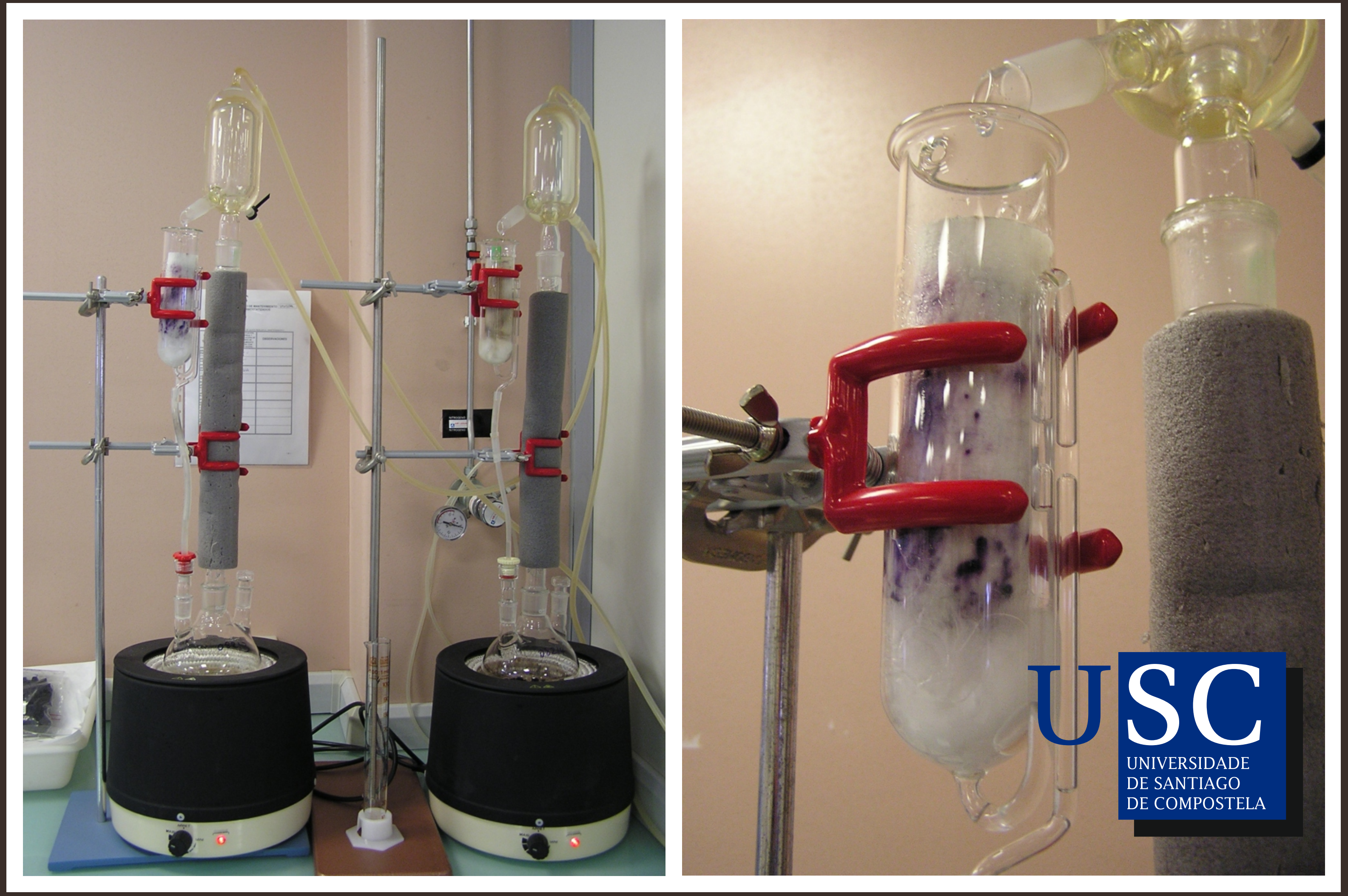
# CONTENIDOS / CONTENTS

SUITABILITY OF ANTHROPOGEOMORPHIC MATERIALS AS SOIL AMENDMENTS: A BIOGEOCHEMICAL STUDY

*Fenxia Yao* *Octubre 2011*

# SUITABILITY OF ANTHROPOGEOMORPHIC MATERIALS AS SOIL AMENDMENTS: A BIOGEOCHEMICAL STUDY



*Tesis Doctoral Presentada por:*
*Fenxia Yao*
*Octubre 2011*

*Departamento de Edafología y Química Agrícola*
*Facultad de Biología, Universidad de Santiago de Compostela*

Departamento de Edafología y Química Agrícola
Facultad de Biología
Universidad de Santiago de Compostela

# SUITABILITY OF ANTHROPOGEOMORPHIC MATERIALS AS SOIL AMENDMENTS: A BIOGEOCHEMICAL STUDY

Tesis Doctoral

Presentado por:

***Fen Xia Yao***

**Octubre 2011.**
**Universidad de Santiago de Compostela.**

*Facultad de Biología*
*DEPARTAMENTO DE EDAFOLOGÍA Y QUÍMICA AGRÍCOLA*
*Campus Universitario Sur*
*15706 Santiago de Compostela*

**Dra. Marta Camps Arbestain**, Profesora Titular del Instituto de Recursos Naturales de la Universidad de Massey, en Nueva Zelanda, y **Dr. Felipe Macías Vázquez**, Catedrático del Departamento de Edafología y Química Agrícola de la Facultad de Biología perteneciente a la Universidad de Santiago de Compostela,

CERTIFICAN:

> Que el presente trabajo titulado "***Suitability of anthropogeomorphic materials as soil amendments: a biogeochemical study***", que para optar al grado de Doctor en Biología presenta **Dª. Fen Xia Yao**, ha sido realizado bajo nuestra dirección y supervisión en los laboratorios del Departamento de Edafología de la Facultad de Biología (Universidad de Santiago de Compostela) y en los del **Departamento de Calidad Ambiental de NEIKER A.B. (*Nekazal Ikerketa eta Garpenerako Euskal Erakundea)*** del *Instituto Vasco de investigación y Desarrollo Agrario (Derio, Bizkaia)*

Considerando que representa trabajo de Tesis Doctoral, autorizamos su presentación como Tesis Europea ante la Comisión de Doctorado de la Universidad de Santiago de Compostela.

Y para que así conste, expedimos el presente certificado en Santiago de Compostela a 14 de Octubre de 2011.

Fdo. Dra. Marta Camps Arbestain

Fdo. Dr. Felipe Macías Vázquez

# Agradecimientos

En primer lugar, quiero agradecer a mis directores: la Dra. Marta Camps Arbestain y el Dr. Felipe Macías Vázquez. Ha sido un honor para mí realizar el doctorado bajo su dirección. Agradezco sinceramente todas sus contribuciones de tiempo e ideas para hacer mi experiencia de doctorado productiva y estimulante. La alegría y el entusiasmo que tienen para su investigación fue la motivación para mí, incluso durante los tiempos difíciles en la persecución de doctorado. Cada vez que hablaba con ellos, me sentía con fuerza y llena de confianza para seguir adelante, a pesar de mis preocupaciones previas. Estoy especialmente agradecida a la Dra. Marta Camps Arbestain por darme la oportunidad de estudiar en España. Sin ella, no habría tenido la gran experiencia como la que he tenido durante los últimos cuatro años. También estoy agradecida por el excelente ejemplo que la Dra. Marta Camps Arbestain ha proporcionado como una exitosa mujer científica. También, quería reconocer al Dr. Felipe Macías Vázquez por mostrarme el campo visual de un científico de prestigio mundial como él representa. También estoy agradecida con él por la financiación que me ha ofrecido al finalizar la beca FPI y que me ha ayudado a sobrevivir hasta terminar la tesis.

En segundo lugar, me gustaría expresar mi gratitud y admiración al Dr. Georges Pédro. Este trabajo se ha basado, en gran medida, en la metodología propuesta y utilizada por Dr. Georges Pédro en la década de 1960 para el estudio de la distribución geoquímica de los principales tipos y procesos de alteración de rocas. En particular, las condiciones de alteración de biocarbón (Capítulo 6) y cenizas (Capítulo 7) conducen rápidamente a situaciones que él había definido como: alkalinolisis. Sin duda, la influencia del drenaje y del tiempo de residencia origina cambios significativos en la movilidad y productos de reacción cuya interpretación sería más difícil sin los trabajos de Dr. Pédro.

Agradezco enormemente a los muchos investigadores y compañeros de trabajo que se convirtieron en parte de mi vida durante mi estudio de doctorado en Neiker-Tecnalia (Instituto Vasco de Investigación y Desarrollo Agrario) y que hicieron que mi estancia fuera agradable. Los miembros del instituto han contribuido inmensamente a mi tiempo personal y profesional durante los últimos cuatro años. El grupo ha sido una fuente de la amistad, así como de buenos consejos y de la

colaboración. Mis agradecimientos a ellos están más allá de las palabras. Sin embargo, todavía quiero mostrarles mis agradecimientos más profundos.

Agradezco sinceramente al Dr. Gerardo Besga y la Dra. Susana Virgel. Por un lado, han actuado como mis tutores y sin ellos la tesis no habría sido posible; por otro lado, me han ofrecido un apoyo paternal en todos los aspectos de la vida y el estudio. Ellos se han alegrado de cada pequeño logro que he conseguido, se han preocupado por todo lo que me preocupa, me siguen fomentando y apoyando incondicionalmente en los momentos duros, siempre están dispuestos a darme una mano o prestarme un hombro cada vez que lo que necesito.

Entre muchas otras personas que han contribuido a esta tesis, me gustaría agradecer a Ander Santesteban y Marta Anza por su importante contribución a los experimentos y análisis. La incontable asistencia técnica de Dr. Fernando Blanco en el laboratorio es muy apreciada. También estoy agradecida con el Dr. Ander González Arias, por su ayuda en la estadística con el software Statview.

Durante los últimos cuatro años, he tenido una experiencia maravillosa en España que no sólo atribuye al trabajo estimulante, sino también que he tenido la suerte de gozar de muchos amigos agradables y serviciales. Estoy especialmente agradecida a Haritz Arriaga por su apoyo y ayuda, cada vez que me dirijo a él. Me gustaría dar las gracias a Xeider Gerrikagoitia y Lur Epelde por guiarme para disfrutar de la belleza natural del País Vasco, lo cual me hizo enamorar de la Euskadi. Doy las gracias a Ainara Artetxe por mostrarme el magnífico baile clásico del pueblo vasco, lo que causó mi gran afecto por dicha cultura, siempre apasionante y amigable. Estoy muy agradecida con Roberto Pérez por su generosidad y amabilidad; Roberto es uno de esos amigos con quien siempre se puede confiar. También debo agradecer a Iker, Oscar, Nahia, Esti, Arrate, Carmen, Asier, Goio, Berdaitz, Mireia, José Antonio, Isabel, Sorkune, Ander, Olatz, Aitor, Laura, Yoli, Lidia, Lucía, Annick, Maialen, Ania,... Gracias a todos ellos, mi estancia en España fue colorida y significativa.

Me gustaría agradecer particularmente a la Dra. Miriam Pinto, la Dra. Ana Aizpurua y la Dra. Pilar Merino por todo su apoyo y ánimo en mi estudio de doctorado y la búsqueda de empleo. Agradezco inmensamente a la Dra. Ana Aizpurua por dejarme empadronar en su casa, lo cual fue crucial para vivir legalmente en España. Doy las gracias a todo el personal de Neiker, en especial a

Joakin Salazar, Mikel Aguirre, Iratxe Elorriaga, Rosa Iturralde, Jon Azua, Idoia Ziluaga, Iñigo Amarika, e Iranzu Telletxea,...

En lo que respecta a la Universidad de Santiago de Compostela, agradezco sinceramente el Dr. José Ramón Verde, el Dr. Roberto Calvelo, Carmen Pérez y Maca Marques por su amable ayuda en el aspecto del estudio y papeleo de la universidad. Estoy especialmente apreciada al Dr. José Ramón Verde por su incontable ayuda durante la última fase de la tesis. También estoy agradecida a Rebeca Pardo por el análisis de actividad microbiana.

Agradezco también al Prof. Javier Aróstegui de la Universidad de País Vasco por el análisis de difracción de rayos X (DRX) y microscopía electrónica de barrido y energía dispersiva de espectroscopia de rayos X (SEM-EDX). Agradezco también al Dr. Juan Antonio Macía Agulló del Instituto Nacional del Carbón por el análisis de espectroscopia fotoelectrones de rayos X (XPS).

Me gustaría agradecer a la Dra. Evelyn Krull y Janine McGowan de CSIRO Land & Water (Australia) por la ayuda aportada en el pretratamiento del análisis de estado sólido de $^{13}$C espectroscopia de resonancia magnética nuclear (RMN) y todos los otros tipos de ayuda durante mi estancia en CSIRO. Doy las gracias a Yvonne Gibbon por alojarme durante tres meses y me hizo sentir en casa. Aprecio la amistad con Anna McBeath, Jia Wen y Bo Li, que hizo mi vida más colorida en Australia.

Agradezco las fuentes de financiación que hizo el trabajo de doctorado posible. He sido financiada por el Ministerio Español de Educación y Ciencia por cuatro años. Mi trabajo durante el año pasado también fue financiado por el Gobierno del País Vasco.

Por último, me gustaría agradecer a mi familia por todo su amor, apoyo y ánimo. Gracias a mis padres que me criaron con amor y me apoyaron en todas mis actividades. Gracias a mi hermano, que trae alegría a la familia. Estoy muy agradecida a mi marido Dazhou por su cuidado con el amor, apoyo, ánimo y paciencia en los últimos cuatro años. Gracias.

Fen Xia Yao
Octubre 2011

A mis padres y mi marido
To my parents and my husband
献给我的父母和我的爱人

# Index

# Capítulo 1

# Introducción

# Capítulo 1. Introducción

## 1.1. Producción de residuos

Se entiende por “residuo” cualquier sustancia u objeto perteneciente a alguna de las categorías que figuran en el anexo de la Ley 10, de Residuos de 21 de abril de 1998 (BOE de 22 de abril) del cual el poseedor se desprende o del que tenga obligación de desprenderse. El concepto legal de residuo es consecuencia de la Directiva Comunitaria 75/442/CEE, que fue modificada posteriormente por la 91/156/CEE, mediante la cual se modernizan y unifican conceptos y se establecen nuevas políticas de residuos.

En las últimas décadas la cantidad de residuos producidos por el hombre se ha incrementado considerablemente. La sociedad exige cada vez más altos estándares de producción y calidad, lo que lleva a la producción de mayores volúmenes de residuos y consecuentemente a un incremento en los riesgos asociados de contaminación.

En esta tesis, se utilizaron fundamentalmente lodos derivados de aguas residuales, cenizas de combustión y residuos de la siderurgia (arena de fundición y escorias de Linz-Donawitz) que, son residuos de amplia producción en el Pais Vasco que podrían ser valorizados en función de sus componentes y propiedades. Por lo tanto, la generación de estos residuos se trata en detalle a continuación.

### *1.1.1. Lodos de depuradora*

Con el fin de satisfacer las exigencias de calidad del agua, es esencial la depuración y el tratamiento de las aguas residuales antes de su vertido. Los lodos de depuradora son un subproducto producido por las plantas de tratamiento de aguas residuales durante su proceso de depuración. Como resultado de la aplicación de la Directiva Europea 91/271/CEE, se han creado muchas nuevas plantas de tratamiento de aguas y la generación de lodos se ha incrementado considerablemente. Por ejemplo, en España, la producción total de lodos en el 2008 alcanzó 1,2 millones de Mg y las plantas de tratamiento de aguas residuales en el País Vasco produjeron 24000 Mg durante el mismo año (Ministerio de Medio Ambiente y Medio Rural y Marino de 2010).

### *1.1.2. Cenizas volantes procedentes de la combustión de carbón y biomasa*

Los combustibles fósiles han sido la fuente de energía principal para las sociedades modernas, en este último siglo. El carbón es uno de los más importantes combustibles fósiles, cuya combustión produce gran cantidad de subproductos. La producción total de subproductos de la combustión del carbón (CCPs) se estima que fue aproximadamente de 65 millones Mg en Europa en 2003, entre los cuales el 67,8% fueron cenizas volantes (ECOBA, 2003); la producción total de cenizas volantes en Europa en 2006 fue de más de 40 millones de Mg (ECOBA, 2006). La producción de cenizas volantes de carbón en Estados Unidos fue de 63 millones Mg (ACAA, 2009). La producción mundial de cenizas de carbón se estima que superará los 550 millones Mg por año (Clarke, 1994).

Como los combustibles fósiles son limitados y no renovables, y además, el consumo de energía de la quema de combustibles fósiles es la principal causa del aumento de la concentración de $CO_2$ en la atmósfera, los biocombustibles se están convirtiendo mundialmente, en una alternativa cada vez más importante, tanto en el presente como en el futuro, frente a los combustibles fósiles (Hansen et al., 2001). Según el libro blanco de la Comisión de la UE (KOM/97/0599) uno de los objetivos de la UE es aumentar la proporción de energía renovable al 12% del consumo total de energía. Entre otras medidas, se ha fomentado la construcción de instalaciones de combustión de biomasa. En Europa, en la actualidad, se encuentran varias combinaciones de plantas generadoras de energía y calefacción, que se basan en la combustión de biomasa (Obernberger, 1998). Por lo tanto, empiezan a acumularse, cada vez más, mayores cantidades de cenizas de biomasa de las centrales eléctricas, de las industrias de la madera y de la industria papelera; por ejemplo, en Austria se producen alrededor de 100 mil Mg de cenizas de biomasa cada año (Kuba et al., 2008); en Suecia se produce anualmente alrededor de 200 mil Mg de ceniza de madera (Charholm, 1994).

### *1.1.3. Arena de fundición*

La arena de fundición se utiliza ampliamente en la industria de fundición de metal para crear el molde en el que se vierte el metal fundido (Guney et al., 2006). La generación anual de arena de fundición es aproximadamente de 9 a 12 millones de toneladas métricas en Europa y los Estados Unidos, respectivamente, y la mayor parte de esta arena se dispone en las instalaciones de confinamiento de residuos

(Abichou et al., 2004). La generación anual de arena de fundición en el País Vasco fue de más de 200 mil toneladas.

### *1.1.4. Escoria Linz-Donawitz*

La escoria de Linz-Donawitz es un subproducto de la industria del acero, en el proceso de refinado utilizando convertidores LD. La producción de escorias es de 464 kg por cada tonelada de acero producido, representando el 71-77% en peso total de todos los residuos generado durante la producción de acero (Virgel, 2002). En España, la generación de escoria de LD es de alrededor de 37 millones de toneladas por año. En ACERALIA, se han producido en el año 2000, 565.485 t de escoria LD (Virgel, 2002). La escoria se produce en grandes cantidades en Europa y por ello se plantea un problema de eliminación sustancial (Pinto et al., 1995).

## **1.2. El problema creciente de la gestión de los residuos**

En las dos últimas décadas, diferentes políticas ambientales, como las de depuración de aguas residuales, y los criterios, cada vez más exigentes, de gestión de los bioresiduos generados obligan a nuevos desarrollos y a métodos más eficientes de utilización y valorización de los residuos que permitan la rápida integración de sus componentes en los ciclos biogeoquímicos superficiales de forma sanitaria y ambientalmente correcta. Sin duda, gran parte de estos objetivos puede realizarse a través de los sistemas edáficos pero, en todo caso, debe realizarse de forma compatible con la conservación de la calidad y funciones relevantes de estos sistemas.

La Estrategia Temática Europea de Protección del Suelo, elaborada en el período 2002-2004 (EU, 2006), señala que la producción de materia orgánica exógena superaba ya los 1.000 millones de toneladas al año, exigiendo la adopción de medidas de gestión eficaces que eviten o mitiguen el deterioro de los sistemas superficiales, es decir del agua, aire, suelo y biota. De estos sistemas, el suelo es el que puede regular más eficientemente la movilidad de los contaminantes pero con una capacidad de amortiguación finita y diferente para cada tipo de suelo que debe ser conocida, conservada y, en lo posible, mejorada.

Aspectos como el incremento del espesor, capacidad de adsorción, neutralización y transformación, así como incremento de la diversidad y actividad biológica son los factores relevantes que deben ser incentivados mediante los procesos de recuperación de suelos degradados y/o contaminados, para lo cual una gestión integral de algunos residuos y suelos puede resultar el sistema más eficiente de gestión ambiental al conseguir, de forma simultánea, y generalmente económica, varios objetivos relevantes (Power y Dick, 2000).

## 1.3. Legislación y principios de gestión de los residuos

Con el crecimiento de las zonas urbanas y la creciente demanda de unos estilos de vida de alta calidad, ha adquirido una gran importancia la gestión de todos los tipos de residuos para evitar la degradación medioambiental y riesgos en la salud pública. Se ha establecido una infraestructura de gestión de residuos para la recogida y eliminación de residuos, basado en una jerarquía de los siguientes principios: (i) prevención, (ii) reciclaje/re-uso, (iii) el uso de residuos como fuente de energía, y (iv) su disposición final controlada, normalmente en vertederos. La disposición final, sin embargo, es la menos deseable ya que causa enormes emisiones de contaminantes a la atmósfera, agua superficial y el subsuelo. Además, esto implica la pérdida de muchos elementos y componentes que podrían ser de gran beneficio para mejorar las funciones de suelo. Gran parte del enfoque de gestión de residuos se centra en los residuos orgánicos, como se ilustra en Europa mediante la expedición de la Directiva de vertidos (99/31/EC), la Directiva de lodos de depuradora de aguas residuales (86/278/ECC), la Directiva Europea del tratamiento de residuos urbanos 91/271/ECC, la reciente Directiva de Residuos (2006/12/EC), la regulación de la UE respecto a los subproductos animales no destinados al consumo humano (EC/1774/2002), así como la Estrategia Temática del Suelo (2004).

## 1.4. Fertilización convencional y pérdida del C orgánico del suelo

Durante las últimas décadas, la aplicación de fertilizantes inorgánicos en los suelos ha resultado en un uso de suelo más “eficiente” en cuanto a la productividad se refiere, lo que permite (i) cultivo continuo, sin barbecho y (ii) el uso de zonas marginales. Los abonos inorgánicos, por un lado, tienen la ventaja de ser fáciles de almacenar, están listos para usar y son fáciles de aplicar. Su uso requiere menos mano de obra que el tradicional estiércol y los abonos verdes, y su manejo no causa el tipo de problemas que normalmente se producen con materiales fermentables (olores desagradables, etc.). Por otra parte, como fertilizantes inorgánicos contienen mayores niveles de nutrientes que los fertilizantes orgánicos, por lo que siempre se requieren menores cantidades. Además, el uso de fertilizantes inorgánicos no requiere la presencia cercana de ganado. Sobre todo, la reducción de los costos asociados con la necesidad de menos mano de obra ha sido un factor decisivo en la sustitución de los fertilizantes orgánicos por los inorgánicos. Sin embargo, el abandono de la aplicación de estiércol a los suelos, junto con la mecanización de la labranza durante las últimas décadas, ha llevado a (i) una drástica disminución en las cantidades de carbón (C) orgánico en los suelos agrícolas, (ii) junto con una importante pérdida de la estructura del suelo ya sea debido a la compactación o dispersión del suelo y (iii) un incremento de los procesos relacionados con la pérdida de los coloides, como la disminución de la capacidad de retención de agua, la erosión o la desertificación.

La pérdida del C orgánico del suelo durante las últimas décadas ha sido acompañada de una gran cantidad de residuos producida por los seres humanos. Se estima que aproximadamente un 50% de la materia orgánica de los suelos cultivados en Europa se ha perdido. Para Galicia se dan cifras del mismo orden (30 al 40%) para la pérdida de C edáfico en el paso a cultivo (Calvo de Anta et al., 1992; Macías Vázquez, 2004). Otras zonas de España presentan valores superiores de pérdida, especialmente las del sur de la Península con regimenes hídricos xéricos o incluso arídicos, en los que pueden alcanzarse cifras de pérdida en el paso a cultivo superiores al 80% (Macías Vázquez y Camps Arbestain, 2010). Esto ha llevado a diferentes investigadores a considerar que los usos agronómicos realizados a lo largo de los últimos siglos han invertido la función del suelo en el ciclo del carbono, pasando estos sistemas de actuar como “sumidero” a hacerlo como “fuente” (Lal, 2001). Este mismo autor señala que hasta 1970 la emisión de $CO_2$ producida por las actividades agrícolas y silvícolas superaba a la del conjunto de las actividades industriales y el transporte y que aún hoy representa el 25% del total de emisiones (Lal, 2001). Junto a esto, los procesos de erosión y desertificación (particularmente en los países del sur de Europa, Sánchez et al., 2001) y las actividades de urbanización, industrialización y extracción de recursos geológicos (EU, 2006) constituyen importantes amenazas para el mantenimiento de la calidad de las funciones del suelo en Europa. Todo ello se contempla en la Estrategia Europea de Protección del Suelo donde, si bien se admite que el porcentaje de materia orgánica existente en la mayoría de ellos es suficiente para mantener su fertilidad y productividad, hay ya una importante disminución de la capacidad del sumidero de C edáfico que obliga a proponer, como uno de los objetivos fundamentales, el incremento de los stocks edáficos de C orgánico. Dicho incremento conllevaría además efectos beneficiosos sobre la actividad biológica, la biodiversidad, la estructura del suelo y su resistencia a la erosión, así como sobre la productividad y la ralentización del incremento del C atmosférico por lo que el incremento del C de los suelos puede considerarse una estrategia win-win (Lal, 2004).

El C orgánico afecta a las propiedades físicas, químicas y biológicas del suelo y su pérdida ha tenido consecuencias muy negativas en funciones de suelo. Esto ha planteado la necesidad de aumentar las existencias de C orgánico en el suelo (a promover el suelo como sumidero de C), que, así como la mejora de las propiedades del suelo (la fertilidad del suelo, la retención de agua del suelo, la capacidad de amortiguación frente a los contaminantes, el aumento de la biodiversidad, etc.), en parte puede mitigar los efectos de las emisiones de los gases de efecto invernadero.

## 1.5. Modificación de suelos por los residuos

Desde que existen suelos en la Tierra, una de sus principales funciones ha sido la del reciclaje de los restos orgánicos incorporando una pequeña parte de ellos en materia orgánica del suelo y descomponiendo el resto hasta formas elementales que son liberadas a la atmósfera, absorbidas por los organismos del suelo o eliminadas en forma disuelta en las aguas de drenaje, participando el suelo, de los ciclos de los principales elementos biogénicos (C, N, P y S). La capacidad para transformar las sustancias orgánicas está relacionada con factores muy diversos pero, en último término, todas las moléculas orgánicas son inestables en las condiciones existentes en los suelos y otros sistemas superficiales, debido a que han sido formadas a partir de procesos y condiciones de fuerte reducción (fotosíntesis: $Eh \leq -600$ mV), por lo que, en presencia de agentes oxidantes tienden a reaccionar y transformarse en compuestos estables y en equilibrio con las condiciones del suelo mediante reacciones oxidativas.

Además, estas reacciones oxidativas pueden ser catalizadas por microorganismos que obtienen la energía necesaria para sus funciones vitales a través de las transformaciones metabólicas de las sustancias orgánicas. Por tanto, (i) inestabilidad termodinámica, (ii) presencia de oxidantes, y (iii) catálisis metabólica son los factores que explican la descomposición de las sustancias orgánicas en los suelos y el papel reciclador del suelo de los restos orgánicos.

La adición antrópica a los suelos de restos orgánicos, arenas de las playas, excrementos animales, restos vegetales y de alimentos, etc., ha sido una consecuencia natural y lógica de la observación de la existencia de determinadas ventajas asociadas. Entre ellas, la propia eliminación de los residuos y, sobre todo, la mejora en las condiciones físicas (estructurales) del suelo y el incremento de la disponibilidad de nutrientes para la biomasa del suelo y las plantas cultivadas. Las culturas antiguas practicaban diferentes formas de aportar periódicamente sustancias orgánicas procedentes de diferentes orígenes (restos forestales, excrementos, cadáveres y residuos de cosecha) que venían a compensar las pérdidas de fertilidad y contenido de C orgánico del suelo que se producían a consecuencia del laboreo y la cosecha. De hecho, la adición antropogénica de residuos orgánicos a los suelos agrícolas a lo largo de la historia ha mejorado en gran medida las propiedades de estos suelos y, en algunos casos, se han formado suelos antrópicos de altas tasas de fertilidad, por ejemplo, suelos de Plaggen del norte de Europa, “Terra Preta do Indio” en Brasil… (Macías Vázquez et al., 2007).

La adición de residuos a los suelos es una importante alternativa que ha demostrado su eficacia cuando se conocen adecuadamente tanto las condiciones del medio inicial como las características de los materiales residuales utilizados y su evolución en el tiempo. Diversos residuos se han agregado a los suelos en muchos lugares y se han utilizado en los procesos de remediación de suelos con especial intensidad en los últimos años, por ejemplo, conchas de mejillón, purines, algas, crustáceos, arena de playa, lodos de depuradora, cenizas de combustión, residuos silvícolas, ganaderos y agroalimentarios, serrines de rocas ornamentales, residuos de demolición, estériles de explotaciones mineras, etc.

### *1.5.1. Efectos de la adición de los residuos utilizados en las propiedades físicas del suelo*

La prevalencia principalmente del tamaño limo de las cenizas volantes podría mejorar el agua disponible para las plantas y la capacidad del suelo de retención de agua, debido a que la gran superficie esférica de las partículas de cenizas volantes es propicia para aumentar la microporosidad del suelo mejorando el espacio aéreo de suelo, lo que equivale a la capacidad de retención de agua en el suelo (Adriano y Weber, 2001). Se ha informado que la adición de cenizas volantes en general produce la disminución de la densidad aparente de suelo, que a su vez mejora la porosidad de suelo y promueve una mejor aireación y percolación (filtración) (Page et al., 1979; Jala y Goyanes, 2006). También se ha señalado que la adición de cenizas volantes puede modificar la textura de los suelos arenosos y arcillosos a suelos francos (Fail y Wochok, 1977; Capp, 1978). La capacidad de retención del agua en los suelos arenosos/arcillosos aumentó un 8% debido a la enmienda de cenizas volantes (Chang et al., 1977) y este aumento, acompañado de la conductividad hidráulica, ayudó a reducir la formación de la superficie de incrustación y a reducir la compactación de suelo (Jal y Goyal, 2006). Un alto contenido de Ca en las cenizas volantes también podría mejorar la floculación/agregación de las partículas del suelo, manteniendo los suelos friables. Sin embargo, la adición única de cenizas volantes puede conducir a la compactación del suelo, tal como se ha producido en la mina de Touro en algunas situaciones similares a los procesos de compactación característicos de los suelos de tendencia excesivamente limosa (Macías Vázquez, 2011). Además, las cenizas generalmente oscurecen el color del suelo y, por tanto, aumentan la temperatura del mismo, al absorber más energía radiante que los suelos de colores claros, teniendo este efecto consecuencias positivas o negativas según el uso y condiciones del suelo.

La densidad del suelo, en general, disminuye a medida que la tasa de aplicación de lodos de depuradora aumenta debido a un efecto de dilución resultante de la mezcla de la adición de materia orgánica con la fracción mineral más densa (Khaleel et al., 1981). Además, se ha visto que la adición de lodos de depuradora es un método eficaz para aumentar la agregación del suelo, especialmente favorable cuando se forman agregados estables (Clapp et al., 1986). El espacio poroso total es atribuido a un aumento de la agregación incrementada por la adición de lodos de depuradora (Khaleel et al., 1981). Sin embargo, según De María et al. (2010), la macroporosidad aumenta, mientras que la microporosidad disminuye después de la aplicación de lodos. Además, la adición de los lodos de depuradora también podría aumentar la retención de agua en el suelo, pero el efecto depende de la textura inicial del suelo; por ejemplo la aplicación de 56 Mg ha$^{-1}$ de lodo anaeróbico a un suelo franco limoso Blount provocó un aumento de la capacidad de campo y del punto de marchitez de 14,9 y 14,7%, respectivamente, mientras que la tasa de la misma aplicación en un suelo franco arenoso aumentó los mismos parámetros en un 17,1 y 51,7% , respectivamente (Clapp et al., 1986).

### *1.5.2. Efectos de la adición de residuos en las propiedades químicas del suelo*

La adición de cenizas volantes al suelo podría aumentar el pH del suelo y la capacidad amortiguadora del mismo (Matsi y Keramidas, 1999). Las cenizas volantes contienen nutrientes como K, Ca y Mg (Demeyer et al., 2001), y por lo tanto, su disponibilidad en el suelo tiende a aumentar mientras que (i) contrarrestan la sodicidad del suelo, (ii) reducen la toxicidad del aluminio y (iii) reducen la toxicidad del Mn (Fail y Wochok, 1977; Demeyer et al., 2001; Jala y Goyanes, 2006). La adición de cenizas volantes a los suelos también puede conducir a la inmovilización de los metales pesados a través de reacciones de precipitación y adsorción. (Ciccu et al., 2001). Sin embargo, las cenizas volantes también pueden contener trazas de metales pesados, como el Cu, Cd, Pb, B, y U, que pueden llegar a contaminar las aguas superficiales y subterráneas (Jala y Goyal, 2006). Otros efectos posibles como producir una alta disponibilidad de B (Page et al., 1979; Aitken y Bell, 1985), una mayor acumulación de selenio (Furr et al., 1977; Straughan et al., 1978) pueden causar efectos tóxicos en plantas y animales.

Las cenizas volantes podrían aumentar el contenido de materia orgánica, no sólo porque contienen carbono orgánico inquemado, sino también porque pueden catalizar el secuestro de carbono atmosférico (Amonette et al., 2003) y, al aumentar la producción vegetal fijar C en biomasa y suelo. Sin embargo, también se ha informado que la adición de cenizas volantes protegidas de la intemperie en suelos arenosos inhibió severamente la respiración microbiana, la actividad enzimática y procesos del ciclo de nitrógeno en el suelo como la nitrificación y la mineralización (Cerevelli et al., 1986; Wong y Wong, 1986; Pitchel, 1990; Pitchel y Hayes, 1990; Garau et al., 1991) con consecuencias positivas o negativas según los casos.

La adición de lodos al suelo aumentó significativamente el contenido de materia orgánica del suelo en un 20.6%; incrementó el contenido de N total y disponible en un 33% y 220%, respectivamente; aumentó el contenido de P total y disponible para las plantas en un 11% y 170%, respectivamente; y llevó el aumento del contenido de K total y disponible para la planta hasta un 70% y 47%, respectivamente (Suhadolc et al., 2010). La materia orgánica aportada por los lodos afecta la disponibilidad de los metales, disminuyendo los coeficientes de transferencia de los mismos cuando el contenido de materia orgánica es elevada (Antoniadis et al., 2010). Por otra parte, la adición de lodos a los suelos también puede aumentar la capacidad de intercambio catiónico de suelo, lo que a su vez causa un incremento de la productividad y fertilidad de suelos.

Sin embargo, han surgido muchos problemas ambientales con la aplicación de residuos a los suelos debido a la gran variabilidad de tipos de residuos añadidos (por ejemplo, residuos urbanos e industriales), y porque el objetivo final de la aplicación de residuos a los suelos es a menudo la eliminación de éstos en lugar de mejorar la fertilidad del suelo (Macías Vázquez, 2001, 2004). La adición de grandes cantidades de restos agrícolas, ganaderos, industriales urbanos y compost puede, en muchos casos, aportar elementos nutritivos e influir en la mejora de las propiedades físicas del suelo, pero estos residuos pueden ir acompañados de sustancias indeseables que pueden hacer disminuir, más o menos rápidamente, la calidad del suelo e incluso pueden llegar a causar graves problemas de contaminación convirtiendo al suelo de sumidero en fuente de contaminantes. Por ejemplo, después de la aplicación inicial de lodos al suelo, han aparecido muchos problemas, tales como acidificación del suelo (Sajwan et al., 2003; Sajwan et al., 2006) o toxicidad de metales pesados y patógenos (Wong y Su, 1997a, 1997b; Reynolds et al., 1999; Schumann y Sumner 1999; Su y Wong, 2002). En muchos casos, el aumento previsto de las existencias C es casi insignificante, principalmente porque el C orgánico en los suelos no se ha estabilizado previamente.

Debido a la magnitud de la actual producción de materia orgánica exógena en Europa, es esencial adoptar medidas de gestión eficaces para evitar o mitigar el deterioro de los sistemas superficiales, es decir, del agua, aire, suelo y biota. Para una correcta reutilización y reciclaje de los productos de desecho, deben desarrollarse nuevos métodos y tecnologías que permitan una rápida y ambientalmente segura incorporación de los componentes de residuos en sus ciclos biogeoquímicos. Sin duda, muchos de estos objetivos podrían alcanzarse a través de sistemas de suelo; sin embargo, esto debe ser llevado a cabo siguiendo un procedimiento que sea compatible con la preservación de las funciones principales del suelo y la calidad de los sistemas. En todo caso, el suelo es el más eficiente de los sistemas superficiales en la regulación de la movilidad de los contaminantes y es el único que tiene capacidad tampón para muchos de ellos, si bien ésta puede verse superada cuando las concentraciones y cantidades aportadas superan la carga crítica de dicho contaminante en el suelo (Macías Vázquez et al., 2002).

## 1.6. Compostaje de residuos orgánicos

El compostaje es un proceso biológico natural, que cuando se lleva a cabo en condiciones controladas acelera la descomposición de residuos orgánicos y reduce su volumen, creando materia orgánica poco estable pero capaz de liberar nutrientes que son aprovechados por la biomasa vegetal y microbiana. Sin embargo, debe tenerse en cuenta que, (i) el proceso de compostaje no es per se, un proceso que maximiza ni la recuperación del C orgánico ni la de otros nutrientes volatilizables, (como por ejemplo, la del N); (ii) el uso final del compost obtenido dependerá del origen del residuo compostado, por ejemplo, restos de hierba, hojas, matorral, en comparación con lodos o estiércol, con la primera siendo una enmienda del suelo y la segunda, un abono orgánico. Además, son motivo de preocupación los posibles riesgos de salud asociados con la exposición a los gases biológicos generados desde el proceso y manejo de materiales orgánicos compostados.

## 1.7. El concepto de Tecnosoles

Al igual que existen procesos de formación de suelos sobre materiales consolidados o desagregados de origen natural, determinados productos derivados de actuaciones antrópicas pueden presentar características de composición y evolución similares a los materiales geológicos cuando son sometidos a los factores de formación de suelos. Estos materiales han sido definidos por la WRB (1996) como “materiales antropogeomórficos”, que incluyen a aquellos residuos derivados de actividades antropogénicas, con características similares a los componentes geológicos y biogénicos de los suelos que pueden actuar como material original de los mismos a través de los procesos de edafogénesis. Cuando estos materiales o las mezclas de ellos, están expuestas a la intemperie, se darán sobre ellos procesos de erosión y edafogénicos, en un grado mayor o menor, dependiendo de las diferentes interacciones que tienen lugar entre la litosfera, la hidrosfera, la biosfera y la atmósfera en el tiempo, dando lugar a suelos derivados de residuos que cumplen con los conceptos de definición de Tecnosoles (WRB, 2006) (Macías-García, 2006; Macías Vázquez et al., 2007; Macías Vázquez and Camps Arbestain, 2010).

La biosfera incluye la vegetación, la fauna, y los seres humanos, aunque la influencia de estos últimos en la edafogénesis apenas ha estado reflejada en los primeros sistemas de clasificación de suelos. Actualmente las nuevas revisiones y las nuevas clasificaciones progresivamente incorporan la importancia de la influencia del factor humano en los procesos de formación de los suelos. Macías-García (2006) realizó una revisión de los cambios en la incorporación de estos nuevos conceptos en las clasificaciones y, especialmente en los sucesivos esquemas propuestos por la FAO. Así, en el sistema de clasificación de suelos propuesto por la FAO-ISRIC-IUSS en 1998, conocido como WRB (Base Mundial de Referencia de los Recursos Edáficos) (FAO/ISRIC/ISSS, 1998), se incluyen los denominados suelos antropogénicos, dentro de los cuales se distinguen cinco tipos distintos según Dudal et al., 2002:

(i) Aquellos en los que la influencia antrópica induce cambios en la clase de suelo (p.e., Cambisoles que han pasado a ser Solonchaks como resultado del riego en zonas áridas; Plinthosoles resultantes de la emergencia de la plintita cerca de la superficie como consecuencia de la erosión o remoción producida por el hombre de Acrisoles plínticos), etc. En estos casos la morfología de los suelos alterados por influencia antrópica no difiere excesivamente de la de suelos “naturales”.

(ii) Aquellos suelos agrícolas en los que la influencia antrópica se refleja en la formación de horizontes de diagnóstico específicos (p.e., horizontes térrico, irrágrico, plággico, hórtico, antrácuico, e hidrárgico de los Anthrosoles). Son el resultado de la aplicación continuada de materia orgánica (Anthrosoles térricos, plággicos, hórticos) o del cultivo en zonas inundadas (Anthrosoles irrágricos, antrácuicos, e hidrágricos) durante largos períodos de tiempo.

(iii) Aquellos en los que la influencia antrópica se refleja en el material original (materiales antropogeomórficos). En estos suelos los procesos edafogénicos no han tenido lugar durante suficiente tiempo como para ser incluidos en el grupo de los Antrosoles. Se clasificaban en la propuesta de 1998 como Regosoles, a nivel de grupo, y a nivel de subgrupo de acuerdo con el origen del material antropogeomórfico diferenciándose los siguientes subgrupos: (a) *materiales aricos*: son los materiales procedentes de suelos minerales que han sido movilizados o perturbados por actuaciones de laboreo, (b) *materiales gárbicos*: cuando los componentes dominantes son residuos orgánicos fermentables, (c) *materiales redúcticos*: cuando los materiales producen emisiones de gases resultantes de las condiciones anaerobias en las que se encuentran, (d) *materiales espólicos*: cuando se producen o quedan en la superficie a consecuencia de actividades extractivas, (e) *materiales úrbicos*: cuando se trata de materiales generados en actividades urbanas o industriales o infraestructuras viarias, como las cenizas de combustión, residuos de demolición de edificios, capas compactadas en hormigón o cemento, etc.

(iv) Aquellos en los que la influencia antrópica induce grandes perturbaciones en los suelos (p.e., la realización de terrazas, excavaciones, minas a cielo abierto, etc.). Estos suelos o bien no tienen horizontes de diagnóstico o sólo tienen fragmentos de éstos.

(v) Aquellos en los que la influencia antrópica induce cambios en el horizonte superficial (p.e., como resultado del laboreo, deforestación, encalando, fertilización, adición de estiércol, drenaje, incendios, etc.). Se incluyen en subunidades ántricas.

En la Reunión de la IUSS en Philadelphia (2006) se ha presentado un intento de clasificación de los Antrosoles. La IUSS en su nueva clasificación (IUSS Working Group WRB, 2006) los incluye en las unidades: Anthrosol, cuando derivan de una actuación agraria de larga duración e intensidad de transformación o Technosol cuando contienen grandes volúmenes, >20% de artefactos, definiendo este concepto como un material de diagnóstico sólido o líquido que tiene una o ambas de las siguientes: (a) ha ido creado o modificado substancialmente por humanos como parte de un proceso de fabricación industrial o artesanal; (b) ha sido transportado a la superficie como consecuencia de una actividad humana desde una profundidad en la que no estaría influenciado por los procesos superficiales y tiene propiedades substancialmente diferentes de las del ambiente en que es colocado. c) Tiene substancialmente las mismas propiedades que cuando fue manufacturado, modificado o excavado.

Ejemplos de artefactos son: ladrillos, cerámicas, vidrios, piedras trituradas o revestidas, residuos industriales, residuos fermentables, productos de procesado de hidrocarburos, residuos de minería y petróleos. Es decir, se incluye como "*artefactos*" lo que anteriormente se definía en la WRB (1998) como *materiales antropogeomórficos.* En esta nueva clasificación, define como materiales de diagnóstico el concepto de *"technic hard rock"* entendiendo por tales los materiales consolidados producidos en un proceso industrial, con propiedades substancialmente diferentes de las de los materiales naturales. De acuerdo con WRB (2006), estos suelos son llamados Tecnosoles – suelos cuyas propiedades y pedogénesis están dominados por su origen técnico (IUSS, grupo WRB, 2006).

Además de las dos grandes unidades anteriores (Anthrosoles y Tecnosoles), en todas las unidades de suelos inorgánicos se incluye el prefijo calificador *"technic"* para aquellos suelos que tengan 10% o más (en volumen o en peso medio) de artefactos en los 100 cm superficiales o hasta la roca continua o una capa cementada o endurecida cuando es más pequeña (p.e.: Technic Leptosol; Technic Ferralsol).

Si se elaboran Tecnosoles "a la carta" (Macías Vázquez y Camps Arbestain, 2010), las proporciones de cada componente deben ser ajustadas para proporcionar un ambiente adecuado para la formación de un nuevo suelo, que debe ser adaptada a los objetivos deseados (ambientales, productivos, etc.,) las condiciones de edafoclimáticas y los tipos de suelos y edafogénesis de la zona en cuestión. Los problemas ambientales derivados de la utilización de estas mezclas pueden evitarse si las características de los materiales empleados son bien conocidas y adecuadas para tales fines. La producción de Tecnosoles de mezclas de residuos no consolidados presenta, pues, los desafíos medioambientales actuales, tales como el comportamiento de los suelos y su evolución, lo cuál debe ser probado para asegurar que se cumplan las principales funciones del suelo (EU, 2006).

## 1.8. Primeros ensayos sobre los suelos artificiales en Galicia

En Galicia, desde la década de 1980 viene proponiéndose la adición de residuos en la restauración de diferentes espacios degradados. Por ejemplo, en las escombreras de la mina de As Pontes (Gil et al., 1990; Monterroso y Macías Vázquez, 1991; Monterroso, 1995; Monterroso et al., 1998; Macías Vázquez, 2004) han utilizado entre otros productos, gallinazas, concha y vianda de mejillones afectados por el vertido de hidrocarburos, sueros de quesería, lodos de depuradora y grandes cantidades de cenizas de combustión del carbón, buscando los efectos positivos de un incremento de nutrientes, una reducción de la velocidad de oxidación de los sulfuros o una subida del pH y neutralización de aguas ácidas. En la corta y escombrera de la corta de Aríns se realizaron ensayos con biodepósitos producidos bajo las bateas de mejillón (Macías Vázquez et al., 1991; Quintás y Macías Vázquez, 1992, 1993), lodos de depuradora (García Arrese et al., 1993) y residuos de demolición. En la mina Touro se han utilizado, entre otros, cenizas de combustión de biomasa, concha de mejillón con y sin vianda, dreggs de lejías verdes, lodos de depuradora anaerobios y anaerobios (Macías Vázquez y Calvo de Anta, 2001). Otros investigadores (López Mosquera; Merino, etc.) han realizado actuaciones similares de incorporación de diferentes residuos en suelos de cultivo y forestales.

Los efectos de los residuos eran, generalmente positivos, pero no siempre muy eficaces por la descompensación de nutrientes y propiedades que tenía cada uno de ellos individualmente, de modo que eran frecuentes situaciones de mejora inicial que luego venían precedidas de daños a la vegetación por la aparición de un elemento nutritivo o de una condición físico-química limitante que estaba inducida por el propio residuo añadido. En la mina Touro, plantas de eucalipto que no se establecerían en las escombreras sin ningún tipo de tratamiento se mantuvieron y desarrollaron tras la aplicación, por los técnicos de Norfor, de una cobertura de 40-50 cm de cenizas de combustión en superficie. El crecimiento se mantuvo durante 3-4 años, pero al cabo de este tiempo comenzó a ralentizarse y los árboles mostraron serias carencias de nitrógeno, con decaimiento, amarillamiento, defoliación, incremento de la intensidad de los ataques de los parásitos como el Gonypterus y, con frecuencia, la muerte de los árboles. Otras experiencias demostraban que la aplicación de un solo tipo de residuo, como las cenizas de combustión de biomasa, producía efectos positivos cuando se necesitaba incrementar el pH del suelo en sistemas acidificados, controlar el Al tóxico y suministrar P, Ca o K, etc, pero aparecían problemas cuando las necesidades ecológicas de la planta no estaban satisfechas por falta de N o por una excesiva alcalinidad. Otros muchos ejemplos del efecto negativo de los desequilibrios generados por la adición individualizada de residuos son bien conocidos y obedecen a la relación bien conocida de la productividad con la denomina “Ley del Mínimo”.

Experiencias posteriores han demostrado que la aplicación conjunta y equilibrada de diferentes residuos es uno de los procedimientos de gestión de residuos más avanzados ambientalmente, con beneficios de restauración de suelos, aguas y biota mucho mayores que los producidos cuando se usa un único tipo de residuo. El resultado era lógico si se tiene en cuenta que los residuos suelen ser descompensados en su contenido de nutrientes y cuando se produce una carencia grave de uno de los elementos prioritarios el crecimiento cesa. La conocida “Ley del mínimo”. Por otra parte, las necesidades nutritivas de las plantas pasan por diferentes etapas, de modo que sus exigencias no son las mismas en los estadios incipientes de evolución que los que se requieren en las fases posteriores. Además, en el caso de la ceniza se observó que, aunque se cubría superficialmente con musgo y aparecían algunas plantas espontáneas, por debajo de unos dos centímetros el material aparecía desestructurado y con una fuerte tendencia a la compactación. Por todo ello, se pensó que una mezcla de residuos que pudiese evolucionar como un material edáfico y contuviese materiales alterables, similares a los de los sedimentos y suelos sería más adecuada.

Esta mezcla de residuos, dirigida a la sustitución de suelo natural cuando faltase por erosión o cuando existiese un problema de contaminación y/o degradación fuerte que impidiese el desarrollo normal de las funciones del suelo, fue denominada inicialmente como *"suelos artificiales"* (Bao y Macías Vázquez, 1998) y, más tarde, como *"suelos derivados de residuos"*, entendiendo actualmente por ellos la mezcla sólida de materiales naturales o sintéticos, minerales u orgánicos que, colocado en superficie, permite el cumplimiento de las funciones del suelo, en especial el anclaje y soporte del sistema radicular y el aporte de nutrientes y elementos esenciales para el desarrollo de las plantas mejorando la situación ambiental precedente (Macías Vázquez, 2004).

Según esta concepción, los residuos no son otra cosa que recursos naturales desaprovechados. El objetivo es valorizarlos y/o integrarlos en los ciclos biogeoquímicos mediante procesos sostenibles y con garantía ambiental, lo que requiere un conocimiento preciso no sólo de la naturaleza y cantidad de cada residuo, sino también de la capacidad de acogida de los medios receptores (en último término la biosfera). Dentro de la biosfera, el suelo representa el papel central ambiental (Estrategia Europea de Protección del Suelo, EU, 2006) tanto por su capacidad amortiguadora intrínseca como por el control que realiza de la mayor parte de los procesos superficiales y ciclos de elementos a través de una multitud de reacciones y operaciones físico-químicas y biocatalizadas que ponen en contacto los diferentes compartimentos biogeoquímicos de la biosfera (suelo, gea, aire, agua y biota) y deciden la movilidad, biodisponibilidad y tiempo de residencia en cada compartimiento de las diferentes especies químicas que pueden originarse. Por ello, los suelos derivados de residuos deben ser capaces de realizar funciones ambientales y productivas de modo similar a los suelos y, en todo caso, deben mejorar la situación precedente (Macías Vázquez et al., 2005, 2006, 2007). Parece lógico, por tanto, que estos suelos sólo se utilicen en situaciones de deterioro previo (contaminación o degradación) difícilmente reversible a escala humana, fuera de áreas consideradas de protección natural como, p.e. la Red Natura y que para garantizar la calidad ambiental no incorporen o sean mínimas las cantidades de residuos tóxicos y peligrosos que entran en su composición, si bien esto es matizable según los casos.

Las primeras experiencias de campo con suelos derivados de residuos fueron realizadas por Caínzos (2000), Soler (2001) y Naveira (2001), bajo la dirección de Manuel Bao y las determinaciones analíticas y el seguimiento ambiental posterior por miembros del Laboratorio de Edafología coordinados por Macías Vázquez. Los primeros ensayos se realizaron en terrenos de Resifor, en Bastavales, (municipio de Brión). Se ensayaron en caballones de aproximadamente un metro de altura, sobre un geotextil impermeable, 5 suelos derivados de residuos elaborados con arena de cuarzo, astillas de madera, serrines graníticos, lodos de depuradora, desechos de extracción de arcillas caoliníticas de Cavisa, concha de mejillón y cenizas de biomasa en diferentes proporciones, funcionando los cinco adecuadamente pero dando el mejor resultado tanto para el crecimiento de las plantas ensayadas (eucalipto, pino, cerezo, roble y vid) como para el crecimiento de especies espontáneas.

Se observó que los suelos derivados de residuos tenían un pH mucho más alto y mayores contenidos de Ca y Mg de cambio y P asimilable que los suelos de la zona, en su mayor parte derivados de rocas graníticas. En este sentido, los suelos derivados de residuos recuerdan a un material original en el sentido de que el pH de abrasión en los suelos de Galicia desciende de forma continuada hasta que alcanza el equilibrio con el tampón aluminio y, paralelo a este descenso, se produce la eliminación de las bases móviles y la inmovilización y pérdida de biodisponibilidad del P. Es decir, el suelo derivado de residuos se comporta como una roca alterable en su fase inicial, pero se presenta como un material suelto (similar a un sedimento no consolidado) que permite la penetración de las raíces y, además, presenta mayores contenidos de elementos biogénicos. Es decir, se parece a un material original sedimentario (suelto) rico en bases y fósforo disponible y moderadamente rico en elementos biogénicos.

La segunda experiencia se realizó en la mina Barquiña, Santa Cristina de Frecha, (municipio de Santiago de Compostela) en colaboración con Norfor y el Departamento Forestal de Lourizán, dirección de M. Bao y F. Macías Vázquez, y determinaciones analíticas efectuadas en el Departamento de Edafología de la Facultad de Biología, Universidad de Santiago de Compostela. La tercera experiencia se realizó en suelos de las escombreras de la mina Puentes, en colaboración del Servicio de Restauración de ENDESA, la empresa de gestión de residuos Xiloga y la dirección de M. Bao. En este caso se añadieron otros suelos derivados de residuos.

En todos los casos, el uso de materiales residuales para la preparación de “suelos derivados de residuos” conlleva una mejora en la eliminación de estos subproductos y aporta una posibilidad de reutilización frente a las alternativas de vertido o recuperación energética, y, también, frente a la depuración anaerobia y el compostaje. Al mismo tiempo, proporciona la posibilidad de regeneración de espacios degradados. Las ventajas económicas y ambientales que presentan este tipo de recuperación derivan de dos aspectos básicos:

(i) Los materiales residuales tienen un coste muy bajo y muchas veces el productor puede pagar por su recogida.

(ii) Las cantidades que se necesitan para elaborar suelos son relativamente altas. Así, una Ha de suelo con 30 cm de espesor eficiente de densidad en torno a 1 g/cm$^3$ requiere volúmenes de suelo del orden de 3.000 Tm, pero si tenemos en cuenta que la densidad de la mayor parte de los residuos suele ser más baja, el contenido de agua, las pérdidas por volatilización de compuestos gaseosos, etc., la cifra real se encuentra entre 5.000 y 10.000 Tm.

En cuanto a los beneficios ambientales y sociales pueden señalarse, entre otros, los siguientes: (i) Se contribuye a la recuperación de suelos degradados y/o contaminados mejorando el cumplimiento de sus principales funciones.

(ii) Se minimizan los residuos a llevar a vertedero o planta de tratamiento con la consiguiente disminución de la producción de gases de efecto invernadero.

(iii) Se minimiza el impacto negativo de los residuos integrándolos en los ciclos biogeoquímicos.

(iv) Se ahorran recursos naturales, en especial “tierra vegetal” para labores de recuperación o sellado de vertederos y otros espacios degradados.

(v) Se reduce drásticamente el alto coste de gestión de residuos minimizando el gasto energético para su tratamiento y eliminación y reduciendo las superficies destinadas a la contención y almacenamiento de residuos.

(vi) Se aprovechan más adecuadamente los nutrientes incorporándolos a la cadena trófica. Esto es especialmente importante en el caso de los residuos ricos en N, P, K, Mg, Ca,…, lo que reduce los costes en obtención y acondicionamiento de fertilizantes y enmendantes.

(vii) Los suelos derivados de residuos contribuyen al secuestro de carbono en suelos y en la biomasa que sostienen.

(viii) Incrementan la actividad biológica y la biodiversidad.

(ix) Se mejora el paisaje incrementando la superficie revegetada y protegida de la erosión.

(x) Se mejora la calidad de las aguas superficiales y freáticas.

(xi) Se reducen los riesgos de contaminación.

(xii) La elaboración de suelos derivados de residuos no produce nuevos residuos como las otras técnicas de gestión.

Por todo ello, los suelos artificiales, para muchos tipos de residuos, sustituyen de modo más eficiente a las alternativas tradicionales: vertido incontrolado, vertido controlado, procesos de inactivación e incineración, valorización y recuperación de materiales útiles, compostaje, etc. A los vertederos con mayor eficacia en la redistribución superficial de materia y energía biodisponible y la drástica reducción de los gases de efecto invernadero derivados de los residuos, lo mismo, aunque en menor medida se producen en la comparación con otros procesos de gestión de residuos por el mayor aprovechamiento de los nutrientes y enmendantes, el menor coste energético y la importante reducción en las emisiones de gases de efecto invernadero.

Por supuesto, estos beneficios sólo deberán ser aceptados si los procesos van acompañados de un estricto control de los posibles efectos negativos sobre los ecosistemas a corto, medio y largo plazo y sólo si son aplicados en las situaciones previstas y aprobadas por la Administración. En este sentido, el proceso de elaboración de suelos derivados de residuos supone cumplir con los criterios de gestión europeos al cumplirse la definición dada por la Ley para el proceso de "valorización": *Todo procedimiento que permite el aprovechamiento de los recursos contenidos en los residuos sin poner en peligro la salud humana y sin utilizar métodos que puedan causar perjuicios al medio ambiente.*

## 1.9. Bibliografía.

Abichou, T., Benson, C.H., Edil, T.B., Tawfiq, K., 2004. Hydraulic conductivity of foundry sands and their use as hydraulic barriers. In: Aydilek A.H., Wartman J. (Eds.), Recycled Materials in Geotechnics, Geotechnical Special Publication 127. ASCE, Baltimore, Maryland.

Adriano, D.C., Weber, J.T., 2001. Influence of fly ash on soil physical properties and turfgrass establishment. J. Environ. Qual. 30, 596-601.

Aitken, R.L., Bell, L.C., 1985. Plant uptake and phytotoxicity of Boron in Australian fly ashes. Plant Soil 84, 245–257.

American Coal Ash Association (ACAA). Corrected 2009 Coal Combustion Product (CCP) Production and Use Survey. 2009.

Amonette, J.E., Kim J., Russell, C.K., Palumbo, A.V., Daniels, W.L. 2003. Fly ash amendments catalyze soil carbon sequestration. Second Annual Conference on Carbon Sequestration, May 5-8.

Antoniadis, V., Tsadilas, C.D., Samarasb, V., 2010. Trace element availability in a sewage sludge-amended cotton grown Mediterranean soil. Chemosphere 80, 1308-1313.

Calvo de Anta, R., 2001. Influencia de diferentes especies forestales sobre las propiedades del suelo en Galicia.  En: XXII Reunión Nacional de la Sociedad Española de la Ciencia del Suelo. Universidad de Santiago de Compostela. 112-116 pp.

Calvo de Anta, R., Macías Vázquez, F. , Riveiro, A., 1992. Aptitud agronómica de los suelos de la provincia de La Coruña (Cultivos, pinos, robles, eucaliptos y castaños). Diputación Provincial. La Coruña.

Calvo de Anta, R., Macías Vázquez, F., 2001. XXII Reunión Nacional de La Sociedad Española de Ciencia del Suelo. Santiago de Compostela.

Capp, J.P., 1978. Power plant fly ash utilization for land reclamation in the eastern United States. In: Schaller, F.W., Sutton, P. (Eds.), Reclamation of Drastically Disturbed Lands. ASA, Madison, WI, pp. 339–353.

Cerevelli, S., Petruzzelli, G., Perna, A., Menicagli, R., 1986. Soil nitrogen and fly ash utilization: a laboratory investigation. Agrochemica 30, 27–33.

Ciccu, R., Ghiani, M., Peretti, R., Serci, A., Zucca, A., 2001. www.flyash.info/2001/mining1/06perret.pdf.

Clapp, C.E., Stark, S.A., Clay, D.E., Larson, W.E., 1986. Sewage sludge organic matter and soil properties. In: Chen, Y., Avnimelech, Y. (Eds.). The Role of

Organic Matter in Modern Agriculture. Martinus Nijhoff Publishers, Dordrecht. Netherlands, pp. 209-248.

Chang, A.C., Lund, L.J., Page, A.L., Warneke, J.E., 1977. Physical properties of fly ash amended soils. J. Environ. Qual. 6, 267– 270.

Charholm, M. 1994. Granulated wood ash and a N-free fertilizer to a forest soil-effects on P availability. Forest Ecol. Manag. 66, 127-136.

De María, I.C., Chiba, M.K., Costa, A., Berton R.S., 2010. Sewage sludge application to agricultural land as soil physical conditioner. Revista Brasileira de Ciencia do Solo 34, 967-974

Demeyer, A., Voundi Nkana, J.C., Verloo, M.G., 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. Bioresource Technol. 77, 287-295.

Dudal, R., Nachtergaele, F.O., Purnell, M.F., 2002. The human factor of soil formation. Symposium No. 18. 17th World Congress of Soil Science, Thailand.

ECOBA. European Coal Combustion Products Association e.V. Production and utilization of CCPs in Europe (EU 15) in 2003.

ECOBA. European Coal Combustion Products Association e.V. Production and utilization of CCPs in Europe (EU 15) in 2006.

EU, 2006. Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Thematic Strategy for Soil Protection plus Summary of the Impact Assessment. COM 231 (2006) final. Brussels. pp. 1-12; 1-8.

Fail Jr., J.L., Wochok, Z.S., 1977. Soyabean growth on fly ash amended strip mine spoils. Plant Soil 48, 473–484.

FAO/ISRIC/ISSS, 1998. World Reference Base for Soil Resources. www.fao.org/ag/agl/agll/wrb

Furr, A.K., Parkinson, T.F., Hinrichs, R.A., Van Campen, D.R., Bache, C.A., Gutenmann, W.H., St. John Jr., L.E., Pakkala, I.S., Lisk, D.J., 1977. National survey of elements and radioactivity in fly ashes. Absorption of elements by cabbage grown in fly ash soil mixtures. Environ. Sci. Technol. 11, 1194–1201.

Garau, M.A., Dalmau, J.L., Felipo, M.T., 1991. Nitrogen mineralization in soil amended with sewage sludge and fly ash. Biol. Fert. Soils 12, 199–201.

Garcia Arrese, A., Quintas, Y., Macías Vázquez, F., 1993. Aprovechamiento de lodos de distinto origen para la recuperación de escombreras de mina: ensayos de mineralización de nitrógeno en laboratorio. En: Ortiz, R. (Ed.) Problemática Geoambiental y Desarrollo Tomo I, pp. 335- 343.

Gil Bueno, A., Val Caballero, C., Macías Vázquez, F., Monterroso, C., 1990. Influence of waste selection in the dump reclamation at Puentes Mine. In: Reclamation, Treatment and Utilization of Coal Mining wastes. Rainbow (Ed.). pp. 203-208. Balkema. Rotterdam.

Guney, Y., Aydilek, A.H., Demirkan, M.M., 2006. Geoenvironmental behavior of foundry sand amended mixtures for highway subbases. Waste Manage. 26, 932-945.

Hansen, H.K., Pedersen, A.J., Ottosen, L.M., Villumsen, A., 2001. Speciation and mobility of cadmium in straw and wood combustion fly ash. Chemosphere 45, 123-128.

IUSS Working Group WRB. 2006. World Reference Base for Soil Resources – A Framework for International Classification, Correlation and Communication. World Soil Resources Reports No. 103. FAO, Rome, Italy.

Jala, S., Goyal, D., 2006. Fly ash as a soil ameliorant for improving crop production-a review. Bioresource Technol. 97, 1136-1147.

Khaleel, R., Reddy, K.R., Overcash, M.R., 1981. Changes in soil physical properties due to organic waste applications: a review. J. Environ. Qual. 10, 133-141.

Kuba, T., Tscholl, A., Partl, C., Meyer, K., Insam, H., 2008. Wood ash admixture to organic wastes improves compost and its performance. Agr. Ecosyst. Environ. 127, 43-49.

Lal, R. (Ed.), 2001. Soil Carbon Sequestration and the Greenhouse Effect. SSSA Special publication number 57.

Lal, R., 2004. Soil carbon sequestration impacts on global climate change and food security. Science 304, 1623-1627.

Macías Vázquez, F., Bao, M., Macías-García, F., Camps Arbestain, M., 2007. Valorización biogeoquímica de residuos por medio de la elaboración de Tecnosoles con diferentes aplicaciones ambientales. Aguas & Residuos 5, 12–25.

Macías Vázquez, F., 2001. Perspectivas de la aplicación de residuos orgánicos al suelo. Aplicación agrícola de residuos orgánicos: 5º Curso de Ingeniería Ambiental, Lleida 23-24-25 de abril de 2001, ISBN 84-8409-093-0, pp. 329-354.

Macías Vázquez, F., 2004. Recuperación de suelos degradados, reutilización de residuos y secuestro de carbono. Una alternativa integral de mejora de la calidad ambiental. Recursos Rurais, 1, 49-56.

Macías Vázquez, F., 2011. Communicación Personal.

Macías Vázquez, F., Bao, M., Macías-García, F., 2007. Valorización biogeoquímica de residuos por medio de la elaboración de Tecnosoles con diferentes aplicaciones ambientales. Agua Residuos 5,12–25.

Macías Vázquez, F., Camps Arbestain, M., 2010. Soil carbon sequestration in a changing global environment. Mitig. Adapt. Strateg. Glob. Change. DOI 10.1007/s11027-010-9231-4.

Macías Vázquez, F., Camps Arbestain, M., Rodríguez, L., Barreal, M.E., 2002. Soil sensitivity to acidification: an estimation based on the buffer mechanisms of different soils of the world. In: Faz, A., Ortiz, R., Mermut, A. (Eds.). Sustainable Use and Mangement of Soils in Arid and Semiarid Regions. Quaderna Editorial. 262-275. Murcia.

Macías Vázquez, F., Camps Arbestain, M., Rodríguez-Lado, L., 2005. Alternativas de secuestro de carbono orgánico en suelos y biomasa de Galicia. Recursos Rurais 1, 71-85.

Macías Vázquez, F., Camps Arbestain, M., Rodríguez-Lado, L., Barreal, M.E., 2002. Cargas críticas de contaminantes: Un criterio de evaluación de la sensibilidad de la naturaleza para la ordenación de las actividades humanas. En: Ramos, P., Márquez, M.C. (Eds.) Avances en Calidad Ambiental. 2002. 19-50.

Macías Vázquez, F., Fernandez de Landa, J.L.A., Calvo de Anta, R., 1991. Composición química y mineralógica de biodepósitos bajo bateas de mejillón. Datos para la evaluación de su uso como fertilizante y/o enmendante de suelos de Galicia. Thalassas, 9, pp. 23–29.

Macías Vázquez, F., Macías-García, F., Camps Arbestain, M., 2006. Compost y sistemas edáficos: Algunas consideraciones sobre su utilización. En: Aspectos Normativos, Tecnológicos y Medioambientales del Compostaje. Red Española de Compostaje. Valencia, pp.168-179.

Macías Vázquez, F., Saiz, J.L., Monterroso, C., 2001. Corrección de la acidez en suelos contaminados por actividades de minería pirítica. Aplicación práctica a la corrección de la acidez en los suelos de la ribera del Guadiamar afectados por el vertido tóxico provocado por la mina de Aznalcóllar. Congreso Forestal, Granada.

Macías-García, F., 2006. Elaboración de suelos derivados de residuos con diferentes aplicaciones ambientales. Trabajo de investigación tutelado. Universidad de Santiago de Compostela.

Matsi, T., Keramidas, V.Z., 1999. Fly ash application on two acid soils and its effect on soil salinity, pH, B, P and on ryegrass growth and composition. Environ. Pollut. 104, 107-112.

Ministerio de Medio Ambiente y Medio Rural y Marino. 2010. Anuario de Estadistica 2009.

Monterroso, C., 1995. Caracterización de los procesos edafogeoquímicos en una escombrera de lignitos en proceso de restauración ambiental. Tesis. Departamento de Edafología y Química Agrícola. Universidad de Santiago.

Monterroso, C., Macías Vázquez, F., Gil Bueno, A., Val Caballero, C., 1998. Evaluation of the land reclamation project at the As Pontes Mine (NW Spain) in relation to the suitability of the soil for plant growth. Land Degradation & Development. 9, 441-451.

Monterroso, M., Macías Vázquez, F., 1991. Utilización de ceniza como enmendante deescombreras ácidas de mina. V Encontro Galego-Portugués de Química, La Coruña, España.

Obernberger, I., 1998. Decentralized biomass combustion: state of the art and future developments. Biomass Bioenerg. 14, 33-56.

Page, A.L., Elseewi, A.A., Straughan, I.R., 1979. Physical and chemical properties of fly ash from coal-fired power plants with special reference to environmental impacts. Residue Rev. 71, 83–120.

Pinto, M., Rodringuez, M., Besga, G., Balcazar, N., Lopez, F.A., 1995. Effects of Linz-Donawitz (LD) slag on soil properties and pasture production in the Basque country (Nothern Spain). New Zeal. J. Agr. Res. 38, 143-155.

Pitchel, J.R., 1990. Microbial respiration in fly ash/sewage sludge amended soils. Environ. Pollut. 63, 225–237.

Pitchel, J.R., Hayes, J.M., 1990. Influence of fly ash on soil microbial activity and populations. J. Environ. Qual. 19, 593–597.

Power, J.F., Dick, W.A., 2000, “Land application of agricultural, industrial and municipal by-products”, SSSA Publ. Madison, WI.

Quintas, Y., Macías Vázquez, F., 1992. Datos para la recuperación de suelos de minas de Galicia: capacidad natural y alternativas de mejora. Cuaderno Lab. Xeolóxico de Laxe 17, 97-106.

Quintas, Y., Macías Vázquez, F., 1993. Recuperación de escombreras de minas de Galicia con biodepósitos de fondos marinos. En: Ortiz, R. (Ed.) Problemática Geoambiental y Desarrollo Tomo I, pp. 325-334.

Reynolds, K.A., Kruger, R.A., Rethman, N.F.G., 1999. The manufacture and evaluation of an artificial soil (SLASH) prepared from fly ash and sewage sludge. Fly Ash Utilization Symposium, Lexington, KY, USA.

Sajwan, K.S., Paramasivam, S., Alva, A.K., Adriano, D.C., Hooda, P.S., 2003. Assessing the feasibility of land application of fly ash, sewage sludge and their mixtures. Adv. Environ. Res. 8, 77-91.

Sajwan, K.S., Paramasivam, S., Alva, A.K., Sahi, S.V., 2006. Fly ash-organic byproduct mixture as soil amendment. In: Twardowska, I., Allen, H.E., Haggblom, M.M., Stefaniak, A. (Eds.) Soil and Water Pollution Monitoring, Protection and Remediation. Springer, Dordrecht, the Netherlands, pp. 387-399.

Sánchez, J., Recatalá, L., Colomer, J.C., Añó, C., 2001. Assessment of soil erosion at national level: a comparative analysis for Spain using several existing maps. In: Ecosystems and Sustainable Development III. Edited By: Y. VILLACAMPA ESTEVE, Universidad de Alicante, Spain and C. A. BREBBIA, Wessex Institute of Technology, United Kingdom and J-L. USO, Universitat Jaume I, Spain. Transaction: Ecology and the Environment volume 46. Transactions of the Wessex Institute.

Schumann, A.W., Sumner, M.E., 1999. Plant nutrient availability from mixtures of fly ashes and biosolids. J. Environ. Qual. 28, 1651-1657.

Su, D.C., Wong, J.W.C., 2002. The growth of corn seedlings in alkaline coal fly ash stabilized sewage sludge. Water Air Soil Poll. 133, 1-13.

Suhadolc, M., Schroll, R., Hagn, A., Dorfler, U., Schloter, M., Lobnik, F., 2010. Single application of sewage sludge – Impact on the quality of an alluvial agricultural soil. Chemosphere 81, 1536-1543.

Virgel Mentxaka, S., 2002. Efecto de la aplicación de escoria siderúrgica LD y fertilizante NPK en sistemas agrarios (Tesis Doctoral). Universidad de País Vasco.

Wong, J.W.C., Cheung, K.C., Wong, M.H., 2000. Environmental implication of soils amended with anaerobically digested sewage sludge in Hong Kong. Water Air Soil Poll. 124, 23-26.

Wong, J.W.C., Su, D.C., 1997a. Reutilization of coal fly-ash and sewage sludge as an artificial soil-mix: effects of preincubation on soil physico-chemical properties. Bioresource Technol. 59, 97-102.

Wong, J.W.C., Su, D.C., 1997b. The growth of agropyron elongatum in an artificial soil mix from coal fly ash and sewage sludge. Bioresource Technol. 59, 57-62.

Wong, M.H., Wong, J.W.C., 1986. Effects of fly ash on soil microbial activity. Environ. Pollut. A 40, 127–144.

# Chapter 2

# Influence of the acid buffering capacity of different types of Technosols on the chemistry of their leachates

This chapter has been published in:
Chemosphere 74: 250-258
(2009)

# Chapter 2. Influence of the acid buffering capacity of different types of Technosols on the chemistry of their leachates

## 2.1. Abstract

The preparation of tailor-made Technosols from wastes may be a novel and prospective option for the re-use of wastes and restoration of degraded areas. A two-month study with pilot columns was conducted to evaluate the influence of the acid buffering capacity of different Technosols on the chemistry of their leachates. The Technosols were made from mixtures of organic and inorganic wastes at a ratio of 56:44 (w/w). The organic components used were an anaerobic (AN) and an aerobic (AE) sewage sludge. The inorganic wastes used – referred to as “conditioners” – were Linz-Donawitz slag (LD) and foundry sand (FS). A mixture of the two conditioners at a ratio of 50:50 (w/w) was made to provide a third type of conditioner (LD + FS). Controls consisted of columns filled with organic waste only (either AN or AE sludges). Changes in pH, electrical conductivity, concentrations of major ions and dissolved organic carbon in the leachates were evaluated periodically. The main processes determining the pH of the systems were nitrification and leaching, but organic matter decomposition and carbonation may also have had an influence. Nitrification was strongly retarded in the AN sludge (attributed to the probable absence of nitrifiers in this waste after the AN wastewater treatment) and was impeded in those mixtures in which LD was used as a component (due to the liming effect). Final pH values ranged from 5.0 and 5.4 (in AE and AE + FS, respectively) to 11.1 (in AN + LD). The pH of the other mixtures finally ranged between 7 and 8. In formulating mixtures of wastes, their acid buffering capacity should be taken into account in addition to the nutrient contents and the limits of contaminants established by local regulations.

*Keywords*: Organic waste; Nitrification; Leaching; Carbonation; Bases; Carbonates.

## 2.2. Introduction

Sewage sludges produced by wastewater treatment plants constitute one of the most important types of organic wastes in developed countries. As a result of the application of European Directive 91/271/EEC many new treatment plants are being created and generation of sewage sludge is expected to increase sharply. Sewage sludges contain high levels of major plant nutrients (e.g., N and P) and are enriched in organic matter (OM) (Ferrier et al., 1996; Bramryd, 2002; Sajwan et al., 2006). Good quality sewage sludges are applied to agricultural land and have been shown to favour crop production and improve soil properties (Valiela et al., 1975; Basta, 1995; Debosza et al., 2002; Adegbidi et al., 2003). However, sludges may contain high levels of contaminants and pathogens that may adversely affect soil and groundwater quality, and may be toxic to plants (Sajwan et al., 2007) and lead to contamination of the food chain. Moreover, these wastes may become acidified as a result of proton release from decomposition of OM and nitrification reactions after their application to soils (Sajwan et al., 2006, 2007), when they are not sufficiently alkaline to counterbalance the acidity generated by the former processes (Lundin et al., 2004; Egiarte et al., 2005, 2006). This is of special concern when the wastes used may be acidified through oxidative processes (e.g., wastes that are rich in sulphides or easily oxidisable OM).

Sewage sludges are frequently blended with inorganic materials to impede soil acidification (Sajwan et al., 2003, 2006), reduce the availability of heavy metals and eliminate pathogens (Wong and Su, 1997a, 1997b; Reynolds et al., 1999; Schumann and Sumner, 1999; Su and Wong, 2002) and promote OM stabilisation (Macías Vázquez et al., 2007). This is largely consistent with the idea proposed by Macías Vázquez (2004), who suggested the formulation of tailor-made Technosols – soils whose properties and pedogenesis are dominated by their technical origin (IUSS Working Group WRB, 2006) – from mixtures of unconsolidated wastes, in order to improve on the characteristics of the individual components. In this process, the proportions of each component should be adjusted to provide an appropriate environment for the formation of a new soil, which should be suited to the pedoclimatic conditions and the type of soil in the area concerned. Environmental problems resulting from the use of these mixtures can be avoided if the characteristics of the materials employed are well known and adequate for such purposes.

The production of Technosols from mixtures of unconsolidated wastes thus presents on-going environmental challenges, as the behaviour of the soils and their evolution must be tested to ensure that the main soil functions (EU, 2006) are fulfilled. Within this framework, the aims of the present study were to evaluate the changes in the chemistry of the leachates eluting from Technosols made from mixtures of organic and inorganic wastes and to compare the leachates with those eluting from organic wastes alone. The main emphasis of the study was to investigate the influence of the different acid buffering capacity of the components, on the chemistry of these leachates. Knowledge of the acid buffering capacity of the tailor-made Technosols is of special interest when the final use of these products is to restore hyper-acid systems, such as sulphide and lignite mine areas. The organic components used were an anaerobic (AN) and an aerobic (AE) sludge. The inorganic wastes used – referred to as "conditioners" – were Linz-Donawitz slag (LD) and foundry sand (FS). These inorganic wastes mainly differ in their liming capacity, as LD has a high content of $Ca(OH)_2$, whereas FS mainly consists of silica sand and smectite (Camps Arbestain et al., 2008).

## 2.3. Materials and methods

### *2.3.1. Components of the Technosols*

Two municipal sewage sludges were used in this column study: (i) a dewatered AN digested sludge from the wastewater treatment plant in Vigo (Galicia, NW Spain), and (ii) an AE sludge that had undergone physicochemical treatment at the wastewater treatment plant in A Estrada (Galicia, NW Spain). The green FS produced from steel foundries was provided by INASMET (Basque Country, N Spain). The LD was obtained from a steel production plant (ACERALIA, ARCELOR group) in Avilés (Asturias, NW Spain). The main chemical characteristics of the materials used in this study are presented in Table 2.1, and the mineralogy and particle-size distribution of the $\leq$2 mm fraction of the two conditioners (FS and LD) are shown in Table 2.2.

### *2.3.2. Experimental design*

The sludges (AN and AE) were air-dried and passed through a 4 mm sieve, and the conditioners (FS and LD) were passed through a 2 mm sieve before use. The sludges and the conditioners were mixed at a ratio of 56:44 (w/w). The conditioners were added either as single amendments or as mixture of the two (50:50 w/w). As a result, there were eight mixtures, including the two controls: AE, AE + FS, AE + LD, AE + FS + LD, AN, AN + FS, AN + LD, and AN + FS + LD. Three replicates per mixture were used.

**Table 2.1** Chemical characterisation of the wastes used as components.

| | **Aerobic sludge** | **Anaerobic sludge** | **Green foundry sand** | **LD slag** |
|---|---|---|---|---|
| pH | 6.7 | 7.9 | 9.6 | 12.1 |
| Organic C (g kg$^{-1}$) | 354 | 275 | 10 | 21 |
| Inorganic C (g kg$^{-1}$) | - | - | 1.5 | 31.7 |
| TN (g kg$^{-1}$) | 59 | 36 | - | - |
| TP (g kg$^{-1}$) | 1.86 | 1.52 | 0.17 | 1.14 |
| Fe (g kg$^{-1}$) | 8.9 | 18.5 | 6.2 | 135.3 |
| TAl (g kg$^{-1}$) | 20.6 | 37.6 | 0.5 | 0.2 |
| TS (g kg$^{-1}$) | 1.3 | 1.3 | 0.1 | 0.5 |
| TK (g kg$^{-1}$) | 4.9 | 2.9 | 0.85 | 0.1 |
| TMg (mg kg$^{-1}$) | 4.5 | 5.1 | 2.4 | 7.7 |
| TCa (mg kg$^{-1}$) | 684 | 1084 | 1.8 | 292 |
| TCd (mg kg$^{-1}$) | 0.7 | 1.2 | 1 | 3 |
| TCu (mg kg$^{-1}$) | 460 | 745 | 31 | 14 |
| TNi (mg kg$^{-1}$) | 31 | 58 | 86 | 20 |
| TPb (mg kg$^{-1}$) | 86 | 291 | 15 | 47 |
| TZn (mg kg$^{-1}$) | 740 | 1470 | 122 | 33 |
| TCr (mg kg$^{-1}$) | 28 | 89 | 233 | 468 |
| THg (mg kg$^{-1}$) | 1.6 | 2.9 | 0.06 | 0.06 |

**Table 2.2** Mineralogy and particle-size distribution of the ≤2 mm fraction of the conditioners used in the experiment.

| **Wastes** | **Mineralogy** | **Coarse sand (%)** | **Fine sand (%)** | **Silt (%)** | **Clay (%)** |
|---|---|---|---|---|---|
| Green foundry sand | Quartz ($SiO_2$); Microcline ($KAlSi_3O_8$); Smectite ($Na_x(Al,Mg)_2Si_4O_{10}(OH)_2$-$zH_2O$) | 24.8 | 46.3 | 8.5 | 20.4 |
| LD slag | Wustite (FeO); Portlandite ($Ca(OH)_2$); Calcite ($CaCO_3$); Lamite ($Ca_2SiO_4$); Aragonite ($CaCO_3$) | 44.8 | 35.9 | 16.5 | 2.9 |

**Table 2.3** Initial dry weight (DW) of the wastes used in the columns and water content at field capacity, grouped by treatments.

| **Treatment** | **Mean DW of each column (g)** | **DW sludge (g)** | **DW FS (g)** | **DW LD (g)** | **Water content at field capacity (%)** |
|---|---|---|---|---|---|
| AE | 48.9 | 48.9 | 0.0 | 0.0 | 108 |
| AE + FS | 85.7 | 48.0 | 37.7 | 0.0 | 136 |
| AE + LD | 105.6 | 59.1 | 0.0 | 46.5 | 97 |
| AE + FS + LD | 86.1 | 48.1 | 19.0 | 19.0 | 74 |
| AN | 77.0 | 77.0 | 0.0 | 0.0 | 98 |
| AN + FS | 99.0 | 55.5 | 43.5 | 0.0 | 87 |
| AN + LD | 136.0 | 76.2 | 0.0 | 59.8 | 52 |
| AN + FS + LD | 112.8 | 63.2 | 24.8 | 24.8 | 77 |

The mixtures and the controls were moistened to field capacity (Table 2.3) before adding them to the pilot columns. Twenty four polypropylene columns (4.5 cm wide and 14 cm long) were manually packed with the corresponding mixtures/controls for each treatment, to a total volume of 222.7 mL, leaving 1 cm headspace on the top of the columns. The amount of dry mass of each mixture is indicated in Table 2.3.

As shown in Fig 2.1, a fibreglass panel (0.5 cm thick) was placed underneath each column, under which there was a layer of polypropylene (0.75 cm thick), which had been previously perforated with 12 holes of 0.45 cm diameter each and 1 hole of 1 cm diameter, to allow drainage. Another layer of fibreglass (0.5 cm thick) was placed underneath this. The top of the columns were covered with a layer of fibreglass (0.5 cm thick) to facilitate uniform flow of the deionised water added to the columns. The columns were closed with polypropylene screw caps in which there was a hole through which the columns were watered.

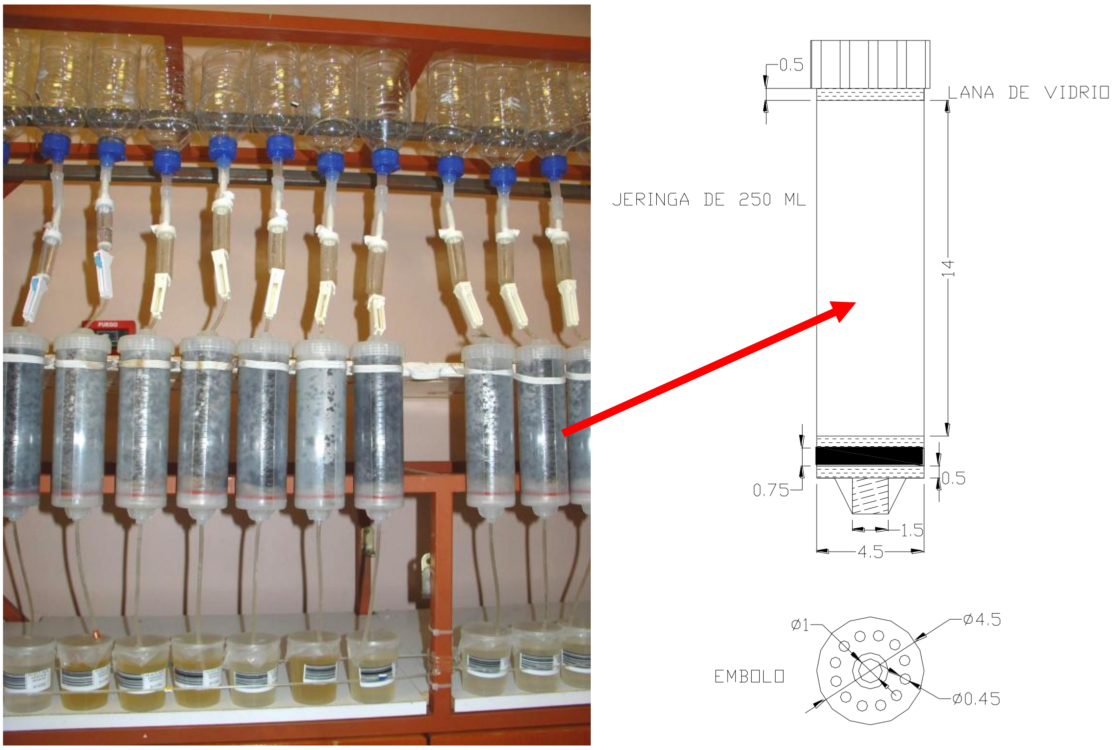


**Fig. 2.1.** Assembling of the leaching system and schematic diagram of the leaching column.

Aluminium foil was used to protect the columns from light. During the 8-wk experimental period, the columns were watered with 100 mL of deionised water twice a week, by use of individual top fill feeding canisters with a preattached delivery gravity setting. This amount of water was calculated by assuming an annual rainfall of 1000 L $m^{-2}$, concentrated in two months. Leachates were collected in polyethylene bottles and stored at ≤4 °C before analysis.

### *2.3.3. Analytical determinations*

Ammonium was determined following the methodology described by Kandeler and Gerber (1988), $PO_4^{3-}$ by the molybdenum blue colorimetric method (Murphy and Riley, 1962), and $SO_4^{2-}$ and $Cl^-$ following the methodologies described by Hoeft et al. (1973) and Zall et al. (1956), respectively, with a UVIKON 930 spectrophotometer (Kontron Instruments, Milan, Italy); Dissolved organic carbon (DOC) was determined by the Walkley-Black method and $NO_3^-$ was determined with a Flowsys – Third generation continuous flow analyzer (SYSTEA, s.r.l., Rome, Italy). The metal elements $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$ were determined with a ICP (Inductively Coupled Plasma) (Varian Ibérica S.L., Barcelona, Spain). Aluminium was determined with a DU730 UV/Vis Spectrophotometer (Beckman Coulter). The pH and the electrical conductivity (EC) of the leachates were also determined at each sampling time.

The acid buffering capacity of the four components was calculated by determining the pH of the suspensions after adding various amount of acid to the wastes (the amount of acid added to FS was one tenth of the amounts used for the organic wastes, while for LD it was five times these amounts) and equilibrating for 48 h, following the methodology described by Hartikainen (1992).

All the above mentioned chemical determinations were carried out, although some results were not reported here. Carbonate, $HCO_3^-$, and $CO_3^{2-}$ species were estimated with the USGS aqueous modelling software PHREEQC. This programme uses the mass balance and electro-neutrality equations to simulate geochemical reactions, such as mixing of water, addition of net irreversible reactions to solution, dissolving and precipitation phases to achieve equilibrium with the aqueous phase (Parkhurst and Appelo, 1999). Another geochemical model – VMINTEQ (Visual MINTEQ) ver 2.53, a Windows version of MINTEQA2 ver 4.0, was also used (Gustafsson, 2007). MINTEQA2 is a geochemical equilibrium speciation model for dilute aqueous systems, in which complexation of metals by DOC was incorporated (Allison et al., 1991).

### *2.3.4. Statistical analysis*

To assess the statistical differences among physicochemical properties of different Technosols and their leachates, a one-way analysis of variance followed by a *post hoc* (Bonferroni) multiple comparison test (significance level at 0.05) was computed with StatView 5.0.1 for Windows (SAS Institute Inc.). Mean separation was also carried out with a Student's *t*-test.

## 2.4. Results

### *2.4.1. Acid buffering capacity of the components*

The effect of increasing the acid load on the pH of the suspensions made with the components is shown in Fig. 2.2. Hartikainen (1992) defined acid buffering capacity as the reciprocal of the slope of the titration graph standards, that is, the meq of $H^+$ that must be added to 1 kg of substrate to lower pH by one unit. The acid buffering capacity of the components were 370, 312, and 29 meq $kg^{-1}$ for AE, AN, and FS, respectively. For LD, there was strong buffering effect above pH 11; thereafter the pH decreased gradually to pH < 2 after the addition of an amount of acid that was four times higher than the amount of acid added to the sewage sludges.

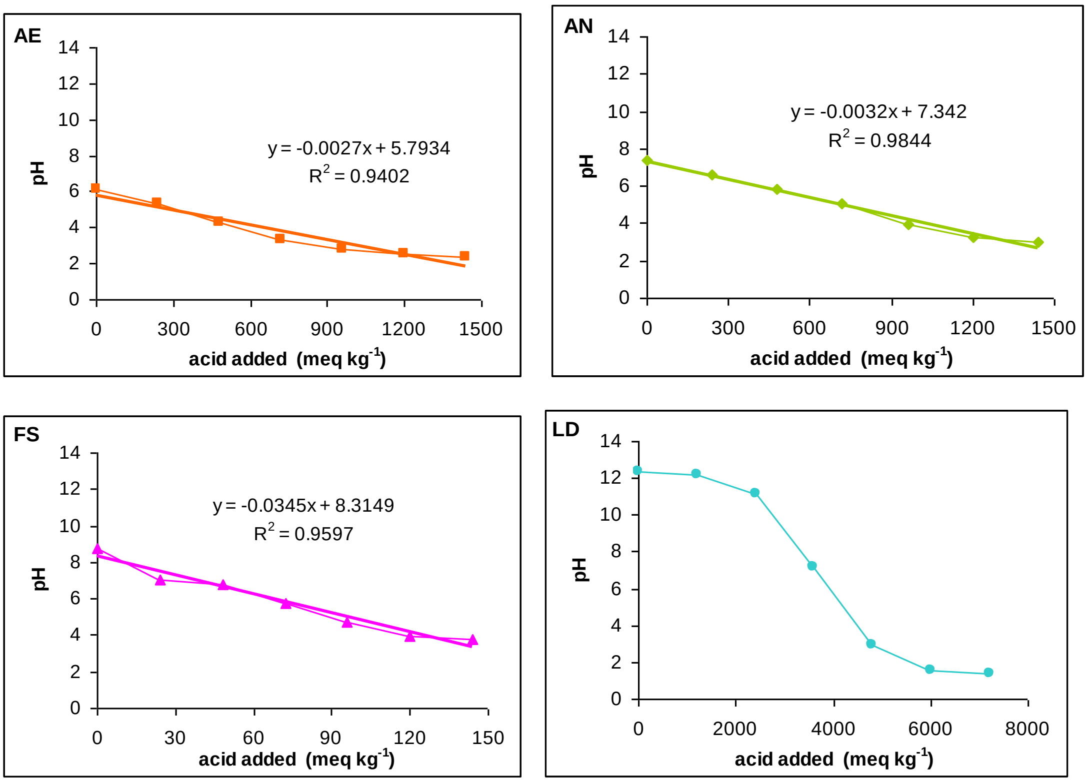


**Fig. 2.2.** Acid buffering capacity of the four components.

### *2.4.2. Chemical characteristics of the leachates throughout the experiment*

#### *2.4.2.1. Changes in pH*

For both controls (AE and AN) and mixtures made with FS only (AE + FS and AN + FS), the initial pH values were ~6.4 and remained below 8.0 during the entire experimental period (Fig. 2.3a and b). During the first 20 d, the changes in pH in these four mixtures were similar, and increased slightly (up to 7.9). Thereafter, the pH values of AE and AE + FS decreased sharply, reaching final values of 5.0 and 5.4, respectively (Fig. 2.3a). These were significantly lower ($P < 0.05$) than the corresponding initial values. For AN and AN + FS, a slight decrease in pH was observed during the same time period, and final values of, respectively, 7.0 and 6.7 were reached (Fig. 2.3b). However, compared to their initial pH, there was an increase of about 0.5 pH unit.

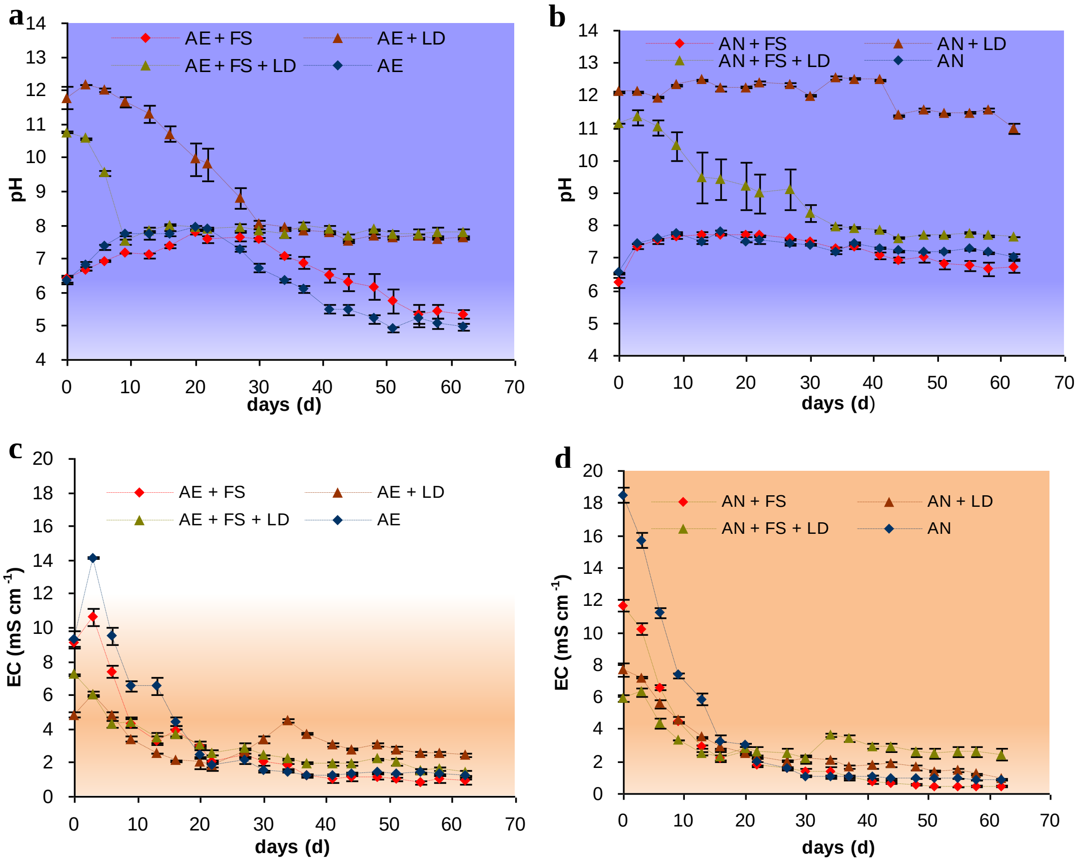


**Fig. 2.3.** Evolution of pH and EC in the leachates from Technosols with different compositions.

The initial pH values of all mixtures made with LD were extremely high (>10) (Fig. 2.3a and b). The mixtures with LD added as a single conditioner had initial pH values (11.8 and 12.1 for AE + LD and AN + LD, respectively) 1.0 unit higher than the pH of the FS + LD mixtures (Fig. 2.3a and b). The pH values of the AE + LD mixture decreased to 8.1 during the first month of experiment and fluctuated between 7.6 and 8.0 during the second month (Fig. 2.3a). For the AE + FS + LD mixture, the pH decreased sharply during the first 9 d and then remained at a pH value ~7.6 in the following days (Fig. 2.3a). In the AN + LD mixture, there was only a gradual decrease (of 1.0 unit) in the pH during the entire experimental period (Fig. 2.3b). This contrasted with the behaviour of the AN + FS + LD mixture, in which the pH values experienced a decrease of 2.8 units during the first month, and oscillated thereafter between 7.6 and 8.0 (Fig. 2.3b).

### *2.4.2.2 Changes in EC*

The initial EC value of the AN control was almost double that of the AE control, with values of 18.5 and 9.3 mS $cm^{-1}$, respectively (Fig. 2.3c and d). However, differences between the EC values of the two sludges were rapidly reduced as the leaching process proceeded. The EC values of the AN control decreased dramatically during the first 22 d, and there was a more gradual decrease thereafter, with a final value of 0.8 mS $cm^{-1}$ being reached (Fig. 2.3d). EC values in the AE control showed a small peak at day 3 (14.1 mS $cm^{-1}$) and thereafter decreased in parallel with the AN control, with a final value of 1.2 mS $cm^{-1}$ (Fig. 2.3c). The trends in changes of the EC values of the mixtures made with the FS conditioner only (AE + FS and AN + FS) were very similar to those in the corresponding controls, except that they were lower, especially during the first two weeks of the experiment in which the differences were significant at $P < 0.05$ (Fig. 2.3c and d).

The initial EC values of the all mixtures made with LD conditioner (range between 4.8 and 7.6 mS $cm^{-1}$) were significantly lower ($P < 0.05$) than in the mixtures that did not contain this conditioner (Fig. 2.3c and d). There was a general gradual decrease from the initial day until the end of the experiment, and values ranging between 0.9 and 2.4 mS $cm^{-1}$ were reached (Fig. 2.3c and d). The AE + LD and AN + FS + LD mixtures showed a small peak in EC between day 22 and day 34, which then remained significantly higher ($P < 0.05$) than in the other AE and AN treatments until the end of the experiment (Fig. 2.3c).

### *2.4.2.3. Changes in concentrations of DOC*

The initial concentrations of DOC in the different mixtures differed widely (Fig. 2.4a and b), and ranged from 5.6 to 10.6 g L$^{-1}$ for both types of sludges (Fig. 2.4a and b). During the first 9 d of experiment, DOC concentrations decreased sharply, although a peak at day 3 was detected for AE, AN + LD and AN + FS + LD (Fig. 2.4a and b). From day 9 to 30, the decrease in DOC concentration was more gradual, and from then on the concentration was very low, and fell to below the detection limit after day 51. For the mixtures containing AE sludge, the DOC concentrations in AE + LD were significantly higher ($P < 0.05$) than in the rest of these mixtures (Fig. 2.4a). In the mixtures containing AN sludge, the DOC concentrations were significantly lower ($P < 0.05$) in AN + FS than in the rest of these mixtures (Fig. 2.4b).

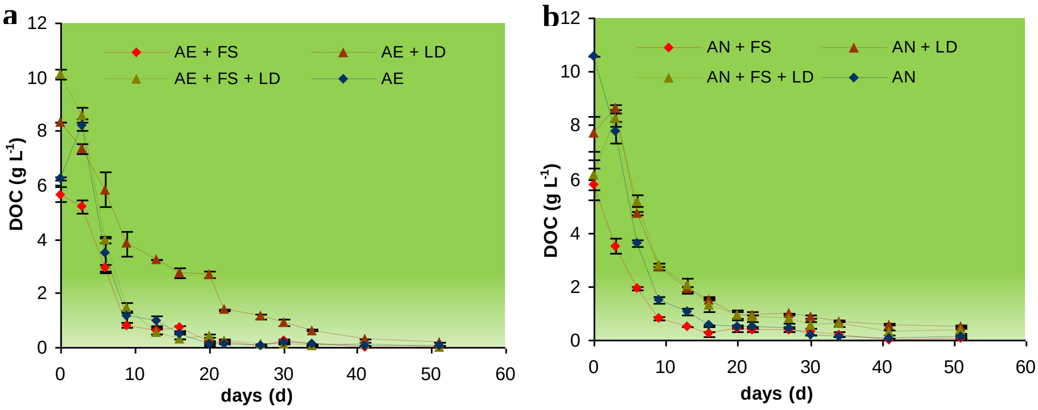


**Fig. 2.4.** Evolution of DOC in the leachates from Technosols with different compositions.

### *2.4.2.4. Changes in concentrations of $NO_3^-$*

Concentrations of $NO_3^-$ in all mixtures containing AE were very low during the first two weeks (Fig. 2.5a). Maximum concentrations were reached in AE and AE + FS on day 27 (758 and 445 mg L$^{-1}$, respectively), and fluctuated thereafter, with final concentrations of 502 mg L$^{-1}$ and 341 mg L$^{-1}$, respectively. The limits established in Spanish Royal Decree 1138/1990 for drinking water standards for $NO_3^-$ (50 mg L$^{-1}$) were thus exceeded in these two treatments. In the AE + FS + LD mixture, the concentrations of $NO_3^-$ did not peak until the last week of the experiment, although at much lower values than the AE control (389 mg L$^{-1}$). In the AE + LD mixture, $NO_3^-$ concentrations began to rise only at the end of the experiment, up to 107 mg L$^{-1}$. In all mixtures containing AN, concentrations of $NO_3^-$ were very low until the end of the experimental period (Fig. 2.5b).

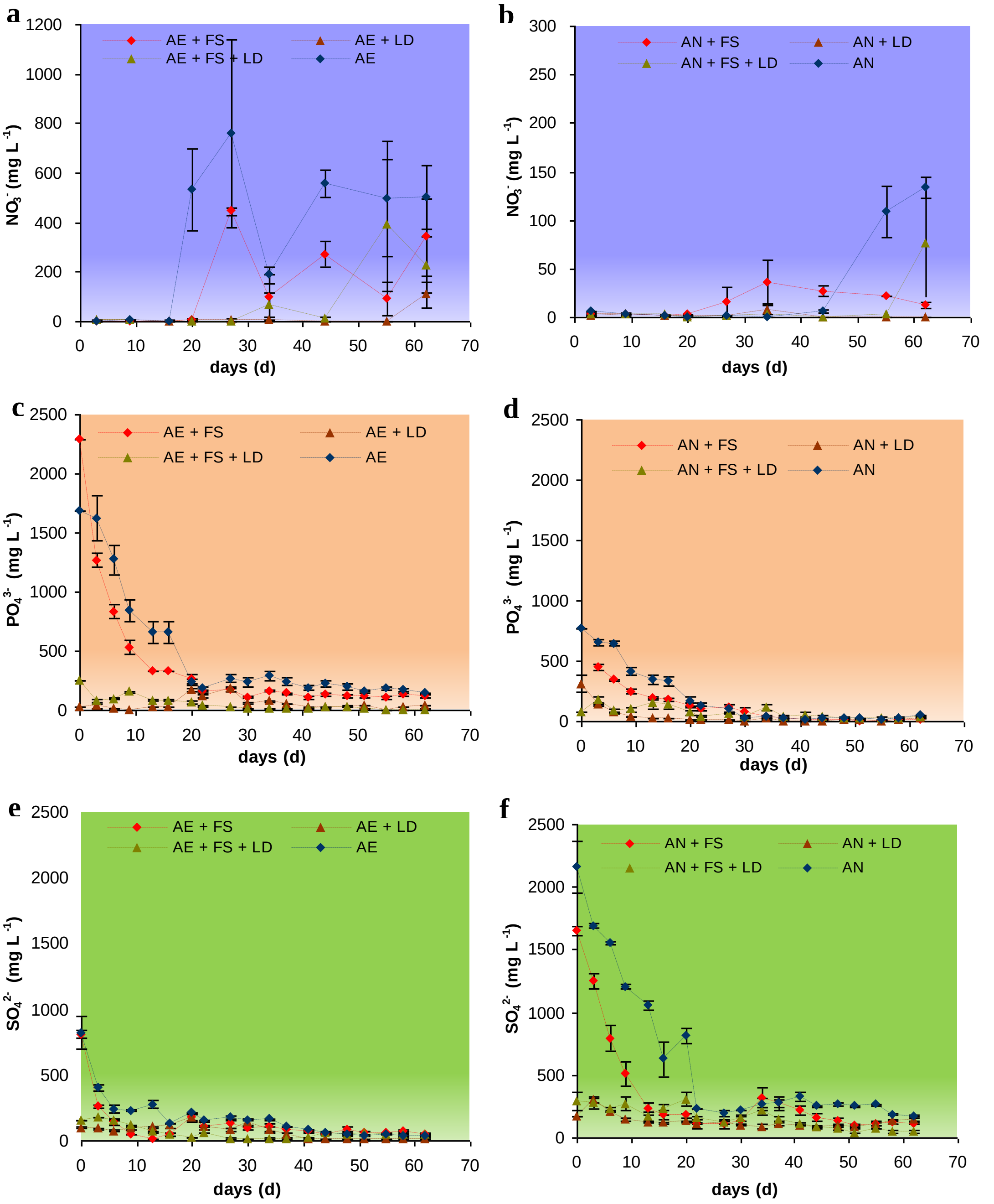


**Fig. 2.5.** Evolution of $NO_3^-$, $PO_4^{3-}$, and $SO_4^{2-}$ in the leachates from Technosols with different compositions.

### *2.4.2.5. Changes in concentrations of phosphate*

The initial concentrations of phosphate in AE and AE + FS (1689 and 2284 mg $L^{-1}$, respectively) (Fig. 2.5c) were significantly higher ($P < 0.05$) than in AN and AN + FS (768 and 452 mg $L^{-1}$; the latter value corresponds to the second sampling time)

(Fig. 2.5d). Speciation calculations indicated that the main species of phosphate in these four Technosols were $H_2PO_4^-$ and $HPO_4^{2-}$ (Table 2.4). During the first 22 d of experiment, phosphate concentrations in these four mixtures were significantly higher ($P < 0.05$) than in mixtures containing LD (Fig. 2.5c and d). In the latter, $CaPO_4^-$ was the dominant phosphate species, as inferred from the PHREEQC programme (Table 2.4).

**Tabla 2.4** Percentage of each species of phosphate in the leachates of all treatments.

| | **main phosphate species** | | | |
|---|---|---|---|---|
| **treatment** | **$H_2PO_4^-$** | **$HPO_4^{2-}$** | **$PO_4^{3-}$** | **$CaPO_4^-$** |
| AE | 69.2% | 25.0% | 0.0% | 0.0% |
| AE + FS | 66.3% | 26.7% | 0.0% | 0.0% |
| AE + LD | 0.0% | 1.4% | 1.5% | 96.9% |
| AE + FS + LD | 0.0% | 9.9% | 1.0% | 88.0% |
| AN | 53.5% | 32.8% | 0.0% | 0.0% |
| AN + FS | 74.1% | 19.8% | 0.0% | 0.0% |
| AN + LD | 0.0% | 0.3% | 0.8% | 98.9% |
| AN + FS + LD | 0.0% | 2.0% | 0.5% | 97.2% |

During this period, phosphate concentrations in AE, AE + FS, AN and AN + FS decreased sharply to values between 100 and 200 mg $L^{-1}$ (Fig. 2.5c and d). Thereafter, concentrations of phosphate in AE and AE + FS fluctuated at around 150 mg $L^{-1}$ (Fig. 2.5c), whereas those in AN and AN + FS fluctuated around 50 mg $L^{-1}$ (Fig. 2.5d), with the former being significantly higher ($P < 0.05$) than the latter. In the treatments containing LD, concentrations of phosphate were seldom higher than 150 mg $L^{-1}$ during the entire experimental period (Fig. 2.5c and d)

### *2.4.2.6. Changes in concentrations of $SO_4^{2-}$*

In contrast to phosphate, the initial concentrations of $SO_4^{2-}$ in mixtures containing AE (820 and 811 mg $L^{-1}$ in AE and AE + FS, respectively) (Fig. 2.5e) were significantly lower ($P < 0.05$) than in mixtures containing AN (2161 and 1647 mg $L^{-1}$ in AN and AN + FS, respectively) (Fig. 2.5f). With the leaching process, concentrations of $SO_4^{2-}$ in all of these mixtures decreased sharply, and reached values ranging between 95 and 220 mg $L^{-1}$ at the end of the first month. Thereafter, concentrations of $SO_4^{2-}$ were low, especially in AE and AE + FS (differences significant at $P < 0.05$), in which final concentrations as low as 30 mg $L^{-1}$ were obtained. In the mixtures containing LD, the initial concentrations of $SO_4^{2-}$ were significantly lower ($P < 0.05$) than in mixtures that did not contain this waste product, with values that ranged between 100 and 291 mg $L^{-1}$. Thereafter, concentrations oscillated between 37 and 307 mg L$^{-1}$ in the LD amended AN sludge and between 7 and 182 mg L$^{-1}$ in the corresponding AE + LD mixture.

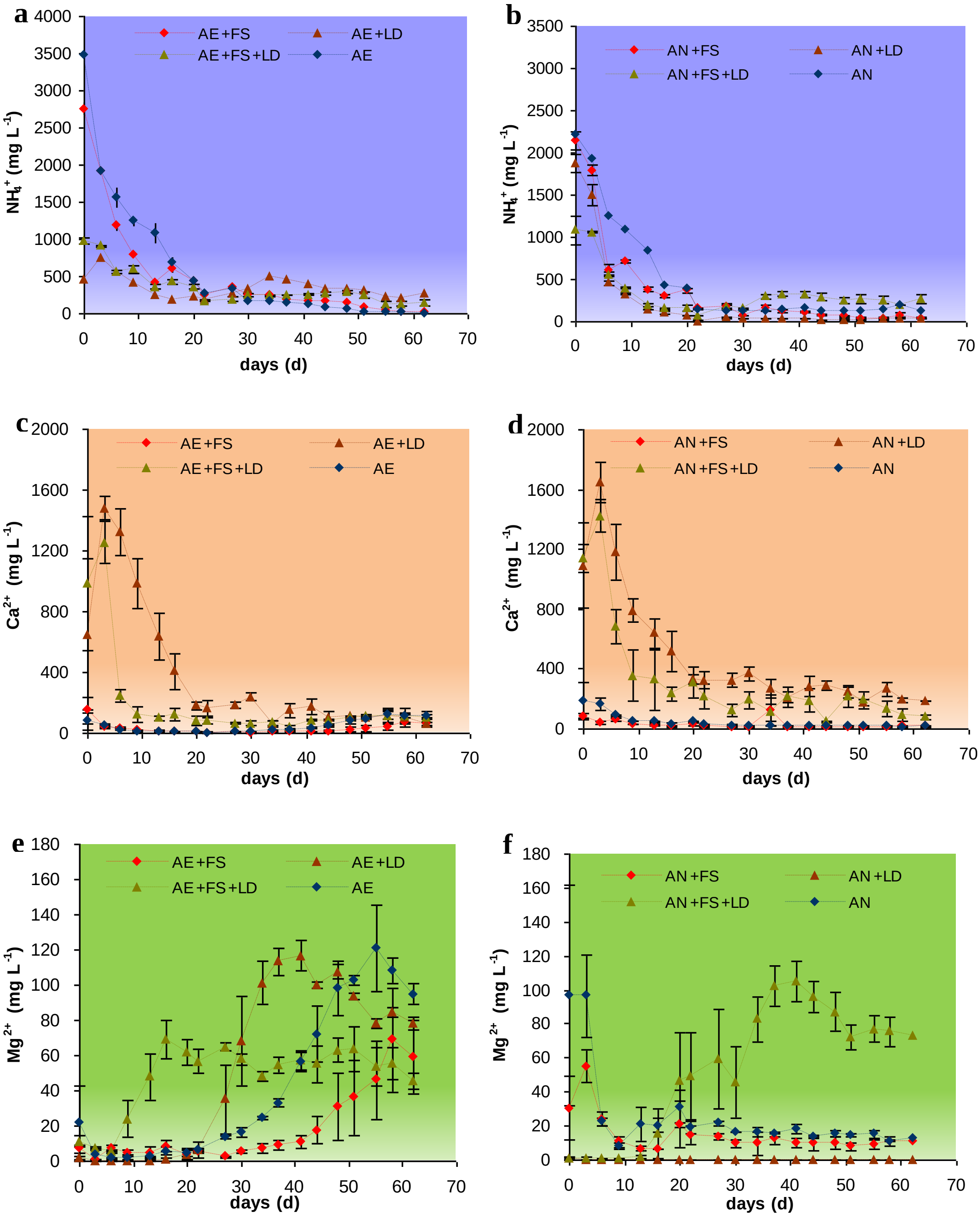


**Fig. 2.6.** Evolution of $NH_4^+$, $Ca^{2+}$ and $Mg^{2+}$ in the leachates from Technosols with different compositions.

### 2.4.2.7. *Changes in concentrations of $NH_4^+$*

The initial concentrations of $NH_4^+$ in AE and AE + FS (3480 and 2759 mg L$^{-1}$, respectively) were significantly higher ($P < 0.05$) than in AN and AN + FS (2219 and 2145 mg L$^{-1}$) (Fig. 2.6a and b). Moreover, during the first 22 d of experiment, the concentrations of $NH_4^+$ in these four mixtures were significantly higher ($P < 0.05$) than in mixtures containing LD as a component. During this period, concentrations of $NH_4^+$ in all mixtures decreased sharply to concentrations of between 7 and 267 mg $L^{-1}$. During the last 40 d, concentrations $NH_4^+$ in all mixtures, except AE + LD and AN + FS + LD, remained very low. For the latter two mixtures there was a slight increase in concentrations of $NH_4^+$ from day 34, as occurred for EC values, which were maintained until the end of the experiment. The differences were significant at $P < 0.05$.

### *2.4.2.8. Changes in concentrations of $Ca^{2+}$*

The changing trends in concentrations of $Ca^{2+}$ can be grouped into two sets: (i) one followed by the mixtures in which LD was used as a component, and (ii) another followed by the mixtures that did not contain LD (Fig. 2.6c and d). The initial concentrations of $Ca^{2+}$ in the first group (ranging between 643 and 1143 mg $L^{-1}$) were significantly higher ($P < 0.05$) than those of the second group (ranging between 87 and 186 mg $L^{-1}$). Moreover, in the first group, all treatments peaked on day 3, with a value of 1649 mg $L^{-1}$. In the second group, which was constituted by the two controls and the mixtures with FS as single conditioner, concentrations were always below 200 mg $L^{-1}$ during the entire experimental period.

### *2.4.2.9. Changes in concentrations of $Mg^{2+}$*

The initial concentrations of $Mg^{2+}$ in AN and AN + FS (97 and 31 mg $L^{-1}$, respectively) were significantly higher ($P < 0.05$) (Fig. 2.6f) than in AE and AE + FS (22 and 7 mg $L^{-1}$, respectively) (Fig. 2.6e). The initial concentrations of $Mg^{2+}$ were lower than 11 mg $L^{-1}$ in all mixtures containing LD (Fig. 2.6e and f). Thereafter, changes in concentrations of $Mg^{2+}$ were closely related to changes in pH (Fig. 2.3a and b), as discussed further below.

Concentrations of $Mg^{2+}$ in AE + FS + LD began to increase on day 9, and reached a maximum value of 69 mg $L^{-1}$ on day 16 and fluctuated between 45 and 65 mg $L^{-1}$ until the end of the experiment (Fig. 2.6e). The corresponding concentrations in AE + LD began to increase by day 20, reaching a maximum value of 117 mg $L^{-1}$ on day 41, and thereafter decreased slowly to a final value of 78 mg $L^{-1}$ (Fig. 2.6e). Concentrations of $Mg^{2+}$ in AE also began to increase by day 20, but at a slower rate than in AE + LD, and peaked on day 55 with a concentration of 121 mg $L^{-1}$ (Fig.

2.4e). Finally, the concentration in AE + FS began to increase slowly by day 30, and peaked on day 58 with a concentration of 69 mg $L^{-1}$ (Fig. 2.6e).

As regards the AN sludge, only the mixture with FS + LD showed a considerable increase in concentrations of $Mg^{2+}$ (Fig. 2.6f), with a peak of 105 mg $L^{-1}$ on day 41. For AN and AN + FS, after the sharp decrease detected at the end of the first week, concentrations of $Mg^{2+}$ increased slightly (on day 20, with values of 32 and 21 mg $L^{-1}$, respectively), and thereafter remained relatively constant, fluctuating around 8 and 22 mg $L^{-1}$. Finally, concentrations of $Mg^{2+}$ in AN + LD remained very low, with values always <1 mg $L^{-1}$.

### *2.4.2.10. Changes in concentrations of other ions ($K^+$, $Na^+$, $Cl^-$)*

The patterns of changes in concentration of these ions were very similar, i.e., a sharp decrease as the leaching process proceeded – especially in the first 20 d – followed by a slight decrease, and concentrations around the detection limit were finally reached (Fig. 2.7). These ions mainly differed in their initial contents, which were in turn influenced by the composition of each of the components and the mixture ratios, as expected. Generally, the initial concentrations of $K^+$ in AE mixtures (ranging from 495 to 610 mg $L^{-1}$) were significantly higher ($P < 0.05$) than in the AN mixtures (ranging from 178 to 433 mg $L^{-1}$), while the initial concentrations of $Na^+$ in AN mixtures (ranging from 736 to 251 mg $L^{-1}$) were higher than in the AE mixtures (ranging from 469 to 129 mg $L^{-1}$). Initial concentrations of $Cl^-$ in the AN mixtures were 6-18 times higher than in the AE mixtures.

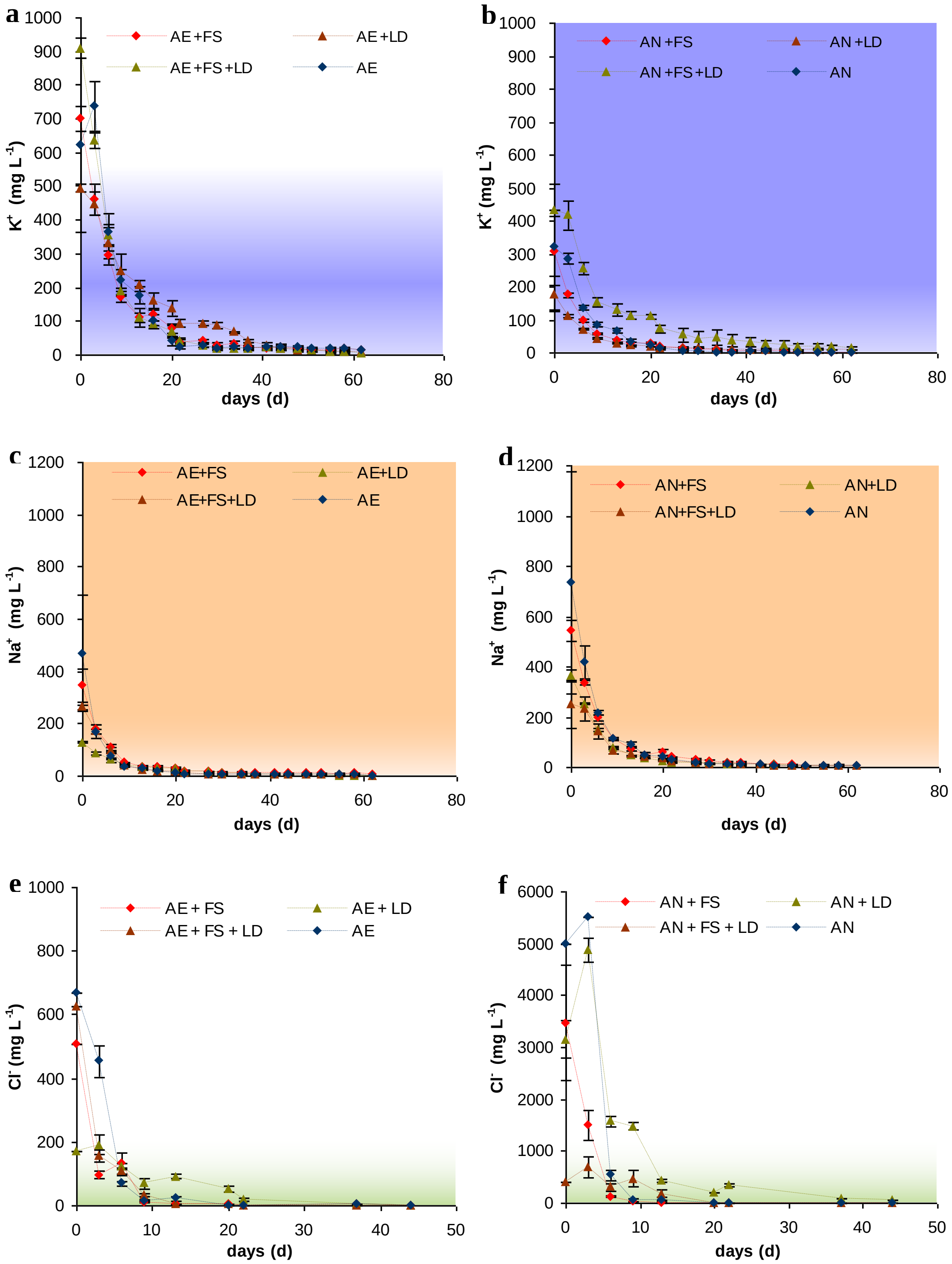


**Fig. 2.7.** Evolution of $K^+$, $Na^+$ and $Cl^-$ in the leachates from Technosols with different compositions.

## 2.5. Discussion

### *2.5.1. Acid buffering capacity of the components*

On the basis of the pH values attained after acidifying the different wastes, it can be inferred that the main buffer system acting in the two organic wastes was probably that of the carbonates; concentrations of $CO_3^{2-}$, $HCO_3^-$ and $H_2CO_3$ species in solution estimated by use of the PHREEQC programme further corroborated this point (Table 2.5); the concentration of Al in the leachates indicated that there was no release of Al during the leaching process (Table 2.6), and thus, the Al buffer did not make contribution.

**Table 2.5** Percentage of each species of inorganic carbon in the leachates of all treatments.

| Treatments | $H_2CO_3$ (%) | $HCO_3^-$ (%) | $CO_3^{2-}$ (%) | $CaCO_3$ (%) | $CaHCO_3^+$ (%) |
|---|---|---|---|---|---|
| AE | 42.3 | 56.7 | 0.0 | 0.0 | 0.4 |
| AE + FS | 38.7 | 60.0 | 0.0 | 0.0 | 0.8 |
| AE + LD | 0.0 | 0.4 | 72.2 | 26.4 | 0.0 |
| AE + FS + LD | 0.0 | 11.1 | 73.1 | 12.2 | 0.1 |
| AN | 30.9 | 67.0 | 0.0 | 0.0 | 0.9 |
| AN + FS | 49.3 | 49.7 | 0.0 | 0.0 | 0.4 |
| AEN+ LD | 0.0 | 0.5 | 76.8 | 18.4 | 0.0 |
| AN + FS + LD | 0.0 | 4.5 | 67.0 | 24.3 | 0.1 |

**Table 2.6** Evolution of $Al^{3+}$ in the leachates of the Technosols and controls.

| | Concentration of $Al^{3+}$ in the leachates (mg $L^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Leaching time (days)** | **3** | **9** | **16** | **20** | **27** | **34** | **44** | **55** | **62** |
| AE | 0.90 | 0.06 | 0.35 | 0.12 | 0.29 | 0.30 | - | 0.03 | 0.07 |
| AE + FS | 0.56 | - | 0.45 | 0.20 | 0.29 | 0.18 | - | - | - |
| AE + LD | 3.34 | 3.88 | 3.38 | 2.48 | 0.90 | 0.56 | 0.07 | 0.05 | 0.07 |
| AE + FS + LD | 1.62 | 0.17 | 0.69 | 0.23 | 0.36 | 0.47 | 0.14 | 0.04 | 0.11 |
| AN | 1.63 | 0.11 | - | 0.07 | 0.35 | 0.47 | - | - | 0.01 |
| AN + FS | 0.62 | -0.13 | 0.49 | 0.09 | 0.34 | 0.57 | 0.67 | - | - |
| AEN+ LD | 3.31 | 1.00 | 4.01 | 0.59 | 3.75 | 3.24 | 4.32 | 3.95 | 2.92 |
| AN + FS + LD | 4.22 | 3.31 | 1.81 | 1.49 | 0.83 | 0.70 | 0.06 | 0.10 | 0.22 |

The practically constant downslope obtained with the acidification of the FS sample suggests that there were no strong buffers able to stabilise the pH of the system, except that of the exchange sites of the smectite, as expected. Finally, since LD contained a large amount of $Ca(OH)_2$, the dominant buffer was a strong base. In addition, $CaCO_3$ was the dominant carbonate species at pH > 11, whereas $HCO_3^-$ predominated in the neutral range. Precipitates of $CaCO_3$ were identified in this waste (Table 2.2), but only in minor amounts as they probably originated through carbonation processes: this may explain the practical absence of any other strong buffer, in addition to $Ca(OH)_2$.

### *2.5.2. Characteristics of the leachates from the AE and AN controls at time 0*

Leachates from the two sludges at time 0 mainly differed in that the values of EC, DOC, $SO_4^{2-}$ and $Cl^-$ were higher in the AN sludge than in the AE sludge, whereas the inverse was observed for $NO_3^-$, $PO_4^{3-}$ and $K^+$, which were present at higher concentrations in the latter. These differences can mainly be attributed to the type of waste treatment at the wastewater treatment plant, with AE treatment favouring loss of the most soluble species – although the fact that the AN sludge originates from a coastal city may also contribute to the higher concentrations of $SO_4^{2-}$ and $Cl^-$ in the leachates from the former. In addition, under the reduced conditions of the AN sludge at the wastewater treatment plant, short-chain organic acids were produced (Kirchmann and Lundvall, 1993), thus explaining the higher initial concentrations of DOC in the AN control. These reduced conditions also favoured the dominance of anaerobic microorganisms, with aerobic microorganisms, such as nitrifiers, being almost totally absent. No microbiological studies have been carried out to confirm this, but differences in types of microorganisms may explain the observed differences between AN and AE treatments in terms of concentrations of $NO_3^-$ (Siripong and Rittmann, 2007), as discussed later.

### *2.5.3. Characteristics of the leachates from mixtures at time 0*

The addition of FS as a conditioner did not modify the pH of the original sludge, but decreased the initial concentrations of the main ions and DOC relative to the controls. This was mainly attributed to the presence of smectite, which has high sorption properties, in this waste (Table 2.2). The addition of LD as a conditioner had a greater impact on the chemistry of the leachates as there was an increase in pH from ~6.4 to ≥10.8; this was mainly attributed to the addition of liming material to the mixture (Table 2.2). An important increase in concentration of $Ca^{2+}$ in the leachates from the mixtures containing LD as conditioner was also observed relative to the controls, as expected. All these changes were less accentuated in FS + LD than in LD mixtures, as the former contained half the amount of LD as in the latter. In all mixtures containing LD conditioner, there was an important decrease in other ions (e.g., phosphate, $SO_4^{2-}$, and $Mg^{2+}$), which was mainly attributed to precipitation reactions caused by the high concentrations of $Ca^{2+}$ and $CO_3^{2-}$ in the limed mixtures, although sorption onto Fe oxides and $CaCO_3$ compounds may also have contributed to this. The concentrations of $NH_4^+$ in the leachates from the mixtures containing LD were also considerably lower than those from the controls; this decrease was attributed to volatilisation of $NH_3$ at high pH values (Rao and Batra, 1983). All this explains the decrease in EC detected in these mixtures.

### *2.5.4. Description of changes in leachate chemistry throughout the experimental period*

The results indicate that changes in the chemistry of the different leachates throughout the experimental period were mainly the response of the acid buffering systems of the different mixtures (e.g., strong bases, carbonates, cation exchange processes) to the acidifying processes taking place (leaching, nitrification, carbonation, OM matter mineralisation) and the need for charge balance within the solution.

The changing trend in the AE, AE + FS, AN, and AN + FS mixtures indicates that the pH of the system during the first three weeks of experiment (≈7.5) was controlled by the carbonate buffer ($HCO_3^-$ was the species of these systems as estimated from the PHREEQC model). The gradual decrease in pH in the AE and AE + FS mixtures until the end of the experiment began to take place at the same time as the sharp increase in the concentrations of $NO_3^-$; this suggests that the acidification caused by nitrification could not be counterbalanced by the carbonate buffer. The decrease in pH caused the dissolution of Mg compounds, as inferred by the release of $Mg^{2+}$ into solution, and by the end of the experiment, the pH of the system reached a value of 5. The fact that the above mentioned changes were less accentuated in the AE + FS mixture than in the AE mixture throughout the experimental period, may be due to retention of $NH_4^+$ on reactive surfaces of smectites, which may have decreased the availability of this cation to the nitrifying population. In AN and AN + FS, nitrification was only detectable at the end of the experiment and this was attributed to the lack of nitrifiers in the original AN sludge and the possible need for a long lag period for their establishment and growth (Diab et al., 1993). The acidification processes in action – leaching and OM mineralisation – were buffered by the acid buffering capacity of the system, and the pH of the system remained close to neutral. There was a small release of Mg throughout the experimental period, which contrasted with what observed in the AE and AE + FS treatments.

The changing trend of the chemistry of the leachates from AE + LD treatment indicates that the high pH of the system (≈12) was initially determined by the strong alkali present in the system, but only for a short time. The gradual decrease in pH (from ≈12 to ≈8) observed after the first week – until day 30 – was paralleled by release of $Ca^{2+}$ into solution. A similar pattern was observed in the AE + FS + LD mixture, although the decrease down to pH ≈ 8 took place during the first week of experiment. There are three acidifying processes that may be occurring simultaneously in these two systems: leaching of the ions, carbonation of the system and OM mineralisation (the latter probably to a lesser extent). Once pH ≈ 8 was reached, it remained fairly constant, although $Mg^{2+}$ was released thereafter. These results suggest that from day 30 onwards, the carbonate buffer (as inferred from the estimations of carbonate species – $HCO_3^-$ and $CaHCO_3^+$ – from the PHREEQC program) determined the pH of the system and the acidification originated by the leaching of the column (and also probably by OM mineralisation) was neutralized by the dissolution of Mg compounds. Nitrification only occurred at the end of the experiment, as the addition of liming material probably retarded the growth of nitrifying bacteria (Wong et al., 1996). Volatilisation of $NH_3$ may have been favoured under the alkaline conditions, although we did not monitor this process. The results obtained also suggest that the high pH of the system enhanced OM dissolution, as confirmed by the DOC concentrations detected in the leachates. In addition, the VMINTEQ calculation indicated that substantial DOC formed complexes with Ca at high pH (data not shown).

The changing trend in the chemistry of the leachates from the AN + LD mixture indicates that the pH of the system (which slightly decreased from 12.1 and 11.1) was determined by a strong base during the entire experimental period, and that there was a constant release of $Ca^{2+}$, but not of $Mg^{2+}$, throughout. Carbonation was probably the main process that caused release of $H^+$, which was buffered by the high alkalinity of the system. No nitrification was observed throughout the experiment, as the addition of liming material probably impeded the growth of nitrifying bacteria. Again, volatilisation of $NH_3$ was probably favoured under the alkaline conditions, and the high pH also enhanced OM dissolution. Finally, the changing trend in the chemistry of the leachates from the AN + FS + LD mixture, as far as pH, $Mg^{2+}$, $Ca^{2+}$,

$NO_3^-$, and $NH_4^+$ are concerned, followed a very similar pattern to that of AE + LD mixture. The results thus suggest that the AE sludge required double the amount of alkaline material to halt nitrification than the AN sludge, at least for the duration of the experiment.

## 2.6. Conclusions

Although the AE sludge has a greater acid buffering capacity than the AN sludge (370 compared with 312 meq $H^+$ $kg^{-1}$), the former suffered greater acidification throughout the 2-month experimental period. This greater acidification was attributed to the fact the AE sludge already contained an aerobic microbial population that was able to degrade the OM, as well as a nitrifying population able to oxidize the $NH_4^+$ released by the ammonifiers. The decrease in pH of the AE leachates was closely related to the release of $NO_3^-$. It is possible that, in the long term, once the nitrifier population would have become important in the AN sludge, acidification of the AN column would have occurred. The results suggest an important role of microbial processes in the kinetics of buffering processes.

The mixtures containing LD conditioner had a high acid buffering capacity, as expected, which is consistent with the important presence of alkaline compounds. Changes in the leachate chemistry of the different treatments in which LD was used as a component differed depending on (i) the type of organic waste to which they were added – the mixtures with the AE sludge acidified fastest (see above), and (ii) the amount of LD added, as the mixtures with only half the amount of LD (FS + LD) had only half of the acid buffering capacity compared with the mixtures with LD only, and this had a great influence on the chemistry of the leachates.

The leachates from the mixtures made with FS as the only conditioner behaved similarly to the respective controls. This was expected, as this waste is mainly composed of silica sand. The small amount of smectite present only had a small effect, probably because this clay was not very reactive after being exposed to high temperature during the blasting process (Vingas and Zrimsek, 1964).

The main acid buffering systems acting in the mixtures were (i) strong bases (mainly $Ca(OH)_2$ at high pH values), (ii) the carbonate system at pH values close to 8 (the fact that pH values were slightly lower may be attributed to lack of equilibrium of the leachates with the solid phase and also to carbonation of the solution), and (iii) exchange reactions at the pH between 7 and 5. No release of Al was detected at the lowest pH values, thus the Al buffer did not play a role as a pH buffer under the conditions studied.

Overall, the results indicate that when formulating Technosols from mixtures of wastes, the acid buffering capacity of the wastes should be taken into account in addition to their nutrient contents and the limits of contaminants established by local regulations.

### 2.7. Acknowledgements

We gratefully acknowledge INASMET and ACERALIA for supplying the conditioners. We would also like to thank the Universidad de País Vasco (UPV) for the StatView software. The research was funded by the Spanish Ministry of the Environment (Project Nos. 093/2004/3; 2.5-206/2005/2-B; 208/2006/1-2.5), and the Spanish Ministry of Science and Education (Project No. CTM 2006-13748-CO2). Fenxia Yao is in receipt of an FPI fellowship from the Spanish Ministry of Science and Education.

### 2.8. References

Adegbidi, H.G., Briggs, R.D., Volk, T.A., White. E.H., Abrahamson, L.P., 2003. Effect of organic amendments and slow-release nitrogen fertilizer on willow biomass production and soil chemical characteristics. Biomass Bioenerg. 25, 389-398.

Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 Users Manual. U.S. Environmental Protection Agency, Athen, GA, EPA/600/3-91/021.

Basta, N.T., 1995. Land Application of Biosolids: A Review of Research Concerning Benefits, Environmental Impacts, and Regulation of Applying Treated Sewage Sludge. Oklahoma Agricultural Experiment Station, Division of Agricultural Sciences and Natural Resources, Oklahoma State University, Stillwater, USA.

Bramryd, T., 2002. Impact of sewage sludge application on the long-term nutrient balance in acid soils of Scots pine (*Pinus sylvestris, L.*) forests. Water Air Soil Poll. 140, 381-399.

Camps Arbestain, M., Madinabeitia, Z., Hortala, M.A., Macías-García, F., Virgel, S., Macías Vázquez, F., 2008. Extractability and leachability of heavy metal in Technosols prepared from mixtures of unconsolidated wastes. Waste Manage. doi:10.1016/j.1016/j.wasman.2008.01.08

Debosza, K., Petersen, S.O., Kure, L.K., Ambus, P., 2002. Evaluating effects of sewage sludge and household compost on soil physical, chemical and microbiological properties. Appl. Soil Ecol. 19, 237-248.

Diab, S., Kochba, M., Avnimelech, Y., 1993. Nitrification pattern in a fluctuating anaerobic-aerobic pond environment. Water Res. 27, 1469-475.

Egiarte, G., Camps Arbestain, M., Alonso, A., Ruíz-Romera, E., Pinto, M., 2005. Effect of repeated applications of sewage sludge on the fate of N in soils under Monterey pine stands. Forest Ecol. Manag. 216, 257-269.

Egiarte, G., Camps Arbestain, M., Ruíz-Romera, E., Pinto, M., 2006. Study of the chemistry of an acid soil column and of the corresponding leachates after the addition of an anaerobic municipal sludge. Chemosphere 65, 2456-2467.

EU, 2006. Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Thematic Strategy for Soil Protection plus Summary of the Impact Assessment. COM 231 (2006) final. Brussels. pp. 1-12; 1-8.

Ferrier, R.C., Edward, A.C., Dutch, J., Wolstenholme, R., Mitchell, D.S., 1996. Sewage sludge as a fertilizer of pole stage forests: Short-term hydrochemical fluxes and foliar response. Soil Use Manage. 12, 1-7.

Gustafsson, J.P., 2007. Visual MINTEQ ver 2.53 http://www.lwr.kth.se/english/OurSoftWare/vminteq/index.htm.

Hartikainen, H., 1992. Soil response to acid input in a titration experiment. Agr. Sci. Finland 1, 577-586.

Hoeft, R.G., Walsh, L.M., Keeney, D.R., 1973. Evaluation of various extractants for available soil sulphur. Soil Sci. Soc. Am. J. 37, 401-404.

IUSS Working Group WRB. 2006. World Reference Base for Soil Resources – A Framework for International Classification, Correlation and Communication. World Soil Resources Reports No. 103. FAO, Rome, Italy.

Kandeler, E., Gerber, H., 1988. Short-term assay of soil urease activity using colorimetric determination of ammonium. Biol. Fert. Soils 6, 68-72.

Kirchmann, H., Lundvall, A., 1993. Relationship between N immobilization and volatile fatty acids decomposition in soil after application of cattle and pig slurry. Biol. Fert. Soils 15, 161-164.

Lundin, M., Olofsson, M., Pettersson, G.J., Zetterlund, H., 2004. Environmental and economic assessment of sewage sludge handling options. Resour. Conserv. Recy. 41, 255-278.

Macías Vázquez, F., 2004. Recuperación dos solos degradados, reutilización de residuos e secuestro de carbono. Una alternativa integral de mellora da calidade ambiental (in Galego). Recursos Rurais 1, 49-56.

Macías Vázquez, F., Bao, M., Macías-García, F., Camps Arbestain. M., 2007. Valorización biogeoquímica de residuos por medio de la elaboración de Tecnosoles con diferentes aplicaciones ambientales. Agua & Residuos 5, 12-25.

Murphy, J., Riley, J. P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31-36.

Parkhurst, D.L., Appelo, C.A.J., 1999. User´s guide to PHREEQC (version 2) □ A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS Water-Resources Investigations Report 99-4259. Denver, Colorado, USA.

Rao, D.L.N., Batra, L., 1983. Ammonia volatilization from applied nitrogen in alkali soils. Plant Soil 70, 219-228.

Reynolds, K.A., Kruger, R.A., Rethman, N.F.G., 1999. The manufacture and evaluation of an artificial soil (SLASH) prepared from fly ash and sewage sludge. Fly Ash Utilization Symposium, Lexington, KY, USA.

Sajwan, K.S., Paramasivam, S., Alva, A.K., 2007. Effects of different rates of fly ash and sewage sludge mixture amendment on cation availability and their leachability. J. Environ. Sci. Heal. A 42, 1155-1160.

Sajwan, K.S., Paramasivam, S., Alva, A.K., Adriano, D.C., Hooda, P.S., 2003. Assessing the feasibility of land application of fly ash, sewage sludge and their mixtures. Adv. Environ. Res. 8, 77-91.

Sajwan, K.S., Paramasivam, S., Alva, A.K., Sahi, S.V., 2006. Fly ash-organic byproduct mixture as soil amendment. In: Twardowska, I., Allen, H.E., Haggblom, M.M., Stefaniak, A. (Eds.) Soil and Water Pollution Monitoring, Protection and Remediation. Springer, Dordrecht, the Netherlands, pp. 387-399.

Schumann, A.W., Sumner, M.E., 1999. Plant nutrient availability from mixtures of fly ashes and biosolids. J. Environ. Qual. 28, 1651-1657

Siripong, S., Rittmann, B.E., 2007. Diversity study of nitrifying bacteria in full-scale municipal wastewater treatment plants. Water Res. 41, 1110-1120.

Su, D.C., Wong, J.W.C., 2002. The growth of corn seedlings in alkaline coal fly ash stabilized sewage sludge. Water Air Soil Poll. 133, 1-13.

Valiela, I., Teal, J.M., Sass, W.J., 1975. Production and dynamics of salt marsh vegetation and the effects of experimental treatment with sewage sludge – Biomass, production and species composition. J. Appl. Ecol. 12, 973-981.

Vingas, G.J., Zrimsek, A.H., 1964. Thermal stability of bentonites in foundry molding sand. Proceedings of the Thirteenth National Conference on Clays and Clay Minerals. 367-380.

Wong, J.W.C., Li, G.X., Wong, M.H., 1996. The growth of Brassica chinensis in heavy-metal-contaminated sewage sludge compost from Hong Kong. Bioresource Technol. 58, 309–313.

Wong, J.W.C., Su, D.C., 1997a. Reutilization of coal fly-ash and sewage sludge as an artificial soil-mix: effects of preincubation on soil physico-chemical properties. Bioresource Technol. 59, 97-102.

Wong, J.W.C., Su, D.C., 1997b. The growth of agropyron elongatum in an artificial soil mix from coal fly ash and sewage sludge. Bioresource Technol. 59, 57-62.

Zall, D.M., Fisher, M.D., Garner, Q.M., 1956. Photometric determination of chlorides in water. Anal. Chem. 28, 1665-1678.

# Chapter 3

# Chemical changes in heavy metals in the leachates from Technosols

This chapter has been published in:
Chemosphere 77, 29-35
(2009)

# Chapter 3. Chemical changes in heavy metals in the leachates from Technosols

## 3.1. Abstract

A 2 month long column study was conducted to evaluate the mobility of heavy metals eluting from Technosols constituted from sewage sludges (aerobic or anaerobic) (as controls) or a mixture of different types of sewage sludges with green foundry sand (FS) or/and Linz-Donawitz slag (LD). The organic and inorganic wastes were mixed at a ratio of 56:44 (w/w). The mixtures and the controls were moistened to field capacity before adding them to the polypropylene columns (4.5 cm wide and 14 cm long). During the 8-week experimental period, the columns were watered, twice a week, with 100 mL of deionised water. The concentrations of heavy metals (Cu, Zn, Ni, Pb, Cd, and Cr) in the leachates were determined periodically. The concentrations of all the heavy metals were generally higher in the leachates from the Technosols containing anaerobic sewage sludge as a component. The concentration of Cu was strongly dependent on pH and was significantly higher ($P < 0.05$) in the most alkaline leachates (pH > 10) than in the other leachates. More Zn was mobilized in the most acidic leachates (pH < 6) than in other leachates. The concentration of Ni in 80% of the leachates exceeded the EU drinking water limit for Ni (0.02 mg $L^{-1}$). The concentrations of Pb were lower in the Technosols containing FS. The concentrations of Cd in the leachates from Technosols containing the conditioners were relatively high, while concentrations of Cr were higher in the controls. As far as the potential toxicity of heavy metals is concerned, the combination of aerobic sludge, inorganic conditioners able to buffer the pH to around neutrality, and reactive aluminosilicates, can be regarded as suitable choice for formulating Technosols from wastes.

*Keywords:* sewage sludge; inorganic conditioner; heavy metals; fractionation; leaching.

## 3.2. Introduction

According to Douglas (1966), “waste is a matter out of place,” and therefore, as waste flows are related to natural cycles, they should be treated in accordance with the characteristics of the cycles involved (Moll, 2004). Moreover, waste management schemes should not only be developed from a technical viewpoint, but also from environmental and economic perspectives (Moll, 2004).

Several researchers have recently proposed the preparation of tailor-made mixtures of unconsolidated wastes (e.g., sludges, fly ashes, foundry sand, etc.) in order to improve on the characteristics (pH, nutrient availability, toxicity, acid buffering capacity, etc.) of the individual ingredients (Punshon et al., 2002; Macías Vázquez, 2004; Macías Vázquez et al., 2007; Camps Arbestain et al., 2008; Yao et al., 2009) so that they can be used to restore degraded areas. These artificial soils, currently denominated as Technosols by the IUSS Working Group WRB (2006), are soils whose properties and pedogenesis are dominated by their technical origin. The preparation of Technosols may be an economically feasible method of re-using waste products and of returning the elements that they contain to their biogeochemical cycles.

The new artificial soils (Technosols) should fulfill the main soil functions, as defined by the EC-COM 231/2006 (EU, 2006) and, as such, should represent an environmentally sound mixture (e.g., low pollutant availability, low ecotoxicity). The positive functions of newly prepared soils do not guarantee, however, that the contaminants will be stored safely and indefinitely. In a lysimeter study, the leachate Zn content was observed to increase in anaerobic sewage sludge amended soil columns (Wong et al., 2000). Al-Wabel et al. (2002) also found that addition of biosolids to soils increased the Cu concentration in the effluents in a column study. Various authors have reported increases in the concentrations of heavy metals in leachates after the application of biosolids to soils, although their mobility was highly influenced by pH, as well as some other properties, such as DOC, EC and redox conditions (Wong et al., 2000; Al-Wabel et al., 2002). These properties may change in response to alterations in the environment, resulting in their sudden mobilisation. This has been defined as a “chemical time bomb” by Stigliani (1991). The “chemical time bomb” effect of stored heavy metals is of particular concern, as unlike hazardous organics, they cannot be degraded and tend to accumulate in wastes and soils. Some metals (e.g., Cr, Hg) can be transformed to other oxidation states in soils, thus altering their mobility and toxicity, while most metals are prone to adsorption and precipitation reactions that are strongly pH-dependent. Other changes in soil environmental conditions, such as degradation of the organic fraction, may also affect the availability of these contaminants.

Under aerobic conditions, the mobility and bioavailability of heavy metals present in the newly made Technosols will depend to a great extent on the pH of the system, with cationic forms of the metals being particularly susceptible to becoming mobilized at low pH values. The acid buffering capacity (BC) of the wastes used in the preparation of Technosols and the proportions used will therefore play an important role in the potential risk of heavy metal mobility, as well as the environmental conditions in the area to be restored.

The objective of this study was to evaluate the mobility of heavy metals eluting from Technosol columns, which were prepared by combining different types of sewage sludges with a variety of inorganic by-products such as green foundry sand (FS) and Linz-Donawitz slag (LD), with very different acid BC. A previous study of the chemistry of the leachates from the same experimental system (Chapter 1) suggested that the main processes influencing the acid BC of the final mixtures were nitrification and leaching, although organic matter (OM) decomposition and carbonation may also have played a role.

## 3.3. Materials and methods

### *3.3.1. Components of the Technosols*

Two municipal sewage sludges were used in this column study: (i) a dewatered anaerobic (AN) digested sludge from the wastewater treatment plant in Vigo (Galicia, NW Spain), and (ii) an aerobic (AE) sludge that had undergone physicochemical treatment at the wastewater treatment plant in A Estrada (Galicia, NW Spain). The FS produced from steel foundries was provided by INASMET (Basque Country, N Spain). The LD was obtained from a steel production plant (ACERALIA, ARCELOR group) in Avilés (Asturias, NW Spain). The inorganic ingredients are referred to as conditioners. The main chemical characteristics of the materials used in this study are shown in Table 3.1, and the mineralogy and particle-size distribution of the ≤2 mm fraction of the two conditioners (FS and LD) are shown in Table 2.2 (Chapter 2).

The ingredients with the highest pH values were LD and FS, with values of 12.1 and 9.6, respectively; the pH values of the AE and AN were 6.7 and 7.9, respectively (Table 3.1). Both the FS and the LD were of very sandy nature, and contained 71% and 81% sand, respectively (Table 2.2, Chapter 2). The FS was mainly comprised of sand sized quartz particles, although it also contained a large clay fraction (20%) – mostly smectite – added to the sand as a binder to form the moulds for metal castings. The LD, in contrast, contained no quartz but rather FeO, $Ca(OH)_2$, $CaCO_3$ and $Ca_2SiO_4$ (Table 2.2, Chapter 2). This conditioner thus contained a large fraction of liming material added during the production of steel to neutralize the acidity.

**Table 3.1** Chemical characterisation of the wastes used as components.

| | Aerobic sludge | Anaerobic sludge | Foundry sand | LD slag |
|---|---|---|---|---|
| pH | 6.7 | 7.9 | 9.6 | 12.1 |
| Organic C (g $kg^{-1}$) | 354 | 275 | 10 | 21 |
| TCu (mg $kg^{-1}$) | 460 | 745 | 31 | 14 |
| TZn (mg $kg^{-1}$) | 740 | 1470 | 122 | 33 |
| TNi (mg $kg^{-1}$) | 31 | 58 | 86 | 20 |
| TPb (mg $kg^{-1}$) | 86 | 291 | 15 | 47 |
| TCd (mg $kg^{-1}$) | 0.7 | 1.2 | 1 | 3 |
| TCr (mg $kg^{-1}$) | 28 | 89 | 233 | 468 |
| BC[a] (meq $kg^{-1}$) | 370 | 312 | 29 | 2000[b]<br>291[c] |

[a]BC = Acid buffering capacity; [b]2000: for the pH range 12-11, the BC of LD is 2000; [c]291: for the pH range 11-3, the BC of LD is 291

### *3.3.2. Experimental design*

The sludges (AN and AE) were air-dried and passed through a 4 mm sieve, and the conditioners (FS and LD) were passed through a 2 mm sieve before use. The sludges and the conditioners were mixed at a ratio of 56:44 (w/w). The conditioners were added either as single amendments or as a mixture (50:50 w/w). As a result, there were eight combinations, including the two controls: AE, AE + FS, AE + LD, AE + FS + LD, AN, AN + FS, AN + LD, and AN + FS + LD. Three replicates per mixture were used.

The mixtures and the controls were moistened to field capacity before adding them to the pilot columns. The mean dry weights of each treatment were as follows: 48.9, 85.7, 105.6, 86.1, 77.0, 99.0, 136.0, and 112.8 g for AE, AE + FS, AE + LD, AE + FS + LD, AN, AN + FS, AN + LD, and AN + FS + LD, respectively (Table 2.3, Chapter 2). The corresponding water content were 108%, 136%, 97%, 74%, 98%, 87%, 52%, and 77%, respectively (Table 2.3, Chapter 2). Twenty-four polypropylene columns (4.5 cm wide and 14 cm long) were manually packed with the corresponding mixtures/controls for each treatment, to a total volume of 222.7 mL, leaving 1 cm headspace on the top of the columns. The set-up of the pilot columns is as described in Chapter 2 (Section 2.3.2).

During the 8-week experimental period, the columns were watered with 100 mL of deionised water twice a week, by use of individual top-fill feeding canisters with a preattached delivery gravity setting. The amount of water was calculated by assuming an annual rainfall of 1000 L $m^{-2}$, concentrated in two months. Leachates were collected in polyethylene bottles and stored at $\leq 4$ °C before analysis.

### *3.3.3. Analytical determinations*

The acid BC of the four components was determined following the methodology described by Hartikainen (1992) (summarised in Chapter 2, section 2.3.3). For the selective sequential extraction of heavy metals in each component, the methodology of Berna et al. (2000) was followed, with slight modifications. Concentrations of Cu, Zn, Cd, Cr, Ni and Pb in the leachates were determined by ICP–OES (Varian Ibérica S.L., Barcelona, Spain). The pH was also determined at each sampling time. $HCO_3^-$ and $CO_3^{2-}$ species were estimated with the USGS aqueous modeling software, PHREEQC. This program uses mass balance and electro-neutrality equations to simulate geochemical reactions, such as mixing of water, addition of net irreversible reactions to solution, dissolution and precipitation phases to achieve equilibrium with the aqueous phase (Parkhurst and Appelo, 1999). Another geochemical model – VMINTEQ (Visual MINTEQ) version 2.53, a Windows version of MINTEQA2 version 4.0, was also used (Gustafsson, 2007). MINTEQA2 is a geochemical equilibrium speciation model for dilute aqueous systems, in which complexation of metals by DOC was incorporated (Allison et al., 1991).

### *3.3.4. Statistical analysis*

To assess the statistical differences among physicochemical properties of different Technosols and their leachates, a one-way analysis of variance followed by a *post hoc* (Bonferroni) multiple comparison test (significance level at 0.05) was computed with StatView 5.0.1 for Windows (SAS Institute Inc.). Mean separation was also carried out with a Student's *t*- test.

## 3.4. Results and discussion

### *3.4.1. Leaching of copper*

Maximum concentrations of Cu in the leachates were observed during the first week of the experiment and, specifically, in the mixtures containing the LD conditioner, following the order AN + FS + LD > AN + LD > AE + FS + LD > AE + LD (46.6, 41.5, 29.6 and 25.3 mg $L^{-1}$, respectively) (Fig. 3.1a and b). In these LD-containing treatments, initial concentrations of Cu were much higher than the EU drinking water threshold of 2.0 mg $L^{-1}$ (EU Directive 98/83) (EC, 1998); a sharp decrease was observed as the pH of the leachate decreased below 10 (Fig. 2.3a and b, Chapter 2). A pH-dependent trend was apparent: in AN + LD, the pH remained above 11 and the concentration of Cu was higher than 5.0 mg $L^{-1}$ throughout the duration of the experiment; the pH of leachates from the treatments without LD was always below 6.5, and the concentration of Cu was generally below 0.5 mg $L^{-1}$, except at the very beginning of the experiment. In addition, the concentrations of Cu throughout the experimental period also paralleled the concentrations of Ca (Fig. 2.6c and d, Chapter 2), which suggests that mobilisation of Cu occurred along with solubilisation of $Ca(OH)_2$ – present in the LD slag. The latter process was accelerated by the leaching, as well as by carbonation of the systems under study (Yao et al., 2009). High concentrations of Ca in solution may have promoted the displacement of Cu from exchange sites. In fact, Cavallaro and McBride (1978) found that adsorption of Cu decreased in the presence of 0.01 M $CaCl_2$ and attributed this to competition with Ca for adsorption sites. In the leachates from LD-containing Technosols, the dominant thermodynamically stable Cu species was $Cu(OH)_3^-$ (VMINTEQ data not shown).

**Table 3.2** Percentage of each species of copper in the leachates of all treatments.

| Treatments | $CuCl_2^-$ (%) | $CuHCO_3^+$ (%) | $CuCO_3$ (%) | $Cu(CO_3)_2^{2-}$ (%) | $CuNH_3^{2+}$ (%) | $Cu(OH)_3$ $(\%)^-$ | $Cu(OH)_4^{2-}$ (%) |
|---|---|---|---|---|---|---|---|
| AE | 5.1 | 7.8 | 44.2 | 4.9 | 30.5 | 0.0 | 0.0 |
| AE + FS | 3.5 | 7.4 | 51.9 | 5.3 | 24.9 | 0.0 | 0.0 |
| AE + LD | 0.0 | 0.0 | 0.0 | 0.8 | 0.0 | 61.3 | 36.8 |
| AE + FS + LD | 0.0 | 0.0 | 0.1 | 99.7 | 0.0 | 0.2 | 0.0 |
| AN | 53.2 | 2.6 | 21.9 | 10.0 | 6.2 | 0.0 | 0.0 |
| AN + FS | 69.7 | 2.7 | 12.2 | 0.7 | 5.7 | 0.0 | 0.0 |
| AEN+ LD | 0.0 | 0.0 | 0.0 | 1.7 | 0.0 | 58.3 | 38.9 |
| AN + FS + LD | 0.0 | 0.0 | 0.2 | 89.2 | 0.0 | 8.4 | 0.4 |

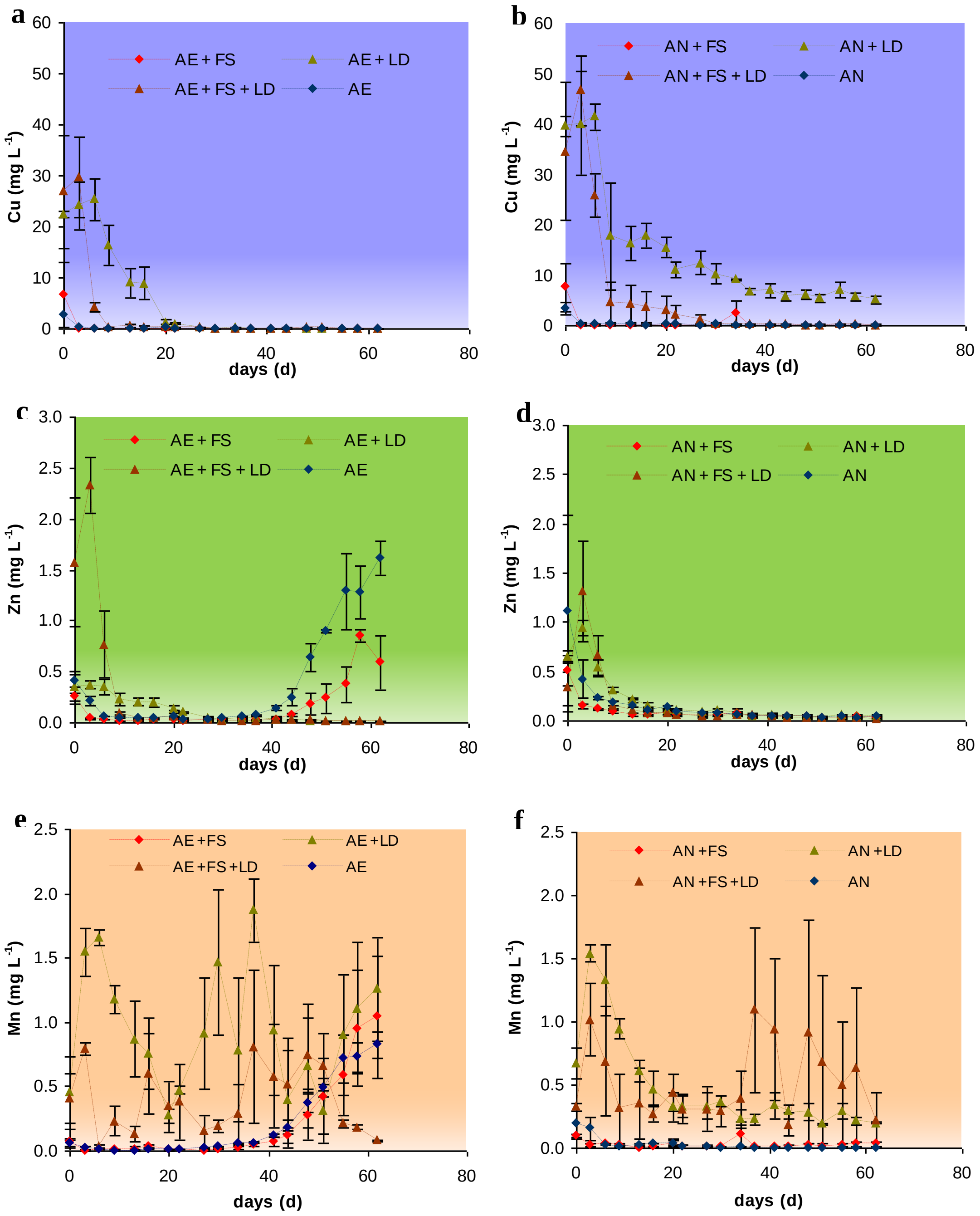


**Fig. 3.1.** Changes throughout the experiment in concentrations of Cu, Zn and Mn in leachates from Technosols with different compositions.

As OM solubilisation generally increases at high pH – favoured by the increased deprotonation of organic functional groups and the further repulsion among them – this may have further promoted mobilisation of OM-bound Cu. In the leachates from Technosols without LD, most Cu was complexed with DOM (Table 3.2). In the present study, some relationship between the concentrations of Cu and DOC (Fig. 2.4, Chapter 2) in the leachate from the AE + LD treatment was observed, but not for the other treatments. Finally, it should be noted that the concentrations of

Cu in solution were slightly influenced by the initial total Cu contents of the solid phase; the concentrations of Cu in the leachate from Technosols comprising AN were generally higher than in the corresponding AE treatment, probably because of the higher total Cu content in AN than AE (460 and 745 mg kg$^{-1}$ for AE and AN, respectively).

### *3.4.2. Leaching of zinc*

At the beginning of the experiment, pulses of Zn in the leachates from the AE + FS + LD, AN + FS + LD and AN treatments were observed, with maxima of 2.3, 1.3 and 1.1 mg L$^{-1}$, respectively (Fig. 3.1c and d). None of these values exceeded the EU drinking water Zn limiting value of 3.0 mg L$^{-1}$ (EU Directive 98/83) (EC, 1998). In the leachates from AE, AE + FS and AN + FS, the main species of Zn was $Zn^{2+}$, while in the LD-containing treatments, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ were the dominant species. In AN, the main species was $ZnHCO_3^+$ (Table 3.3).

At the end of the experiment, a sharp increase in the concentrations of Zn in the leachates from the AE and AE + FS treatments was observed (Fig. 3.1c) as the pH decreased below six (Fig. 2.2a in Chapter 2), reaching values of 1.6 and 0.9 mg L$^{-1}$, respectively, which corresponded with the sharp increase in concentrations of Mn in the leachates during the same experimental period (Fig 3.1e). This may be attributed to the presence of a major portion of Zn bound to Fe-Mn oxide in AE (Table 3.4), and the fact that these oxides are only soluble under acidic conditions (Chuan et al., 1996). Moreover, there was no relationship between solubilised Zn and the initial total Zn contents of the solid phase (740, 1470, 122 and 33 mg kg$^{-1}$, for the AE, AN, FS and LD, respectively), which can be explained by the fact that most of the Zn was generally present in very recalcitrant forms (Table 3.4).

**Tabla 3.3** Percentage of each species of zinc in the leachates of all treatments.

| Treatment | $Zn^{2+}$ (%) | $ZnHCO_3^+$ (%) | $Zn(OH)_3^-$ (%) | $Zn(OH)_4^{2-}$ (%) |
|---|---|---|---|---|
| AE | 50.8 | 37.7 | 0.0 | 0.0 |
| AE + FS | 53.0 | 37.8 | 0.0 | 0.0 |
| AE + LD | 0.0 | 0.0 | 40.0 | 59.3 |
| AE + FS + LD | 0.0 | 0.0 | 70.3 | 10.8 |
| AN | 30.9 | 46.4 | 0.0 | 0.0 |
| AN + FS | 50.6 | 30.6 | 0.0 | 0.0 |
| AN + LD | 0.0 | 0.0 | 22.8 | 77.0 |
| AN + FS + LD | 0.0 | 0.0 | 75. | 17.4 |

**Table 3.4** Percentage of each fraction of the heavy metals in the four components of the Technosols.

| | | Percentage of each fraction (%) | | | |
|---|---|---|---|---|---|
| | | Aerobic sludge | Anaerobic sludge | Foundry sand | LD slag |
| Water soluble and exchangeable | Cu | 1.18 | 1.62 | 0.00 | 0.00 |
| | Zn | 1.56 | 0.60 | 0.00 | 0.00 |
| | Ni | 12.2 | 21.95 | 19.92 | 46.25 |
| | Pb | 11.88 | 8.45 | 74.56 | 25.46 |
| | Cd | 85.71 | 95.83 | 100.00 | 42.78 |
| | Cr | 0.00 | 0.00 | 0.00 | 0.00 |
| Carbonate or weekly absorbed | Cu | 1.48 | 7.12 | 0.00 | 0.00 |
| | Zn | 16.41 | 24.91 | 27.31 | 3.08 |
| | Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| | Pb | 7.95 | 0.00 | 0.00 | 0.00 |
| | Cd | 0.00 | 0.00 | 0.00 | 0.00 |
| | Cr | 0.00 | 0.00 | 0.00 | 0.00 |
| Al oxide | Cu | 13.60 | 17.15 | 0.00 | 0.00 |
| | Zn | 21.07 | 16.28 | 3.67 | 0.00 |
| | Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| | Pb | 0.00 | 0.00 | 0.00 | 0.00 |
| | Cd | 0.00 | 0.00 | 0.00 | 0.00 |
| | Cr | 0.00 | 0.00 | 0.00 | 0.00 |
| Fe-Mn oxides | Cu | 69.35 | 9.69 | 41.12 | 34.52 |
| | Zn | 51.38 | 14.91 | 23.20 | 45.11 |
| | Ni | 25.70 | 48.59 | 13.64 | 43.90 |
| | Pb | 76.30 | 24.78 | 0.00 | 37.40 |
| | Cd | 0.00 | 0.00 | 0.00 | 40.89 |
| | Cr | 16.79 | 58.36 | 6.89 | 6.56 |
| Organic matter | Cu | 36.45 | 12.58 | 0.00 | 0.00 |
| | Zn | 1.39 | 1.38 | 5.60 | 0.00 |
| | Ni | 0.00 | 0.00 | 0.00 | 0.00 |
| | Pb | 0.00 | 0.00 | 0.00 | 0.00 |
| | Cd | 0.00 | 0.00 | 0.00 | 0.00 |
| | Cr | 42.95 | 26.17 | 0.88 | 3.21 |
| Mineral | Cu | 0.00 | 51.84 | 58.88 | 65.48 |
| | Zn | 8.20 | 41.93 | 40.23 | 51.81 |
| | Ni | 62.10 | 29.46 | 66.43 | 9.85 |
| | Pb | 3.87 | 66.77 | 25.44 | 37.13 |
| | Cd | 14.29 | 4.17 | 0.00 | 16.33 |
| | Cr | 40.27 | 15.47 | 92.23 | 90.23 |

### *3.4.3. Leaching of nickel*

There was a sharp decrease in the concentration of Ni as the leaching process proceeded, especially in the first 2 weeks, from as high as 3.25 to as low as 0.16 mg $L^{-1}$ (Fig. 3.2a and b). The maximum concentration of Ni was observed during the first two sampling times, and specifically for the treatments containing the AN sludge, with values ranging from 0.85 to 3.25 mg L$^{-1}$, which were well above the limit of 0.02 mg L$^{-1}$ proposed in the 98/83/EC Directive (EC, 1998). The concentrations of Ni in leachates from all AN treatments were significantly greater ($P$< 0.05) than the corresponding leachates from the AE treatments (Fig. 3.2a); this may be explained by the fact that the AN sludge contained almost twice as much Ni as the AE sludge (58 compared with 31 mg kg$^{-1}$), and also by the fact that the water soluble fraction, as estimated by extraction with the solution of MgCl$_2$ (1 M), was more than three times higher (Table 3.4). In AN + LD and AN + FS + LD, the main species of Ni was Ni(OH)$_3^-$, while in AN and AN + FS it was NiHCO$_3^+$ (Table 3.5).

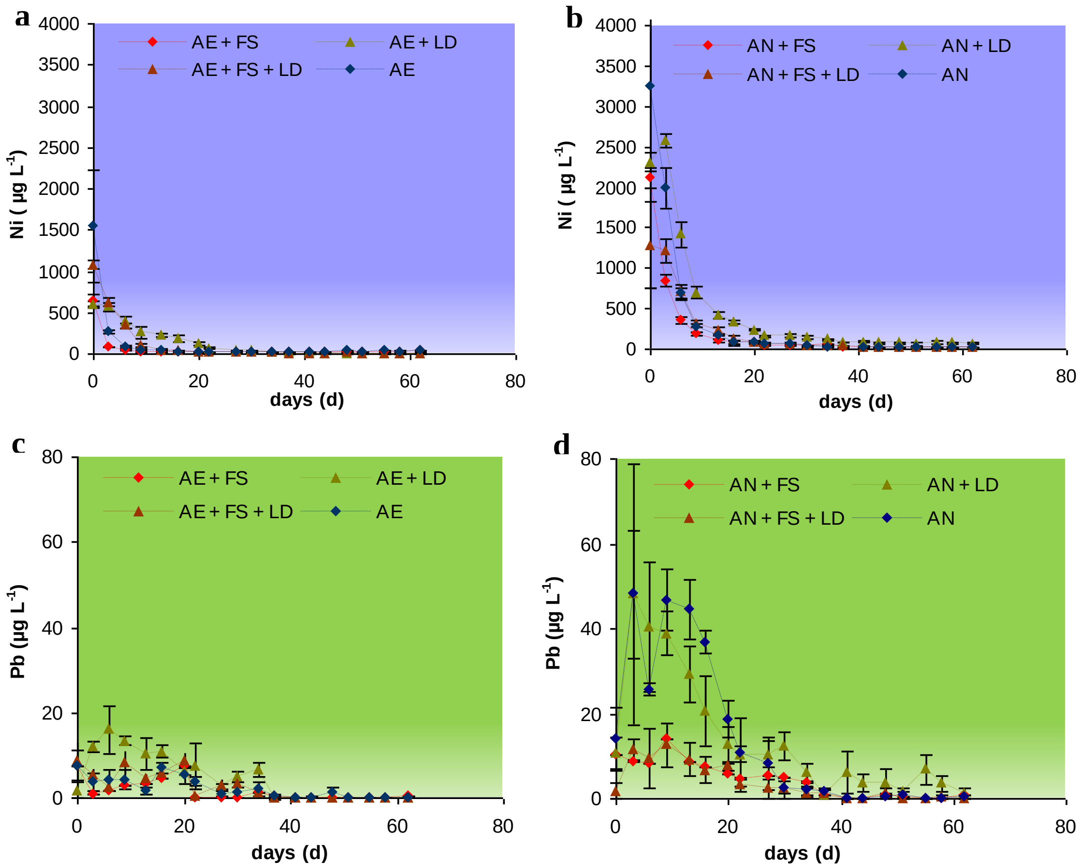


**Fig. 3.2.** Changes throughout the experiment in concentrations of Ni and Pb in leachates from Technosols with different compositions.

The leaching pattern of Ni indicates that the water soluble fraction of Ni present in the mixtures at the start of the experiment was mostly lost as the leaching process proceeded. No relationship with the pH of the corresponding leachates was observed, whereas the type of waste did have an effect, more specifically the type of sewage sludge used in the mixture. The waste containing most Ni was the FS (86 mg kg$^{-1}$), however, this was not reflected in the concentrations of Ni in the leachates, despite the fact that almost 20% was extractable with $MgCl_2$ (1 M). This suggests the occurrence of precipitation reactions when FS and sewage sludges were mixed together.

**Table 3.5** Percentage of each species of nickel in the leachates of all treatments.

| Treatment | $NiHCO_3^+$ (%) | $Ni^{2+}$ (%) | $Ni(OH)_2$ (%) | $Ni(OH)_3^-$ (%) |
|---|---|---|---|---|
| AE | 66.0 | 22.8 | 0.0 | 0.0 |
| AE + FS | 66.7 | 24.0 | 0.0 | 0.0 |
| AE + LD | 0.0 | 0.0 | 8.2 | 91.2 |
| AE + FS + LD | 0.0 | 0.0 | 4.4 | 4.8 |
| AN | 75.3 | 12.8 | 0.0 | 0.0 |
| AN + FS | 62.1 | 26.3 | 0.0 | 0.0 |
| AN + LD | 0.0 | 0.0 | 3.9 | 95.7 |
| AN + FS + LD | 0.0 | 0.0 | 18.0 | 39.7 |

### *3.4.4. Leaching of lead*

The maximum concentrations of Pb in the leachates were observed in the AN and AN + LD treatments during the first 3 weeks of the experiment, with values of up to 48 µg $L^{-1}$ (Fig. 3.2c and d). In both of these treatments, the concentrations of Pb in solution were higher than the limit for drinking water quality established by the EU regulation (EU Directive 98/83) (10 µg $L^{-1}$) (EC, 1998), while for the rest of the treatments, values were generally below this limit, except on a few occasions. In addition, there was no clear relationship with the pH of the corresponding leachates, while the total concentration of Pb in the ingredients used to prepare the mixtures (Table 3.1) may have played a role, especially considering that the water soluble fraction concentrations of Pb in the AN and LD ingredients were the highest (24.6 and 12 mg $kg^{-1}$, respectively) (Table 3.4). In the AN leachates, Pb was mainly combined with $Pb(CO_3)_2^{2-}$ while in the AN + LD leachate, Pb was present as $Pb(OH)_4^{2-}$ (Table 3.6).

**Table 3.6** Percentage of each species of lead in the leachates of all treatments.

| Treatment | $Pb(CO_3)_2^{2-}$ (%) | $PbCO_3$ (%) | $PbHCO_3^+$ (%) | $Pb(OH)_3^-$ (%) | $Pb(OH)_4^{2-}$ (%) |
|---|---|---|---|---|---|
| AE | 2.1 | 18.1 | 73.2 | 0.0 | 0.0 |
| AE + FS | 2.4 | 21.5 | 70.4 | 0.0 | 0.0 |
| AE + LD | 27.8 | 0.0 | 0.0 | 7.1 | 64.5 |
| AE + FS + LD | 99.9 | 0.1 | 0.0 | 0.0 | 0.0 |
| AN | 10.7 | 21.9 | 60.0 | 0.0 | 0.0 |
| AN + FS | 0.9 | 13.5 | 70.0 | 0.0 | 0.0 |
| AN + LD | 1.2 | 0.0 | 0.0 | 4.5 | 94.1 |
| AN + FS + LD | 96.8 | 0.2 | 0.0 | 1.0 | 1.5 |

Lead is retained by soils and soil constituents to a great extent, as it is either precipitated or adsorbed on reactive surfaces (McLean and Bledsoe, 1992). The results obtained suggest that the higher mobility of Pb in the AN and AN + LD treatments was probably associated with the water soluble and exchangeable fractions (Table 3.4), and not with either the pH of the systems or the complexation by enhanced OM dissolution relation with the available Pb. The fact that the AN + FS and AN + FS + LD did not follow this pattern may be attributed to the retention of Pb by the smectite present in the FS conditioner. The results thus suggest an important role for this aluminosilicate in the immobilisation of Pb.

### *3.4.5. Leaching of cadmium*

Cadmium concentrations in the leachates from all treatments were extremely low, with values below 2 µg $L^{-1}$, except for the initial Cd concentrations of the AE + FS + LD and AN + FS + LD treatments, which reached values as high as 15 µg $L^{-1}$ at the beginning of the experiment (Fig. 3.3a and b). This level was well above the limit established in Directive 98/83/EC (5 µg $L^{-1}$) (EC, 1998), but rapidly decreased as the leaching proceeded. Total concentrations of Cd in the wastes used for preparation of the mixtures were 0.7, 1.2, 1.0 and 3.0 mg $kg^{-1}$, for the AE, AN, FS and LD wastes, respectively. In both AE + FS + LD and AN + FS + LD, the main Cd species is $Cd(CO3)_2^{2-}$ (Table 3.7).

The fact that the only those mixtures with the simultaneous presence of the two conditioners (FS + LD) showed a pulse of Cd at the beginning of the experiment suggests that the high concentration of Ca present in the LD slag may have displaced the small amount of Cd present at the exchange sites of the smectite in the FS.

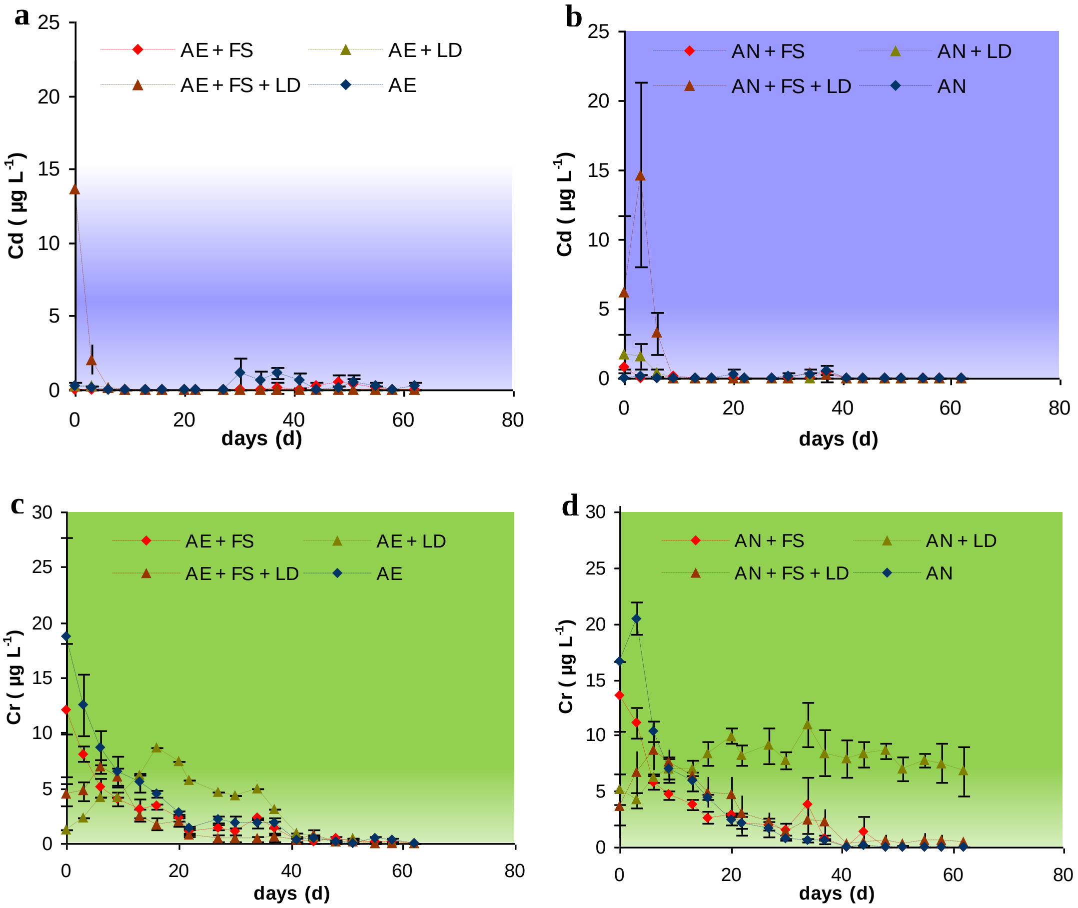


**Fig. 3.3**. Changes throughout the experiment in concentrations of Cd and Cr in leachates from Technosols with different compositions.

**Table 3.7** Percentage of each species of cadmium in the leachates of all treatments.

| Treatment | $Cd(CO3)_2^{2-}$ (%) | $CdCO_3$ (%) | CdOHCl (%) |
|---|---|---|---|
| AE | 0.0 | 0.0 | 0.0 |
| AE + FS | 0.0 | 0.0 | 0.0 |
| AE + LD | 0.0 | 0.0 | 0.0 |
| AE + FS + LD | 99.7 | 0.3 | 0.0 |
| AN | 0.0 | 0.0 | 0.0 |
| AN + FS | 0.0 | 0.4 | 0.0 |
| AN + LD | 86.8 | 0.3 | 1.7 |
| AN + FS + LD | 98.9 | 0.9 | 0.1 |

### *3.4.6. Leaching of chromium*

The highest concentrations of Cr were detected at the beginning of the experiment, and in both controls (AE and AN treatments), with values up to 20 µg L$^{-1}$ (Fig. 3.3c and d). After 2 weeks of experiment, the AE + LD and the AN + LD treatments showed different patterns compared with the other treatments: in both cases, there was an increase in concentration of Cr; however, in the AE + LD treatment the concentration decreased 3 weeks later, and in the AN + LD treatment the concentration remained at around 8 µg $L^{-1}$ until the end of the experiment (Fig. 3.3c and d). Throughout the experiment, concentrations of Cr were always below the limit established in EU Directive 98/83 (50 µg $L^{-1}$) (EC, 1998). In AE and AN, the main species of Cr was $Cr(OH)^{2+}$. In AE + LD and AN + LD, the main species of Cr was $CrO_4^{2-}$ (Table 3.8).

There are two possible oxidation states for Cr in soils: Cr(III) and Cr(VI). The trivalent cation has a strong affinity for negatively-charged ions and colloids in soil and is therefore relatively immobile and non-toxic in these environments (Fendorf, 1995). The Cr(III) form predominates in sewage sludge, either bound to organic compounds or as inorganic precipitates (Milacic and Stupar, 1995). However, Cr(VI) is more soluble, mobile, bioavailable, and toxic, and its presence is favoured under highly oxidizing conditions or in the presence of Mn oxides (Guertin et al., 2005).

**Table 3.8** Percentage of each species of cromo in the leachates of all treatments.

| **Treatment** | **$Cr(OH)^{2+}$ (%)** | **$Cr(OH)_2^{+}$ (%)** | **$CrO4^{2-}$ (%)** |
|---|---:|---:|---:|
| AE | 61.4 | 32.9 | 0.0 |
| AE + FS | 55.7 | 40.8 | 0.0 |
| AE + LD | 0.0 | 0.0 | 97.9 |
| AE + FS + LD | 0.0 | 0.0 | 95.3 |
| AN | 55.5 | 38.0 | 0.0 |
| AN + FS | 63.7 | 28.1 | 0.0 |
| AN + LD | 0.0 | 0.0 | 97.3 |
| AN + FS + LD | 0.0 | 0.0 | 96.9 |

Under the conditions of the system studied, in which OM is abundant, this would tend to reduce any Cr(VI), if present (Bartlett and Kimble, 1976; Bolan and Duraisamy, 2003). Thus, Cr was probably present as Cr(III) and, as such, it should have been relatively immobile. The presence of Cr in the leachates has been attributed to its downward transfer in the column, while bound to particulate matter (Egiarte et al., 2008). This transfer was possibly favoured at the start of the experiment in the treatments with sludges only (AE and AN treatments), i.e., in the absence of an inorganic conditioner able to retain downward flowing organic colloids. The presence of smectite in the FS treatments may have favoured organo-mineral interactions and aggregation, and impeded particulate dispersion. On the other hand, the high pH of the LD mixtures may have favoured dispersion of organic colloids, thus promoting the downward movement of Cr-bound OM particles.

## 3.5. Conclusions

The total amount of heavy metals (Cu, Zn, Ni, Pb, Cd and Cr) was higher in AN than in AE, and thus the concentrations of these heavy metals in the leachates from Technosols constituted with AN were generally higher than the AE. This phenomenon was particularly evident for Cu, Ni and Pb, because concentrations of water soluble Cu, Ni and Pb in AN were considerably higher than in AE. In addition, release of Cu was stimulated by the high pH and high Ca content of the conditioner. On the contrary, although concentrations of Zn in all the leachates during all sampling times were far below the Zn limiting value for drinking water (3.0 mg $L^{-1}$) (EU Directive 98/83) (EC, 1998), the concentrations tended to increase at $pH < 6$. As far as Cu and Zn are concerned, an inorganic conditioner with neutral pH and strong acid buffering capacity is strongly recommended.

Ni was the most potentially hazardous metals in this study, as almost 80% of the leachates contained more Ni than the established threshold value for drinking water (0.02 mg $L^{-1}$) (EU Directive 98/83) (EC, 1998). Release of Pb may be partly retarded by FS due to the presence of smectite, although FS has a low acid buffering capacity.

In conclusion, the results indicate that for formulating Technosols from sewage sludges, the AE sludge under study was better than the AN sludge in terms of release of heavy metals, although longer term studies would be needed to confirm this. In addition, inorganic conditioners with neutral pH, strong acid buffering capacity and reactive aluminosilicates are strongly recommended for use as amendments.

## 3.6. Acknowledgements

We gratefully acknowledge the Universidad de País Vasco (UPV) for the StatView software. The research was funded by the Spanish Ministry of Science and Education (Project No. CTM 2006-13748-CO2). Fenxia Yao is in receipt of an FPI fellowship from the Spanish Ministry of Science and Education.

## 3.7. References

Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 Users Manual. U.S. Environmental Protection Agency, Athen, GA, EPA/600/3-91/021.

Al-Wabel, M.A., Heil, D.M., Westfall, D.G., Barbarick, K.A., 2002. Solution chemistry influence on metal mobility in biosolids-amended soils. J. Environ. Qual. 31, 1157–1165.

Bartlett, R.J., Kimble, J.M., 1976. Behavior of Chromium in soils: II. Hexavalent forms. J. Environ. Qual. 5, 383-386.

Berna, F., Corti, G., Ugolini, F.C., Agnelli, A., 2000. Assessment of the role of rock fragments in the retention of Cadmium and Lead in irrigated arid stony soils. Annali di Chimica 90, 209-217.

Bolan, N.S., Duraisamy, V.P., 2003. Role of inorganic and organic soil amendments on immobilization and phytoavailability of heavy metals: a review involving specific case studies. Aust. J. Soil Res. 41, 533-555.

Camps Arbestain, M., Madinabeitia, Z., Hortalà, A.M., Macías-García, F., Virgel, S., Macías Vázquez, F., 2008. Extractability and leachability of heavy metals in Technosols prepared from mixtures of unconsolidated wastes. Waste Manage. 28:2653-2666.

Cavallaro, N., McBride, M.B., 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. Soil Sci. Soc. Am. J. 42, 550-556.

Chuan, M.C., Shu, G.Y., Liu, J.C., 1996. Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH. Water Air Soil Poll. 90, 543-556.

Douglas, M., 1966. Purity and danger: an analysis of the concepts of pollution and taboo. Routledge and Kegan Paul, London and New York.

EC, European Commission Council Directive 98/83/EC of 3 November 1998, on the Quality of Water Intended for Human Consumption. EN L 330/42, 5.12.98.

Egiarte, G., Pinto, M., Ruíz-Romera, Camps Arbestain, M., 2008. Monitoring heavy metal concentrations in leachates from a forest soil subjected to repeated applications of sewage sludge. Environ. Pollut. 156, 840-848.

EU, 2006. Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the regions. Thematic Strategy for Soil Protection plus Summary of the impact Assessment. COM 231 (2006) final. Brussels, pp. 1-12, 1-8.

Fendorf, S.E., 1995. Surface reactions of chromium in soils and waters. Geoderma 67, 55-71.

Guertin, J., 2005. Toxicity and health effects of chromium (all oxidation states). In: Guertin, J., Jacobs, J.A., Avakian, C.P. (Eds.) Chromium (VI) Handbook. CRC Press, London, UK, pp. 216-230.

Gustafsson, J.P., 2007. Visual MINTEQ ver 2.53. http: // www.lwr.kth.se/english/OurSoftWare/vminteq/index.htm.

Hartikainen, H., 1992. Soil response to acid input in a titration experiment. Agric. Sci. Finland 1, 577-586.

IUSS Working Group WRB, 2006. World Refence Base for Soil Resources – A Framework for International Classification, Correlation and Commucation. World Soil Resources Reports No. 103. FAO, Rome, Italy.

Macías, F., 2004. Recuperación de suelos degradados, reutilización de residuos y secuestro de carbono. Una alternativa integral de mejora de la calidad ambiental. Recursos Rurais, 1, 49-56.

Macías Vázquez, F., Bao, M., Macías-García, F., Camps Arbestain, M., 2007. Valorización biogeoquímica de residuos por medio de la elaboración de Tecnosoles con diferentes aplicaciones ambientales. Agua & Residuos 5, 12-25.

McLean, J.E., Bledsoe, B.E., 1992. Behaviour of metals in soils. Groups water Issue. EPA/540/S-92/018.

Milacic, R., Stupar, J., 1995. Fractionation and oxidation of chromium in tannery waste- and sewage sludge-amended soils. Environ. Sci. Technol. 29, 506-514.

Moll, H.C., 2004. Material metabolism through society and environment: a new view on waste management. In: Lens, P., Hamelers, B., Hoitink, H., Bildlingmaier, W. (Eds.) Resource Recovery and Reuse in Organic Solid Waste Management, IWA Publishing, Londen, UK, pp. 3-22.

Parkhurst, D.L., Appelo, C.A.J., 1999. User’s guide to PHREEQC (version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS Water-Resources Investigations Report 99-4259. Denver, Colorado, USA.

Punshon, T., Adriano, D.C., Weber, J.T., 2002. Restoration of drastically eroded land using coal fly ash and poultry biosolid. Sci. Total Environ. 296, 209-225.

Stigliani, W.M., 1991. Chemical Time Bombs: Definition, Concepts, and Examples. International Institute for Applied Systems Analysis A-2361 Laxenburg, Austria.

Wong, J.W.C., Cheung, K.C., Wong, M.H., 2000. Environmental implication of soils amended with anaerobically digested sewage sludge in Hong Kong. Water Air Soil Pollut. 124, 23–26.

Yao, F.X., Macías Vázquez, F., Santesteban, A., Virgel, S., Blanco, F., Jiang, X., Camps Arbestain, M., 2009. Influence of the acid buffering capacity of different Technosols on the chemistry of their leachates. Chemosphere 74, 250-258.

# Chapter 4

# Elaborating Technosols from mixtures of wastes for ryegrass growth: I. Characteristics of soil and soil solution

This chapter has been sent to:
Waste Management
(2011)

# Chapter 4. Elaborating Technosols from mixtures of wastes for ryegrass growth: I. Characteristics of soil and soil solution

## 4.1. Abstract

The preparation of tailor-made Technosols from wastes has been proposed as a novel and prospective option for valorisation of wastes, sequestration of carbon and restoration of degraded areas. A greenhouse experiment was carried out to evaluate the feasibility of different tailor-made Technosols for plant growth. They were formulated from sewage sludges and conditioners mixed at two ratios: 60:40 and 50:50 (w/w, DW). Three types of sludges were used as main component: aerobic sewage sludge (AE), anaerobic sewage sludge (AN) and CaO-treated aerobic sludge (AL). Four kinds of conditioners – 5% of green foundry sand (FS), 10% of Linz-Donawitz slag (LD), 2% of barley straw (BS) and 23 or 33% of fly ash from pine bark combustion (FA) - were used as amendments. Three Technosols containing 60% of sludge and 23% of FA were referred to as M1-AE, M1-AN and M1-AL. Another three with 50% of sludge and 33% of FA were identified as M2-AE, M2-AN and M2-AL. Controls were set for each type of sludge only (AE, AN, and AL sludges). Changes in pH, concentrations of major ions and dissolved organic carbon in the soil solution were evaluated periodically. The chemical composition of the soil was also analyzed at the start and at the end of the incubation. The results showed that the Technosols elaborated from AN sludge contained the highest contents of both nutrients (N and P) and OC, while the Technosols derived from AE sludge had the lowest level of OC and macro nutrients. AL sludge had the lowest availability of P, due to precipitation by large amount of Ca. Addition of conditioners is not only in favour of anti-acidification and immobilisation of heavy metals, but also promotes OM stabilisation and thus protects it from decomposition. The tailor-made Technosols from unconsolidated anthropogenic wastes should be a promising technology for sound waste disposal.

*Keywords*: Sewage sludge; Biomass fly ash; Green foundry sand; Linz-Donawitz slag; Waste treatment

## 4.2. Introduction

As a result of the application of European Directive 91/271/EEC, many new wastewater treatment plants have been created and generation of sludge has increased sharply, e.g. in Spain, the total production of sludge in 2008 reached 1.2 million Mg and the wastewater treatment plants in Basque Country produced 24 thousand Mg during the same year (Ministerio de Medio Ambiente y Medio Rural y Marino, 2010). How to dispose the increasingly large amount of sewage sludge in an environmental-friendly way at lowest cost arouses world-wide concern. As sewage sludge contains high content of organic matter (OC) and nutrients that are required by plant growth, application of sewage sludge to agricultural soil is a common practice around the world. However, many side-effects have appeared from such kind of application, such as soil acidification and contamination of pathogens and heavy metals to soil and plants (Wong and Su, 1997a, 1997b).

Wastes with liming effects, i.e. fly ash and LD slag, could increase soil pH and kill the pathogens (Wong and Su, 1997 a, 1997b; Su and Wong, 2002). Residues derived from a wide variety of sources (e.g. fly ash, red-mud gypsum, sugar foam, dolomite residues, etc.) could also function as chemical stabilising agents to reduce the mobility of heavy metals (Kumpiene et al., 2008). Some minerals rich in Al and/or Fe oxy-hydroxides may promote OM stabilisation through the formation of stable bonds (Eusterhues et al., 2003; Kögel-Knabner et al., 2008). Therefore, it is suggested that mixtures of different types of wastes be made before their application (Sajwan et al., 2003, 2006, 2007). This is largely consistent with the idea proposed by Macías Vázquez (2004), who suggested the formulation of tailor-made Technosols – soils whose properties and pedogenesis are dominated by their technical origin (WRB, 2006).

The preparation of Technosols from mixtures of unconsolidated wastes, e.g. sewage sludge, fly ash, has been proved to be a promising alternative to reuse waste products. Through this technology, tailor-made Technosols can be artificially produced with the final objective of fulfilling soil functions, as defined by the EC-COM 231/2006 (EU, 2006). While disposing the wastes, recycling the nutrients, eliminating the pathogens, reducing the availability of heavy metals, promoting the OM stabilisation could also be achieved (Macías Vázquez, 2004; Macías Vázquez et al., 2007; Camps Arbestain et al., 2008, 2009; Yao et al., 2009a, 2009b). Technosols derived from residues have been successfully utilized in the restoration of degraded mine lands in Galicia (N Spain) (Macías-García et al., 2009). Production of Technosols is also considered to be an important option for managing waste in an environmental-friendly way with minimum greenhouse gas (GHG) emission (Macías Vázquez and Camps Arbestain, 2010).

To ensure the artificially formulated Technosols fulfil the main soil functions (EU, 2006), distinct types of residues and different percentage of each ingredient need to be tested. The objective of this study was to evaluate the feasibility of six types of Technosols elaborated from mixtures of anthropogenic residues for growing perennial ryegrass in a greenhouse experiment. This chapter focused on the changes in the concentrations of nutrients and heavy metals in both the soil solution and soil. Biomass production, uptake of nutrients and accumulation of heavy metals in the plants are reported in Chapter 5.

## 4.3. Materials and methods

### *4.3.1. Ingredients of the Technosols*

Three types of municipal sewage sludge were used: (i) an anaerobic digested sludge (AN), (ii) an aerobic sludge (AE), both from the Lagares wastewater treatment plant in Vigo (Galicia, NW Spain), and (iii) a CaO-treated aerobic sludge (AL) from the Silvouta wastewater treatment plant in Santiago de Compostela, (Galicia, NW Spain). The fly ash from pine bark (*Pinus radiata and Pinus pinaster*) combustion (FA) was obtained from a paper production plant (Smurfit Kappa Group) in Durango (Basque Country, N Spain).

**Table 4.1** Chemical characterisation of the four conditioners (Source: Camps Arbestain et al., 2009).

| | **Green foundry sand** | **LD slag** | **Fly ash** | **Barley straw** |
|---|---:|---:|---:|---:|
| pH | 9.6 | 12.1 | 8.0 | - |
| Inorganic C (g kg$^{-1}$) | 1.5 | 31.7 | 8.5 | - |
| Organic C (g kg$^{-1}$) | 9.9 | 21.2 | 234.1 | 375 |
| TN (g kg$^{-1}$) | 0.1 | 0.1 | 1.1 | 4.6 |
| TP (g kg$^{-1}$) | 0.17 | 1.14 | 1.86 | 0.65 |
| TS (g kg$^{-1}$) | 0.1 | 0.5 | 21.9 | - |
| TK (g kg$^{-1}$) | 0.85 | 0.14 | 20.87 | 17 |

| | | | | |
|---|---|---|---|---|
| TCa (mg $kg^{-1}$) | 1.8 | 291.7 | 52.5 | 4 |
| TMg (mg $kg^{-1}$) | 2.4 | 7.7 | 2.9 | 5 |
| TFe (g $kg^{-1}$) | 6.2 | 135.3 | 18.1 | - |
| TMn (mg $kg^{-1}$) | 432 | 25400 | 873 | - |
| TCu (mg $kg^{-1}$) | 31 | 14 | 111 | 2.0 |
| TZn (mg $kg^{-1}$) | 122 | 33 | 873 | 6.0 |
| TNi (mg $kg^{-1}$) | 86 | 20 | 27 | - |
| TPb (mg $kg^{-1}$) | 15 | 47 | 454 | - |
| TCd (mg $kg^{-1}$) | 1.0 | 3.0 | 5.0 | - |
| TCr (mg $kg^{-1}$) | 233 | 468 | 56 | 24 |

The green foundry sand (FS) was provided by INASMET (Basque Country, N Spain). The Linz-Donawitz slag (LD) was obtained from a steel production plant ACERALIA (ARCELOR group) in Avilés (Asturias, N Spain). Besides, barley straw (BS) was also used as an ingredient to formulate Technosols in this study. The inorganic ingredients and BS were referred to as conditioners. The main chemical characteristics of all the conditioners are detailed in Table 4.1. The mineralogy and particle-size distribution of the three inorganic conditioners are presented in Table 4.2. The description of the characterisation of the conditioners was detailed in Camps Arbestain et al. (2009).

**Table 4.2** Mineralogy and particle-size distribution of the <2 mm fraction of the three inorganic conditioners (Source: Camps Arbestain et al., 2009).

| Waste | Mineralogy | Coarse sand | Fine sand | Silt | Clay |
|---|---|---|---|---|---|
| Green foundry sand | Quartz ($SiO_2$); Microcline ($KAlSi_3O_8$); Smectite ($(Na_x(Al,Mg)_2Si_4O_{10}(OH)_2\text{-}zH_2O)$) | 24.8% | 46.3% | 8.5% | 20.4% |
| LD slag | Wustite (FeO); Portlandite ($Ca(OH)_2$); Calcite ($CaCO_3$); Lamite ($Ca_2SiO_4$); Aragonite ($CaCO_3$) | 44.8% | 35.9% | 16.5% | 2.9% |
| Fly ash | Quartz ($SiO_2$); Calcite ($CaCO_3$); Halloysite ($Al_2O_3SiO_2\text{-}xH_2O$); Dolomite ($CaMg(CO_3)_2$) | 15.7% | 30.4% | 48.6% | 5.2% |

In addition, two sludges (AE and AN) and three conditioners (FS, LD and FA) were checked for the presence of toxic organic compounds. Concentrations of major organic contaminants in the ingredients are displayed in Table 4.3. The AE sludge had high BTEX (the sum of benzene, toluene, ethylbenzene, and xylene) concentrations (35 mg $kg^{-1}$) whereas the rest of ingredients had low or negligible

BTEX concentrations (Table 4.3). On the other hand, concentration of total polycyclic aromatic hydrocarbons (PAHs) in the FA ingredient (20.4 mg kg$^{-1}$) (Table 4.3) was well above the limit value for sludges to be used on land (6 mg kg$^{-1}$) (EU, 2000), although only a small fraction of these PAHs were carcinogen (0.4 mg kg$^{-1}$) (Table 2). The rest of ingredients had total PAHs contents ≤ 1.1 mg kg$^{-1}$ (Table 4.3). None of the residues had detectable concentrations of polychlorinated biphenyls (PCB) (Table 4.3). It should be highlighted that limits for organic contaminants listed in the "Working document on sludge" (EU, 2000) only refer to these organic residues and not to inorganic wastes, such as FA.

**Table 4.3** Organic contaminants in two sewages sludges and three inorganic conditioners.

| Contaminants (mg kg$^{-1}$) | Aerobic sludge | Anaerobic sludge | Green foundry sand | LD slag | Fly ash |
|---|---|---|---|---|---|
| BTEXs | 35 | <1.0 | <1.0 | <1.0 | 1.5 |
| PAHs | 0.17 | 1.17 | 0.86 | 0.95 | 20.40 |
| PAHs carcinogenic | <0.01 | 0.17 | <0.01 | 0.31 | 0.40 |
| PAHs no carcinogenic | 0.16 | 1.10 | 0.85 | 0.64 | 20.40 |

BTEXs – sum of compounds of benzene, toluene, ethylbenzene and xylene; PAHs – sum of polycyclic aromatic hydrocarbons.

### *4.3.2. Formulation of the Technosols*

The sludges (AN, AE and AL) were air-dried and passed through a 4 mm sieve, and the conditioners (FS, LD, FA and BS) were passed through a 2 mm sieve before use.

**Table 4.4** The weight percentage of each component in every treatment (air-dry weight) and their water content at field capacity of each mixture and control.

| | Aerobic sludge | Anaerobic sludge | CaO-treated aerobic sludge | Green foundry sand | LD slag | Fly ash | Barley straw | Water content at field capacity |
|---|---|---|---|---|---|---|---|---|
| AE | 100% | 0 | 0 | 0 | 0 | 0 | 0 | 57% |
| AN | 0 | 100% | 0 | 0 | 0 | 0 | 0 | 150% |
| AL | 0 | 0 | 100% | 0 | 0 | 0 | 0 | 107% |
| M1-AE | 60% | 0 | 0 | 5% | 10% | 23% | 2% | 44% |
| M1-AN | 0 | 60% | 0 | 5% | 10% | 23% | 2% | 92% |
| M1-AL | 0 | 0 | 60% | 5% | 10% | 23% | 2% | 82% |
| M2-AE | 50% | 0 | 0 | 5% | 10% | 33% | 2% | 50% |
| M2-AN | 0 | 50% | 0 | 5% | 10% | 33% | 2% | 85% |
| M2-AL | 0 | 0 | 50% | 5% | 10% | 33% | 2% | 80% |

As shown in Table 4.4, Technosols were formulated through mixing each type of sewage sludge with the four conditioners. Two doses of each sewage sludge (60% and 50%, DW) and two doses of FA (23 and 33%, DW) were considered. The rest conditioners were added at fixed percentage (5% of FS, 10% of LD and 2% of BS). Three Technosols containing 60% of sludge and 23% of FA were referred to as M1-AE, M1-AN and M1-AL. Another three with 50% of sludge and 33% of FA were identified as M2-AE, M2-AN and M2-AL. Besides, there were also three controls consisted of only sewage sludge without any addition of conditioners (AE, AN and AL controls).

### *4.3.3. Stabilisation of the samples*

The field capacity of each mixture was determined with a series of the soil moisture pressure extraction equipment (Soil Moisture Equipment Corp., Santa Barbara, CA) at the pressure of -0.33 bar. In order to reduce the adverse effects of high ammonium concentrations, all mixtures were then incubated at field capacity under greenhouse conditions for two months until they showed no phytotoxicity. The phytotoxicity of the substrates during the stabilisation process was determined by the germination index of *Lepidium sativum* L. (Zucconi et al., 1981). After stabilisation process, microbiological analysis was carried out to test the presence of pathogens in all the controls and Technosols. The results are shown in Table 4.5.

**Table 4.5** Microbiology of each mixture and control after stabilisation.

| **Samples** | **Cultivo *Salmonella* enriquecimiento (Bacsalenr)** | **Recuento *coniformes* totales alimentos (Rctocolital) (NMP g$^{-1}$)** | **Recuento *E.Coli* alimentos (Rctoecoal) (NMP g$^{-1}$)** | **Recuento *Clostridium* perfringen alimentos (Rctoperal) (UFC g$^{-1}$)** |
|---|---|---|---|---|
| AE | Absence | 240 | <3 | >1000 |
| AN | Absence | 240 | <3 | 48000 |
| AL | Absence | <3 | <3 | 900 |
| M1-AE | Absence | 240 | <3 | >1000 |
| M1-AN | Absence | 240 | <3 | >1000 |
| M1-AL | Absence | 93 | <3 | 3000 |
| M2-AE | Absence | 460 | <3 | >1000 |
| M2-AN | Absence | 460 | <3 | >1000 |
| M2-AL | Absence | 7 | <3 | 2000 |

### *4.3.4. Greenhouse experiment design*

Polypropylene (PP) plastic pots (12 cm in diameter, 17 cm in height) – with 1 cm of glass wool placed at the bottom – were filled with the previously stabilized samples (Fig.4.1). Four pots were prepared for each treatment and three of them were pierced with two Rhizon Soil Moisture Sampler (10 cm Tube, Eijkelkamp Agrisearch Equipment) to collect soil solution periodically. One was set at a height of 4.5 cm and the other at a height of 5.5 cm. Given the small volumes of solution sampled, these were mixed previous to analyses. The fourth pot of each treatment was used to collect the soil sample for analysis every two weeks with a mini soil corer, although here only the characteristics of the initial and final soil samples have been reported. Deionised water was added daily into each pot using an individualised drip system to maintain moisture at field capacity. After one week, all pots were sown with 15 seeds of perennial ryegrass (*Lolium perenne* L.).

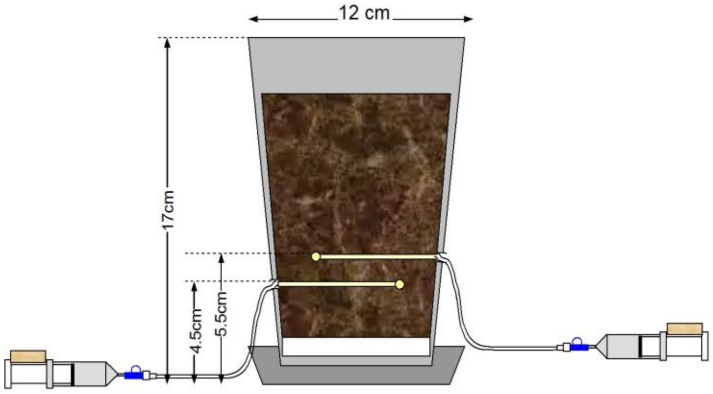


**Fig. 4.1.** Schematic diagram of the pot used in the greenhouse experiment.

### *4.3.5. Soil and soil solution samples collection and chemical analyses*

Soil solution samples were collected once or twice weekly from the first day of the experiment until day 136. All of the solutions were analyzed for pH; ammonium following the modified method of Berthelot (Kandeler and Gerber, 1988); dissolved organic carbon (DOC) after digestion by acid potassium dichromate solution (Heanes, 1984; Nelson and Sommers, 1996) based on the Walkley-Black method using UVIKON 930 spectrophotometer (Kontron Instruments, Milan, Italy); total P, K, Ca, Mg, S, Cu, Zn, Ni, Pb, Cd and Cr in the soil solution using a charge coupled device (CCD) Simultaneous ICP-OES VISTA-MPX (Varian Ibérica S.L., Madrid, Spain); sulphate, nitrate and chloride using ionic chromatograph (Dionex-4500i, Dionex Corp., Sunnyvale, CA).

Soil samples at the beginning and end of the experiment were oven-dried at 35 ºC until constant weight, and then ground to pass 2 mm sieve for analysis. The pH of the soil was measured in deionised water at a water/soil ratio of 2.5/1 (v/w). The organic carbon (OC) was digested by acid potassium dichromate solution (Heanes, 1984; Nelson and Sommers, 1996) and then measured with UVIKON 930 spectrophotometer (Kontron Instruments, Milan, Italy). Total C and N were determined by a TruSpec CHN analyzer (LECO Corporation, Michigan USA). Total P, S, K, Ca, Mg, Cu, Zn, Ni, Pb, Cd and Cr were analysed by charge coupled device (CCD) Simultaneous ICP-OES VISTA-MPX (Varian Ibérica S.L., Madrid, Spain) after digestion with a mixture of nitric and perchloric acid (85%:15%, v/v).

### *4.3.6. Other characterisation of soil samples.*

#### *4.3.6.1. Solid-state nuclear magnetic resonance spectroscopy (NMR)*

Solid-state $^{13}C$ nuclear magnetic resonance (NMR) spectra were obtained (Bruker Avance DSX300 NMR spectrometer, Bruker Corporation) after pre-treatment of the samples with HF solution. Variable amplitude cross-polarisation magic angle spinning (CP/MAS) experiments were run with a 4-mm MAS probe, with a spin rate of approximately 8,000 Hz. The contact time was 1 ms and the delay time was 2 s. An average of 50,000 transients was recorded for each sample.

#### *4.3.6.2. Estimation of microbial activity by substrate induced respiration (SIR) technique*

Microbial activity in the soils was estimated through the substrate induced respiration (SIR) technique (Anderson and Domsch, 1973) using a Micro-Oxymax Respirometer (Columbus Instruments, Columbus, OH). After two-day stabilisation of each sample (the amount was the equivalent to 2 g dry weight) in 100 mL Schott Duran bottles, evolved $CO_2$ was continuously measured during 24 h. Then 1 mL glucose solution (4 g $L^{-1}$) was injected into each bottle through a septum. The bottle was agitated to homogenize the sample with the glucose solution. The emitted $CO_2$ was measured at 2, 4, 8 and 24 h.

### *4.3.7. Statistical analysis*

To assess the statistical differences among chemical properties of the soil solution, a one-way analysis of variance followed by a *post hoc* (Bonferroni) multiple comparison test (at $P < 0.05$) was computed with SPSS version 11.0 for PC-Windows (SPSS Inc., Chicago, IL, USA).

## **4.4. Results and discussion**

### *4.4.1. Chemical properties of the Technosols*

At the beginning of the experiment, the AE and AN controls showed pH values slightly below neutrality (6.3 and 6.7, respectively), whereas the pH values of their respective Technosols were significantly higher, with mean values of 7.8, 8.0, 7.3 and 7.6 for the treatments M1-AE, M2-AE, M1-AN and M2-AN, respectively (Table 4.6), owing to the amendment of inorganic conditioners (FS, LD and FA) that contained substantial amount of alkaline materials (Table 4.2). In the AE and AN Technosols, an increase in the FA dose (M2 treatments) produced a higher pH values compared to the low FA dose (M1 treatments), as expected, but this was not observed in the AL treatments. The pH of the AL control was 7.0 and that of the Technosols M1-AL and M2-AL was 7.1. This was attributed to the fact that the CaO pre-treatment at the wastewater treatment plant conferred this sludge a high acid-alkali buffering capacity. The pH of the AN control decreased to 5.3 at the end of the experiment while there was no obvious decrease in the pH of other treatments (Table 4.7).

The AN control had the highest amount of TC (234 g $kg^{-1}$) and OC (189 g $kg^{-1}$) (Table 4.6), which could be the result of the low rates of OM decomposition under the reduced conditions at which the AN sludge was treated. The content of TC and OC (Table 4.6) in the AN Technosols was significantly lower than the control (>25 and > 45%, respectively), caused by the dilution effect of the conditioners. In the AL sludge, the addition of CaO at the wastewater treatment plant halted OM degradation. This may explain the fact that this treatment had the second highest concentration of OC (112 g $kg^{-1}$) (Table 4.6). Secondary carbonation associated with the alkalinity of the CaO explains the high values of inorganic C, estimated by subtracting OC from TC. The FA conditioner had higher OC content than the AL and AE sludges (136 vs. 112 and 55 g $kg^{-1}$) (Table 4.1 and 4.6), due to the presence of charred material in the former. This caused an increase in OC content as the dose of FA in the AL and AE Technosol mixtures increased (Table 4.6). The AE sludge and their corresponding Technosols were those that had the lowest amount of OC (55 g kg$^{-1}$ in the AE control, 48 g kg$^{-1}$ in M1-AE and 68 g kg$^{-1}$ in M2-AE) (Table 4.6). The AE control had the greatest reduction in TC and OC contents during the experiment (28% in TC and 21% in OC, respectively; Table 4.7).

**Table 4.6** Chemical characterisation of the sample of each treatment at the beginning of the greenhouse experiment (after stabilisation).

| Properties | AE | AN | AL | M1-AE | M1-AN | M1-AL | M2-AE | M2-AN | M2-AL |
|---|---|---|---|---|---|---|---|---|---|
| pH | 6.3 | 6.7 | 7.0 | 7.8 | 7.3 | 7.1 | 8.0 | 7.6 | 7.1 |
| Total C (g kg$^{-1}$) | 63 | 234 | 188 | 82 | 161 | 156 | 83 | 172 | 155 |
| Organic C (g kg$^{-1}$) | 55 | 189 | 112 | 48 | 104 | 81 | 68 | 87 | 103 |
| TN (g kg$^{-1}$) | 6.2 | 33.2 | 19.1 | 4.2 | 15.0 | 12.8 | 3.6 | 14.2 | 10.2 |
| TP (g kg$^{-1}$) | 7.9 | 18.8 | 8.2 | 6.3 | 11.3 | 6.1 | 5.5 | 9.7 | 6.1 |
| TS (g kg$^{-1}$) | 4.2 | 10.3 | 3.0 | 6.9 | 10.9 | 7.0 | 8.0 | 13.0 | 11.1 |
| TK (g kg$^{-1}$) | 7.9 | 5.5 | 1.6 | 7.0 | 5.0 | 2.8 | 6.2 | 4.8 | 3.8 |
| TCa (g kg$^{-1}$) | 11.2 | 16.8 | 214.7 | 55.8 | 67.3 | 179.0 | 64.5 | 95.4 | 185.9 |
| TMg (g kg$^{-1}$) | 9.7 | 4.7 | 3.5 | 11.9 | 9.7 | 10.7 | 11.4 | 12.2 | 11.2 |
| TFe (g kg$^{-1}$) | 26.5 | 19.2 | 29.9 | 31.1 | 30.7 | 34.7 | 28.6 | 30.3 | 29.9 |
| TMn (g kg$^{-1}$) | 0.36 | 0.29 | 0.25 | 3.43 | 3.95 | 4.30 | 3.74 | 7.07 | 4.35 |
| TAl (g kg$^{-1}$) | 39 | 37 | 10 | 28 | 27 | 11 | 24 | 22 | 12 |
| TCu (mg kg$^{-1}$) | 264 | 920 | 259 | 170 | 501 | 169 | 144 | 395 | 172 |
| TZn (mg kg$^{-1}$) | 508 | 807 | 328 | 405 | 521 | 282 | 346 | 499 | 316 |
| TNi (mg kg$^{-1}$) | 60 | 35 | 26 | 127 | 123 | 138 | 149 | 185 | 181 |
| TPb (mg kg$^{-1}$) | 119 | 137 | 51 | 116 | 110 | 68 | 94 | 120 | 89 |
| TCd (mg kg$^{-1}$) | 2.86 | 2.88 | 2.73 | 2.98 | 3.37 | 3.39 | 5.54 | 3.32 | 2.79 |
| TCr (mg kg$^{-1}$) | 109 | 77 | 94 | 211 | 172 | 240 | 219 | 234 | 201 |

The AN control had greater TN (33.2 g kg$^{-1}$) than the other two controls (6.2 and 19.1 g kg$^{-1}$ in AE and AL control, respectively) (Table 4.6), and this was again attributed to the different treatments underwent at the wastewater treatment plants. The TN content became diluted with the addition of the conditioners, given their scarce N content. The highest initial concentration of P was also found in the AN control (18.8 g kg$^{-1}$), being more than double compared to those of the AE and AL controls (7.9 and 8.2 g kg$^{-1}$, respectively) (Table 4.6). Phosphorus concentration in all the Technosols was significantly lower than in the controls owing to the poor P contribution of the conditioners.

**Table 4.7** Chemical characterisation of the sample of each treatment at the end of the greenhouse experiment.

| Properties | AE | AN | AL | M1-AE | M1-AN | M1-AL | M2-AE | M2-AN | M2-AL |
|---|---|---|---|---|---|---|---|---|---|
| pH | 6.2 | 5.3 | 7.8 | 8.3 | 7.7 | 8.2 | 8.7 | 8.0 | 8.1 |
| Total C (g kg$^{-1}$) | 45 | 222 | 172 | 71 | 142 | 148 | 80 | 150 | 147 |
| Organic C (g kg$^{-1}$) | 43 | 161 | 103 | 54 | 88 | 91 | 57 | 92 | 86 |
| TN (g kg$^{-1}$) | 4.3 | 27.7 | 17.2 | 3.7 | 8.6 | 11.2 | 3.7 | 9.5 | 10.1 |
| TP (g kg$^{-1}$) | 6.3 | 16.8 | 8.8 | 5.3 | 7.2 | 5.9 | 5.0 | 7.5 | 5.5 |
| TS (g kg$^{-1}$) | 2.7 | 9.9 | 3.2 | 5.5 | 10.2 | 6.4 | 6.6 | 10.7 | 8.1 |
| TK (g kg$^{-1}$) | 6.7 | 4.4 | 1.2 | 5.6 | 2.3 | 1.3 | 5.3 | 2.4 | 1.3 |
| TCa (g kg$^{-1}$) | 8.6 | 16.0 | 252.9 | 48.3 | 83.9 | 183.1 | 63.4 | 94.6 | 177.3 |
| TMg (g kg$^{-1}$) | 8.2 | 3.9 | 2.9 | 10.6 | 8.5 | 9.5 | 13.7 | 13.1 | 10.2 |
| TFe (g kg$^{-1}$) | 29.1 | 19.8 | 39.8 | 40.8 | 36.2 | 36.0 | 37.5 | 34.5 | 33.0 |
| TMn (g kg$^{-1}$) | 0.31 | 0.28 | 0.27 | 3.00 | 4.60 | 2.98 | 3.73 | 5.42 | 3.24 |
| TAl (g kg$^{-1}$) | 45 | 53 | 11 | 32 | 19 | 12 | 31 | 22 | 13 |
| TCu (mg kg$^{-1}$) | 248 | 872 | 274 | 191 | 261 | 241 | 169 | 292 | 165 |
| TZn (mg kg$^{-1}$) | 472 | 780 | 354 | 403 | 458 | 300 | 394 | 481 | 308 |
| TNi (mg kg$^{-1}$) | 49 | 53 | 26 | 125 | 178 | 121 | 216 | 194 | 145 |
| TPb (mg kg$^{-1}$) | 121 | 134 | 49 | 120 | 93 | 66 | 123 | 106 | 77 |
| TCd (mg kg$^{-1}$) | 2.22 | 2.57 | 2.42 | 2.61 | 2.67 | 2.41 | 2.61 | 2.74 | 2.26 |
| TCr (mg kg$^{-1}$) | 52 | 87 | 101 | 205 | 509 | 297 | 392 | 374 | 225 |

The anaerobic treatment underwent by the AN sludge at the wastewater treatment plant, caused S to be reduced to sulphides with their subsequent precipitation due to their very low solubility. This explains the higher concentration of S in the AN control (10.3 g kg$^{-1}$) and the AN Technosols (10.9 and 13.0 g kg$^{-1}$ in M1-AN and M2-AN, respectively) compared to the rest of treatments. The concentration of S rose up as the percentage of sludge was decreased in the Technosols, which was caused by higher content of S in the FA (21.9 g kg$^{-1}$) than in the sludge (Tables 4.1 and 4.6). The concentration of K and Mg followed the order AE > AN > AL and this trend was also observed in their corresponding Technosols (Table 4.6). The concentration of Ca in the AL control was more than 10 times higher than in the other controls, which was due to the addition of CaO into the AL sludge at the wastewater treatment plant. This was also reflected in their corresponding Technosols.

With regard to heavy metals, the AN control had the highest Cu (920 mg $kg^{-1}$), Zn (807 mg $kg^{-1}$) and Pb (137 mg $kg^{-1}$) concentrations among all the treatments whereas AE control contained the highest amount of Ni (60.1 mg $kg^{-1}$) and Cr (109 mg $kg^{-1}$) (Table 4.6). Cadmium concentration was < 3 mg $kg^{-1}$ in the three controls (Table 4.5). The addition of conditioners tended to dilute the concentrations of Cu and Zn, whereas it significantly increased the concentrations of Cr and Ni (Table 4.6), resulting from the high concentration of Cr in FS (233 mg $kg^{-1}$) and LD (468 mg $kg^{-1}$), and Ni in FS (86 mg $kg^{-1}$) (Table 4.1).

### *4.4.2. Changes in pH of the soil solution*

The pH values in the soil solution from the controls at time 0 followed the order: AN (7.6) > AE (6.9) > AL (6.6) (Fig. 4.2A). During the first 31 days, the pH values of the AN control soil solution were always the highest among the three controls, whereas after 73 days they were the lowest among all the treatments. The AE and AL controls remained relatively constant, with a slight decrease of the former from 6.5 to 6.3 after the first 6 weeks of experiment. Both the AE and AL sludges have a higher acid buffering capacity than the AN sludge, the first owing to the presence of a more humified organic matter (Yao et al., 2009a), and the latter due to the CaO pre-treatment undergone at the wastewater treatment plant. The soil solution of the Technosols under study had significantly higher pH values than the corresponding controls and remained relatively stable during the experiment, which could be attributed to the acid buffering effect provided by the conditioners.

### *4.4.3. Changes in the concentrations of the DOC in the soil solution*

The concentration values of DOC in the AL control solution were significantly higher than those found in the rest of treatments studied during the whole experimental period, with an initial DOC concentration of 3.9 mg $L^{-1}$ and a maximum of 5.3 mg $L^{-1}$ at day 17 (Fig. 4.2B). Thereafter, DOC values declined continuously to 1.9 mg $L^{-1}$ at day 136. The concentration values of DOC in the AL Technosols (M1-AL and M2-AL) were significantly lower than the AL control ($P < 0.05$), with mean concentrations of 1.0 and 0.9 mg $L^{-1}$ for the M1-AL and M2-AL treatments, respectively (Fig. 4.2B).

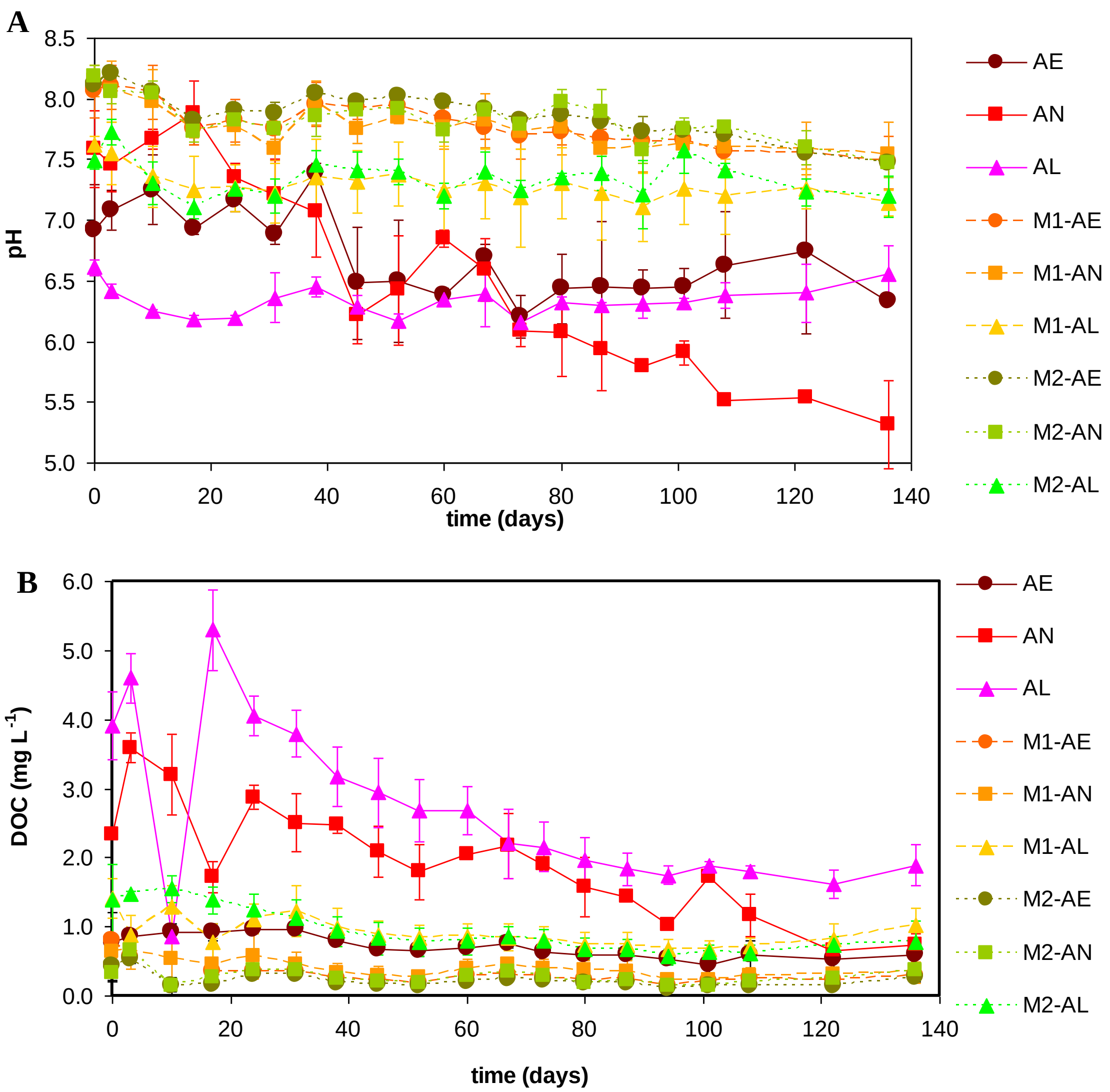


**Fig. 4.2.** Changes in (A) pH and concentrations of (B) DOC in the leachates of controls and different Technososls.

The concentration values of DOC in the AN control were significantly lower than those of the AL control, with an average concentration of 1.8 mg $L^{-1}$ during the experiment and a peak of 3.2 mg $L^{-1}$ at day 10 (Fig. 4.2B). The DOC concentrations in the soil solution of M1-AN and M2-AN Technosols were significantly lower than the AN control, oscillating around 0.3-0.4 mg $L^{-1}$.

The concentration values of DOC in the solution of the AE control was the lowest among the three controls, with an initial value of 0.8 mg $L^{-1}$ and a final value of 0.6 mg $L^{-1}$ (Fig. 4.2B). The aerobic treatment of AE at the wastewater treatment plant favoured the decomposition of organic matter and, therefore, the decomposition of the most soluble species (Bernal and Kirchmann, 1992; Yao et al., 2009a). In the soil solution of M1-AE and M2-AE treatments, DOC concentration was even lower than that of the AE control. The DOC concentrations in the solution of the

Technosols were lower than of the controls, not only because of the dilution effect of the conditioners but also due to the protection of OC from decomposition by the conditioners through sorption reactions. These results were in agreement with the results obtained using the SIR technique (Fig. 4.8, as discussed below).

### *4.4.4. Evolution of ammonium and nitrate concentrations in the soil solution*

The concentration of ammonium in the initial soil solution of the AL control, was as high as 1174 mg $L^{-1}$ and went up to 1355 mg $L^{-1}$ at day 10 (Fig. 4.3A), attributed to the addition of CaO with high pH to the AL sludge. During the experiment there was a continuous decline in the ammonium concentration mainly attributed to plant uptake as described in Chapter 5, reaching a concentration of 75 mg $L^{-1}$ at day 136.

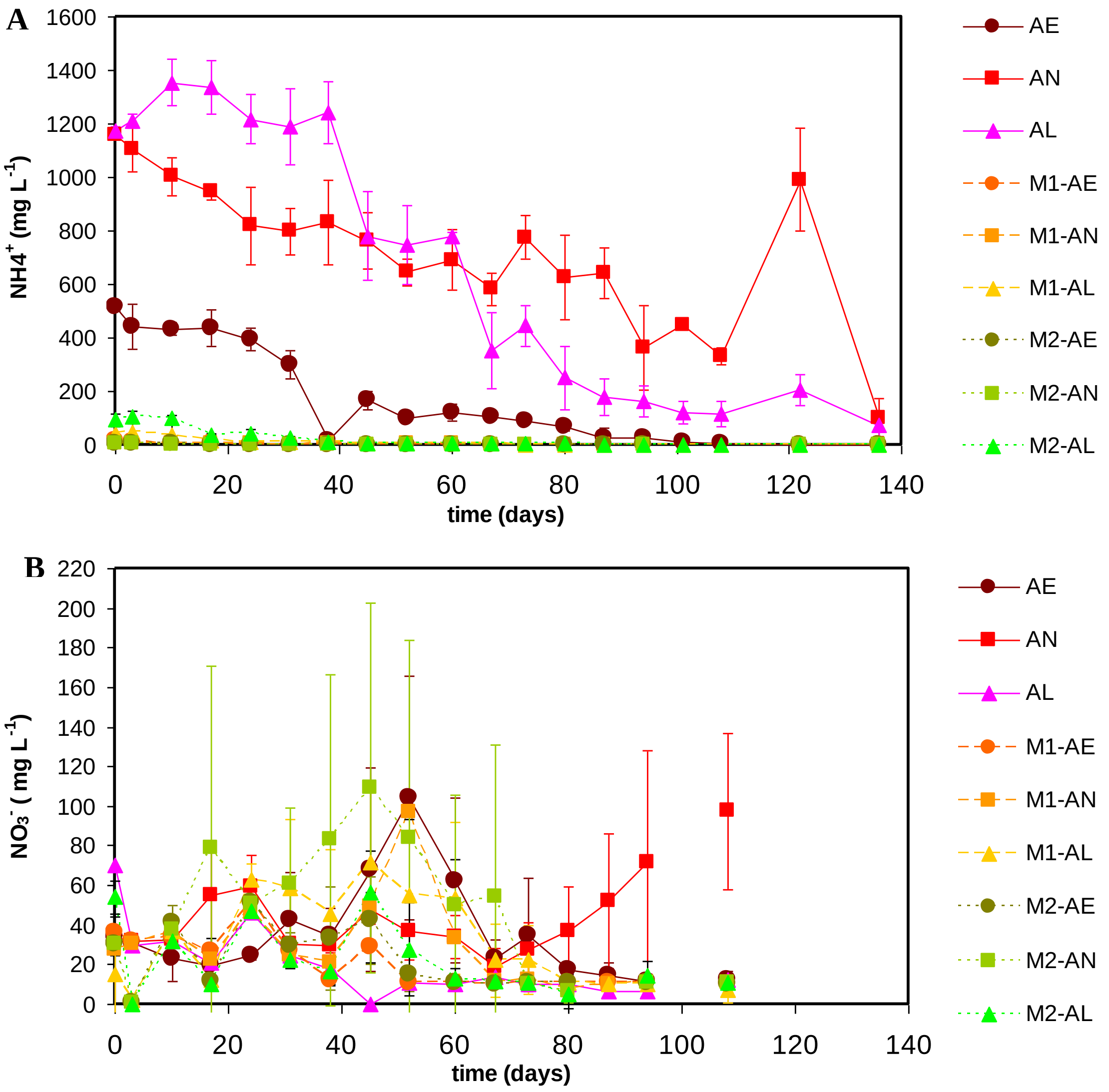


**Fig. 4.3.** Changes in concentrations of (A) ammonium and (B) nitrate in the leachates of controls and different Technososls.

In the AN control, initial ammonium concentration was 1157 mg $L^{-1}$ and this decreased with some fluctuations, to a concentration of 101 mg $L^{-1}$ at day 136 (Fig. 4.3A). The concentration of ammonium in the AE control was the lowest among the three controls, which may explain the low N uptake observed in the ryegrass and described in Chapter 5 (Fig. 5.2). Its peak value was 518 mg $L^{-1}$ at the beginning and declined to as low as 0.7 mg $L^{-1}$ at day 136. Ammonium concentrations in solution of the Technosols, were lower than 17 mg $L^{-1}$, except for the AL mixtures, which had a highest value of 103 mg $L^{-1}$ (Fig. 4.3A). The addition of conditioners with reactive surfaces able to adsorb ammonium and the presence of a fresh organic residue – barley straw – with a high C/N ratio might explain the differences from the control treatments observed.

The initial nitrate concentration in the AL control was the highest (70 mg $L^{-1}$) among all the controls but it decreased, with oscillations, during the experiment and reached 12 mg $L^{-1}$ at day 108 (Fig. 4.3B). There was an apparent increase in the nitrate concentration of the AN control from day 67 on, which was paralleled by a decrease in pH values, evidencing the acidification associated with nitrification processes (Fig. 4.3B). However, the nitrifying process did not cause significant decrease in the pH in the Technosols (Fig. 4.2A) owing to the high acid capacity of the mixtures. The concentrations of ammonium in the solution of the Technosols were significantly lower than the controls whereas the reverse trend was observed in the nitrate concentrations, although the fact that microbes and plants were taking up both forms of N made the interpretation of these results difficult. Total N contents absorbed by the ryegrass grown on the Technosols were generally lower than those of the controls (Fig. 5.2B, Chapter 5).

### *4.4.5. Evolution of phosphorus in the soil solution*

Phosphorus concentration in the solution of the AN control (Fig. 4.4A) was the highest, with the initial value above 200 mg $L^{-1}$ and the final value of 72 mg $L^{-1}$. The high solubility of P in the AN sludge was also evidenced in the amount of P taken up by the plants grown in this substrate, as discussed in Chapter 5 (Fig. 5.3).

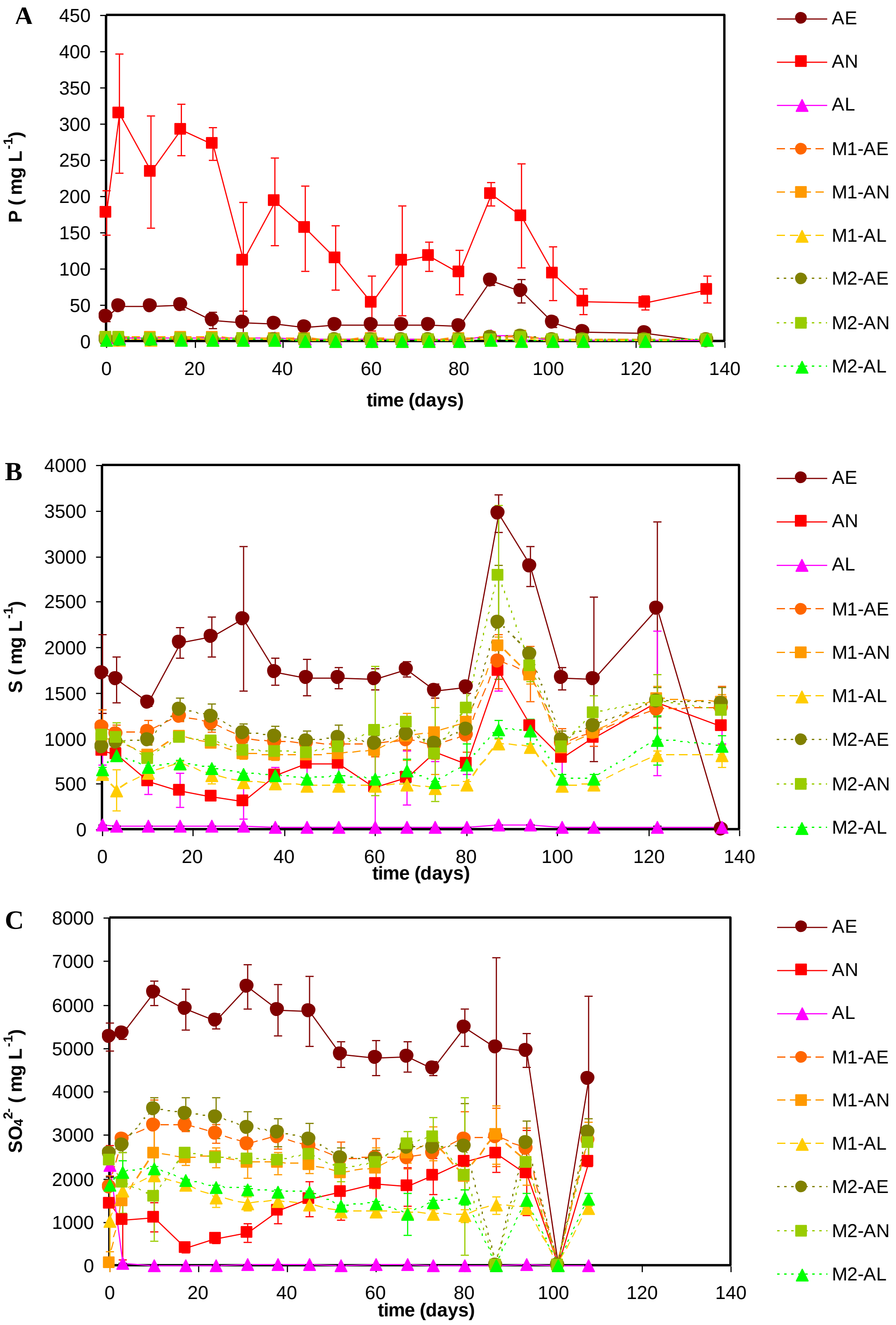


**Fig. 4.4.** Changes in the concentrations of (A) P, (B) S, and (C) sulphate in the leachates of controls and different Technososls.

The concentrations of P in the AE control oscillated between 20 and 50 mg $L^{-1}$ during the first 80 days; It suddenly increased to 83 mg $L^{-1}$ at day 87 when the first clipping of ryegrass was cut; after that, it decreased continuously to 0.1 mg $L^{-1}$ at day 136 (Fig. 4.4A), probably due to rapid uptake by the ryegrass which was cut at day 132 (Chapter 5).

Total P concentrations in the soil solution of the AL control and all the Technosols were lower than 8.0 mg $L^{-1}$ at all solution sampling times (Fig. 4.4A). This was attributed to the high content of Ca in the AL sludge and conditioners, which induced the formation of Ca phosphates with the subsequent decline in their solubility. Also, the addition of conditioners lowered P concentration in solution, through (i) dilution and (ii) sorption and/or precipitation reactions. The extremely low availability of P in the AL treatments was reflected in the low P concentrations of ryegrass plants grown on these substrates (Fig. 5.3, Chapter 5).

### *4.4.6. Evolution of total sulphur in the soil solution*

The concentration of soluble S (Fig. 4.4B) – found mostly as sulphate (Fig 4.4C) –was the highest in the solution of the AE control (varying between 1394 and 3474 mg $L^{-1}$) and the lowest in the AL control with values always below 50 mg $L^{-1}$ (Fig. 4.4C). The peak value of S concentration observed in all treatments except the AL control at day 87 was probably attributed to the fact that roots reached that depth by such sampling time. The concentration of soluble S in the AE Technosols was lower than the AE control, and this was attributed to precipitation reactions caused by the conditioners added. The opposite tendency was found in the soil solution of the AN and AL Technosols in relation with their corresponding controls. The greater presence of DOC in these two sludges than in the AE sludge might have favoured the displacement of sulphate from sorption sites in the conditioners. Also, the greater presence of organic S associated with DOC (data not shown) might also explain these patterns.

### *4.4.7. Evolution of basic cations in the soil solution*

The concentrations of K in the soil solution of the AE and AL controls were lower than those of the respective Technosols (Fig. 4.5A), reflecting the positive role of the conditioners on K availability (mainly through the addition of K with the fly ashes and barley straw). In all the treatments, a sudden decrease was observed from day 80, and this could be attributed, as above, to the fact that by that time roots probably reached the depth at which the sampling devices were placed.

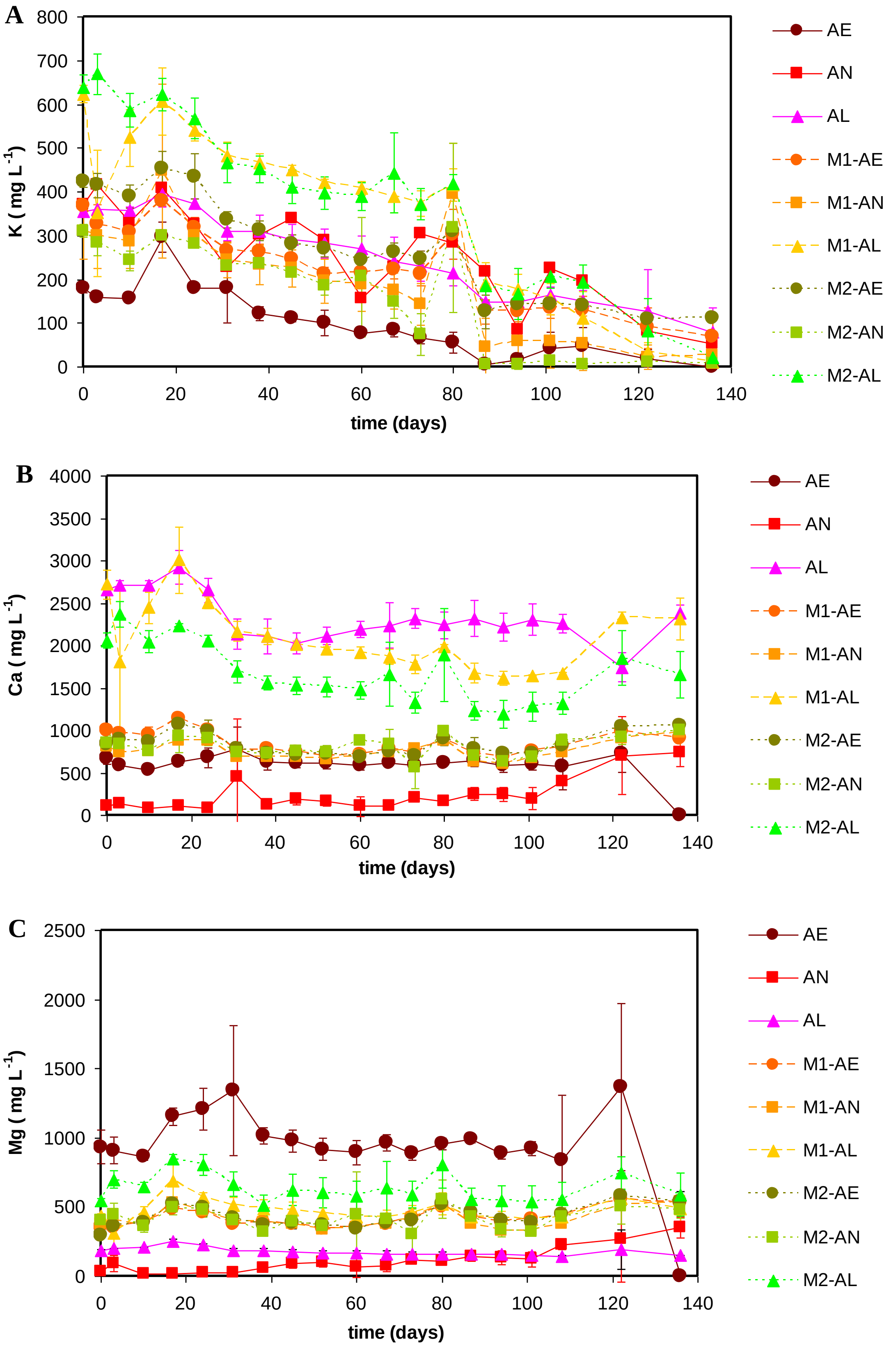


**Fig. 4.5.** Changes in the concentrations of (A) K, (B) Ca and (C) Mg in the leachates of controls and different Technosols.

Calcium concentration of all treatments remained relatively constant throughout the experiment (Fig. 4.5B), which indicates that its concentration was controlled by inorganic Ca precipitates. The highest Ca concentrations were found in the treatments in which the AL sludge was used as ingredient (Fig. 4.5B), as expected. In these treatments, Ca solubility decreased in the presence of conditioners, probably due to additional precipitation and adsorption reactions. In contrast, the soil solution of the AE and AN Technosols had higher Ca concentrations than their respective controls, resulting from the high content of Ca supplied by the conditioners. Calcium concentrations in the solution were paralleled by the total Ca taken up by the plants (Fig. 5.5, Chapter 5).

The highest Mg concentration was found in the soil solution of the AE control, reaching a peak value of 1367 mg $L^{-1}$ at day 122 (Fig. 4.5C), due to the highest Mg content in the AE sludge (9.7 g $kg^{-1}$) (Table 4.5). The high Mg availability in this treatment was manifested in the Mg concentrations of the ryegrass grown in the AE control (Fig. 5.6, Chapter 5). Magnesium concentrations in the soil solution of the M1-AE and M2-AE Technosols were significantly lower than the AE control, which was attributed to precipitation and adsorption reactions. The soil solution of the AN and AL controls had the lowest Mg concentration, with values ranging from 144.7 to 247.9 mg $L^{-1}$ (Fig. 4.5C). Those of their respective Technosols were higher, as expected, given the Mg concentrations of the conditioners relative to these sludges.

### *4.4.8. Evolution of heavy metals in the soil solution*

The Cu concentrations in the soil solution of AN control were generally higher than in the other treatments and the addition of conditioners effectively decreased Cu solubility and mobility (Fig. 4.6A) and thus Cu bioavailability (Fig. 5.9A, Chapter 5). None of the Cu concentrations exceeded the EU drinking water threshold (2.0 mg $L^{-1}$) (EU Directive 98/83) – it should be noted that soil solution was sampled at field capacity and that drainage water would be even further diluted.

The concentrations of Zn in the soil solution of the Technosols were significantly lower than those of the corresponding controls (Fig. 4.6B), suggesting stabilisation of Zn by the conditioners. None of the Zn concentration has surpassed the EU drinking water threshold (3.0 mg $L^{-1}$) (EU Directive 98/83).

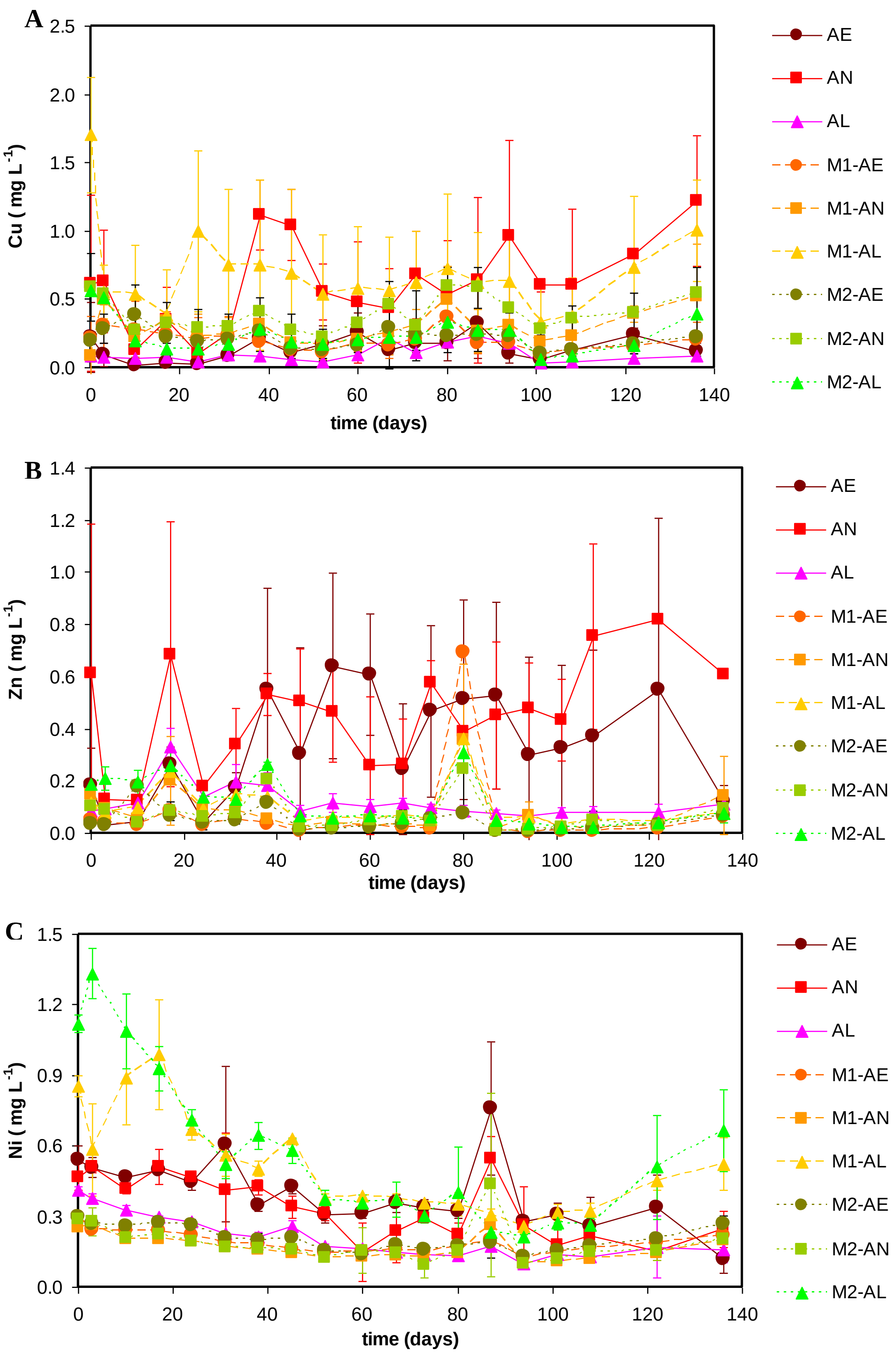


**Fig. 4.6.** Changes in concentrations of (A) Cu, (B) Zn and (C) Ni in the leachates of controls and different Technosols.

The concentrations of Ni in most of the solutions at different sampling times have exceeded the limit value (0.02 mg $L^{-1}$) of EU drinking water (EU Directive 98/83) (Fig. 4.6C), which could be brought by the high portion of water-soluble fraction of Ni in the sludges (Yao et al., 2009b). However, as the drainage water was few under this irrigating condition, there would be minimum hazards to the ground water. The concentrations of Pb, Cd and Cr in the soil solution were extremely low (data not shown).

### *4.4.9. Carbon characterisation and microbial activity in the Technosols*

The CP/MAS $^{13}$C NMR spectra of the three controls are displayed in Fig. 4.7. The three sludges showed a dominant band at 45-110 ppm characteristic of O-alkyl. This can be attributed to cellulose and hemicellulose, but also to protein and lignin side chains. The peak at 100 ppm could be attributed to acetyl groups (di-O-alkyl) attributed to anomeric C-1 cellulosic structures. The three sludges showed a dominant band at 162-190 ppm that could be attributed either to carboxylic acids and/or secondary amides. The intensity of the alkyl C band, at 0-45 ppm, was less intense in the AE sludge, followed by the AN and the AL sludges. The ratio of alkyl C to O-alkyl C is recognised as a sensitive indicator of the extent of decomposition of soil organic matter (Baldock et al., 1997). The alkyl C/O-alkyl C ratios were the highest in the AE sludge (0.95), followed by the AN sludge (0.79) and the AL sludge (0.47), in agreement with the degree of decomposition undergone by the different sludges.

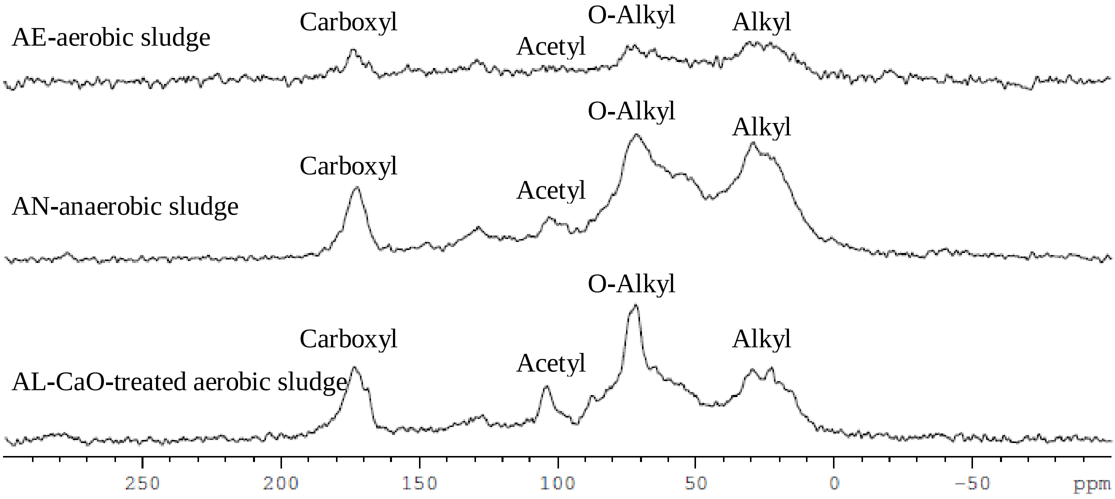


**Fig. 4.7.** CP/MAS $^{13}$C NMR spectra of the three sludges.

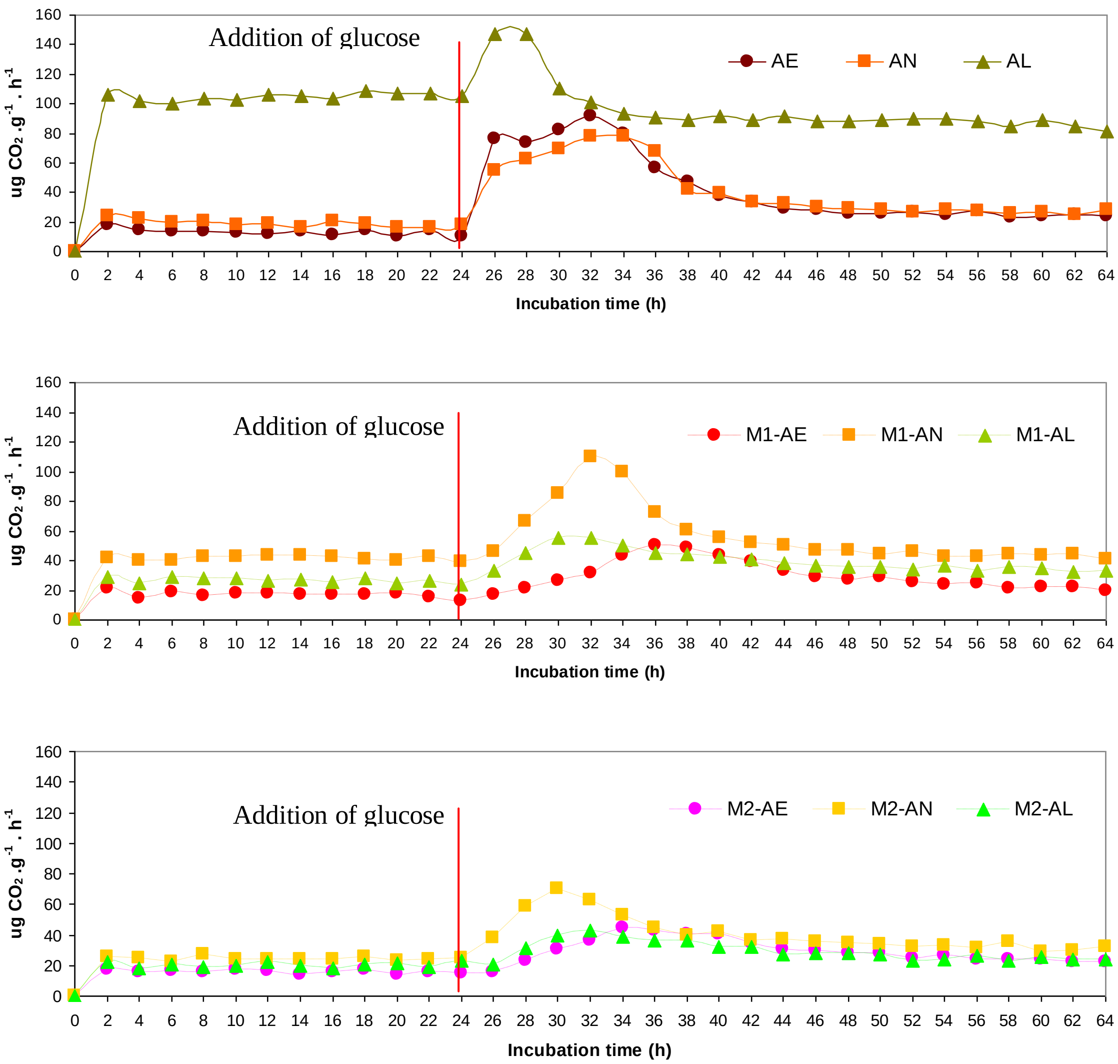


**Fig. 4.8**. The release rate of carbon dioxide of the Technosols and controls using substrate induced respiration (SIR) technique at day 118; glucose was added at 24 h.

Samples on day 118 were incubated during 64 h and the rate of $CO_2$ evolved is reported in Fig. 4.8. The greatest $CO_2$ released among the 3 controls was from the AL sludge, which mostly occurred during the first 2 hours and was attributed to the evolution of $CO_2$ from carbonates, present in important amounts in this sludge. All the three controls released a significant amount of $CO_2$ right after the amendment of glucose. This released was steadily maintained for 14 h in the AE and AN treatments, due to a burst in microbial activity and growth, whereas that of the AL treatment was short and probably attributed to a further dissolution of carbonates, although some microbial activity could also be responsible for this. These results reflect the presence of an active microbial biomass in the AE and AN sludges. In the AL treatment, the small microbial activity detected could be explained by the negative effect of CaO treatment undergone previously at the wastewater treatment plant on microbial activity.

The $CO_2$ evolution of the mixtures was more homogeneous among treatments (e.g. M1-AE, M1-AN, M1-AL) compared to the patterns observed among controls (AE, AN, AL), as the amount of sludge was diluted and all treatments received the same amount of barley straw. The highest rate of $CO_2$ evolved from the mixtures was always from the AN treatment, in agreement with the high organic C concentrations of this sludge, followed by the AL and then the AE treatment, although these differences almost disappeared at the lowest dose of sludge (M2 treatments). When these values were normalised per unit of initial TC content, this order was modified; the highest value was found in the AL control (0.47 g $CO_2$ $kg^{-1}$ TC $h^{-1}$), followed by AE control (0.43 g $CO_2$ $kg^{-1}$ TC $h^{-1}$) and the lowest was found in the AN control (0.13 g $CO_2$ $kg^{-1}$ TC $h^{-1}$).

## 4.5. Conclusions

The properties of the Technosols were highly influenced by the type of the sewage sludge used. The Technosols made with anaerobic sludge contained the highest content of N, P, K and OC, while those elaborated from aerobic sludge had the lowest amount of such nutrients and OM. The Technosols formulated from CaO-treated aerobic sludge contained the highest amount of Ca and lowest availability of P. Amendment of conditioners, i.e. green foundry sand, Linz-Donawitz slag and fly ash not only have increased the acid buffering capacity, lowered the acidification rate, but also decreased the decomposition rate of OC through protection by minerals. The addition of barley straw as a conditioner has also increased the K availability. Furthermore, the conditioners have also favoured the immobilisation of heavy metals although the effect of “chemical time bomb” should not be ignored. The technology of elaborating Technosols from mixtures of residues is an optimum option for incorporating the nutrients in the wastes into the biogeochemical cycle. It should be tailor-made according to various factors, among which the property and rate of each ingredient are the most important.

## 4.6. Acknowledgements

We gratefully acknowledge Smurfit Kappa Group, INASMET and ACERALIA for supplying the conditioners. The research was funded by the Spanish Ministry of

Environment (Project Nos. 093/2004/3; 2.5-206/2005/2-B; 208/2006/1-2.5), the Diputacion Foral de Bizkaia (Project No. 7/12/EK/2005), and the Spanish Ministry of Science and Education (Project No. CTM 2006-13748 -CO2). Fenxia Yao is in receipt of an FPI fellowship from the Spanish Ministry of Science and Education.

## 4.7. References

Anderson, J.P.E. and Domsch, K.H., 1973. Quantification of bacterial and fungal contributions to soil respiration. Arch. Microbiol. 93, 113-27.

Camps Arbestain, M., Ibargoitia, M.L., Madinabeitia, Z., Gil, M.V., Virgel, S., Morán, A., Pereira, R.C., Macías Vázquez, F., 2009. Laboratory appraisal of organic carbon changes in mixtures made with different inorganic wastes. Waste Manage. 29, 2931-2938.

Camps Arbestain, M., Madinabeitia, Z., Anza Hortalà, M., Macías-García, F., Virgel, S., Macías Vázquez, F., 2008. Extractability and leachability of heavy metals in Technosols prepared from mixtures of unconsolidated wastes. Waste Manage. 28, 2653-2666.

EC, European Commission Council Directive 98/83/EC of 3 November 1998, on the Quality of Water Intended for Human Consumption. EN L 330/42, 5.12.98.

EU, 2006. Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste, in: Union, E. (Ed.), Strasbourg.

EU. 2000. Working document on sludge. 3rd Draft. Unpublished. 19 p.

Eusterhues, K., Rumpela, C., Kleber, M., Kögel-Knabner, I., 2003. Stabilisation of soil organic matter by interactions with minerals as revealed by mineral dissolution and oxidative degradation. Org. Geochem. 34, 1591-1600.

Heanes, D.L., 1984. Determination of total organic-C in soils by an improved chromic acid digestion and spectrophotometric procedure. Comm. Soil Sci. Plant Anal. 15, 1191-1213.

Kandeler, E. and Gerber, H., 1988. Short-term assay of soil urease activity using colorimetric determination of ammonium. Biol. Fert. Soils 6, 68-72.

Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K., Leinweber, P., 2008. Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry. J. Plant Nutr. Soil Sc. 171, 61-82.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Manage. 28, 215-225.

Macías-García, F., Camps Arbestain, M., Macías Vázquez, F., 2009. Utilización de Tecnosoles derivados de residuos en procesos de restauración de suelos de la mina Touro. In: Cámara Oficial Mineira de Galicia (Ed.) Minería Sostenible, A Coruña, p 651-661.

Macías Vázquez, F. and Camps Arbestain, M., 2010. Soil carbon sequestration in a changing global environment. Mitig. Adapt. Strat. Global Change 15, 511-529

Macías Vázquez, F., 2004. Recuperación dos solos degradados, reutilización de residuos e secuestro de carbono. Una alternativa integral de mellora da calidade ambiental (in Galego). Recursos Rurais 1, 49-56.

Macías Vázquez, F., Bao, M., Macías-García, F., Camps Arbestain, M., 2007. Valorización biogeoquímica de residuos por medio de la elaboración de tecnosoles con diferentes aplicaciones ambientales. Agua & Residuos 5, 12–25.

Ministerio de Medio Ambiente y Medio Rural y Marino. 2010. Anuario de Estadistica 2009.

Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon and organic matter. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Summer, M.E. (Eds.). Methods of Soil Analysis. Part 3. Chemical Methods. Soil Science Society of America, Inc., Madison, USA, pp. 961-1010.

Sajwan, K.S., Paramasivam, S., Alva, A.K., 2007. Effects of different rates of fly ash and sewage sludge mixture amendment on cation availability and their leachability. J. Environ. Sci. Heal. A 42, 1155-1160.

Sajwan, K.S., Paramasivam, S., Alva, A.K., Adriano, D.C., Hooda, P.S., 2003. Assessing the feasibility of land application of fly ash, sewage sludge and their mixtures. Adv. Environ. Res. 8, 77-91.

Sajwan, K.S., Paramasivam, S., Alva, A.K., Sahi, S.V., 2006. Fly ash-organic byproduct mixture as soil amendment. In: Twardowska, I., Allen, H.E., Haggblom, M.M., Stefaniak, A. (Eds.) Soil and Water Pollution Monitoring, Protection and Remediation. Springer, Dordrecht, the Netherlands, pp. 387-399.

Su, D.C. and Wong, J.W.C., 2002. The growth of corn seedlings in alkaline coal fly ash stabilized sewage sludge. Water Air Soil Poll. 133, 1-13.

Wong, J.W.C. and Su, D.C., 1997a. The growth of Agropyron elongatum in an artificial soil mix from coal fly ash and sewage sludge. Bioresource Technol. 59, 57-62.

Wong, J.W.C. and Su, D.C., 1997b. Reutilization of coal fly-ash and sewage sludge as an artificial soil-mix: Effects of preincubation on soil physico-chemical properties. Bioresource Technol. 59, 97-102.

WRB, 2006. World Reference Base for Soil Resources, FAO, Rome, p. 95.

Yao, F.X., Macías Vázquez, F., Santesteban, A., Virgel, S., Blanco, F., Jiang, X., Camps Arbestain, M., 2009a. Influence of the acid buffering capacity of different types of Technosols on the chemistry of their leachates. Chemosphere 74, 250-258.

Yao, F.X., Macías Vázquez, F., Virgel, S., Blanco, F., Jiang, X., Camps Arbestain, M., 2009b. Chemical changes in heavy metals in the leachates from Technosols. Chemosphere 77, 29-35.

Zucconi, F., Forte, M., Monac, A. Beritodi, M. 1981. Biological evaluation of compost maturity. Biocycle 22, 28-29.

# Chapter 5

# Elaborating Technosols from mixtures of wastes for ryegrass growth: II. Plant analysis

# Chapter 5. Elaborating Technosols from mixtures of wastes for ryegrass growth: II. Plant analysis

## 5.1. Abstract

The preparation of tailor-made Technosols from wastes has been proposed as a novel and prospective option for the re-use of wastes and restoration of degraded areas. A greenhouse experiment was carried out to evaluate the feasibility of different tailor-made Technosols for perennial ryegrass growth. They were formulated from sewage sludges and conditioners mixed at two ratios: 60:40 and 50:50 (w/w, DW). Three types of sludges were used as main component: aerobic sewage sludge (AE), anaerobic sewage sludge (AN) and CaO-treated aerobic sludge (AL). Four kinds of conditioners – 5% of green foundry sand (FS), 10% of Linz-Donawitz slag (LD), 2% of barley straw (BS) and 23 or 33% of fly ash from pine bark combustion (FA) – were used as amendments. Three Technosols containing 60% of sludge and 23% of FA were referred to as M1-AE, M1-AN and M1-AL. Another three with 50% of sludge and 33% of FA were identified as M2-AE, M2-AN and M2-AL. Controls were set for each type of sludge only (AE, AN, and AL sludges). The biomass yields and chemical compositions of four clipping harvests were reported. The results showed that the total above-ground biomass yields was in the order of M2-AN (21.1 g) ~ M1-AL (20.2 g) ~ M2-AL (19.9 g) ~ AN (19.8 g) ~ M1-AN (19.6 g) > AE (11.2 g) ~ M1-AE (11.0 g) > AL (9.8 g) ~ M2-AE (9.4 g) ("~" denotes the lack of significant differences at $P < 0.05$). The addition of conditioners to the AN sludge did not improve plant yield significantly ($P < 0.05$); the addition of conditioners to the AL sludge significantly increased ($P < 0.05$) plant yield compared to the AL control; the addition of conditioners to the AE sludge significantly reduced ($P < 0.05$) plant yield compared to the AE control. The concentrations of Cu in the ryegrass of the unamended AN sludge were above the Cu toxicity level for plants (20 mg $kg^{-1}$) (Chapman, 1966); in general, the addition of conditioners efficiently decreased the bioavailability of heavy metals. The results obtained thus indicate that (i) the type of sludge selected for the preparation of Technosols has an important role on the final properties of them, and (ii) the addition of conditioners to sewage sludges should be made carefully to ensure the most suitable conditions for plant growth while ensuring the production of an environmental-friendly mixture.

*Keywords*: Sewage sludge; Conditioners; Nutrients; Heavy metals; Perennial ryegrass.

## 5.2. Introduction

In recent decades, the amount of waste produced by humans has increased greatly. World-wide production of coal-ash was estimated to exceed 550 million Mg per year (Clarke, 1994). In order to meet the demands of water quality, purification and treatment of wastewater is essential before their discharge. As a result of the application of European Directive 91/271/EEC, many new wastewater treatment plants have been created and generation of sludge has increased sharply; e.g. in Spain, the total production of sludge in 2008 reached 1.2 million Mg and the wastewater treatment plants in Basque Country (N Spain) produced 24 thousand Mg during the same year (Ministerio de Medio Ambiente y Medio Rural y Marino, 2010).

With the growth of urban areas and the increasing demand for high quality lifestyles, the importance of managing all types of wastes to avoid environmental degradation and public health risk has gained importance. A waste management infrastructure has been established both in the EU and in other non-EU countries based on a hierarchy of the following principles: (i) waste prevention; (ii) recycling/re-use; (iii) the use of waste as a source of energy; and (iv) controlled final disposal. In the thought of recycling waste streams there have been numerous studies in which mixtures of organic and inorganic by-products have been prepared with the purpose of improving the characteristics of the individual ingredients as soil amendments (Camps Arbestain et al., 2008, 2009; Yao et al., 2009a, 2009b). In recent years, Technosols – soils whose properties and pedogenesis are dominated by their technical origin (WRB, 2006) – elaborated from mixtures of unconsolidated wastes has been proposed as an alternative to reuse waste products, recycle essential nutrients and stabilise the organic matter (Macías Vázquez, 2004; Macías Vázquez et al., 2007). This technology entails not only sound waste management but also fulfilment of soil functions, as defined by the EC-COM 231/2006 (EU, 2006).

Many anthropogenic residues have beneficial effects on soil quality and productivity. No detrimental effects on turfgrass growth of high rates (1120 Mg ha$^{-1}$) of coal fly ash added as amendment to a silt loamy soil has been described by Adriano et al. (2002). Wong and Su (1997) reported that the addition of coal fly ash-sewage sludge mixture significantly improved the seedling emergence and dry weight yields of Agropyron. Matsi and Keramidas (1999) also found that the biomass yields significantly increased with fly ash application to acid soils. Camps Arbestain et al. (2008, 2009) and Yao et al. (2009a, 2009b) have studied the chemistry of the waste mixtures but not on their agronomic performance. Since one of the most important soil functions is biomass production, plant growth is an important index that needs to be evaluated in order to determine the suitability of specific tailor-made Technosols.

The objective of this study was to assess the feasibility of six types of Technosols – produced from mixtures of three types of sewage sludges and four kinds of conditioners – for growing perennial ryegrass (*Lolium perenne* L.) in a greenhouse experiment. This chapter focused on biomass production and plant availability of macro and micro nutrients and heavy metals.

## 5.3. Materials and methods

### *5.3.1. Ingredients of the Technosols*

Three types of municipal sewage sludge were used: (i) an anaerobic digested sludge (AN), (ii) an aerobic sludge (AE), both from the Lagares wastewater treatment plant in Vigo (Galicia, NW Spain), and (iii) a CaO-treated aerobic sludge (AL) from the Silvouta wastewater treatment plant in Santiago de Compostela (Galicia, NW Spain). The fly ash from pine bark (*Pinus radiata and Pinus pinaster*) combustion (FA) was obtained from a paper production plant (Smurfit Kappa Group) in Durango (Basque Country, N Spain). The green foundry sand (FS) was provided by INASMET (Basque Country, N Spain). The Linz-Donawitz slag (LD) was obtained from a steel production plant ACERALIA (ARCELOR group) in Avilés (Asturias, N Spain). Besides, barley straw (BS) was also used as a conditioner. The main chemical characteristics of all the conditioners are detailed in Table 4.1 (Chapter 4); the mineralogy and particle-size distribution of the three inorganic conditioners are presented in Table 4.2 (Chapter 4). In addition, two sludges (AE and AN) and three conditioners (FS, LD and FA) were checked for the presence of toxic organic compounds. Concentrations of major organic contaminants in the ingredients are displayed in Table 4.3 (Chapter 4).

### *5.3.2. Formulation of the Technosols*

The sludges (AE, AN and AL) were air-dried and passed through a 4 mm sieve, and the conditioners (FS, LD, FA and BS) were passed through a 2 mm sieve before use. As shown in Table 4.4 (Chapter 4), Technosols were formulated through mixing each type of sewage sludge with the four conditioners. Two doses of each sewage sludge (60% and 50%, DW) and two doses of FA (23 and 33%, DW) were considered. The rest conditioners were added at fixed percentage (5% of FS, 10% of LD and 2% of BS). Three Technosols containing 60% of sludge and 23% of FA were referred to as M1-AE, M1-AN and M1-AL. Another three with 50% of sludge and 33% of FA were identified as M2-AE, M2-AN and M2-AL. Besides, there were also three controls consisted of only sewage sludge without any addition of conditioners (AE, AN and AL controls).

### *5.3.3. Stabilisation of the samples*

The field capacity of each mixture was determined with a series of the soil moisture pressure extraction equipment (Soil Moisture Equipment Corp., Santa Barbara, CA) at the pressure of -0.33 bar. In order to reduce the adverse effects of high ammonium concentrations, all mixtures were then incubated at field capacity under greenhouse conditions for two months until they showed no phytotoxicity. The phytotoxicity of the substrates during the stabilisation process was determined by the germination index of *Lepidium sativum* L. (Zucconi et al., 1981). After stabilisation process, microbiological analysis was carried out to test the presence of pathogens in all the controls and Technosols. The results are shown in Table 4.5 (Chapter 4).

### *5.3.4. Technosols characteristics and greenhouse experiment design*

The chemical characteristics of the stabilized samples are reported in Table 4.6 (Chapter 4). Basically, the Technosols with the greater content of OC and total N were the AN and AL treatments. The AN treatments also contained the highest P content. The Technosols with the greater K content were the AE treatments.

Polypropylene (PP) plastic pots (12 cm in diameter, 17 cm in height) – with 1 cm of glass wool placed at the bottom – were filled with the previously stabilized samples. Deionised water was added daily into each pot using an individualised drip system to maintain moisture at field capacity. All the pots were sown with 15 seeds of perennial ryegrass (*Lolium perenne* L.) a week after the pots were prepared.

Changes in soil and soil solution properties during the experimental period are reported in Chapter 4.

### *5.3.5. Plant characterisation*

The ryegrass plants were cut to 5 cm height four times (on day 87, 132, 159, and 523 after the start of the experiment). All plant samples were oven-dried at 75 ºC until constant weight and ground. Total C and N in the plants were determined by a TruSpec CHN analyzer (LECO Corporation, Michigan USA). Total P, S, K, Ca, Mg, Cu, Zn, Ni, Pb, Cd and Cr in the plants of first and second harvest, and total P, S, Ni, Pb, Cd and Cr in the plants of third and fourth harvest were analysed by charge coupled device (CCD) Simultaneous ICP-OES VISTA-MPX (Varian Ibérica S.L., Madrid, Spain) after digestion with a mixture of nitric and perchloric acid (85%:15%, v/v). The concentrations of K, Na, Ca, Mg, Fe, Mn, Cu and Zn in the plants of third and fourth harvest were determined by atomic absorption spectrophotometer (SpectrAA 250) equipped with a SPS-5 auto-sampler (Varian Ibérica S.L., Barcelona, Spain) after digestion with the same mixture as above. A standard sample of peach leaves (Standard Reference Materials NBS NIST) was used to ensure the quality control.

### *5.3.6. Statistical analysis*

To assess the statistical differences among the biomass yields and chemical compositions of plants of different treatments, a one-way analysis of variance followed by a *post hoc* (Bonferroni) multiple comparison test (at $P < 0.05$) was computed with SPSS version 11.0 for PC-Windows (SPSS Inc., Chicago, IL, USA).

## **5.4. Results and discussion**

### *5.4.1. Biomass yields*

The above-ground biomass of ryegrass at each cutting time is reported in Fig. 5.1. In the first harvest, treatments M1-AN and M2-AN produced a significantly higher ($P < 0.05$) yield (2.3 and 2.9 g, respectively) than the rest of treatments studied, which had values below 1.5 g, and the ryegrass in the AL control showed barely no growth. The higher yield of ryegrass grown in the AN Technosols was attributed to the high content of available N in the AN sludge (Table 4.6, Chapter 4), as a greater fraction of organic N from the anaerobic treatment is easily mineralisable compared to aerobic treatment (Bernal and Kirchmann, 1992). In addition, the amendment of conditioners to the AN sludge favoured the uptake of K, Ca and Mg, as described below, which promoted plant growth compared to the AN control. In the second and third harvest, biomass yields in the AN control (5.6 and 6.8 g, respectively) were significantly higher than all the other treatments ($P < 0.05$), as well as total N uptake (described below). In the fourth harvest, treatments M1-AN, M2-AN, M1-AL and M2-AL had significantly higher yields (all of which were above 10.0 g; Fig. 5.1) than the rest of treatments ($P < 0.05$). The M2-AE treatment produced the lowest total biomass yield (9.4 g). This was mainly attributed to the low available N content in the AE sludge and the dilution effects of the conditioners (Table 4.6, Chapter 4).

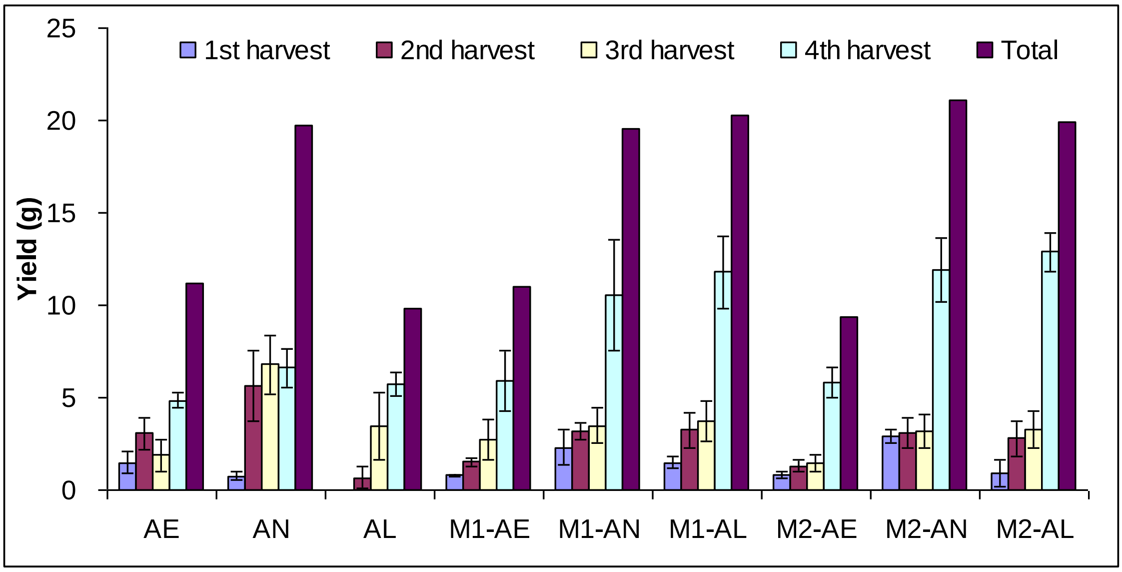


**Fig. 5.1.** Dry weights of the harvested clippings of perennial ryegrass.

### *5.4.2. Macro nutrients in perennial ryegrass*

Nitrogen is the most important nutrient for plants because it is an integral component of many essential plant compounds and a major part of proteins, nucleic acids and chlorophyll (Brady and Weil, 1999). Among all harvests, N concentrations in the ryegrass of the AN and AL controls (25.8-52.2 g $kg^{-1}$) were significantly higher ($P < 0.05$) than those in other treatments (Fig. 5.2A). The lower N availability in the AN and AL Technosols compared to the corresponding controls was mainly attributed to the immobilisation of N caused by the addition of a high C/N ratio in the barley straw, as shown in Chapter 4.

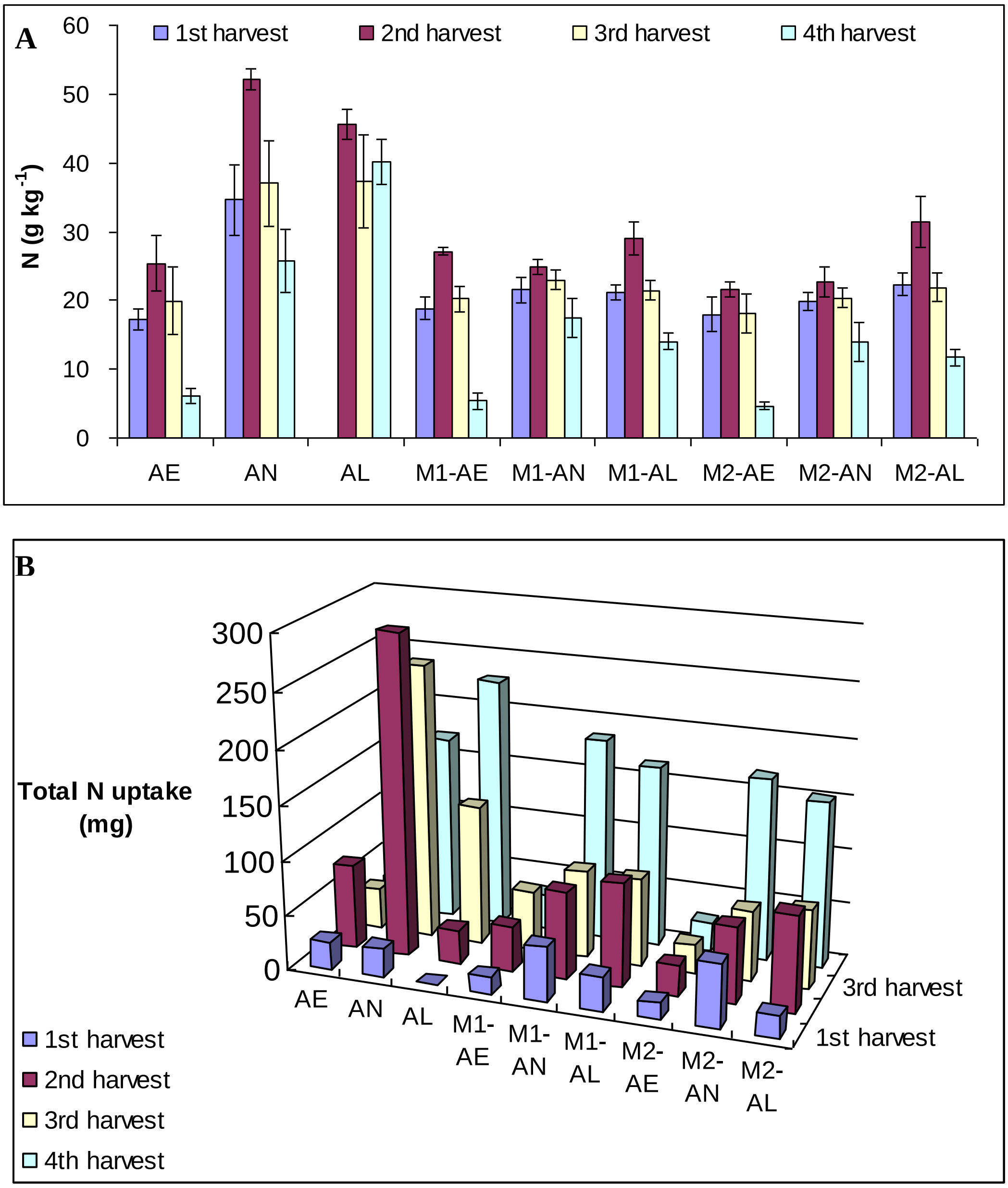


**Fig. 5.2.** Concentrations and total contents of N in the harvested clippings of perennial ryegrass grown in different Technosols.

Total N uptake of the second and third harvest of ryegrass grown in AN control were significantly higher ($P < 0.05$) than the rest of treatments, with values of 294 and 252 mg, respectively (Fig. 5.2B), in agreement with the high $NH_4^+$ concentration in soil solution (Fig. 4.3A, Chapter 4). The N concentrations in the perennial ryegrass plants of all treatments peaked at the second harvest. This is not consistent with the results of Cheng et al. (2007), who suggested that composted sewage sludge served as a long-term source of nitrogen in the soil. The treatments that gave rise to plants with low N concentrations were those in which the AE sludge was an ingredient, in agreement with the lower N content – and specifically, that of available N, as shown in Fig. 4.3A of Chapter 4 – of this sludge compared to the other two sludges under study; in these AE treatments, the N concentrations in the fourth harvest were below the N deficiency level in plants (15 g kg$^{-1}$) (Chapman, 1966). The results obtained thus indicate that the type of sludge was the most determining factor affecting plant N availability.

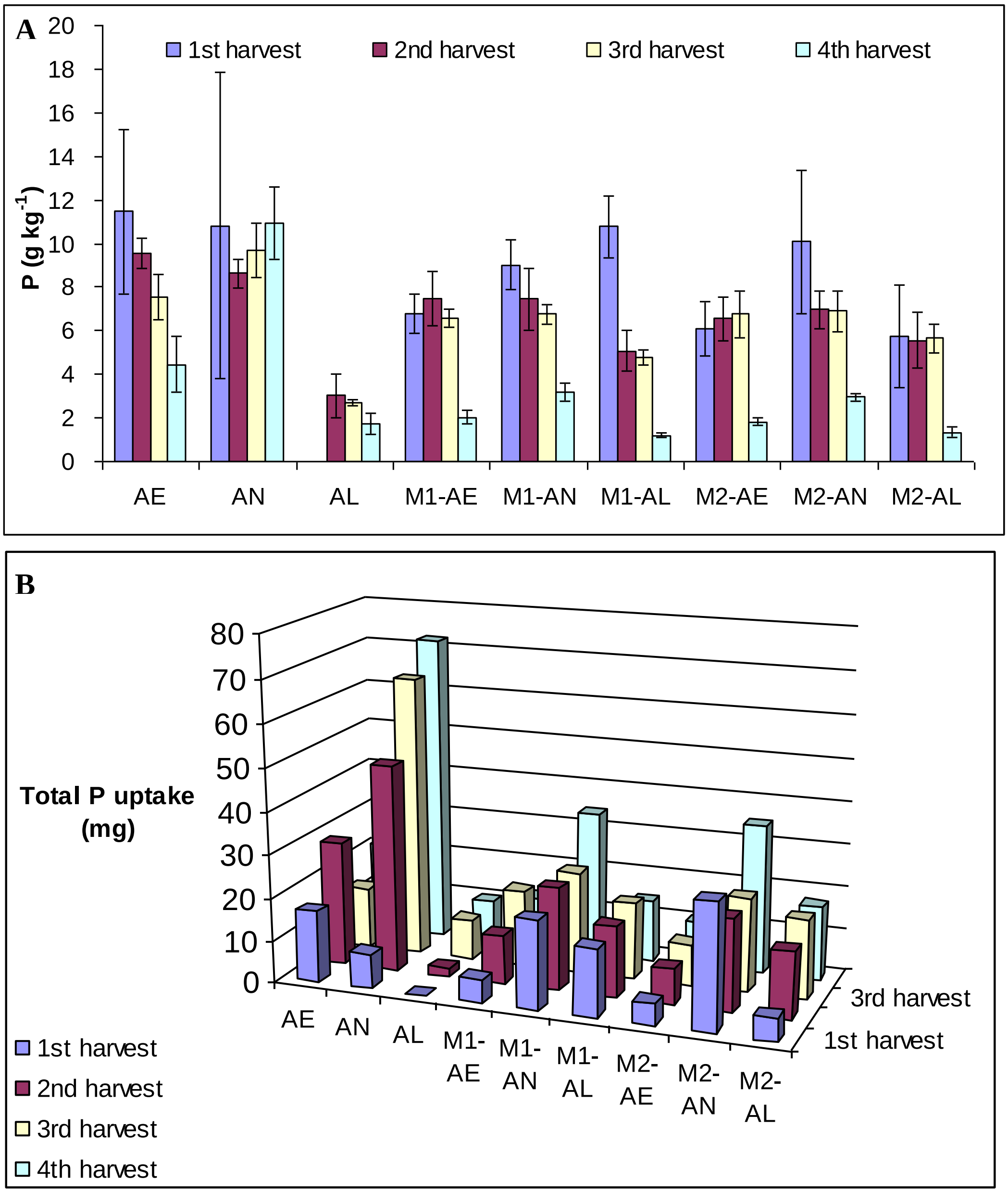


**Fig. 5.3.** Concentrations and total contents of P in the harvested clippings of perennial ryegrass grown in different Technosols.

Phosphorous is the second most essential element for plant growth and it is an essential component of organic compounds of the living cells, including adenosine triphosphate (ATP), deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and phospholipids (Brady and Weil, 1999; Cheng et al., 2007). In the first harvest, the P concentrations in the ryegrass grown on the AE and AN controls were the highest, with values of 11.5 and 10.8 g $kg^{-1}$, respectively (Fig. 5.3A). The total P uptake in the second harvest of AN control was as high as 48.5 mg (Fig. 5.3B). This could be attributed to the relative solubility of P in the AE and AN sludge, as shown in the previous chapter (Fig. 4.4A, Chapter 4). Among all the harvests, P concentrations in the plants grown on the AL control were the lowest; Based on the fact that the biomass yield was also low (Fig. 5.1), the results suggest that P was the limiting nutrient in this treatment. This could be attributed to the CaO treatment at the wastewater plant, which limited P solubility due to the large amount of Ca. The role of conditioners on P availability was not as negative as the CaO treatment. As shown in the previous chapter (Chapter 4), the addition of conditioners reduced the solubility of P. However, the plant tissue analyses reveal that this did not limited P uptake in the corresponding Technosol treatments, at least for those prepared with the AN sludge. In the fourth harvest, the P concentrations of ryegrass grown in the AL control, M1-AL, M2-AE and M2-AL Technosols were below the P deficiency limit in plants (2.0 g $kg^{-1}$) (Chapman, 1966).

Potassium is the third most essential plant nutrient, after N and P (Brady and Weil, 1999; Cheng et al., 2007). The highest K concentrations were found in the first harvest, probably due to the fact that other nutrients, especially N were limiting at early stages while K is highly bioavailable (Fig. 5.4A). In the following harvests, the K concentrations of the ryegrass were significantly lower than their corresponding concentrations in the first harvest ($P < 0.05$), as the K in the soils solutions were also decreasing rapidly (Fig. 4.5A, Chapter 4). In the second and third harvests, no significant difference was found in the K concentrations of the ryegrass. Potassium concentration in the AL control was the lowest in the fourth harvest (4 g $kg^{-1}$), with values below the K deficiency level (7.0-1.5 g $kg^{-1}$) (Chapman, 1966). All amended sludges showed a higher K uptake than the sludges without amendments, evidencing the contribution of the conditioners (and especially of the barley straw) to the uptake of this nutrient, which was corroborated by the corresponding K concentration in soil solutions (Fig. 4.5A, Chapter 4).

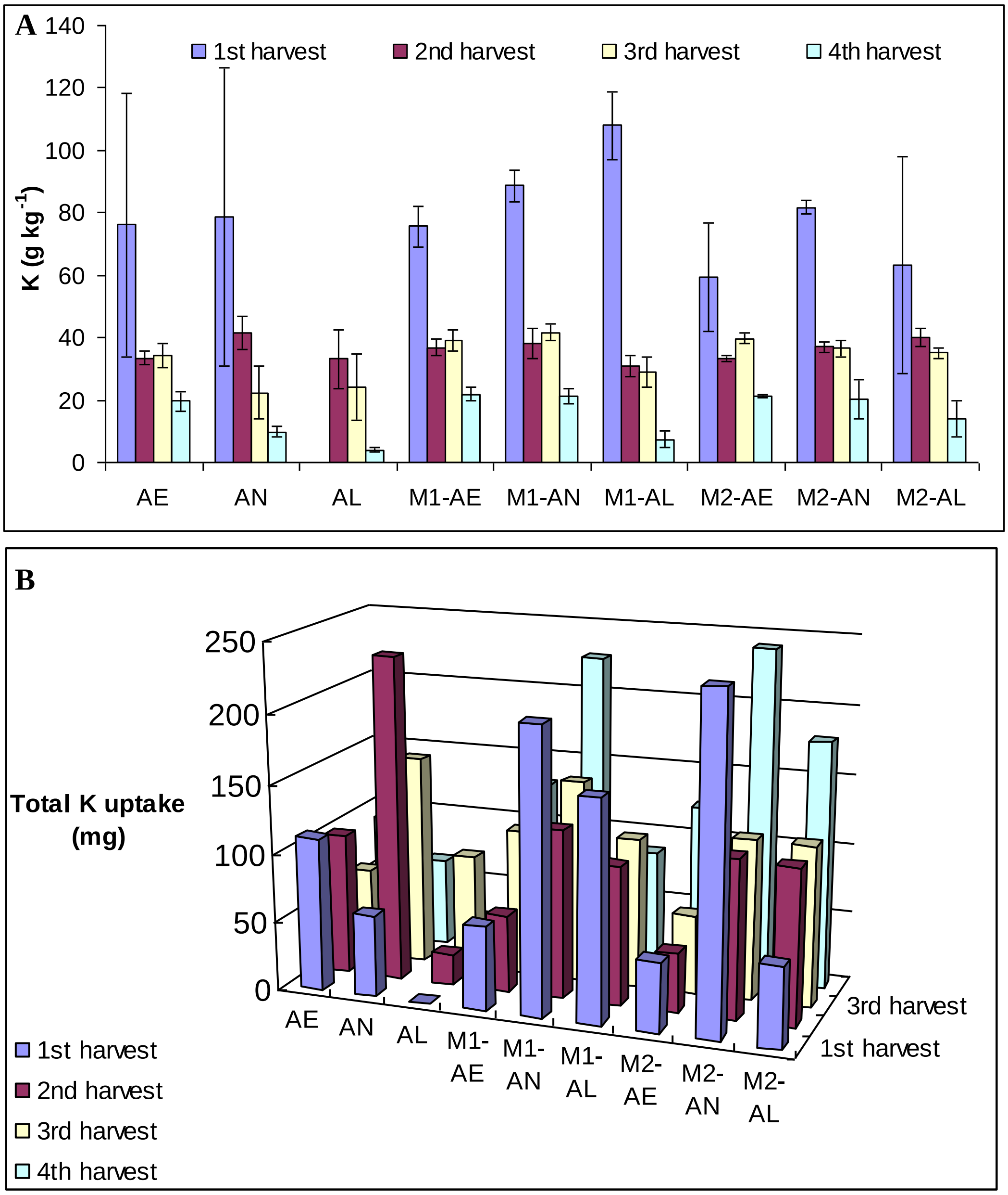


**Fig. 5.4.** Concentrations and total contents of K in the harvested clippings of perennial ryegrass grown in different Technosols.

Calcium concentrations in the perennial ryegrass of the AL control were the highest (>13 g kg$^{-1}$) among all harvests while those of AE and AN controls were the lowest (<5.0 g kg$^{-1}$) (Fig. 5.5A); this was as expected, given the higher content of Ca in the AL sludge compared to the AE and AN sludges (Table 4.6, Chapter 4). The Ca concentrations in the ryegrass grown in the AE and AN Technosols were higher than their corresponding controls, owing to the Ca contents in the conditioners (especially foundry sand and LD slag). These results were consistent with the corresponding Ca concentration in soil solutions (Fig. 4.5B, Chapter 4). All Ca concentrations in the ryegrass were above the deficiency level (1.4 g kg$^{-1}$) (Chapman, 1966). Total Ca uptake was the highest in the fourth harvest ryegrass – specifically in the plants grown in AL control, M1-AL and M2-AL Technosols (>100 mg) (Fig. 5.5B) –, which was attributed to the highest clipping yields.

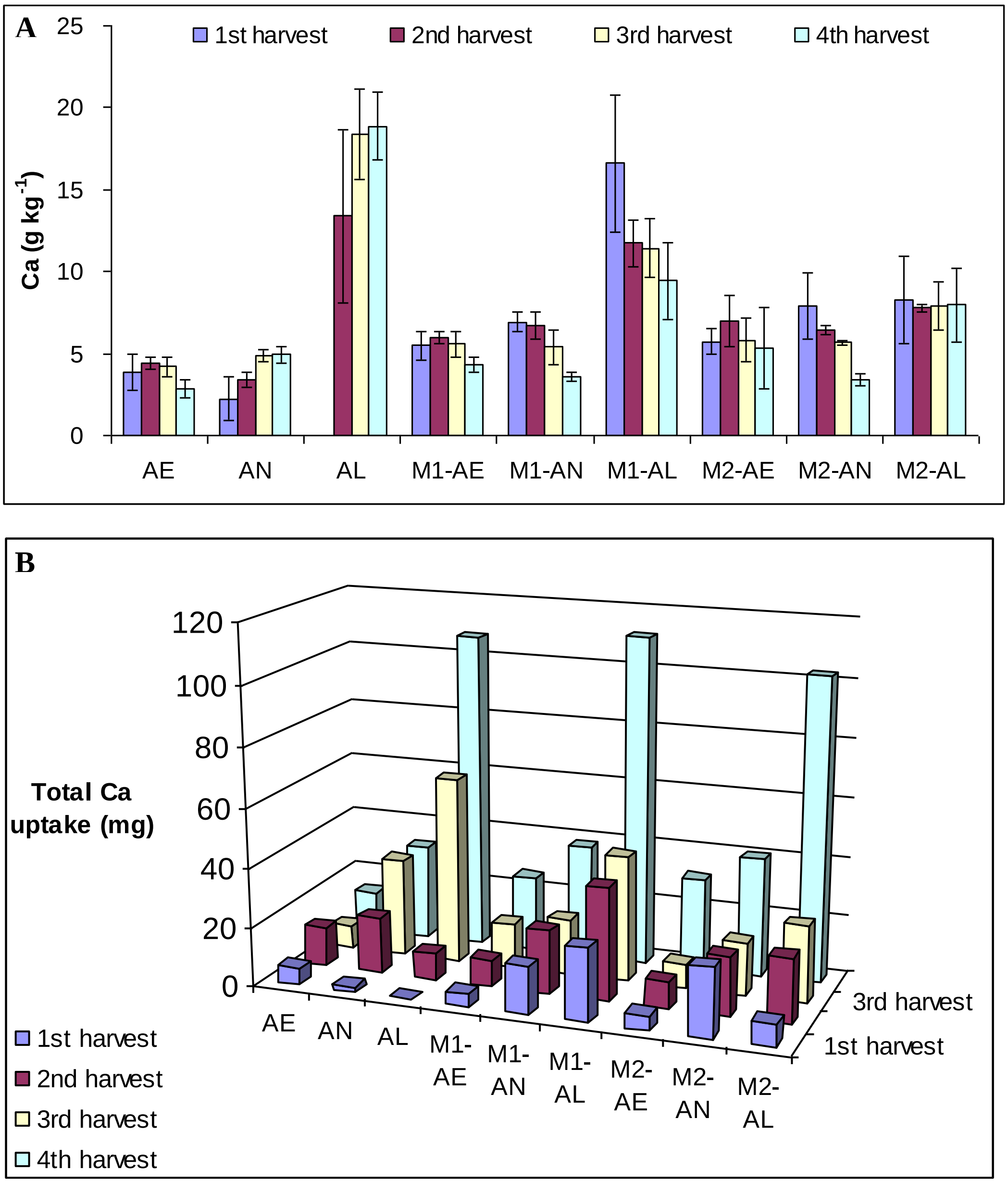


**Fig. 5.5.** Concentrations and total contents of Ca in the harvested clippings of perennial ryegrass grown in different Technosols.

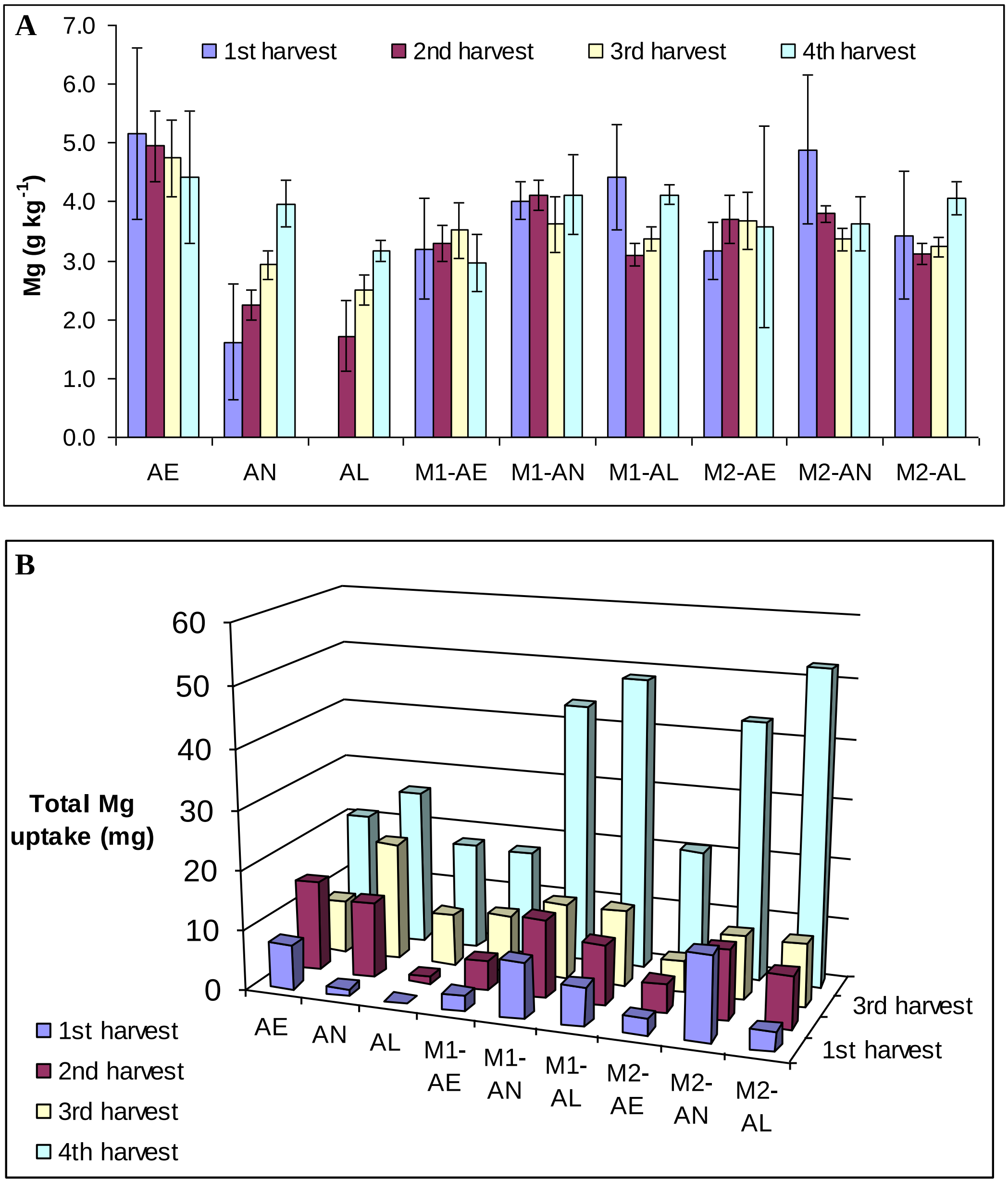


**Fig. 5.6.** Concentrations and total contents of Mg in the harvested clippings of perennial ryegrass grown in different Technosols.

Magnesium concentrations in the ryegrass of the AE control was the highest among all the harvests and was significantly higher ($P < 0.05$) than other treatments in the second and third harvest (Fig. 5.6A); this was paralleled by high concentrations of Mg in the AE soil solutions (Fig. 4.5C, Chapter 4). In contrast, Mg concentrations in the ryegrass of the AL control were the lowest among all harvests; this was mainly attributed to the competition effect of Ca (Marschner, 1986) – present in very high concentration. Nonetheless, Mg concentrations were well above the deficiency level (0.6 g $kg^{-1}$) (Chapman, 1966). The total Mg uptake were the highest in the fourth harvest of M1-AL and M2-AL Technosols, 48.6 and 52.5 mg, respectively (Fig. 5.6B), which was again attributed to their high clipping yields (Fig. 5.1).

### *5.4.3. Micro nutrients in perennial ryegrass*

The highest Fe concentration was observed in the fourth harvest ryegrass of the AL control, with a mean value of 273 mg kg$^{-1}$ (Fig. 5.7A); this was paralleled by a high concentration of Fe in the AL soil solutions (data not shown). The above-ground biomass of this treatment was the lowest among all the treatments studied (Fig. 5.1). This may explain the concentration effect in plant tissue observed for this element. The ingredient with the highest content of Fe was the LD slag (135 g kg$^{-1}$) (Table 4.1, Chapter 4), which was added to all Technosols. However, no effect of the addition of this conditioner on Fe uptake was observed; this was probably due to the fact that the Fe forms added (wustite FeO) were mostly unavailable, at least, in the short term (Table 4.2, Chapter 4). The Fe concentrations in all the clippings were among the intermediate range of Fe in plants (Chapman, 1966). Plants have three means at their disposal to make Fe bioavailable: protonation, reduction and chelation (Guerinot and Yi, 1994). It is possible that the slight increase in Fe concentration in the biomass clipped during the fourth harvest could be attributed to the greater root density and enriched presence of chelating substances exuded by roots. The fourth harvest ryegrass grown in the M1-AN Technosols contained the highest amount of Fe (2.79 mg) (Fig. 5.7B).

The ryegrass of the AL control contained the lowest Mn concentrations, as low as 54 mg kg$^{-1}$ (Fig. 5.8A), owing to the low content of Mn in the AL sludge, but still above the deficiency limit of 20 mg kg$^{-1}$ (Chapman, 1966). The Mn concentrations in the ryegrass grown on Technosols were significantly higher ($P < 0.05$) than in the AN and AL controls, probably due to the high content of Mn in the conditioners (Table 4.1, Chapter 4). Manganese concentrations in the plants were consistent with the Mn concentrations in the soil solutions (data not shown), as expected. The highest uptake of Mn was found in the fourth harvest of ryegrass in the Technosols M2-AL (11.19 mg) (Fig. 5.8B). The results obtained reflect an increase in the Mn concentrations as the harvests proceeded, suggesting the gradual release of Mn during the experiment. This could be attributed as above, to the increasing root density and the correspondingly increase of chelating substances exuded by roots. As for Fe, Mn solubility is highly dependent on redox conditions, pH, and the presence of chelating substances (Godo and Reisenauer, 1980).

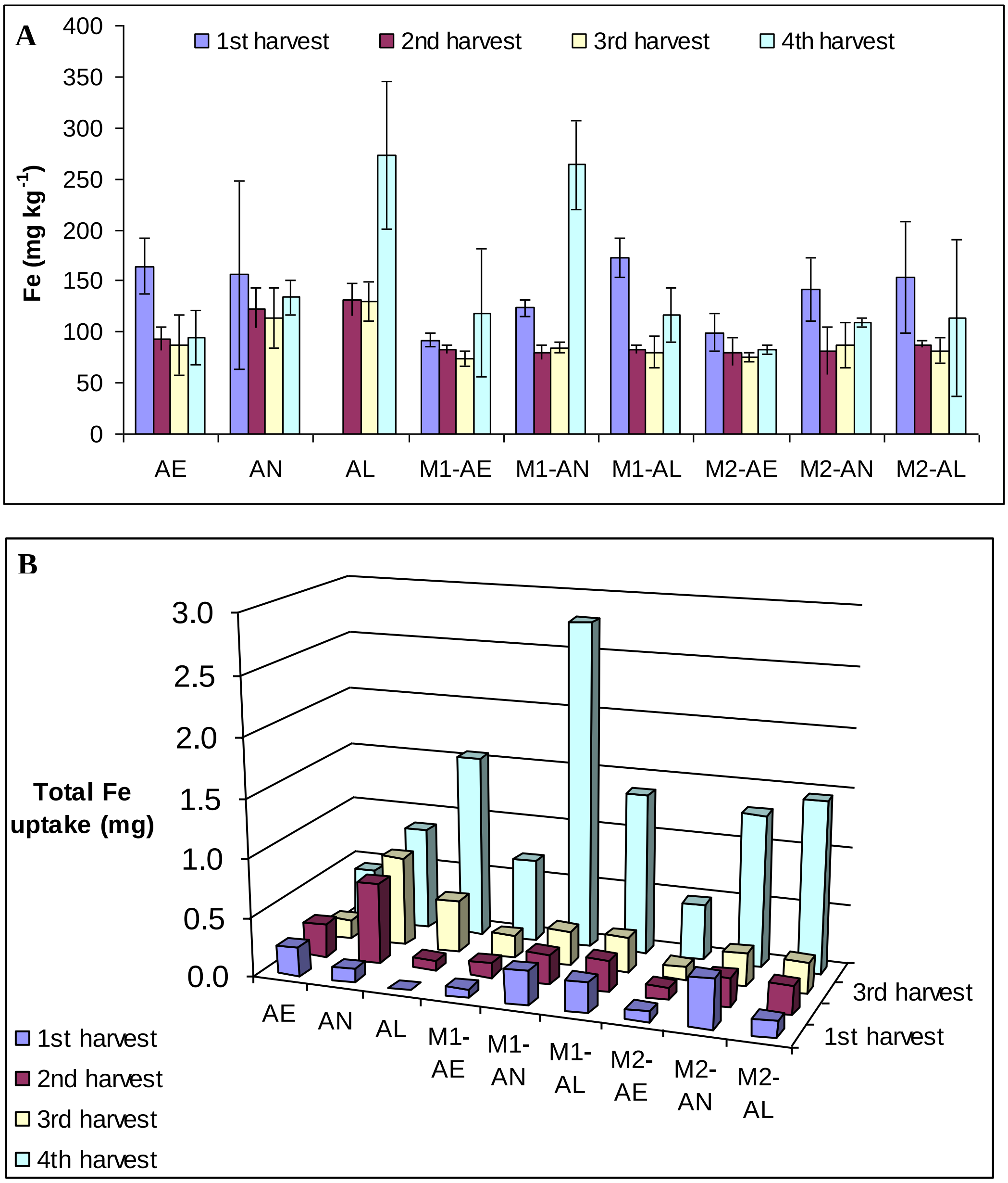


**Fig. 5.7.** Concentrations and total contents of Fe in the harvested clippings of perennial ryegrass grown in different Technosols.

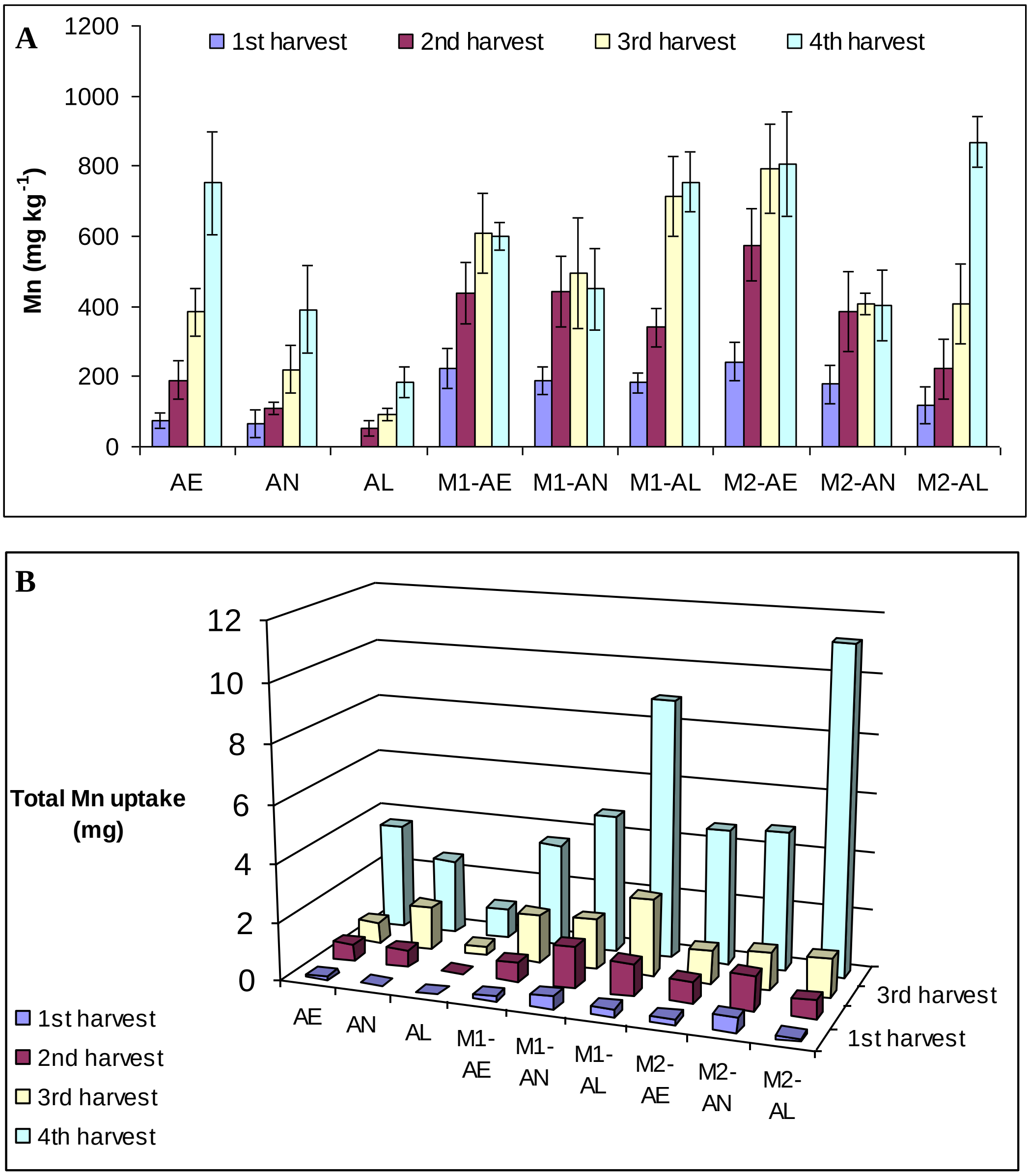


**Fig. 5.8.** Concentrations and total contents of Mn in the harvested clippings of perennial ryegrass grown in different Technosols.

### *5.4.4. Heavy metals in perennial ryegrass*

The concentrations of Cu in the ryegrass from the first harvest were generally higher than in the following harvests (Fig. 5.9A). From the second harvest on, Cu concentrations in the ryegrass of the AN control were significantly higher than in the other treatments ($P < 0.05$), there being no significant difference among the latter (Fig. 5.9A). The Cu concentrations in the ryegrass of all harvests of the AN control were the highest and all of the values were above the Cu toxicity level for plants (20 mg kg$^{-1}$) (Chapman, 1966). This was attributed to the particularly high Cu content in the AN sludge (920 mg kg$^{-1}$) (Table 4.6, Chapter 4). The ryegrass grown in the AN

Technosols contained significantly lower content of Cu than the control, mainly due to the dilution effect of the conditioners although the Ca in the conditioners may have displaced some Cu from the exchange sites and increased its mobility (Yao et al., 2009b). The results obtained were consistent with the Cu concentrations in the soil solutions (Fig. 4.6A, Chapter 4). The ryegrass of the first harvest of AE control, M1-AL and M2-AN Technosols, and the fourth harvest of AL control also exceeded the Cu toxicity level for plants (20 mg kg$^{-1}$) (Chapman, 1966).

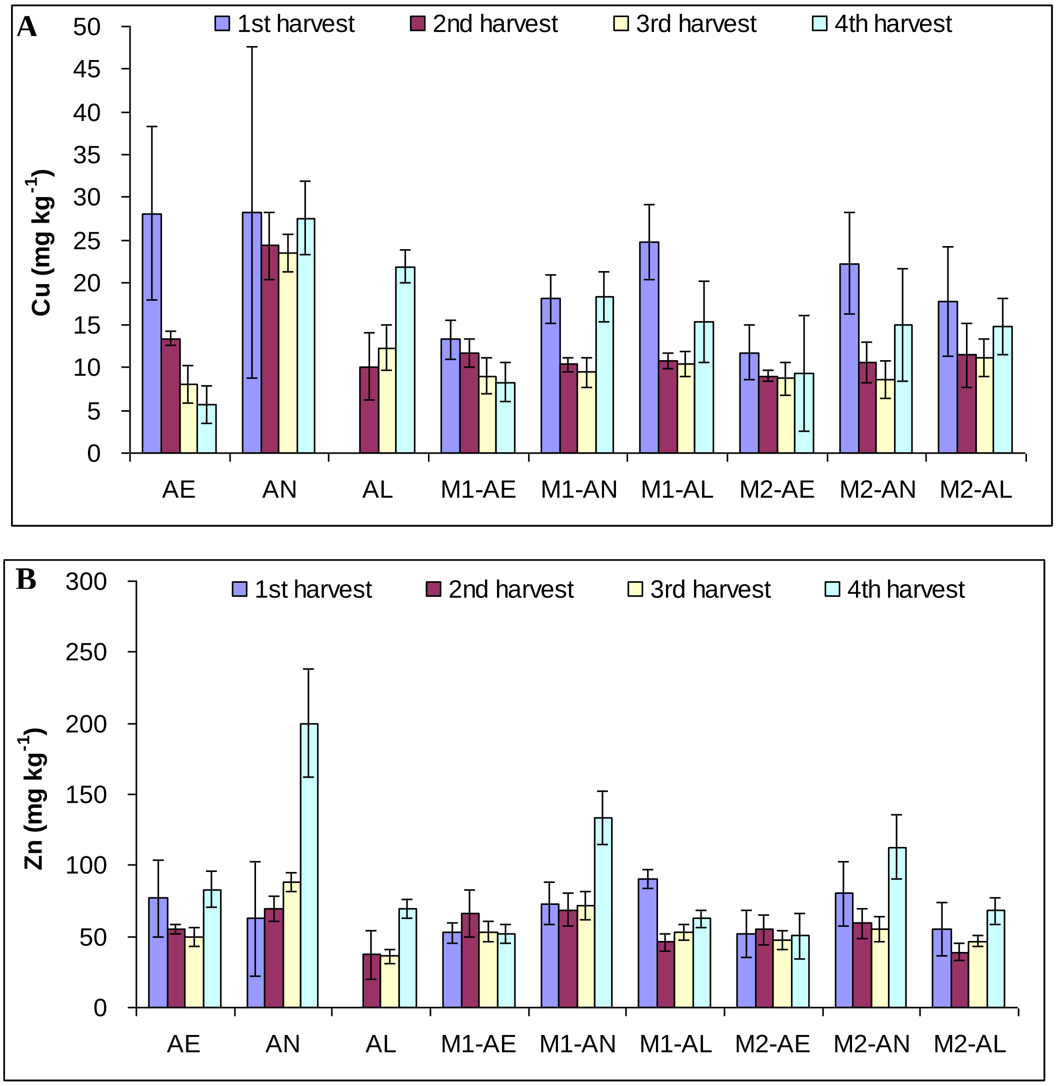


**Fig. 5.9.** Concentrations of Cu and Zn in the harvested clippings of perennial ryegrass grown in different Technosols.

Zinc concentrations in the ryegrass grown on the AN control were the highest among all treatments from the second harvest onwards (Fig. 5.9B); specifically that from the fourth harvest was above the toxicity limit of Zn in plants (150 mg kg$^{-1}$) (Chapman, 1966) and was significantly higher than all the other treatments ($P <$ 0.05). These results indicated some toxicity hazards of Zn in the AN sludge to plants, which was attributed to high available content of Zn in the AN sludges (Table 4.6, Chapter 4). Amendment of conditioners has significantly decreased the Zn concentration in the fourth harvest ryegrass (Fig. 5.9B).The Zn concentrations in the ryegrass of the AL control and corresponding Technosols were the lowest, in agreement with the fact that this ingredient had the lowest Zn content. Zinc concentrations in the ryegrass of the fourth harvest were generally higher than the former harvests, suggesting that the Zn availability increased gradually as the experiment proceeded, owing to the decrease in soil pH and increase in root density.

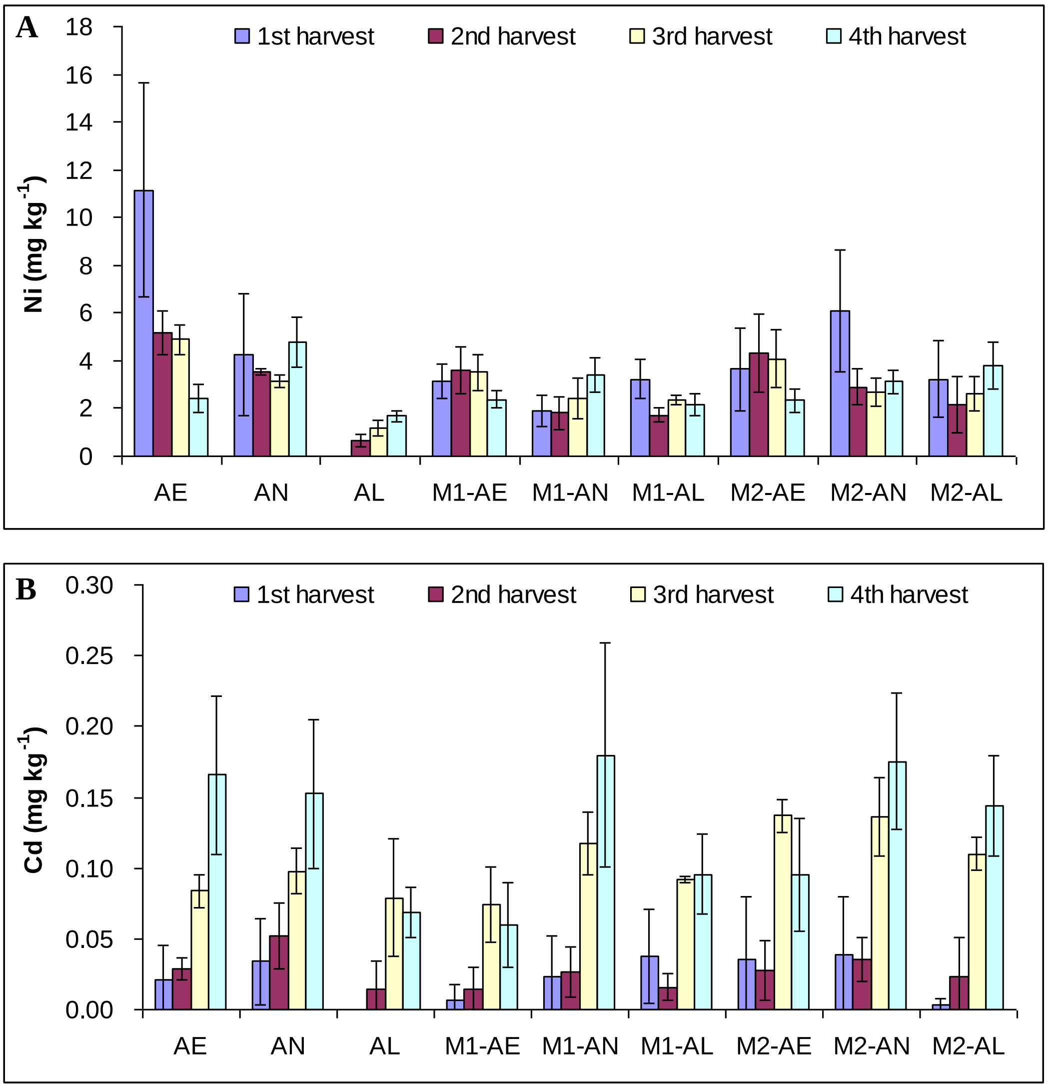


**Fig. 5.10.** Concentrations of Ni and Cd in the harvested clippings of perennial ryegrass grown in different Technosols.

For the first three harvests, the concentration of Ni in the ryegrass of the AE control was always higher than those in other soils, being that of the first harvest (11 mg kg$^{-1}$) significantly higher than the rest of treatments (Fig. 5.10A). This was attributed to higher content of Ni in the AE sludge than in the AN and AL sludges.

Addition of conditioners decreased the mobility and availability of Ni, which might be due to the possible precipitation reactions between foundry sand and sewage sludges (Yao et al., 2009b). The Ni concentrations in the ryegrass of the first and second harvest of AE control, and the first harvest of M2-AN Technosols exceeded the intermediate range of Ni concentration (1-5 mg kg$^{-1}$) in plant tissues (Mas and Azcue, 1993). The ryegrass grown in the AL control contained the lowest concentration of Ni among all the harvests. These results were consistent with the Ni content in the soils (Table 4.6, Chapter 4).

Cadmium concentrations of ryegrass were found to significantly increase ($P < 0.05$) as the harvests proceeded, especially from the second to the third harvest (Fig. 5.10B), which suggested the bioavailability of Cd had been gradually increased along the experiment. The fourth harvest ryegrass grown in the M1-AN Technosols contained the highest concentration of Cd (0.18 mg kg$^{-1}$) (Fig. 5.10B). All the Cd concentrations were in the normal range of Cd concentrations in the plants (0.1-2.4 mg kg$^{-1}$) (Mas and Azcue, 1993).

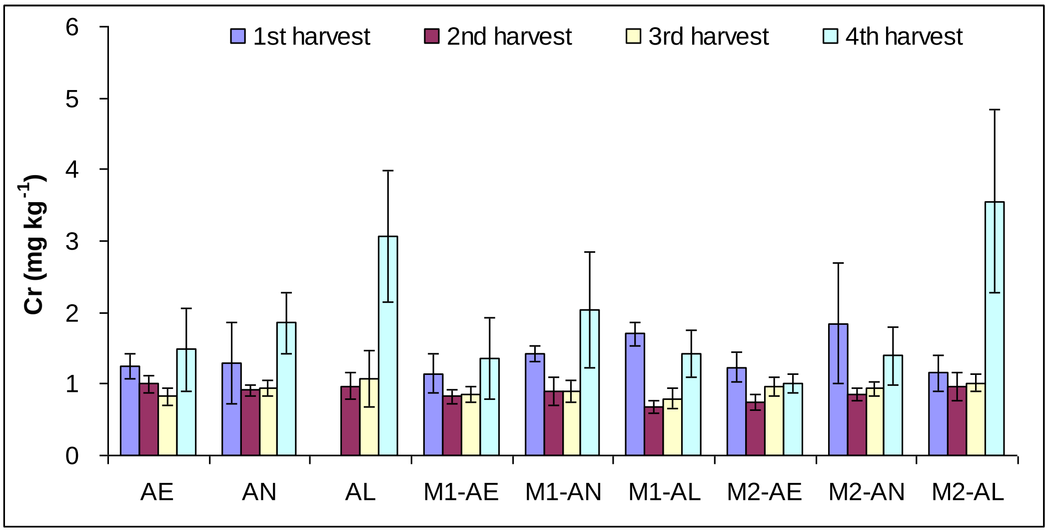


**Fig. 5.11.** Concentrations of Cr in the harvested clippings of perennial ryegrass grown in different Technosols.

No significant difference in the Cr concentrations of ryegrass among the first three harvests was found (Fig. 5.11). All the Cr concentrations were in the intermediate range of Cr concentrations in the plants (0.03-10 mg kg$^{-1}$) (Mas and Azcue, 1993). The concentration of Pb in the ryegrass of all harvest ranged from 0.57 to 2.19 mg kg$^{-1}$ and no significant difference was found among different treatments (data not shown).

## 5.5. Conclusions

Organic ingredient in the formulated Technosols (sewage sludge in this study) is the principal source of nutrients (especially N and P) for plants and the treatment of sludge has great influence on its properties, which then determines the plant growth to a large extent. The AN sludge contained the highest available content of N and P, which together with the fact that the other nutrients were not limiting plant growth, it was the sludge that promoted plant growth the most. The AE sludge had the lowest content of N, which led to the lowest biomass yields. Low content of K and low bioavailability of P caused by high content of Ca in the AL sludge have greatly restricted the plant growth, which needs extra supplement of K and P fertilizer to ensure balanced nutrient supply to plants. Conditioners such as foundry sand, LD slag, fly ash and barley straw, on one hand, made extra contribution of K, Ca, Mg and Mn to plants; on the other hand, increased the pH and decreased the mobility and bioavailability of heavy metals such as Cu, Zn and Ni, etc.

The formulation of Technosols from these residues was feasible to support plant growth as far as essential nutrients are concerned. However, the concept of "chemical time bomb" (Stigliani, 1991) should not be disregarded although conditioners may decrease the mobility and bioavailability of heavy metals during a short period of time. This means that such buffering mechanisms for heavy metals are vulnerable and the harmful effects will become manifested with any change in the condition of the system (e.g. decrease in pH). Therefore, it is recommended that the heavy metals be extracted before elaborating Technosols or certain hyperaccumulators be grown the first a few years.

## 5.6. Acknowledgements

We gratefully acknowledge Smurfit Kappa Group, INASMET and ACERALIA for supplying the conditioners. The research was funded by the Spanish Ministry of Environment (Project Nos. 093/2004/3; 2.5-206/2005/2-B; 208/2006/1-2.5), the Diputacion Foral de Bizkaia (Project No. 7/12/EK/2005), and the Spanish Ministry of Science and Education (Project No. CTM 2006-13748 -CO2). Fenxia Yao is in receipt of an FPI fellowship from the Spanish Ministry of Science and Education.

## 5.7. References

Adriano, D.C., Weber, J., Bolsa, N.S., Paramasivam, S., Koo, B.J., Sajwan, K.S., 2002. Effects of high rates of coal fly ash on soil, turfgrass, and groundwater quality. Water Air Soil Poll. 139, 365-385.

Bernal, M.P. and Kirchmann, H., 1992. Carbon and nitrogen mineralization and ammonia volatilization from fresh, aerobically and anaerobically treated pig manure during incubation with soil. Biol. Fert. Soils 13, 135-141.

Brady, N.C. and Weil, R.R., 1999. The nature and properties of soils, 12th ed. Prentice Hall, Upper Saddle River, NJ.

Camps Arbestain, M., Ibargoitia, M.L., Madinabeitia, Z., Gil, M.V., Virgel, S., Morán, A., Pereira, R.C., Macías Vázquez, F., 2009. Laboratory appraisal of organic carbon changes in mixtures made with different inorganic wastes. Waste Manage. 29, 2931-2938.

Camps Arbestain, M., Madinabeitia, Z., Anza Hortalà, M., Macías-García, F., Virgel, S., Macías Vázquez, F., 2008. Extractability and leachability of heavy metals in Technosols prepared from mixtures of unconsolidated wastes. Waste Manage 28, 2653-2666.

Chapman, H.D., 1966. Diagnostic criteria for plants and soils. University of California.

Cheng, H., Xu, W., Liu, J., Zhao, Q., He, Y., Chen, G., 2007. Application of composed sewage sludge (CSS) as a soil amendment for turfgrass growth. Ecol. Eng. 29, 96-104.

EU, 2006. Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste, in: Union, E. (Ed.), Strasbourg.

Godo, G.H. and Reisenauer, H.M., 1980. Plant effects on soil manganese availability. Soil Sci. Soc. Am. J. 44, 993-995.

Guerinot, M.L. and Yi, Y., 1994. Iron: Nutritious, noxious, and not readily. Plant Physiol. 104, 815-820.

Macías, F., 2004. Recuperación de suelos degradados, reutilización de residuos y secuestro de carbono. Una alternativa integral de mejora de la calidad ambiental. Recursos Rurais 1, 49-56.

Macías Vázquez, F., Bao, M., Macías-García, F., Camps Arbestain, M., 2007. Valorización biogeoquímica de residuos por medio de la elaboración de tecnosoles con diferentes aplicaciones ambientales. Agua & Residuos 5, 12–25.

Marschner, H., 1986. Mineral nutrition in higher plants. Academic Press.

Mas, A., Azcue, J.M., 1993. Metales en sistemas biológicos. Promociones y Publicaciones Universitarias, S.A. Barcelona.

Matsi, T. and Keramidas, V.Z., 1999. Fly ash application on two acid soils and its effects on soil salinity, pH, B, P and on ryegrass growth and composition. Environ. Pollut. 104, 107-112.

Ministerio de Medio Ambiente y Medio Rural y Marino. 2010. Anuario de Estadistica 2009.

Stigliani, W.M., 1991. Chemical Time Bombs: Definition, Concepts, and Examples. International Institute for Applied Systems Analysis A-2361 Laxenburg, Austria.

Wong, J.W.C. and Su, D.C., 1997. The growth of Agropyron elongatum in an artificial soil mix from coal fly ash and sewage sludge. Bioresource Technol. 59, 57-62.

WRB, 2006. World Reference Base for Soil Resources, FAO, Rome, p. 95.

Yao, F.X., Macías Vázquez, F., Santesteban, A., Virgel, S., Blanco, F., Jiang, X., Camps Arbestain, M., 2009a. Influence of the acid buffering capacity of different types of Technosols on the chemistry of their leachates. Chemosphere 74, 250-258.

Yao, F.X., Macías Vázquez, F., Virgel, S., Blanco, F., Jiang, X., Camps Arbestain, M., 2009b. Chemical changes in heavy metals in the leachates from Technosols. Chemosphere 77, 29-35.

Zucconi, F., Forte, M., Monac, A. Beritodi, M., 1981. Biological evaluation of compost maturity. Biocycle 22, 28-29.

# Chapter 6

# Simulated geochemical weathering of a mineral ash-rich biochar in a modified Soxhlet reactor

This chapter has been published in:
Chemosphere 80, 724-732
(2010)

# Chapter 6. Simulated geochemical weathering of a mineral ash-rich biochar in a modified Soxhlet reactor

## 6.1. Abstract

Although there are many studies on the characterisation of C in biochar and its C sequestration potential, there is little knowledge on the mineral fraction in biochar and its weathering. The latter, however, can have powerful implications on nutrient availability. In the present study, a modified Soxhlet reactor was used to simulate the long-term geochemical weathering of an ash-rich biochar produced from sewage sludge of a non-industrial area in New Zealand. The weathering process took place during a period of 300 h, with and without the addition of humic acid (1.00 g added to 20.00 g of biochar), and the treatments were referred to as treatment BC-HA and BC-B, respectively. Both the leaching kinetics and the transformations within the solid phase were studied. The results revealed that substantial amounts of K (8.5–10.2%) and S (20.2–28.3%) were recovered in the weathering solutions. Noticeable Ca (17.9–20.7%) and P (15.4%) in the solid were released but only a few were recovered in the weathering solutions because of the precipitation. The presence of humic acids increased this dissolution and thus the availability of K, S, Ca, Mg and P, but induced N immobilisation. Nitrogen availability was already very low (<1.0% of the total N) due to the probable recalcitrant heterocyclic N structure. The pH of the biochar samples dropped from 8.4 to 7.5; this was mainly attributed to loss of base cations through leaching and probable carbonation of the system. The XPS spectra evidenced the oxidation of C in biochar during the weathering process with the formation of carbonyl and carboxylic functional groups. The results obtained in this study showed some promise for the positive use of modified Soxhlet extractor in simulating the geochemical weathering in ash-rich biochars and providing a better understanding on the kinetics of nutrient release. This will be key information in assessing the added value of biochars as soil amendments.

*Keywords:* Sewage sludge; Biochar; Nutrients; Oxidation; Climate change.

## 6.2. Introduction

Biochar is a charcoal-rich substance produced to be used as soil amendment for agronomic and/or environmental gain (Lehmann and Joseph, 2009). The conversion of biomass into biochar by pyrolysis rapidly locks up a fraction of the C present in the original feedstock in a much more durable form (Lehmann, 2007a, 2007b), which can remain in soils for hundreds to thousands of years (Lehmann et al., 2008). In light of the increasingly higher levels of atmospheric greenhouse gases (GHGs) (IPCC, 2008) and the longevity of C in biochar, many studies have been carried out to explore the potential of biochar for sequestering atmospheric C in terrestrial systems to offset carbon emissions and combat global climate change (Lehmann et al., 2006, 2008; Kuzyakov et al., 2009; Nguyen and Lehmann, 2009).

The active surface and porous properties of biochar that develop during the producing process enable it to retain nutrients (Tryon, 1948; Lehmann et al., 2003; Liang et al., 2006) and hold water, thereby increasing soil productivity (Lehmann et al., 2003). In fact, Amazonian Dark Earth soils (Terra Preta) – anthropogenic soils enriched in biochar several centuries ago – have been found to maintain high cation availability (Lima et al., 2002) compared with adjacent soils of similar mineralogy, and despite the high leaching conditions in humid tropical Amazonia. More recent evidence further corroborates the beneficial effects of biochar amendments on soil nutrient dynamics (Glaser et al., 2001; Lehmann et al., 2003; Chan et al., 2007, 2008), although different soils and crops might respond differently, and not always in a positive way (van Zwieten et al., 2010). Knowledge on soil and biochar characteristics is fundamental to maximize the positive effect of this soil amendment.

The generally observed favourable effects of biochar on soil fertility may be promoted by the use of biochar rich in plant nutrients. The nutrient contents of biochar largely depend on the type of feedstock (Gundale and DeLuca, 2006; Chan et al., 2008), whereas the availability of nutrients present in biochar is element dependent. For example, most of the N in biochar might be present as heterocyclic N (Knicker et al., 1996), and thus not readily available, although some researchers have observed a considerable N availability from chicken litter manures (Chan et al., 2008). Phosphorus is mainly found in the ash fraction, and its solubilisation is determined by pH-dependent reactions and the presence of chelating substances (DeLuca et al., 2009). Since sewage sludge contains high levels of major plant nutrients (e.g., N and P) and is rich in organic matter (OM) (Ferrier et al., 1996; Bramryd, 2002), it is supposed to be an ideal pyrolysis feedstock for biochar production, in spite of the fact that ash-rich biochar might be less recalcitrant than that produced from wood or other lignocellulosic materials (McBeath and Smernik, 2009). Conversion of sewage sludge into biochar through slow pyrolysis also has further environmental advantages (e.g., reduction of the problems related to its disposal in landfills).

Despite the great interest in the application of nutrient-rich biochars to agricultural systems, there is inadequate information available regarding their geochemical weathering. To improve our understanding of the long-time behaviour of mineral ash-rich biochars, we simulated the geochemical weathering of a biochar produced from sewage sludge under laboratory conditions, through the use of the methodology developed in pedological studies of rock weathering (Pédro, 1961,…). The specific objectives of the present study were: (i) to determine the release kinetics of major elements, (ii) to establish the organic and mineral transformations undergone in the biochar during weathering, and (iii) to examine whether humic acids (HA) accelerates biochar weathering. We hypothesized that biochar produced from sewage sludge contains nutritional elements that are favourable for plant growth when applied to soil, and that the release of these elements will be influenced by the addition of HA.

## 6.3. Materials and methods

### *6.3.1. Weathering system*

The experiment was conducted with a modified Soxhlet reactor, as shown in Fig. 6.1, following the methodology used by Pédro (1961) to study the geochemical weathering of rocks. The reactor was modified and used to investigate the long-term release of compounds from solidified/stabilized wastes (Humez et al., 1997; Humez and Prost, 1999; Badreddine et al., 2004). The working principle of the modified Soxhlet extractor is as follows: the deionised water in a round-bottom flask evaporates because of the constant heating and then condenses in the condenser that is connected to the flask; water drips into the extractor that holds the sample; when the water level reaches the top of the siphon of the extractor it returns to the three-neck round-bottom flask via a tube; water cycles round the system (Humez et al., 1997; Humez and Prost, 1999). In the present study, the extractor was further modified – only one condenser was used – maintaining the leaching water temperature at around 30 °C. The flow rate of water in the extractor is a function of the heating temperature of water in the three-neck round-bottom flask (Humez et al., 1997; Humez and Prost, 1999). In our study, it was controlled to approximately 30 mL every 6 min (equivalent to the rainfall of 273 mm per hour).

**Fig. 6.1.** The modified Soxhlet extractor for simulating geochemical weathering of biochar.

### *6.3.2. Experimental design*

The biochar used in the study was produced from sewage sludge in a gas-fired rotating kiln at 550 °C at a heating rate of 18 °C min$^{-1}$. A cellulose cartridge of the Soxhlet reactor was filled with 20.00 g biochar to investigate the weathering of biochar alone (BC-B). In addition, another cellulose cartridge was filled with a mixture of 20.00 g biochar and 1.00 g HA in order to simulate the exposure of biochar in soils (BC-HA). The HA was extracted from an alu-andic Andosol (Lopez et al., 2008), which contains 48.36% of C, 5.72% of H and 4.63% of N (dry weight basis). The first cycle (the first time the weathering solution flowed back to the flask through the siphon) was considered to be time zero and the weathering solution was collected separately. At the beginning of the experiment, weathering solutions were sampled each cycle, and after half an hour samplings were then spaced out to daily or weekly until 300 h. The kinetics of the release of elements was studied during the 300-h weathering period.

### *6.3.3. Analysis of weathering solution*

Weathering solutions were measured for pH, electrical conductivity (EC), with the electrode SCHOTT CG-843 and CRISON GLP-32 conductimeter, respectively. Chemical composition was determined as follows: dissolved organic carbon (DOC) was determined by the Walkley-Black method; nitrate was determined with a Flowsys – Third generation continuous flow analyzer (SYSTEA, s.r.l., Rome, Italy); ammonium was determined following the methodology described by Kandeler and Gerber (1988); phosphate by the molybdenum blue colorimetric method (Murphy and Riley, 1962); and sulphate following the methodology described by Hoeft et al. (1973), with a UVIKON 930 spectrophotometer (Kontron Instruments, Milan, Italy). The metal elements $K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ were determined with an atomic absorption spectrophotometer SpectrAA 250 Plus equipped with a SPS-5 auto-sampler (Varian Ibérica S.L., Barcelona, Spain). Carbonate and bicarbonate were determined by the chemical titration method, with phenolphthalein and mixed bromcresol green-methyl red as indicators. The released kinetics of elements corresponded to the cumulative percentage of one element released with respect to the initial amount in the sample relative to time in hours. The heavy metals in the weathering solutions were determined by CCD Simultaneous ICP-OES VISTA-MPX (Varian Ibérica S.L., Madrid, Spain), but the data are not shown here as all concentrations were below the detection limit. Organic pollutants (PAH and PCBs) were also measured, and all were below the limit of detection.

Saturation indices in each weathering solution were estimated with the USGS aqueous modelling software, PHREEQC. This program uses mass balance and electro-neutrality equations to simulate geochemical reactions, such as the mixing of water, the addition of net irreversible reactions to solution, dissolution and precipitation phases to achieve equilibrium with the aqueous phase (Parkhurst and Appelo, 1999). The activities of each species and saturation index of minerals clacurated by PHREEQC for the solutions at different weathering times were presented in the Annex 1 and 2.

### *6.3.4. Analysis of solid materials*

#### *6.3.4.1. Elemental analysis*

The pH of the biochar was measured at a ratio of 1:20 (w/v) in water. Total carbon (C), H, N and S (at 1350 °C) in the HA and biochar samples were analyzed with a TruSpec CHN(S) analyzer (LECO Corporation, Michigan USA). In addition, S analyzed at 950 °C was considered to be organic S (OS). The carbonate-C content of the biochar was determined using a modification of common static chamber methods (Bundy and Bremner, 1972; Tiessen et al., 1983). The organic C was determined as the difference between total C and carbonate-C. As carbonate-C content of the fresh biochar was below 0.1% and that of the weathered biochars was undetectable, total C was basically all organic C. The moisture content of the biochar samples was determined by weighing the sample moist, drying the sample at 105 °C, weighing the same sample dry and calculating moisture content as the mass difference (water content) divided by the mass of the dry sample. Ash content of the biochar samples was determined by heating the dry samples in a furnace up to 900 °C for 30 min in air atmosphere and dividing the residue (ash) weight by the weight of the initial dry sample. The mass sample used in each case was around 1.24 g. The elemental compositions of organic C, H, N and organic S of biochar samples were presented on both dry weight and dry ash-free basis (the elemental concentration on dry weight basis divided by the concentration of the non-ash fraction of the biochar). Concentrations of total P, K, Ca and Mg were determined by CCD Simultaneous ICP-OES VISTA-MPX (Varian Ibérica S.L., Madrid, Spain) after $HNO_3$–$HClO_4$ digestion.

#### *6.3.4.2. Mineralogical and morphological analysis*

Changes in the crystalline fraction of the solid phase were assessed by X-ray diffraction (XRD) (Philips PW 1710, Cu Ka1.2). Morphological and elemental analyses were carried out by scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) (Jeol JSM-6400).

#### *6.3.4.3. X-ray photoelectron spectroscopy (XPS)*

Surface analysis of the biochars was conducted by X-ray photoelectron spectroscopy (XPS) with Mg Kα (1253.6 eV) radiation emitted from a double anode at 50 W. Binding energies for the high-resolution spectra were calibrated by setting C to 1s at 284.6 eV. A non-linear least squares curve fit, with a Gaussian–Lorentzian mix function and Shirley background subtraction, was used for the deconvolution of the XPS spectra.

### *6.3.4.4. Solid-state nuclear magnetic resonance spectroscopy (NMR)*

Solid-state $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained (Bruker Avance DSX300 NMR spectrometer: Bruker Corporation) after pre-treatment of the samples with 2% HF solution, according to Skjemstad et al. (1994). Variable amplitude cross-polarisation magic angle spinning (CP/MAS) experiments were run with a 4-mm MAS probe, with a spin rate of approximately 11 000 Hz. The contact time was 1 ms and the delay time was 2 s. An average of 40,000 transients was recorded for each sample.

## 6.4. Results and discussion

### *6.4.1. Changes in pH and EC*

The pH of the weathering solution (9.2) from the treatment BC-B at time zero was slightly higher than the pH of the fresh biochar (8.4) (Fig. 6.2a), probably because of initial solubilisation of the most alkaline base cations (as it was shown in the next section). The pH of the weathering solution then decreased to ~8.6 during the first half hour of the weathering. During the following 40 h, the pH decreased towards neutrality, fluctuated thereafter, and finally increased slightly to 7.8 at the end of 300-h weathering period. The initial pH value (7.5) of the weathering solution from the BC-HA treatment was considerably lower than the pH of the BC-B treatment, which reflects the acidifying effect of the added HA. The pH decreased to 7.2 immediately after the second cycle, and then increased linearly to 8.0 after the first half hour of weathering. Between 0.5 and 3 h, the pH decreased by 0.9 units to reach neutrality and then remained almost stable except for a slight decrease at 42 h. During the last 200 h, the pH fluctuated between 7.0 and 7.4. The acidification observed in both treatments during the 300-h-weathering period was mainly attributed to be the result of the leaching of alkaline ions, although carbonation of the system might also have had an influence.

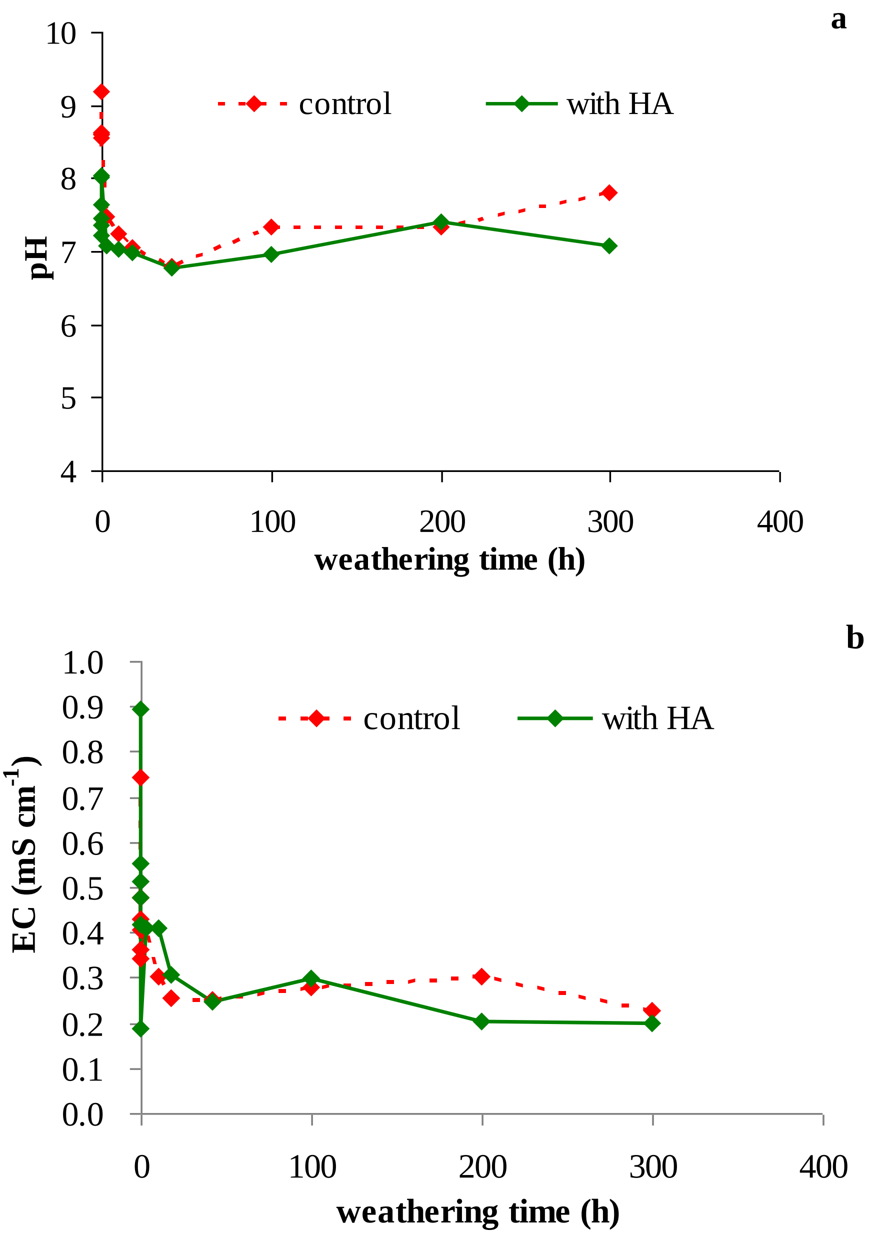


**Fig. 6.2.** Changes in (a) pH and (b) EC in the biochar weathering solutions from simulated weathering in a modified Soxhlet reactor. HA stands for humic acids.

The initial EC values for the BC-B and BC-HA treatments were 0.7 and 0.9 mS cm$^{-1}$, respectively (Fig. 6.2b). After 6 min, they decreased rapidly to 0.4 and 0.6 mS cm$^{-1}$, respectively, and then continued decreasing to 0.2 mS cm$^{-1}$ by the end of the experiment, except for slight fluctuations at around 3 h. The results thus show that, under the high leaching conditions of the Soxhlet system, the EC values of the weathering solutions from both of the two treatments tended to decrease rapidly to low values, as expected. However, under field conditions, initial EC values around particles of this biochar from sewage sludge might reach relatively high values, especially if placed in a non-leaching environment. This should be considered when choosing the type of biochar, dose and timing of application to non-subtractive systems if beneficial effects of biochars on crops are to be attained.

### *6.4.2. Weathering of the mineral ash fraction of the biochar (K, S, Ca, P, Mg, carbonate-C and bicarbonate-C)*

#### *6.4.2.1. Potassium*

The dissolution of mineral components, with the concomitant leaching of their constituent elements is an important process during the weathering of a mineral ash-rich biochar. Potassium was readily released due to the high solubility of K-containing salts as expected, the amount of $K^+$ in the initial weathering solutions reaching 5.9% and 6.5% of the total K in the fresh biochar at the end of 18 h in the BC-B and the BC-HA treatments, respectively (Fig. 6.3a). Thereafter, the amount of $K^+$ in the weathering solutions increased steadily until 300 h, reaching around 8.5% and 10.2% of the total K in the fresh biochar for the BC-B and the BC-HA treatments, respectively. The K in the solid fraction decreased correspondingly, from 8.01 to 7.06 g $kg^{-1}$ in the BC-B treatment and to 6.82 g $kg^{-1}$ in the BC-HA treatment during the entire experimental period (Table 6.1).

#### *6.4.2.2. Sulphur*

The amount of sulphate-S in the weathering solutions from the treatment BC-B increased from 2.5% to 9.3% of the total S in the fresh biochar during the first 18 h, followed by another slower linear release until 20.2% was reached at the end of the 300-h weathering period (Fig. 6.3b). The presence of HA also favoured sulphate solubilisation and attributed to its role as chelating agent for cations. The pattern of changes in the sulphate-S concentration of the weathering solutions from the BC-HA treatment was similar to the BC-B treatment, although values were higher. Overall, 28.3% of total S in the fresh biochar was recovered in the weathering solutions from the BC-HA treatment at the end of the 300-h experimental period. As far as solid S is concerned, the amount of S decreased by 23.8% in the BC-B treatment and by 21.4% in the BC-HA treatment during the weathering period. The values obtained reflect the fact that most of the sulphate-S remained in solution without re-precipitation. The sulphate-S released probably originated from amorphous sulphate precipitates, as no crystalline sulphate compounds were detected in the XRD analysis, whereas substantial S was detected in the inorganic particles analyzed by means of EDX.

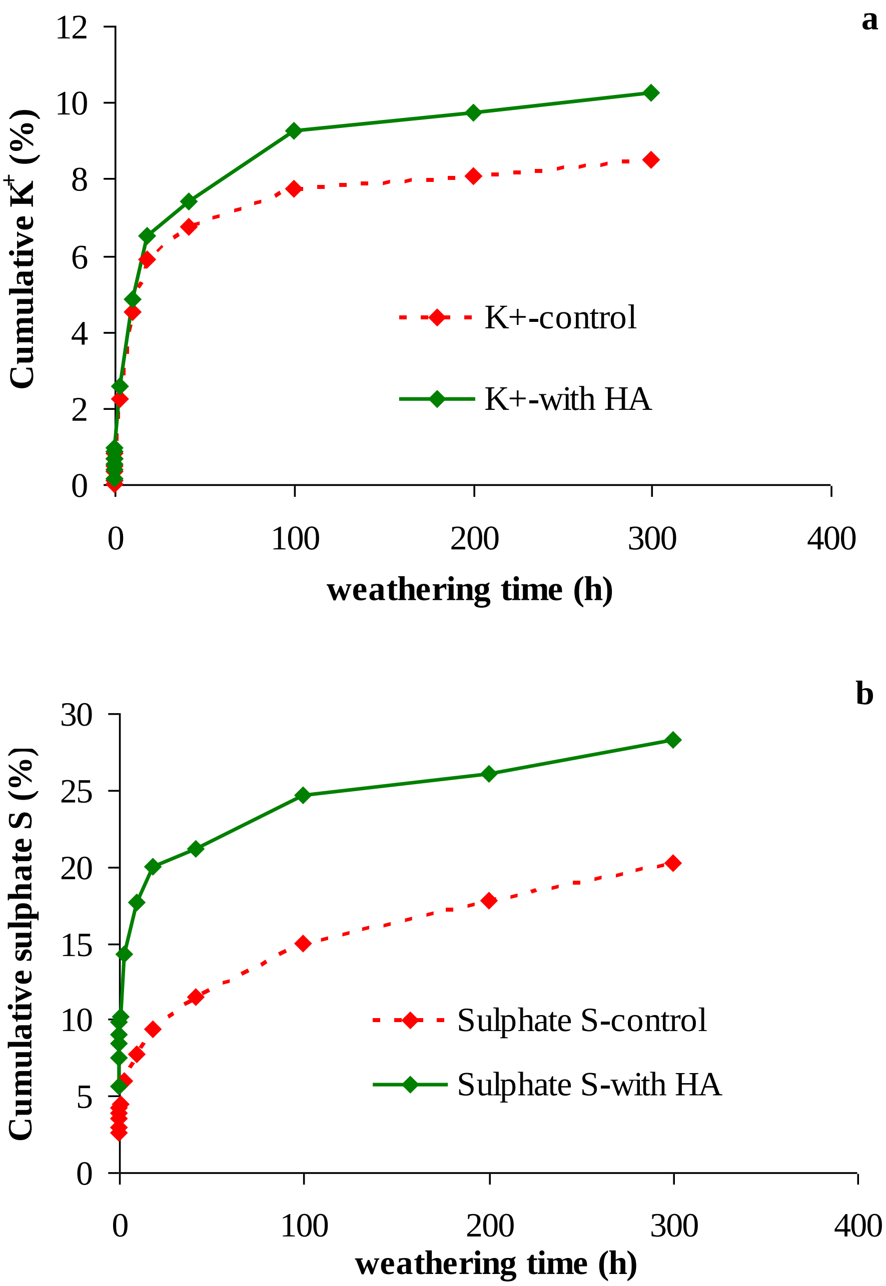


**Fig. 6.3.** Changes in cumulative (a) potassium and (b) sulphate-S (expressed as a percentage of the total K and S, respectively in the fresh biochar) in the biochar weathering solutions with weathering time. HA stands for humic acids.

**Table 6.1** The chemical properties and elemental composition of fresh and weathered biochar from simulated weathering in a modified Soxhlet reactor. BC-HA and BC-B are weathered biochar with and without the addition of humic acids, respectively.

| | Parameters | Fresh biochar | BC-B | BC-HA |
|---|---|---|---|---|
| Dry-weight basis | pH[a] | 8.4 | 7.5 | 7.5 |
| | Ash% | 60.95 | 58.54 | 58.14 |
| | C% | 28.77 | 28.80 | 31.03 |
| | OC% [b] | 28.67 | 28.80 | 31.03 |
| | H% | 1.62 | 2.32 | 2.85 |
| | N% | 3.17 | 3.20 | 3.32 |
| | S% | 0.42 | 0.32 | 0.33 |
| | OS%[c] | 0.11 | 0.13 | 0.10 |
| | P (g kg$^{-1}$) | 26.4 | 22.4 | 22.4 |
| | K (g kg$^{-1}$) | 8.01 | 7.06 | 6.82 |
| | Ca (g kg$^{-1}$) | 33.0 | 26.1 | 27.1 |
| | Mg (g kg$^{-1}$) | 5.30 | 4.76 | 4.66 |
| Dry ash-free basis | OC% | 73.42 | 69.47 | 74.12 |
| | H% | 4.14 | 5.60 | 6.82 |
| | N% | 8.11 | 7.73 | 7.93 |
| | OS% | 0.28 | 0.31 | 0.24 |
| | H/C | 0.68 | 0.97 | 1.10 |
| | C/N | 10.56 | 10.49 | 10.91 |

[a]pH: pH in water (1:20 w/v); [b]OC% organic C concentration; [c]OS%: organic S concentration (analyzed at 950 °C).

### *6.4.2.3. Calcium*

Relatively lower concentrations of Ca$^{2+}$ were detected in the weathering solutions compared with K$^{+}$ and sulphate-S. The amount of Ca$^{2+}$ recovered in the first half hour of the experiment barely exceeded 0.5% of the total Ca in the fresh biochar (Fig. 6.4a). Recovery increased during the 0.5–3 h time interval, with 0.9% of the total Ca in the fresh biochar being found in the weathering solutions from both the BC-B and the BC-HA treatments. At the end of the 300-h weathering period, recoveries of Ca$^{2+}$ in the weathering solutions were 2.0% and 2.2% of the total Ca for the BC-B and the BC-HA treatments, respectively. However, in the solid fraction, Ca decreased by 20.7% in the BC-B treatment and by 17.9% in the BC-HA treatment, which indicated that most of the Ca lost in the both treatments was re-precipitated in the inner surface of the flask, as corroborated by the data obtained by the PHREEQC geochemical program (data not shown). The smaller total loss of Ca from the BC-HA biochar compared with the BC-B biochar is attributed to the precipitation of Cahumates in the former, whereas the greater Ca concentrations in the BC-HA leachates reflect the fact that precipitation of Ca-components in the bottom flask was favoured in the absence of chelating compounds.

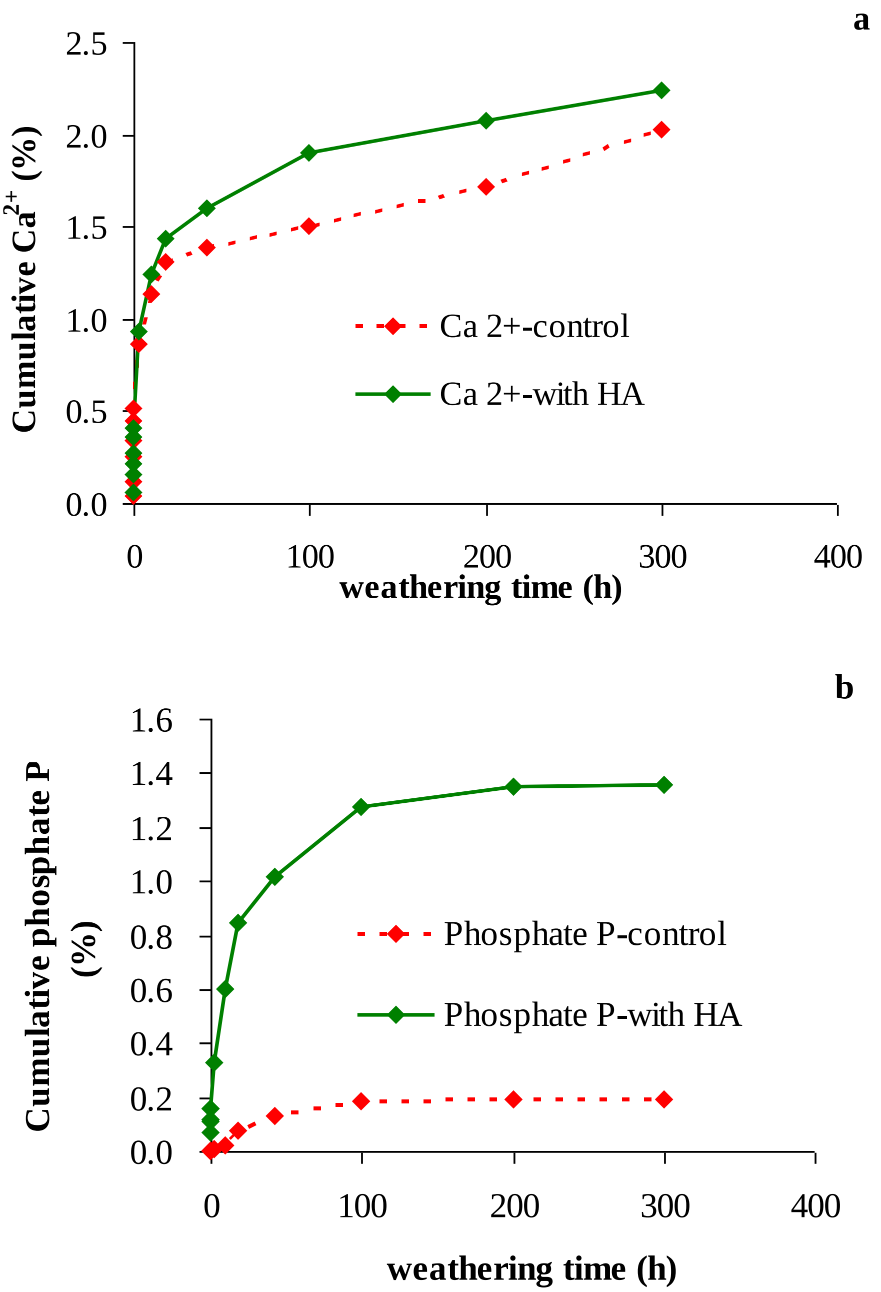


**Fig. 6.4.** Changes in cumulative (a) calcium and (b) phosphate-P (expressed as a percentage of the total Ca and P, respectively in the fresh biochar) in the biochar weathering solutions with weathering time. HA stands for humic acids.

#### *6.4.2.4. Phosphate*

Similarly, scarce phosphate-P was detected in the weathering solution from the BC-B treatment (Fig. 6.4b) and the total amount recovered at the end of the experiment barely exceeded 0.2% of the total P in the fresh biochar (Fig. 6.4b). However, there was relatively more phosphate-P in the weathering solutions from the BC-HA treatment. Within the first 18 h of weathering, the amount of phosphate-P in the BC-HA solution reached 0.84% of the total P in the fresh biochar. An additional 0.5% of the total P was then detected in the following 282 h of weathering. Apparently, the solubilisation of less readily soluble salts, such as phosphate salts, was particularly favoured by the presence of HA probably through cation complexation. The P content in the solid fraction decreased by 15.4% in both the BC-B and the BC-HA treatments compared with the fresh biochar. As with Ca, this indicates that a large fraction of the released P was precipitated on the inner surface of the flask, which according to PHREEQC modelling (data not shown), was supposed to be hydroxyapatites, and that this precipitation was favoured in the absence of chelating compounds. Overall, the low solubility of Ca–P compounds would explain the low recovery of P and Ca in the weathering solutions (0.2% of P and 2.0% of Ca in the BC-B weathering solutions) compared with the important decrease in P and Ca detected in the solid fraction (15.4% decrease in P and 20.7% decrease in Ca in the BC-B biochar).

#### *6.4.2.5. Magnesium*

Magnesium was also detected in low concentrations in the weathering solutions. Only 0.2% of total Mg in the fresh biochar was recovered in the aqueous phase from both the BC-B and the BC-HA treatments during the first half hour of the experiment (Fig. 6.5a). Thereafter, differences between the two treatments began to become evident and, at the end of the experiment final recoveries of 1.6% and 2.4% were obtained for BC-B and BC-HA treatments respectively. The Mg content of the solid fraction in the BC-B and BC-HA treatments decreased by 10.2% and 12.1%, respectively. The data obtained thus suggest that precipitation reactions are taking place. The PHREEQC geochemical program, however, did not indicate the existence of supersaturating conditions for any of the Mg compounds considered in the model.

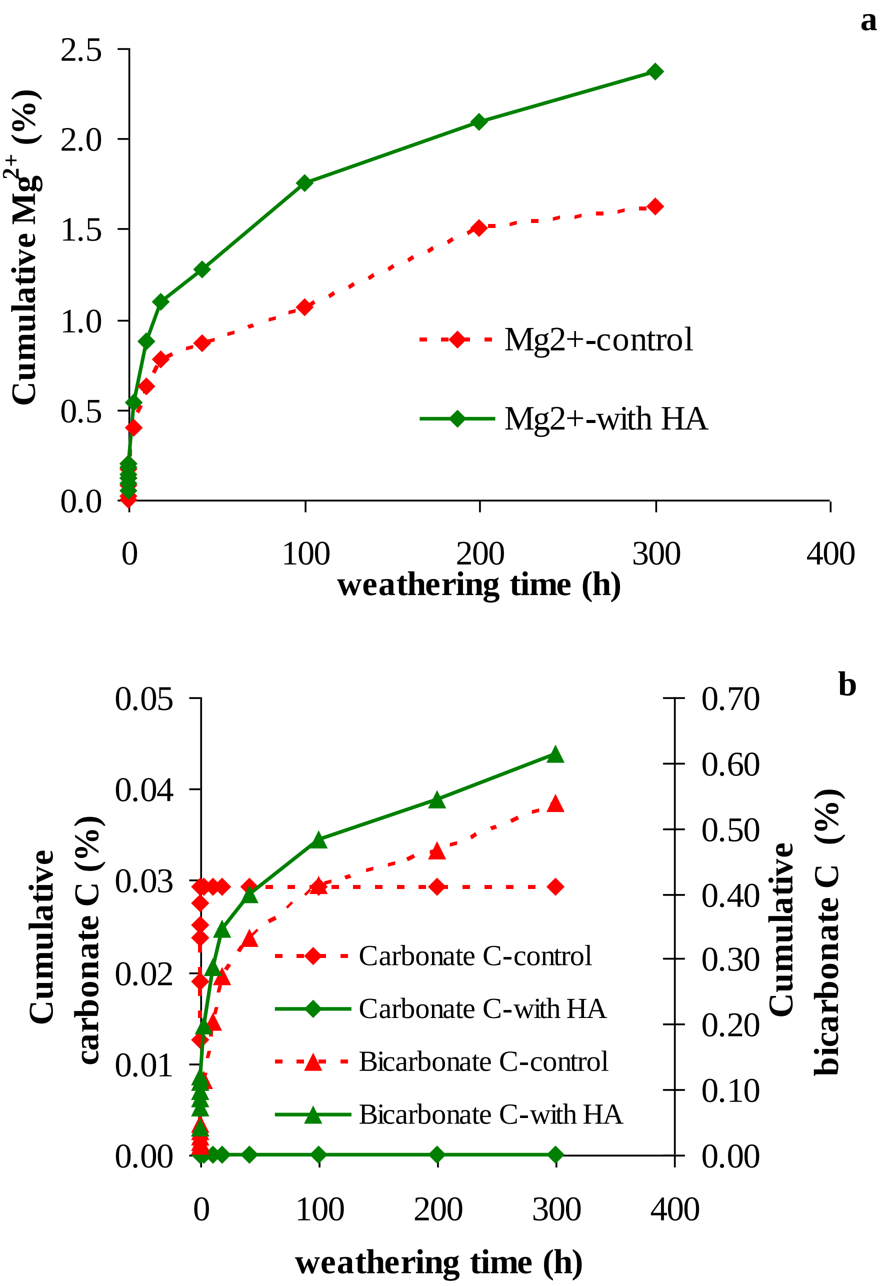


**Fig. 6.5.** Changes in cumulative (a) magnesium and (b) carbonate- and bicarbonate-C (expressed as a percentage of the total Mg and C, respectively in the fresh biochar) in the biochar weathering solutions with weathering time. HA stands for humic acids.

### *6.4.2.6. Carbonate and bicarbonate*

Carbonate-C was only detected in the first four weathering solutions from the BC-B treatment, making up 0.04% of the total C in the fresh biochar (Fig. 6.5b). This ion was present in solution when the system pH was higher than 8.6, which occurred in the BC-B treatment throughout the first half hour of the experiment. The amount of bicarbonate-C in solution was considerably higher than that of carbonate-C. During the first 18 h, 0.27% and 0.35% of the total C in the fresh biochar were detected as bicarbonate-C in the weathering solutions for BC-B and the BC-HA treatments, respectively. In the subsequent period, the increase was much slower but still considerable by the end of the experiment, total bicarbonate-C in the weathering solutions of the BC-B and BC-HA treatments reached 0.54% and 0.61% of the total C in the fresh biochar, respectively. These values are higher than the initial carbonate-C content of the fresh biochar (~0.03% carbonate-C/total C), suggesting that the carbonate-C originated from other processes, in addition to the dissolution of carbonates, including: (i) dissolution of gaseous $CO_2$ into the aqueous phase under the initial high pH conditions of the system, (ii) $CO_2$ released from abiotic oxidation of the biochar, and (iii) microbial processes associated with decomposition of HA and/or biochar.

### *6.4.2.7. Mineral composition and morphological characterisation of biochars*

According to the results of the XRD analysis (data not shown), the fresh and weathered biochars contained a few crystalline minerals, including quartz, traces amounts of albite, Ti-magnetite and olivine. In addition, traces of calcite were detected in the fresh biochar, but not in the weathered treatments, owing to the enhanced solubilisation through leaching and acidification of the system. The EDX analysis of some mineral particles in the biochar before and after weathering is shown in Fig. 6.6. Particles presented a considerable roughness and abundant microparticle adhesions on their surfaces, affecting the brightness of the images, which hampered the interpretation of the data from a compositional view point. Figure 6.6a illustrates the composition of a fresh biochar particle consisting of a combination of Al, Si, P, K, Ca, Ti and Fe. Figure 6.6b denotes the presence of a quartz particle in the BC-B biochar sample. Fig. 6.6c corresponds to an image of another BC-B biochar particle, where Fe, Ca and S predominated. Finally, Fig. 6.6d shows an image of a BC-HA biochar particle with high Fe and Ca concentrations, and lower amounts of Al, P, S and Ti. The presence of Cu and Zn is likely to be related to the composition of the sample holder (brass).

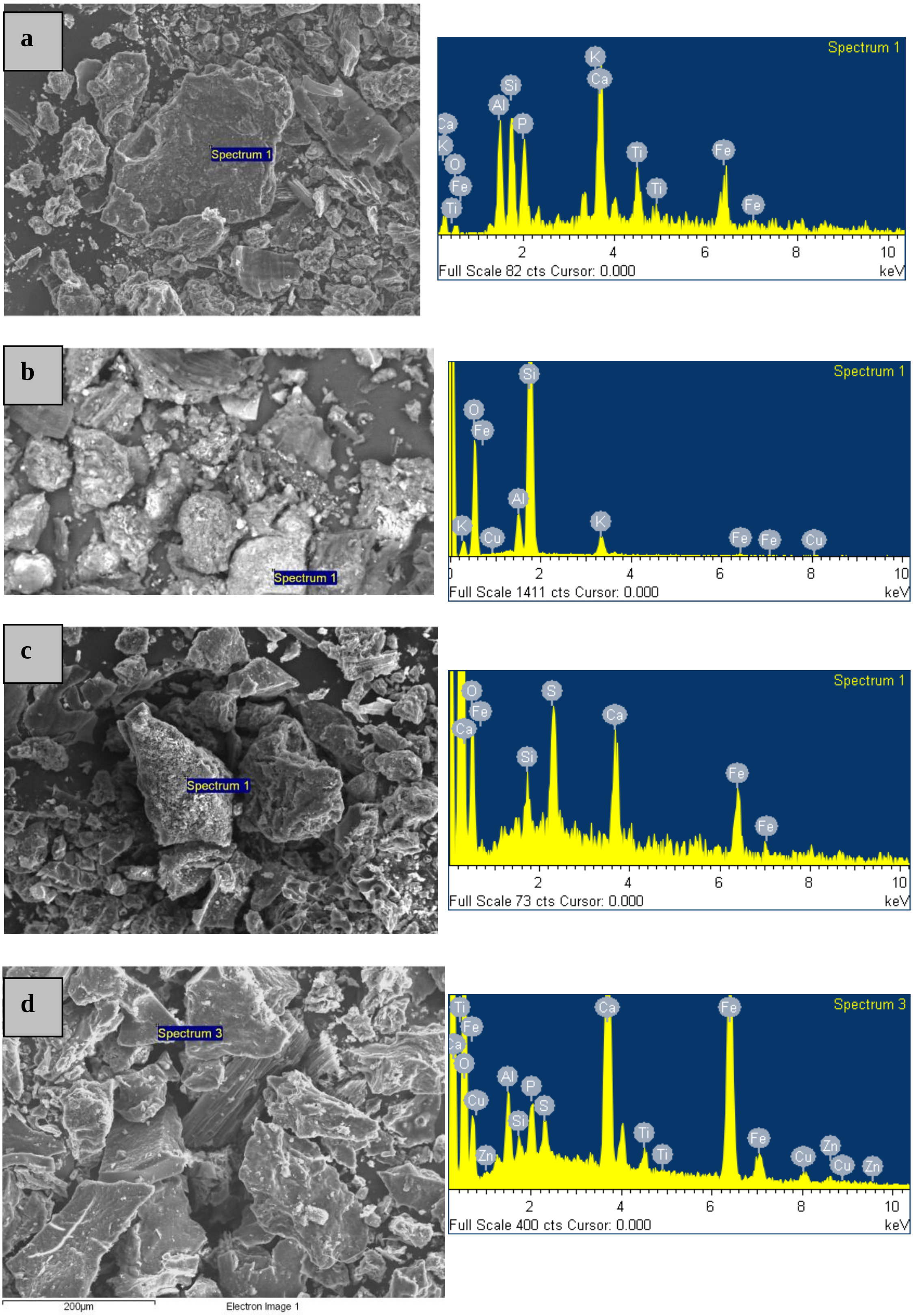


**Fig. 6.6.** Scanning electron micrographs and EDX spectrograms of mineral particles found in fresh and weathered biochar from simulated weathering in a modified Soxhlet reactor: (a) in fresh biochar, (b) in BC-B biochar, (c) in BC-B biochar (no humic acids addition), and (d) in BC-HA biochar (with humic acids addition).

The EDX analysis of the mineral particles in the biochar before and after the experiment showed no evident pattern associated with the weathering process. However, it was useful to identify the presence of amorphous inorganic components, in addition to the crystalline minerals identified with XRD. Other technologies, such as EDS in conjunction with scanning transmission electron microscopy (STEM), might be needed to determine the changes occurring at the surface of ash-rich biochars through weathering (Joseph et al., 2010).

### *6.4.3. Weathering of the charcoal fraction of the biochar (total organic C, H and N)*

The addition of HA resulted in 0.5% of the total organic C in the fresh biochar released as DOC during the first 3 h of the weathering, while only 0.1% of the total organic C in the fresh biochar was released during the same period in the BC-B treatment (Fig. 6.7a). This DOC could originate from either the biochar and/or the HA; however, the experimental design used in this study does not allow us to distinguish the source of this C. Most of the DOC detected in the weathering solutions of both the BC-B and the BC-HA treatments was found during the first 18 h of weathering (0.2% and 0.6% of the total organic C in the fresh biochar for the BC-B and the BC-HA treatment, respectively). During the following 282 h of weathering, only an additional 0.1% of the total organic C in the fresh biochar was released in the weathering solutions. The total amount of DOC in the weathering solutions was as low as 0.3% and 0.8% of the total organic C in the fresh biochar, for the BC-B and BC-HA treatments, respectively, reflecting the low solubility in water of the organic C in the solid phase.

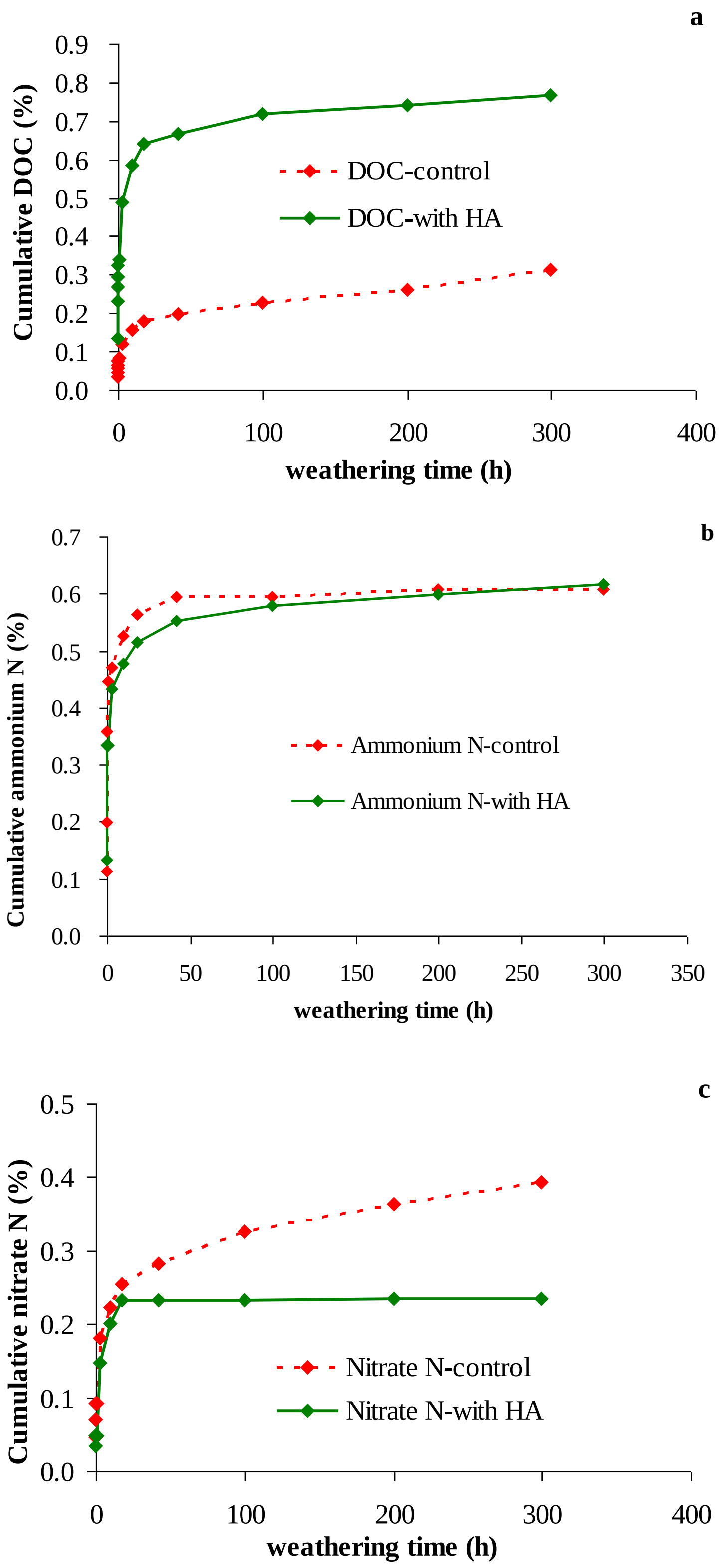


**Fig. 6.7.** Changes in cumulative (a) DOC, (b) ammonium-N and (c) nitrate-N (expressed as a percentage of the total C and N in the fresh biochar, respectively) in the biochar weathering solutions from simulated weathering in a modified Soxhlet reactor. HA stands for humic acids.

As far as the solid biochar is concerned, the 300-h-simulated weathering of biochar with water resulted in a decrease in the concentration of total organic C and increase in the concentration of H. The total organic C content in the ash-free fraction of biochar decreased from 73.68% to 69.47% after 300 h weathering in the BC-B treatment, while an increase of 0.44% was observed in the BC-HA treatment as a result of the additional C in the HA (Table 6.1). Fresh biochar contained less H (4.14%) than the weathered biochar (BC-B), which contained 5.60% of H. Treatment with HA resulted in 6.82% of H at the end of the experiment (Table 6.1). Concomitantly, in the BC-B treatment, the H/C atomic ratio increased from 0.67 to 0.97 and in the BC-HA treatment it rose to 1.10. The three CP/MAS $^{13}$C NMR spectra showed a dominant band characteristic of aromatic C at about 127 ppm, with substantially lower intensity of alkyl C at 0–50 ppm (Fig. 6.8). An additional peak at 73 ppm in the spectrum of BC-HA suggests the presence of a small amount of O-alkyl C added with the HA. Overall, the spectra obtained showed the presence of a highly aromatic C, and therefore reflected the highly recalcitrant nature of this charcoal to decomposition (Singh and Cowie, 2008).

The oxygen functionalities present at the outer surface of the biochar particles were analyzed by XPS. The C 1s core level spectra obtained for fresh biochar samples, BC-B and BC-HA treatments, are shown in Fig. 6.9 along with the peak-fitting of the envelope. For these materials, the C 1s envelope contains four signals attributed, respectively, to aliphatic/aromatic carbon groups (CHx, C–C/C=C) (284.6 eV), hydroxyl and ether groups (-C-OR) (285.8 eV), carbonyl groups (>C=O) (287.2 eV) and carboxylic groups, esters and lactones (–COOR) (288.8–288.9 eV).Generally, the XPS results showed that the two weathered biochars contained higher proportions of carbonyl and carboxylic groups than the fresh biochar, which might have resulted from biochar oxidation (in the BC-HA treatment, also from the added HA). The increase of carboxylic groups has clear implications on surface reactions of biochars (Cheng et al., 2006, 2008; Joseph et al., 2010). In the system studied, water dripped into the reactor cartridge and when the water level reached the height of the siphon, it drained immediately. Thus, the biochar sample was in alternating saturated–unsaturated condition, which ensured the availability of $O_2$ for both biotic and abiotic decomposition of biochar. Nguyen and Lehmann (2009) incubated oak and corn biochars inoculated with microbes under different water regimes, and observed a greater decomposition of the oak biochar under alternative saturated–unsaturated conditions, whereas that of corn biochar was favoured under continuous unsaturated conditions. In our study, no microbial inoculum was added to the system, but microbial activity could be inferred from the pattern of dissolved N species, as described below.

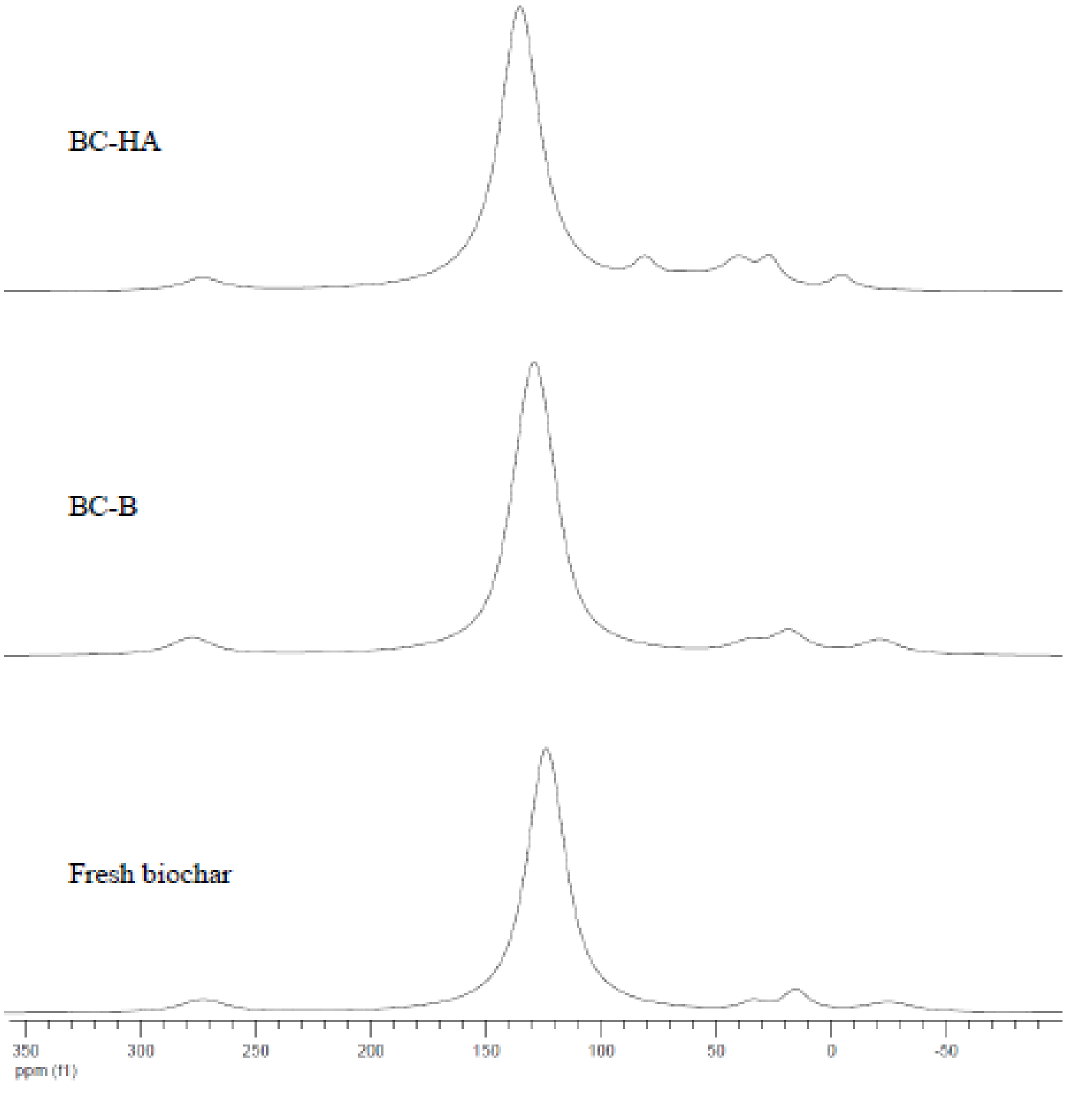


**Fig. 6.8.** CP/MAS $^{13}$C NMR spectra of fresh and weathered biochar (BC-HA and BC-B are with and without the addition of humic acids, respectively) from simulated weathering in a modified Soxhlet reactor.

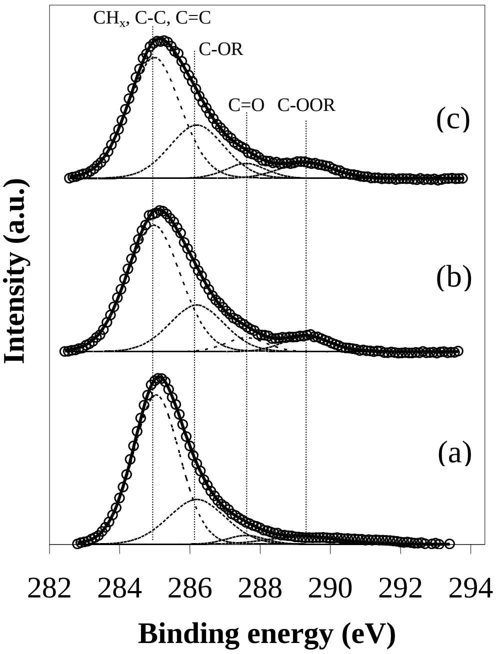


**Fig. 6.9.** C 1s core level spectra of fresh and weathered biochar from simulated weathering in a modified Soxhlet reactor measured by XPS (a) fresh biochar, (b) BC-B (no humic acids addition), and (c) BC-HA (with humic acids addition). Dashed lines correspond to deconvoluted peaks, circles are the experimental data and continuous lines are the global fit (sum of the different deconvolutions).

The content of total N in the ash-free fraction of biochar decreased from 8.11% to 7.73% and 7.93% in the BC-B and BC-HA treatments, respectively (Table 6.1). Both ammonium-N (as low as 0.6% of the total N in the fresh biochar) and nitrate-N (less than 0.4% of the total N in the fresh biochar) were found to be at very low concentrations in the biochar weathering solution (Fig. 6.7b and c), in spite of the low C/N ratio of this biochar (Table 6.1), which agrees with the results of Gaskin et al. (2008). In contrast to the rest of ionic species studied, ammonium-N and nitrate-N concentrations were generally lower in the BC-HA biochar than in the BC-B biochar. This was probably caused by an enhanced microbial N immobilisation in the former, which resulted from the addition of a more easily degradable C form (e.g., humic acids) compared with charcoal into the system.

A greenhouse study carried out by our research team using the same biochar from sewage sludge as the one in the present study to amend ray grass-soil system confirmed the low availability of N in this biochar produced from sewage sludge at 550 °C (Wisnubroto et al., 2010). These results contrast with those of Chan et al.

(2008), who described an increase in N uptake by radish after the application of poultry litter biochars produced at 450 and 550 °C, and indicated that nitrate-N was mainly found at the surface of the poultry litter biochar particles (Joseph et al., 2010). We thus need to improve our understanding of how pyrolysis conditions of high-N feedstocks affects the availability of N. We hypothesize that, in our biochar, most of the N was present as recalcitrant heterocyclic N within the charcoal structure (Knicker, 2007), although more research is needed in this area to confirm this.

## 6.5. Conclusions

The evolutionary trend of this biochar mineral-weathering experiment shows that, under the neutral-slightly alkaline conditions of the system, the presence of metallic oxy-hydroxides will lead to the formation of carbonate-bicarbonates (the former only at the initial high pH values) and phosphates salts. Sulphate seems to remain mostly in solution, although the re-precipitation of sulphates in more insoluble forms than those originally present in the biochar cannot be discarded. The effect of HA is evident from the pattern observed in the weathering solutions and seems to be more related to the kinetics of weathering (apparently accelerating it) than to the thermodynamic evolution. The mobility of elements follows the order Ca >> Mg ~ K, which is different from that of silicate systems, as these follow the order Mg > K >> Ca. This further reflects the dominance of metal oxy-hydroxides and relatively soluble salts (e.g., sulphate salts) in relation to the presence of silicates.

The results obtained from the 300-h experimental period of geochemical weathering thus demonstrated the potential of this biochar derived from sewage sludge as a source of some plant essential nutrients (e.g., K, Ca, S, P, and Mg). Nitrogen availability was restricted and this was attributed to its high recalcitrance. The pH of the system was lowered by the leaching of base cations and possibly carbonation through $CO_2$ dissolution in the initial alkaline system and/or $CO_2$ released from the biotic and abiotic oxidation of the biochar. Although the weathering time was limited, a considerable increase in carbonyl and carboxylic functional groups was detected at the surface of biochar particles, which indicated oxidation of the biochar during geochemical weathering. Nevertheless, the C mass balance indicates that C in biochar suffered little decomposition, in spite of the favourable environmental conditions (e.g., 30 ºC and fluctuating moisture conditions), which was as expected, given the short duration of the study and the fact that we did not inoculate the system with microbes.

This is the first study to use a Soxhlet extractor in this context. The modified Soxhlet reactor used here has been proved to be successful in simulating the mineral weathering of this mineral ash-rich biochar, although the present study is mainly limited to the fact that the biochar was not mixed with soil (and microbes) and the pH weathering conditions of this biochar mostly simulated neutral to alkaline systems but not acid soils. Stronger acidification and long-term geochemical weathering study of the biochar mixed with the soil to which it will be applied should be conducted to be able to predict the mid-term nutrient availability and the mineralogical transformation of biochar.

## 6.6. Acknowledgements

We are grateful to Carmen Perez Llaguno at University of Santiago de Compostela, Iñaki Basañez Llantada at NEIKER-TECNALIA and Janine McGowan at CSIRO Land and Water for their kind help in the laboratory. We acknowledge financial support for the research provided by the Spanish Ministry of Science and Education (Project No. CTM 2006-13748-CO2) and through an FPI fellowship from the Spanish Ministry of Science and Education. In addition, J.A. Macía Agulló acknowledges the assistance of the Spanish Ministry of Science and Education for its award of a Juan de la Cierva contract. Marta Camps Arbestain is very grateful for financial support from the New Zealand Ministry of Agriculture and Forestry. We thank Palmerston North City Council for providing the sewage sludge used as feedstock. The authors also thank the anonymous reviewers for their valuable suggestions.

## 6.7. References

Badreddine, R., Humez, A.N., Mingelgrin, U., Benchare, A., Meducin, F., Prost, R., 2004. Retention of trace metals by solidified/stabilized wastes: Assessment of long-term metal release. Environ. Sci. Technol. 38, 1383–1398.

Bramryd, T., 2002. Impact of sewage sludge application on the long-term nutrient balance in acid soils of Scots pine (Pinus sylvestris, L.) forests. Water Air Soil Poll. 140, 381-399.

Bundy, L.G., Bremner, J.M., 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. J. 36, 273-275.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie A., Joseph, S., 2007. Agronomic values of greenwaste biochar as a soil amendment. Aust. J. Soil Res. 45, 629-634.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph S., 2008. Using poultry litter biochars as soil amendments. Aust. J. Soil Res. 46, 437-444.

Cheng, C.H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochim Cosmochim Acta 72, 1598-1610.

Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006. Oxidation of black carbon by biotic and abiotic processes. Org. Geochem. 37, 1477-1488.

DeLuca, T., Derek MacKenzie, M., Gundale, M.J., 2009. Biochar effects on soil nutrient transformations. In: Lehmann, J., Joseph, H. (Eds.). Biochar for Environmental Management: Science and Technology. Earthscan Press, London, pp. 251-269.

Ferrier, R.C., Edward, A.C., Dutch, J., Wolstenholme, R., Mitchell, D.S., 1996. Sewage sludge as a fertilizer of pole stage forests: Short-term hydrochemical fluxes and foliar response. Soil Use Manage. 12, 1-7.

Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., 2008. Effect of low-temperature pyrolysis condition on biochar for agricultural use. T. ASABE 51, 2061-2069.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 2001. The ‘Terra Preta’ phenomenon: A model for sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37–41.

Gundale, M.J., DeLuca, T.H., 2006. Temperature and source material influence ecological attributes of ponderosa pine and Douglas-fir charcoal. Forest Ecol. Manag. 231, 86-93.

Hoeft, R.G., Walsh, L.M., Keeney, D.R., 1973. Evaluation of various extractants for available soil sulfur. Soil Sci. Soc. Am. J. 37, 401–404.

Humez, N., Prost, R., 1999. A new experimental approach to study the long-term behaviour of solidified/stabilized wastes. Chem. Spec. Bioavailab. 11, 1–24.

Humez, N., Humez, A.L., Juste, C. and Prost R. (1997) A new assessment of mobility of elements in sediments and wastes. Chem. Spec. Bioavailab. 9, 57–65.

IPCC (Pachauri, R.K., Reisinger, A.), 2008. Climate Change 2007: Synthesis Report. Intergovernmental Panel on Climate Change, Sweden.

Joseph, S, Camps Arbestain, M., Lin, Y, Munroe, P., Chia, C.H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J., Foidl, N., Smernik, R.J., Amonette J.E. 2010. An investigation into the reactions of biochar in soils. Soil Res. 48, 501-515.

Kandeler, E., Gerber, H., 1988. Short-term assay of soil urease activity using colorimetric determination of ammonium. Biol. Fert. Soils 6, 68–72.

Knicker, H., 2007. How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. Biogeochemistry-US 85, 91–118.

Knicker, H., Almendros, G., Gonzáles-Vila, F.J., Martin, F., Lüdemann, H.D., 1996. 13C- and 15N-NMR spectroscopic examination of the transformation of organic nitrogen in plant biomass during thermal treatment. Soil Biol. Biochem. 28, 1053-1060.

Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I., Xu, X., 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. Soil Biol Biochem. 41, 210-219.

Lehmann, J., 2007a. A handful of carbon. Nature 447, 143–144.

Lehmann, J., 2007b. Bio-energy in the black. Front. Ecol. Environ. 5, 381–387.

Lehmann, J., Joseph, S., 2009. Biochar for environmental management: an introduction. In: Lehmann, J., Joseph, H. (Eds.). Biochar for Environmental Management: Science and Technology. Earthscan Press, London, pp. 1-10.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems-a review. Mit. Adapt. Strat. Global. Change 11, 403-427.

Lehmann, J., Pereira da Silva, Jr.J., Steiner, C., Nehls, T., Zech, W., Glaser, B. 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferrasol of the central Amazon basin: fertilizer, manure and charcoal amendments. Plant Soil 249, 343–357.

Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E., 2008. Australian climate-carbon cycle feedback reduced by soil black carbon. Nat. Geosci. 1, 832–835.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizao, F.J., Petersen, J., Neves, E.G., 2006. Black carbon increases cation exchange capacity in soils. Soil Sci. Soc. Am. J. 70, 1719–1730.

Lima, H.N., Schaefer, C.E.R., Mello, J.W.V., Gilkes, R.J., Ker, J.C., 2002. Pedogenesis and pre-Colombian land use of "Terra Preta Anthrosols" ("Indian black earth") of Western Amazonia. Geoderma 110, 1–17.

Lopez, R., Gondar, D., Iglesias, A., Fiol, S., Antelo, J., Arce, F., 2008. Acid properties of fulvic and humic acids isolated from two acid forest soils under different vegetation cover and soil depth. Eur. J. Soil Sci. 59, 892-899.

McBeath, A.V., Smernik, R.J. 2009. Variation in the degree of aromatic condensation of chars. Org Geochem. 40, 1161-1168.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36.

Nguyen, B.T., Lehmann J. 2009. Black carbon decomposition under varying water regimes. Org. Geochem. 40, 846-853.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS Water-Resources Investigations Report 99–4259. Denver, Colorado, USA.

Pédro, G., 1961. An experimental study on the geochemical weathering of crystalline rocks by water. Clay Miner Bull. 4, 266–281.

Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., Newman, R.H., 1994. The removal of magnetic materials from surface soils-a solid state 13C CP/MAS NMR study. Aust. J. Soil Res. 32, 1215–1229.

Singh, B.P., Cowie, A.L. 2008. A novel approach, using 13C natural abundance, for measuring decomposition of biochars in soil. In: Currie, L.D. and Yates, L.J. (Eds.). Carbon and Nutrient Management in Agriculture, Fertilizer and Lime Research Centre Workshop Proceedings. Massey University, Palmerston North, New Zealand, pp. 549.

Tiessen, H., Roberts T., Stewart J. 1983. Carbonate analysis in soils and minerals by acid digestion and two-endpoint titration. Communications in Soil Science and Plant Analysis 14, 161-166.

Tryon, E.H., 1948. Effect of charcoal on certain physical, chemical and biological properties of forest soils. Eco. Monogr. 18, 81–115.

Wisnubroto, E.I., Hedley, M., Hina, K., Camps Arbestain, M., 2010. The use of biochar from biosolids on Waitarere sandy soils: Effects on the growth of Rye grass. New Zealand Biochar Research Centre Workshop 2010. http://www.biochar.co.nz /workshop.html.

# Chapter 7

# Simulated geochemical weathering of biomass fly ash in a modified Soxhlet reactor

# Chapter 7. Simulated geochemical weathering of biomass fly ash in a modified Soxhlet reactor

## 1. Abstract

Fly ash has abundant aluminosilicate glass, as volcanic ash does; it has been hypothesized that, as fly ash weathers with time after exposure to outdoor conditions, andic soil properties can developed. In the present study, a modified Soxhlet reactor was utilized to evaluate the long-term geochemical weathering of a carbon-rich fly ash produced from bark combustion. The weathering process took place at 30 °C, with a flow rate of water of 5 mL $\text{min}^{-1}$ (equivalent to the rainfall of 273 mm $\text{h}^{-1}$). Seven weathering periods were set: 1 h, 24 h, 120 h, 300 h, 800 h, 1304 h and 1808 h. The kinetics of elements released at different sampling times were studied, along with the transformations occurred within the solid phase at the end of the experiment. The results showed that S, Na and K were the most mobile elements, followed by Si, Ca and Mg. The maximum loss of K and S were 34% at 800 h and 55% at 120 h, respectively, and the loss of Na reached 99% at the end of the study. The maximum loss of Ca, Si, and Mg was 4.75%, 6.41% and 1.25%, respectively, there being an obvious decrease thereafter, attributed to neoformation and/or adsorption. No sulphates have reached saturation despite of the high concentration of $SO_4^{2-}$. The heavy metals in the weathering solutions were negligible. Calcite disappeared after weathering for 800 h. The results proved that this modified Soxhlet reactor and the weathering concepts established by Pédro was considered applicable to the simulation of geochemical weathering of fly ash.

.*Keywords:* Aluminosilicate glass; Clay formation; Secondary minerals; Parker index; Species activity

## 7.2. Introduction

Fly ash refers to the ash and non-combustible minerals that are released from coal or biomass combustion and that “fly” up and out of the boiler with the flue gases (Halverson et al., 2001). The United States produced 72.4 million tons of fly ash in 2006 (ACAA, 2007); India produces about 80 million tons of fly ash per year (Kumar and Sharma, 1998). The environmentally-sound use or disposal of such huge quantities of fly ash raises global concerns. Apart from coal fly ash, there is another kind of fly ash derived from biomass combustion, which contains considerable amounts of plant nutrients and is appeal to agricultural utilization (Biedermann and Obernberger, 2005).

Both fly ash and volcanic ash contain abundant aluminosilicate glass, which are themselves materials of low degree of order and often of glassy structure, and/or weather to non-crystalline clay (Warren and Dudas, 1985; Zevenbergen et al, 1999). The formation rate of amorphous compounds was observed to be even greater in the former due to the effect of the high pH on the glass dissolution (Zevenbergen et al., 1999). Since soil formation on volcanic ash can give rise to Andosols under good drainage conditions at early stages of weathering (WRB, 2006), it is hypothesized that, under suitable conditions, new soils with andic soil properties could develop from fly ashes exposed to outdoor conditions. Fly ashes originally met many properties that relate to the criteria definition of andic soils, e.g. among others, they have low bulk density, high anion-binding capacity, especially with specific adsorption of anions (phosphates, fluorides, sulphates, arsenates, etc) (Warren and Dudas, 1985; Zevenbergen et al, 1999).

Considering that the fly ash would subject to the same natural weathering process as rocks and other residues, we propose to carry out the simulated geochemical weathering of fly ash in a modified Soxhlet reactor, following the methodology of Pédro (1961), Humez et al. (1997), Humez and Prost (1999) and Badreddine et al. (2004). The working principle of the reactor is as follows: the deionized water in a three-neck round-bottom flask evaporates because of the constant heating and then condenses in the condenser that is connected to the flask; water drips into the extractor that holds the sample; when the water level reaches the top of the siphon of the extractor it returns to the flask via a silicone tube; water cycles round the system (Humez et al., 1997; Humez and Prost, 1999). This modified Soxhlet reactor was also successfully employed to study the geochemical weathering of biochar in our laboratory (Yao et al., 2010).

Weathering time is a key factor in the reaction processes in a fundamental way not only because it modifies the reaction kinetics, but also because it alters the end products that the thermodynamics of the system leads to. Under natural conditions, the weathering time is regulated by the drainage conditions, which in turn is influenced by factors among others, related to topography and permeability of materials. The present study on the weathering of the fly ash from pine park combustion has been carried out in a modified Soxhlet reactor to obtain the weathering solutions with different weathering time: 1, 24, 120, 300, 800, 1304 and 1808 h. The objective was to investigate the long-term weathering behavior of biomass fly ash through tracing the release kinetics of elements and mineralogical and chemical changes within the fly ash.

## 7.3. Materials and methods

### *7.3.1. Experimental design*

Fly ash (FA) from combustion of pine bark (*Pinus radiata and Pinus pinaster*) at more than 1000 °C and with sufficient oxygen was provided by Smurfit Kappa (Durango, Basque Country, N Spain). It was air-dried and then sieved to <2 mm after collection.

About 20.00 g of FA were weighed to fill each cellulose cartridge of the Soxhlet reactor. The weathering time series were set to be 1 h, 24 h, 120 h, 300 h, 800 h, 1304 h and 1808 h. The temperature of the leaching water was controlled around 30°C and the flow rate was approximately 5 mL $min^{-1}$ (equivalent to a rainfall of 273 mm $h^{-1}$). The first cycle (the first time the weathering solution flowed back to the flask through the siphon) was considered to be time zero. The chemical and mineralogical changes of the fly ash as well as the composition of the weathering solutions were studied along the weathering period.

### *7.3.2. Analysis of weathering solutions*

Weathering solutions were measured for pH, electrical conductivity (EC) and Eh with suitable electrodes. The concentrations of $F^-$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$, and $PO_4^{3-}$ were determined using ionic chromatograph (Dionex-4500i, Dionex Corp., Sunnyvale, CA). The concentration of $CO_3^{2-}$ was measured with titration method. The concentration of $NH_4^+$ was determined colorimetrically, following the modified method of Berthelot (Kandeler and Gerber, 1988). Total concentrations of Al, Fe, Mn, Ni, Pb, Si, Zn, Cd, Cu, Ca, K, Mg, Na, Co and Cr were determined by atomic absorption spectrophotometer (AAS). The analytic results of the solutions are presented in the Fig.7.1-7.3.

The data of concentration were utilized in the calculation of the activities de different species. Mineral saturation indices and thermodynamic equilibrium diagrams in each weathering solution were computed using the USGS aqueous modelling software, PHREEQC (Parkhurst and Appelo, 1999). The activities of each species and saturation index of minerals clacurated by PHREEQC for the solutions at different weathering times were presented in Annex 3.

### *7.3.3. Chemical analysis of solid samples*

The pH of the FA was measured at a ratio of 1:20 (w/v) in water. Total carbon (C), H and N were analyzed with a TruSpec CHN analyzer (LECO Corporation, Michigan USA). Total P, S, K, Na, Ca, Mg, Fe, Mn, Al, Cu, Zn, Ni, Pb, Cd and Cr were analysed by Charge coupled device (CCD) simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES) (VISTA-MPX, Varian Ibérica S.L., Madrid, Spain) after digestion with a mixture of nitric and perchloric acid (85%:15%, v/v). In addition, 0.5 g of each solid sample was microwave digested with 9.0 mL concentrated nitric acid + 3 mL concentrated hydrochloric acid + 2 mL hydrofluoric acid (48%) for the determination of total Si.

### *7.3.4. Mineralogical analysis and solid-state nuclear magnetic resonance spectroscopy (NMR)*

Changes in the crystalline fraction of the solid phase were assessed by X-ray diffraction (XRD) (Philips PW 1710, CuKa1.2).

Solid-state $^{13}C$ nuclear magnetic resonance (NMR) spectra were obtained (Bruker Avance DSX300 NMR spectrometer: Bruker Corporation) after pre-treatment of the samples with 2% HF solution, according to Skjemstad et al. (1994). Variable amplitude cross-polarization magic angle spinning (CP/MAS) experiments were run with a 4-mm MAS probe, with a spin rate of approximately 10,000 Hz. The contact time was 1 ms and the delay time was 2 s. An average of 40,000 transients was recorded for each sample.

## **7.4. Results and discussion**

### *7.4.1. Evolution of weathering solutions over time*

It was observed that, for most of the elements, the distribution of the concentrations followed an exponential model until saturation or equilibrium with variations (Fig. 7.1-7.4). These trends are related to processes of neoformation or adsorption in new colloidal components.

The pH of 1 h-weathering solution was 9.2 (Fig. 7.1), meaning that strong bases are released even within this small weathering time. With the increase of the weathering time, three stages of the evolution of pH could be discerned: the first with gradual release of alkali to the solution, causing the value of pH arising to 10.2 at 300 h; the second stage corresponded to the phase of balance or saturation between 300 and 800 h, during which there was hardly any change of pH; the third during the weathering time more than 800 h, presented an obvious decrease of pH (around 9.3), which related to the removal process of alkalinity to form secondary minerals. All of these processes correspond to the weathering conditions defined by Pédro (1961) as “alkalinolisis”.

The electrical conductivity (EC) increased with the weathering time up to values around 1120 μS $cm^{-1}$ at 300 h (Fig. 7.1). It was stable with this value during the following weathering periods, indicating that it has practically reached equilibrium.

The redox potential (Eh) followed a similar evolution trend of EC, stabilized at 1304 h, with values of 108 mv (Fig. 7.1). However, it was always remained within “suboxide” conditions.

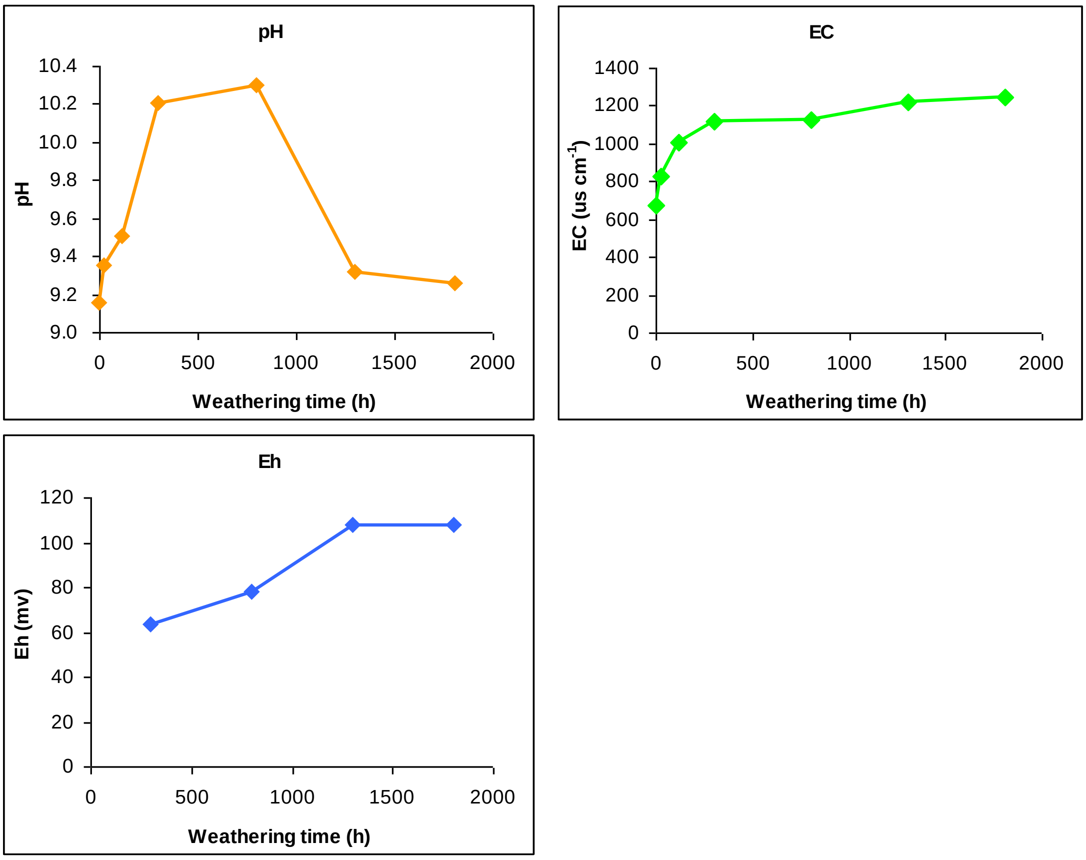


**Fig. 7.1.** Changes of pH, EC and Eh of the weathering solutions.

The evolution sequence of the most abundant cations ($K^+$ and $Na^+$) were characterised by an increase in the concentrations with weathering time and stabilised between 300 and 800 h (Fig. 7.2). The saturation concentrations were about 200 and 100 mg $L^{-1}$ for $K^+$ and $Na^+$, respectively (Fig. 7.2).

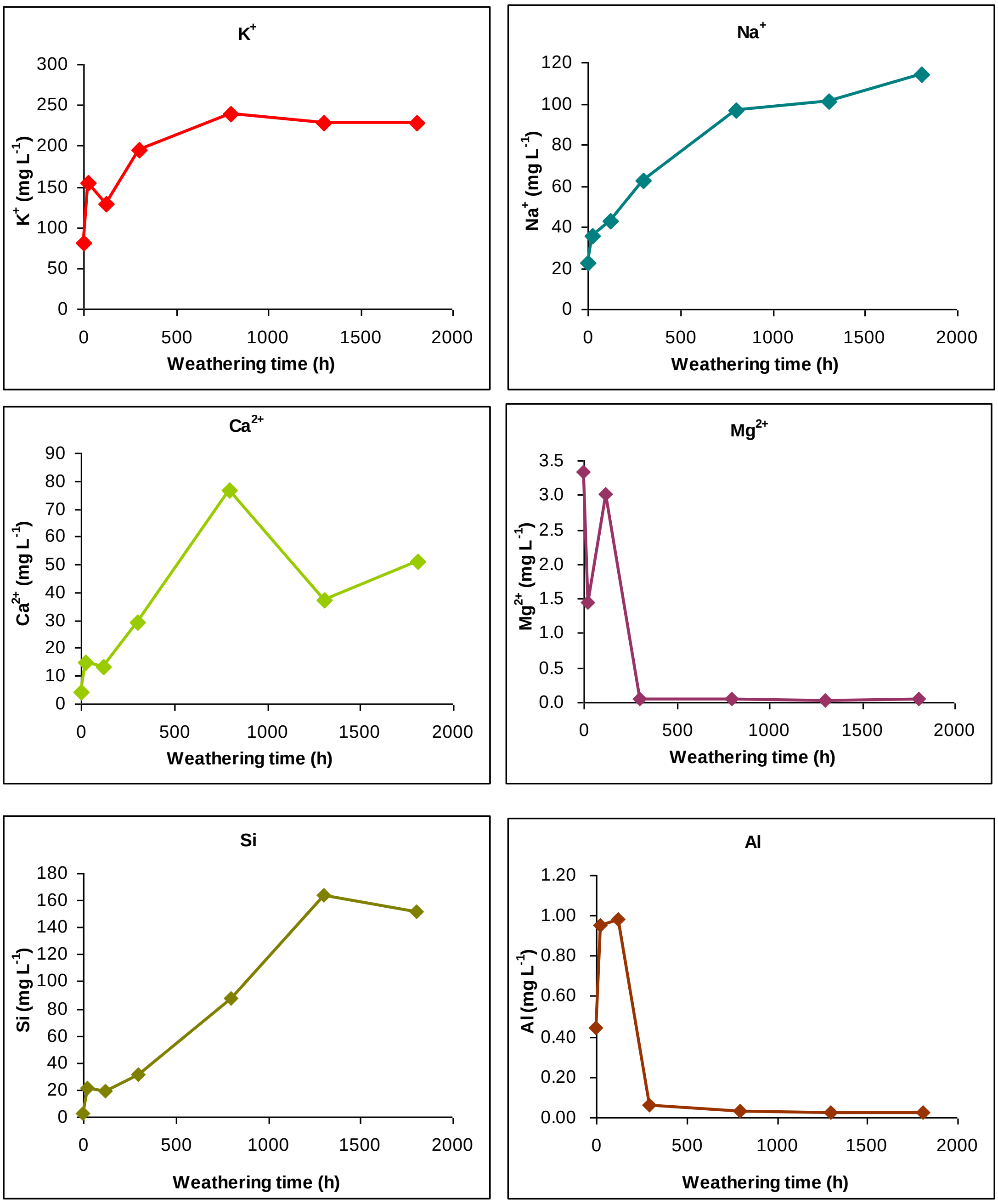


**Fig. 7.2.** Changes of concentrations of $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, Si and Al in the weathering solutions.

The evolution trend of the concentrations of $Ca^{2+}$ and $Mg^{2+}$ were more irregular (Fig. 7.2), which appeared to be related to the greater tendency to be incorporated into the secondary products of these elements. After 800 h of weathering, the concentration of $Ca^{2+}$ decreased from values 77 to around 40 mg $L^{-1}$. In the case of

$Mg^{2+}$, the variation was more dramatic, with a concentration of 3 mg $L^{-1}$ at 120 h and almost completely eliminated from the dissolved phase thereafter.

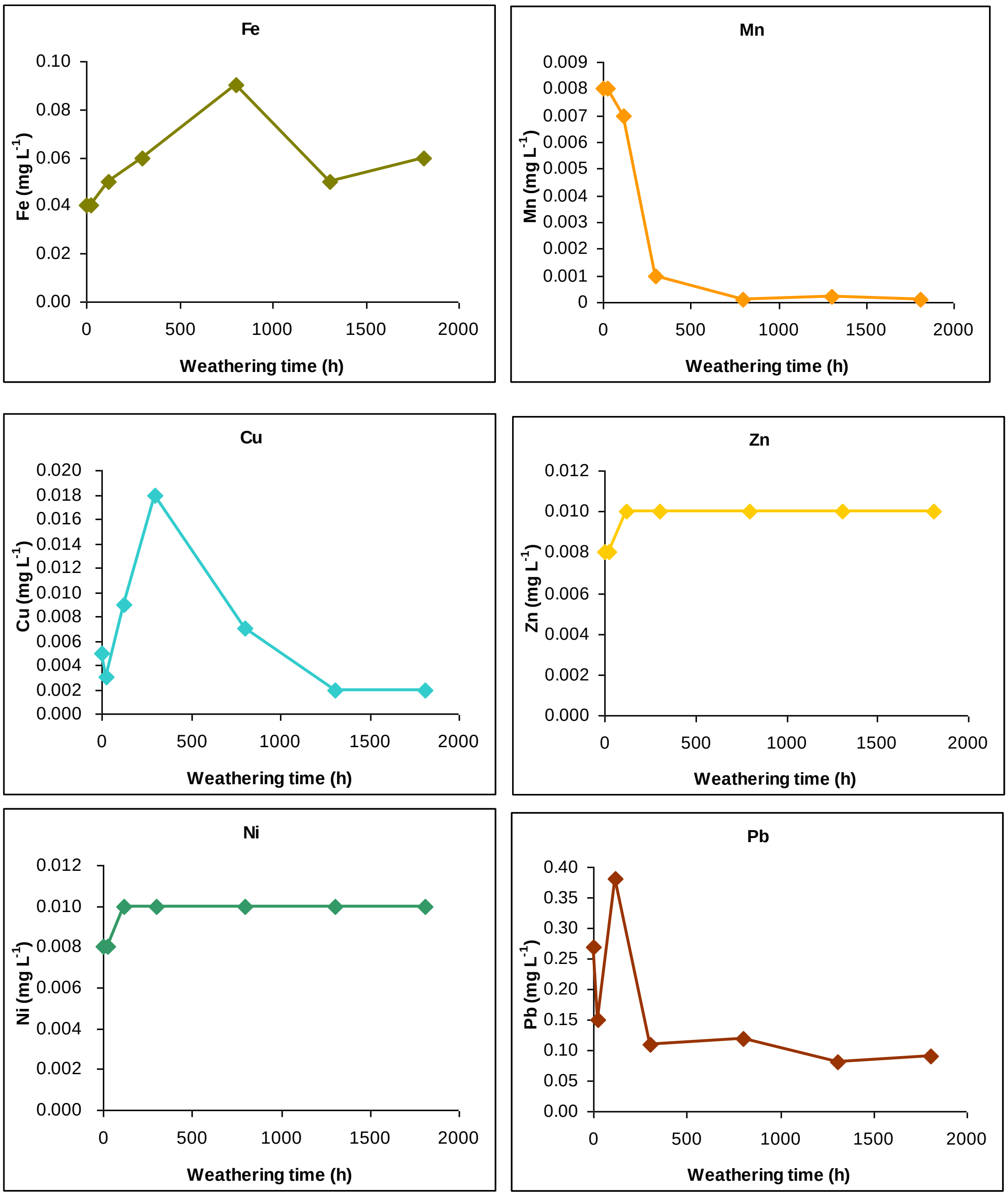


**Fig. 7.3.** Changes of concentrations of heavy metals in the weathering solutions.

A gradual increase in the Si concentration with weathering time has been observed under the alkalinolisis conditions favoring the dissolution of Si (Fig. 7.2), as expected, as Si dissolution is enhanced at high pH values, reaching values of 163 mg $L^{-1}$ at 1304 h and then declined slightly as weathering proceeded. During most of the weathering time, Si concentration was very high (21-163 mg $L^{-1}$) compared to that in the natural water systems. The decrease of Si concentration at increasing weathering time was probably associated with the neoformation of Si-containing secondary products.

The evolution of Al concentration followed a similar behaviour to that of Mg although the concentration was much lower (Fig. 7.2). The maximum concentration of Al was 0.98 mg $L^{-1}$ at 120h and then decreased to below 0.1 mg $L^{-1}$, which was, definitely related to its incorporation into the neoformed compounds.

The concentration of heavy metals was very low, practically irrelevant, which indicates that, under these weathering conditions, the risk of groundwater contamination was negligible (Fig. 7.3).

Initially, the main anion in the weathering solution was sulphate (Fig. 7.4). The concentration of sulphate increased from 165 mg $L^{-1}$ at 1 h to 218 mg $L^{-1}$ at 120 h; thereafter it stabilised at concentrations >200 mg $L^{-1}$ (Fig. 7.4), which is close to the maximum sulphate concentration (250 mg $L^{-1}$) authorised in drinking waters (EC, 1998).

Another important anion was $CO_3^{2-}$. Although its initial concentration was as low as 30 mg $L^{-1}$, it kept increasing during the whole weathering process and reached a concentration of 213 mg $L^{-1}$ at 1808 h (Fig. 7.4). This is partly due to the carbonation process occurring under the alkaline conditions of the system (pH > 9), as time proceed.

The concentrations of $F^-$ and $Cl^-$ had the same evolution trend: their concentrations increased from the beginning to 300 h and then stabilised at 2.7 and 40.2 mg $L^{-1}$ for $F^-$ and $Cl^-$, respectively (Fig. 7.4). Both of the concentrations of $F^-$ and $Cl^-$ are much higher than those usually present in river waters including coastal areas. The evolution trend of nitrate concentration was similar to those of $F^-$ and $Cl^-$, but it reached the saturation at 800 h, with concentration of about 13 mg $L^{-1}$ (Fig. 7.4).

The $PO_4^{3-}$ concentration followed an irregular trend (Fig. 7.4). It reached its maximum concentration of 0.67 mg $L^{-1}$ at 120 h and then declined to 0.14 mg $L^{-1}$ at 300 h; after that, there were almost no variations of the concentration. Undoubtedly, the observed variations must be related to precipitation or adsorption processes.

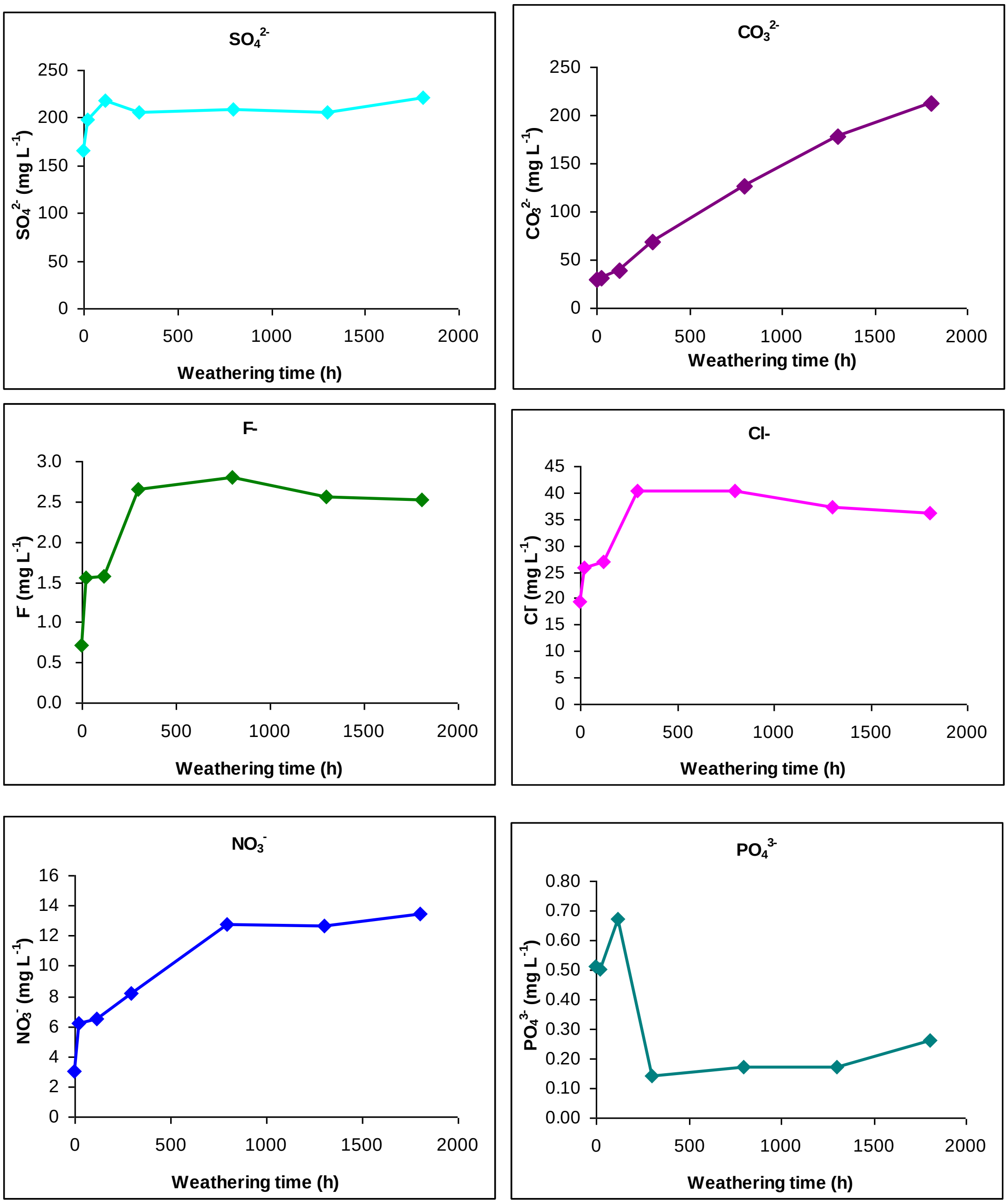


**Fig. 7.4.** Changes of concentrations of $SO_4^{2-}$, $CO_3^{2-}$, $F^-$, $Cl^-$, $NO_3^-$ and $PO_4^{3-}$ in the weathering solutions.

### *7.4.2. Activity of different species in the weathering solutions*

The modelling with the PHREEQC software allows the calculation of the activities of the different species of each element. The output obtained for the solutions at different weathering times was found in the Annex 3.

A synthesis of the activity obtained for the species of greater interest is presented in Table 7.1.

**Table 7.1** Variation of the activity of the most active species for each element and other environmentally relevant species at different weathering time*.

| | FA 1 | FA 24 | FA 120 | FA 300 | FA 800 | FA 1304 | FA 1808 |
|---|---|---|---|---|---|---|---|
| $Al(OH)_4^-$ | $1.50\ 10^{-5}$ | $3.20\ 10^{-5}$ | $3.30\ 10^{-5}$ | $2.00\ 10^{-6}$ | $9.85\ 10^{-7}$ | $6.59\ 10^{-7}$ | $6.57\ 10^{-7}$ |
| $Al^{+3}$ | $1.84\ 10^{-19}$ | $6.22\ 10^{-20}$ | $1.61\ 10^{-20}$ | $1.55\ 10^{-24}$ | $3.03\ 10^{-25}$ | $1.69\ 10^{-21}$ | $2.93.10^{-21}$ |
| $HCO_3^-$ | $4.23\ 10^{-4}$ | $4.01\ 10^{-4}$ | $4.78\ 10^{-4}$ | $4.27\ 10^{-4}$ | $5.61\ 10^{-4}$ | $2.18\ 10^{-3}$ | $2.61\ 10^{-3}$ |
| $CO_3^{2-}$ | $2.80\ 10^{-5}$ | $4.21\ 10^{-5}$ | $7.09\ 10^{-5}$ | $3.17\ 10^{-4}$ | $5.25\ 10^{-4}$ | $2.18\ 10^{-3}$ | $2.23\ 10^{-4}$ |
| $Ca^{+2}$ | $5.91\ 10^{-5}$ | $2.01\ 10^{-4}$ | $1.71\ 10^{-4}$ | $3.11\ 10^{-4}$ | $6.92\ 10^{-4}$ | $4.10\ 10^{-4}$ | $5.47\ 10^{-4}$ |
| $CaSO_4$ | $1.62\ 10^{-5}$ | $6.12\ 10^{-5}$ | $5.68\ 10^{-5}$ | $9.15\ 10^{-5}$ | $1.86\ 10^{-4}$ | $1.15\ 10^{-4}$ | $1.58.10^{-4}$ |
| $CaCO_3$ | $2.62\ 10^{-6}$ | $1.34\ 10^{-5}$ | $1.92\ 10^{-5}$ | $1.56\ 10^{-4}$ | $5.76\ 10^{-4}$ | $1.39\ 10^{-4}$ | $1.93\ 10^{-4}$ |
| $Cl^-$ | $4.98\ 10^{-4}$ | $6.59\ 10^{-4}$ | $6.84\ 10^{-4}$ | $1.02\ 10^{-3}$ | $1.01\ 10^{-3}$ | $9.31.10^{-4}$ | $9.02\ 10^{-4}$ |
| $CuCO_3$ | $3.56\ 10^{-8}$ | $1.65\ 10^{-8}$ | $4.41\ 10^{-8}$ | $1.95\ 10^{-8}$ | $6.93\ 10^{-9}$ | $1.38\ 10^{-8}$ | $1.38\ 10^{-8}$ |
| $Cu(OH)_2$ | $2.75\ 10^{-8}$ | $2.14\ 10^{-8}$ | $6.76\ 10^{-8}$ | $1.68\ 10^{-7}$ | $5.70\ 10^{-8}$ | $3.05\ 10^{-9}$ | $2.23\ 10^{-9}$ |
| $CuOH^+$ | $9.69\ 10^{-9}$ | $4.75\ 10^{-9}$ | $1.06\ 10^{-8}$ | $5.28\ 10^{-9}$ | $1.42\ 10^{-9}$ | $7.27\ 10^{-10}$ | $6.10\ 10^{-10}$ |
| $Cu^{+2}$ | $2.15\ 10^{-10}$ | $6.67\ 10^{-11}$ | $1.06\ 10^{-10}$ | $1.05\ 10^{-11}$ | $2.24\ 10^{-12}$ | $1.09\ 10^{-11}$ | $1.53\ 10^{-11}$ |
| $F^-$ | $3.41\ 10^{-5}$ | $7.37\ 10^{-5}$ | $7.38\ 10^{-5}$ | $1.25\ 10^{-4}$ | $1.29\ 10^{-4}$ | $1.19\ 10^{-4}$ | $1.16\ 10^{-4}$ |
| $Fe(OH)_4^-$ | $3.79\ 10^{-7}$ | $4.49\ 10^{-7}$ | $6.19\ 10^{-7}$ | $9.13\ 10^{-7}$ | $1.37\ 10^{-6}$ | $5{,}41\ 10^{-7}$ | $6.16\ 10^{-7}$ |
| $Fe(OH)_3$ | $2.86\ 10^{-7}$ | $2.14\ 10^{-7}$ | $2.09\ 10^{-7}$ | $6.14\ 10^{-8}$ | $7.31\ 10^{-8}$ | $2.76\ 10^{-7}$ | $3.61\ 10^{-7}$ |
| $K^+$ | $1.89\ 10^{-3}$ | $3.57\ 10^{-3}$ | $2.94\ 10^{-3}$ | $4.46\ 10^{-3}$ | $5.39\ 10^{-3}$ | $5.14\ 10^{-3}$ | $5.14\ 10^{-3}$ |
| $KSO_4^-$ | $1.60\ 10^{-5}$ | $3.36\ 10^{-5}$ | $3.03\ 10^{-5}$ | $4.05\ 10^{-5}$ | $4.47\ 10^{-5}$ | $4.44\ 10^{-5}$ | $4.58\ 10^{-5}$ |
| $Mg^{+2}$ | $8.32\ 10^{-5}$ | $3.36\ 10^{-5}$ | $6.74\ 10^{-5}$ | $7.73\ 10^{-7}$ | $6.87\ 10^{-7}$ | $6.02\ 10^{-7}$ | $7.85\ 10^{-7}$ |
| $MgSO_4$ | $1.81\ 10^{-5}$ | $8.11\ 10^{-6}$ | $1.78\ 10^{-5}$ | $1.81\ 10^{-7}$ | $1.46\ 10^{-7}$ | $1.34\ 10^{-7}$ | $1.80\ 10^{-7}$ |
| $MgCO_3$ | $1.94\ 10^{-6}$ | $1.17\ 10^{-6}$ | $3.98\ 10^{-6}$ | $2.04\ 10^{-7}$ | $3.00\ 10^{-7}$ | $1.07\ 10^{-7}$ | $1.45\ 10^{-7}$ |
| $Mn^{+2}$ | $8.57\ 10^{-8}$ | $7.88\ 10^{-8}$ | $6.66\ 10^{-8}$ | $7.80\ 10^{-9}$ | $7.07\ 10^{-10}$ | $1.77\ 10^{-9}$ | $8.62\ 10^{-10}$ |
| $NH_4^+$ | $7.48\ 10^{-7}$ | $8.94\ 10^{-7}$ | $7.32\ 10^{-7}$ | $4.91\ 10^{-7}$ | $5.12\ 10^{-7}$ | $4.27\ 10^{-6}$ | $7.50\ 10^{-6}$ |
| $NH_3$ | $6.02\ 10^{-7}$ | $1.14\ 10^{-6}$ | $1.32\ 10^{-6}$ | $4.44\ 10^{-6}$ | $5.83\ 10^{-6}$ | $5.09\ 10^{-6}$ | $7.78\ 10^{-6}$ |
| $NO_3^-$ | $1.98\ 10^{-4}$ | $3.99\ 10^{-4}$ | $4.18\ 10^{-4}$ | $5.21\ 10^{-4}$ | $8.04\ 10^{-4}$ | $8.04\ 10^{-4}$ | $8.45\ 10^{-4}$ |
| $Na^+$ | $8.84\ 10^{-4}$ | $1.39\ 10^{-3}$ | $1.68\ 10^{-3}$ | $2.41\ 10^{-3}$ | $3.67\ 10^{-3}$ | $3.86\ 10^{-3}$ | $4.34\ 10^{-3}$ |
| $NaSO_4$- | $5.67\ 10^{-6}$ | $9.91\ 10^{-6}$ | $1.31\ 10^{-5}$ | $1.66\ 10^{-5}$ | $2.31\ 10^{-5}$ | $2.53\ 10^{-5}$ | $2.93\ 10^{-5}$ |
| $NaCO_3^-$ | $4.61\ 10^{-7}$ | $1.09\ 10^{-6}$ | $2.22\ 10^{-6}$ | $1.42\ 10^{-5}$ | $3.59\ 10^{-5}$ | $1.54\ 10^{-5}$ | $1.80\ 10^{-5}$ |
| $Ni^{+2}$ | $5.43\ 10^{-8}$ | $4.06\ 10^{-8}$ | $2.85\ 10^{-8}$ | $3.70\ 10^{-9}$ | $2.30\ 10^{-9}$ | $1.56\ 10^{-8}$ | $1.52\ 10^{-8}$ |
| $NiCO_3$ | $5.68\ 10^{-8}$ | $6.37\ 10^{-8}$ | $7.54\ 10^{-8}$ | $4.38\ 10^{-8}$ | $4.50\ 10^{-8}$ | $1.25\ 10^{-7}$ | $1.27\ 10^{-7}$ |
| $NiSO_4$ | $1.29\ 10^{-8}$ | $1.08\ 10^{-8}$ | $8.27\ 10^{-9}$ | $9.49\ 10^{-10}$ | $5.37\ 10^{-10}$ | $3.81\ 10^{-9}$ | $3.82\ 10^{-9}$ |
| $Ni(OH)_2$ | $1.10\ 10^{-8}$ | $2.06\ 10^{-8}$ | $2.89\ 10^{-8}$ | $9.43\ 10^{-8}$ | $9.27\ 10^{-8}$ | $6.92\ 10^{-9}$ | $5.12\ 10^{-9}$ |
| $HPO_4^{-2}$ | $3.32\ 10^{-6}$ | $2.36\ 10^{-6}$ | $2.99\ 10^{-6}$ | $1.77\ 10^{-7}$ | $8.48\ 10^{-8}$ | $5.84\ 10^{-7}$ | $8.23\ 10^{-7}$ |
| $CaPO_4^-$ | $3.37\ 10^{-7}$ | $1.30\ 10^{-6}$ | $1.96\ 10^{-6}$ | $1.06\ 10^{-6}$ | $1.42\ 10^{-6}$ | $6.08\ 10^{-7}$ | $9.97\ 10^{-7}$ |
| $MgHPO_4$ | $1.74\ 10^{-7}$ | $5.01\ 10^{-8}$ | $1.27\ 10^{-7}$ | $8.61\ 10^{-11}$ | $3.67\ 10^{-11}$ | $2.22\ 10^{-10}$ | $4.08\ 10^{-10}$ |
| $PO_4^{-3}$ | $1.98\ 10^{-9}$ | $2.23\ 10^{-9}$ | $3.98\ 10^{-9}$ | $1.18\ 10^{-9}$ | $7.13\ 10^{-10}$ | $5.14\ 10^{-10}$ | $5.52\ 10^{-16}$ |
| $PbCO_3$ | $7.23\ 10^{-7}$ | $3.56\ 10^{-7}$ | $8.57\ 10^{-7}$ | $9.64\ 10^{-8}$ | $8.78\ 10^{-8}$ | $1.74\ 10^{-7}$ | $1.92\ 10^{-7}$ |
| $PbOH^+$ | $3.06\ 10^{-7}$ | $1.60\ 10^{-7}$ | $3.22\ 10^{-7}$ | $4.06\ 10^{-8}$ | $2.80\ 10^{-8}$ | $1.43\ 10^{-8}$ | $1.32.10^{-8}$ |
| $Pb(OH)_2$ | $1.38\ 10^{-7}$ | $1.14\ 10^{-7}$ | $3.24\ 10^{-7}$ | $2.05\ 10^{-7}$ | $1.78\ 10^{-7}$ | $9.51\ 10^{-9}$ | $7.64\ 10^{-9}$ |
| $Pb^{+2}$ | $8.58\ 10^{-9}$ | $2.82\ 10^{-9}$ | $2.87\ 10^{-9}$ | $1.01\ 10^{-10}$ | $5.56\ 10^{-11}$ | $2.71\ 10^{-10}$ | $2.87\ 10^{-10}$ |
| $SO_4^{-2}$ | $1.20\ 10^{-3}$ | $1.33\ 10^{-3}$ | $1.45\ 10^{-3}$ | $1.28\ 10^{-3}$ | $1.17\ 10^{-3}$ | $1.22\ 10^{-3}$ | $1.26\ 10^{-3}$ |
| $MgSO_4$ | $1.81\ 10^{-5}$ | $8.11\ 10^{-6}$ | $1.78\ 10^{-5}$ | $1.81\ 10^{-7}$ | $1.46\ 10^{-7}$ | $1.34\ 10^{-7}$ | $1.80\ 10^{-7}$ |
| $KSO_4^-$ | $1.60\ 10^{-5}$ | $3.36\ 10^{-5}$ | $3.03\ 10^{-5}$ | $4.05\ 10^{-5}$ | $4.47\ 10^{-5}$ | $4.44\ 10^{-5}$ | $4.58\ 10^{-5}$ |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CaSO_4$ | $1.62\ 10^{-5}$ | $6.13\ 10^{-5}$ | $5.68\ 10^{-5}$ | $9.15\ 10^{-5}$ | $1.86\ 10^{-4}$ | $1.14\ 10^{-4}$ | $1.58\ 10^{-4}$ |
| $NaSO_4^-$ | $5.67\ 10^{-6}$ | $9.90\ 10^{-6}$ | $1.31\ 10^{-5}$ | $1.66\ 10^{-5}$ | $2.31\ 10^{-5}$ | $2.53\ 10^{-5}$ | $2.93\ 10^{-5}$ |
| $H_4SiO_4$ | $2.52\ 10^{-5}$ | $2.58\ 10^{-4}$ | $2.06\ 10^{-4}$ | $1.44\ 10^{-4}$ | $3.39\ 10^{-4}$ | $2.03\ 10^{-3}$ | $1.94.10^{-3}$ |
| $Zn(OH)_2$ | $5.89\ 10^{-8}$ | $7.78\ 10^{-8}$ | $8.64\ 10^{-8}$ | $7.61\ 10^{-8}$ | $6.76\ 10^{-8}$ | $4.36\ 10^{-8}$ | $3.56\ 10^{-8}$ |
| $ZnCO_3$ | $2.96\ 10^{-8}$ | $2.34\ 10^{-8}$ | $2.19\ 10^{-8}$ | $3.44\ 10^{-9}$ | $3.20\ 10^{-9}$ | $7.65\ 10^{-8}$ | $8.57\ 10^{-8}$ |
| $ZnOH^+$ | $2.61\ 10^{-8}$ | $2.18\ 10^{-8}$ | $1.71\ 10^{-8}$ | $3.01\ 10^{-9}$ | $2.12\ 10^{-9}$ | $1.31\ 10^{-8}$ | $1.23.10^{-8}$ |
| $Zn^{+2}$ | $1.84\ 10^{-8}$ | $9.67\ 10^{-9}$ | $5.38\ 10^{-9}$ | $1.89\ 10^{-10}$ | $1.06\ 10^{-10}$ | $6.22\ 10^{-9}$ | $6.69\ 10^{-9}$ |
| $ZnSO_4$ | $4.81\ 10^{-9}$ | $2.81\ 10^{-9}$ | $1.71\ 10^{-9}$ | $5.30\ 10^{-11}$ | $2.71\ 10^{-11}$ | $1.66\ 10^{-9}$ | $1.84\ 10^{-9}$ |

* The species of Fe are not included because the Eh were not incorporated in the modelling.

From Table 7.2 it can be inferred that the dominant species in the weathering solutions of the fly ash were $K^+$ and $SO_4^{2-}$, with activities greater than $10^{-3}$. The species $H_4SiO_4$ achieved activities of similar orders only after 1304 h of weathering. The weathering of the fly ash leading to solutions rich in $K_2SO_4$ would only form under evaporitic conditions. Ions such as $Na^+$, $NO_3^-$, $Cl^-$, and $HCO_3^-$ reached activities of $10^{-4}$ at every weathering time, while $Ca^{2+}$, $CaSO_4$, $F^-$, $H_4SiO_4$ and $CaCO_3$ required variable weathering time to achieve this order of activity. Other ions (see Table 7.2) reached activities of between $10^{-5}$ and $10^{-6}$ under different conditions. The observation leads to the conclusion that it is primarily sulphate what forms ion pairs and complexes with Ca, K, Mg and Na; therefore, the corresponding sulphates could form in solutions, either by the alteration and dissolution of the fly ash or by evaporation of the weathering solution. Similarly, the possible formation of carbonates, bicarbonates of Ca, Mg, and Na, as well as Ca phosphates was observed; they would be the main compounds more easily neoformed in the process of neoformation. Among the heavy metals, only Pb species ($PbCO_3$, $PbOH^+$, $Pb(OH)_2$)) reached an activity that could be considered of environmental concern..

**Table 7.2** Species with significant activities in the solutions at different weathering time.

| | Species |
|---|---|
| $10^{-3}$ | $K^+$, $SO_4^{2-}$, $H_4SiO_4$ (>1304 h) |
| $10^{-4}$ | $HCO_3^-$, $Cl^-$, $NO_3^-$, $Na^+$, $Ca^{2+}$ (>24 h), $CaSO_4$ (>800 h), $F^-$ (>300 h), $H_4SiO_4$ (>24 h), $CaCO_3$ (>300 h) |
| $10^{-5}$ | $CO_3^{2-}$, $F^-$ (>24 h), $KSO_4^-$, $Mg^{2+}$ (<300 h), $MgSO_4$ (<300 h), $H_4SiO_4$, $CaCO_3$, $CaSO_4$, $NaSO_4^-$ (>120 h), $NaCO_3^-$ (>300 h), |
| $10^{-6}$ | $CaCO_3$, $MgCO_3$, $NaSO_4^-$, $NaCO_3^-$ (>24 h), $HPO_4^{2-}$ (<300 h), $CaPO_4^-$ (between 24 and 800 h) |
| $10^{-7}$ | $PbCO_3$, $PbOH^+$, $Pb(OH)_2$ |

In conclusion, the weathering of the fly ash under suboxic alkalinolisis conditions underwent dissolution, reaching saturation relatively quickly for many ions and the concomitant formation of ion pairs and complex of sulphates of metals, alkali and alkaline earth, the corresponding carbonates and Ca phosphates. These complexes and ion pairs are the precursors of the neoformed products. Likewise, the thermodynamic modelling allows concluding that there is a significant saturation in Si, which should lead to the formation of secondary silicates or – if there is not enough activity of metals – the precipitation of secondary silica phases.

### *7.4.3. Mineralogical change*

Mineralogically, quartz ($SiO_2$) was the dominant crystalline mineral in the fly ash. In addition, there were traces of calcite ($CaCO_3$) and albite ($NaAlSi_3O_8$) (Fig. 7.5). The total mineralogy spectra showed that calcite disappeared after weathering for 800 h. In addition, traces of clay formation have been detected (Fig. 7.5).

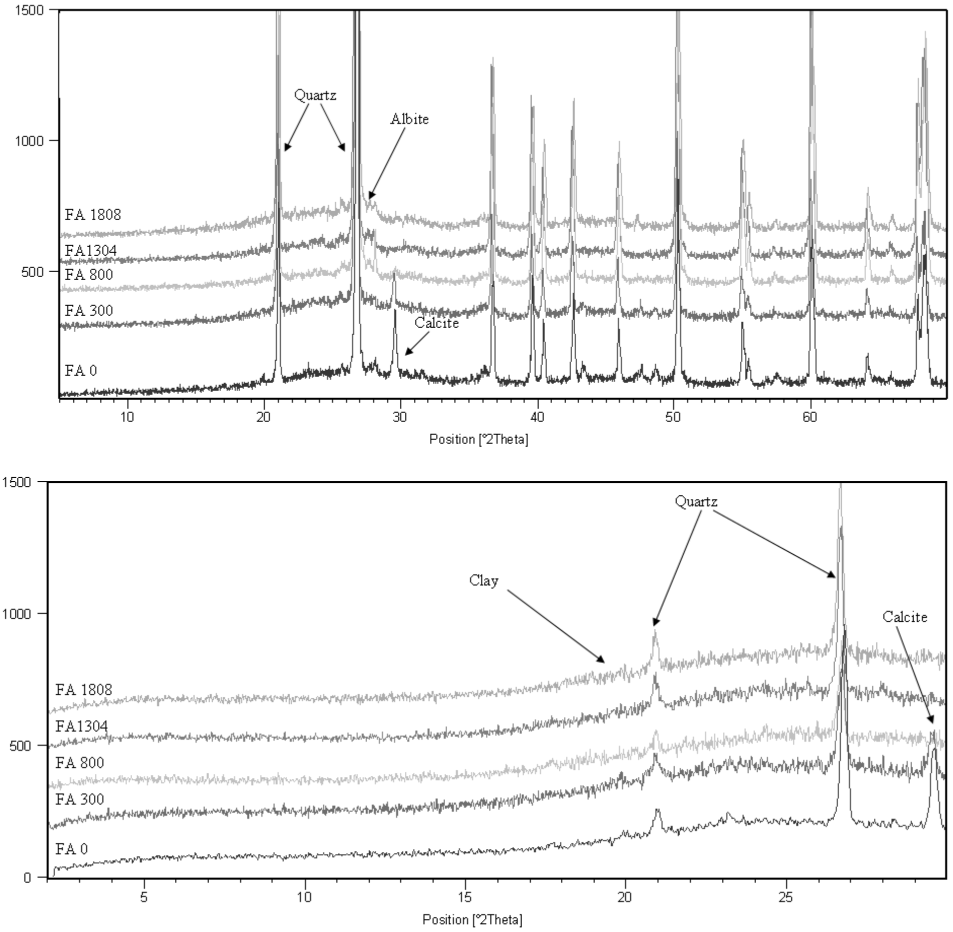


**Fig. 7.5.** X-ray spectrum of total mineralogy and clay of fresh and weathered fly ash.

It was observed that among all the crystalline minerals initially present in the fly ash, such as quartz, calcite and albite, the calcite was unstable even after short period of weathering (less than 1 hour), but both this and its polymorph (aragonite) were stable at increasing weathering time. There is no doubt that the increasing carbonation (Fig 7.3) has progressively increased the stability and the possibility of the neoformation of these carbonates and others, such as dolomite, and in some cases, malachite, cerrucite and hidrocerrucite can also be stable, and therefore the neoformed products. In contrast, carbonates of alkaline elements could only be formed in evaporitic conditions.

**Table 7.3** Saturation index of minerals that present conditions of stability or metastability in the weathering solutions.

| Mineral | FA 1 | FA 24 | FA 120 | FA 300 | FA 800 | FA 1304 | FA 1808 |
|---|---|---|---|---|---|---|---|
| Aragonite | -0.48 | 0.23 | 0.38 | 1.29 | 1.86 | 1.24 | 1.39 |
| Calcite | -0.3 | 0.41 | 0.56 | 1.47 | 2.04 | 1.42 | 1.57 |
| Dolomite | -0.32 | 0.17 | 0.85 | 0.47 | 1.21 | 0.14 | 0.42 |
| $Ca_3(PO_4)_2$ | -1.17 | 0.53 | 0.82 | 0.54 | 1.15 | 0.18 | 0.74 |
| Hydroxylapatite | 6.23 | 9.25 | 9.8 | 10.21 | 11.39 | 8.85 | 9.68 |
| F-CO3-Apatite | 15 | 21.27 | 22.15 | 23.17 | 25.71 | 22.36 | 23.99 |
| Sepiolite | -1.11 | 1.93 | 2.84 | 1.29 | 2.7 | 1 | 0.94 |
| Chrysotile | 1.27 | 3.3 | 4.92 | 2.98 | 4.17 | -0.33 | -0.38 |
| Manganite | -0.96 | -0.39 | -0.02 | 1.15 | 0.41 | -2.13 | -2.62 |
| $MnHPO_4$ | 0.48 | 0.3 | 0.32 | -1.84 | -3.2 | -1.96 | -2.12 |
| Bixbyite | -1.29 | -0.16 | 0.59 | 2.93 | 1.44 | -3.64 | -4.63 |
| Hausmannite | -1.03 | 0.46 | 1.44 | 4.25 | 1.92 | -4.73 | -6.14 |
| Gibbsite | 0.42 | 0.55 | 0.42 | -1.5 | -1.91 | -1.1 | -1.05 |
| Boehmite | 0.14 | 0.27 | 0.13 | -1.79 | -2.2 | -1.39 | -1.33 |
| Diaspore | 1.84 | 1.97 | 1.83 | -0.08 | -0.49 | 0.31 | 0.37 |
| Kaolinite | 0.8 | 3.08 | 2.61 | -1.54 | -1.61 | 1.56 | 1.63 |
| Halloysite | -1.34 | 0.94 | 0.47 | -3.68 | -3.75 | -0.58 | -0.57 |
| Chalcedony | -1.05 | -0.04 | -0.14 | -0.29 | 0.08 | 0.86 | 0.84 |
| Cristobalite | -1.25 | -0.24 | -0.34 | -0.49 | -0.12 | 0.66 | 0.64 |
| Quartz | -0.6 | 0.41 | 0.31 | 0.16 | 0.53 | 1.31 | 1.29 |
| $SiO_2$ am | -1.88 | -0.86 | -0.98 | -1.13 | -0.76 | 0.02 | 0.03 |
| $Cu(OH)_2$ | -0.04 | -0.15 | 0.35 | 0.75 | 0.28 | -1 | -1.13 |
| Cerrusite | 0.51 | 0.2 | 0.59 | -0.36 | -0.4 | -0.11 | -0.06 |
| Hidrocerrusite | 3.77 | 3.07 | 4.29 | 2.19 | 2.05 | 1.37 | 1.36 |
| Hydroxylpyromorphite | 5.5 | 3.44 | 5.12 | -3.77 | -5.62 | -3.59 | -3.26 |
| Malachite | -0.28 | -0.72 | 0.2 | 0.25 | -0.67 | -1.65 | -1.78 |
| $Pb(OH)_2$ | 2.08 | 2 | 2.45 | 2.25 | 2.19 | 0.92 | 0.83 |
| $Pb_3(PO_4)_2$ | 1.93 | 0.58 | 1.55 | -4.31 | -5.53 | -3.75 | -3.5 |
| Pyromorphite | 14.69 | 12.55 | 14.09 | 4.68 | 2.72 | 5.69 | 6.08 |
| Tenorite | 0.99 | 0.88 | 1.38 | 1.78 | 1.31 | 0.03 | -0.1 |
| Tsumevite | 2.74 | 1.91 | 3.12 | 0.49 | -0.62 | -1.64 | -1.69 |

The phosphates of Pb and the type of apatite are the minerals that have higher saturation indices and therefore they were the most likely to be newly formed (Table 7.3). This confirms what was suggested by the calculations of the activity, i.e. the presence of ion pairs and complexes with phosphate, and their virtual disappearance from the dissolution after 300 h of weathering.

Despite the high activity of sulphate, no saturation of any sulphate mineral (including gypsum) has been observed because they could only be newly formed under evaporitic conditions, which is, without any doubt, due to its high solubility.

With regards to Al minerals, given the relatively low concentration of this element in the fly ash under study, its neoformation under the present study was limited. Gibbsite, boehmite, diaspore, kaolinite and halloysite are oversaturated at some sampling times (Table 7.3), among which kaolinite was the most stable, but at increasing weathering time all of them became unstable. This suggests that the formation of secondary 2:1 minerals should be dominant among the Al minerals. Probably, minerals of the type of smectites, feldspathoids and/or more or less disordered zeolites would be the Al minerals with greater chances of neoformation. Silicon is very abundant in the solution and able to react with metallic elements, such as Mg and Al, to form 2:1-type minerals. The saturation of the sepiolite – or in some solutions chrysotile – suggests the possibility of neoformation, but its kinetics may be restricted under low temperature conditions. Therefore, based on the excess of Si in the solution, the most possible formation of secondary silica are chalcedony, cristobalite, quartz, and amorphous $SiO_2$. However, the XRD analysis of the residual fraction could not identify any secondary mineral listed above, probably because of the low grade order or low amounts of the neoformed minerals.

Obviously, various macroscopic geochemical changes were discerned during the weathering process. The weathering solution changed from transparent to a milky opalescence and then some white flakes appeared over the inner surface of the receiving flask. The weathering reactor was an open system and the dissolution of $CO_2$ in the alkaline leaching water was inevitable, which led to the acidifying of the fly ash or more probably to the decreased ability of neutralization of acids, although no change in pH has been produced, the system being saturated under alkalinosis conditions. However, the minor decrease of pH facilitated the precipitation of secondary minerals in the lessivage. Most of the mobile elements were leached out of the system after the first hour of weathering and all the elements reached saturation concentrations at variable weathering time between 300 and 800 h.

### *7.4.4. Geochemistry of charcoal present in the fly ash*

There was only one peak of aryl C (at 124-126 ppm) in the NMR spectra of both the fresh fly ash and the weathered one (Fig. 7.6), reflecting the presence of charred material in the ash. No changes in the spectra were detected with the weathering.

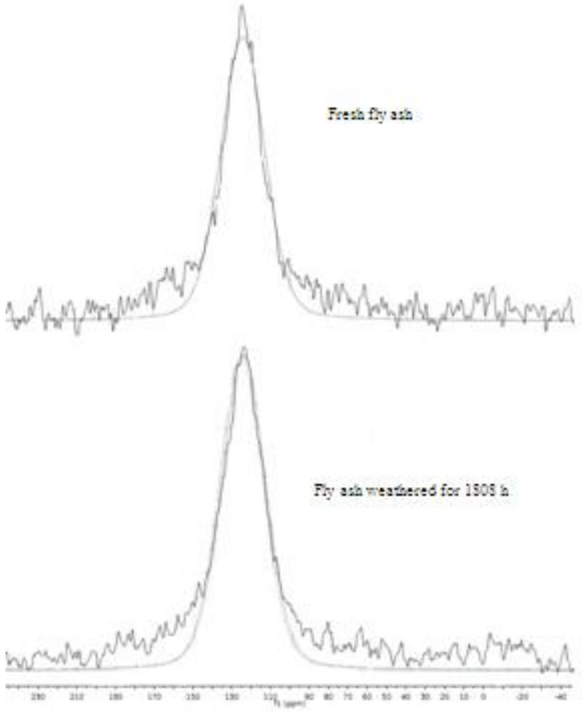


**Fig. 7.6.** CP/MAS $^{13}$C NMR spectra of fresh and weathered fly ash.

*7.4.5. Weathering balance: mobility and weathering intensity of each element*

The weathering of the fly ash produced two solid phases: (i) one was the residual phase, where the recalcitrant elements and components accumulated, and (ii) another phase, which was that of the secondary products. Only the elements that stayed in the soluble phase could be mobilised and removed from the system. A multitude of mechanisms and procedures for establishing the weathering balance have been developed by many researchers, e.g. balance of iso-quartz, iso-volumetric, iso-aluminum, iso-iron, iso-invariant component (Macías Vázquez, 1991; Macías Vázquez and Chesworth, 1992; Martini and Chesworth, 1992). However, when the data of weathering solutions and the composition of the starting material are available, a direct mass balance can be calculated and the geochemical mobility of each element can be established. Furthermore, multitude indices of geochemical or biogeochemical weathering that have been used satisfactorily by different authors in tracking the weathering of original material of soil can also be used. Among them, Parker index (Parker, 1970; Macías Vázquez et al., 1981) has been chosen in this thesis because it measures the mobility of the most mobile elements (the alkali and alkaline).

Parker Index = (Ca/0.7 + Mg/0.9 + K/0.25 + Na/0.35) * 100 (Parker, 1970; Macías Vázquez et al., 1979, 1981)

The Parker Index of the fly ash at different weathering time is presented in Fig 7.7. It can be observed that the initial Parker index is similar to the acidic igneous rocks such as granite or metamorphic rocks of low grade, such as many shales. The weathering would be faster and more easily in basic rocks (gabbros, amphibolites, basalt ...) or ultrabasic (peridotite, serpentinites ...) with higher Parker index ( >70) in fresh materials and lower (<20) in the residual systems of weathering anf soil formation.

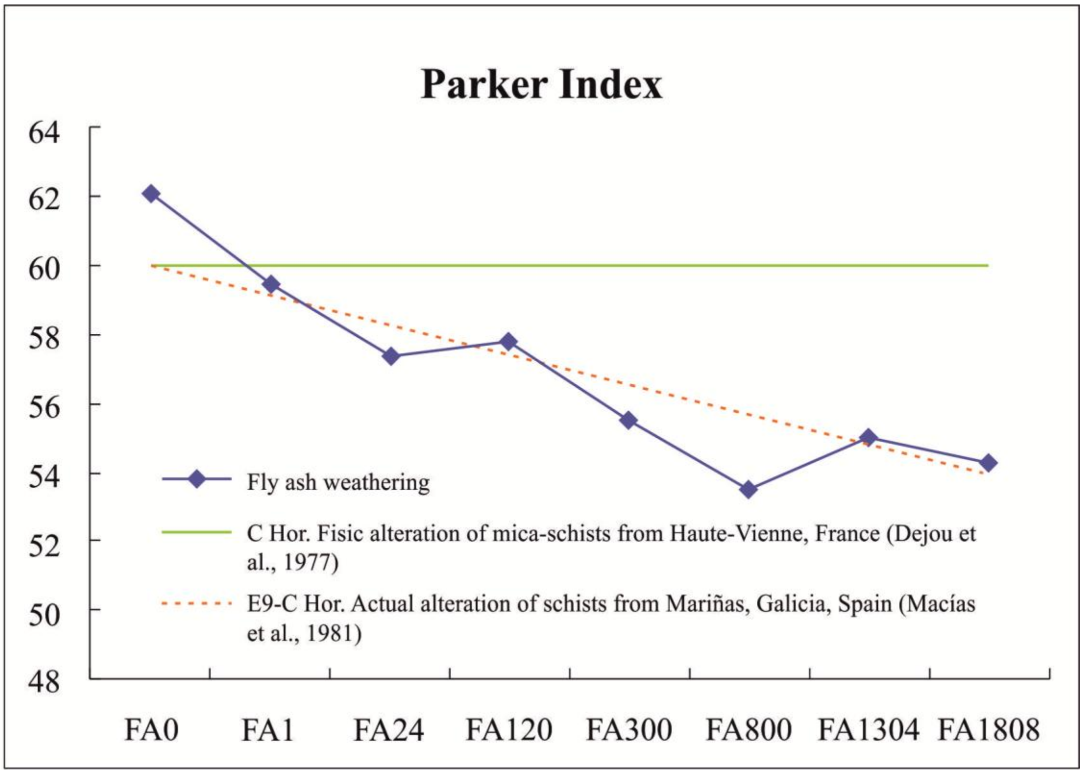


**Fig. 7.7.** Parker index of fly ash weathering.

The Parker indices obtained in this study (Fig. 7.7) were compared with some specific rock weathering examples and soil formation under temperate environments (e.g. Galicia, Spain) (Macías Vázquez et al., 1981) and cold environments (e.g. Haute Viane, France) (Dejou et al., 1977). In cold conditions there is no chemical change but the isochemical breakdown. In the Mariñas there were losses of base cations although the rock was slightly altered. The behaviour of the fly ash in the alkalinolinitic alteration is very similar to the schistose rocks and inicpiet soil formation in the Mariñas (Galicia, NW Spain).

Data depicted in Fig. 7.7 evidences that the weathering intensity is scarce under the conditions of this study, but more important than the mere physical isochemical breakdown under the cold conditions. The trend of the alteration of the fly ash is the loss of cations, including under the alkalinolisis conditions, and very similar to what occurs in the alteration of schistose rocks of the Mariñas to form actual incipient soil C horizons. Practically, the factor of weathering time had very little influence when equilibrium of loss of elements has been established in, i.e. from 300-800 h.

Table 7.4 shows the loss percentage of each element during the 1808h- period of fly ash weathering. The most mobile elements were S, Na and K. The maximum loss of K and S were 34% at 800 h and 55% at 120 h, respectively, and after that they became stable. The loss of Na kept increasing during the whole weathering period, reaching as high as 99% at 1808 h, indicating that all the Na in the fly ash was easily dissolved. At increasing weathering time Na is the element of greater mobility of the weathering system while at short time the most mobile element is S.

**Table 7.4** The loss percentage of each element at different weathering time.

| Loss percentage | FA 1 | FA 24 | FA 120 | FA 300 | FA 800 | FA 1304 | FA 1808 |
|---|---|---|---|---|---|---|---|
| C | 0.10% | 0.10% | 0.12% | 0.22% | 0.35% | 0.43% | 0.52% |
| N | 0.62% | 1.26% | 1.32% | 1.69% | 2.63% | 2.65% | 2.86% |
| P | 0.24% | 0.24% | 0.32% | 0.07% | 0.08% | 0.08% | 0.12% |
| S | 41% | 50% | 55% | 52% | 53% | 52% | 55% |
| K | 11% | 22% | 18% | 28% | 34% | 32% | 32% |
| Na | 19% | 31% | 37% | 54% | 84% | 88% | 99% |
| Ca | 0.25% | 0.93% | 0.83% | 1.82% | 4.75% | 2.32% | 3.17% |
| Mg | 1.25% | 0.54% | 1.13% | 0.02% | 0.02% | 0.01% | 0.02% |
| Si | 0.07% | 0.82% | 0.73% | 1.21% | 3.41% | 6.41% | 5.94% |
| Al | 0.04% | 0.08% | 0.08% | 0.00% | 0.00% | 0.00% | 0.00% |
| Fe | 0.01% | 0.01% | 0.01% | 0.01% | 0.02% | 0.01% | 0.01% |
| Mn | 0.03% | 0.03% | 0.03% | 0.00% | 0.00% | 0.00% | 0.00% |
| Cu | 0.23% | 0.14% | 0.41% | 0.82% | 0.32% | 0.09% | 0.09% |
| Zn | 0.08% | 0.08% | 0.11% | 0.11% | 0.11% | 0.11% | 0.11% |
| Ni | 0.90% | 0.90% | 1.12% | 1.12% | 1.12% | 1.12% | 1.12% |
| Pb | 15.31% | 8.51% | 21.55% | 6.24% | 6.80% | 4.54% | 5.10% |
| Cd | 0.05% | 0.02% | 0.01% | 0.02% | 0.04% | 0.01% | 0.01% |

The maximum loss of Ca was 4.75% at 800 h and the maximum of Si was 6.41% at 1304 h, respectively, there being an obvious decrease thereafter, suggesting the neoformation of Ca and Si-containing minerals. The dissolution trend of Mg, P and Al were similar to that of Ca and Si while the loss percentage was much lower, which was attributed to the extremely low solubility of Mg, P, Al-containing compounds and the low mobility of these elements.

Among the heavy metals, Pb was the most mobile, with a loss percentage of 15.3% after one hour of weathering, but it decreased with time due to secondary neoformation. The loss of Ni was stable after 120 h of weathering, with 1.12% of the total Ni in the initial fly ash lost. The loss percentage of Cu reached its maximum value (0.82%) at 300 h and decreased sharply thereafter whereas that of Zn was stable at 0.11% after 120 h. The contents of Fe, Mn and Cd in the weathering solutions have never exceeded 0.05% of the total contents in the initial fly ash.

## 7.5. Conclusion

During the geochemical weathering of this specific fly ash from pine bark combustion, S, Na and K were the most mobile elements. This was verified not only by the high concentrations of these elements in the weathering solutions but also proved by their higher percentage of loss calculated through mass balance. In contrast, although Ca, Si, Mg, P and Al dissolved and leached out of the reactor during the first period of weathering, the content of these elements in the weathering solutions tended to decrease during the later period of weathering. This was attributed to neoformation of secondary stable compounds of these elements. The chemical nature of the fly ash induced the formation of the weathering conditions that corresponded to alkalinolisis even with very short weathering time (1 h) in which the loss of alkali and alkaline earth elements is important for Na and to a lesser extent for K, but little for Ca and Mg. The change in the Parker index indicates a type of weathering with few chemical variations, similar to what occurred during the incipient weathering of low-grade metamorphic rocks with few alterable minerals in Galicia. The high pH of this type of fly ash stimulated the rapid dissolution of aluminosilicate glass components at the beginning of weathering, so that between 300 and 800 h most elements reach saturating or supersaturating conditions, with Ca and Pb phosphates, Ca carbonates and the minerals of greater thermodynamic stability. The alkaline carbonates had never reached saturation, because they could only be neoformed under evaporitic conditions. The same reason applies to the sulphates, including gypsum. The new formation of 1:1 and 2:1 minerals is possible, particularly with short weathering time, but the low activity of Al and Mg seemed to minimize their formation, so that Si should concentrate as amorphous silica or in other poor tectosilicates poor in Al and Mg with low crystallinity. The concentrations of heavy metals were negligible, as well as their potential environmental risk. This modified Soxhlet reactor and the weathering concepts established by Pédro was considered applicable to the simulation of geochemical weathering of fly ash.

## 7.6. Acknowledgements

We are grateful to Carmen Perez Llaguno at University of Santiago de Compostela and Iñaki Basañez Llantada at NEIKER-TECNALIA for their kind help in the laboratory. We acknowledge financial support for the research provided by the Spanish Ministry of Science and Education (Project No. CTM 2006-13748-CO2) and through an FPI fellowship from the Spanish Ministry of Science and Education. We also thank the Basque government for the financial support of the project TECNOSOX (Project No. 61.0263.0).

## 7.7. References

ACAA. American Coal Ash Association 2007. Coal combustion Product (CCP) Production and Use Results 2006. Available from: http://www.acaa-usa.org.

Badreddine R., Humez A.N., Mingelgrin U., Benchare A., Meducin F., Prost R., 2004. Retention of trace metals by solidified/stabilized wastes: Assessment of long-term metal release. Environ. Sci. Technol. 38, 1383-1398.

Biedermann F., Obernberger I., 2005. Ash-related problems during biomass combustion and possibilities for a sustainable ash utilization. Available from: http://www.bios-bioenergy.at/en/downloads-publications/ashes.html

Borja and Collins, 2004. Oceanography and marine environment of the Basque Country. P 98. Elsevier B.V. Amsterdam, The Netherlands.

Cawse, P.A., 1967. The determination of nitrate in soil solutions by ultraviolet spectrophotometry. Analyst 92, 311-315.

Dejou, J., Guyot, J., Robert, M., 1977. Évolution superficielle des roches christallines et cristallophylliennes dans les régions tempérées. Institu National de la Recherche Agronomique, Paris, 463 pp.

EC, European Commission Council Directive 98/83/EC of 3 November 1998, on the Quality of Water Intended for Human Consumption. EN L 330/42, 5.12.98.

Halverson, R.R., Boggs, B., Enyart, J., Madden, G., 2001. “Accelerated non-pozzolanic reactions of high volume coal fly ash concrete.” Proceedings of the 14th International Symposium on Management and Use of Coal Combustion Products. Provided courtesy of the American Coal Ash Association: Alexandria, VA.

Hoeft, R.G., Walsh, L.M., Keeney, D.R., 1973. Evaluation of various extractants for available soil sulfur. Soil Sci. Soc. Am. J. 37, 401–404.

Humez, N., Humez, A.L., Juste, C., Prost, R., 1997. A new assessment of mobility of elements in sediments and wastes. Chem. Spec. Bioavailab. 9, 57–65.

Humez, N., Prost, R., 1999. A new experimental approach to study the long-term behaviour of solidified/stabilized wastes. Chem. Spec. Bioavailab. 11, 1–24.

Kandeler, E., Gerber, H., 1988. Short-term assay of soil urease activity using colorimetric determination of ammonium. Biol. Fertil. Soils 6, 68-72.

Kumar V., Sharma P., 1998. In proceedings of the International Conference Fly Ash Disposal and Utilisation; India Central Board of Irrigation and Power: New Delhi, pp 1-7.

Macías Vázquez, F., 1991. Alteración y edafogénesis de rocas plutónicas y metamórficas. En: Instituto Geológico Minero y Sociedad Española de Geomorfología (Ed.). Alteraciones y Paleoalteraciones en La Morfología del Oeste Peninsular. Monog. Nº 6, pp.121-159.

Macías Vázquez, F., Camps Arbestain, M., 2010. Soil carbon sequestration in a changing global environment. Mitig. Adapt. Strateg. Glob. Change 15, 511-529.

Macías Vázquez, F., Chesworth, W., 1992. Weathering in humid regions, with emphasis on igneous rocks and their metamorphic equivalents. In: Martini, P. and Chesworth, W. (Ed.). Weathering, Soils and Paleosols. Elsevier. Holanda. Chapter 12, pp. 283-306.

Macías Vázquez, F., García Paz, C., Giménez de Azcárate, M., Villar M.C., 1979. El factor material de partida de los suelos de las mariñas. 1. Alteracion de las rocas metabasicas. Reun. Geol. del N. O. del Laboratorio Xeolóxico de laxe 205-223.

Macías Vázquez, F., García Paz, C., Giménez de Azcárate, M., Villar M.C., 1981. El factor material de partida de los suelos de las mariñas. 2. Alteracion de los esquistos en medios bien drenados. Acta Científica Compostelana XVII, 265-291.

Martini, P., Chesworth, W., 1992. Weathering, Soils and Paleosols. Elsevier. Holanda.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36.

Parker, A., 1970. An index of weathering for silicate rocks. Geol. Magaz. 501-504.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS Water-Resources Investigations Report 99–4259. Denver, Colorado, USA.

Pédro, G., 1961. An experimental study on the geochemical weathering of crystalline rocks by water. Clay Miner. Bull. 4, 266–281.

Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., Newman, R.H., 1994. The removal of magnetic materials from surface soils-a solid state $^{13}$C CP/MAS NMR study. Aust. J. Soil Res. 32, 1215–1229.

Vance, E.D., Brookes, P.C., Jenkinson, D.S., 1987. An extraction method for measuring soil microbial biomass C. Soil Biol. Biochem. 19, 703-707.

Warren, C.J., Dudas, M.J., 1985. Formation of secondary minerals in artificially weathered fly ash. J. Environ. Qual. 14, 405-410.

Zevenbergen, C., Bradley, J. P., Piet Van Reeuwijk, L., Shyam, A. K., Hjelmar, O., Comans, R. J., 1999. Clay formation and metal fixation during weathering of coal fly ash. Environ. Sci. Technol. 33, 3405-3409.

# Capítulo 8 / Chapter 8

## Resumen / Abstract

# Capítulo 8. Resumen

En las últimas décadas, la cantidad de residuos de origen antrópico ha aumentado considerablemente. La sociedad exige estándares de producción y calidad cada vez más altos, lo que lleva a la producción de mayores volúmenes de desechos con el consiguiente incremento de los riesgos de contaminación asociados. Ello explica la urgente necesidad de gestionar todo tipo de residuos de forma sostenible para con ello evitar la degradación del medio ambiente y riesgos para la salud pública. Cabe mencionar que la aplicación de residuos al suelo, como excrementos de animales o residuos vegetales, se ha llevado a cabo desde tiempos remotos. Sin embargo, muchos de los problemas ambientales actuales asociados con la gestión de residuos se deben a que el objetivo final de la adición de residuos al suelo es la eliminación de los desechos en lugar de la mejora de la fertilidad o condiciones físicas del suelo.

El objetivo de esta tesis ha sido evaluar la idoneidad de los residuos antropogeomórficos como enmienda o fertilizante del suelo. Para ello se han realizado diferentes estudios, distribuidos en seis capítulos: cuatro de ellos sobre el estudio de Tecnosoles y dos sobre el estudio de la alteración geoquímica acelerada de biocarbones y de cenizas volantes de biomasa.

Los capítulos 2 y 3 corresponden al estudio de lixiviación de Tecnosoles en columnas. Los Tecnosoles se elaboraron a partir de mezclas de residuos orgánicos e inorgánicos en una proporción de 56:44 (en peso). Los componentes orgánicos utilizados fueron un lodo de depuradora anaerobio (AN) y un lodo de depuradora aerobio (AE). Los residuos inorgánicos utilizados fueron la escoria de acería Linz-Donawitz (LD) y la arena verde de fundición (FS). También se realizó una mezcla de los dos residuos en una proporción de 50:50 (peso/peso) (FS + LD). Los residuos LD, FS y FS + LD se denominaron acondicionadores. Los residuos orgánicos fermentables sin acondicionadores se consideraron los controles (AN o AE). Se estudiaron ocho tratamientos en total: AE, AE + FS, AE + LD, AE + FS + LD, AN, AE + FS, AN + LD, y AN + FS + LD. Los objetivos fueron evaluar la influencia de la capacidad de neutralización de ácidos en la química de los lixiviados de diferentes Tecnosoles y el estudio de la movilidad de los metales pesados en los lixiviados.

Los resultados demostraron que los procesos de mayor influencia en el pH de estos sistemas fueron la nitrificación y la lixiviación de cationes básicos, aunque la descomposición de materia orgánica y la carbonatación también influyeron en menor grado. Los valores más bajos de pH de los lixiviados al final del experimento se observaron en el control de AE (5,0) y en el tratamiento AE + FS (5,4), mientras que los más altos (11,1) se produjeron en el tratamiento AN + LD; el pH final del resto de lixiviados osciló entre 7,0 y 8,0. Se observó un retraso considerable de la nitrificación en los tratamientos de lodo anaeróbico, hecho que se atribuyó tanto a un valor de Eh inicial más bajo (en relación al resto de los tratamientos) como a la probable ausencia de bacterias nitrificantes. La nitrificación se vio inhibida en las mezclas en las que la escoria LD se utilizó como uno de los acondicionadores (por el efecto del encalado).

Los resultados de las concentraciones de metales pesados en los mismos lixiviados indicaron que las concentraciones de Cu, Ni y Pb en los tratamientos con lodo AN fueron generalmente más altos que los de lodo AE. La concentración de Cu fue significativamente mayor en los lixiviados de los Tecnosoles en los que se usó escorias LD como ingrediente. Las concentraciones de Zn en los lixiviados del control AE y del Tecnosol AE + FS fueron significativamente mayores a $pH < 6,0$ debido a la mayor solubilidad del elemento y a su menor adsorción sobre los óxihidróxidos de Fe y Mn en estas condiciones. Las concentraciones de Ni en 80% de los lixiviados superaron el límite europeo para Ni (0,02 mg $L^{-1}$). Las concentraciones de Pb fueron menores en los lixiviados de los Tecnosoles en los que se usó arena de fundición, como ingrediente, hecho que se atribuyó a la retención de Pb por parte de las esmectitas presentes en la arena de fundición. Las concentraciones de Cd en los lixiviados de todos los Tecnosoles fueron relativamente más elevadas que los controles, mientras que las concentraciones de Cr fueron mayores en los controles. Esto pone de manifiesto que la elaboración de los Tecnosoles modifica de forma significativa el comportamiento de los elementos presentes en los residuos de partida.

Los capítulos 4 y 5 corresponden a un ensayo de Tecnosoles en el invernadero, en el que se evaluó la viabilidad de los diferentes Tecnosoles como substratos de ray-grass. Los Tecnosoles se realizaron a partir de mezclas de lodos de depuradora y acondicionadores en dos proporciones de 60:40 y 50:50 (en peso). Se utilizaron tres tipos de lodos: lodo aeróbico (AE), anaeróbico (AN) y un lodo aeróbico con cal (AL). En cuanto a los acondicionadores, se utilizaron arena de fundición (FS) 5%, escorias de acería (LD) 10%, paja de cebada (BS) 2% y cenizas de combustión (FA) 23% o 33%. Los Tecnosoles realizados a partir de un 60% de lodos (y el correspondiente 23% de FA) se denominaron M1-AE, M1-AN y M1- AL. Los Tecnosoles realizados a partir de un 50% de lodos (y el correspondiente 33% de FA) fueron identificados como M2-AE, M2-AN y M2-AL. Lodos AE, AN o AL sin la adición de acondicionadores se utilizaron como controles.

Los resultados de los análisis de suelos y disoluciones del suelo extraídas *in situ* indicaron que los Tecnosoles elaborados a partir de lodos anaeróbicos contenían el mayor contenido de N y P, así como de carbono orgánico (OC), mientras que los Tecnosoles derivados de lodo aeróbico contienen los niveles más bajos de OC y macro nutrientes. El lodo aeróbico tratado con CaO presentó una menor disponibilidad de P en relación al resto de lodos, hecho que se atribuyó a la precipitación de fosfatos con Ca.

Los resultados de los análisis de la fracción vegetal mostraron que el total biomasa aérea seguía el siguiente orden: M2-AN (21,1 g) ~ M1-AL (20,2 g) ~ M2-AL (19,9 g) ~ AN (19,8 g) ~ M1-AN (19.6 g) > AE (11,2 g) ~ M1-AE (11,0 g) > AL (9,8 g) ~ M2-AE (9,4 g). La adición de acondicionadores al lodo AN no incrementó el crecimiento de la planta de forma significativa; si fue el caso de la adición de acondicionadores al lodo AL aumentó significativamente; en el caso del lodo AE, el crecimiento vegetal se redujo significativamente ($P < 0,05$) con la adición de los mismos. Las concentraciones de Cu en el rye-grass del lodo AN control estaban por encima del nivel de toxicidad para las plantas (20 mg $kg^{-1}$). En general, la adición de acondicionadores disminuyó de manera eficiente la biodisponibilidad de metales pesados.

Los capítulos 6 y 7 corresponden a los ensayos de meteorización geoquímica acelerada de biocarbón de lodos de depuradora y de cenizas volantes de la combustión de corteza de pino rico en carbono, respectivamente. Se realizaron en un reactor de Soxhlet modificado. La simulación de la alteración geoquímica se llevó a cabo a 30 °C, con un flujo de 5 mL $min^{-1}$ (equivalente a una precipitación de 273 mm $h^{-1}$). El ensayo de biocarbón tuvo dos tratamientos, con y sin adición de ácidos húmicos (tratamientos BC-HA y BC-B respectivamente) y el tiempo de reacción duró 300 horas. El ensayo de meteorización geoquímica de cenizas se realizó con diferentes tiempos de residencia: 1, 24, 120, 300, 800, 1304, y 1808 horas (h).

Los resultados del estudio de meteorización geoquímica del biocarbón revelaron que importantes cantidades de K (8,5-10,2%) y S (20,2-28,3%) fueron solubilizados permaneciendo fundamentalmente en forma disuelta. Calcio (17,9 a 20,7%) y P (15,4%) también fueron solubilizados durante el proceso de alteración, pero luego precipitaron formando fases sólidas neoformadas. La presencia de ácidos húmicos incrementó la capacidad de disolución de las cenizas presentes en el biocarbón y, con ello, la disponibilidad en la disolución de K, S, Ca, Mg y P. Por el contrario, los ácidos húmicos favorecieron la inmovilización del poco N disponible. Probablemente la baja disponibilidad de N (<1,0% del total de N) se deba a la existencia de este elemento en las estructuras heterocíclicas de la fracción carbonosa las cuales son resultado del proceso térmico al que fue sometido el biocarbon. El pH del biocarbón descendió de 8,4 a 7,5, lo que se atribuyó principalmente a la pérdida de cationes básicos por lixiviación y a la probable carbonatación de las disoluciones alcalinas en presencia de $CO_2$.

Los resultados del estudio de meteorización geoquímica de cenizas demostraron que el proceso de alteración transcurre por mecanismos de alcalinolisis desde (i) los tiempos más cortos (1 h), en los que se produce la disolución y movilización de cationes alcalinos y sulfatos, y (ii) a medida que aumenta el tiempo de residencia con la progresiva carbonatación de las disoluciones alcalinas . Los principales procesos que se producen en la meteorización de estos materiales serían (i) la carbonatación, (ii) la neoformación de algunos productos secundarios (fundamentalmente fosfatos y, en menor medida sílice amorfa y minerales 2:1 de bajo grado de orden), y (iii)el lavado de los cationes alcalinos y los sulfatos, siempre con diferente intensidad según el tiempo de residencia. Inicialmente el catión dominante en la disolución es el $K^+$, seguido por el $Na^+$, siendo el $SO_4^{2-}$ el principal anión neutralizante y el de mayor movilidad en los ensayos con tiempos de reacción cortos (< 300 h), mientras que a tiempos largos es el $Na^+$ el elemento de mayor movilidad, seguido del $SO_4^{2-}$ y $K^+$. Estos tres iones son, en toda la secuencia de tiempos los que presentan las mayores concentraciones en disolución y los que tienen mayor movilidad geoquímica. Los siguientes elementos en importancia en cuanto a la concentración en la fase líquida y a la movilidad geoquímica son Si, $Ca^{2+}$ y $Mg^{2+}$. Su comportamiento es muy diferente. Tras alcanzar las concentraciones máximas – que se interpretan como las concentraciones de sobresaturación en las condiciones alcalinas del proceso experimental seguido – debido a la aparición de procesos de neoformación y/o de adsorción relacionados con el equilibrio termoquímico del sistema en las condiciones finales, su actividad y su concentración disminuyeron considerablemente, indicando la neoformación de fases, en su mayor parte amorfas o de bajo grado de orden, que no dan cristalinidad en los análisis de DRX. La presencia de pares y complejos iónicos de $SO_4^{2-}$ de alcalino térreos y también de los alcalinos indica que $SO_4^{2-}$ minerales podrían ser una fase importante en condiciones evaporíticas, pero en las condiciones de relación sólido: disolución del presente estudio no se alcanza ninguna condición de sobresaturación y estabilidad termodinámica para las mismas. Los iones $F^-$, $Cl^-$ y $NO_3^-$ también siguen reacciones exponenciales aunque con diferentes concentraciones y tiempos, alcanzan el equilibrio a partir de las 300 h, los dos primeros, y de las 800 h, el tercero. Las concentraciones de metales pesados presentes en las disoluciones de meteorización de estas cenizas volantes son despreciables dada su baja actividad, lo cual está relacionado con el pH alcalino de las disoluciones finales. Los fosfatos son los minerales para los que se producen mayoritariamente condiciones de sobresaturación, por lo que siempre se formarán. En el caso del silicio, parece posible la formación de arcillas 2:1 y de tectosilicatos (feldespatoides y/o zeolitas) asociadas a formas secundarias de cuarzo. La formación de los fosfatos puede estar limitada por las bajas concentraciones de Al y Mg en las disoluciones de largos tiempos de reacción y, quizás, por razones cinéticas. En condiciones evaporíticas además de los sulfatos, podrían formarse carbonatos y, en algunos, casos hidróxidos, especialmente cuando se trata de tiempos largos de reacción. En ambos casos el ensayo de alteración con Soxhlet y los conceptos y mecanismos de meteorización propuestos por Pédro han demostrado su importancia en la interpretación de los proceso de alteración de biocarbones y cenizas de combustión.

*Palabras clave*: Lodos de depuradora; cenizas volantes de combustión de biomasa; Escoria Linz-Donawitz; Arena de fundición; Tecnosoles; Biocarbón; secuestro de carbono.

# Chapter 8. Abstract

In recent decades, the amount of waste produced by humans has increased greatly. Society demands increasingly high standards of production and quality, leading to the production of greater volumes of waste and consequent increases in the associated risks of contamination. There is international concern regarding the management of all types of wastes and the consequent environmental degradation and public health risks. Land application of wastes, such as animal excrement or vegetable residues, has been carried out since long time ago. However, many environmental problems have now appeared primary because the final goal of the addition of wastes to soils is often the elimination of wastes rather than the enhancement of soil fertility or improvement of soil physical properties.

The objective of this thesis was to evaluate the suitability of anthropogeomorphic wastes as soil amendment or fertilizer. For this, different studies have been carried out and described in six chapters: four of them describe the study of Technosols and the other two describe the geochemical accelerated weathering study of biochar and biomass fly ash.

Chapters 2 and 3 correspond to a column study of Technosols. The Technosols were formulated from the mixtures of organic and inorganic wastes at a ratio of 56:44 (w/w). The organic components used were an anaerobic (AN) and an aerobic (AE) sewage sludge. The inorganic wastes used were Linz-Donawitz slag (LD) and green foundry sand (FS) and were termed conditioners. A mixture of the two conditioners at a ratio of 50:50 (w/w) was made to provide a third type of conditioner (FS + LD). Controls consisted of columns filled with organic waste only (AN or AE). There were eight treatments in total: AE, AE + FS, AE + LD, AE + FS + LD, AN, AN + FS, AN + LD, and AN + FS + LD. The objectives were to evaluate the influence of the acid buffering capacity of the ingredients on the chemistry of the leachates of different Technosols and to assess the mobility of the heavy metals.

The results demonstrated that the main processes determining the pH of the systems were nitrification and leaching of alkaline cations, but organic matter decomposition and carbonation may also have had an effect, although to a lesser degree. The lowest final pH values of the leachates were found in the AE sludge

control (5.0) and the treatment AE + FS (5.4), whereas the highest was 11.1 in the treatment AN + LD slag; the final pH of the other leachates ranged between 7.0 and 8.0. Nitrification was strongly retarded in the treatment of anaerobic sludge attributed to both the low initial Eh and the probable absence of nitrifiers. Nitrification was also impeded in those mixtures in which LD slag was used as a component (due to the liming effect).

The results of the heavy metal concentrations in the same leachates indicated that the concentrations of Cu, Ni and Pb in the leachates of anaerobic sludge treatments were generally higher than those of aerobic sludge treatments. The concentration of Cu was significantly higher in the leachates of the Technosols containing LD slag than the others. The concentrations of Zn in the leachates of the aerobic sludge control and the aerobic sludge + foundry sand Technosols were significantly higher at $pH < 6.0$ due to more Zn bound to Fe-Mn oxide was dissolved. The concentrations of Ni in 80% of the leachates exceeded the EU drinking water limiting for Ni ($0.02 \text{ mg L}^{-1}$). The concentrations of Pb were lower in the leachates of Technosols containing foundry sand attributed to the retention of Pb by the smectite present in the foundry sand. The concentrations of Cd in the leachates of all the Technosols were relatively higher than the controls, while the concentrations of Cr were higher in the controls. These results showed that the elaboration of Technosols has significantly altered the behaviour of the elements present in the starting waste material.

Chapters 4 and 5 correspond to a greenhouse experiment of Technosols in which the feasibility of different Technosols as substrates for ryegrass was evaluated. The Technosols were made from mixtures of sewage sludges and conditioners at two ratios: 60:40 and 50:50 (w/w, DW). Three types of sludges were used: aerobic sludge (AE), anaerobic sludge (AN) and CaO-treated aerobic sludge (AL). Four kinds of conditioners – 5% of green foundry sand (FS), 10% of Linz-Donawitz slag (LD), 2% of barley straw (BS) and 23 or 33% of fly ash from pine bark combustion (FA) – were used as amendments. Three Technosols containing 60% of sludge and 23% of FA were referred to as M1-AE, M1-AN and M1-AL. Another three with 50% of sludge and 33% of FA were identified as M2-AE, M2-AN and M2-AL. Controls were set for each type of sludge only (AE, AN, and AL sludges).

The analyses of soils and soil solutions (sampled *in situ*) showed that the Technosols elaborated from anaerobic sludge contained the highest contents of N and P, and organic carbon (OC), while the Technosols derived from aerobic sludge had the lowest level of OC and macro nutrients. Aerobic sludge treated with CaO had the lowest availability of P, due to precipitation of large amount of phosphates with Ca.

The analyses of plants showed that the total above-ground biomass yields was in the order of M2-AN (21.1 g) ~ M1-AL (20.2 g) ~ M2-AL (19.9 g) ~ AN (19.8 g) ~ M1-AN (19.6 g) > AE (11.2 g) ~ M1-AE (11.0 g) > AL (9.8 g) ~ M2-AE (9.4 g) ("~" denotes the lack of significant differences at $P < 0.05$). The addition of conditioners to the AN sludge did not improve the plant yield significantly; the addition of conditioners to the AL sludge significantly increased the plant yield; the addition of conditioners to the AE sludge significantly reduced the plant yield. The concentration of Cu in the ryegrass of the unamended AN sludge was above the Cu toxicity level for plants (20 mg $kg^{-1}$). In general, the addition of conditioners efficiently decreased the bioavailability of heavy metals.

Chapters 6 and 7 corresponded to the simulated geochemical weathering studies of biochar produced from biosolids and fly ash produced from pine bark combustion, respectively. The experiments were realized in a modified Soxhlet reactor. The weathering process took place at 30 °C, with a flow rate of water of 5 mL $min^{-1}$ (equivalent to the rainfall of 273 mm $h^{-1}$). The study of biochar weathering had two treatments, with and without the addition of humic acid (treatment BC-HA and BC-B, respectively) and the weathering time lasted for 300 hours in total. The study of fly ash geochemical weathering was conducted with different weathering periods: 1, 24, 120, 300, 800, 1304 and 1808 hours (h).

The results of the geochemical weathering study of biochar revealed that substantial amounts of K (8.5–10.2%) and S (20.2–28.3%) were recovered in the weathering solutions. Noticeable Ca (17.9–20.7%) and P (15.4%) in the solid were released but only a few were recovered in the weathering solutions because of the precipitation. The presence of humic acids increased this dissolution of the mineral ash fraction of the biochar and thus the availability of K, S, Ca, Mg and P. On the contrary, the humic acid induced N immobilisation. Nitrogen availability in the biochar was already very low (< 1.0% of the total N) due to the probable recalcitrant heterocyclic N structure. The pH of the biochar dropped from 8.4 to 7.5; this was mainly attributed to loss of base cations through leaching and probable carbonation of the alkaline solutions exposed to the air.

The results of the geochemical accelerated weathering of fly ash showed that the weathering process is mainly through alkalinolisis. At the shortest time (1 h) there is already dissolution and mobilisation of alkaline cations and sulphates; at increasing weathering time, there is the progressive carbonation of the alkaline solution. The main processes that occur during the weathering of these materials are: (i) the neoformation of some secondary products, mainly phosphates, and lower quantity of amorphous silica and low order grade 2:1 mineral during the carbonation process, (ii) carbonation, and (iii) the leaching of alkaline cations and sulphates. These occur with different intensity depending on the weathering time. Initially, the dominant cation in solution was $K^+$ followed by $Na^+$, and $SO_4^{2-}$ being the main neutralizing anion and with major mobility at short weathering times (< 300 h). However, at long weathering times, Na had the highest mobility, followed by $SO_4^{2-}$ and $K^+$. These three ions had the highest concentrations and geochemical mobility in all the time sequence. The following important elements, based in their concentrations, are Si, $Ca^{2+}$ and $Mg^{2+}$, whose behaviours were very different from the former three ions. After reaching peak concentrations – which were interpreted as the concentrations of oversaturation under the alkaline conditions of the experiment – , their concentrations and activities decreased considerably due to neoformation and/or adsorption, related to the thermochemical equilibrium of the system under the final conditions. This suggested the formation secondary minerals, most of which were amorphous or of low order grade that could not be detected by the XRD analysis. The presence of ion pair and complexes of sulphates of alkaline earth elements and bases indicated that sulphate minerals should be an important phase under evaporitic conditions. However, under the conditions of the present study none of the oversaturation and thermodynamic stability of sulphates has been found. The ions $F^-$, $Cl^-$ and $NO_3^-$ also followed exponential reactions, although at different concentrations and time: $F^-$ and $Cl^-$ reached equilibrium from 300 h on and $NO_3^-$ after 800 h. Concentrations of heavy metals in the weathering solutions were negligible, due to their low activity at the alkaline pH of the final solutions. The phosphates were the minerals most oversaturated. In the case of silica, the formation of 2:1 clay

and tectosilicates (feldespatoides and/or zeolites) associated with the secondary form of quartz seems plausible. The formation of the former could be inhibited or limited due to the low concentrations of Al and Mg in the solution at long weathering time and due to kinetic reasons. Under evaporitic conditions, carbonates could be formed, in addition to sulphates and, in some cases, hydroxides, especially at long weathering time.

In both cases, the geochemical weathering study with Soxhlet reactor, the weathering concepts and mechanisms proposed by Pédro have demonstrated its importance in the interpretation of the weathering processes of biochar and fly ash.

*Keywords:* Sewage sludge; Fly ash from biomass combustion; Linz-Donawitz slag; Foundry sand; Technosols; Biochar; Carbon sequestration.

# Capítulo 9 / Chapter 9

# Conclusiones principales / Main conclusions

# Capítulo 9. Conclusiones principales

Nota introductoria: en el capítulo actual, sólo se recogen las principales conclusiones. Para llegar a conclusiones más específicas sobre los diferentes temas tratados durante el desarrollo de este trabajo deben consultarse los capítulos correspondientes (Capítulos 2-7).

Conclusiones:

1. Los Tecnosoles formulados a partir de los lodos aeróbicos estudiados tienen una mayor capacidad de neutralización de ácidos inicial, pero también presentan un mayor potencial acidificante como consecuencia del incremento progresivo de la nitrificación y la degradación de la materia orgánica que contienen.

2. Los Tecnosoles elaborados con lodos anaeróbicos tienen un mayor contenido de metales pesados (especialmente Cu, Ni, Pb y Zn) que los elaborados con lodos aeróbicos.

3. La adición de escorias LD aumenta el pH y el contenido de Ca de los Tecnosoles, lo que favorece la liberación y lixiviación de Cu.

4. Los Tecnosoles elaborados con lodos aeróbicos liberan grandes cantidades de Fe y Mn que, rápidamente, forman oxi-hidróxidos y pueden incorporar Zn adsorbido o coprecipitado cuando el pH es inferior a 6.

5. Las principales sistemas de neutralización de ácidos que actúan en los Tecnosoles son: (i) las bases fuertes (principalmente $Ca(OH)_2$ a valores de pH>9,0), (ii) el sistema $CO_3^{=}$-$CO_2$-$H_2O$, a valores de pH en torno a 8, y (iii) las reacciones de intercambio de cationes alcalinos y alcalino-térreos en el intervalo de pH entre 7 y 5.

6. Al formular Tecnosoles a partir de mezclas de residuos debe tenerse en cuenta la capacidad de neutralización de ácido de los residuos y su potencial de

acidificación, además de su contenido de nutrientes y de los límites de contaminantes establecidos por las diferentes normativas ambientales.

7. Los Tecnosoles elaborados con lodos anaerobios tienen mayores contenidos de N, P, K y carbono orgánico, lo que promueve un mayor crecimiento de las plantas.

8. Los Tecnosoles elaborados a partir de lodos aeróbicos tienen las menores cantidades de macronutrientes, lo que conduce a rendimientos de producción de biomasa más bajos.

9. El bajo contenido de K y la baja biodisponibilidad de P, causada por el alto contenido de Ca en los lodos aeróbicos tratados con CaO restringe, en gran medida, el crecimiento de las plantas en los Tecnosoles formulados con lodos aeróbicos floculados con CaO.

10. Los acondicionadores (arena verde de fundición, escorias LD, cenizas volantes de combustión de biomasa y paja de cebada) no sólo aumentan el pH y la capacidad de neutralización de ácidos reduciendo, por tanto, la tasa de acidificación, sino que deben ser valorados por el aporte de K, Ca, Mg y Mn que realizan al sistema. Además, reducen la tasa de descomposición del carbono orgánico. Este proceso de estabilización del C, además de permitir una mayor cantidad de C fijado durante más tiempo, debe tiene la ventaja añadida de favorecer la inmovilización de metales pesados como Cu, Zn y Ni,.., en el Tecnosol, todo lo cual reduce considerablemente el impacto ambiental.

11. La tecnología de elaboración de Tecnosoles a partir de mezclas de residuos es una opción óptima para la incorporación de los nutrientes de los residuos en el ciclo biogeoquímico. Deben ser hechos “a la carta”, teniendo en cuenta las necesidades del medio en el que se van a aplicar y las propiedades y el porcentaje de cada ingrediente que debe formar parte del Tecnosol.

12. El efecto de “bomba química de tiempo” debe ser tenido en cuenta en la aplicación de Tecnosoles elaborados a partir de los residuos.

13. La meteorización geoquímica simulada del biocarbón de lodos indica que, la presencia de oxi-hidróxidos metálicos en su composición conduce a la formación de fosfatos, carbonatos (sólo al inicio de la alteración cuando el pH es elevado) y bicarbonatos.

14. A pesar de que se ha comprobado la precipitación de algunos sulfatos en formas más insolubles que las originalmente presentes en el biocarbón, la mayor parte de los sulfatos liberados en la meteorización permanecen en la fase disuelta.

15. La presencia de ácidos húmicos en el sistema de alteración de los biocarbones incrementa la cinética de las reacciones, pero no modifica las tendencias termodinámicas de la alteración de los biocarbones.

16. La movilidad de los cationes básicos en la alteración de los biocarbones sigue el orden Ca>> Mg ~ K.

17. La meteorización geoquímica acelerada de estos biocarbones de biosolidos producidos a 550 °C ha demostrado su potencial como fuente de algunos nutrientes esenciales (por ejemplo, K, Ca, S, P y Mg). Por el contrario, no es importante como fuente de N.

18. El pH del sistema de alteración de los biocarbones se redujo debido a la lixiviación de cationes básicos y la carbonatación de las disoluciones. Este último efecto puede atribuirse a la captura de $CO_2$ atmosférico en sistemas alcalinos y al $CO_2$ liberado por la oxidación biótica y abiótica de los biocarbones.

19. El incremento considerable de los grupos funcionales carbonilo y carboxílo ponen de manifiesto la oxidabilidad de los biocarbones en procesos de meteorización geoquímica.

20. El estudio de la meteorización geoquímica de las cenizas volantes de combustión de biomasa ha demostrado que incluso con tiempos de reacción muy bajos el proceso se realiza en condiciones de alcalinolisis (pH>9,0), siendo K, Na y S los elementos más intensa y rápidamente movilizados. Son necesarios tiempos de residencia de 300-800 h para que se alcancen las máximas concentraciones en disolución de todos los elementos, acelerándose, a partir de este tiempo de reacción, la formación de compuestos secundarios neoformados con reducción de la actividad de Al, Mg y P en disolución.

21. La variación del índice de Parker indica que la alteración de las cenizas produce una pequeña variación química, similar a la que se ha observado en los procesos de alteración incipientes de rocas metamórficas con pocos minerales alterables en Galicia.

22. Los fosfatos de Ca y Pb son los minerales de mayor estabilidad termodinámica de los productos neoformados. Aunque existen pares y complejos iónicos con presencia de carbonatos y sulfatos estos no alcanzan nunca condiciones de saturación, por lo que sólo podrían neoformarse en condiciones evaporíticas.

23. La neoformación de minerales 1:1 y 2:1 es termodinámicamente posible, especialmente a tiempos cortos de reacción, pero la escasa actividad de Al y Mg parecen minimizar su formación, por lo que el Si debe concentrarse como sílice amorfa o bien en otros tectosilicatos pobres en Al y Mg con baja cristalinidad.

24. El reactor Soxhlet modificado y los conceptos sobre la alteración establecidos por Pédro han demostrado su utilidad para la interpretación de los procesos de meteorización geoquímica de las cenizas volantes de combustión de biomasa y de los biocarbones.

# Chapter 9. Main conclusions

Introductory note: in the current chapter, only the main conclusions from this work are included. For more specific conclusions regarding the different topics dealt with during the development of this work, please refer to the corresponding chapters (Chapters 2-7).

Conclusions:

1. The Technosols formulated from aerobic sludge had greater acid buffering capacity but suffered greater acidification than those from the anaerobic sludge due to the intense nitrification and degradation of organic matter.

2. The Technosols formulated with anaerobic sludge contained higher amount of heavy metals (especially Cu, Ni, and Pb) than the aerobic sludge.

3. Addition of LD slag increased the pH and Ca content of the Technosols, which favoured the release and leaching of Cu.

4. Large amount of Fe/Mn-oxide combined Zn was released from Technosols of aerobic sludge when the pH was lower than 6.

5. The main acid buffering systems in the Technosols were (i) strong bases (mainly $Ca(OH)_2$ at pH>9.0), (ii) the carbonate system at pH values close to 8, and (iii) exchange reactions of alkaline cations at the pH between 7 and 5.

6. When formulating Technosols from mixtures of wastes, the acid buffering capacity of the wastes should be taken into account, as well as their nutrient contents and the limits of contaminants established by local regulations.

7. The Technosols made with anaerobic sludge contained the highest content of N, P, K and organic C, which induced the greatest plant growth.

8. The Technosols elaborated from aerobic sludge had the lowest amount of macro nutrients which led to the lowest biomass yields.

9. Low content of K and low bioavailability of P – caused by high content of Ca in the CaO-treated aerobic sludge – have greatly restricted the plant growth in the Technosols formulated with CaO-treated aerobic sludge.

10. Amendment of conditioners (green foundry sand, LD slag, biomass fly ash and barley straw) not only have increased the pH and the acid buffering capacity, lowered the acidification rate, and made extra contribution of K, Ca, Mg and Mn to plants. In addition decreased the decomposition rate of organic C. This stabilisation, apart from permitting a great quantity of C fixed during long time favoured the immobilisation of heavy metals such as Cu, Zn and Ni, etc. All of these could considerably reduce the negative impacts of wastes on the environment.

11. The technology of elaborating Technosols from mixtures of wastes is an adequate option for incorporating the nutrients in the wastes into the biogeochemical cycle. It should be tailor-made according to various factors, among which the necessity of application means, the property and rate of each ingredient are the most important.

12. The effect of “chemical time bomb” should not be ignored during the application of Technosols elaborated from wastes.

13. The simulated geochemical weathering of the sludge-born biochar indicated that, the presence of metallic oxy-hydroxides will lead to the formation of phosphates, carbonates (only at the initial high pH values), and bicarbonates.

14. Sulphate seems to remain mostly in solution after weathering, although the precipitated sulphates were in more insoluble forms than those originally present in the biochar.

15. The effect of humic acid on the weathering seems to be more related to the kinetics of the weathering (apparently accelerating it) than to the thermodynamic evolution of the biochar.

16. The mobility of elements in the biochar follows the order Ca >> Mg ~ K.

17. The geochemical weathering demonstrated the potential of this biochar as a source of some plant essential nutrients (e.g., K, Ca, S, P, and Mg), while the nitrogen availability was restricted due to its high recalcitrance.

18. The pH of the system was lowered by the leaching of base cations and possibly carbonation through atmospheric $CO_2$ dissolution in the initial alkaline system and/or $CO_2$ released from the biotic and abiotic oxidation of the biochar.

19. Considerable increases in carbonyl and carboxylic functional groups indicated oxidation of the biochar during geochemical weathering.

20. The geochemical weathering study of the biomass fly ash demonstrated that even with short weathering time the process was realized under alkalinolisis conditions (pH > 9.0), where K, Na and S were the most intense and rapidly mobilised elements. Weathering time of 300-800 h was necessary for the attainment of the highest concentrations of all elements in the solution. Thereafter, the formation of neoformed secondary compounds was accelerated with reductions in the activities of Al, Mg and P in the solution.

21. The variation of the Parker index indicates that the alteration of the fly ash produced a small chemical change, similar to what has been observed in the incipient alteration processes of metamorphic rocks with few weathered minerals in Galicia.

22. Phosphates of Ca and Pb were the minerals with the highest thermodynamic stability among the newly formed products. Although there were ion pairs and

complexes with the presence of carbonates and sulphates, they never reached saturation, because they could only neoform under evaporitic conditions.

23. The neoformation of 1:1 and 2:1 minerals was thermodynamically possible, especially at short weathering time, but the low activity of Al and Mg seemed to minimize their formation, so that Si should concentrate as amorphous silica or other tectosilicates poor in Al and Mg with low crystallinity.

24. The modified Soxhlet reactor and the weathering concepts established by Pédro have been proved to be useful for the interpretation of geochemical weathering processes of biochar and fly ash from biomass combustion.

# Anexos / Annex

## Todos los anexos se encuentran incluidos en el Cd adjunto /

## All Annexes are included in the attached Cd

**Annex 1.** PHREEQC modelling of weathering solutions of biochar at different time.
**Annex 2.** PHREEQC modelling of weathering solutions of mixtures of biochar and humic acid (HA) at different time.
**Annex 3.** PHREEQC modelling of weathering solutions of fly ash at different time.

## Annex 1. PHREEQC modeling of weathering solutions of biochar at different time.

Initial solution 1-Biochar 0 h.

```
-----------------------------Solution composition-------------------------------

        Elements           Molality       Moles

        C                8.160e-004  8.160e-004
        Ca               1.498e-004  1.498e-004
        N(-3)            1.531e-003  1.531e-003
        N(5)             2.286e-003  2.286e-003
        Na               6.567e-003  6.567e-003
        P                2.261e-006  2.261e-006
        S(6)             1.654e-003  1.654e-003

----------------------------Description of solution-----------------------------

                                       pH  =   9.190
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  8.855e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.445e-003
                       Total CO2 (mol/kg)  =  8.160e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  1.355e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   9.58
                               Iterations  =   8
                                  Total H  = 1.110188e+002
                                  Total O  = 5.552216e+001

---------------------------------Redox couples----------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           3.7358      0.2173

----------------------------Distribution of species-----------------------------

                                                    Log       Log         Log
   Species                  Molality    Activity  Molality  Activity     Gamma

   OH-                   1.160e-005  1.051e-005    -4.935    -4.978    -0.043
   H+                    7.034e-010  6.457e-010    -9.153    -9.190    -0.037
   H2O                   5.551e+001  9.998e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -86.425   -86.424     0.001
C(4)            8.160e-004
   HCO3-                 7.383e-004  6.721e-004    -3.132    -3.173    -0.041
   CO3-2                 6.381e-005  4.384e-005    -4.195    -4.358    -0.163
   CaCO3                 5.770e-006  5.782e-006    -5.239    -5.238     0.001
   NaCO3-                4.126e-006  3.745e-006    -5.384    -5.427    -0.042
   NaHCO3                2.236e-006  2.241e-006    -5.650    -5.650     0.001
   CO2                   1.044e-006  1.046e-006    -5.981    -5.981     0.001
   CaHCO3+               7.439e-007  6.773e-007    -6.128    -6.169    -0.041
Ca              1.498e-004
   Ca+2                  1.252e-004  8.598e-005    -3.902    -4.066    -0.163
   CaSO4                 1.774e-005  1.777e-005    -4.751    -4.750     0.001
   CaCO3                 5.770e-006  5.782e-006    -5.239    -5.238     0.001
   CaHCO3+               7.439e-007  6.773e-007    -6.128    -6.169    -0.041
   CaPO4-                2.088e-007  1.895e-007    -6.680    -6.722    -0.042
   CaHPO4                5.681e-008  5.693e-008    -7.246    -7.245     0.001
   CaOH+                 2.435e-008  2.210e-008    -7.614    -7.656    -0.042
   CaH2PO4+              3.123e-011  2.834e-011   -10.505   -10.548    -0.042
   CaHSO4+               6.980e-014  6.335e-014   -13.156   -13.198    -0.042
H(0)            6.196e-030
   H2                    3.098e-030  3.104e-030   -29.509   -29.508     0.001
```

```
N(-3)           1.531e-003
   NH4+                  9.757e-004  8.815e-004    -3.011    -3.055    -0.044
   NH3                   5.420e-004  5.431e-004    -3.266    -3.265     0.001
   NH4SO4-               1.359e-005  1.234e-005    -4.867    -4.909    -0.042
N(5)            2.286e-003
   NO3-                  2.286e-003  2.068e-003    -2.641    -2.684    -0.044
Na              6.567e-003
   Na+                   6.526e-003  5.929e-003    -2.185    -2.227    -0.042
   NaSO4-                3.444e-005  3.126e-005    -4.463    -4.505    -0.042
   NaCO3-                4.126e-006  3.745e-006    -5.384    -5.427    -0.042
   NaHCO3                2.236e-006  2.241e-006    -5.650    -5.650     0.001
   NaOH                  6.053e-008  6.066e-008    -7.218    -7.217     0.001
   NaHPO4-               1.691e-008  1.535e-008    -7.772    -7.814    -0.042
O(0)            1.972e-035
   O2                    9.858e-036  9.878e-036   -35.006   -35.005     0.001
P               2.261e-006
   HPO4-2                1.961e-006  1.328e-006    -5.708    -5.877    -0.169
   CaPO4-                2.088e-007  1.895e-007    -6.680    -6.722    -0.042
   CaHPO4                5.681e-008  5.693e-008    -7.246    -7.245     0.001
   NaHPO4-               1.691e-008  1.535e-008    -7.772    -7.814    -0.042
   H2PO4-                1.564e-008  1.421e-008    -7.806    -7.847    -0.042
   PO4-3                 2.013e-009  8.376e-010    -8.696    -9.077    -0.381
   CaH2PO4+              3.123e-011  2.834e-011   -10.505   -10.548    -0.042
S(6)            1.654e-003
   SO4-2                 1.589e-003  1.086e-003    -2.799    -2.964    -0.165
   NaSO4-                3.444e-005  3.126e-005    -4.463    -4.505    -0.042
   CaSO4                 1.774e-005  1.777e-005    -4.751    -4.750     0.001
   NH4SO4-               1.359e-005  1.234e-005    -4.867    -4.909    -0.042
   HSO4-                 6.752e-011  6.128e-011   -10.171   -10.213    -0.042
   CaHSO4+               6.980e-014  6.335e-014   -13.156   -13.198    -0.042

------------------------------Saturation indices--------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.69   -7.03   -4.34  CaSO4
        Aragonite        -0.12   -8.42   -8.31  CaCO3
        Calcite           0.03   -8.42   -8.45  CaCO3
        CH4(g)          -83.61  -86.42   -2.82  CH4
        CO2(g)           -4.57   -5.98   -1.41  CO2
        Gypsum           -2.45   -7.03   -4.58  CaSO4:2H2O
        H2(g)           -26.38  -29.51   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    1.77   -1.20   -2.97  Ca5(PO4)3OH
        NH3(g)           -5.14   -3.27    1.87  NH3
        O2(g)           -32.15  -35.01   -2.85  O2

Initial solution 2-Biochar 0.1 h.

-----------------------------Solution composition-------------------------------

        Elements           Molality       Moles

        C                4.426e-004  4.426e-004
        Ca               7.037e-004  7.037e-004
        K                1.893e-004  1.893e-004
        Mg               4.937e-005  4.937e-005
        N(-3)            2.373e-003  2.373e-003
        Na               1.692e-003  1.692e-003
        P                1.292e-006  1.292e-006
        S(6)             4.923e-004  4.923e-004

----------------------------Description of solution-----------------------------

                                       pH  =   8.590
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  4.524e-003
```

```
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  7.551e-004
                       Total CO2 (mol/kg)  =  4.426e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  4.020e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  59.84
                               Iterations  =   8
                                  Total H  = 1.110221e+002
                                  Total O  = 5.550952e+001

----------------------------Distribution of species----------------------------

                                                   Log       Log          Log
   Species                  Molality    Activity  Molality  Activity     Gamma

   OH-                   2.840e-006  2.641e-006    -5.547    -5.578    -0.032
   H+                    2.744e-009  2.570e-009    -8.562    -8.590    -0.028
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -81.256   -81.255     0.000
C(4)            4.426e-004
   HCO3-                 4.232e-004  3.947e-004    -3.373    -3.404    -0.030
   CO3-2                 8.553e-006  6.466e-006    -5.068    -5.189    -0.121
   CaCO3                 4.970e-006  4.975e-006    -5.304    -5.303     0.000
   CaHCO3+               2.488e-006  2.320e-006    -5.604    -5.634    -0.030
   CO2                   2.442e-006  2.444e-006    -5.612    -5.612     0.000
   NaHCO3                3.488e-007  3.491e-007    -6.457    -6.457     0.000
   MgCO3                 2.012e-007  2.014e-007    -6.696    -6.696     0.000
   MgHCO3+               1.715e-007  1.596e-007    -6.766    -6.797    -0.031
   NaCO3-                1.575e-007  1.466e-007    -6.803    -6.834    -0.031
Ca              7.037e-004
   Ca+2                  6.639e-004  5.017e-004    -3.178    -3.300    -0.122
   CaSO4                 3.205e-005  3.208e-005    -4.494    -4.494     0.000
   CaCO3                 4.970e-006  4.975e-006    -5.304    -5.303     0.000
   CaHCO3+               2.488e-006  2.320e-006    -5.604    -5.634    -0.030
   CaHPO4                1.696e-007  1.698e-007    -6.771    -6.770     0.000
   CaPO4-                1.525e-007  1.420e-007    -6.817    -6.848    -0.031
   CaOH+                 3.479e-008  3.239e-008    -7.458    -7.490    -0.031
   CaH2PO4+              3.615e-010  3.365e-010    -9.442    -9.473    -0.031
   CaHSO4+               4.891e-013  4.552e-013   -12.311   -12.342    -0.031
H(0)            9.830e-029
   H2                    4.915e-029  4.920e-029   -28.308   -28.308     0.000
K               1.893e-004
   K+                    1.889e-004  1.757e-004    -3.724    -3.755    -0.031
   KSO4-                 4.078e-007  3.796e-007    -6.390    -6.421    -0.031
   KHPO4-                2.498e-010  2.325e-010    -9.602    -9.634    -0.031
   KOH                   2.367e-010  2.369e-010    -9.626    -9.625     0.000
Mg              4.937e-005
   Mg+2                  4.650e-005  3.525e-005    -4.333    -4.453    -0.120
   MgSO4                 2.433e-006  2.436e-006    -5.614    -5.613     0.000
   MgCO3                 2.012e-007  2.014e-007    -6.696    -6.696     0.000
   MgHCO3+               1.715e-007  1.596e-007    -6.766    -6.797    -0.031
   MgOH+                 3.379e-008  3.145e-008    -7.471    -7.502    -0.031
   MgHPO4                1.611e-008  1.613e-008    -7.793    -7.792     0.000
   MgPO4-                1.446e-008  1.346e-008    -7.840    -7.871    -0.031
   MgH2PO4+              3.235e-011  3.011e-011   -10.490   -10.521    -0.031
N(-3)           2.373e-003
   NH4+                  2.067e-003  1.919e-003    -2.685    -2.717    -0.032
   NH3                   2.968e-004  2.971e-004    -3.528    -3.527     0.000
   NH4SO4-               8.928e-006  8.310e-006    -5.049    -5.080    -0.031
Na              1.692e-003
   Na+                   1.689e-003  1.573e-003    -2.772    -2.803    -0.031
   NaSO4-                2.756e-006  2.566e-006    -5.560    -5.591    -0.031
   NaHCO3                3.488e-007  3.491e-007    -6.457    -6.457     0.000
   NaCO3-                1.575e-007  1.466e-007    -6.803    -6.834    -0.031
   NaOH                  4.039e-009  4.043e-009    -8.394    -8.393     0.000
   NaHPO4-               2.237e-009  2.082e-009    -8.650    -8.682    -0.031
O(0)            7.859e-038
```

```
   O2                   3.929e-038  3.934e-038   -37.406   -37.405     0.000
P               1.292e-006
   HPO4-2               9.048e-007  6.787e-007    -6.043    -6.168    -0.125
   CaHPO4               1.696e-007  1.698e-007    -6.771    -6.770     0.000
   CaPO4-               1.525e-007  1.420e-007    -6.817    -6.848    -0.031
   H2PO4-               3.104e-008  2.891e-008    -7.508    -7.539    -0.031
   MgHPO4               1.611e-008  1.613e-008    -7.793    -7.792     0.000
   MgPO4-               1.446e-008  1.346e-008    -7.840    -7.871    -0.031
   NaHPO4-              2.237e-009  2.082e-009    -8.650    -8.682    -0.031
   CaH2PO4+             3.615e-010  3.365e-010    -9.442    -9.473    -0.031
   KHPO4-               2.498e-010  2.325e-010    -9.602    -9.634    -0.031
   PO4-3                2.054e-010  1.075e-010    -9.687    -9.968    -0.281
   MgH2PO4+             3.235e-011  3.011e-011   -10.490   -10.521    -0.031
S(6)            4.923e-004
   SO4-2                4.457e-004  3.361e-004    -3.351    -3.474    -0.123
   CaSO4                3.205e-005  3.208e-005    -4.494    -4.494     0.000
   NH4SO4-              8.928e-006  8.310e-006    -5.049    -5.080    -0.031
   NaSO4-               2.756e-006  2.566e-006    -5.560    -5.591    -0.031
   MgSO4                2.433e-006  2.436e-006    -5.614    -5.613     0.000
   KSO4-                4.078e-007  3.796e-007    -6.390    -6.421    -0.031
   HSO4-                8.109e-011  7.548e-011   -10.091   -10.122    -0.031
   CaHSO4+              4.891e-013  4.552e-013   -12.311   -12.342    -0.031

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.43   -6.77   -4.34  CaSO4
        Aragonite        -0.18   -8.49   -8.31  CaCO3
        Calcite          -0.04   -8.49   -8.45  CaCO3
        CH4(g)          -78.44  -81.26   -2.82  CH4
        CO2(g)           -4.20   -5.61   -1.41  CO2
        Dolomite         -1.16  -18.13  -16.97  CaMg(CO3)2
        Gypsum           -2.19   -6.77   -4.58  CaSO4:2H2O
        H2(g)           -25.18  -28.31   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    2.33   -0.64   -2.97  Ca5(PO4)3OH
        NH3(g)           -5.40   -3.53    1.87  NH3
        O2(g)           -34.55  -37.41   -2.85  O2

Initial solution 3-Biochar 0.2 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 4.937e-004  4.937e-004
        Ca                9.583e-004  9.583e-004
        K                 4.144e-004  4.144e-004
        Mg                1.111e-004  1.111e-004
        N(-3)             3.859e-003  3.859e-003
        N(5)              2.072e-003  2.072e-003
        Na                1.022e-003  1.022e-003
        P                 1.615e-006  1.615e-006
        S(6)              6.922e-004  6.922e-004

----------------------------Description of solution----------------------------

                                       pH  =   8.620
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  6.910e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.019e-003
                       Total CO2 (mol/kg)  =  4.937e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  2.958e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  27.96
```

```
                               Iterations  =   7
                                  Total H  = 1.110278e+002
                                  Total O  = 5.551669e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           4.3762      0.2545

----------------------------Distribution of species----------------------------

                                                      Log       Log         Log
   Species                  Molality    Activity  Molality  Activity       Gamma

   OH-                    3.091e-006  2.830e-006    -5.510    -5.548      -0.038
   H+                     2.593e-009  2.399e-009    -8.586    -8.620      -0.034
   H2O                    5.551e+001  9.998e-001     1.744    -0.000       0.000
C(-4)           0.000e+000
   CH4                    0.000e+000  0.000e+000   -81.488   -81.487       0.001
C(4)            4.937e-004
   HCO3-                  4.685e-004  4.307e-004    -3.329    -3.366      -0.037
   CO3-2                  1.059e-005  7.561e-006    -4.975    -5.121      -0.146
   CaCO3                  7.386e-006  7.398e-006    -5.132    -5.131       0.001
   CaHCO3+                3.503e-006  3.220e-006    -5.456    -5.492      -0.037
   CO2                    2.485e-006  2.489e-006    -5.605    -5.604       0.001
   MgCO3                  4.945e-007  4.953e-007    -6.306    -6.305       0.001
   MgHCO3+                3.995e-007  3.663e-007    -6.398    -6.436      -0.038
   NaHCO3                 2.263e-007  2.267e-007    -6.645    -6.645       0.001
   NaCO3-                 1.112e-007  1.020e-007    -6.954    -6.992      -0.038
Ca              9.583e-004
   Ca+2                   8.943e-004  6.379e-004    -3.049    -3.195      -0.147
   CaSO4                  5.265e-005  5.274e-005    -4.279    -4.278       0.001
   CaCO3                  7.386e-006  7.398e-006    -5.132    -5.131       0.001
   CaHCO3+                3.503e-006  3.220e-006    -5.456    -5.492      -0.037
   CaHPO4                 2.340e-007  2.343e-007    -6.631    -6.630       0.001
   CaPO4-                 2.291e-007  2.100e-007    -6.640    -6.678      -0.038
   CaOH+                  4.813e-008  4.413e-008    -7.318    -7.355      -0.038
   CaH2PO4+               4.728e-010  4.335e-010    -9.325    -9.363      -0.038
   CaHSO4+                7.618e-013  6.984e-013   -12.118   -12.156      -0.038
H(0)            8.557e-029
   H2                     4.279e-029  4.285e-029   -28.369   -28.368       0.001
K               4.144e-004
   K+                     4.133e-004  3.784e-004    -3.384    -3.422      -0.038
   KSO4-                  1.153e-006  1.057e-006    -5.938    -5.976      -0.038
   KHPO4-                 5.930e-010  5.436e-010    -9.227    -9.265      -0.038
   KOH                    5.460e-010  5.469e-010    -9.263    -9.262       0.001
Mg              1.111e-004
   Mg+2                   1.034e-004  7.412e-005    -3.985    -4.130      -0.145
   MgSO4                  6.612e-006  6.623e-006    -5.180    -5.179       0.001
   MgCO3                  4.945e-007  4.953e-007    -6.306    -6.305       0.001
   MgHCO3+                3.995e-007  3.663e-007    -6.398    -6.436      -0.038
   MgOH+                  7.730e-008  7.087e-008    -7.112    -7.150      -0.038
   MgHPO4                 3.676e-008  3.681e-008    -7.435    -7.434       0.001
   MgPO4-                 3.590e-008  3.291e-008    -7.445    -7.483      -0.038
   MgH2PO4+               6.996e-011  6.414e-011   -10.155   -10.193      -0.038
N(-3)           3.859e-003
   NH4+                   3.336e-003  3.047e-003    -2.477    -2.516      -0.039
   NH3                    5.046e-004  5.054e-004    -3.297    -3.296       0.001
   NH4SO4-                1.860e-005  1.706e-005    -4.730    -4.768      -0.038
N(5)            2.072e-003
   NO3-                   2.072e-003  1.895e-003    -2.684    -2.722      -0.039
Na              1.022e-003
   Na+                    1.020e-003  9.359e-004    -2.991    -3.029      -0.037
   NaSO4-                 2.152e-006  1.973e-006    -5.667    -5.705      -0.038
   NaHCO3                 2.263e-007  2.267e-007    -6.645    -6.645       0.001
   NaCO3-                 1.112e-007  1.020e-007    -6.954    -6.992      -0.038
   NaOH                   2.573e-009  2.577e-009    -8.590    -8.589       0.001
```

```
   NaHPO4-              1.467e-009  1.345e-009    -8.834    -8.871    -0.038
O(0)           1.035e-037
   O2                   5.177e-038  5.185e-038   -37.286   -37.285     0.001
P              1.615e-006
   HPO4-2               1.044e-006  7.368e-007    -5.981    -6.133    -0.151
   CaHPO4               2.340e-007  2.343e-007    -6.631    -6.630     0.001
   CaPO4-               2.291e-007  2.100e-007    -6.640    -6.678    -0.038
   MgHPO4               3.676e-008  3.681e-008    -7.435    -7.434     0.001
   MgPO4-               3.590e-008  3.291e-008    -7.445    -7.483    -0.038
   H2PO4-               3.192e-008  2.929e-008    -7.496    -7.533    -0.037
   NaHPO4-              1.467e-009  1.345e-009    -8.834    -8.871    -0.038
   KHPO4-               5.930e-010  5.436e-010    -9.227    -9.265    -0.038
   CaH2PO4+             4.728e-010  4.335e-010    -9.325    -9.363    -0.038
   PO4-3                2.741e-010  1.251e-010    -9.562    -9.903    -0.341
   MgH2PO4+             6.996e-011  6.414e-011   -10.155   -10.193    -0.038
S(6)           6.922e-004
   SO4-2                6.110e-004  4.345e-004    -3.214    -3.362    -0.148
   CaSO4                5.265e-005  5.274e-005    -4.279    -4.278     0.001
   NH4SO4-              1.860e-005  1.706e-005    -4.730    -4.768    -0.038
   MgSO4                6.612e-006  6.623e-006    -5.180    -5.179     0.001
   NaSO4-               2.152e-006  1.973e-006    -5.667    -5.705    -0.038
   KSO4-                1.153e-006  1.057e-006    -5.938    -5.976    -0.038
   HSO4-                9.933e-011  9.106e-011   -10.003   -10.041    -0.038
   CaHSO4+              7.618e-013  6.984e-013   -12.118   -12.156    -0.038

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.21   -6.56   -4.34  CaSO4
        Aragonite        -0.01   -8.32   -8.31  CaCO3
        Calcite           0.14   -8.32   -8.45  CaCO3
        CH4(g)          -78.67  -81.49   -2.82  CH4
        CO2(g)           -4.20   -5.60   -1.41  CO2
        Dolomite         -0.60  -17.57  -16.97  CaMg(CO3)2
        Gypsum           -1.98   -6.56   -4.58  CaSO4:2H2O
        H2(g)           -25.24  -28.37   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    3.07    0.11   -2.97  Ca5(PO4)3OH
        NH3(g)           -5.17   -3.30    1.87  NH3
        O2(g)           -34.43  -37.29   -2.85  O2

Initial solution 4-Biochar 0.3 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 5.207e-004  5.207e-004
        Ca                1.046e-003  1.046e-003
        K                 4.323e-004  4.323e-004
        Mg                1.193e-004  1.193e-004
        Na                8.571e-004  8.571e-004
        P                 6.781e-006  6.781e-006
        S(6)              6.468e-004  6.468e-004

----------------------------Description of solution----------------------------

                                       pH  =   8.550
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  4.233e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  5.455e-004
                    Total CO2 (mol/kg)  =  5.207e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  1.773e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  34.57
```

```
                               Iterations  =   6
                                  Total H  = 1.110129e+002
                                  Total O  = 5.551039e+001

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                Molality    Activity  Molality  Activity     Gamma

   OH-                   2.584e-006  2.409e-006    -5.588    -5.618    -0.031
   H+                    3.003e-009  2.818e-009    -8.522    -8.550    -0.028
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -80.827   -80.826     0.000
C(4)            5.207e-004
   HCO3-                 4.951e-004  4.627e-004    -3.305    -3.335    -0.029
   CO3-2                 9.069e-006  6.913e-006    -5.042    -5.160    -0.118
   CaCO3                 7.828e-006  7.836e-006    -5.106    -5.106     0.000
   CaHCO3+               4.288e-006  4.007e-006    -5.368    -5.397    -0.029
   CO2                   3.139e-006  3.142e-006    -5.503    -5.503     0.000
   MgCO3                 5.146e-007  5.151e-007    -6.289    -6.288     0.000
   MgHCO3+               4.798e-007  4.476e-007    -6.319    -6.349    -0.030
   NaHCO3                2.074e-007  2.076e-007    -6.683    -6.683     0.000
   NaCO3-                8.521e-008  7.948e-008    -7.070    -7.100    -0.030
Ca              1.046e-003
   Ca+2                  9.699e-004  7.390e-004    -3.013    -3.131    -0.118
   CaSO4                 6.139e-005  6.145e-005    -4.212    -4.211     0.000
   CaCO3                 7.828e-006  7.836e-006    -5.106    -5.106     0.000
   CaHCO3+               4.288e-006  4.007e-006    -5.368    -5.397    -0.029
   CaHPO4                1.162e-006  1.163e-006    -5.935    -5.934     0.000
   CaPO4-                9.511e-007  8.872e-007    -6.022    -6.052    -0.030
   CaOH+                 4.665e-008  4.351e-008    -7.331    -7.361    -0.030
   CaH2PO4+              2.710e-009  2.528e-009    -8.567    -8.597    -0.030
   CaHSO4+               1.025e-012  9.562e-013   -11.989   -12.019    -0.030
H(0)            1.182e-028
   H2                    5.910e-029  5.915e-029   -28.228   -28.228     0.000
K               4.323e-004
   K+                    4.311e-004  4.018e-004    -3.365    -3.396    -0.031
   KSO4-                 1.211e-006  1.129e-006    -5.917    -5.947    -0.030
   KHPO4-                2.652e-009  2.473e-009    -8.576    -8.607    -0.030
   KOH                   4.938e-010  4.943e-010    -9.306    -9.306     0.000
Mg              1.193e-004
   Mg+2                  1.103e-004  8.432e-005    -3.957    -4.074    -0.117
   MgSO4                 7.571e-006  7.578e-006    -5.121    -5.120     0.000
   MgCO3                 5.146e-007  5.151e-007    -6.289    -6.288     0.000
   MgHCO3+               4.798e-007  4.476e-007    -6.319    -6.349    -0.030
   MgHPO4                1.793e-007  1.794e-007    -6.747    -6.746     0.000
   MgPO4-                1.464e-007  1.365e-007    -6.834    -6.865    -0.030
   MgOH+                 7.356e-008  6.862e-008    -7.133    -7.164    -0.030
   MgH2PO4+              3.938e-010  3.673e-010    -9.405    -9.435    -0.030
Na              8.571e-004
   Na+                   8.549e-004  7.979e-004    -3.068    -3.098    -0.030
   NaSO4-                1.814e-006  1.692e-006    -5.741    -5.771    -0.030
   NaHCO3                2.074e-007  2.076e-007    -6.683    -6.683     0.000
   NaCO3-                8.521e-008  7.948e-008    -7.070    -7.100    -0.030
   NaHPO4-               5.266e-009  4.912e-009    -8.279    -8.309    -0.030
   NaOH                  1.869e-009  1.870e-009    -8.728    -8.728     0.000
O(0)            5.438e-038
   O2                    2.719e-038  2.722e-038   -37.566   -37.565     0.000
P               6.781e-006
   HPO4-2                4.172e-006  3.157e-006    -5.380    -5.501    -0.121
   CaHPO4                1.162e-006  1.163e-006    -5.935    -5.934     0.000
   CaPO4-                9.511e-007  8.872e-007    -6.022    -6.052    -0.030
   MgHPO4                1.793e-007  1.794e-007    -6.747    -6.746     0.000
   H2PO4-                1.580e-007  1.474e-007    -6.801    -6.831    -0.030
   MgPO4-                1.464e-007  1.365e-007    -6.834    -6.865    -0.030
   NaHPO4-               5.266e-009  4.912e-009    -8.279    -8.309    -0.030
   CaH2PO4+              2.710e-009  2.528e-009    -8.567    -8.597    -0.030
```

```
   KHPO4-               2.652e-009  2.473e-009    -8.576    -8.607    -0.030
   PO4-3                8.544e-010  4.562e-010    -9.068    -9.341    -0.273
   MgH2PO4+             3.938e-010  3.673e-010    -9.405    -9.435    -0.030
S(6)            6.468e-004
   SO4-2                5.748e-004  4.371e-004    -3.241    -3.359    -0.119
   CaSO4                6.139e-005  6.145e-005    -4.212    -4.211     0.000
   MgSO4                7.571e-006  7.578e-006    -5.121    -5.120     0.000
   NaSO4-               1.814e-006  1.692e-006    -5.741    -5.771    -0.030
   KSO4-                1.211e-006  1.129e-006    -5.917    -5.947    -0.030
   HSO4-                1.154e-010  1.076e-010    -9.938    -9.968    -0.030
   CaHSO4+              1.025e-012  9.562e-013   -11.989   -12.019    -0.030

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.15   -6.49   -4.34  CaSO4
        Aragonite         0.01   -8.29   -8.31  CaCO3
        Calcite           0.16   -8.29   -8.45  CaCO3
        CH4(g)          -78.01  -80.83   -2.82  CH4
        CO2(g)           -4.10   -5.50   -1.41  CO2
        Dolomite         -0.55  -17.53  -16.97  CaMg(CO3)2
        Gypsum           -1.91   -6.49   -4.58  CaSO4:2H2O
        H2(g)           -25.10  -28.23   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    5.01    2.04   -2.97  Ca5(PO4)3OH
        O2(g)           -34.71  -37.57   -2.85  O2

Initial solution 5-Biochar 0.4 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                4.185e-004  4.185e-004
        Ca               8.435e-004  8.435e-004
        K                3.939e-004  3.939e-004
        Mg               1.028e-004  1.028e-004
        N(-3)            2.234e-003  2.234e-003
        N(5)             1.944e-003  1.944e-003
        Na               5.351e-004  5.351e-004
        P                5.167e-006  5.167e-006
        S(6)             4.785e-004  4.785e-004

----------------------------Description of solution----------------------------

                                       pH  =   8.600
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  5.286e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  7.232e-004
                       Total CO2 (mol/kg)  =  4.185e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  1.426e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  18.05
                               Iterations  =   6
                                  Total H  = 1.110215e+002
                                  Total O  = 5.551524e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           4.4271      0.2575

----------------------------Distribution of species----------------------------
```

```
                                                       Log       Log        Log
   Species              Molality    Activity  Molality  Activity      Gamma

   OH-                2.922e-006  2.703e-006    -5.534    -5.568     -0.034
   H+                 2.693e-009  2.512e-009    -8.570    -8.600     -0.030
   H2O                5.551e+001  9.999e-001     1.744    -0.000      0.000
C(-4)            0.000e+000
   CH4                0.000e+000  0.000e+000   -81.374   -81.373      0.001
C(4)             4.185e-004
   HCO3-              3.986e-004  3.698e-004    -3.399    -3.432     -0.033
   CO3-2              8.368e-006  6.201e-006    -5.077    -5.208     -0.130
   CaCO3              5.615e-006  5.622e-006    -5.251    -5.250      0.001
   CaHCO3+            2.761e-006  2.562e-006    -5.559    -5.591     -0.033
   CO2                2.236e-006  2.238e-006    -5.651    -5.650      0.001
   MgCO3              3.951e-007  3.956e-007    -6.403    -6.403      0.001
   MgHCO3+            3.309e-007  3.063e-007    -6.480    -6.514     -0.033
   NaHCO3             1.028e-007  1.029e-007    -6.988    -6.987      0.001
   NaCO3-             4.776e-008  4.422e-008    -7.321    -7.354     -0.033
Ca               8.435e-004
   Ca+2               7.981e-004  5.911e-004    -3.098    -3.228     -0.130
   CaSO4              3.558e-005  3.562e-005    -4.449    -4.448      0.001
   CaCO3              5.615e-006  5.622e-006    -5.251    -5.250      0.001
   CaHCO3+            2.761e-006  2.562e-006    -5.559    -5.591     -0.033
   CaHPO4             7.348e-007  7.357e-007    -6.134    -6.133      0.001
   CaPO4-             6.799e-007  6.296e-007    -6.168    -6.201     -0.033
   CaOH+              4.217e-008  3.905e-008    -7.375    -7.408     -0.033
   CaH2PO4+           1.539e-009  1.425e-009    -8.813    -8.846     -0.033
   CaHSO4+            5.335e-013  4.940e-013   -12.273   -12.306     -0.033
H(0)             9.386e-029
   H2                 4.693e-029  4.699e-029   -28.329   -28.328      0.001
K                3.939e-004
   K+                 3.931e-004  3.637e-004    -3.405    -3.439     -0.034
   KSO4-              7.999e-007  7.406e-007    -6.097    -6.130     -0.033
   KHPO4-             1.912e-009  1.770e-009    -8.719    -8.752     -0.033
   KOH                5.013e-010  5.019e-010    -9.300    -9.299      0.001
Mg               1.028e-004
   Mg+2               9.712e-005  7.219e-005    -4.013    -4.142     -0.129
   MgSO4              4.697e-006  4.702e-006    -5.328    -5.328      0.001
   MgCO3              3.951e-007  3.956e-007    -6.403    -6.403      0.001
   MgHCO3+            3.309e-007  3.063e-007    -6.480    -6.514     -0.033
   MgHPO4             1.213e-007  1.215e-007    -6.916    -6.915      0.001
   MgPO4-             1.120e-007  1.037e-007    -6.951    -6.984     -0.033
   MgOH+              7.120e-008  6.592e-008    -7.148    -7.181     -0.033
   MgH2PO4+           2.394e-010  2.216e-010    -9.621    -9.654     -0.033
N(-3)            2.234e-003
   NH4+               1.942e-003  1.793e-003    -2.712    -2.746     -0.035
   NH3                2.836e-004  2.840e-004    -3.547    -3.547      0.001
   NH4SO4-            7.902e-006  7.317e-006    -5.102    -5.136     -0.033
N(5)             1.944e-003
   NO3-               1.944e-003  1.796e-003    -2.711    -2.746     -0.034
Na               5.351e-004
   Na+                5.341e-004  4.949e-004    -3.272    -3.305     -0.033
   NaSO4-             8.216e-007  7.607e-007    -6.085    -6.119     -0.033
   NaHCO3             1.028e-007  1.029e-007    -6.988    -6.987      0.001
   NaCO3-             4.776e-008  4.422e-008    -7.321    -7.354     -0.033
   NaHPO4-            2.602e-009  2.409e-009    -8.585    -8.618     -0.033
   NaOH               1.300e-009  1.302e-009    -8.886    -8.886      0.001
O(0)             8.615e-038
   O2                 4.308e-038  4.313e-038   -37.366   -37.365      0.001
P                5.167e-006
   HPO4-2             3.399e-006  2.496e-006    -5.469    -5.603     -0.134
   CaHPO4             7.348e-007  7.357e-007    -6.134    -6.133      0.001
   CaPO4-             6.799e-007  6.296e-007    -6.168    -6.201     -0.033
   MgHPO4             1.213e-007  1.215e-007    -6.916    -6.915      0.001
   H2PO4-             1.122e-007  1.039e-007    -6.950    -6.983     -0.033
   MgPO4-             1.120e-007  1.037e-007    -6.951    -6.984     -0.033
   NaHPO4-            2.602e-009  2.409e-009    -8.585    -8.618     -0.033
   KHPO4-             1.912e-009  1.770e-009    -8.719    -8.752     -0.033
```

```
   CaH2PO4+             1.539e-009  1.425e-009    -8.813    -8.846    -0.033
   PO4-3                8.108e-010  4.047e-010    -9.091    -9.393    -0.302
   MgH2PO4+             2.394e-010  2.216e-010    -9.621    -9.654    -0.033
S(6)            4.785e-004
   SO4-2                4.287e-004  3.167e-004    -3.368    -3.499    -0.131
   CaSO4                3.558e-005  3.562e-005    -4.449    -4.448     0.001
   NH4SO4-              7.902e-006  7.317e-006    -5.102    -5.136    -0.033
   MgSO4                4.697e-006  4.702e-006    -5.328    -5.328     0.001
   NaSO4-               8.216e-007  7.607e-007    -6.085    -6.119    -0.033
   KSO4-                7.999e-007  7.406e-007    -6.097    -6.130    -0.033
   HSO4-                7.508e-011  6.952e-011   -10.124   -10.158    -0.033
   CaHSO4+              5.335e-013  4.940e-013   -12.273   -12.306    -0.033

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.38   -6.73   -4.34  CaSO4
        Aragonite        -0.13   -8.44   -8.31  CaCO3
        Calcite           0.02   -8.44   -8.45  CaCO3
        CH4(g)          -78.56  -81.37   -2.82  CH4
        CO2(g)           -4.24   -5.65   -1.41  CO2
        Dolomite         -0.81  -17.78  -16.97  CaMg(CO3)2
        Gypsum           -2.15   -6.73   -4.58  CaSO4:2H2O
        H2(g)           -25.20  -28.33   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    4.42    1.45   -2.97  Ca5(PO4)3OH
        NH3(g)           -5.42   -3.55    1.87  NH3
        O2(g)           -34.51  -37.37   -2.85  O2

Initial solution 6-Biochar 0.5 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                3.822e-004  3.822e-004
        Ca               6.463e-004  6.463e-004
        K                3.044e-004  3.044e-004
        Mg               8.639e-005  8.639e-005
        Na               4.046e-004  4.046e-004
        P                3.875e-006  3.875e-006
        S(6)             3.420e-004  3.420e-004

----------------------------Description of solution----------------------------

                                       pH  =   8.610
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  2.582e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  3.998e-004
                       Total CO2 (mol/kg)  =  3.822e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  1.087e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  34.80
                               Iterations  =   6
                                  Total H  = 1.110128e+002
                                  Total O  = 5.550875e+001

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                  2.925e-006  2.766e-006    -5.534    -5.558    -0.024
   H+                   2.584e-009  2.455e-009    -8.588    -8.610    -0.022
   H2O                  5.551e+001  1.000e+000     1.744    -0.000     0.000
```

```
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -81.492   -81.492     0.000
C(4)            3.822e-004
   HCO3-                 3.654e-004  3.461e-004    -3.437    -3.461    -0.024
   CO3-2                 7.377e-006  5.939e-006    -5.132    -5.226    -0.094
   CaCO3                 4.504e-006  4.507e-006    -5.346    -5.346     0.000
   CaHCO3+               2.119e-006  2.007e-006    -5.674    -5.697    -0.024
   CO2                   2.046e-006  2.047e-006    -5.689    -5.689     0.000
   MgCO3                 3.471e-007  3.473e-007    -6.460    -6.459     0.000
   MgHCO3+               2.778e-007  2.628e-007    -6.556    -6.580    -0.024
   NaHCO3                7.438e-008  7.443e-008    -7.129    -7.128     0.000
   NaCO3-                3.458e-008  3.272e-008    -7.461    -7.485    -0.024
Ca              6.463e-004
   Ca+2                  6.149e-004  4.948e-004    -3.211    -3.306    -0.094
   CaSO4                 2.374e-005  2.375e-005    -4.625    -4.624     0.000
   CaCO3                 4.504e-006  4.507e-006    -5.346    -5.346     0.000
   CaHCO3+               2.119e-006  2.007e-006    -5.674    -5.697    -0.024
   CaHPO4                5.153e-007  5.156e-007    -6.288    -6.288     0.000
   CaPO4-                4.772e-007  4.515e-007    -6.321    -6.345    -0.024
   CaOH+                 3.536e-008  3.345e-008    -7.452    -7.476    -0.024
   CaH2PO4+              1.032e-009  9.760e-010    -8.987    -9.011    -0.024
   CaHSO4+               3.402e-013  3.219e-013   -12.468   -12.492    -0.024
H(0)            8.969e-029
   H2                    4.485e-029  4.487e-029   -28.348   -28.348     0.000
K               3.044e-004
   K+                    3.039e-004  2.874e-004    -3.517    -3.542    -0.024
   KSO4-                 4.927e-007  4.661e-007    -6.307    -6.331    -0.024
   KHPO4-                1.238e-009  1.171e-009    -8.907    -8.931    -0.024
   KOH                   4.057e-010  4.059e-010    -9.392    -9.392     0.000
Mg              8.639e-005
   Mg+2                  8.209e-005  6.618e-005    -4.086    -4.179    -0.094
   MgSO4                 3.431e-006  3.433e-006    -5.465    -5.464     0.000
   MgCO3                 3.471e-007  3.473e-007    -6.460    -6.459     0.000
   MgHCO3+               2.778e-007  2.628e-007    -6.556    -6.580    -0.024
   MgHPO4                9.318e-008  9.324e-008    -7.031    -7.030     0.000
   MgPO4-                8.610e-008  8.146e-008    -7.065    -7.089    -0.024
   MgOH+                 6.536e-008  6.184e-008    -7.185    -7.209    -0.024
   MgH2PO4+              1.757e-010  1.662e-010    -9.755    -9.779    -0.024
Na              4.046e-004
   Na+                   4.040e-004  3.824e-004    -3.394    -3.418    -0.024
   NaSO4-                4.947e-007  4.681e-007    -6.306    -6.330    -0.024
   NaHCO3                7.438e-008  7.443e-008    -7.129    -7.128     0.000
   NaCO3-                3.458e-008  3.272e-008    -7.461    -7.485    -0.024
   NaHPO4-               1.647e-009  1.558e-009    -8.783    -8.807    -0.024
   NaOH                  1.028e-009  1.029e-009    -8.988    -8.988     0.000
O(0)            9.454e-038
   O2                    4.727e-038  4.730e-038   -37.325   -37.325     0.000
P               3.875e-006
   HPO4-2                2.608e-006  2.090e-006    -5.584    -5.680    -0.096
   CaHPO4                5.153e-007  5.156e-007    -6.288    -6.288     0.000
   CaPO4-                4.772e-007  4.515e-007    -6.321    -6.345    -0.024
   MgHPO4                9.318e-008  9.324e-008    -7.031    -7.030     0.000
   H2PO4-                8.982e-008  8.502e-008    -7.047    -7.071    -0.024
   MgPO4-                8.610e-008  8.146e-008    -7.065    -7.089    -0.024
   NaHPO4-               1.647e-009  1.558e-009    -8.783    -8.807    -0.024
   KHPO4-                1.238e-009  1.171e-009    -8.907    -8.931    -0.024
   CaH2PO4+              1.032e-009  9.760e-010    -8.987    -9.011    -0.024
   PO4-3                 5.709e-010  3.467e-010    -9.243    -9.460    -0.217
   MgH2PO4+              1.757e-010  1.662e-010    -9.755    -9.779    -0.024
S(6)            3.420e-004
   SO4-2                 3.138e-004  2.523e-004    -3.503    -3.598    -0.095
   CaSO4                 2.374e-005  2.375e-005    -4.625    -4.624     0.000
   MgSO4                 3.431e-006  3.433e-006    -5.465    -5.464     0.000
   NaSO4-                4.947e-007  4.681e-007    -6.306    -6.330    -0.024
   KSO4-                 4.927e-007  4.661e-007    -6.307    -6.331    -0.024
   HSO4-                 5.718e-011  5.410e-011   -10.243   -10.267    -0.024
   CaHSO4+               3.402e-013  3.219e-013   -12.468   -12.492    -0.024
```

```
------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.56   -6.90   -4.34  CaSO4
        Aragonite        -0.23   -8.53   -8.31  CaCO3
        Calcite          -0.08   -8.53   -8.45  CaCO3
        CH4(g)          -78.67  -81.49   -2.82  CH4
        CO2(g)           -4.28   -5.69   -1.41  CO2
        Dolomite         -0.97  -17.94  -16.97  CaMg(CO3)2
        Gypsum           -2.32   -6.90   -4.58  CaSO4:2H2O
        H2(g)           -25.22  -28.35   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    3.84    0.87   -2.97  Ca5(PO4)3OH
        O2(g)           -34.47  -37.33   -2.85  O2

Initial solution 7-Biochar 3 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 4.545e-004  4.545e-004
        Ca                6.963e-004  6.963e-004
        K                 7.878e-004  7.878e-004
        Mg                1.070e-004  1.070e-004
        N(-3)             1.664e-004  1.664e-004
        N(5)              2.346e-003  2.346e-003
        Na                1.527e-003  1.527e-003
        P                 1.292e-006  1.292e-006
        S(6)              5.060e-004  5.060e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.460
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  5.078e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.260e-004
                       Total CO2 (mol/kg)  =  4.545e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  3.026e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   3.93
                               Iterations  =   5
                                  Total H  = 1.110135e+002
                                  Total O  = 5.551661e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           5.9965      0.3488

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                   2.114e-007  1.958e-007    -6.675    -6.708    -0.033
   H+                    3.713e-008  3.467e-008    -7.430    -7.460    -0.030
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -71.093   -71.092     0.001
C(4)            4.545e-004
   HCO3-                 4.180e-004  3.884e-004    -3.379    -3.411    -0.032
   CO2                   3.241e-005  3.245e-005    -4.489    -4.489     0.001
   CaHCO3+               2.412e-006  2.241e-006    -5.618    -5.650    -0.032
```

```
   CO3-2                 6.332e-007  4.717e-007    -6.198    -6.326    -0.128
   MgHCO3+               3.633e-007  3.369e-007    -6.440    -6.473    -0.033
   CaCO3                 3.557e-007  3.561e-007    -6.449    -6.448     0.001
   NaHCO3                3.085e-007  3.088e-007    -6.511    -6.510     0.001
   MgCO3                 3.148e-008  3.152e-008    -7.502    -7.501     0.001
   NaCO3-                1.037e-008  9.611e-009    -7.984    -8.017    -0.033
Ca              6.963e-004
   Ca+2                  6.611e-004  4.923e-004    -3.180    -3.308    -0.128
   CaSO4                 3.221e-005  3.224e-005    -4.492    -4.492     0.001
   CaHCO3+               2.412e-006  2.241e-006    -5.618    -5.650    -0.032
   CaCO3                 3.557e-007  3.561e-007    -6.449    -6.448     0.001
   CaHPO4                1.375e-007  1.377e-007    -6.862    -6.861     0.001
   CaPO4-                9.207e-009  8.537e-009    -8.036    -8.069    -0.033
   CaH2PO4+              3.971e-009  3.682e-009    -8.401    -8.434    -0.033
   CaOH+                 2.541e-009  2.356e-009    -8.595    -8.628    -0.033
   CaHSO4+               6.657e-012  6.172e-012   -11.177   -11.210    -0.033
H(0)            1.789e-026
   H2                    8.943e-027  8.953e-027   -26.049   -26.048     0.001
K               7.878e-004
   K+                    7.861e-004  7.283e-004    -3.105    -3.138    -0.033
   KSO4-                 1.739e-006  1.612e-006    -5.760    -5.793    -0.033
   KHPO4-                8.592e-010  7.966e-010    -9.066    -9.099    -0.033
   KOH                   7.273e-011  7.282e-011   -10.138   -10.138     0.001
Mg              1.070e-004
   Mg+2                  1.012e-004  7.561e-005    -3.995    -4.121    -0.127
   MgSO4                 5.346e-006  5.352e-006    -5.272    -5.271     0.001
   MgHCO3+               3.633e-007  3.369e-007    -6.440    -6.473    -0.033
   MgCO3                 3.148e-008  3.152e-008    -7.502    -7.501     0.001
   MgHPO4                2.856e-008  2.859e-008    -7.544    -7.544     0.001
   MgOH+                 5.394e-009  5.001e-009    -8.268    -8.301    -0.033
   MgPO4-                1.908e-009  1.769e-009    -8.720    -8.752    -0.033
   MgH2PO4+              7.766e-010  7.201e-010    -9.110    -9.143    -0.033
N(-3)           1.664e-004
   NH4+                  1.639e-004  1.516e-004    -3.785    -3.819    -0.034
   NH3                   1.737e-006  1.739e-006    -5.760    -5.760     0.001
   NH4SO4-               7.250e-007  6.722e-007    -6.140    -6.172    -0.033
N(5)            2.346e-003
   NO3-                  2.346e-003  2.171e-003    -2.630    -2.663    -0.034
Na              1.527e-003
   Na+                   1.524e-003  1.414e-003    -2.817    -2.849    -0.033
   NaSO4-                2.548e-006  2.363e-006    -5.594    -5.627    -0.033
   NaHCO3                3.085e-007  3.088e-007    -6.511    -6.510     0.001
   NaCO3-                1.037e-008  9.611e-009    -7.984    -8.017    -0.033
   NaHPO4-               1.668e-009  1.547e-009    -8.778    -8.811    -0.033
   NaOH                  2.691e-010  2.694e-010    -9.570    -9.570     0.001
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -41.926   -41.925     0.001
P               1.292e-006
   HPO4-2                7.597e-007  5.610e-007    -6.119    -6.251    -0.132
   H2PO4-                3.475e-007  3.224e-007    -6.459    -6.492    -0.033
   CaHPO4                1.375e-007  1.377e-007    -6.862    -6.861     0.001
   MgHPO4                2.856e-008  2.859e-008    -7.544    -7.544     0.001
   CaPO4-                9.207e-009  8.537e-009    -8.036    -8.069    -0.033
   CaH2PO4+              3.971e-009  3.682e-009    -8.401    -8.434    -0.033
   MgPO4-                1.908e-009  1.769e-009    -8.720    -8.752    -0.033
   NaHPO4-               1.668e-009  1.547e-009    -8.778    -8.811    -0.033
   KHPO4-                8.592e-010  7.966e-010    -9.066    -9.099    -0.033
   MgH2PO4+              7.766e-010  7.201e-010    -9.110    -9.143    -0.033
   PO4-3                 1.304e-011  6.589e-012   -10.885   -11.181    -0.296
S(6)            5.060e-004
   SO4-2                 4.635e-004  3.443e-004    -3.334    -3.463    -0.129
   CaSO4                 3.221e-005  3.224e-005    -4.492    -4.492     0.001
   MgSO4                 5.346e-006  5.352e-006    -5.272    -5.271     0.001
   NaSO4-                2.548e-006  2.363e-006    -5.594    -5.627    -0.033
   KSO4-                 1.739e-006  1.612e-006    -5.760    -5.793    -0.033
   NH4SO4-               7.250e-007  6.722e-007    -6.140    -6.172    -0.033
   HSO4-                 1.125e-009  1.043e-009    -8.949    -8.982    -0.033
   CaHSO4+               6.657e-012  6.172e-012   -11.177   -11.210    -0.033
```

```
------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.43   -6.77   -4.34  CaSO4
        Aragonite        -1.33   -9.63   -8.31  CaCO3
        Calcite          -1.18   -9.63   -8.45  CaCO3
        CH4(g)          -68.27  -71.09   -2.82  CH4
        CO2(g)           -3.08   -4.49   -1.41  CO2
        Dolomite         -3.11  -20.08  -16.97  CaMg(CO3)2
        Gypsum           -2.19   -6.77   -4.58  CaSO4:2H2O
        H2(g)           -22.92  -26.05   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite   -2.48   -5.45   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.63   -5.76    1.87  NH3
        O2(g)           -39.07  -41.93   -2.85  O2

Initial solution 8-Biochar 10 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                3.221e-004  3.221e-004
        Ca               4.217e-004  4.217e-004
        K                8.697e-004  8.697e-004
        Mg               9.668e-005  9.668e-005
        N(-3)            2.756e-004  2.756e-004
        N(5)             7.876e-004  7.876e-004
        Na               1.344e-003  1.344e-003
        P                2.196e-005  2.196e-005
        S(6)             4.204e-004  4.204e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.220
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  3.578e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.987e-004
                       Total CO2 (mol/kg)  =  3.221e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  1.577e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  29.42
                               Iterations  =   8
                                  Total H  = 1.110138e+002
                                  Total O  = 5.551128e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.2095      0.3612

----------------------------Distribution of species----------------------------

                                                      Log       Log         Log 
   Species                    Molality    Activity  Molality  Activity     Gamma

   OH-                      1.202e-007  1.127e-007    -6.920    -6.948    -0.028
   H+                       6.393e-008  6.026e-008    -7.194    -7.220    -0.026
   H2O                      5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                      0.000e+000  0.000e+000   -69.099   -69.099     0.000
C(4)            3.221e-004
   HCO3-                    2.819e-004  2.647e-004    -3.550    -3.577    -0.027
```

```
   CO2                 3.840e-005  3.843e-005     -4.416    -4.415     0.000
   CaHCO3+             1.030e-006  9.671e-007     -5.987    -6.015    -0.027
   CO3-2               2.379e-007  1.850e-007     -6.624    -6.733    -0.109
   MgHCO3+             2.310e-007  2.166e-007     -6.636    -6.664    -0.028
   NaHCO3              1.873e-007  1.874e-007     -6.728    -6.727     0.000
   CaCO3               8.838e-008  8.845e-008     -7.054    -7.053     0.000
   MgCO3               1.165e-008  1.166e-008     -7.934    -7.933     0.000
   NaCO3-              3.579e-009  3.356e-009     -8.446    -8.474    -0.028
Ca                4.217e-004
   Ca+2                4.011e-004  3.117e-004     -3.397    -3.506    -0.109
   CaSO4               1.808e-005  1.809e-005     -4.743    -4.743     0.000
   CaHPO4              1.319e-006  1.321e-006     -5.880    -5.879     0.000
   CaHCO3+             1.030e-006  9.671e-007     -5.987    -6.015    -0.027
   CaCO3               8.838e-008  8.845e-008     -7.054    -7.053     0.000
   CaH2PO4+            6.544e-008  6.136e-008     -7.184    -7.212    -0.028
   CaPO4-              5.025e-008  4.711e-008     -7.299    -7.327    -0.028
   CaOH+               9.156e-010  8.585e-010     -9.038    -9.066    -0.028
   CaHSO4+             6.418e-012  6.018e-012    -11.193   -11.221    -0.028
H(0)              5.403e-026
   H2                  2.702e-026  2.704e-026    -25.568   -25.568     0.000
K                 8.697e-004
   K+                  8.679e-004  8.133e-004     -3.062    -3.090    -0.028
   KSO4-               1.701e-006  1.595e-006     -5.769    -5.797    -0.028
   KHPO4-              1.437e-008  1.347e-008     -7.843    -7.870    -0.028
   KOH                 4.676e-011  4.680e-011    -10.330   -10.330     0.000
Mg                9.668e-005
   Mg+2                9.152e-005  7.131e-005     -4.038    -4.147    -0.108
   MgSO4               4.469e-006  4.472e-006     -5.350    -5.349     0.000
   MgHPO4              4.081e-007  4.084e-007     -6.389    -6.389     0.000
   MgHCO3+             2.310e-007  2.166e-007     -6.636    -6.664    -0.028
   MgH2PO4+            1.906e-008  1.788e-008     -7.720    -7.748    -0.028
   MgPO4-              1.550e-008  1.454e-008     -7.810    -7.838    -0.028
   MgCO3               1.165e-008  1.166e-008     -7.934    -7.933     0.000
   MgOH+               2.895e-009  2.714e-009     -8.538    -8.566    -0.028
N(-3)             2.756e-004
   NH4+                2.729e-004  2.554e-004     -3.564    -3.593    -0.029
   NH3                 1.685e-006  1.686e-006     -5.774    -5.773     0.000
   NH4SO4-             1.070e-006  1.003e-006     -5.971    -5.999    -0.028
N(5)              7.876e-004
   NO3-                7.876e-004  7.375e-004     -3.104    -3.132    -0.029
Na                1.344e-003
   Na+                 1.342e-003  1.259e-003     -2.872    -2.900    -0.028
   NaSO4-              1.987e-006  1.863e-006     -5.702    -5.730    -0.028
   NaHCO3              1.873e-007  1.874e-007     -6.728    -6.727     0.000
   NaHPO4-             2.225e-008  2.086e-008     -7.653    -7.681    -0.028
   NaCO3-              3.579e-009  3.356e-009     -8.446    -8.474    -0.028
   NaOH                1.379e-010  1.380e-010     -9.860    -9.860     0.000
O(0)              0.000e+000
   O2                  0.000e+000  0.000e+000    -42.886   -42.885     0.000
P                 2.196e-005
   HPO4-2              1.100e-005  8.497e-006     -4.959    -5.071    -0.112
   H2PO4-              9.045e-006  8.485e-006     -5.044    -5.071    -0.028
   CaHPO4              1.319e-006  1.321e-006     -5.880    -5.879     0.000
   MgHPO4              4.081e-007  4.084e-007     -6.389    -6.389     0.000
   CaH2PO4+            6.544e-008  6.136e-008     -7.184    -7.212    -0.028
   CaPO4-              5.025e-008  4.711e-008     -7.299    -7.327    -0.028
   NaHPO4-             2.225e-008  2.086e-008     -7.653    -7.681    -0.028
   MgH2PO4+            1.906e-008  1.788e-008     -7.720    -7.748    -0.028
   MgPO4-              1.550e-008  1.454e-008     -7.810    -7.838    -0.028
   KHPO4-              1.437e-008  1.347e-008     -7.843    -7.870    -0.028
   PO4-3               1.026e-010  5.743e-011     -9.989   -10.241    -0.252
S(6)              4.204e-004
   SO4-2               3.931e-004  3.050e-004     -3.405    -3.516    -0.110
   CaSO4               1.808e-005  1.809e-005     -4.743    -4.743     0.000
   MgSO4               4.469e-006  4.472e-006     -5.350    -5.349     0.000
   NaSO4-              1.987e-006  1.863e-006     -5.702    -5.730    -0.028
   KSO4-               1.701e-006  1.595e-006     -5.769    -5.797    -0.028
   NH4SO4-             1.070e-006  1.003e-006     -5.971    -5.999    -0.028
```

```
   HSO4-                 1.713e-009  1.606e-009    -8.766    -8.794    -0.028
   CaHSO4+               6.418e-012  6.018e-012   -11.193   -11.221    -0.028

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.68   -7.02   -4.34  CaSO4
        Aragonite        -1.93  -10.24   -8.31  CaCO3
        Calcite          -1.79  -10.24   -8.45  CaCO3
        CH4(g)          -66.28  -69.10   -2.82  CH4
        CO2(g)           -3.01   -4.42   -1.41  CO2
        Dolomite         -4.15  -21.12  -16.97  CaMg(CO3)2
        Gypsum           -2.44   -7.02   -4.58  CaSO4:2H2O
        H2(g)           -22.44  -25.57   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite   -0.89   -3.86   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.65   -5.77    1.87  NH3
        O2(g)           -40.03  -42.89   -2.85  O2

Initial solution 9-Biochar 18 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                2.257e-004  2.257e-004
        Ca               3.032e-004  3.032e-004
        K                6.177e-004  6.177e-004
        Mg               6.993e-005  6.993e-005
        N(-3)            2.164e-004  2.164e-004
        N(5)             6.333e-004  6.333e-004
        Na               7.635e-004  7.635e-004
        P                9.429e-005  9.429e-005
        S(6)             4.315e-004  4.315e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.050
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  2.834e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.336e-004
                       Total CO2 (mol/kg)  =  2.257e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  5.195e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  12.77
                               Iterations  =   9
                                  Total H  = 1.110136e+002
                                  Total O  = 5.551086e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.4232      0.3736

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   H+                    9.402e-008  8.913e-008    -7.027    -7.050    -0.023
   OH-                   8.075e-008  7.617e-008    -7.093    -7.118    -0.025
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -67.744   -67.744     0.000
```

```
C(4)            2.257e-004
   HCO3-                 1.870e-004  1.767e-004    -3.728    -3.753    -0.025
   CO2                   3.791e-005  3.794e-005    -4.421    -4.421     0.000
   CaHCO3+               4.972e-007  4.698e-007    -6.303    -6.328    -0.025
   MgHCO3+               1.117e-007  1.054e-007    -6.952    -6.977    -0.025
   CO3-2                 1.047e-007  8.349e-008    -6.980    -7.078    -0.098
   NaHCO3                7.145e-008  7.150e-008    -7.146    -7.146     0.000
   CaCO3                 2.903e-008  2.905e-008    -7.537    -7.537     0.000
   MgCO3                 3.835e-009  3.837e-009    -8.416    -8.416     0.000
   NaCO3-                9.171e-010  8.656e-010    -9.038    -9.063    -0.025
Ca              3.032e-004
   Ca+2                  2.846e-004  2.269e-004    -3.546    -3.644    -0.098
   CaSO4                 1.410e-005  1.411e-005    -4.851    -4.850     0.000
   CaHPO4                3.565e-006  3.567e-006    -5.448    -5.448     0.000
   CaHCO3+               4.972e-007  4.698e-007    -6.303    -6.328    -0.025
   CaH2PO4+              2.598e-007  2.452e-007    -6.585    -6.611    -0.025
   CaPO4-                9.116e-008  8.604e-008    -7.040    -7.065    -0.025
   CaCO3                 2.903e-008  2.905e-008    -7.537    -7.537     0.000
   CaOH+                 4.476e-010  4.225e-010    -9.349    -9.374    -0.025
   CaHSO4+               7.356e-012  6.942e-012   -11.133   -11.158    -0.025
H(0)            1.182e-025
   H2                    5.912e-026  5.915e-026   -25.228   -25.228     0.000
K               6.177e-004
   K+                    6.164e-004  5.815e-004    -3.210    -3.235    -0.025
   KSO4-                 1.295e-006  1.222e-006    -5.888    -5.913    -0.025
   KHPO4-                3.788e-008  3.575e-008    -7.422    -7.447    -0.025
   KOH                   2.261e-011  2.262e-011   -10.646   -10.645     0.000
Mg              6.993e-005
   Mg+2                  6.511e-005  5.201e-005    -4.186    -4.284    -0.098
   MgSO4                 3.493e-006  3.496e-006    -5.457    -5.456     0.000
   MgHPO4                1.105e-006  1.106e-006    -5.957    -5.956     0.000
   MgHCO3+               1.117e-007  1.054e-007    -6.952    -6.977    -0.025
   MgH2PO4+              7.583e-008  7.157e-008    -7.120    -7.145    -0.025
   MgPO4-                2.819e-008  2.661e-008    -7.550    -7.575    -0.025
   MgCO3                 3.835e-009  3.837e-009    -8.416    -8.416     0.000
   MgOH+                 1.418e-009  1.339e-009    -8.848    -8.873    -0.025
N(-3)           2.164e-004
   NH4+                  2.145e-004  2.022e-004    -3.668    -3.694    -0.026
   NH4SO4-               9.019e-007  8.513e-007    -6.045    -6.070    -0.025
   NH3                   9.019e-007  9.025e-007    -6.045    -6.045     0.000
N(5)            6.333e-004
   NO3-                  6.333e-004  5.972e-004    -3.198    -3.224    -0.026
Na              7.635e-004
   Na+                   7.621e-004  7.196e-004    -3.118    -3.143    -0.025
   NaSO4-                1.209e-006  1.141e-006    -5.917    -5.943    -0.025
   NaHCO3                7.145e-008  7.150e-008    -7.146    -7.146     0.000
   NaHPO4-               4.688e-008  4.425e-008    -7.329    -7.354    -0.025
   NaCO3-                9.171e-010  8.656e-010    -9.038    -9.063    -0.025
   NaOH                  5.331e-011  5.334e-011   -10.273   -10.273     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -43.565   -43.565     0.000
P               9.429e-005
   H2PO4-                4.933e-005  4.657e-005    -4.307    -4.332    -0.025
   HPO4-2                3.975e-005  3.153e-005    -4.401    -4.501    -0.101
   CaHPO4                3.565e-006  3.567e-006    -5.448    -5.448     0.000
   MgHPO4                1.105e-006  1.106e-006    -5.957    -5.956     0.000
   CaH2PO4+              2.598e-007  2.452e-007    -6.585    -6.611    -0.025
   CaPO4-                9.116e-008  8.604e-008    -7.040    -7.065    -0.025
   MgH2PO4+              7.583e-008  7.157e-008    -7.120    -7.145    -0.025
   NaHPO4-               4.688e-008  4.425e-008    -7.329    -7.354    -0.025
   KHPO4-                3.788e-008  3.575e-008    -7.422    -7.447    -0.025
   MgPO4-                2.819e-008  2.661e-008    -7.550    -7.575    -0.025
   PO4-3                 2.426e-010  1.441e-010    -9.615    -9.841    -0.226
S(6)            4.315e-004
   SO4-2                 4.105e-004  3.268e-004    -3.387    -3.486    -0.099
   CaSO4                 1.410e-005  1.411e-005    -4.851    -4.850     0.000
   MgSO4                 3.493e-006  3.496e-006    -5.457    -5.456     0.000
   KSO4-                 1.295e-006  1.222e-006    -5.888    -5.913    -0.025
```

```
   NaSO4-                1.209e-006  1.141e-006    -5.917    -5.943    -0.025
   NH4SO4-               9.019e-007  8.513e-007    -6.045    -6.070    -0.025
   HSO4-                 2.696e-009  2.545e-009    -8.569    -8.594    -0.025
   CaHSO4+               7.356e-012  6.942e-012   -11.133   -11.158    -0.025

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.79   -7.13   -4.34  CaSO4
        Aragonite        -2.42  -10.72   -8.31  CaCO3
        Calcite          -2.27  -10.72   -8.45  CaCO3
        CH4(g)          -64.93  -67.74   -2.82  CH4
        CO2(g)           -3.01   -4.42   -1.41  CO2
        Dolomite         -5.11  -22.08  -16.97  CaMg(CO3)2
        Gypsum           -2.55   -7.13   -4.58  CaSO4:2H2O
        H2(g)           -22.10  -25.23   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite   -0.56   -3.52   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.92   -6.04    1.87  NH3
        O2(g)           -40.71  -43.57   -2.85  O2

Initial solution 10-Biochar 42 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 2.137e-004  2.137e-004
        Ca                1.759e-004  1.759e-004
        K                 4.514e-004  4.514e-004
        Mg                5.142e-005  5.142e-005
        N(-3)             2.178e-004  2.178e-004
        N(5)              7.448e-004  7.448e-004
        Na                8.657e-004  8.657e-004
        P                 9.526e-005  9.526e-005
        S(6)              7.049e-004  7.049e-004

----------------------------Description of solution----------------------------

                                       pH  =   6.790
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  3.088e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.875e-004
                       Total CO2 (mol/kg)  =  2.137e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -4.478e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -10.32
                               Iterations  =   9
                                  Total H  = 1.110136e+002
                                  Total O  = 5.551224e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.7567      0.3930

----------------------------Distribution of species----------------------------

                                                         Log       Log       Log
   Species               Molality    Activity  Molality  Activity     Gamma

   H+                    1.714e-007  1.622e-007    -6.766    -6.790    -0.024
   OH-                   4.448e-008  4.186e-008    -7.352    -7.378    -0.026
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
```

```
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -65.484   -65.484     0.000
C(4)            2.137e-004
   HCO3-                 1.559e-004  1.470e-004    -3.807    -3.833    -0.026
   CO2                   5.740e-005  5.744e-005    -4.241    -4.241     0.000
   CaHCO3+               2.324e-007  2.191e-007    -6.634    -6.659    -0.026
   NaHCO3                6.719e-008  6.723e-008    -7.173    -7.172     0.000
   MgHCO3+               6.613e-008  6.227e-008    -7.180    -7.206    -0.026
   CO3-2                 4.830e-008  3.817e-008    -7.316    -7.418    -0.102
   CaCO3                 7.442e-009  7.447e-009    -8.128    -8.128     0.000
   MgCO3                 1.245e-009  1.245e-009    -8.905    -8.905     0.000
   NaCO3-                4.751e-010  4.473e-010    -9.323    -9.349    -0.026
Ca              1.759e-004
   Ca+2                  1.610e-004  1.272e-004    -3.793    -3.896    -0.102
   CaSO4                 1.302e-005  1.303e-005    -4.885    -4.885     0.000
   CaHPO4                1.427e-006  1.428e-006    -5.845    -5.845     0.000
   CaHCO3+               2.324e-007  2.191e-007    -6.634    -6.659    -0.026
   CaH2PO4+              1.897e-007  1.786e-007    -6.722    -6.748    -0.026
   CaPO4-                2.011e-008  1.893e-008    -7.697    -7.723    -0.026
   CaCO3                 7.442e-009  7.447e-009    -8.128    -8.128     0.000
   CaOH+                 1.382e-010  1.302e-010    -9.859    -9.886    -0.026
   CaHSO4+               1.239e-011  1.167e-011   -10.907   -10.933    -0.026
H(0)            3.915e-025
   H2                    1.957e-025  1.959e-025   -24.708   -24.708     0.000
K               4.514e-004
   K+                    4.499e-004  4.234e-004    -3.347    -3.373    -0.026
   KSO4-                 1.557e-006  1.466e-006    -5.808    -5.834    -0.026
   KHPO4-                1.975e-008  1.859e-008    -7.704    -7.731    -0.026
   KOH                   9.045e-012  9.052e-012   -11.044   -11.043     0.000
Mg              5.142e-005
   Mg+2                  4.663e-005  3.692e-005    -4.331    -4.433    -0.101
   MgSO4                 4.084e-006  4.087e-006    -5.389    -5.389     0.000
   MgHPO4                5.602e-007  5.606e-007    -6.252    -6.251     0.000
   MgH2PO4+              7.012e-008  6.603e-008    -7.154    -7.180    -0.026
   MgHCO3+               6.613e-008  6.227e-008    -7.180    -7.206    -0.026
   MgPO4-                7.872e-009  7.413e-009    -8.104    -8.130    -0.026
   MgCO3                 1.245e-009  1.245e-009    -8.905    -8.905     0.000
   MgOH+                 5.545e-010  5.221e-010    -9.256    -9.282    -0.026
N(-3)           2.178e-004
   NH4+                  2.158e-004  2.029e-004    -3.666    -3.693    -0.027
   NH4SO4-               1.494e-006  1.407e-006    -5.826    -5.852    -0.026
   NH3                   4.972e-007  4.976e-007    -6.303    -6.303     0.000
N(5)            7.448e-004
   NO3-                  7.448e-004  7.005e-004    -3.128    -3.155    -0.027
Na              8.657e-004
   Na+                   8.634e-004  8.133e-004    -3.064    -3.090    -0.026
   NaSO4-                2.257e-006  2.125e-006    -5.647    -5.673    -0.026
   NaHCO3                6.719e-008  6.723e-008    -7.173    -7.172     0.000
   NaHPO4-               3.793e-008  3.572e-008    -7.421    -7.447    -0.026
   NaCO3-                4.751e-010  4.473e-010    -9.323    -9.349    -0.026
   NaOH                  3.311e-011  3.313e-011   -10.480   -10.480     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -44.605   -44.605     0.000
P               9.526e-005
   H2PO4-                6.426e-005  6.054e-005    -4.192    -4.218    -0.026
   HPO4-2                2.866e-005  2.252e-005    -4.543    -4.647    -0.105
   CaHPO4                1.427e-006  1.428e-006    -5.845    -5.845     0.000
   MgHPO4                5.602e-007  5.606e-007    -6.252    -6.251     0.000
   CaH2PO4+              1.897e-007  1.786e-007    -6.722    -6.748    -0.026
   MgH2PO4+              7.012e-008  6.603e-008    -7.154    -7.180    -0.026
   NaHPO4-               3.793e-008  3.572e-008    -7.421    -7.447    -0.026
   CaPO4-                2.011e-008  1.893e-008    -7.697    -7.723    -0.026
   KHPO4-                1.975e-008  1.859e-008    -7.704    -7.731    -0.026
   MgPO4-                7.872e-009  7.413e-009    -8.104    -8.130    -0.026
   PO4-3                 9.727e-011  5.656e-011   -10.012   -10.247    -0.235
S(6)            7.049e-004
   SO4-2                 6.825e-004  5.384e-004    -3.166    -3.269    -0.103
   CaSO4                 1.302e-005  1.303e-005    -4.885    -4.885     0.000
```

```
   MgSO4                 4.084e-006  4.087e-006    -5.389    -5.389     0.000
   NaSO4-                2.257e-006  2.125e-006    -5.647    -5.673    -0.026
   KSO4-                 1.557e-006  1.466e-006    -5.808    -5.834    -0.026
   NH4SO4-               1.494e-006  1.407e-006    -5.826    -5.852    -0.026
   HSO4-                 8.102e-009  7.629e-009    -8.091    -8.118    -0.026
   CaHSO4+               1.239e-011  1.167e-011   -10.907   -10.933    -0.026

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.82   -7.16   -4.34  CaSO4
        Aragonite        -3.01  -11.31   -8.31  CaCO3
        Calcite          -2.86  -11.31   -8.45  CaCO3
        CH4(g)          -62.67  -65.48   -2.82  CH4
        CO2(g)           -2.83   -4.24   -1.41  CO2
        Dolomite         -6.19  -23.16  -16.97  CaMg(CO3)2
        Gypsum           -2.58   -7.16   -4.58  CaSO4:2H2O
        H2(g)           -21.58  -24.71   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite   -3.29   -6.26   -2.97  Ca5(PO4)3OH
        NH3(g)           -8.18   -6.30    1.87  NH3
        O2(g)           -41.75  -44.61   -2.85  O2

Initial solution 11-Biochar 100 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                2.408e-004  2.408e-004
        Ca               1.759e-004  1.759e-004
        K                3.709e-004  3.709e-004
        Mg               7.611e-005  7.611e-005
        N(5)             7.619e-004  7.619e-004
        Na               1.333e-003  1.333e-003
        P                6.490e-005  6.490e-005
        S(6)             7.998e-004  7.998e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.330
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  3.432e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.590e-004
                       Total CO2 (mol/kg)  =  2.408e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -4.771e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -9.97
                               Iterations  =  10
                                  Total H  = 1.110127e+002
                                  Total O  = 5.551266e+001

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                   1.547e-007  1.451e-007    -6.810    -6.838    -0.028
   H+                    4.957e-008  4.677e-008    -7.305    -7.330    -0.025
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -70.202   -70.202     0.000
C(4)            2.408e-004
   HCO3-                 2.169e-004  2.040e-004    -3.664    -3.690    -0.027
   CO2                   2.297e-005  2.298e-005    -4.639    -4.639     0.000
```

```
   CaHCO3+              3.163e-007  2.974e-007    -6.500    -6.527    -0.027
   CO3-2                2.351e-007  1.836e-007    -6.629    -6.736    -0.107
   NaHCO3               1.431e-007  1.432e-007    -6.844    -6.844     0.000
   MgHCO3+              1.331e-007  1.249e-007    -6.876    -6.903    -0.027
   CaCO3                3.502e-008  3.504e-008    -7.456    -7.455     0.000
   MgCO3                8.657e-009  8.664e-009    -8.063    -8.062     0.000
   NaCO3-               3.519e-009  3.303e-009    -8.454    -8.481    -0.027
Ca              1.759e-004
   Ca+2                 1.593e-004  1.244e-004    -3.798    -3.905    -0.107
   CaSO4                1.427e-005  1.428e-005    -4.846    -4.845     0.000
   CaHPO4               1.810e-006  1.811e-006    -5.742    -5.742     0.000
   CaHCO3+              3.163e-007  2.974e-007    -6.500    -6.527    -0.027
   CaPO4-               8.866e-008  8.324e-008    -7.052    -7.080    -0.027
   CaH2PO4+             6.958e-008  6.532e-008    -7.157    -7.185    -0.027
   CaCO3                3.502e-008  3.504e-008    -7.456    -7.455     0.000
   CaOH+                4.702e-010  4.414e-010    -9.328    -9.355    -0.027
   CaHSO4+              3.927e-012  3.687e-012   -11.406   -11.433    -0.027
H(0)            3.256e-026
   H2                   1.628e-026  1.629e-026   -25.788   -25.788     0.000
K               3.709e-004
   K+                   3.694e-004  3.466e-004    -3.432    -3.460    -0.028
   KSO4-                1.432e-006  1.344e-006    -5.844    -5.872    -0.027
   KHPO4-               2.102e-008  1.973e-008    -7.677    -7.705    -0.027
   KOH                  2.567e-011  2.569e-011   -10.591   -10.590     0.000
Mg              7.611e-005
   Mg+2                 6.821e-005  5.339e-005    -4.166    -4.273    -0.106
   MgSO4                6.616e-006  6.621e-006    -5.179    -5.179     0.000
   MgHPO4               1.050e-006  1.051e-006    -5.979    -5.978     0.000
   MgHCO3+              1.331e-007  1.249e-007    -6.876    -6.903    -0.027
   MgPO4-               5.132e-008  4.818e-008    -7.290    -7.317    -0.027
   MgH2PO4+             3.802e-008  3.570e-008    -7.420    -7.447    -0.027
   MgCO3                8.657e-009  8.664e-009    -8.063    -8.062     0.000
   MgOH+                2.789e-009  2.618e-009    -8.555    -8.582    -0.027
N(5)            7.619e-004
   NO3-                 7.619e-004  7.144e-004    -3.118    -3.146    -0.028
Na              1.333e-003
   Na+                  1.329e-003  1.249e-003    -2.876    -2.904    -0.027
   NaSO4-               3.892e-006  3.654e-006    -5.410    -5.437    -0.027
   NaHCO3               1.431e-007  1.432e-007    -6.844    -6.844     0.000
   NaHPO4-              7.571e-008  7.107e-008    -7.121    -7.148    -0.027
   NaCO3-               3.519e-009  3.303e-009    -8.454    -8.481    -0.027
   NaOH                 1.762e-010  1.763e-010    -9.754    -9.754     0.000
O(0)            0.000e+000
   O2                   0.000e+000  0.000e+000   -42.446   -42.445     0.000
P               6.490e-005
   HPO4-2               3.760e-005  2.920e-005    -4.425    -4.535    -0.110
   H2PO4-               2.410e-005  2.263e-005    -4.618    -4.645    -0.027
   CaHPO4               1.810e-006  1.811e-006    -5.742    -5.742     0.000
   MgHPO4               1.050e-006  1.051e-006    -5.979    -5.978     0.000
   CaPO4-               8.866e-008  8.324e-008    -7.052    -7.080    -0.027
   NaHPO4-              7.571e-008  7.107e-008    -7.121    -7.148    -0.027
   CaH2PO4+             6.958e-008  6.532e-008    -7.157    -7.185    -0.027
   MgPO4-               5.132e-008  4.818e-008    -7.290    -7.317    -0.027
   MgH2PO4+             3.802e-008  3.570e-008    -7.420    -7.447    -0.027
   KHPO4-               2.102e-008  1.973e-008    -7.677    -7.705    -0.027
   PO4-3                4.493e-010  2.542e-010    -9.347    -9.595    -0.247
S(6)            7.998e-004
   SO4-2                7.736e-004  6.031e-004    -3.111    -3.220    -0.108
   CaSO4                1.427e-005  1.428e-005    -4.846    -4.845     0.000
   MgSO4                6.616e-006  6.621e-006    -5.179    -5.179     0.000
   NaSO4-               3.892e-006  3.654e-006    -5.410    -5.437    -0.027
   KSO4-                1.432e-006  1.344e-006    -5.844    -5.872    -0.027
   HSO4-                2.625e-009  2.465e-009    -8.581    -8.608    -0.027
   CaHSO4+              3.927e-012  3.687e-012   -11.406   -11.433    -0.027

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT
```

```
        Anhydrite         -2.78   -7.12   -4.34  CaSO4
        Aragonite         -2.34  -10.64   -8.31  CaCO3
        Calcite           -2.19  -10.64   -8.45  CaCO3
        CH4(g)           -67.38  -70.20   -2.82  CH4
        CO2(g)            -3.23   -4.64   -1.41  CO2
        Dolomite          -4.68  -21.65  -16.97  CaMg(CO3)2
        Gypsum            -2.54   -7.12   -4.58  CaSO4:2H2O
        H2(g)            -22.66  -25.79   -3.13  H2
        H2O(g)            -1.64   -0.00    1.64  H2O
        Hydroxyapatite    -0.84   -3.81   -2.97  Ca5(PO4)3OH
        O2(g)            -39.59  -42.45   -2.85  O2

Initial solution 12-Biochar 200 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 4.516e-004  4.516e-004
        Ca                4.741e-004  4.741e-004
        K                 1.982e-004  1.982e-004
        Mg                2.715e-004  2.715e-004
        N(-3)             1.078e-004  1.078e-004
        N(5)              1.062e-003  1.062e-003
        Na                1.081e-003  1.081e-003
        P                 6.458e-007  6.458e-007
        S(6)              1.017e-003  1.017e-003

----------------------------Description of solution----------------------------

                                       pH  =   7.340
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  4.659e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.120e-004
                       Total CO2 (mol/kg)  =  4.516e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -6.300e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -10.35
                               Iterations  =   6
                                  Total H  = 1.110133e+002
                                  Total O  = 5.551479e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.1271      0.3564

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                    1.599e-007  1.485e-007    -6.796    -6.828    -0.032
   H+                     4.883e-008  4.571e-008    -7.311    -7.340    -0.029
   H2O                    5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)            0.000e+000
   CH4                    0.000e+000  0.000e+000   -70.023   -70.023     0.000
C(4)             4.516e-004
   HCO3-                  4.066e-004  3.788e-004    -3.391    -3.422    -0.031
   CO2                    4.167e-005  4.172e-005    -4.380    -4.380     0.000
   CaHCO3+                1.539e-006  1.434e-006    -5.813    -5.843    -0.031
   MgHCO3+                8.607e-007  8.004e-007    -6.065    -6.097    -0.032
   CO3-2                  4.633e-007  3.490e-007    -6.334    -6.457    -0.123
   NaHCO3                 2.133e-007  2.135e-007    -6.671    -6.671     0.000
```

```
   CaCO3                 1.727e-007  1.729e-007    -6.763    -6.762     0.000
   MgCO3                 5.674e-008  5.680e-008    -7.246    -7.246     0.000
   NaCO3-                5.420e-009  5.040e-009    -8.266    -8.298    -0.032
Ca              4.741e-004
   Ca+2                  4.290e-004  3.230e-004    -3.368    -3.491    -0.123
   CaSO4                 4.341e-005  4.346e-005    -4.362    -4.362     0.000
   CaHCO3+               1.539e-006  1.434e-006    -5.813    -5.843    -0.031
   CaCO3                 1.727e-007  1.729e-007    -6.763    -6.762     0.000
   CaHPO4                4.215e-008  4.219e-008    -7.375    -7.375     0.000
   CaPO4-                2.134e-009  1.984e-009    -8.671    -8.702    -0.032
   CaH2PO4+              1.599e-009  1.487e-009    -8.796    -8.828    -0.032
   CaOH+                 1.261e-009  1.173e-009    -8.899    -8.931    -0.032
   CaHSO4+               1.179e-011  1.097e-011   -10.928   -10.960    -0.032
H(0)            3.109e-026
   H2                    1.554e-026  1.556e-026   -25.808   -25.808     0.000
K               1.982e-004
   K+                    1.973e-004  1.834e-004    -3.705    -3.737    -0.032
   KSO4-                 8.966e-007  8.337e-007    -6.047    -6.079    -0.032
   KHPO4-                1.007e-010  9.368e-011    -9.997   -10.028    -0.032
   KOH                   1.389e-011  1.391e-011   -10.857   -10.857     0.000
Mg              2.715e-004
   Mg+2                  2.438e-004  1.842e-004    -3.613    -3.735    -0.122
   MgSO4                 2.675e-005  2.678e-005    -4.573    -4.572     0.000
   MgHCO3+               8.607e-007  8.004e-007    -6.065    -6.097    -0.032
   MgCO3                 5.674e-008  5.680e-008    -7.246    -7.246     0.000
   MgHPO4                3.249e-008  3.253e-008    -7.488    -7.488     0.000
   MgOH+                 9.938e-009  9.241e-009    -8.003    -8.034    -0.032
   MgPO4-                1.641e-009  1.526e-009    -8.785    -8.816    -0.032
   MgH2PO4+              1.161e-009  1.080e-009    -8.935    -8.967    -0.032
N(-3)           1.078e-004
   NH4+                  1.060e-004  9.833e-005    -3.975    -4.007    -0.033
   NH4SO4-               9.633e-007  8.958e-007    -6.016    -6.048    -0.032
   NH3                   8.549e-007  8.558e-007    -6.068    -6.068     0.000
N(5)            1.062e-003
   NO3-                  1.062e-003  9.857e-004    -2.974    -3.006    -0.032
Na              1.081e-003
   Na+                   1.077e-003  1.002e-003    -2.968    -2.999    -0.031
   NaSO4-                3.699e-006  3.440e-006    -5.432    -5.463    -0.032
   NaHCO3                2.133e-007  2.135e-007    -6.671    -6.671     0.000
   NaCO3-                5.420e-009  5.040e-009    -8.266    -8.298    -0.032
   NaHPO4-               5.507e-010  5.121e-010    -9.259    -9.291    -0.032
   NaOH                  1.447e-010  1.449e-010    -9.839    -9.839     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -42.406   -42.405     0.000
P               6.458e-007
   HPO4-2                3.507e-007  2.620e-007    -6.455    -6.582    -0.127
   H2PO4-                2.133e-007  1.985e-007    -6.671    -6.702    -0.031
   CaHPO4                4.215e-008  4.219e-008    -7.375    -7.375     0.000
   MgHPO4                3.249e-008  3.253e-008    -7.488    -7.488     0.000
   CaPO4-                2.134e-009  1.984e-009    -8.671    -8.702    -0.032
   MgPO4-                1.641e-009  1.526e-009    -8.785    -8.816    -0.032
   CaH2PO4+              1.599e-009  1.487e-009    -8.796    -8.828    -0.032
   MgH2PO4+              1.161e-009  1.080e-009    -8.935    -8.967    -0.032
   NaHPO4-               5.507e-010  5.121e-010    -9.259    -9.291    -0.032
   KHPO4-                1.007e-010  9.368e-011    -9.997   -10.028    -0.032
   PO4-3                 4.498e-012  2.335e-012   -11.347   -11.632    -0.285
S(6)            1.017e-003
   SO4-2                 9.413e-004  7.071e-004    -3.026    -3.150    -0.124
   CaSO4                 4.341e-005  4.346e-005    -4.362    -4.362     0.000
   MgSO4                 2.675e-005  2.678e-005    -4.573    -4.572     0.000
   NaSO4-                3.699e-006  3.440e-006    -5.432    -5.463    -0.032
   NH4SO4-               9.633e-007  8.958e-007    -6.016    -6.048    -0.032
   KSO4-                 8.966e-007  8.337e-007    -6.047    -6.079    -0.032
   HSO4-                 3.037e-009  2.824e-009    -8.518    -8.549    -0.032
   CaHSO4+               1.179e-011  1.097e-011   -10.928   -10.960    -0.032

------------------------------Saturation indices-------------------------------
```

```
        Phase               SI log IAP  log KT

        Anhydrite        -2.30   -6.64   -4.34  CaSO4
        Aragonite        -1.64   -9.95   -8.31  CaCO3
        Calcite          -1.49   -9.95   -8.45  CaCO3
        CH4(g)          -67.21  -70.02   -2.82  CH4
        CO2(g)           -2.97   -4.38   -1.41  CO2
        Dolomite         -3.17  -20.14  -16.97  CaMg(CO3)2
        Gypsum           -2.06   -6.64   -4.58  CaSO4:2H2O
        H2(g)           -22.68  -25.81   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite   -4.87   -7.84   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.94   -6.07    1.87  NH3
        O2(g)           -39.55  -42.41   -2.85  O2

Initial solution 13-Biochar 300 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                4.360e-004  4.360e-004
        Ca               4.978e-004  4.978e-004
        K                1.752e-004  1.752e-004
        Mg               5.348e-005  5.348e-005
        N(5)             6.077e-004  6.077e-004
        Na               7.048e-004  7.048e-004
        P                6.458e-007  6.458e-007
        S(6)             6.169e-004  6.169e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.800
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  3.142e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.240e-004
                       Total CO2 (mol/kg)  =  4.360e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -2.834e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -6.92
                               Iterations  =   7
                                  Total H  = 1.110129e+002
                                  Total O  = 5.551180e+001

----------------------------Distribution of species----------------------------

                                                         Log       Log         Log
   Species                 Molality    Activity  Molality  Activity      Gamma

   OH-                   4.554e-007  4.283e-007    -6.342    -6.368     -0.027
   H+                    1.676e-008  1.585e-008    -7.776    -7.800     -0.024
   H2O                   5.551e+001  9.999e-001     1.744    -0.000      0.000
C(-4)               0.000e+000
   CH4                   0.000e+000  0.000e+000   -74.147   -74.147      0.000
C(4)                4.360e-004
   HCO3-                 4.169e-004  3.929e-004    -3.380    -3.406     -0.026
   CO2                   1.499e-005  1.500e-005    -4.824    -4.824      0.000
   CaHCO3+               1.786e-006  1.683e-006    -5.748    -5.774     -0.026
   CO3-2                 1.324e-006  1.044e-006    -5.878    -5.981     -0.103
   CaCO3                 5.850e-007  5.854e-007    -6.233    -6.233      0.000
   MgHCO3+               1.876e-007  1.766e-007    -6.727    -6.753     -0.026
   NaHCO3                1.462e-007  1.463e-007    -6.835    -6.835      0.000
   MgCO3                 3.611e-008  3.614e-008    -7.442    -7.442      0.000
   NaCO3-                1.058e-008  9.958e-009    -7.975    -8.002     -0.026
Ca                  4.978e-004
   Ca+2                  4.637e-004  3.656e-004    -3.334    -3.437     -0.103
```

```
   CaSO4                 3.171e-005  3.173e-005    -4.499    -4.499     0.000
   CaHCO3+               1.786e-006  1.683e-006    -5.748    -5.774    -0.026
   CaCO3                 5.850e-007  5.854e-007    -6.233    -6.233     0.000
   CaHPO4                6.546e-008  6.551e-008    -7.184    -7.184     0.000
   CaPO4-                9.440e-009  8.885e-009    -8.025    -8.051    -0.026
   CaOH+                 4.067e-009  3.828e-009    -8.391    -8.417    -0.026
   CaH2PO4+              8.506e-010  8.006e-010    -9.070    -9.097    -0.026
   CaHSO4+               2.950e-012  2.776e-012   -11.530   -11.557    -0.026
H(0)            3.739e-027
   H2                    1.869e-027  1.871e-027   -26.728   -26.728     0.000
K               1.752e-004
   K+                    1.747e-004  1.643e-004    -3.758    -3.784    -0.027
   KSO4-                 5.121e-007  4.820e-007    -6.291    -6.317    -0.026
   KHPO4-                1.224e-010  1.152e-010    -9.912    -9.939    -0.026
   KOH                   3.592e-011  3.595e-011   -10.445   -10.444     0.000
Mg              5.348e-005
   Mg+2                  4.957e-005  3.917e-005    -4.305    -4.407    -0.102
   MgSO4                 3.672e-006  3.674e-006    -5.435    -5.435     0.000
   MgHCO3+               1.876e-007  1.766e-007    -6.727    -6.753    -0.026
   MgCO3                 3.611e-008  3.614e-008    -7.442    -7.442     0.000
   MgHPO4                9.483e-009  9.489e-009    -8.023    -8.023     0.000
   MgOH+                 6.023e-009  5.669e-009    -8.220    -8.247    -0.026
   MgPO4-                1.364e-009  1.284e-009    -8.865    -8.891    -0.026
   MgH2PO4+              1.161e-010  1.092e-010    -9.935    -9.962    -0.026
N(5)            6.077e-004
   NO3-                  6.077e-004  5.712e-004    -3.216    -3.243    -0.027
Na              7.048e-004
   Na+                   7.030e-004  6.620e-004    -3.153    -3.179    -0.026
   NaSO4-                1.557e-006  1.465e-006    -5.808    -5.834    -0.026
   NaHCO3                1.462e-007  1.463e-007    -6.835    -6.835     0.000
   NaCO3-                1.058e-008  9.958e-009    -7.975    -8.002    -0.026
   NaHPO4-               4.929e-010  4.639e-010    -9.307    -9.334    -0.026
   NaOH                  2.757e-010  2.759e-010    -9.559    -9.559     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -40.565   -40.565     0.000
P               6.458e-007
   HPO4-2                4.582e-007  3.594e-007    -6.339    -6.444    -0.106
   H2PO4-                1.002e-007  9.439e-008    -6.999    -7.025    -0.026
   CaHPO4                6.546e-008  6.551e-008    -7.184    -7.184     0.000
   MgHPO4                9.483e-009  9.489e-009    -8.023    -8.023     0.000
   CaPO4-                9.440e-009  8.885e-009    -8.025    -8.051    -0.026
   MgPO4-                1.364e-009  1.284e-009    -8.865    -8.891    -0.026
   CaH2PO4+              8.506e-010  8.006e-010    -9.070    -9.097    -0.026
   NaHPO4-               4.929e-010  4.639e-010    -9.307    -9.334    -0.026
   KHPO4-                1.224e-010  1.152e-010    -9.912    -9.939    -0.026
   MgH2PO4+              1.161e-010  1.092e-010    -9.935    -9.962    -0.026
   PO4-3                 1.595e-011  9.235e-012   -10.797   -11.035    -0.237
S(6)            6.169e-004
   SO4-2                 5.794e-004  4.562e-004    -3.237    -3.341    -0.104
   CaSO4                 3.171e-005  3.173e-005    -4.499    -4.499     0.000
   MgSO4                 3.672e-006  3.674e-006    -5.435    -5.435     0.000
   NaSO4-                1.557e-006  1.465e-006    -5.808    -5.834    -0.026
   KSO4-                 5.121e-007  4.820e-007    -6.291    -6.317    -0.026
   HSO4-                 6.712e-010  6.317e-010    -9.173    -9.199    -0.026
   CaHSO4+               2.950e-012  2.776e-012   -11.530   -11.557    -0.026

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.43   -6.78   -4.34  CaSO4
        Aragonite        -1.11   -9.42   -8.31  CaCO3
        Calcite          -0.96   -9.42   -8.45  CaCO3
        CH4(g)          -71.33  -74.15   -2.82  CH4
        CO2(g)           -3.42   -4.82   -1.41  CO2
        Dolomite         -2.83  -19.81  -16.97  CaMg(CO3)2
        Gypsum           -2.20   -6.78   -4.58  CaSO4:2H2O
        H2(g)           -23.60  -26.73   -3.13  H2
```

```
H2O(g)            -1.64   -0.00    1.64  H2O
Hydroxyapatite    -2.35   -5.32   -2.97  Ca5(PO4)3OH
O2(g)            -37.71  -40.57   -2.85  O2
```

Annex 2. PHREEQC modeling of weathering solutions of mixtures of biochar and humic acid (HA) at different time.

Initial solution 1-Biochar + HA 0 h.

```
-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                3.488e-003  3.488e-003
        Ca               2.872e-004  2.872e-004
        K                1.549e-004  1.549e-004
        Mg               5.970e-005  5.970e-005
        N(-3)            1.994e-003  1.994e-003
        N(5)             1.835e-003  1.835e-003
        Na               1.074e-002  1.074e-002
        P                3.196e-004  3.196e-004
        S(6)             4.066e-003  4.066e-003

----------------------------Description of solution----------------------------

                                       pH  =   7.450
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  1.761e-002
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  3.506e-003
                       Total CO2 (mol/kg)  =  3.488e-003
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -2.134e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.80
                               Iterations  =   9
                                  Total H  = 1.110240e+002
                                  Total O  = 5.553949e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           5.8622      0.3410

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                   2.187e-007  1.913e-007    -6.660    -6.718    -0.058
   H+                    3.964e-008  3.548e-008    -7.402    -7.450    -0.048
   H2O                   5.551e+001  9.996e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -70.139   -70.138     0.002
C(4)            3.488e-003
   HCO3-                 3.219e-003  2.841e-003    -2.492    -2.547    -0.054
   CO2                   2.419e-004  2.429e-004    -3.616    -3.615     0.002
   NaHCO3                1.483e-005  1.489e-005    -4.829    -4.827     0.002
   CO3-2                 5.559e-006  3.372e-006    -5.255    -5.472    -0.217
   CaHCO3+               4.929e-006  4.350e-006    -5.307    -5.362    -0.054
   MgHCO3+               9.900e-007  8.693e-007    -6.004    -6.061    -0.057
   CaCO3                 6.729e-007  6.757e-007    -6.172    -6.170     0.002
   NaCO3-                5.158e-007  4.529e-007    -6.287    -6.344    -0.057
   MgCO3                 7.915e-008  7.947e-008    -7.102    -7.100     0.002
Ca              2.872e-004
   Ca+2                  2.155e-004  1.307e-004    -3.667    -3.884    -0.217
   CaSO4                 5.686e-005  5.709e-005    -4.245    -4.243     0.002
   CaHPO4                8.385e-006  8.419e-006    -5.077    -5.075     0.002
   CaHCO3+               4.929e-006  4.350e-006    -5.307    -5.362    -0.054
   CaCO3                 6.729e-007  6.757e-007    -6.172    -6.170     0.002
   CaPO4-                5.809e-007  5.100e-007    -6.236    -6.292    -0.057
```

```
   CaH2PO4+          2.623e-007  2.303e-007    -6.581    -6.638    -0.057
   CaOH+             6.958e-010  6.109e-010    -9.158    -9.214    -0.057
   CaHSO4+           1.274e-011  1.118e-011   -10.895   -10.951    -0.057
H(0)            1.867e-026
   H2                9.337e-027  9.375e-027   -26.030   -26.028     0.002
K               1.549e-004
   K+                1.526e-004  1.335e-004    -3.816    -3.874    -0.058
   KSO4-             2.246e-006  1.972e-006    -5.649    -5.705    -0.057
   KHPO4-            3.832e-008  3.365e-008    -7.417    -7.473    -0.057
   KOH               1.299e-011  1.304e-011   -10.886   -10.885     0.002
Mg              5.970e-005
   Mg+2              4.354e-005  2.667e-005    -4.361    -4.574    -0.213
   MgSO4             1.255e-005  1.260e-005    -4.902    -4.900     0.002
   MgHPO4            2.314e-006  2.324e-006    -5.636    -5.634     0.002
   MgHCO3+           9.900e-007  8.693e-007    -6.004    -6.061    -0.057
   MgPO4-            1.600e-007  1.404e-007    -6.796    -6.852    -0.057
   MgCO3             7.915e-008  7.947e-008    -7.102    -7.100     0.002
   MgH2PO4+          6.820e-008  5.988e-008    -7.166    -7.223    -0.057
   MgOH+             1.963e-009  1.724e-009    -8.707    -8.764    -0.057
N(-3)           1.994e-003
   NH4+              1.919e-003  1.670e-003    -2.717    -2.777    -0.060
   NH4SO4-           5.626e-005  4.940e-005    -4.250    -4.306    -0.057
   NH3               1.864e-005  1.872e-005    -4.729    -4.728     0.002
N(5)            1.835e-003
   NO3-              1.835e-003  1.601e-003    -2.736    -2.796    -0.059
Na              1.074e-002
   Na+               1.060e-002  9.323e-003    -1.975    -2.030    -0.056
   NaSO4-            1.183e-004  1.039e-004    -3.927    -3.983    -0.057
   NaHCO3            1.483e-005  1.489e-005    -4.829    -4.827     0.002
   NaHPO4-           2.676e-006  2.349e-006    -5.573    -5.629    -0.057
   NaCO3-            5.158e-007  4.529e-007    -6.287    -6.344    -0.057
   NaOH              1.728e-009  1.735e-009    -8.762    -8.761     0.002
O(0)            0.000e+000
   O2                0.000e+000  0.000e+000   -41.967   -41.965     0.002
P               3.196e-004
   HPO4-2            2.187e-004  1.292e-004    -3.660    -3.889    -0.228
   H2PO4-            8.646e-005  7.599e-005    -4.063    -4.119    -0.056
   CaHPO4            8.385e-006  8.419e-006    -5.077    -5.075     0.002
   NaHPO4-           2.676e-006  2.349e-006    -5.573    -5.629    -0.057
   MgHPO4            2.314e-006  2.324e-006    -5.636    -5.634     0.002
   CaPO4-            5.809e-007  5.100e-007    -6.236    -6.292    -0.057
   CaH2PO4+          2.623e-007  2.303e-007    -6.581    -6.638    -0.057
   MgPO4-            1.600e-007  1.404e-007    -6.796    -6.852    -0.057
   MgH2PO4+          6.820e-008  5.988e-008    -7.166    -7.223    -0.057
   KHPO4-            3.832e-008  3.365e-008    -7.417    -7.473    -0.057
   PO4-3             4.843e-009  1.483e-009    -8.315    -8.829    -0.514
S(6)            4.066e-003
   SO4-2             3.820e-003  2.297e-003    -2.418    -2.639    -0.221
   NaSO4-            1.183e-004  1.039e-004    -3.927    -3.983    -0.057
   CaSO4             5.686e-005  5.709e-005    -4.245    -4.243     0.002
   NH4SO4-           5.626e-005  4.940e-005    -4.250    -4.306    -0.057
   MgSO4             1.255e-005  1.260e-005    -4.902    -4.900     0.002
   KSO4-             2.246e-006  1.972e-006    -5.649    -5.705    -0.057
   HSO4-             8.109e-009  7.120e-009    -8.091    -8.148    -0.057
   CaHSO4+           1.274e-011  1.118e-011   -10.895   -10.951    -0.057

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.18   -6.52   -4.34  CaSO4
        Aragonite        -1.05   -9.36   -8.31  CaCO3
        Calcite          -0.90   -9.36   -8.45  CaCO3
        CH4(g)          -67.32  -70.14   -2.82  CH4
        CO2(g)           -2.21   -3.61   -1.41  CO2
        Dolomite         -2.43  -19.40  -16.97  CaMg(CO3)2
        Gypsum           -1.94   -6.52   -4.58  CaSO4:2H2O
        H2(g)           -22.90  -26.03   -3.13  H2
```

```
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    1.68   -1.29   -2.97  Ca5(PO4)3OH
        NH3(g)           -6.60   -4.73    1.87  NH3
        O2(g)           -39.11  -41.97   -2.85  O2

Initial solution 2-Biochar + HA 0.1 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 3.192e-003  3.192e-003
        Ca                5.717e-004  5.717e-004
        K                 3.442e-004  3.442e-004
        Mg                6.996e-005  6.996e-005
        N(-3)             3.880e-003  3.880e-003
        N(5)              1.034e-003  1.034e-003
        Na                3.025e-003  3.025e-003
        P                 2.827e-004  2.827e-004
        S(6)              1.739e-003  1.739e-003

----------------------------Description of solution----------------------------

                                       pH  =   7.210
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  1.016e-002
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  3.012e-003
                       Total CO2 (mol/kg)  =  3.192e-003
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  7.260e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   4.61
                               Iterations  =   9
                                  Total H  = 1.110311e+002
                                  Total O  = 5.552660e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.0938      0.3544

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                   Molality    Activity  Molality  Activity     Gamma

   OH-                   1.223e-007  1.101e-007    -6.913    -6.958    -0.046
   H+                    6.749e-008  6.166e-008    -7.171    -7.210    -0.039
   H2O                   5.551e+001  9.998e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -68.029   -68.028     0.001
C(4)            3.192e-003
   HCO3-                 2.797e-003  2.532e-003    -2.553    -2.596    -0.043
   CO2                   3.754e-004  3.763e-004    -3.426    -3.424     0.001
   CaHCO3+               1.052e-005  9.525e-006    -4.978    -5.021    -0.043
   NaHCO3                3.856e-006  3.865e-006    -5.414    -5.413     0.001
   CO3-2                 2.575e-006  1.730e-006    -5.589    -5.762    -0.173
   MgHCO3+               1.248e-006  1.126e-006    -5.904    -5.948    -0.045
   CaCO3                 8.494e-007  8.514e-007    -6.071    -6.070     0.001
   NaCO3-                7.497e-008  6.763e-008    -7.125    -7.170    -0.045
   MgCO3                 5.911e-008  5.924e-008    -7.228    -7.227     0.001
Ca              5.717e-004
   Ca+2                  4.781e-004  3.209e-004    -3.320    -3.494    -0.173
   CaSO4                 6.494e-005  6.509e-005    -4.187    -4.186     0.001
   CaHPO4                1.581e-005  1.585e-005    -4.801    -4.800     0.001
   CaHCO3+               1.052e-005  9.525e-006    -4.978    -5.021    -0.043
```

```
   CaCO3                 8.494e-007  8.514e-007    -6.071    -6.070     0.001
   CaH2PO4+              8.352e-007  7.535e-007    -6.078    -6.123    -0.045
   CaPO4-                6.124e-007  5.525e-007    -6.213    -6.258    -0.045
   CaOH+                 9.572e-010  8.636e-010    -9.019    -9.064    -0.045
   CaHSO4+               2.456e-011  2.216e-011   -10.610   -10.654    -0.045
H(0)            5.649e-026
   H2                    2.825e-026  2.831e-026   -25.549   -25.548     0.001
K               3.442e-004
   K+                    3.418e-004  3.078e-004    -3.466    -3.512    -0.045
   KSO4-                 2.338e-006  2.109e-006    -5.631    -5.676    -0.045
   KHPO4-                6.588e-008  5.944e-008    -7.181    -7.226    -0.045
   KOH                   1.726e-011  1.730e-011   -10.763   -10.762     0.001
Mg              6.996e-005
   Mg+2                  5.737e-005  3.876e-005    -4.241    -4.412    -0.170
   MgSO4                 8.476e-006  8.496e-006    -5.072    -5.071     0.001
   MgHPO4                2.582e-006  2.588e-006    -5.588    -5.587     0.001
   MgHCO3+               1.248e-006  1.126e-006    -5.904    -5.948    -0.045
   MgH2PO4+              1.285e-007  1.159e-007    -6.891    -6.936    -0.045
   MgPO4-                9.977e-008  9.001e-008    -7.001    -7.046    -0.045
   MgCO3                 5.911e-008  5.924e-008    -7.228    -7.227     0.001
   MgOH+                 1.598e-009  1.442e-009    -8.796    -8.841    -0.045
N(-3)           3.880e-003
   NH4+                  3.806e-003  3.416e-003    -2.419    -2.467    -0.047
   NH4SO4-               5.199e-005  4.690e-005    -4.284    -4.329    -0.045
   NH3                   2.199e-005  2.204e-005    -4.658    -4.657     0.001
N(5)            1.034e-003
   NO3-                  1.034e-003  9.291e-004    -2.986    -3.032    -0.046
Na              3.025e-003
   Na+                   3.005e-003  2.714e-003    -2.522    -2.566    -0.044
   NaSO4-                1.556e-005  1.404e-005    -4.808    -4.853    -0.045
   NaHCO3                3.856e-006  3.865e-006    -5.414    -5.413     0.001
   NaHPO4-               5.809e-007  5.241e-007    -6.236    -6.281    -0.045
   NaCO3-                7.497e-008  6.763e-008    -7.125    -7.170    -0.045
   NaOH                  2.900e-010  2.907e-010    -9.538    -9.537     0.001
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -42.926   -42.925     0.001
P               2.827e-004
   HPO4-2                1.499e-004  9.904e-005    -3.824    -4.004    -0.180
   H2PO4-                1.121e-004  1.012e-004    -3.950    -3.995    -0.044
   CaHPO4                1.581e-005  1.585e-005    -4.801    -4.800     0.001
   MgHPO4                2.582e-006  2.588e-006    -5.588    -5.587     0.001
   CaH2PO4+              8.352e-007  7.535e-007    -6.078    -6.123    -0.045
   CaPO4-                6.124e-007  5.525e-007    -6.213    -6.258    -0.045
   NaHPO4-               5.809e-007  5.241e-007    -6.236    -6.281    -0.045
   MgH2PO4+              1.285e-007  1.159e-007    -6.891    -6.936    -0.045
   MgPO4-                9.977e-008  9.001e-008    -7.001    -7.046    -0.045
   KHPO4-                6.588e-008  5.944e-008    -7.181    -7.226    -0.045
   PO4-3                 1.661e-009  6.542e-010    -8.780    -9.184    -0.405
S(6)            1.739e-003
   SO4-2                 1.596e-003  1.066e-003    -2.797    -2.972    -0.175
   CaSO4                 6.494e-005  6.509e-005    -4.187    -4.186     0.001
   NH4SO4-               5.199e-005  4.690e-005    -4.284    -4.329    -0.045
   NaSO4-                1.556e-005  1.404e-005    -4.808    -4.853    -0.045
   MgSO4                 8.476e-006  8.496e-006    -5.072    -5.071     0.001
   KSO4-                 2.338e-006  2.109e-006    -5.631    -5.676    -0.045
   HSO4-                 6.365e-009  5.743e-009    -8.196    -8.241    -0.045
   CaHSO4+               2.456e-011  2.216e-011   -10.610   -10.654    -0.045

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.12   -6.47   -4.34  CaSO4
        Aragonite        -0.95   -9.26   -8.31  CaCO3
        Calcite          -0.80   -9.26   -8.45  CaCO3
        CH4(g)          -65.21  -68.03   -2.82  CH4
        CO2(g)           -2.02   -3.42   -1.41  CO2
        Dolomite         -2.46  -19.43  -16.97  CaMg(CO3)2
```

```
        Gypsum            -1.88   -6.47   -4.58  CaSO4:2H2O
        H2(g)            -22.42  -25.55   -3.13  H2
        H2O(g)            -1.64   -0.00    1.64  H2O
        Hydroxyapatite     2.33   -0.64   -2.97  Ca5(PO4)3OH
        NH3(g)            -6.53   -4.66    1.87  NH3
        O2(g)            -40.07  -42.93   -2.85  O2

Initial solution 3-Biochar + HA 0.2 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 2.330e-003  2.330e-003
        Ca                7.051e-004  7.051e-004
        K                 4.388e-004  4.388e-004
        Mg                7.612e-005  7.612e-005
        Na                2.147e-003  2.147e-003
        P                 7.170e-005  7.170e-005
        S(6)              1.661e-003  1.661e-003

----------------------------Description of solution----------------------------

                                       pH  =   7.350
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  6.865e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.175e-003
                       Total CO2 (mol/kg)  =  2.330e-003
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -1.419e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -15.38
                               Iterations  =  10
                                  Total H  = 1.110146e+002
                                  Total O  = 5.551993e+001

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                    1.660e-007  1.520e-007    -6.780    -6.818    -0.038
   H+                     4.827e-008  4.467e-008    -7.316    -7.350    -0.034
   H2O                    5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)            0.000e+000
   CH4                    0.000e+000  0.000e+000   -69.405   -69.405     0.001
C(4)             2.330e-003
   HCO3-                  2.105e-003  1.935e-003    -2.677    -2.713    -0.037
   CO2                    2.079e-004  2.083e-004    -3.682    -3.681     0.001
   CaHCO3+                1.052e-005  9.676e-006    -4.978    -5.014    -0.037
   CO3-2                  2.554e-006  1.824e-006    -5.593    -5.739    -0.146
   NaHCO3                 2.128e-006  2.131e-006    -5.672    -5.671     0.001
   CaCO3                  1.192e-006  1.194e-006    -5.924    -5.923     0.001
   MgHCO3+                1.106e-006  1.014e-006    -5.956    -5.994    -0.038
   MgCO3                  7.351e-008  7.363e-008    -7.134    -7.133     0.001
   NaCO3-                 5.614e-008  5.148e-008    -7.251    -7.288    -0.038
Ca               7.051e-004
   Ca+2                   5.975e-004  4.267e-004    -3.224    -3.370    -0.146
   CaSO4                  8.923e-005  8.937e-005    -4.050    -4.049     0.001
   CaHCO3+                1.052e-005  9.676e-006    -4.978    -5.014    -0.037
   CaHPO4                 6.110e-006  6.120e-006    -5.214    -5.213     0.001
   CaCO3                  1.192e-006  1.194e-006    -5.924    -5.923     0.001
   CaPO4-                 3.212e-007  2.945e-007    -6.493    -6.531    -0.038
   CaH2PO4+               2.299e-007  2.108e-007    -6.639    -6.676    -0.038
   CaOH+                  1.728e-009  1.585e-009    -8.762    -8.800    -0.038
   CaHSO4+                2.403e-011  2.204e-011   -10.619   -10.657    -0.038
H(0)             2.967e-026
```

```
   H2                 1.484e-026  1.486e-026   -25.829   -25.828     0.001
K               4.388e-004
   K+                 4.357e-004  3.991e-004    -3.361    -3.399    -0.038
   KSO4-              3.080e-006  2.825e-006    -5.511    -5.549    -0.038
   KHPO4-             2.441e-008  2.238e-008    -7.612    -7.650    -0.038
   KOH                3.092e-011  3.097e-011   -10.510   -10.509     0.001
Mg              7.612e-005
   Mg+2               6.366e-005  4.566e-005    -4.196    -4.340    -0.144
   MgSO4              1.032e-005  1.034e-005    -4.986    -4.986     0.001
   MgHCO3+            1.106e-006  1.014e-006    -5.956    -5.994    -0.038
   MgHPO4             8.842e-007  8.856e-007    -6.053    -6.053     0.001
   MgCO3              7.351e-008  7.363e-008    -7.134    -7.133     0.001
   MgPO4-             4.637e-008  4.252e-008    -7.334    -7.371    -0.038
   MgH2PO4+           3.133e-008  2.873e-008    -7.504    -7.542    -0.038
   MgOH+              2.557e-009  2.345e-009    -8.592    -8.630    -0.038
Na              2.147e-003
   Na+                2.134e-003  1.958e-003    -2.671    -2.708    -0.037
   NaSO4-             1.141e-005  1.046e-005    -4.943    -4.980    -0.038
   NaHCO3             2.128e-006  2.131e-006    -5.672    -5.671     0.001
   NaHPO4-            1.198e-007  1.099e-007    -6.922    -6.959    -0.038
   NaCO3-             5.614e-008  5.148e-008    -7.251    -7.288    -0.038
   NaOH               2.892e-010  2.896e-010    -9.539    -9.538     0.001
O(0)            0.000e+000
   O2                 0.000e+000  0.000e+000   -42.366   -42.365     0.001
P               7.170e-005
   HPO4-2             4.073e-005  2.877e-005    -4.390    -4.541    -0.151
   H2PO4-             2.320e-005  2.130e-005    -4.634    -4.672    -0.037
   CaHPO4             6.110e-006  6.120e-006    -5.214    -5.213     0.001
   MgHPO4             8.842e-007  8.856e-007    -6.053    -6.053     0.001
   CaPO4-             3.212e-007  2.945e-007    -6.493    -6.531    -0.038
   CaH2PO4+           2.299e-007  2.108e-007    -6.639    -6.676    -0.038
   NaHPO4-            1.198e-007  1.099e-007    -6.922    -6.959    -0.038
   MgPO4-             4.637e-008  4.252e-008    -7.334    -7.371    -0.038
   MgH2PO4+           3.133e-008  2.873e-008    -7.504    -7.542    -0.038
   KHPO4-             2.441e-008  2.238e-008    -7.612    -7.650    -0.038
   PO4-3              5.735e-010  2.623e-010    -9.241    -9.581    -0.340
S(6)            1.661e-003
   SO4-2              1.547e-003  1.101e-003    -2.811    -2.958    -0.148
   CaSO4              8.923e-005  8.937e-005    -4.050    -4.049     0.001
   NaSO4-             1.141e-005  1.046e-005    -4.943    -4.980    -0.038
   MgSO4              1.032e-005  1.034e-005    -4.986    -4.986     0.001
   KSO4-              3.080e-006  2.825e-006    -5.511    -5.549    -0.038
   HSO4-              4.685e-009  4.296e-009    -8.329    -8.367    -0.038
   CaHSO4+            2.403e-011  2.204e-011   -10.619   -10.657    -0.038

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -1.98   -6.33   -4.34  CaSO4
        Aragonite        -0.80   -9.11   -8.31  CaCO3
        Calcite          -0.66   -9.11   -8.45  CaCO3
        CH4(g)          -66.59  -69.40   -2.82  CH4
        CO2(g)           -2.27   -3.68   -1.41  CO2
        Dolomite         -2.22  -19.19  -16.97  CaMg(CO3)2
        Gypsum           -1.75   -6.33   -4.58  CaSO4:2H2O
        H2(g)           -22.70  -25.83   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    1.90   -1.07   -2.97  Ca5(PO4)3OH
        O2(g)           -39.51  -42.37   -2.85  O2

Initial solution 4-Biochar + HA 0.3 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 2.047e-003  2.047e-003
```

```
        Ca               8.698e-004  8.698e-004
        K                5.040e-004  5.040e-004
        Mg               9.875e-005  9.875e-005
        Na               1.754e-003  1.754e-003
        S(6)             1.490e-003  1.490e-003

----------------------------Description of solution----------------------------

                                        pH  =   7.640
                                        pe  =   4.000
                         Activity of water  =   1.000
                            Ionic strength  =  6.515e-003
                        Mass of water (kg)  =  1.000e+000
                  Total alkalinity (eq/kg)  =  1.957e-003
                        Total CO2 (mol/kg)  =  2.047e-003
                       Temperature (deg C)  =  20.000
                   Electrical balance (eq)  = -7.417e-004
  Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -8.61
                                Iterations  =   7
                                   Total H  = 1.110144e+002
                                   Total O  = 5.551822e+001

----------------------------Distribution of species----------------------------

                                                      Log       Log        Log
   Species                Molality    Activity  Molality  Activity      Gamma

   OH-                   3.229e-007  2.963e-007    -6.491    -6.528     -0.037
   H+                    2.471e-008  2.291e-008    -7.607    -7.640     -0.033
   H2O                   5.551e+001  9.999e-001     1.744    -0.000      0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -72.053   -72.052      0.001
C(4)            2.047e-003
   HCO3-                 1.927e-003  1.775e-003    -2.715    -2.751     -0.036
   CO2                   9.782e-005  9.797e-005    -4.010    -4.009      0.001
   CaHCO3+               1.225e-005  1.128e-005    -4.912    -4.948     -0.036
   CO3-2                 4.532e-006  3.263e-006    -5.344    -5.486     -0.143
   CaCO3                 2.711e-006  2.715e-006    -5.567    -5.566      0.001
   NaHCO3                1.598e-006  1.600e-006    -5.796    -5.796      0.001
   MgHCO3+               1.359e-006  1.249e-006    -5.867    -5.903     -0.037
   MgCO3                 1.766e-007  1.769e-007    -6.753    -6.752      0.001
   NaCO3-                8.204e-008  7.538e-008    -7.086    -7.123     -0.037
Ca              8.698e-004
   Ca+2                  7.540e-004  5.425e-004    -3.123    -3.266     -0.143
   CaSO4                 1.009e-004  1.011e-004    -3.996    -3.995      0.001
   CaHCO3+               1.225e-005  1.128e-005    -4.912    -4.948     -0.036
   CaCO3                 2.711e-006  2.715e-006    -5.567    -5.566      0.001
   CaOH+                 4.276e-009  3.929e-009    -8.369    -8.406     -0.037
   CaHSO4+               1.391e-011  1.278e-011   -10.857   -10.893     -0.037
H(0)            7.805e-027
   H2                    3.902e-027  3.908e-027   -26.409   -26.408      0.001
K               5.040e-004
   K+                    5.008e-004  4.597e-004    -3.300    -3.338     -0.037
   KSO4-                 3.149e-006  2.894e-006    -5.502    -5.539     -0.037
   KOH                   6.947e-011  6.957e-011   -10.158   -10.158      0.001
Mg              9.875e-005
   Mg+2                  8.488e-005  6.134e-005    -4.071    -4.212     -0.141
   MgSO4                 1.233e-005  1.235e-005    -4.909    -4.908      0.001
   MgHCO3+               1.359e-006  1.249e-006    -5.867    -5.903     -0.037
   MgCO3                 1.766e-007  1.769e-007    -6.753    -6.752      0.001
   MgOH+                 6.683e-009  6.141e-009    -8.175    -8.212     -0.037
Na              1.754e-003
   Na+                   1.744e-003  1.604e-003    -2.759    -2.795     -0.036
   NaSO4-                8.291e-006  7.618e-006    -5.081    -5.118     -0.037
   NaHCO3                1.598e-006  1.600e-006    -5.796    -5.796      0.001
   NaCO3-                8.204e-008  7.538e-008    -7.086    -7.123     -0.037
   NaOH                  4.617e-010  4.624e-010    -9.336    -9.335      0.001
O(0)            0.000e+000
```

```
   O2                   0.000e+000  0.000e+000   -41.206   -41.205     0.001
S(6)            1.490e-003
   SO4-2                1.365e-003  9.790e-004    -2.865    -3.009    -0.144
   CaSO4                1.009e-004  1.011e-004    -3.996    -3.995     0.001
   MgSO4                1.233e-005  1.235e-005    -4.909    -4.908     0.001
   NaSO4-               8.291e-006  7.618e-006    -5.081    -5.118    -0.037
   KSO4-                3.149e-006  2.894e-006    -5.502    -5.539    -0.037
   HSO4-                2.133e-009  1.960e-009    -8.671    -8.708    -0.037
   CaHSO4+              1.391e-011  1.278e-011   -10.857   -10.893    -0.037

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -1.93   -6.27   -4.34  CaSO4
        Aragonite        -0.45   -8.75   -8.31  CaCO3
        Calcite          -0.30   -8.75   -8.45  CaCO3
        CH4(g)          -69.23  -72.05   -2.82  CH4
        CO2(g)           -2.60   -4.01   -1.41  CO2
        Dolomite         -1.48  -18.45  -16.97  CaMg(CO3)2
        Gypsum           -1.69   -6.27   -4.58  CaSO4:2H2O
        H2(g)           -23.28  -26.41   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        O2(g)           -38.35  -41.21   -2.85  O2

Initial solution 5-Biochar + HA 0.4 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                1.547e-003  1.547e-003
        Ca               7.999e-004  7.999e-004
        K                4.797e-004  4.797e-004
        Mg               9.052e-005  9.052e-005
        Na               1.462e-003  1.462e-003
        P                3.753e-004  3.753e-004
        S(6)             1.112e-003  1.112e-003

----------------------------Description of solution----------------------------

                                       pH  =   8.020
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  5.825e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.884e-003
                       Total CO2 (mol/kg)  =  1.547e-003
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -7.608e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -10.05
                               Iterations  =  10
                                  Total H  = 1.110143e+002
                                  Total O  = 5.551678e+001

----------------------------Distribution of species----------------------------

                                                         Log       Log       Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                  7.713e-007  7.108e-007    -6.113    -6.148    -0.035
   H+                   1.027e-008  9.550e-009    -7.989    -8.020    -0.031
   H2O                  5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                  0.000e+000  0.000e+000   -75.582   -75.582     0.001
C(4)            1.547e-003
   HCO3-                1.492e-003  1.380e-003    -2.826    -2.860    -0.034
   CO2                  3.171e-005  3.175e-005    -4.499    -4.498     0.001
```

```
   CaHCO3+               8.425e-006  7.791e-006    -5.074    -5.108    -0.034
   CO3-2                 8.320e-006  6.085e-006    -5.080    -5.216    -0.136
   CaCO3                 4.490e-006  4.496e-006    -5.348    -5.347     0.001
   NaHCO3                1.041e-006  1.042e-006    -5.983    -5.982     0.001
   MgHCO3+               9.106e-007  8.402e-007    -6.041    -6.076    -0.035
   MgCO3                 2.850e-007  2.854e-007    -6.545    -6.545     0.001
   NaCO3-                1.277e-007  1.178e-007    -6.894    -6.929    -0.035
Ca              7.999e-004
   Ca+2                  6.591e-004  4.818e-004    -3.181    -3.317    -0.136
   CaSO4                 6.858e-005  6.867e-005    -4.164    -4.163     0.001
   CaHPO4                4.735e-005  4.741e-005    -4.325    -4.324     0.001
   CaPO4-                1.157e-005  1.067e-005    -4.937    -4.972    -0.035
   CaHCO3+               8.425e-006  7.791e-006    -5.074    -5.108    -0.034
   CaCO3                 4.490e-006  4.496e-006    -5.348    -5.347     0.001
   CaH2PO4+              3.784e-007  3.491e-007    -6.422    -6.457    -0.035
   CaOH+                 9.073e-009  8.371e-009    -8.042    -8.077    -0.035
   CaHSO4+               3.924e-012  3.620e-012   -11.406   -11.441    -0.035
H(0)            1.357e-027
   H2                    6.783e-028  6.792e-028   -27.169   -27.168     0.001
K               4.797e-004
   K+                    4.772e-004  4.399e-004    -3.321    -3.357    -0.035
   KSO4-                 2.296e-006  2.119e-006    -5.639    -5.674    -0.035
   KHPO4-                1.835e-007  1.693e-007    -6.736    -6.771    -0.035
   KOH                   1.595e-010  1.597e-010    -9.797    -9.797     0.001
Mg              9.052e-005
   Mg+2                  7.232e-005  5.307e-005    -4.141    -4.275    -0.134
   MgSO4                 8.165e-006  8.176e-006    -5.088    -5.087     0.001
   MgHPO4                7.052e-006  7.061e-006    -5.152    -5.151     0.001
   MgPO4-                1.719e-006  1.586e-006    -5.765    -5.800    -0.035
   MgHCO3+               9.106e-007  8.402e-007    -6.041    -6.076    -0.035
   MgCO3                 2.850e-007  2.854e-007    -6.545    -6.545     0.001
   MgH2PO4+              5.308e-008  4.898e-008    -7.275    -7.310    -0.035
   MgOH+                 1.381e-008  1.275e-008    -7.860    -7.895    -0.035
Na              1.462e-003
   Na+                   1.455e-003  1.343e-003    -2.837    -2.872    -0.035
   NaSO4-                5.293e-006  4.884e-006    -5.276    -5.311    -0.035
   NaHCO3                1.041e-006  1.042e-006    -5.983    -5.982     0.001
   NaHPO4-               5.603e-007  5.170e-007    -6.252    -6.286    -0.035
   NaCO3-                1.277e-007  1.178e-007    -6.894    -6.929    -0.035
   NaOH                  9.281e-010  9.294e-010    -9.032    -9.032     0.001
O(0)            4.123e-040
   O2                    2.062e-040  2.064e-040   -39.686   -39.685     0.001
P               3.753e-004
   HPO4-2                2.726e-004  1.974e-004    -3.565    -3.705    -0.140
   CaHPO4                4.735e-005  4.741e-005    -4.325    -4.324     0.001
   H2PO4-                3.383e-005  3.124e-005    -4.471    -4.505    -0.035
   CaPO4-                1.157e-005  1.067e-005    -4.937    -4.972    -0.035
   MgHPO4                7.052e-006  7.061e-006    -5.152    -5.151     0.001
   MgPO4-                1.719e-006  1.586e-006    -5.765    -5.800    -0.035
   NaHPO4-               5.603e-007  5.170e-007    -6.252    -6.286    -0.035
   CaH2PO4+              3.784e-007  3.491e-007    -6.422    -6.457    -0.035
   KHPO4-                1.835e-007  1.693e-007    -6.736    -6.771    -0.035
   MgH2PO4+              5.308e-008  4.898e-008    -7.275    -7.310    -0.035
   PO4-3                 1.740e-008  8.417e-009    -7.759    -8.075    -0.315
S(6)            1.112e-003
   SO4-2                 1.028e-003  7.491e-004    -2.988    -3.125    -0.137
   CaSO4                 6.858e-005  6.867e-005    -4.164    -4.163     0.001
   MgSO4                 8.165e-006  8.176e-006    -5.088    -5.087     0.001
   NaSO4-                5.293e-006  4.884e-006    -5.276    -5.311    -0.035
   KSO4-                 2.296e-006  2.119e-006    -5.639    -5.674    -0.035
   HSO4-                 6.774e-010  6.251e-010    -9.169    -9.204    -0.035
   CaHSO4+               3.924e-012  3.620e-012   -11.406   -11.441    -0.035

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.10   -6.44   -4.34  CaSO4
```

```
        Aragonite        -0.23   -8.53   -8.31  CaCO3
        Calcite          -0.08   -8.53   -8.45  CaCO3
        CH4(g)          -72.76  -75.58   -2.82  CH4
        CO2(g)           -3.09   -4.50   -1.41  CO2
        Dolomite         -1.05  -18.02  -16.97  CaMg(CO3)2
        Gypsum           -1.86   -6.44   -4.58  CaSO4:2H2O
        H2(g)           -24.04  -27.17   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    7.35    4.38   -2.97  Ca5(PO4)3OH
        O2(g)           -36.83  -39.69   -2.85  O2

Initial solution 6-Biochar + HA 0.5 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                1.180e-003  1.180e-003
        Ca               6.888e-004  6.888e-004
        K                3.850e-004  3.850e-004
        Mg               7.611e-005  7.611e-005
        Na               1.022e-003  1.022e-003
        S(6)             7.133e-004  7.133e-004

----------------------------Description of solution----------------------------

                                       pH  =   8.000
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  4.007e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.165e-003
                       Total CO2 (mol/kg)  =  1.180e-003
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  3.459e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   6.55
                               Iterations  =   7
                                  Total H  = 1.110136e+002
                                  Total O  = 5.551259e+001

----------------------------Distribution of species----------------------------

                                                   Log       Log          Log
   Species                 Molality    Activity  Molality  Activity       Gamma

   OH-                   7.271e-007  6.789e-007    -6.138    -6.168    -0.030
   H+                    1.064e-008  1.000e-008    -7.973    -8.000    -0.027
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -75.515   -75.514     0.000
C(4)            1.180e-003
   HCO3-                 1.137e-003  1.064e-003    -2.944    -2.973    -0.029
   CO2                   2.562e-005  2.564e-005    -4.591    -4.591     0.000
   CaHCO3+               6.466e-006  6.052e-006    -5.189    -5.218    -0.029
   CO3-2                 5.842e-006  4.483e-006    -5.233    -5.348    -0.115
   CaCO3                 3.332e-006  3.335e-006    -5.477    -5.477     0.000
   MgHCO3+               7.001e-007  6.541e-007    -6.155    -6.184    -0.029
   NaHCO3                5.698e-007  5.704e-007    -6.244    -6.244     0.000
   MgCO3                 2.120e-007  2.122e-007    -6.674    -6.673     0.000
   NaCO3-                6.587e-008  6.155e-008    -7.181    -7.211    -0.029
Ca              6.888e-004
   Ca+2                  6.325e-004  4.851e-004    -3.199    -3.314    -0.115
   CaSO4                 4.643e-005  4.647e-005    -4.333    -4.333     0.000
   CaHCO3+               6.466e-006  6.052e-006    -5.189    -5.218    -0.029
   CaCO3                 3.332e-006  3.335e-006    -5.477    -5.477     0.000
   CaOH+                 8.616e-009  8.051e-009    -8.065    -8.094    -0.029
   CaHSO4+               2.746e-012  2.565e-012   -11.561   -11.591    -0.029
H(0)            1.488e-027
```

```
   H2                    7.440e-028  7.447e-028   -27.128   -27.128     0.000
K               3.850e-004
   K+                    3.837e-004  3.583e-004    -3.416    -3.446    -0.030
   KSO4-                 1.241e-006  1.160e-006    -5.906    -5.936    -0.029
   KOH                   1.241e-010  1.242e-010    -9.906    -9.906     0.000
Mg              7.611e-005
   Mg+2                  6.964e-005  5.357e-005    -4.157    -4.271    -0.114
   MgSO4                 5.540e-006  5.545e-006    -5.256    -5.256     0.000
   MgHCO3+               7.001e-007  6.541e-007    -6.155    -6.184    -0.029
   MgCO3                 2.120e-007  2.122e-007    -6.674    -6.673     0.000
   MgOH+                 1.315e-008  1.229e-008    -7.881    -7.911    -0.029
Na              1.022e-003
   Na+                   1.019e-003  9.529e-004    -2.992    -3.021    -0.029
   NaSO4-                2.491e-006  2.328e-006    -5.604    -5.633    -0.029
   NaHCO3                5.698e-007  5.704e-007    -6.244    -6.244     0.000
   NaCO3-                6.587e-008  6.155e-008    -7.181    -7.211    -0.029
   NaOH                  6.290e-010  6.296e-010    -9.201    -9.201     0.000
O(0)            3.431e-040
   O2                    1.716e-040  1.717e-040   -39.766   -39.765     0.000
S(6)            7.133e-004
   SO4-2                 6.576e-004  5.034e-004    -3.182    -3.298    -0.116
   CaSO4                 4.643e-005  4.647e-005    -4.333    -4.333     0.000
   MgSO4                 5.540e-006  5.545e-006    -5.256    -5.256     0.000
   NaSO4-                2.491e-006  2.328e-006    -5.604    -5.633    -0.029
   KSO4-                 1.241e-006  1.160e-006    -5.906    -5.936    -0.029
   HSO4-                 4.707e-010  4.399e-010    -9.327    -9.357    -0.029
   CaHSO4+               2.746e-012  2.565e-012   -11.561   -11.591    -0.029

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.27   -6.61   -4.34  CaSO4
        Aragonite        -0.36   -8.66   -8.31  CaCO3
        Calcite          -0.21   -8.66   -8.45  CaCO3
        CH4(g)          -72.70  -75.51   -2.82  CH4
        CO2(g)           -3.18   -4.59   -1.41  CO2
        Dolomite         -1.31  -18.28  -16.97  CaMg(CO3)2
        Gypsum           -2.03   -6.61   -4.58  CaSO4:2H2O
        H2(g)           -24.00  -27.13   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        O2(g)           -36.91  -39.77   -2.85  O2

Initial solution 7-Biochar + HA 3 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                1.466e-003  1.466e-003
        Ca               9.397e-004  9.397e-004
        K                7.048e-004  7.048e-004
        Mg               1.646e-004  1.646e-004
        N(-3)            5.685e-004  5.685e-004
        N(5)             2.115e-003  2.115e-003
        Na               1.677e-003  1.677e-003
        P                3.126e-004  3.126e-004
        S(6)             1.112e-003  1.112e-003

----------------------------Description of solution----------------------------

                                       pH  =   7.070
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  7.430e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.408e-003
                       Total CO2 (mol/kg)  =  1.466e-003
```

```
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -9.005e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -8.45
                               Iterations  =  10
                                  Total H  = 1.110164e+002
                                  Total O  = 5.552243e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.4116      0.3729

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                   Molality    Activity  Molality  Activity     Gamma

   H+                    9.220e-008  8.511e-008    -7.035    -7.070    -0.035
   OH-                   8.737e-008  7.975e-008    -7.059    -7.098    -0.040
   H2O                   5.551e+001  9.998e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -67.122   -67.121     0.001
C(4)            1.466e-003
   HCO3-                 1.224e-003  1.122e-003    -2.912    -2.950    -0.038
   CO2                   2.298e-004  2.302e-004    -3.639    -3.638     0.001
   CaHCO3+               8.337e-006  7.642e-006    -5.079    -5.117    -0.038
   MgHCO3+               1.415e-006  1.294e-006    -5.849    -5.888    -0.039
   NaHCO3                9.630e-007  9.646e-007    -6.016    -6.016     0.001
   CO3-2                 7.864e-007  5.553e-007    -6.104    -6.255    -0.151
   CaCO3                 4.940e-007  4.949e-007    -6.306    -6.306     0.001
   MgCO3                 4.922e-008  4.930e-008    -7.308    -7.307     0.001
   NaCO3-                1.338e-008  1.223e-008    -7.874    -7.913    -0.039
Ca              9.397e-004
   Ca+2                  8.234e-004  5.810e-004    -3.084    -3.236    -0.151
   CaSO4                 7.803e-005  7.817e-005    -4.108    -4.107     0.001
   CaHPO4                2.681e-005  2.686e-005    -4.572    -4.571     0.001
   CaHCO3+               8.337e-006  7.642e-006    -5.079    -5.117    -0.038
   CaH2PO4+              1.928e-006  1.763e-006    -5.715    -5.754    -0.039
   CaPO4-                7.420e-007  6.783e-007    -6.130    -6.169    -0.039
   CaCO3                 4.940e-007  4.949e-007    -6.306    -6.306     0.001
   CaOH+                 1.239e-009  1.133e-009    -8.907    -8.946    -0.039
   CaHSO4+               4.018e-011  3.673e-011   -10.396   -10.435    -0.039
H(0)            1.077e-025
   H2                    5.386e-026  5.395e-026   -25.269   -25.268     0.001
K               7.048e-004
   K+                    7.015e-004  6.405e-004    -3.154    -3.193    -0.040
   KSO4-                 3.185e-006  2.912e-006    -5.497    -5.536    -0.039
   KHPO4-                1.266e-007  1.158e-007    -6.897    -6.936    -0.039
   KOH                   2.604e-011  2.609e-011   -10.584   -10.584     0.001
Mg              1.646e-004
   Mg+2                  1.417e-004  1.005e-004    -3.849    -3.998    -0.149
   MgSO4                 1.458e-005  1.461e-005    -4.836    -4.835     0.001
   MgHPO4                6.268e-006  6.279e-006    -5.203    -5.202     0.001
   MgHCO3+               1.415e-006  1.294e-006    -5.849    -5.888    -0.039
   MgH2PO4+              4.246e-007  3.882e-007    -6.372    -6.411    -0.039
   MgPO4-                1.731e-007  1.582e-007    -6.762    -6.801    -0.039
   MgCO3                 4.922e-008  4.930e-008    -7.308    -7.307     0.001
   MgOH+                 2.961e-009  2.707e-009    -8.529    -8.567    -0.039
N(-3)           5.685e-004
   NH4+                  5.610e-004  5.109e-004    -3.251    -3.292    -0.041
   NH4SO4-               5.090e-006  4.653e-006    -5.293    -5.332    -0.039
   NH3                   2.384e-006  2.388e-006    -5.623    -5.622     0.001
N(5)            2.115e-003
   NO3-                  2.115e-003  1.928e-003    -2.675    -2.715    -0.040
Na              1.677e-003
   Na+                   1.670e-003  1.528e-003    -2.777    -2.816    -0.039
   NaSO4-                5.737e-006  5.244e-006    -5.241    -5.280    -0.039
```

```
   NaHCO3                 9.630e-007  9.646e-007    -6.016    -6.016     0.001
   NaHPO4-                3.022e-007  2.763e-007    -6.520    -6.559    -0.039
   NaCO3-                 1.338e-008  1.223e-008    -7.874    -7.913    -0.039
   NaOH                   1.184e-010  1.186e-010    -9.927    -9.926     0.001
O(0)             0.000e+000
   O2                     0.000e+000  0.000e+000   -43.486   -43.485     0.001
P                3.126e-004
   H2PO4-                 1.429e-004  1.308e-004    -3.845    -3.884    -0.039
   HPO4-2                 1.329e-004  9.271e-005    -3.876    -4.033    -0.156
   CaHPO4                 2.681e-005  2.686e-005    -4.572    -4.571     0.001
   MgHPO4                 6.268e-006  6.279e-006    -5.203    -5.202     0.001
   CaH2PO4+               1.928e-006  1.763e-006    -5.715    -5.754    -0.039
   CaPO4-                 7.420e-007  6.783e-007    -6.130    -6.169    -0.039
   MgH2PO4+               4.246e-007  3.882e-007    -6.372    -6.411    -0.039
   NaHPO4-                3.022e-007  2.763e-007    -6.520    -6.559    -0.039
   MgPO4-                 1.731e-007  1.582e-007    -6.762    -6.801    -0.039
   KHPO4-                 1.266e-007  1.158e-007    -6.897    -6.936    -0.039
   PO4-3                  9.979e-010  4.436e-010    -9.001    -9.353    -0.352
S(6)             1.112e-003
   SO4-2                  1.005e-003  7.070e-004    -2.998    -3.151    -0.153
   CaSO4                  7.803e-005  7.817e-005    -4.108    -4.107     0.001
   MgSO4                  1.458e-005  1.461e-005    -4.836    -4.835     0.001
   NaSO4-                 5.737e-006  5.244e-006    -5.241    -5.280    -0.039
   NH4SO4-                5.090e-006  4.653e-006    -5.293    -5.332    -0.039
   KSO4-                  3.185e-006  2.912e-006    -5.497    -5.536    -0.039
   HSO4-                  5.751e-009  5.258e-009    -8.240    -8.279    -0.039
   CaHSO4+                4.018e-011  3.673e-011   -10.396   -10.435    -0.039

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.04   -6.39   -4.34  CaSO4
        Aragonite        -1.19   -9.49   -8.31  CaCO3
        Calcite          -1.04   -9.49   -8.45  CaCO3
        CH4(g)          -64.30  -67.12   -2.82  CH4
        CO2(g)           -2.23   -3.64   -1.41  CO2
        Dolomite         -2.77  -19.74  -16.97  CaMg(CO3)2
        Gypsum           -1.81   -6.39   -4.58  CaSO4:2H2O
        H2(g)           -22.14  -25.27   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    2.97    0.00   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.49   -5.62    1.87  NH3
        O2(g)           -40.63  -43.49   -2.85  O2

Initial solution 8-Biochar + HA 10 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 9.934e-004  9.934e-004
        Ca                5.578e-004  5.578e-004
        K                 1.059e-003  1.059e-003
        Mg                1.563e-004  1.563e-004
        N(-3)             2.571e-004  2.571e-004
        N(5)              1.209e-003  1.209e-003
        Na                1.793e-003  1.793e-003
        P                 4.828e-004  4.828e-004
        S(6)              9.492e-004  9.492e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.010
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  6.083e-003
                       Mass of water (kg)  =  1.000e+000
```

```
                 Total alkalinity (eq/kg)  =  1.051e-003
                       Total CO2 (mol/kg)  =  9.934e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -1.047e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -1.19
                               Iterations  =  11
                                  Total H  = 1.110150e+002
                                  Total O  = 5.551838e+001

---------------------------------Redox couples----------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           6.4992      0.3780

----------------------------Distribution of species-----------------------------

                                                    Log       Log         Log 
   Species                 Molality    Activity  Molality  Activity     Gamma

   H+                    1.052e-007  9.772e-008     -6.978    -7.010    -0.032
   OH-                   7.550e-008  6.946e-008     -7.122    -7.158    -0.036
   H2O                   5.551e+001  9.999e-001      1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000    -66.757   -66.757     0.001
C(4)            9.934e-004
   HCO3-                 8.116e-004  7.494e-004     -3.091    -3.125    -0.035
   CO2                   1.762e-004  1.765e-004     -3.754    -3.753     0.001
   CaHCO3+               3.346e-006  3.090e-006     -5.475    -5.510    -0.035
   MgHCO3+               9.029e-007  8.318e-007     -6.044    -6.080    -0.036
   NaHCO3                6.929e-007  6.939e-007     -6.159    -6.159     0.001
   CO3-2                 4.443e-007  3.230e-007     -6.352    -6.491    -0.138
   CaCO3                 1.740e-007  1.743e-007     -6.759    -6.759     0.001
   MgCO3                 2.757e-008  2.761e-008     -7.560    -7.559     0.001
   NaCO3-                8.317e-009  7.662e-009     -8.080    -8.116    -0.036
Ca              5.578e-004
   Ca+2                  4.842e-004  3.518e-004     -3.315    -3.454    -0.139
   CaSO4                 4.271e-005  4.277e-005     -4.370    -4.369     0.001
   CaHPO4                2.475e-005  2.478e-005     -4.607    -4.606     0.001
   CaHCO3+               3.346e-006  3.090e-006     -5.475    -5.510    -0.035
   CaH2PO4+              2.027e-006  1.867e-006     -5.693    -5.729    -0.036
   CaPO4-                5.917e-007  5.451e-007     -6.228    -6.264    -0.036
   CaCO3                 1.740e-007  1.743e-007     -6.759    -6.759     0.001
   CaOH+                 6.484e-010  5.974e-010     -9.188    -9.224    -0.036
   CaHSO4+               2.505e-011  2.307e-011    -10.601   -10.637    -0.036
H(0)            1.420e-025
   H2                    7.102e-026  7.112e-026    -25.149   -25.148     0.001
K               1.059e-003
   K+                    1.054e-003  9.704e-004     -2.977    -3.013    -0.036
   KSO4-                 4.327e-006  3.987e-006     -5.364    -5.399    -0.036
   KHPO4-                2.902e-007  2.673e-007     -6.537    -6.573    -0.036
   KOH                   3.438e-011  3.443e-011    -10.464   -10.463     0.001
Mg              1.563e-004
   Mg+2                  1.326e-004  9.673e-005     -3.877    -4.014    -0.137
   MgSO4                 1.269e-005  1.271e-005     -4.896    -4.896     0.001
   MgHPO4                9.200e-006  9.213e-006     -5.036    -5.036     0.001
   MgHCO3+               9.029e-007  8.318e-007     -6.044    -6.080    -0.036
   MgH2PO4+              7.098e-007  6.539e-007     -6.149    -6.184    -0.036
   MgPO4-                2.195e-007  2.022e-007     -6.659    -6.694    -0.036
   MgCO3                 2.757e-008  2.761e-008     -7.560    -7.559     0.001
   MgOH+                 2.464e-009  2.270e-009     -8.608    -8.644    -0.036
N(-3)           2.571e-004
   NH4+                  2.541e-004  2.333e-004     -3.595    -3.632    -0.037
   NH4SO4-               2.084e-006  1.920e-006     -5.681    -5.717    -0.036
   NH3                   9.484e-007  9.497e-007     -6.023    -6.022     0.001
N(5)            1.209e-003
   NO3-                  1.209e-003  1.111e-003     -2.918    -2.954    -0.037
Na              1.793e-003
```

```
   Na+                   1.786e-003  1.647e-003    -2.748    -2.783    -0.035
   NaSO4-                5.541e-006  5.105e-006    -5.256    -5.292    -0.036
   NaHCO3                6.929e-007  6.939e-007    -6.159    -6.159     0.001
   NaHPO4-               4.923e-007  4.536e-007    -6.308    -6.343    -0.036
   NaCO3-                8.317e-009  7.662e-009    -8.080    -8.116    -0.036
   NaOH                  1.111e-010  1.113e-010    -9.954    -9.953     0.001
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -43.726   -43.725     0.001
P               4.828e-004
   H2PO4-                2.482e-004  2.288e-004    -3.605    -3.641    -0.035
   HPO4-2                1.963e-004  1.413e-004    -3.707    -3.850    -0.143
   CaHPO4                2.475e-005  2.478e-005    -4.607    -4.606     0.001
   MgHPO4                9.200e-006  9.213e-006    -5.036    -5.036     0.001
   CaH2PO4+              2.027e-006  1.867e-006    -5.693    -5.729    -0.036
   MgH2PO4+              7.098e-007  6.539e-007    -6.149    -6.184    -0.036
   CaPO4-                5.917e-007  5.451e-007    -6.228    -6.264    -0.036
   NaHPO4-               4.923e-007  4.536e-007    -6.308    -6.343    -0.036
   KHPO4-                2.902e-007  2.673e-007    -6.537    -6.573    -0.036
   MgPO4-                2.195e-007  2.022e-007    -6.659    -6.694    -0.036
   PO4-3                 1.235e-009  5.887e-010    -8.908    -9.230    -0.322
S(6)            9.492e-004
   SO4-2                 8.819e-004  6.389e-004    -3.055    -3.195    -0.140
   CaSO4                 4.271e-005  4.277e-005    -4.370    -4.369     0.001
   MgSO4                 1.269e-005  1.271e-005    -4.896    -4.896     0.001
   NaSO4-                5.541e-006  5.105e-006    -5.256    -5.292    -0.036
   KSO4-                 4.327e-006  3.987e-006    -5.364    -5.399    -0.036
   NH4SO4-               2.084e-006  1.920e-006    -5.681    -5.717    -0.036
   HSO4-                 5.922e-009  5.455e-009    -8.228    -8.263    -0.036
   CaHSO4+               2.505e-011  2.307e-011   -10.601   -10.637    -0.036

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.30   -6.65   -4.34  CaSO4
        Aragonite        -1.64   -9.94   -8.31  CaCO3
        Calcite          -1.49   -9.94   -8.45  CaCO3
        CH4(g)          -63.94  -66.76   -2.82  CH4
        CO2(g)           -2.35   -3.75   -1.41  CO2
        Dolomite         -3.48  -20.45  -16.97  CaMg(CO3)2
        Gypsum           -2.07   -6.65   -4.58  CaSO4:2H2O
        H2(g)           -22.02  -25.15   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    2.19   -0.78   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.89   -6.02    1.87  NH3
        O2(g)           -40.87  -43.73   -2.85  O2

Initial solution 9-Biochar + HA 18 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                6.262e-004  6.262e-004
        Ca               4.018e-004  4.018e-004
        K                8.249e-004  8.249e-004
        Mg               1.234e-004  1.234e-004
        N(-3)            2.278e-004  2.278e-004
        N(5)             7.769e-004  7.769e-004
        Na               1.283e-003  1.283e-003
        P                5.041e-004  5.041e-004
        S(6)             7.292e-004  7.292e-004

----------------------------Description of solution----------------------------

                                       pH  =   6.970
                                       pe  =   4.000
                        Activity of water  =   1.000
```

```
                           Ionic strength  =  4.631e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  7.304e-004
                       Total CO2 (mol/kg)  =  6.262e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  = -8.313e-005
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -1.26
                               Iterations  =  11
                                  Total H  = 1.110146e+002
                                  Total O  = 5.551524e+001

---------------------------------Redox couples----------------------------------

        Redox couple              pe  Eh (volts)

        N(-3)/N(5)            6.5316      0.3799

----------------------------Distribution of species-----------------------------

                                                   Log       Log         Log
   Species                  Molality    Activity  Molality  Activity     Gamma

   H+                     1.145e-007  1.072e-007    -6.941    -6.970    -0.029
   OH-                    6.818e-008  6.335e-008    -7.166    -7.198    -0.032
   H2O                    5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                    0.000e+000  0.000e+000   -66.601   -66.601     0.000
C(4)            6.262e-004
   HCO3-                  5.027e-004  4.684e-004    -3.299    -3.329    -0.031
   CO2                    1.208e-004  1.209e-004    -3.918    -3.917     0.000
   CaHCO3+                1.565e-006  1.459e-006    -5.805    -5.836    -0.031
   MgHCO3+                4.620e-007  4.297e-007    -6.335    -6.367    -0.031
   NaHCO3                 3.133e-007  3.137e-007    -6.504    -6.504     0.000
   CO3-2                  2.442e-007  1.841e-007    -6.612    -6.735    -0.123
   CaCO3                  7.494e-008  7.502e-008    -7.125    -7.125     0.000
   MgCO3                  1.299e-008  1.301e-008    -7.886    -7.886     0.000
   NaCO3-                 3.396e-009  3.159e-009    -8.469    -8.500    -0.031
Ca              4.018e-004
   Ca+2                   3.526e-004  2.657e-004    -3.453    -3.576    -0.123
   CaSO4                  2.609e-005  2.612e-005    -4.584    -4.583     0.000
   CaHPO4                 1.930e-005  1.932e-005    -4.714    -4.714     0.000
   CaH2PO4+               1.716e-006  1.596e-006    -5.765    -5.797    -0.031
   CaHCO3+                1.565e-006  1.459e-006    -5.805    -5.836    -0.031
   CaPO4-                 4.168e-007  3.876e-007    -6.380    -6.412    -0.031
   CaCO3                  7.494e-008  7.502e-008    -7.125    -7.125     0.000
   CaOH+                  4.424e-010  4.115e-010    -9.354    -9.386    -0.031
   CaHSO4+                1.661e-011  1.545e-011   -10.780   -10.811    -0.031
H(0)            1.708e-025
   H2                     8.541e-026  8.550e-026   -25.068   -25.068     0.000
K               8.249e-004
   K+                     8.220e-004  7.639e-004    -3.085    -3.117    -0.032
   KSO4-                  2.728e-006  2.537e-006    -5.564    -5.596    -0.031
   KHPO4-                 2.336e-007  2.173e-007    -6.632    -6.663    -0.031
   KOH                    2.469e-011  2.472e-011   -10.607   -10.607     0.000
Mg              1.234e-004
   Mg+2                   1.058e-004  7.996e-005    -3.976    -4.097    -0.122
   MgSO4                  8.485e-006  8.494e-006    -5.071    -5.071     0.000
   MgHPO4                 7.853e-006  7.862e-006    -5.105    -5.104     0.000
   MgH2PO4+               6.579e-007  6.119e-007    -6.182    -6.213    -0.031
   MgHCO3+                4.620e-007  4.297e-007    -6.335    -6.367    -0.031
   MgPO4-                 1.692e-007  1.574e-007    -6.772    -6.803    -0.031
   MgCO3                  1.299e-008  1.301e-008    -7.886    -7.886     0.000
   MgOH+                  1.840e-009  1.712e-009    -8.735    -8.767    -0.031
N(-3)           2.278e-004
   NH4+                   2.255e-004  2.092e-004    -3.647    -3.679    -0.033
   NH4SO4-                1.497e-006  1.392e-006    -5.825    -5.856    -0.031
   NH3                    7.760e-007  7.768e-007    -6.110    -6.110     0.000
N(5)            7.769e-004
```

```
   NO3-                  7.769e-004  7.214e-004    -3.110    -3.142    -0.032
Na              1.283e-003
   Na+                   1.280e-003  1.191e-003    -2.893    -2.924    -0.031
   NaSO4-                3.210e-006  2.985e-006    -5.494    -5.525    -0.031
   NaHPO4-               3.641e-007  3.387e-007    -6.439    -6.470    -0.031
   NaHCO3                3.133e-007  3.137e-007    -6.504    -6.504     0.000
   NaCO3-                3.396e-009  3.159e-009    -8.469    -8.500    -0.031
   NaOH                  7.334e-011  7.342e-011   -10.135   -10.134     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -43.886   -43.885     0.000
P               5.041e-004
   H2PO4-                2.783e-004  2.590e-004    -3.555    -3.587    -0.031
   HPO4-2                1.951e-004  1.459e-004    -3.710    -3.836    -0.126
   CaHPO4                1.930e-005  1.932e-005    -4.714    -4.714     0.000
   MgHPO4                7.853e-006  7.862e-006    -5.105    -5.104     0.000
   CaH2PO4+              1.716e-006  1.596e-006    -5.765    -5.797    -0.031
   MgH2PO4+              6.579e-007  6.119e-007    -6.182    -6.213    -0.031
   CaPO4-                4.168e-007  3.876e-007    -6.380    -6.412    -0.031
   NaHPO4-               3.641e-007  3.387e-007    -6.439    -6.470    -0.031
   KHPO4-                2.336e-007  2.173e-007    -6.632    -6.663    -0.031
   MgPO4-                1.692e-007  1.574e-007    -6.772    -6.803    -0.031
   PO4-3                 1.066e-009  5.544e-010    -8.972    -9.256    -0.284
S(6)            7.292e-004
   SO4-2                 6.871e-004  5.166e-004    -3.163    -3.287    -0.124
   CaSO4                 2.609e-005  2.612e-005    -4.584    -4.583     0.000
   MgSO4                 8.485e-006  8.494e-006    -5.071    -5.071     0.000
   NaSO4-                3.210e-006  2.985e-006    -5.494    -5.525    -0.031
   KSO4-                 2.728e-006  2.537e-006    -5.564    -5.596    -0.031
   NH4SO4-               1.497e-006  1.392e-006    -5.825    -5.856    -0.031
   HSO4-                 5.200e-009  4.837e-009    -8.284    -8.315    -0.031
   CaHSO4+               1.661e-011  1.545e-011   -10.780   -10.811    -0.031

------------------------------Saturation indices--------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.52   -6.86   -4.34  CaSO4
        Aragonite        -2.00  -10.31   -8.31  CaCO3
        Calcite          -1.86  -10.31   -8.45  CaCO3
        CH4(g)          -63.78  -66.60   -2.82  CH4
        CO2(g)           -2.51   -3.92   -1.41  CO2
        Dolomite         -4.17  -21.14  -16.97  CaMg(CO3)2
        Gypsum           -2.28   -6.86   -4.58  CaSO4:2H2O
        H2(g)           -21.94  -25.07   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    1.46   -1.51   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.98   -6.11    1.87  NH3
        O2(g)           -41.03  -43.89   -2.85  O2

Initial solution 10-Biochar + HA 42 h.

-----------------------------Solution composition-------------------------------

        Elements           Molality       Moles

        C                5.612e-004  3.612e-004
        Ca               3.456e-004  3.456e-004
        K                5.116e-004  5.116e-004
        Mg               9.873e-005  9.873e-005
        N(-3)            2.813e-004  2.813e-004
        Na               9.070e-004  9.070e-004
        P                3.742e-004  3.742e-004
        S(6)             4.433e-004  4.433e-004

----------------------------Description of solution----------------------------

                                       pH  =   6.760
                                       pe  =   4.000
```

```
                        Activity of water  =   1.000
                           Ionic strength  =  2.966e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  3.796e-004
                       Total CO2 (mol/kg)  =  3.612e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  9.481e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  23.28
                               Iterations  =  10
                                  Total H  = 1.110144e+002
                                  Total O  = 5.551047e+001

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                    Molality    Activity  Molality  Activity     Gamma

   H+                    1.835e-007  1.738e-007    -6.736    -6.760    -0.024
   OH-                   4.147e-008  3.907e-008    -7.382    -7.408    -0.026
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -64.995   -64.995     0.000
C(4)            3.612e-004
   HCO3-                 2.581e-004  2.436e-004    -3.588    -3.613    -0.025
   CO2                   1.019e-004  1.020e-004    -3.992    -3.991     0.000
   CaHCO3+               7.607e-007  7.180e-007    -6.119    -6.144    -0.025
   MgHCO3+               2.102e-007  1.981e-007    -6.677    -6.703    -0.026
   NaHCO3                1.169e-007  1.170e-007    -6.932    -6.932     0.000
   CO3-2                 7.439e-008  5.904e-008    -7.128    -7.229    -0.100
   CaCO3                 2.276e-008  2.277e-008    -7.643    -7.643     0.000
   MgCO3                 3.696e-009  3.698e-009    -8.432    -8.432     0.000
   NaCO3-                7.705e-010  7.263e-010    -9.113    -9.139    -0.026
Ca              3.456e-004
   Ca+2                  3.170e-004  2.515e-004    -3.499    -3.600    -0.101
   CaSO4                 1.587e-005  1.588e-005    -4.800    -4.799     0.000
   CaHPO4                1.037e-005  1.037e-005    -4.984    -4.984     0.000
   CaH2PO4+              1.475e-006  1.390e-006    -5.831    -5.857    -0.026
   CaHCO3+               7.607e-007  7.180e-007    -6.119    -6.144    -0.025
   CaPO4-                1.361e-007  1.283e-007    -6.866    -6.892    -0.026
   CaCO3                 2.276e-008  2.277e-008    -7.643    -7.643     0.000
   CaOH+                 2.547e-010  2.401e-010    -9.594    -9.620    -0.026
   CaHSO4+               1.616e-011  1.523e-011   -10.792   -10.817    -0.026
H(0)            4.495e-025
   H2                    2.247e-025  2.249e-025   -24.648   -24.648     0.000
K               5.116e-004
   K+                    5.104e-004  4.809e-004    -3.292    -3.318    -0.026
   KSO4-                 1.088e-006  1.026e-006    -5.963    -5.989    -0.026
   KHPO4-                8.230e-008  7.758e-008    -7.085    -7.110    -0.026
   KOH                   9.588e-012  9.594e-012   -11.018   -11.018     0.000
Mg              9.873e-005
   Mg+2                  8.915e-005  7.088e-005    -4.050    -4.149    -0.100
   MgSO4                 4.833e-006  4.837e-006    -5.316    -5.315     0.000
   MgHPO4                3.951e-006  3.953e-006    -5.403    -5.403     0.000
   MgH2PO4+              5.294e-007  4.990e-007    -6.276    -6.302    -0.026
   MgHCO3+               2.102e-007  1.981e-007    -6.677    -6.703    -0.026
   MgPO4-                5.176e-008  4.879e-008    -7.286    -7.312    -0.026
   MgCO3                 3.696e-009  3.698e-009    -8.432    -8.432     0.000
   MgOH+                 9.924e-010  9.355e-010    -9.003    -9.029    -0.026
N(-3)           2.813e-004
   NH4+                  2.795e-004  2.631e-004    -3.554    -3.580    -0.026
   NH4SO4-               1.193e-006  1.125e-006    -5.923    -5.949    -0.026
   NH3                   6.019e-007  6.023e-007    -6.221    -6.220     0.000
Na              9.070e-004
   Na+                   9.053e-004  8.538e-004    -3.043    -3.069    -0.025
   NaSO4-                1.459e-006  1.375e-006    -5.836    -5.862    -0.026
   NaHPO4-               1.461e-007  1.377e-007    -6.835    -6.861    -0.026
   NaHCO3                1.169e-007  1.170e-007    -6.932    -6.932     0.000
   NaCO3-                7.705e-010  7.263e-010    -9.113    -9.139    -0.026
```

```
   NaOH                3.244e-011  3.246e-011   -10.489   -10.489     0.000
O(0)            0.000e+000
   O2                  0.000e+000  0.000e+000   -44.725   -44.725     0.000
P               3.742e-004
   H2PO4-              2.527e-004  2.383e-004    -3.597    -3.623    -0.025
   HPO4-2              1.048e-004  8.274e-005    -3.980    -4.082    -0.103
   CaHPO4              1.037e-005  1.037e-005    -4.984    -4.984     0.000
   MgHPO4              3.951e-006  3.953e-006    -5.403    -5.403     0.000
   CaH2PO4+            1.475e-006  1.390e-006    -5.831    -5.857    -0.026
   MgH2PO4+            5.294e-007  4.990e-007    -6.276    -6.302    -0.026
   NaHPO4-             1.461e-007  1.377e-007    -6.835    -6.861    -0.026
   CaPO4-              1.361e-007  1.283e-007    -6.866    -6.892    -0.026
   KHPO4-              8.230e-008  7.758e-008    -7.085    -7.110    -0.026
   MgPO4-              5.176e-008  4.879e-008    -7.286    -7.312    -0.026
   PO4-3               3.301e-010  1.939e-010    -9.481    -9.712    -0.231
S(6)            4.433e-004
   SO4-2               4.189e-004  3.318e-004    -3.378    -3.479    -0.101
   CaSO4               1.587e-005  1.588e-005    -4.800    -4.799     0.000
   MgSO4               4.833e-006  4.837e-006    -5.316    -5.315     0.000
   NaSO4-              1.459e-006  1.375e-006    -5.836    -5.862    -0.026
   NH4SO4-             1.193e-006  1.125e-006    -5.923    -5.949    -0.026
   KSO4-               1.088e-006  1.026e-006    -5.963    -5.989    -0.026
   HSO4-               5.345e-009  5.038e-009    -8.272    -8.298    -0.026
   CaHSO4+             1.616e-011  1.523e-011   -10.792   -10.817    -0.026

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.73   -7.08   -4.34  CaSO4
        Aragonite        -2.52  -10.83   -8.31  CaCO3
        Calcite          -2.38  -10.83   -8.45  CaCO3
        CH4(g)          -62.18  -64.99   -2.82  CH4
        CO2(g)           -2.58   -3.99   -1.41  CO2
        Dolomite         -5.23  -22.21  -16.97  CaMg(CO3)2
        Gypsum           -2.50   -7.08   -4.58  CaSO4:2H2O
        H2(g)           -21.52  -24.65   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite   -0.24   -3.20   -2.97  Ca5(PO4)3OH
        NH3(g)           -8.09   -6.22    1.87  NH3
        O2(g)           -41.87  -44.73   -2.85  O2

Initial solution 11-Biochar + HA 100 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                3.793e-004  3.793e-004
        Ca               3.818e-004  3.818e-004
        K                5.973e-004  5.973e-004
        Mg               1.604e-004  1.604e-004
        N(-3)            1.021e-004  1.021e-004
        Na               1.281e-003  1.281e-003
        P                3.336e-004  3.336e-004
        S(6)             7.353e-004  7.353e-004

----------------------------Description of solution----------------------------

                                       pH  =   6.960
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  3.830e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.509e-004
                       Total CO2 (mol/kg)  =  3.793e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  8.101e-004
```

```
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  15.99
                            Iterations  =  11
                               Total H  = 1.110137e+002
                               Total O  = 5.551156e+001

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log
   Species                   Molality    Activity  Molality  Activity     Gamma

   H+                       1.165e-007  1.096e-007    -6.934    -6.960    -0.026
   OH-                      6.622e-008  6.191e-008    -7.179    -7.208    -0.029
   H2O                      5.551e+001  9.999e-001     1.744    -0.000     0.000
C(-4)               0.000e+000
   CH4                      0.000e+000  0.000e+000   -66.729   -66.729     0.000
C(4)                3.793e-004
   HCO3-                    3.027e-004  2.837e-004    -3.519    -3.547    -0.028
   CO2                      7.488e-005  7.495e-005    -4.126    -4.125     0.000
   CaHCO3+                  9.311e-007  8.726e-007    -6.031    -6.059    -0.028
   MgHCO3+                  3.777e-007  3.534e-007    -6.423    -6.452    -0.029
   NaHCO3                   1.906e-007  1.908e-007    -6.720    -6.719     0.000
   CO3-2                    1.413e-007  1.090e-007    -6.850    -6.963    -0.113
   CaCO3                    4.382e-008  4.386e-008    -7.358    -7.358     0.000
   MgCO3                    1.045e-008  1.045e-008    -7.981    -7.981     0.000
   NaCO3-                   2.007e-009  1.878e-009    -8.698    -8.726    -0.029
Ca                  3.818e-004
   Ca+2                     3.404e-004  2.624e-004    -3.468    -3.581    -0.113
   CaSO4                    2.653e-005  2.655e-005    -4.576    -4.576     0.000
   CaHPO4                   1.255e-005  1.256e-005    -4.902    -4.901     0.000
   CaH2PO4+                 1.135e-006  1.062e-006    -5.945    -5.974    -0.029
   CaHCO3+                  9.311e-007  8.726e-007    -6.031    -6.059    -0.028
   CaPO4-                   2.631e-007  2.462e-007    -6.580    -6.609    -0.029
   CaCO3                    4.382e-008  4.386e-008    -7.358    -7.358     0.000
   CaOH+                    4.245e-010  3.972e-010    -9.372    -9.401    -0.029
   CaHSO4+                  1.718e-011  1.607e-011   -10.765   -10.794    -0.029
H(0)                1.789e-025
   H2                       8.946e-026  8.953e-026   -25.048   -25.048     0.000
K                   5.973e-004
   K+                       5.951e-004  5.565e-004    -3.225    -3.255    -0.029
   KSO4-                    2.033e-006  1.903e-006    -5.692    -5.721    -0.029
   KHPO4-                   1.113e-007  1.041e-007    -6.954    -6.982    -0.029
   KOH                      1.758e-011  1.760e-011   -10.755   -10.755     0.000
Mg                  1.604e-004
   Mg+2                     1.404e-004  1.086e-004    -3.853    -3.964    -0.112
   MgSO4                    1.186e-005  1.187e-005    -4.926    -4.925     0.000
   MgHPO4                   7.018e-006  7.024e-006    -5.154    -5.153     0.000
   MgH2PO4+                 5.978e-007  5.594e-007    -6.223    -6.252    -0.029
   MgHCO3+                  3.777e-007  3.534e-007    -6.423    -6.452    -0.029
   MgPO4-                   1.468e-007  1.374e-007    -6.833    -6.862    -0.029
   MgCO3                    1.045e-008  1.045e-008    -7.981    -7.981     0.000
   MgOH+                    2.427e-009  2.271e-009    -8.615    -8.644    -0.029
N(-3)               1.021e-004
   NH4+                     1.011e-004  9.439e-005    -3.995    -4.025    -0.030
   NH4SO4-                  6.910e-007  6.465e-007    -6.161    -6.189    -0.029
   NH3                      3.421e-007  3.424e-007    -6.466    -6.465     0.000
Na                  1.281e-003
   Na+                      1.278e-003  1.196e-003    -2.894    -2.922    -0.029
   NaSO4-                   3.298e-006  3.086e-006    -5.482    -5.511    -0.029
   NaHPO4-                  2.392e-007  2.238e-007    -6.621    -6.650    -0.029
   NaHCO3                   1.906e-007  1.908e-007    -6.720    -6.719     0.000
   NaCO3-                   2.007e-009  1.878e-009    -8.698    -8.726    -0.029
   NaOH                     7.200e-011  7.206e-011   -10.143   -10.142     0.000
O(0)                0.000e+000
   O2                       0.000e+000  0.000e+000   -43.926   -43.925     0.000
P                   3.336e-004
   H2PO4-                   1.863e-004  1.744e-004    -3.730    -3.759    -0.029
   HPO4-2                   1.252e-004  9.596e-005    -3.902    -4.018    -0.116
   CaHPO4                   1.255e-005  1.256e-005    -4.902    -4.901     0.000
```

```
   MgHPO4                7.018e-006  7.024e-006    -5.154    -5.153     0.000
   CaH2PO4+              1.135e-006  1.062e-006    -5.945    -5.974    -0.029
   MgH2PO4+              5.978e-007  5.594e-007    -6.223    -6.252    -0.029
   CaPO4-                2.631e-007  2.462e-007    -6.580    -6.609    -0.029
   NaHPO4-               2.392e-007  2.238e-007    -6.621    -6.650    -0.029
   MgPO4-                1.468e-007  1.374e-007    -6.833    -6.862    -0.029
   KHPO4-                1.113e-007  1.041e-007    -6.954    -6.982    -0.029
   PO4-3                 6.490e-010  3.564e-010    -9.188    -9.448    -0.260
S(6)            7.353e-004
   SO4-2                 6.908e-004  5.317e-004    -3.161    -3.274    -0.114
   CaSO4                 2.653e-005  2.655e-005    -4.576    -4.576     0.000
   MgSO4                 1.186e-005  1.187e-005    -4.926    -4.925     0.000
   NaSO4-                3.298e-006  3.086e-006    -5.482    -5.511    -0.029
   KSO4-                 2.033e-006  1.903e-006    -5.692    -5.721    -0.029
   NH4SO4-               6.910e-007  6.465e-007    -6.161    -6.189    -0.029
   HSO4-                 5.444e-009  5.094e-009    -8.264    -8.293    -0.029
   CaHSO4+               1.718e-011  1.607e-011   -10.765   -10.794    -0.029

------------------------------Saturation indices--------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.51   -6.86   -4.34  CaSO4
        Aragonite        -2.24  -10.54   -8.31  CaCO3
        Calcite          -2.09  -10.54   -8.45  CaCO3
        CH4(g)          -63.91  -66.73   -2.82  CH4
        CO2(g)           -2.72   -4.13   -1.41  CO2
        Dolomite         -4.50  -21.47  -16.97  CaMg(CO3)2
        Gypsum           -2.27   -6.86   -4.58  CaSO4:2H2O
        H2(g)           -21.92  -25.05   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    0.85   -2.12   -2.97  Ca5(PO4)3OH
        NH3(g)           -8.34   -6.47    1.87  NH3
        O2(g)           -41.07  -43.93   -2.85  O2

Initial solution 12-Biochar + HA 200 h.

-----------------------------Solution composition-------------------------------

        Elements           Molality       Moles

        C                2.257e-004  2.257e-004
        Ca               2.932e-004  2.932e-004
        K                2.443e-004  2.443e-004
        Mg               1.584e-004  1.584e-004
        N(-3)            1.050e-004  1.050e-004
        Na               1.027e-003  1.027e-003
        P                1.227e-004  1.227e-004
        S(6)             4.490e-004  4.490e-004

----------------------------Description of solution-----------------------------

                                       pH  =   7.390
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  2.635e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.907e-004
                       Total CO2 (mol/kg)  =  2.257e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  9.676e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  28.08
                               Iterations  =   9
                                  Total H  = 1.110132e+002
                                  Total O  = 5.550916e+001

----------------------------Distribution of species-----------------------------
```

```
                                                   Log       Log         Log
   Species                  Molality    Activity  Molality  Activity     Gamma

   OH-                   1.763e-007  1.666e-007    -6.754    -6.778    -0.024
   H+                    4.291e-008  4.074e-008    -7.367    -7.390    -0.023
   H2O                   5.551e+001  1.000e+000     1.744    -0.000     0.000
C(-4)           0.000e+000
   CH4                   0.000e+000  0.000e+000   -70.763   -70.763     0.000
C(4)            2.257e-004
   HCO3-                 2.054e-004  1.944e-004    -3.687    -3.711    -0.024
   CO2                   1.907e-005  1.908e-005    -4.720    -4.719     0.000
   CaHCO3+               5.254e-007  4.974e-007    -6.280    -6.303    -0.024
   MgHCO3+               2.754e-007  2.604e-007    -6.560    -6.584    -0.024
   CO3-2                 2.502e-007  2.010e-007    -6.602    -6.697    -0.095
   NaHCO3                1.059e-007  1.060e-007    -6.975    -6.975     0.000
   CaCO3                 6.725e-008  6.729e-008    -7.172    -7.172     0.000
   MgCO3                 2.072e-008  2.074e-008    -7.684    -7.683     0.000
   NaCO3-                2.969e-009  2.808e-009    -8.527    -8.552    -0.024
Ca              2.932e-004
   Ca+2                  2.718e-004  2.183e-004    -3.566    -3.661    -0.095
   CaSO4                 1.412e-005  1.413e-005    -4.850    -4.850     0.000
   CaHPO4                6.147e-006  6.151e-006    -5.211    -5.211     0.000
   CaHCO3+               5.254e-007  4.974e-007    -6.280    -6.303    -0.024
   CaPO4-                3.432e-007  3.246e-007    -6.464    -6.489    -0.024
   CaH2PO4+              2.043e-007  1.932e-007    -6.690    -6.714    -0.024
   CaCO3                 6.725e-008  6.729e-008    -7.172    -7.172     0.000
   CaOH+                 9.402e-010  8.892e-010    -9.027    -9.051    -0.024
   CaHSO4+               3.360e-012  3.177e-012   -11.474   -11.498    -0.024
H(0)            2.470e-026
   H2                    1.235e-026  1.236e-026   -25.908   -25.908     0.000
K               2.443e-004
   K+                    2.437e-004  2.304e-004    -3.613    -3.638    -0.024
   KSO4-                 5.328e-007  5.038e-007    -6.273    -6.298    -0.024
   KHPO4-                2.685e-008  2.539e-008    -7.571    -7.595    -0.024
   KOH                   1.959e-011  1.961e-011   -10.708   -10.708     0.000
Mg              1.584e-004
   Mg+2                  1.451e-004  1.167e-004    -3.838    -3.933    -0.094
   MgSO4                 8.160e-006  8.165e-006    -5.088    -5.088     0.000
   MgHPO4                4.445e-006  4.448e-006    -5.352    -5.352     0.000
   MgHCO3+               2.754e-007  2.604e-007    -6.560    -6.584    -0.024
   MgPO4-                2.476e-007  2.342e-007    -6.606    -6.630    -0.024
   MgH2PO4+              1.392e-007  1.316e-007    -6.856    -6.881    -0.024
   MgCO3                 2.072e-008  2.074e-008    -7.684    -7.683     0.000
   MgOH+                 6.950e-009  6.573e-009    -8.158    -8.182    -0.024
N(-3)           1.050e-004
   NH4+                  1.036e-004  9.779e-005    -3.985    -4.010    -0.025
   NH3                   9.543e-007  9.549e-007    -6.020    -6.020     0.000
   NH4SO4-               4.531e-007  4.285e-007    -6.344    -6.368    -0.024
Na              1.027e-003
   Na+                   1.025e-003  9.694e-004    -2.989    -3.013    -0.024
   NaSO4-                1.692e-006  1.600e-006    -5.772    -5.796    -0.024
   NaHPO4-               1.130e-007  1.068e-007    -6.947    -6.971    -0.024
   NaHCO3                1.059e-007  1.060e-007    -6.975    -6.975     0.000
   NaCO3-                2.969e-009  2.808e-009    -8.527    -8.552    -0.024
   NaOH                  1.571e-010  1.572e-010    -9.804    -9.804     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -42.205   -42.205     0.000
P               1.227e-004
   HPO4-2                7.069e-005  5.652e-005    -4.151    -4.248    -0.097
   H2PO4-                4.034e-005  3.816e-005    -4.394    -4.418    -0.024
   CaHPO4                6.147e-006  6.151e-006    -5.211    -5.211     0.000
   MgHPO4                4.445e-006  4.448e-006    -5.352    -5.352     0.000
   CaPO4-                3.432e-007  3.246e-007    -6.464    -6.489    -0.024
   MgPO4-                2.476e-007  2.342e-007    -6.606    -6.630    -0.024
   CaH2PO4+              2.043e-007  1.932e-007    -6.690    -6.714    -0.024
   MgH2PO4+              1.392e-007  1.316e-007    -6.856    -6.881    -0.024
   NaHPO4-               1.130e-007  1.068e-007    -6.947    -6.971    -0.024
   KHPO4-                2.685e-008  2.539e-008    -7.571    -7.595    -0.024
```

```
   PO4-3                 9.348e-010  5.650e-010    -9.029    -9.248    -0.219
S(6)            4.490e-004
   SO4-2                 4.241e-004  3.401e-004    -3.373    -3.468    -0.096
   CaSO4                 1.412e-005  1.413e-005    -4.850    -4.850     0.000
   MgSO4                 8.160e-006  8.165e-006    -5.088    -5.088     0.000
   NaSO4-                1.692e-006  1.600e-006    -5.772    -5.796    -0.024
   KSO4-                 5.328e-007  5.038e-007    -6.273    -6.298    -0.024
   NH4SO4-               4.531e-007  4.285e-007    -6.344    -6.368    -0.024
   HSO4-                 1.280e-009  1.211e-009    -8.893    -8.917    -0.024
   CaHSO4+               3.360e-012  3.177e-012   -11.474   -11.498    -0.024

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Anhydrite        -2.79   -7.13   -4.34  CaSO4
        Aragonite        -2.05  -10.36   -8.31  CaCO3
        Calcite          -1.90  -10.36   -8.45  CaCO3
        CH4(g)          -67.94  -70.76   -2.82  CH4
        CO2(g)           -3.31   -4.72   -1.41  CO2
        Dolomite         -4.02  -20.99  -16.97  CaMg(CO3)2
        Gypsum           -2.55   -7.13   -4.58  CaSO4:2H2O
        H2(g)           -22.78  -25.91   -3.13  H2
        H2O(g)           -1.64   -0.00    1.64  H2O
        Hydroxyapatite    1.48   -1.49   -2.97  Ca5(PO4)3OH
        NH3(g)           -7.89   -6.02    1.87  NH3
        O2(g)           -39.35  -42.21   -2.85  O2

Initial solution 13-Biochar + HA 300 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        C                 2.441e-004  2.441e-004
        Ca                2.732e-004  2.732e-004
        K                 2.174e-004  2.174e-004
        Mg                1.234e-004  1.234e-004
        N(-3)             9.068e-005  9.068e-005
        Na                9.636e-004  9.636e-004
        P                 1.614e-005  1.614e-005
        S(6)              5.835e-004  5.835e-004

----------------------------Description of solution----------------------------

                                       pH  =   7.080
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  2.604e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.138e-004
                       Total CO2 (mol/kg)  =  2.441e-004
                      Temperature (deg C)  =  20.000
                  Electrical balance (eq)  =  6.679e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  19.96
                               Iterations  =   8
                                  Total H  = 1.110130e+002
                                  Total O  = 5.550931e+001

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log
   Species                 Molality    Activity  Molality  Activity       Gamma

   H+                    8.758e-008  8.318e-008    -7.058    -7.080    -0.022
   OH-                   8.633e-008  8.162e-008    -7.064    -7.088    -0.024
   H2O                   5.551e+001  1.000e+000     1.744    -0.000     0.000
C(-4)           0.000e+000
```

```
   CH4                   0.000e+000  0.000e+000   -67.975   -67.975     0.000
C(4)            2.441e-004
   HCO3-                 2.043e-004  1.935e-004    -3.690    -3.713    -0.024
   CO2                   3.875e-005  3.878e-005    -4.412    -4.411     0.000
   CaHCO3+               4.905e-007  4.645e-007    -6.309    -6.333    -0.024
   MgHCO3+               2.162e-007  2.046e-007    -6.665    -6.689    -0.024
   CO3-2                 1.218e-007  9.798e-008    -6.914    -7.009    -0.095
   NaHCO3                9.894e-008  9.900e-008    -7.005    -7.004     0.000
   CaCO3                 3.076e-008  3.078e-008    -7.512    -7.512     0.000
   MgCO3                 7.973e-009  7.977e-009    -8.098    -8.098     0.000
   NaCO3-                1.358e-009  1.284e-009    -8.867    -8.891    -0.024
Ca              2.732e-004
   Ca+2                  2.547e-004  2.048e-004    -3.594    -3.689    -0.095
   CaSO4                 1.735e-005  1.736e-005    -4.761    -4.761     0.000
   CaHPO4                5.706e-007  5.710e-007    -6.244    -6.243     0.000
   CaHCO3+               4.905e-007  4.645e-007    -6.309    -6.333    -0.024
   CaH2PO4+              3.871e-008  3.662e-008    -7.412    -7.436    -0.024
   CaCO3                 3.076e-008  3.078e-008    -7.512    -7.512     0.000
   CaPO4-                1.560e-008  1.476e-008    -7.807    -7.831    -0.024
   CaOH+                 4.320e-010  4.087e-010    -9.365    -9.389    -0.024
   CaHSO4+               8.425e-012  7.970e-012   -11.074   -11.099    -0.024
H(0)            1.030e-025
   H2                    5.149e-026  5.152e-026   -25.288   -25.288     0.000
K               2.174e-004
   K+                    2.168e-004  2.050e-004    -3.664    -3.688    -0.024
   KSO4-                 6.205e-007  5.869e-007    -6.207    -6.231    -0.024
   KHPO4-                2.362e-009  2.235e-009    -8.627    -8.651    -0.024
   KOH                   8.540e-012  8.545e-012   -11.069   -11.068     0.000
Mg              1.234e-004
   Mg+2                  1.144e-004  9.213e-005    -3.942    -4.036    -0.094
   MgSO4                 8.433e-006  8.438e-006    -5.074    -5.074     0.000
   MgHPO4                3.470e-007  3.473e-007    -6.460    -6.459     0.000
   MgHCO3+               2.162e-007  2.046e-007    -6.665    -6.689    -0.024
   MgH2PO4+              2.218e-008  2.098e-008    -7.654    -7.678    -0.024
   MgPO4-                9.466e-009  8.954e-009    -8.024    -8.048    -0.024
   MgCO3                 7.973e-009  7.977e-009    -8.098    -8.098     0.000
   MgOH+                 2.686e-009  2.541e-009    -8.571    -8.595    -0.024
N(-3)           9.068e-005
   NH4+                  8.976e-005  8.479e-005    -4.047    -4.072    -0.025
   NH4SO4-               5.142e-007  4.864e-007    -6.289    -6.313    -0.024
   NH3                   4.053e-007  4.055e-007    -6.392    -6.392     0.000
Na              9.636e-004
   Na+                   9.614e-004  9.098e-004    -3.017    -3.041    -0.024
   NaSO4-                2.078e-006  1.966e-006    -5.682    -5.706    -0.024
   NaHCO3                9.894e-008  9.900e-008    -7.005    -7.004     0.000
   NaHPO4-               1.048e-008  9.918e-009    -7.979    -8.004    -0.024
   NaCO3-                1.358e-009  1.284e-009    -8.867    -8.891    -0.024
   NaOH                  7.222e-011  7.226e-011   -10.141   -10.141     0.000
O(0)            0.000e+000
   O2                    0.000e+000  0.000e+000   -43.445   -43.445     0.000
P               1.614e-005
   H2PO4-                8.144e-006  7.707e-006    -5.089    -5.113    -0.024
   HPO4-2                6.984e-006  5.591e-006    -5.156    -5.253    -0.097
   CaHPO4                5.706e-007  5.710e-007    -6.244    -6.243     0.000
   MgHPO4                3.470e-007  3.473e-007    -6.460    -6.459     0.000
   CaH2PO4+              3.871e-008  3.662e-008    -7.412    -7.436    -0.024
   MgH2PO4+              2.218e-008  2.098e-008    -7.654    -7.678    -0.024
   CaPO4-                1.560e-008  1.476e-008    -7.807    -7.831    -0.024
   NaHPO4-               1.048e-008  9.918e-009    -7.979    -8.004    -0.024
   MgPO4-                9.466e-009  8.954e-009    -8.024    -8.048    -0.024
   KHPO4-                2.362e-009  2.235e-009    -8.627    -8.651    -0.024
   PO4-3                 4.516e-011  2.737e-011   -10.345   -10.563    -0.217
S(6)            5.835e-004
   SO4-2                 5.545e-004  4.453e-004    -3.256    -3.351    -0.095
   CaSO4                 1.735e-005  1.736e-005    -4.761    -4.761     0.000
   MgSO4                 8.433e-006  8.438e-006    -5.074    -5.074     0.000
   NaSO4-                2.078e-006  1.966e-006    -5.682    -5.706    -0.024
   KSO4-                 6.205e-007  5.869e-007    -6.207    -6.231    -0.024
```

```
NH4SO4-                5.142e-007  4.864e-007    -6.289    -6.313    -0.024
HSO4-                  3.421e-009  3.236e-009    -8.466    -8.490    -0.024
CaHSO4+                8.425e-012  7.970e-012   -11.074   -11.099    -0.024

------------------------------Saturation indices-------------------------------

     Phase               SI log IAP  log KT

     Anhydrite        -2.70   -7.04   -4.34  CaSO4
     Aragonite        -2.39  -10.70   -8.31  CaCO3
     Calcite          -2.24  -10.70   -8.45  CaCO3
     CH4(g)          -65.16  -67.97   -2.82  CH4
     CO2(g)           -3.00   -4.41   -1.41  CO2
     Dolomite         -4.77  -21.74  -16.97  CaMg(CO3)2
     Gypsum           -2.46   -7.04   -4.58  CaSO4:2H2O
     H2(g)           -22.16  -25.29   -3.13  H2
     H2O(g)           -1.64   -0.00    1.64  H2O
     Hydroxyapatite   -2.91   -5.88   -2.97  Ca5(PO4)3OH
     NH3(g)           -8.26   -6.39    1.87  NH3
     O2(g)           -40.59  -43.45   -2.85  O2
```

Annex 3. PHREEQC modeling of weathering solutions of fly ash at different time.

Initial solution 1-FA 1 h.

```
-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Al                1.631e-005  1.631e-005
        C(4)              5.051e-004  5.051e-004
        Ca                1.018e-004  1.018e-004
        Cd                5.339e-010  5.339e-010
        Cl                5.409e-004  5.409e-004
        Cu                7.871e-008  7.871e-008
        F                 3.738e-005  3.738e-005
        Fe                7.165e-007  7.165e-007
        K                 2.070e-003  2.070e-003
        Mg                1.371e-004  1.371e-004
        Mn                1.457e-007  1.457e-007
        N(-3)             1.428e-006  1.428e-006
        N(5)              2.157e-004  2.157e-004
        Na                9.660e-004  9.660e-004
        Ni                1.704e-007  1.704e-007
        P                 5.361e-006  5.361e-006
        Pb                1.304e-006  1.304e-006
        S(6)              1.718e-003  1.718e-003
        Si                3.080e-005  3.080e-005
        Zn                1.530e-007  1.530e-007

----------------------------Description of solution----------------------------

                                       pH  =   9.150
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  5.968e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  6.445e-004
                    Total CO2 (mol/kg)  =  5.051e-004
                   Temperature (deg C)  =  25.000
                  Electrical balance (eq)  = -1.312e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -16.13
                               Iterations  =  10
                                  Total H  = 1.110143e+002
                                  Total O  = 5.551610e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           3.7501      0.2218

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log
   Species                 Molality    Activity  Molality  Activity     Gamma

   OH-                   1.546e-005  1.422e-005    -4.811    -4.847    -0.036
   H+                    7.684e-010  7.079e-010    -9.114    -9.150    -0.036
   H2O                   5.551e+001  9.999e-001     1.744    -0.000     0.000
Al               1.631e-005
   Al(OH)4-              1.630e-005  1.503e-005    -4.788    -4.823    -0.035
   Al(OH)3               8.395e-009  8.395e-009    -8.076    -8.076     0.000
   Al(OH)2+              3.204e-011  2.959e-011   -10.494   -10.529    -0.035
   AlOH+2                3.602e-015  2.619e-015   -14.443   -14.582    -0.138
   AlF2+                 9.223e-016  8.516e-016   -15.035   -15.070    -0.035
   AlF3                  3.654e-016  3.654e-016   -15.437   -15.437     0.000
   AlF+2                 8.632e-017  6.276e-017   -16.064   -16.202    -0.138
   AlF4-                 6.771e-018  6.242e-018   -17.169   -17.205    -0.035
```

```
   AlSO4+                1.855e-018  1.710e-018   -17.732   -17.767    -0.035
   Al+3                  3.852e-019  1.842e-019   -18.414   -18.735    -0.320
   Al(SO4)2-             2.377e-020  2.191e-020   -19.624   -19.659    -0.035
C(4)            5.051e-004
   HCO3-                 4.583e-004  4.232e-004    -3.339    -3.373    -0.035
   CO3-2                 3.890e-005  2.802e-005    -4.410    -4.552    -0.142
   CaCO3                 2.623e-006  2.623e-006    -5.581    -5.581     0.000
   MgCO3                 1.941e-006  1.941e-006    -5.712    -5.712     0.000
   PbCO3                 7.234e-007  7.234e-007    -6.141    -6.141     0.000
   H2CO3                 6.738e-007  6.738e-007    -6.171    -6.171     0.000
   CaHCO3+               5.035e-007  4.654e-007    -6.298    -6.332    -0.034
   NaCO3-                4.993e-007  4.611e-007    -6.302    -6.336    -0.035
   MgHCO3+               3.914e-007  3.605e-007    -6.407    -6.443    -0.036
   NaHCO3                2.103e-007  2.103e-007    -6.677    -6.677     0.000
   Pb(CO3)2-2            8.400e-008  5.847e-008    -7.076    -7.233    -0.157
   NiCO3                 5.686e-008  5.686e-008    -7.245    -7.245     0.000
   CuCO3                 3.556e-008  3.556e-008    -7.449    -7.449     0.000
   ZnCO3                 2.965e-008  2.965e-008    -7.528    -7.528     0.000
   Cu(CO3)2-2            3.854e-009  2.682e-009    -8.414    -8.571    -0.157
   NiHCO3+               3.106e-009  2.837e-009    -8.508    -8.547    -0.039
   PbHCO3+               2.956e-009  2.700e-009    -8.529    -8.569    -0.039
   MnHCO3+               7.842e-010  7.236e-010    -9.106    -9.140    -0.035
   ZnHCO3+               2.694e-010  2.461e-010    -9.570    -9.609    -0.039
   CdCO3                 1.338e-010  1.338e-010    -9.874    -9.874     0.000
   CuHCO3+               6.300e-012  5.754e-012   -11.201   -11.240    -0.039
   Cd(CO3)2-2            3.994e-012  2.780e-012   -11.399   -11.556    -0.157
   CdHCO3+               2.210e-013  2.018e-013   -12.656   -12.695    -0.039
   FeHCO3+               2.287e-015  2.114e-015   -14.641   -14.675    -0.034
Ca              1.018e-004
   Ca+2                  8.199e-005  5.906e-005    -4.086    -4.229    -0.142
   CaSO4                 1.618e-005  1.618e-005    -4.791    -4.791     0.000
   CaCO3                 2.623e-006  2.623e-006    -5.581    -5.581     0.000
   CaHCO3+               5.035e-007  4.654e-007    -6.298    -6.332    -0.034
   CaPO4-                3.656e-007  3.376e-007    -6.437    -6.472    -0.035
   CaHPO4                8.982e-008  8.982e-008    -7.047    -7.047     0.000
   CaNO3+                4.062e-008  3.710e-008    -7.391    -7.431    -0.039
   CaF+                  2.381e-008  2.197e-008    -7.623    -7.658    -0.035
   CaOH+                 1.813e-008  1.676e-008    -7.742    -7.776    -0.034
   CaNH3+2               6.440e-011  4.482e-011   -10.191   -10.349    -0.157
   CaH2PO4+              5.321e-011  4.913e-011   -10.274   -10.309    -0.035
   Ca(NH3)2+2            1.545e-017  1.076e-017   -16.811   -16.968    -0.157
Cd              5.339e-010
   Cd+2                  2.908e-010  2.095e-010    -9.536    -9.679    -0.142
   CdCO3                 1.338e-010  1.338e-010    -9.874    -9.874     0.000
   CdSO4                 5.873e-011  5.873e-011   -10.231   -10.231     0.000
   CdOH+                 2.591e-011  2.366e-011   -10.587   -10.626    -0.039
   CdCl+                 1.091e-011  9.968e-012   -10.962   -11.001    -0.039
   CdOHCl                5.815e-012  5.815e-012   -11.235   -11.235     0.000
   Cd(CO3)2-2            3.994e-012  2.780e-012   -11.399   -11.556    -0.157
   Cd(OH)2               2.123e-012  2.123e-012   -11.673   -11.673     0.000
   Cd(SO4)2-2            1.361e-012  9.476e-013   -11.866   -12.023    -0.157
   CdHCO3+               2.210e-013  2.018e-013   -12.656   -12.695    -0.039
   CdNO3+                1.441e-013  1.316e-013   -12.841   -12.881    -0.039
   CdF+                  1.239e-013  1.132e-013   -12.907   -12.946    -0.039
   CdCl2                 2.071e-014  2.071e-014   -13.684   -13.684     0.000
   Cd(OH)3-              2.020e-015  1.845e-015   -14.695   -14.734    -0.039
   Cd(NO3)2              1.310e-017  1.310e-017   -16.883   -16.883     0.000
   CdF2                  7.695e-018  7.695e-018   -17.114   -17.114     0.000
   CdCl3-                7.128e-018  6.511e-018   -17.147   -17.186    -0.039
   Cd2OH+3               5.614e-020  2.484e-020   -19.251   -19.605    -0.354
   Cd(OH)4-2             6.170e-021  4.295e-021   -20.210   -20.367    -0.157
Cl              5.409e-004
   Cl-                   5.409e-004  4.983e-004    -3.267    -3.302    -0.036
   ZnOHCl                4.285e-010  4.285e-010    -9.368    -9.368     0.000
   PbCl+                 1.662e-010  1.518e-010    -9.779    -9.819    -0.039
   NiCl+                 7.591e-011  6.933e-011   -10.120   -10.159    -0.039
   MnCl+                 5.826e-011  5.376e-011   -10.235   -10.270    -0.035
   ZnCl+                 2.499e-011  2.302e-011   -10.602   -10.638    -0.036
```

```
   CdCl+                 1.091e-011  9.968e-012    -10.962    -11.001     -0.039
   CuCl                  6.621e-012  6.621e-012    -11.179    -11.179      0.000
   CdOHCl                5.815e-012  5.815e-012    -11.235    -11.235      0.000
   CuCl2-                7.484e-013  6.893e-013    -12.126    -12.162     -0.036
   PbCl2                 3.379e-013  3.379e-013    -12.471    -12.471      0.000
   CuCl+                 1.848e-013  1.702e-013    -12.733    -12.769     -0.036
   MnCl2                 3.784e-014  3.784e-014    -13.422    -13.422      0.000
   CdCl2                 2.071e-014  2.071e-014    -13.684    -13.684      0.000
   ZnCl2                 1.818e-014  1.818e-014    -13.740    -13.740      0.000
   NiCl2                 1.740e-016  1.740e-016    -15.760    -15.760      0.000
   CuCl3-2               1.013e-016  7.344e-017    -15.994    -16.134     -0.140
   PbCl3-                7.340e-017  6.704e-017    -16.134    -16.174     -0.039
   CuCl2                 2.941e-017  2.941e-017    -16.532    -16.532      0.000
   ZnCl3-                7.812e-018  7.195e-018    -17.107    -17.143     -0.036
   CdCl3-                7.128e-018  6.511e-018    -17.147    -17.186     -0.039
   MnCl3-                5.628e-018  5.194e-018    -17.250    -17.285     -0.035
   PbCl4-2               2.194e-020  1.527e-020    -19.659    -19.816     -0.157
   ZnCl4-2               2.473e-021  1.793e-021    -20.607    -20.746     -0.140
   CuCl3-                1.485e-022  1.368e-022    -21.828    -21.864     -0.036
   FeCl+2                7.651e-024  5.547e-024    -23.116    -23.256     -0.140
   FeCl2+                1.338e-026  1.235e-026    -25.874    -25.908     -0.035
   CuCl4-2               4.711e-028  3.415e-028    -27.327    -27.467     -0.140
   FeCl3                 6.153e-031  6.153e-031    -30.211    -30.211      0.000
Cu(1)           1.892e-011
   Cu+                   1.156e-011  1.055e-011    -10.937    -10.977     -0.039
   CuCl                  6.621e-012  6.621e-012    -11.179    -11.179      0.000
   CuCl2-                7.484e-013  6.893e-013    -12.126    -12.162     -0.036
   CuCl3-2               1.013e-016  7.344e-017    -15.994    -16.134     -0.140
Cu(2)           7.869e-008
   CuCO3                 3.556e-008  3.556e-008     -7.449     -7.449      0.000
   Cu(OH)2               2.750e-008  2.750e-008     -7.561     -7.561      0.000
   CuOH+                 1.052e-008  9.691e-009     -7.978     -8.014     -0.036
   Cu(CO3)2-2            3.854e-009  2.682e-009     -8.414     -8.571     -0.157
   Cu(OH)3-              8.783e-010  8.022e-010     -9.056     -9.096     -0.039
   Cu+2                  2.991e-010  2.155e-010     -9.524     -9.667     -0.142
   CuSO4                 5.904e-011  5.904e-011    -10.229    -10.229      0.000
   CuHCO3+               6.300e-012  5.754e-012    -11.201    -11.240     -0.039
   Cu2(OH)2+2            3.390e-012  2.359e-012    -11.470    -11.627     -0.157
   CuNH3+2               1.910e-012  1.329e-012    -11.719    -11.876     -0.157
   CuF+                  5.074e-013  4.634e-013    -12.295    -12.334     -0.039
   CuCl+                 1.848e-013  1.702e-013    -12.733    -12.769     -0.036
   CuNO3+                1.482e-013  1.354e-013    -12.829    -12.868     -0.039
   Cu(OH)4-2             1.290e-013  8.979e-014    -12.889    -13.047     -0.157
   CuCl2                 2.941e-017  2.941e-017    -16.532    -16.532      0.000
   Cu(NO3)2              3.386e-018  3.386e-018    -17.470    -17.470      0.000
   CuCl3-                1.485e-022  1.368e-022    -21.828    -21.864     -0.036
   CuCl4-2               4.711e-028  3.415e-028    -27.327    -27.467     -0.140
F               3.738e-005
   F-                    3.700e-005  3.408e-005     -4.432     -4.467     -0.036
   MgF+                  3.453e-007  3.184e-007     -6.462     -6.497     -0.035
   CaF+                  2.381e-008  2.197e-008     -7.623     -7.658     -0.035
   NaF                   1.900e-008  1.900e-008     -7.721     -7.721      0.000
   MnF+                  1.260e-010  1.163e-010     -9.900     -9.934     -0.035
   NiF+                  5.097e-011  4.656e-011    -10.293    -10.332     -0.039
   HF                    3.569e-011  3.569e-011    -10.447    -10.447      0.000
   PbF+                  2.258e-011  2.062e-011    -10.646    -10.686     -0.039
   ZnF+                  1.369e-011  1.250e-011    -10.864    -10.903     -0.039
   CuF+                  5.074e-013  4.634e-013    -12.295    -12.334     -0.039
   CdF+                  1.239e-013  1.132e-013    -12.907    -12.946     -0.039
   PbF2                  1.383e-014  1.383e-014    -13.859    -13.859      0.000
   HF2-                  5.026e-015  4.625e-015    -14.299    -14.335     -0.036
   AlF2+                 9.223e-016  8.516e-016    -15.035    -15.070     -0.035
   AlF3                  3.654e-016  3.654e-016    -15.437    -15.437      0.000
   AlF+2                 8.632e-017  6.276e-017    -16.064    -16.202     -0.138
   CdF2                  7.695e-018  7.695e-018    -17.114    -17.114      0.000
   AlF4-                 6.771e-018  6.242e-018    -17.169    -17.205     -0.035
   PbF3-                 9.790e-019  8.942e-019    -18.009    -18.049     -0.039
   FeF+2                 1.900e-020  1.377e-020    -19.721    -19.861     -0.140
```

```
   FeF2+                 1.362e-020  1.256e-020   -19.866   -19.901    -0.035
   H2F2                  3.413e-021  3.413e-021   -20.467   -20.467     0.000
   FeF3                  6.042e-022  6.042e-022   -21.219   -21.219     0.000
   PbF4-2                2.096e-023  1.459e-023   -22.679   -22.836    -0.157
   SiF6-2                2.076e-038  1.505e-038   -37.683   -37.823    -0.140
Fe(2)           9.525e-013
   Fe+2                  5.701e-013  3.968e-013   -12.244   -12.401    -0.157
   FeOH+                 2.435e-013  2.246e-013   -12.614   -12.648    -0.035
   FeSO4                 1.165e-013  1.165e-013   -12.934   -12.934     0.000
   Fe(OH)3-              1.237e-014  1.141e-014   -13.908   -13.943    -0.035
   FeHPO4                5.256e-015  5.256e-015   -14.279   -14.279     0.000
   Fe(OH)2               2.538e-015  2.538e-015   -14.596   -14.596     0.000
   FeHCO3+               2.287e-015  2.114e-015   -14.641   -14.675    -0.034
   FeH2PO4+              8.003e-018  7.390e-018   -17.097   -17.131    -0.035
Fe(3)           7.165e-007
   Fe(OH)4-              4.102e-007  3.788e-007    -6.387    -6.422    -0.035
   Fe(OH)3               2.860e-007  2.860e-007    -6.544    -6.544     0.000
   Fe(OH)2+              2.028e-008  1.873e-008    -7.693    -7.728    -0.035
   FeOH+2                4.668e-015  3.385e-015   -14.331   -14.470    -0.140
   FeHPO4+               1.097e-017  1.013e-017   -16.960   -16.994    -0.035
   FeF+2                 1.900e-020  1.377e-020   -19.721   -19.861    -0.140
   FeF2+                 1.362e-020  1.256e-020   -19.866   -19.901    -0.035
   FeSO4+                5.361e-021  4.946e-021   -20.271   -20.306    -0.035
   Fe+3                  7.710e-022  3.686e-022   -21.113   -21.433    -0.320
   FeF3                  6.042e-022  6.042e-022   -21.219   -21.219     0.000
   Fe(SO4)2-             1.385e-022  1.265e-022   -21.859   -21.898    -0.039
   FeCl+2                7.651e-024  5.547e-024   -23.116   -23.256    -0.140
   FeNO3+2               1.052e-024  7.323e-025   -23.978   -24.135    -0.157
   FeH2PO4+2             3.577e-025  2.601e-025   -24.446   -24.585    -0.138
   FeCl2+                1.338e-026  1.235e-026   -25.874   -25.908    -0.035
   Fe2(OH)2+4            1.616e-027  3.793e-028   -26.791   -27.421    -0.630
   FeCl3                 6.153e-031  6.153e-031   -30.211   -30.211     0.000
   Fe3(OH)4+5            9.887e-034  1.027e-034   -33.005   -33.989    -0.984
H(0)            7.087e-030
   H2                    3.543e-030  3.548e-030   -29.451   -29.450     0.001
K               2.070e-003
   K+                    2.052e-003  1.891e-003    -2.688    -2.723    -0.036
   KSO4-                 1.734e-005  1.601e-005    -4.761    -4.796    -0.035
   KHPO4-                5.168e-008  4.772e-008    -7.287    -7.321    -0.035
Mg              1.371e-004
   Mg+2                  1.156e-004  8.325e-005    -3.937    -4.080    -0.142
   MgSO4                 1.812e-005  1.812e-005    -4.742    -4.742     0.000
   MgCO3                 1.941e-006  1.941e-006    -5.712    -5.712     0.000
   MgOH+                 5.095e-007  4.713e-007    -6.293    -6.327    -0.034
   MgHCO3+               3.914e-007  3.605e-007    -6.407    -6.443    -0.036
   MgF+                  3.453e-007  3.184e-007    -6.462    -6.497    -0.035
   MgHPO4                1.748e-007  1.748e-007    -6.758    -6.758     0.000
   MgPO4-                8.055e-009  7.438e-009    -8.094    -8.129    -0.035
   MgH2PO4+              1.615e-010  1.491e-010    -9.792    -9.826    -0.035
Mn(2)           1.457e-007
   Mn+2                  1.231e-007  8.570e-008    -6.910    -7.067    -0.157
   MnSO4                 1.823e-008  1.823e-008    -7.739    -7.739     0.000
   MnOH+                 3.318e-009  3.061e-009    -8.479    -8.514    -0.035
   MnHCO3+               7.842e-010  7.236e-010    -9.106    -9.140    -0.035
   MnF+                  1.260e-010  1.163e-010    -9.900    -9.934    -0.035
   MnCl+                 5.826e-011  5.376e-011   -10.235   -10.270    -0.035
   MnNO3+                2.954e-011  2.698e-011   -10.530   -10.569    -0.039
   MnCl2                 3.784e-014  3.784e-014   -13.422   -13.422     0.000
   Mn(NO3)2              1.347e-014  1.347e-014   -13.871   -13.871     0.000
   Mn(OH)3-              4.147e-015  3.827e-015   -14.382   -14.417    -0.035
   MnCl3-                5.628e-018  5.194e-018   -17.250   -17.285    -0.035
   Mn(OH)4-2             2.424e-019  1.757e-019   -18.616   -18.755    -0.140
Mn(3)           8.007e-029
   Mn+3                  8.007e-029  3.828e-029   -28.097   -28.417    -0.320
Mn(6)           7.087e-037
   MnO4-2                7.087e-037  5.138e-037   -36.150   -36.289    -0.140
Mn(7)           0.000e+000
   MnO4-                 0.000e+000  0.000e+000   -41.625   -41.661    -0.037
```

```
N(-3)           1.428e-006
   NH4+                  8.151e-007  7.485e-007    -6.089    -6.126    -0.037
   NH3                   6.028e-007  6.028e-007    -6.220    -6.220     0.000
   NH4SO4-               1.040e-008  9.592e-009    -7.983    -8.018    -0.035
   CaNH3+2               6.440e-011  4.482e-011   -10.191   -10.349    -0.157
   NiNH3+2               2.529e-011  1.760e-011   -10.597   -10.754    -0.157
   CuNH3+2               1.910e-012  1.329e-012   -11.719   -11.876    -0.157
   Ni(NH3)2+2            2.204e-015  1.534e-015   -14.657   -14.814    -0.157
   Ca(NH3)2+2            1.545e-017  1.076e-017   -16.811   -16.968    -0.157
N(5)            2.157e-004
   NO3-                  2.156e-004  1.987e-004    -3.666    -3.702    -0.036
   CaNO3+                4.062e-008  3.710e-008    -7.391    -7.431    -0.039
   NiNO3+                2.971e-011  2.714e-011   -10.527   -10.566    -0.039
   MnNO3+                2.954e-011  2.698e-011   -10.530   -10.569    -0.039
   PbNO3+                2.762e-011  2.523e-011   -10.559   -10.598    -0.039
   ZnNO3+                1.005e-011  9.176e-012   -10.998   -11.037    -0.039
   CuNO3+                1.482e-013  1.354e-013   -12.829   -12.868    -0.039
   CdNO3+                1.441e-013  1.316e-013   -12.841   -12.881    -0.039
   Mn(NO3)2              1.347e-014  1.347e-014   -13.871   -13.871     0.000
   Pb(NO3)2              8.513e-015  8.513e-015   -14.070   -14.070     0.000
   Zn(NO3)2              3.637e-016  3.637e-016   -15.439   -15.439     0.000
   Cd(NO3)2              1.310e-017  1.310e-017   -16.883   -16.883     0.000
   Cu(NO3)2              3.386e-018  3.386e-018   -17.470   -17.470     0.000
   FeNO3+2               1.052e-024  7.323e-025   -23.978   -24.135    -0.157
Na              9.660e-004
   Na+                   9.591e-004  8.836e-004    -3.018    -3.054    -0.036
   NaSO4-                6.146e-006  5.675e-006    -5.211    -5.246    -0.035
   NaCO3-                4.993e-007  4.611e-007    -6.302    -6.336    -0.035
   NaHCO3                2.103e-007  2.103e-007    -6.677    -6.677     0.000
   NaHPO4-               3.740e-008  3.454e-008    -7.427    -7.462    -0.035
   NaF                   1.900e-008  1.900e-008    -7.721    -7.721     0.000
Ni              1.704e-007
   Ni+2                  7.549e-008  5.438e-008    -7.122    -7.265    -0.142
   NiCO3                 5.686e-008  5.686e-008    -7.245    -7.245     0.000
   NiSO4                 1.298e-008  1.298e-008    -7.887    -7.887     0.000
   Ni(OH)2               1.100e-008  1.100e-008    -7.959    -7.959     0.000
   NiOH+                 1.066e-008  9.736e-009    -7.972    -8.012    -0.039
   NiHCO3+               3.106e-009  2.837e-009    -8.508    -8.547    -0.039
   Ni(OH)3-              1.713e-010  1.564e-010    -9.766    -9.806    -0.039
   NiCl+                 7.591e-011  6.933e-011   -10.120   -10.159    -0.039
   NiF+                  5.097e-011  4.656e-011   -10.293   -10.332    -0.039
   NiNO3+                2.971e-011  2.714e-011   -10.527   -10.566    -0.039
   NiNH3+2               2.529e-011  1.760e-011   -10.597   -10.754    -0.157
   Ni(SO4)2-2            7.384e-013  5.140e-013   -12.132   -12.289    -0.157
   Ni(NH3)2+2            2.204e-015  1.534e-015   -14.657   -14.814    -0.157
   NiCl2                 1.740e-016  1.740e-016   -15.760   -15.760     0.000
O(0)            8.040e-034
   O2                    4.020e-034  4.026e-034   -33.396   -33.395     0.001
P               5.361e-006
   HPO4-2                4.589e-006  3.327e-006    -5.338    -5.478    -0.140
   CaPO4-                3.656e-007  3.376e-007    -6.437    -6.472    -0.035
   MgHPO4                1.748e-007  1.748e-007    -6.758    -6.758     0.000
   CaHPO4                8.982e-008  8.982e-008    -7.047    -7.047     0.000
   KHPO4-                5.168e-008  4.772e-008    -7.287    -7.321    -0.035
   H2PO4-                4.024e-008  3.716e-008    -7.395    -7.430    -0.035
   NaHPO4-               3.740e-008  3.454e-008    -7.427    -7.462    -0.035
   MgPO4-                8.055e-009  7.438e-009    -8.094    -8.129    -0.035
   PO4-3                 4.145e-009  1.982e-009    -8.382    -8.703    -0.320
   MgH2PO4+              1.615e-010  1.491e-010    -9.792    -9.826    -0.035
   CaH2PO4+              5.321e-011  4.913e-011   -10.274   -10.309    -0.035
   FeHPO4                5.256e-015  5.256e-015   -14.279   -14.279     0.000
   H3PO4                 3.699e-015  3.699e-015   -14.432   -14.432     0.000
   FeHPO4+               1.097e-017  1.013e-017   -16.960   -16.994    -0.035
   FeH2PO4+              8.003e-018  7.390e-018   -17.097   -17.131    -0.035
   FeH2PO4+2             3.577e-025  2.601e-025   -24.446   -24.585    -0.138
Pb              1.304e-006
   PbCO3                 7.234e-007  7.234e-007    -6.141    -6.141     0.000
   PbOH+                 3.358e-007  3.067e-007    -6.474    -6.513    -0.039
```

```
   Pb(OH)2               1.380e-007  1.380e-007     -6.860    -6.860     0.000
   Pb(CO3)2-2            8.400e-008  5.847e-008     -7.076    -7.233    -0.157
   Pb+2                  1.192e-008  8.587e-009     -7.924    -8.066    -0.142
   PbSO4                 5.030e-009  5.030e-009     -8.298    -8.298     0.000
   PbHCO3+               2.956e-009  2.700e-009     -8.529    -8.569    -0.039
   Pb(OH)3-              2.148e-009  1.962e-009     -8.668    -8.707    -0.039
   PbCl+                 1.662e-010  1.518e-010     -9.779    -9.819    -0.039
   Pb(SO4)2-2            5.208e-011  3.625e-011    -10.283   -10.441    -0.157
   PbNO3+                2.762e-011  2.523e-011    -10.559   -10.598    -0.039
   PbF+                  2.258e-011  2.062e-011    -10.646   -10.686    -0.039
   Pb(OH)4-2             9.818e-012  6.833e-012    -11.008   -11.165    -0.157
   Pb3(OH)4+2            4.685e-012  3.261e-012    -11.329   -11.487    -0.157
   PbCl2                 3.379e-013  3.379e-013    -12.471   -12.471     0.000
   Pb2OH+3               9.434e-014  4.174e-014    -13.025   -13.379    -0.354
   PbF2                  1.383e-014  1.383e-014    -13.859   -13.859     0.000
   Pb(NO3)2              8.513e-015  8.513e-015    -14.070   -14.070     0.000
   Pb4(OH)4+4            9.476e-016  2.224e-016    -15.023   -15.653    -0.630
   PbCl3-                7.340e-017  6.704e-017    -16.134   -16.174    -0.039
   PbF3-                 9.790e-019  8.942e-019    -18.009   -18.049    -0.039
   PbCl4-2               2.194e-020  1.527e-020    -19.659   -19.816    -0.157
   PbF4-2                2.096e-023  1.459e-023    -22.679   -22.836    -0.157
S(6)            1.718e-003
   SO4-2                 1.660e-003  1.196e-003     -2.780    -2.922    -0.142
   MgSO4                 1.812e-005  1.812e-005     -4.742    -4.742     0.000
   KSO4-                 1.734e-005  1.601e-005     -4.761    -4.796    -0.035
   CaSO4                 1.618e-005  1.618e-005     -4.791    -4.791     0.000
   NaSO4-                6.146e-006  5.675e-006     -5.211    -5.246    -0.035
   MnSO4                 1.823e-008  1.823e-008     -7.739    -7.739     0.000
   NiSO4                 1.298e-008  1.298e-008     -7.887    -7.887     0.000
   NH4SO4-               1.040e-008  9.592e-009     -7.983    -8.018    -0.035
   PbSO4                 5.030e-009  5.030e-009     -8.298    -8.298     0.000
   ZnSO4                 4.811e-009  4.811e-009     -8.318    -8.318     0.000
   HSO4-                 8.975e-011  8.275e-011    -10.047   -10.082    -0.035
   Zn(SO4)2-2            7.201e-011  5.012e-011    -10.143   -10.300    -0.157
   CuSO4                 5.904e-011  5.904e-011    -10.229   -10.229     0.000
   CdSO4                 5.873e-011  5.873e-011    -10.231   -10.231     0.000
   Pb(SO4)2-2            5.208e-011  3.625e-011    -10.283   -10.441    -0.157
   Cd(SO4)2-2            1.361e-012  9.476e-013    -11.866   -12.023    -0.157
   Ni(SO4)2-2            7.384e-013  5.140e-013    -12.132   -12.289    -0.157
   FeSO4                 1.165e-013  1.165e-013    -12.934   -12.934     0.000
   AlSO4+                1.855e-018  1.710e-018    -17.732   -17.767    -0.035
   Al(SO4)2-             2.377e-020  2.191e-020    -19.624   -19.659    -0.035
   FeSO4+                5.361e-021  4.946e-021    -20.271   -20.306    -0.035
   Fe(SO4)2-             1.385e-022  1.265e-022    -21.859   -21.898    -0.039
Si              3.080e-005
   H4SiO4                2.520e-005  2.524e-005     -4.599    -4.598     0.001
   H3SiO4-               5.595e-006  5.153e-006     -5.252    -5.288    -0.036
   H2SiO4-2              6.317e-010  4.593e-010     -9.200    -9.338    -0.138
   SiF6-2                2.076e-038  1.505e-038    -37.683   -37.823    -0.140
Zn              1.530e-007
   Zn(OH)2               5.894e-008  5.894e-008     -7.230    -7.230     0.000
   ZnCO3                 2.965e-008  2.965e-008     -7.528    -7.528     0.000
   ZnOH+                 2.863e-008  2.615e-008     -7.543    -7.583    -0.039
   Zn+2                  2.552e-008  1.839e-008     -7.593    -7.735    -0.142
   ZnSO4                 4.811e-009  4.811e-009     -8.318    -8.318     0.000
   Zn(OH)3-              4.600e-009  4.201e-009     -8.337    -8.377    -0.039
   ZnOHCl                4.285e-010  4.285e-010     -9.368    -9.368     0.000
   ZnHCO3+               2.694e-010  2.461e-010     -9.570    -9.609    -0.039
   Zn(SO4)2-2            7.201e-011  5.012e-011    -10.143   -10.300    -0.157
   ZnCl+                 2.499e-011  2.302e-011    -10.602   -10.638    -0.036
   ZnF+                  1.369e-011  1.250e-011    -10.864   -10.903    -0.039
   ZnNO3+                1.005e-011  9.176e-012    -10.998   -11.037    -0.039
   Zn(OH)4-2             3.417e-012  2.379e-012    -11.466   -11.624    -0.157
   ZnCl2                 1.818e-014  1.818e-014    -13.740   -13.740     0.000
   Zn(NO3)2              3.637e-016  3.637e-016    -15.439   -15.439     0.000
   ZnCl3-                7.812e-018  7.195e-018    -17.107   -17.143    -0.036
   ZnCl4-2               2.473e-021  1.793e-021    -20.607   -20.746    -0.140
```

```
-----------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -2.08    8.72   10.80  Al(OH)3
        Al2O3            -2.22   17.43   19.65  Al2O3
        Al4(OH)10SO4     -9.06   13.64   22.70  Al4(OH)10SO4
        AlOHSO4          -9.28  -12.51   -3.23  AlOHSO4
        Alunite          -8.47   -9.87   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -3.20  -10.99   -7.79  PbSO4
        Anhydrite        -2.79   -7.15   -4.36  CaSO4
        Antlerite        -4.11    4.68    8.79  Cu3(OH)4SO4
        Aragonite        -0.48   -8.78   -8.30  CaCO3
        Artinite         -4.01    5.59    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -2.58    4.81    7.39  Cu2(OH)3Cl
        Azurite          -2.90  -19.80  -16.91  Cu3(OH)2(CO3)2
        Bianchite        -8.89  -10.66   -1.76  ZnSO4:6H2O
        Birnessite       -5.91   12.18   18.09  MnO2
        Bixbyite         -1.29   -1.93   -0.64  Mn2O3
        Boehmite          0.14    8.72    8.58  AlOOH
        Brochantite      -1.91   13.31   15.22  Cu4(OH)6SO4
        Brucite          -2.62   14.22   16.84  Mg(OH)2
        Bunsenite        -1.41   11.04   12.45  NiO
        Ca3(PO4)2(beta)  -1.17  -30.09  -28.92  Ca3(PO4)2
        Ca4H(PO4)3:3H2O  -5.09  -52.17  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -2.81  -22.08  -19.27  CaHPO4
        CaHPO4:2H2O      -3.09  -22.08  -19.00  CaHPO4:2H2O
        Calcite          -0.30   -8.78   -8.48  CaCO3
        Cd(OH)2          -5.02    8.62   13.64  Cd(OH)2
        Cd(OH)2(am)      -5.11    8.62   13.73  Cd(OH)2
        Cd3(OH)2(SO4)2  -23.29  -16.58    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -17.92    4.64   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -13.84  -46.44  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -15.14   13.26   28.40  Cd4(OH)6SO4
        CdCl2           -15.63  -16.28   -0.66  CdCl2
        CdCl2:1H2O      -14.59  -16.28   -1.69  CdCl2:1H2O
        CdCl2:2.5H2O    -14.37  -16.28   -1.91  CdCl2:2.5H2O
        CdF2            -17.40  -18.61   -1.21  CdF2
        Cdmetal(alpha)  -31.19  -17.68   13.51  Cd
        Cdmetal(gamma)  -31.30  -17.68   13.62  Cd
        CdOHCl           -7.37   -3.83    3.54  CdOHCl
        CdSO4           -12.43  -12.60   -0.17  CdSO4
        CdSO4:1H2O      -10.88  -12.60   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -10.73  -12.60   -1.87  CdSO4:2.67H2O
        Cerrusite         0.51  -12.62  -13.13  PbCO3
        CH4(g)          -87.01 -128.05  -41.05  CH4
        Chalcanthite     -9.95  -12.59   -2.64  CuSO4:5H2O
        Chalcedony       -1.05   -4.60   -3.55  SiO2
        Chrysotile        1.27   33.47   32.20  Mg3Si2O5(OH)4
        CO2(g)           -4.71  -22.85  -18.15  CO2
        Cotunnite        -9.89  -14.67   -4.78  PbCl2
        Cristobalite     -1.25   -4.60   -3.35  SiO2
        Cryolite        -20.86  -54.70  -33.84  Na3AlF6
        Cu(OH)2          -0.04    8.63    8.67  Cu(OH)2
        Cu2(OH)3NO3      -4.84    4.41    9.25  Cu2(OH)3NO3
        Cu2SO4          -22.93  -24.88   -1.95  Cu2SO4
        Cu3(PO4)2        -9.56  -46.41  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -11.29  -46.41  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -2.72  -14.22  -11.50  CuCO3
        CuF             -10.54  -15.44   -4.91  CuF
        CuF2            -19.72  -18.60    1.12  CuF2
        CuF2:2H2O       -14.05  -18.60   -4.55  CuF2:2H2O
        Cumetal          -6.22  -14.98   -8.76  Cu
        CuOCuSO4        -14.26   -3.96   10.30  CuOCuSO4
        Cupricferrite    14.68   20.67    5.99  CuFe2O4
        Cuprite          -2.25   -3.65   -1.41  Cu2O
        Cuprousferrite   13.11    4.19   -8.92  CuFeO2
        CuSO4           -15.53  -12.59    2.94  CuSO4
```

```
        Diaspore            1.84    8.72    6.87  AlOOH
        Dolomite(disordered)  -0.87  -17.41  -16.54  CaMg(CO3)2
        Dolomite(ordered)  -0.32  -17.41  -17.09  CaMg(CO3)2
        Epsomite           -4.88   -7.00   -2.13  MgSO4:7H2O
        FCO3Apatite        15.00  -99.40 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
        Fe(OH)2            -7.67    5.90   13.56  Fe(OH)2
        Fe(OH)2.7Cl.3       5.32    2.28   -3.04  Fe(OH)2.7Cl.3
        Fe2(SO4)3         -47.90  -51.63   -3.73  Fe2(SO4)3
        Fe3(OH)8           -2.29   17.93   20.22  Fe3(OH)8
        Ferrihydrite        2.83    6.02    3.19  Fe(OH)3
        Fluorite           -2.66  -13.16  -10.50  CaF2
        Gibbsite            0.42    8.72    8.29  Al(OH)3
        Goethite            5.53    6.02    0.49  FeOOH
        Goslarite          -8.65  -10.66   -2.01  ZnSO4:7H2O
        Greenalite        -12.31    8.50   20.81  Fe3Si2O5(OH)4
        Gypsum             -2.54   -7.15   -4.61  CaSO4:2H2O
        H-Jarosite        -12.30  -24.40  -12.10  (H3O)Fe3(SO4)2(OH)6
        Halite             -7.96   -6.36    1.60  NaCl
        Halloysite         -1.34    8.23    9.57  Al2Si2O5(OH)4
        Hausmannite        -1.03   60.00   61.03  Mn3O4
        Hematite           13.45   12.03   -1.42  Fe2O3
        Hercynite           0.44   23.33   22.89  FeAl2O4
        Hinsdalite        -18.50  -21.00   -2.50  PbAl3PO4SO4(OH)6
        Huntite            -4.71  -34.68  -29.97  CaMg3(CO3)4
        Hydrocerrusite      3.77  -15.00  -18.77  Pb3(OH)2(CO3)2
        Hydromagnesite    -11.54  -20.31   -8.77  Mg5(CO3)4(OH)2:4H2O
        Hydroxylapatite     6.23  -38.10  -44.33  Ca5(PO4)3OH
        Hydroxylpyromorphite   5.50  -57.29  -62.79  Pb5(PO4)3OH
        K-Alum            -22.13  -27.30   -5.17  KAl(SO4)2:12H2O
        K-Jarosite         -3.17  -17.97  -14.80  KFe3(SO4)2(OH)6
        Kaolinite           0.80    8.23    7.43  Al2Si2O5(OH)4
        Langite            -4.18   13.31   17.49  Cu4(OH)6SO4:H2O
        Larnakite          -0.32   -0.75   -0.43  PbO:PbSO4
        Laurionite         -2.84   -2.22    0.62  PbOHCl
        Lepidocrocite       4.65    6.02    1.37  FeOOH
        Lime              -18.63   14.07   32.70  CaO
        Litharge           -2.46   10.23   12.69  PbO
        Maghemite           5.65   12.03    6.39  Fe2O3
        Magnesioferrite     9.39   26.25   16.86  Fe2MgO4
        Magnesite          -1.17   -8.63   -7.46  MgCO3
        Magnetite          14.53   17.93    3.40  Fe3O4
        Malachite          -0.28   -5.59   -5.31  Cu2(OH)2CO3
        Manganite          -0.96   24.38   25.34  MnOOH
        Massicot           -2.66   10.23   12.89  PbO
        Matlockite         -6.86  -15.84   -8.97  PbClF
        Melanothallite    -22.53  -16.27    6.26  CuCl2
        Melanterite       -13.12  -15.32   -2.21  FeSO4:7H2O
        Mg(OH)2(active)    -4.57   14.22   18.79  Mg(OH)2
        Mg3(PO4)2          -6.36  -29.64  -23.28  Mg3(PO4)2
        MgF2               -4.88  -13.01   -8.13  MgF2
        MgHPO4:3H2O        -3.76  -21.93  -18.18  MgHPO4:3H2O
        Minium            -16.52   57.00   73.52  Pb3O4
        Mirabilite         -7.92   -9.03   -1.11  Na2SO4:10H2O
        Mn2(SO4)3         -59.89  -65.60   -5.71  Mn2(SO4)3
        Mn3(PO4)2         -14.78  -38.61  -23.83  Mn3(PO4)2
        MnCl2:4H2O        -16.39  -13.67    2.72  MnCl2:4H2O
        MnHPO4              0.48  -24.92  -25.40  MnHPO4
        MnSO4             -12.57   -9.99    2.58  MnSO4
        Monteponite        -6.48    8.62   15.10  CdO
        Morenosite         -8.04  -10.19   -2.14  NiSO4:7H2O
        Na-Jarosite        -7.10  -18.30  -11.20  NaFe3(SO4)2(OH)6
        Nantokite          -7.55  -14.28   -6.73  CuCl
        Natron             -9.35  -10.66   -1.31  Na2CO3:10H2O
        Nesquehonite       -3.96   -8.63   -4.67  MgCO3:3H2O
        Ni(OH)2            -1.76   11.04   12.79  Ni(OH)2
        Ni3(PO4)2          -7.90  -39.20  -31.30  Ni3(PO4)2
        Ni4(OH)6SO4        -9.08   22.92   32.00  Ni4(OH)6SO4
```

```
        NiCO3            -4.95  -11.82   -6.87  NiCO3
        Nsutite          -5.32   12.18   17.50  MnO2
        O2(g)           -30.49   52.60   83.09  O2
        Otavite          -2.23  -14.23  -12.00  CdCO3
        Pb(OH)2           2.08   10.23    8.15  Pb(OH)2
        Pb10(OH)6O(CO3)6 -26.02  -34.78   -8.76  Pb10(OH)6O(CO3)6
        Pb2(OH)3Cl       -0.78    8.02    8.79  Pb2(OH)3Cl
        Pb2O(OH)2        -5.72   20.47   26.19  Pb2O(OH)2
        Pb2O3           -14.27   46.77   61.04  Pb2O3
        Pb2OCO3          -1.83   -2.38   -0.56  Pb2OCO3
        Pb3(PO4)2         1.93  -41.60  -43.53  Pb3(PO4)2
        Pb3O2CO3         -3.17    7.85   11.02  Pb3O2CO3
        Pb3O2SO4         -1.21    9.48   10.69  Pb3O2SO4
        Pb4(OH)6SO4      -1.39   19.71   21.10  Pb4(OH)6SO4
        Pb4O3SO4         -2.16   19.71   21.88  Pb4O3SO4
        PbF2             -9.56  -17.00   -7.44  PbF2
        PbHPO4           -2.11  -25.92  -23.81  PbHPO4
        Pbmetal         -20.31  -16.07    4.25  Pb
        PbO:0.3H2O       -2.75   10.23   12.98  PbO:0.33H2O
        Periclase        -7.36   14.22   21.58  MgO
        Phosgenite       -7.48  -27.29  -19.81  PbCl2:PbCO3
        Plattnerite     -13.07   36.53   49.60  PbO2
        Plumbgummite     -3.14  -35.93  -32.79  PbAl3(PO4)2(OH)5:H2O
        Portlandite      -8.73   14.07   22.80  Ca(OH)2
        Pyrochroite      -3.96   11.23   15.19  Mn(OH)2
        Pyrolusite       -3.85   37.53   41.38  MnO2
        Pyromorphite     14.69  -69.74  -84.43  Pb5(PO4)3Cl
        Quartz           -0.60   -4.60   -4.00  SiO2
        Retgersite       -8.15  -10.19   -2.04  NiSO4:6H2O
        Rhodochrosite    -1.04  -11.62  -10.58  MnCO3
        Sepiolite        -1.11   14.65   15.76  Mg2Si3O7.5OH:3H2O
        Sepiolite(A)     -4.13   14.65   18.78  Mg2Si3O7.5OH:3H2O
        Siderite         -6.71  -16.95  -10.24  FeCO3
        SiO2(am-gel)     -1.89   -4.60   -2.71  SiO2
        SiO2(am-ppt)     -1.86   -4.60   -2.74  SiO2
        Smithsonite      -2.29  -12.29  -10.00  ZnCO3
        Spinel           -5.20   31.65   36.85  MgAl2O4
        Strengite        -3.74  -30.14  -26.40  FePO4:2H2O
        Tenorite          0.99    8.63    7.64  CuO
        Thenardite       -9.35   -9.03    0.32  Na2SO4
        Thermonatrite   -11.30  -10.66    0.64  Na2CO3:H2O
        Tsumebite         2.74   -7.05   -9.79  Pb2CuPO4(OH)3:3H2O
        Vivianite       -18.61  -54.61  -36.00  Fe3(PO4)2:8H2O
        Zincite          -0.77   10.56   11.33  ZnO
        Zincosite       -14.59  -10.66    3.93  ZnSO4
        Zn(NO3)2:6H2O   -18.45  -15.14    3.32  Zn(NO3)2:6H2O
        Zn(OH)2          -1.64   10.56   12.20  Zn(OH)2
        Zn(OH)2(am)      -1.91   10.56   12.47  Zn(OH)2
        Zn(OH)2(beta)    -1.19   10.56   11.75  Zn(OH)2
        Zn(OH)2(epsilon)  -0.97   10.56   11.53  Zn(OH)2
        Zn(OH)2(gamma)   -1.17   10.56   11.73  Zn(OH)2
        Zn2(OH)2SO4      -7.59   -0.09    7.50  Zn2(OH)2SO4
        Zn2(OH)3Cl       -6.51    8.68   15.19  Zn2(OH)3Cl
        Zn3(PO4)2:4H2O   -5.19  -40.61  -35.42  Zn3(PO4)2:4H2O
        Zn3O(SO4)2      -29.66  -10.75   18.91  Zn3O(SO4)2
        Zn4(OH)6SO4      -7.36   21.04   28.40  Zn4(OH)6SO4
        Zn5(OH)8Cl2     -10.58   27.92   38.50  Zn5(OH)8Cl2
        ZnCl2           -21.39  -14.34    7.05  ZnCl2
        ZnCO3:1H2O       -2.03  -12.29  -10.26  ZnCO3:1H2O
        ZnF2            -16.14  -16.67   -0.53  ZnF2
        Znmetal         -41.52  -15.74   25.79  Zn
        ZnO(active)      -0.62   10.56   11.19  ZnO
        ZnSO4:1H2O      -10.02  -10.66   -0.64  ZnSO4:1H2O

Initial solution 2-FA 24 h.

----------------------------Solution composition------------------------------
```

```
        Elements           Molality       Moles

        Al               3.523e-005  3.523e-005
        C(4)             5.202e-004  5.202e-004
        Ca               3.735e-004  3.735e-004
        Cd               1.780e-010  1.780e-010
        Cl               7.253e-004  7.253e-004
        Cu               4.723e-008  4.723e-008
        F                8.163e-005  8.163e-005
        Fe               7.166e-007  7.166e-007
        K                3.966e-003  3.966e-003
        Mg               5.928e-005  5.928e-005
        Mn               1.457e-007  1.457e-007
        N(-3)            2.143e-006  2.143e-006
        N(5)             4.393e-004  4.393e-004
        Na               1.541e-003  1.541e-003
        Ni               1.705e-007  1.705e-007
        P                5.265e-006  5.265e-006
        Pb               7.243e-007  7.243e-007
        S(6)             2.062e-003  2.062e-003
        Si               3.490e-004  3.490e-004
        Zn               1.530e-007  1.530e-007

----------------------------Description of solution----------------------------

                                       pH  =   9.350
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  8.384e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  8.655e-004
                       Total CO2 (mol/kg)  =  5.202e-004
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  2.422e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   2.01
                               Iterations  =  10
                                  Total H  = 1.110156e+002
                                  Total O  = 5.551955e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           3.5284      0.2087

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log
   Species                 Molality    Activity  Molality  Activity       Gamma

   OH-                   2.484e-005  2.254e-005    -4.605    -4.647    -0.042
   H+                    4.914e-010  4.467e-010    -9.309    -9.350    -0.041
   H2O                   5.551e+001  9.998e-001     1.744    -0.000     0.000
Al              3.523e-005
   Al(OH)4-              3.522e-005  3.204e-005    -4.453    -4.494    -0.041
   Al(OH)3               1.129e-008  1.129e-008    -7.947    -7.947     0.000
   Al(OH)2+              2.754e-011  2.511e-011   -10.560   -10.600    -0.040
   AlOH+2                2.029e-015  1.402e-015   -14.693   -14.853    -0.160
   AlF2+                 1.476e-015  1.345e-015   -14.831   -14.871    -0.040
   AlF3                  1.248e-015  1.248e-015   -14.904   -14.904     0.000
   AlF+2                 6.636e-017  4.586e-017   -16.178   -16.339    -0.160
   AlF4-                 5.069e-017  4.611e-017   -16.295   -16.336    -0.041
   AlSO4+                7.050e-019  6.414e-019   -18.152   -18.193    -0.041
   Al+3                  1.469e-019  6.222e-020   -18.833   -19.206    -0.373
   Al(SO4)2-             1.003e-020  9.126e-021   -19.999   -20.040    -0.041
C(4)            5.202e-004
   HCO3-                 4.396e-004  4.008e-004    -3.357    -3.397    -0.040
   CO3-2                 6.162e-005  4.207e-005    -4.210    -4.376    -0.166
```

```
   CaCO3                 1.343e-005  1.343e-005     -4.872    -4.872     0.000
   CaHCO3+               1.646e-006  1.503e-006     -5.784    -5.823    -0.040
   NaCO3-                1.193e-006  1.088e-006     -5.923    -5.963    -0.040
   MgCO3                 1.174e-006  1.174e-006     -5.930    -5.930     0.000
   H2CO3                 4.027e-007  4.027e-007     -6.395    -6.395     0.000
   PbCO3                 3.565e-007  3.565e-007     -6.448    -6.448     0.000
   NaHCO3                3.131e-007  3.131e-007     -6.504    -6.504     0.000
   MgHCO3+               1.515e-007  1.376e-007     -6.820    -6.861    -0.042
   Pb(CO3)2-2            6.646e-008  4.325e-008     -7.177    -7.364    -0.187
   NiCO3                 6.375e-008  6.375e-008     -7.196    -7.196     0.000
   ZnCO3                 2.341e-008  2.341e-008     -7.631    -7.631     0.000
   CuCO3                 1.652e-008  1.652e-008     -7.782    -7.782     0.000
   Cu(CO3)2-2            2.874e-009  1.871e-009     -8.541    -8.728    -0.187
   NiHCO3+               2.235e-009  2.007e-009     -8.651    -8.697    -0.047
   PbHCO3+               9.347e-010  8.396e-010     -9.029    -9.076    -0.047
   MnHCO3+               6.921e-010  6.304e-010     -9.160    -9.200    -0.041
   ZnHCO3+               1.365e-010  1.226e-010     -9.865    -9.912    -0.047
   CdCO3                 5.425e-011  5.425e-011    -10.266   -10.266     0.000
   Cd(CO3)2-2            2.599e-012  1.692e-012    -11.585   -11.772    -0.187
   CuHCO3+               1.878e-012  1.687e-012    -11.726   -11.773    -0.047
   CdHCO3+               5.748e-014  5.163e-014    -13.240   -13.287    -0.047
   FeHCO3+               4.124e-016  3.765e-016    -15.385   -15.424    -0.040
Ca              3.735e-004
   Ca+2                  2.949e-004  2.014e-004     -3.530    -3.696    -0.166
   CaSO4                 6.125e-005  6.125e-005     -4.213    -4.213     0.000
   CaCO3                 1.343e-005  1.343e-005     -4.872    -4.872     0.000
   CaHCO3+               1.646e-006  1.503e-006     -5.784    -5.823    -0.040
   CaPO4-                1.422e-006  1.297e-006     -5.847    -5.887    -0.040
   CaNO3+                2.829e-007  2.541e-007     -6.548    -6.595    -0.047
   CaHPO4                2.177e-007  2.177e-007     -6.662    -6.662     0.000
   CaF+                  1.778e-007  1.620e-007     -6.750    -6.791    -0.041
   CaOH+                 9.917e-008  9.055e-008     -7.004    -7.043    -0.040
   CaNH3+2               4.443e-010  2.892e-010     -9.352    -9.539    -0.187
   CaH2PO4+              8.239e-011  7.512e-011    -10.084   -10.124    -0.040
   Ca(NH3)2+2            2.018e-016  1.313e-016    -15.695   -15.882    -0.187
Cd              1.780e-010
   Cd+2                  8.287e-011  5.657e-011    -10.082   -10.247    -0.166
   CdCO3                 5.425e-011  5.425e-011    -10.266   -10.266     0.000
   CdSO4                 1.761e-011  1.761e-011    -10.754   -10.754     0.000
   CdOH+                 1.128e-011  1.013e-011    -10.948   -10.994    -0.047
   CdCl+                 3.966e-012  3.562e-012    -11.402   -11.448    -0.047
   CdOHCl                3.293e-012  3.293e-012    -11.482   -11.482     0.000
   Cd(CO3)2-2            2.599e-012  1.692e-012    -11.585   -11.772    -0.187
   Cd(OH)2               1.440e-012  1.440e-012    -11.842   -11.842     0.000
   Cd(SO4)2-2            4.847e-013  3.155e-013    -12.315   -12.501    -0.187
   CdNO3+                7.948e-014  7.139e-014    -13.100   -13.146    -0.047
   CdF+                  7.357e-014  6.608e-014    -13.133   -13.180    -0.047
   CdHCO3+               5.748e-014  5.163e-014    -13.240   -13.287    -0.047
   CdCl2                 9.789e-015  9.789e-015    -14.009   -14.009     0.000
   Cd(OH)3-              2.208e-015  1.983e-015    -14.656   -14.703    -0.047
   Cd(NO3)2              1.428e-017  1.428e-017    -16.845   -16.845     0.000
   CdF2                  9.717e-018  9.717e-018    -17.012   -17.012     0.000
   CdCl3-                4.533e-018  4.072e-018    -17.344   -17.390    -0.047
   Cd(OH)4-2             1.124e-020  7.317e-021    -19.949   -20.136    -0.187
   Cd2OH+3               7.548e-021  2.872e-021    -20.122   -20.542    -0.420
Cl              7.253e-004
   Cl-                   7.253e-004  6.593e-004     -3.140    -3.181    -0.041
   ZnOHCl                4.725e-010  4.725e-010     -9.326    -9.326     0.000
   NiCl+                 7.628e-011  6.851e-011    -10.118   -10.164    -0.047
   PbCl+                 7.341e-011  6.594e-011    -10.134   -10.181    -0.047
   MnCl+                 7.182e-011  6.542e-011    -10.144   -10.184    -0.041
   ZnCl+                 1.762e-011  1.601e-011    -10.754   -10.796    -0.042
   CdCl+                 3.966e-012  3.562e-012    -11.402   -11.448    -0.047
   CdOHCl                3.293e-012  3.293e-012    -11.482   -11.482     0.000
   CuCl                  2.711e-012  2.711e-012    -11.567   -11.567     0.000
   CuCl2-                4.110e-013  3.734e-013    -12.386   -12.428    -0.042
   PbCl2                 1.942e-013  1.942e-013    -12.712   -12.712     0.000
   CuCl+                 7.669e-014  6.968e-014    -13.115   -13.157    -0.042
```

```
   MnCl2               6.092e-014  6.092e-014   -13.215   -13.215     0.000
   ZnCl2               1.673e-014  1.673e-014   -13.776   -13.776     0.000
   CdCl2               9.789e-015  9.789e-015   -14.009   -14.009     0.000
   NiCl2               2.274e-016  2.274e-016   -15.643   -15.643     0.000
   CuCl3-2             7.645e-017  5.263e-017   -16.117   -16.279    -0.162
   PbCl3-              5.674e-017  5.096e-017   -16.246   -16.293    -0.047
   CuCl2               1.593e-017  1.593e-017   -16.798   -16.798     0.000
   MnCl3-              1.214e-017  1.106e-017   -16.916   -16.956    -0.041
   ZnCl3-              9.643e-018  8.761e-018   -17.016   -17.057    -0.042
   CdCl3-              4.533e-018  4.072e-018   -17.344   -17.390    -0.047
   PbCl4-2             2.360e-020  1.536e-020   -19.627   -19.814    -0.187
   ZnCl4-2             4.196e-021  2.888e-021   -20.377   -20.539    -0.162
   CuCl3-              1.079e-022  9.800e-023   -21.967   -22.009    -0.042
   FeCl+2              2.005e-024  1.380e-024   -23.698   -23.860    -0.162
   FeCl2+              4.462e-027  4.064e-027   -26.351   -26.391    -0.041
   CuCl4-2             4.704e-028  3.238e-028   -27.328   -27.490    -0.162
   FeCl3               2.679e-031  2.679e-031   -30.572   -30.572     0.000
Cu(1)           6.759e-012
   Cu+                 3.637e-012  3.266e-012   -11.439   -11.486    -0.047
   CuCl                2.711e-012  2.711e-012   -11.567   -11.567     0.000
   CuCl2-              4.110e-013  3.734e-013   -12.386   -12.428    -0.042
   CuCl3-2             7.645e-017  5.263e-017   -16.117   -16.279    -0.162
Cu(2)           4.723e-008
   Cu(OH)2             2.138e-008  2.138e-008    -7.670    -7.670     0.000
   CuCO3               1.652e-008  1.652e-008    -7.782    -7.782     0.000
   CuOH+               5.231e-009  4.753e-009    -8.281    -8.323    -0.042
   Cu(CO3)2-2          2.874e-009  1.871e-009    -8.541    -8.728    -0.187
   Cu(OH)3-            1.100e-009  9.882e-010    -8.959    -9.005    -0.047
   Cu+2                9.769e-011  6.669e-011   -10.010   -10.176    -0.166
   CuSO4               2.029e-011  2.029e-011   -10.693   -10.693     0.000
   CuHCO3+             1.878e-012  1.687e-012   -11.726   -11.773    -0.047
   CuNH3+2             1.196e-012  7.786e-013   -11.922   -12.109    -0.187
   Cu2(OH)2+2          8.720e-013  5.675e-013   -12.059   -12.246    -0.187
   CuF+                3.453e-013  3.101e-013   -12.462   -12.508    -0.047
   Cu(OH)4-2           2.693e-013  1.753e-013   -12.570   -12.756    -0.187
   CuNO3+              9.370e-014  8.416e-014   -13.028   -13.075    -0.047
   CuCl+               7.669e-014  6.968e-014   -13.115   -13.157    -0.042
   CuCl2               1.593e-017  1.593e-017   -16.798   -16.798     0.000
   Cu(NO3)2            4.228e-018  4.228e-018   -17.374   -17.374     0.000
   CuCl3-              1.079e-022  9.800e-023   -21.967   -22.009    -0.042
   CuCl4-2             4.704e-028  3.238e-028   -27.328   -27.490    -0.162
F               8.163e-005
   F-                  8.108e-005  7.370e-005    -4.091    -4.133    -0.041
   MgF+                3.050e-007  2.775e-007    -6.516    -6.557    -0.041
   CaF+                1.778e-007  1.620e-007    -6.750    -6.791    -0.041
   NaF                 6.459e-008  6.459e-008    -7.190    -7.190     0.000
   MnF+                2.539e-010  2.313e-010    -9.595    -9.636    -0.041
   NiF+                8.372e-011  7.519e-011   -10.077   -10.124    -0.047
   HF                  4.869e-011  4.869e-011   -10.313   -10.313     0.000
   PbF+                1.630e-011  1.464e-011   -10.788   -10.834    -0.047
   ZnF+                1.583e-011  1.422e-011   -10.800   -10.847    -0.047
   CuF+                3.453e-013  3.101e-013   -12.462   -12.508    -0.047
   CdF+                7.357e-014  6.608e-014   -13.133   -13.180    -0.047
   PbF2                2.123e-014  2.123e-014   -13.673   -13.673     0.000
   HF2-                1.504e-014  1.364e-014   -13.823   -13.865    -0.042
   AlF2+               1.476e-015  1.345e-015   -14.831   -14.871    -0.040
   AlF3                1.248e-015  1.248e-015   -14.904   -14.904     0.000
   AlF+2               6.636e-017  4.586e-017   -16.178   -16.339    -0.160
   AlF4-               5.069e-017  4.611e-017   -16.295   -16.336    -0.041
   CdF2                9.717e-018  9.717e-018   -17.012   -17.012     0.000
   PbF3-               3.305e-018  2.968e-018   -17.481   -17.528    -0.047
   FeF2+               1.213e-020  1.105e-020   -19.916   -19.957    -0.041
   FeF+2               8.137e-021  5.601e-021   -20.090   -20.252    -0.162
   H2F2                6.352e-021  6.352e-021   -20.197   -20.197     0.000
   FeF3                1.149e-021  1.149e-021   -20.940   -20.940     0.000
   PbF4-2              1.609e-022  1.047e-022   -21.794   -21.980    -0.187
   SiF6-2              3.617e-036  2.490e-036   -35.442   -35.604    -0.162
Fe(2)           2.242e-013
```

```
   Fe+2                  1.146e-013  7.462e-014   -12.941    -13.127     -0.187
   FeOH+                 7.350e-014  6.695e-014   -13.134    -13.174     -0.041
   FeSO4                 2.432e-014  2.432e-014   -13.614    -13.614      0.000
   Fe(OH)3-              9.379e-015  8.543e-015   -14.028    -14.068     -0.041
   Fe(OH)2               1.199e-015  1.199e-015   -14.921    -14.921      0.000
   FeHPO4                7.025e-016  7.025e-016   -15.153    -15.153      0.000
   FeHCO3+               4.124e-016  3.765e-016   -15.385    -15.424     -0.040
   FeH2PO4+              6.836e-019  6.232e-019   -18.165    -18.205     -0.040
Fe(3)           7.166e-007
   Fe(OH)4-              4.928e-007  4.493e-007    -6.307     -6.347     -0.040
   Fe(OH)3               2.141e-007  2.141e-007    -6.669     -6.669      0.000
   Fe(OH)2+              9.701e-009  8.845e-009    -8.013     -8.053     -0.040
   FeOH+2                1.465e-015  1.009e-015   -14.834    -14.996     -0.162
   FeHPO4+               1.485e-018  1.354e-018   -17.828    -17.868     -0.040
   FeF2+                 1.213e-020  1.105e-020   -19.916    -19.957     -0.041
   FeF+2                 8.137e-021  5.601e-021   -20.090    -20.252     -0.162
   FeF3                  1.149e-021  1.149e-021   -20.940    -20.940      0.000
   FeSO4+                1.134e-021  1.033e-021   -20.945    -20.986     -0.041
   Fe+3                  1.636e-022  6.932e-023   -21.786    -22.159     -0.373
   Fe(SO4)2-             3.264e-023  2.932e-023   -22.486    -22.533     -0.047
   FeCl+2                2.005e-024  1.380e-024   -23.698    -23.860     -0.162
   FeNO3+2               4.250e-025  2.766e-025   -24.372    -24.558     -0.187
   FeH2PO4+2             3.174e-026  2.194e-026   -25.498    -25.659     -0.160
   FeCl2+                4.462e-027  4.064e-027   -26.351    -26.391     -0.041
   Fe2(OH)2+4            1.878e-028  3.369e-029   -27.726    -28.472     -0.746
   FeCl3                 2.679e-031  2.679e-031   -30.572    -30.572      0.000
   Fe3(OH)4+5            6.310e-035  4.308e-036   -34.200    -35.366     -1.166
H(0)            2.820e-030
   H2                    1.410e-030  1.413e-030   -29.851    -29.850      0.001
K               3.966e-003
   K+                    3.929e-003  3.572e-003    -2.406     -2.447     -0.041
   KSO4-                 3.683e-005  3.358e-005    -4.434     -4.474     -0.040
   KHPO4-                7.028e-008  6.408e-008    -7.153     -7.193     -0.040
Mg              5.928e-005
   Mg+2                  4.915e-005  3.356e-005    -4.308     -4.474     -0.166
   MgSO4                 8.109e-006  8.109e-006    -5.091     -5.091      0.000
   MgCO3                 1.174e-006  1.174e-006    -5.930     -5.930      0.000
   MgOH+                 3.294e-007  3.011e-007    -6.482     -6.521     -0.039
   MgF+                  3.050e-007  2.775e-007    -6.516     -6.557     -0.041
   MgHCO3+               1.515e-007  1.376e-007    -6.820     -6.861     -0.042
   MgHPO4                5.007e-008  5.007e-008    -7.300     -7.300      0.000
   MgPO4-                3.705e-009  3.378e-009    -8.431     -8.471     -0.040
   MgH2PO4+              2.957e-011  2.696e-011   -10.529    -10.569     -0.040
Mn(2)           1.457e-007
   Mn+2                  1.211e-007  7.882e-008    -6.917     -7.103     -0.187
   MnSO4                 1.861e-008  1.861e-008    -7.730     -7.730      0.000
   MnOH+                 4.899e-009  4.462e-009    -8.310     -8.350     -0.041
   MnHCO3+               6.921e-010  6.304e-010    -9.160     -9.200     -0.041
   MnF+                  2.539e-010  2.313e-010    -9.595     -9.636     -0.041
   MnCl+                 7.182e-011  6.542e-011   -10.144    -10.184     -0.041
   MnNO3+                5.550e-011  4.985e-011   -10.256    -10.302     -0.047
   MnCl2                 6.092e-014  6.092e-014   -13.215    -13.215      0.000
   Mn(NO3)2              4.997e-014  4.997e-014   -13.301    -13.301      0.000
   Mn(OH)3-              1.538e-014  1.401e-014   -13.813    -13.854     -0.041
   MnCl3-                1.214e-017  1.106e-017   -16.916    -16.956     -0.041
   Mn(OH)4-2             1.481e-018  1.019e-018   -17.830    -17.992     -0.162
Mn(3)           8.310e-029
   Mn+3                  8.310e-029  3.521e-029   -28.080    -28.453     -0.373
Mn(6)           2.732e-035
   MnO4-2                2.732e-035  1.881e-035   -34.564    -34.726     -0.162
Mn(7)           0.000e+000
   MnO4-                 0.000e+000  0.000e+000   -40.055    -40.098     -0.043
N(-3)           2.143e-006
   NH3                   1.141e-006  1.141e-006    -5.943     -5.943      0.000
   NH4+                  9.876e-007  8.938e-007    -6.005     -6.049     -0.043
   NH4SO4-               1.396e-008  1.272e-008    -7.855     -7.896     -0.041
   CaNH3+2               4.443e-010  2.892e-010    -9.352     -9.539     -0.187
   NiNH3+2               3.824e-011  2.489e-011   -10.418    -10.604     -0.187
```

```
   CuNH3+2               1.196e-012  7.786e-013   -11.922   -12.109    -0.187
   Ni(NH3)2+2            6.305e-015  4.104e-015   -14.200   -14.387    -0.187
   Ca(NH3)2+2            2.018e-016  1.313e-016   -15.695   -15.882    -0.187
N(5)            4.393e-004
   NO3-                  4.390e-004  3.991e-004    -3.358    -3.399    -0.041
   CaNO3+                2.829e-007  2.541e-007    -6.548    -6.595    -0.047
   MnNO3+                5.550e-011  4.985e-011   -10.256   -10.302    -0.047
   NiNO3+                4.533e-011  4.072e-011   -10.344   -10.390    -0.047
   PbNO3+                1.852e-011  1.664e-011   -10.732   -10.779    -0.047
   ZnNO3+                1.079e-011  9.693e-012   -10.967   -11.014    -0.047
   CuNO3+                9.370e-014  8.416e-014   -13.028   -13.075    -0.047
   CdNO3+                7.948e-014  7.139e-014   -13.100   -13.146    -0.047
   Mn(NO3)2              4.997e-014  4.997e-014   -13.301   -13.301     0.000
   Pb(NO3)2              1.128e-014  1.128e-014   -13.948   -13.948     0.000
   Zn(NO3)2              7.718e-016  7.718e-016   -15.113   -15.113     0.000
   Cd(NO3)2              1.428e-017  1.428e-017   -16.845   -16.845     0.000
   Cu(NO3)2              4.228e-018  4.228e-018   -17.374   -17.374     0.000
   FeNO3+2               4.250e-025  2.766e-025   -24.372   -24.558    -0.187
Na              1.541e-003
   Na+                   1.528e-003  1.389e-003    -2.816    -2.857    -0.041
   NaSO4-                1.086e-005  9.905e-006    -4.964    -5.004    -0.040
   NaCO3-                1.193e-006  1.088e-006    -5.923    -5.963    -0.040
   NaHCO3                3.131e-007  3.131e-007    -6.504    -6.504     0.000
   NaF                   6.459e-008  6.459e-008    -7.190    -7.190     0.000
   NaHPO4-               4.233e-008  3.859e-008    -7.373    -7.413    -0.040
Ni              1.705e-007
   NiCO3                 6.375e-008  6.375e-008    -7.196    -7.196     0.000
   Ni+2                  5.950e-008  4.062e-008    -7.226    -7.391    -0.166
   Ni(OH)2               2.063e-008  2.063e-008    -7.685    -7.685     0.000
   NiOH+                 1.283e-008  1.153e-008    -7.892    -7.938    -0.047
   NiSO4                 1.076e-008  1.076e-008    -7.968    -7.968     0.000
   NiHCO3+               2.235e-009  2.007e-009    -8.651    -8.697    -0.047
   Ni(OH)3-              5.178e-010  4.651e-010    -9.286    -9.332    -0.047
   NiF+                  8.372e-011  7.519e-011   -10.077   -10.124    -0.047
   NiCl+                 7.628e-011  6.851e-011   -10.118   -10.164    -0.047
   NiNO3+                4.533e-011  4.072e-011   -10.344   -10.390    -0.047
   NiNH3+2               3.824e-011  2.489e-011   -10.418   -10.604    -0.187
   Ni(SO4)2-2            7.271e-013  4.732e-013   -12.138   -12.325    -0.187
   Ni(NH3)2+2            6.305e-015  4.104e-015   -14.200   -14.387    -0.187
   NiCl2                 2.274e-016  2.274e-016   -15.643   -15.643     0.000
O(0)            5.070e-033
   O2                    2.535e-033  2.540e-033   -32.596   -32.595     0.001
P               5.265e-006
   HPO4-2                3.435e-006  2.365e-006    -5.464    -5.626    -0.162
   CaPO4-                1.422e-006  1.297e-006    -5.847    -5.887    -0.040
   CaHPO4                2.177e-007  2.177e-007    -6.662    -6.662     0.000
   KHPO4-                7.028e-008  6.408e-008    -7.153    -7.193    -0.040
   MgHPO4                5.007e-008  5.007e-008    -7.300    -7.300     0.000
   NaHPO4-               4.233e-008  3.859e-008    -7.373    -7.413    -0.040
   H2PO4-                1.828e-008  1.667e-008    -7.738    -7.778    -0.040
   PO4-3                 5.270e-009  2.233e-009    -8.278    -8.651    -0.373
   MgPO4-                3.705e-009  3.378e-009    -8.431    -8.471    -0.040
   CaH2PO4+              8.239e-011  7.512e-011   -10.084   -10.124    -0.040
   MgH2PO4+              2.957e-011  2.696e-011   -10.529   -10.569    -0.040
   H3PO4                 1.047e-015  1.047e-015   -14.980   -14.980     0.000
   FeHPO4                7.025e-016  7.025e-016   -15.153   -15.153     0.000
   FeHPO4+               1.485e-018  1.354e-018   -17.828   -17.868    -0.040
   FeH2PO4+              6.836e-019  6.232e-019   -18.165   -18.205    -0.040
   FeH2PO4+2             3.174e-026  2.194e-026   -25.498   -25.659    -0.160
Pb              7.243e-007
   PbCO3                 3.565e-007  3.565e-007    -6.448    -6.448     0.000
   PbOH+                 1.777e-007  1.596e-007    -6.750    -6.797    -0.047
   Pb(OH)2               1.137e-007  1.137e-007    -6.944    -6.944     0.000
   Pb(CO3)2-2            6.646e-008  4.325e-008    -7.177    -7.364    -0.187
   Pb+2                  4.129e-009  2.819e-009    -8.384    -8.550    -0.166
   Pb(OH)3-              2.854e-009  2.564e-009    -8.545    -8.591    -0.047
   PbSO4                 1.833e-009  1.833e-009    -8.737    -8.737     0.000
   PbHCO3+               9.347e-010  8.396e-010    -9.029    -9.076    -0.047
```

```
   PbCl+                 7.341e-011  6.594e-011   -10.134   -10.181    -0.047
   Pb(SO4)2-2            2.254e-011  1.467e-011   -10.647   -10.834    -0.187
   Pb(OH)4-2             2.174e-011  1.415e-011   -10.663   -10.849    -0.187
   PbNO3+                1.852e-011  1.664e-011   -10.732   -10.779    -0.047
   PbF+                  1.630e-011  1.464e-011   -10.788   -10.834    -0.047
   Pb3(OH)4+2            1.118e-012  7.277e-013   -11.951   -12.138    -0.187
   PbCl2                 1.942e-013  1.942e-013   -12.712   -12.712     0.000
   PbF2                  2.123e-014  2.123e-014   -13.673   -13.673     0.000
   Pb2OH+3               1.874e-014  7.130e-015   -13.727   -14.147    -0.420
   Pb(NO3)2              1.128e-014  1.128e-014   -13.948   -13.948     0.000
   Pb4(OH)4+4            9.082e-017  1.630e-017   -16.042   -16.788    -0.746
   PbCl3-                5.674e-017  5.096e-017   -16.246   -16.293    -0.047
   PbF3-                 3.305e-018  2.968e-018   -17.481   -17.528    -0.047
   PbCl4-2               2.360e-020  1.536e-020   -19.627   -19.814    -0.187
   PbF4-2                1.609e-022  1.047e-022   -21.794   -21.980    -0.187
S(6)            2.062e-003
   SO4-2                 1.945e-003  1.328e-003    -2.711    -2.877    -0.166
   CaSO4                 6.125e-005  6.125e-005    -4.213    -4.213     0.000
   KSO4-                 3.683e-005  3.358e-005    -4.434    -4.474    -0.040
   NaSO4-                1.086e-005  9.905e-006    -4.964    -5.004    -0.040
   MgSO4                 8.109e-006  8.109e-006    -5.091    -5.091     0.000
   MnSO4                 1.861e-008  1.861e-008    -7.730    -7.730     0.000
   NH4SO4-               1.396e-008  1.272e-008    -7.855    -7.896    -0.041
   NiSO4                 1.076e-008  1.076e-008    -7.968    -7.968     0.000
   ZnSO4                 2.809e-009  2.809e-009    -8.551    -8.551     0.000
   PbSO4                 1.833e-009  1.833e-009    -8.737    -8.737     0.000
   HSO4-                 6.371e-011  5.796e-011   -10.196   -10.237    -0.041
   Zn(SO4)2-2            4.992e-011  3.249e-011   -10.302   -10.488    -0.187
   Pb(SO4)2-2            2.254e-011  1.467e-011   -10.647   -10.834    -0.187
   CuSO4                 2.029e-011  2.029e-011   -10.693   -10.693     0.000
   CdSO4                 1.761e-011  1.761e-011   -10.754   -10.754     0.000
   Ni(SO4)2-2            7.271e-013  4.732e-013   -12.138   -12.325    -0.187
   Cd(SO4)2-2            4.847e-013  3.155e-013   -12.315   -12.501    -0.187
   FeSO4                 2.432e-014  2.432e-014   -13.614   -13.614     0.000
   AlSO4+                7.050e-019  6.414e-019   -18.152   -18.193    -0.041
   Al(SO4)2-             1.003e-020  9.126e-021   -19.999   -20.040    -0.041
   FeSO4+                1.134e-021  1.033e-021   -20.945   -20.986    -0.041
   Fe(SO4)2-             3.264e-023  2.932e-023   -22.486   -22.533    -0.047
Si              3.490e-004
   H4SiO4                2.572e-004  2.577e-004    -3.590    -3.589     0.001
   H3SiO4-               9.178e-005  8.339e-005    -4.037    -4.079    -0.042
   H2SiO4-2              1.705e-008  1.178e-008    -7.768    -7.929    -0.160
   SiF6-2                3.617e-036  2.490e-036   -35.442   -35.604    -0.162
Zn              1.530e-007
   Zn(OH)2               7.785e-008  7.785e-008    -7.109    -7.109     0.000
   ZnOH+                 2.426e-008  2.179e-008    -7.615    -7.662    -0.047
   ZnCO3                 2.341e-008  2.341e-008    -7.631    -7.631     0.000
   Zn+2                  1.416e-008  9.670e-009    -7.849    -8.015    -0.166
   Zn(OH)3-              9.791e-009  8.794e-009    -8.009    -8.056    -0.047
   ZnSO4                 2.809e-009  2.809e-009    -8.551    -8.551     0.000
   ZnOHCl                4.725e-010  4.725e-010    -9.326    -9.326     0.000
   ZnHCO3+               1.365e-010  1.226e-010    -9.865    -9.912    -0.047
   Zn(SO4)2-2            4.992e-011  3.249e-011   -10.302   -10.488    -0.187
   ZnCl+                 1.762e-011  1.601e-011   -10.754   -10.796    -0.042
   ZnF+                  1.583e-011  1.422e-011   -10.800   -10.847    -0.047
   Zn(OH)4-2             1.212e-011  7.891e-012   -10.916   -11.103    -0.187
   ZnNO3+                1.079e-011  9.693e-012   -10.967   -11.014    -0.047
   ZnCl2                 1.673e-014  1.673e-014   -13.776   -13.776     0.000
   Zn(NO3)2              7.718e-016  7.718e-016   -15.113   -15.113     0.000
   ZnCl3-                9.643e-018  8.761e-018   -17.016   -17.057    -0.042
   ZnCl4-2               4.196e-021  2.888e-021   -20.377   -20.539    -0.162

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -1.96    8.84   10.80  Al(OH)3
        Al2O3            -1.96   17.69   19.65  Al2O3
```

```
        Al4(OH)10SO4     -8.90   13.80   22.70  Al4(OH)10SO4
        AlOHSO4          -9.50  -12.73   -3.23  AlOHSO4
        Alunite          -8.32   -9.72   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -3.64  -11.43   -7.79  PbSO4
        Anhydrite        -2.21   -6.57   -4.36  CaSO4
        Antlerite        -4.79    4.00    8.79  Cu3(OH)4SO4
        Aragonite         0.23   -8.07   -8.30  CaCO3
        Artinite         -4.22    5.38    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -2.87    4.52    7.39  Cu2(OH)3Cl
        Azurite          -3.67  -20.58  -16.91  Cu3(OH)2(CO3)2
        Bianchite        -9.13  -10.89   -1.76  ZnSO4:6H2O
        Birnessite       -5.14   12.95   18.09  MnO2
        Bixbyite         -0.16   -0.81   -0.64  Mn2O3
        Boehmite          0.27    8.84    8.58  AlOOH
        Brochantite      -2.70   12.52   15.22  Cu4(OH)6SO4
        Brucite          -2.62   14.23   16.84  Mg(OH)2
        Bunsenite        -1.14   11.31   12.45  NiO
        Ca3(PO4)2(beta)   0.53  -28.39  -28.92  Ca3(PO4)2
        Ca4H(PO4)3:3H2O  -3.01  -50.09  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -2.42  -21.70  -19.27  CaHPO4
        CaHPO4:2H2O      -2.70  -21.70  -19.00  CaHPO4:2H2O
        Calcite           0.41   -8.07   -8.48  CaCO3
        Cd(OH)2          -5.19    8.45   13.64  Cd(OH)2
        Cd(OH)2(am)      -5.28    8.45   13.73  Cd(OH)2
        Cd3(OH)2(SO4)2  -24.51  -17.80    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -18.78    3.78   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -15.44  -48.04  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -16.17   12.23   28.40  Cd4(OH)6SO4
        CdCl2           -15.95  -16.61   -0.66  CdCl2
        CdCl2:1H2O      -14.92  -16.61   -1.69  CdCl2:1H2O
        CdCl2:2.5H2O    -14.70  -16.61   -1.91  CdCl2:2.5H2O
        CdF2            -17.30  -18.51   -1.21  CdF2
        Cdmetal(alpha)  -31.76  -18.25   13.51  Cd
        Cdmetal(gamma)  -31.87  -18.25   13.62  Cd
        CdOHCl           -7.62   -4.08    3.54  CdOHCl
        CdSO4           -12.95  -13.12   -0.17  CdSO4
        CdSO4:1H2O      -11.40  -13.12   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -11.25  -13.12   -1.87  CdSO4:2.67H2O
        Cerrusite         0.20  -12.93  -13.13  PbCO3
        CH4(g)          -88.83 -129.88  -41.05  CH4
        Chalcanthite    -10.41  -13.05   -2.64  CuSO4:5H2O
        Chalcedony       -0.04   -3.59   -3.55  SiO2
        Chrysotile        3.30   35.50   32.20  Mg3Si2O5(OH)4
        CO2(g)           -4.93  -23.08  -18.15  CO2
        Cotunnite       -10.13  -14.91   -4.78  PbCl2
        Cristobalite     -0.24   -3.59   -3.35  SiO2
        Cryolite        -18.73  -52.57  -33.84  Na3AlF6
        Cu(OH)2          -0.15    8.52    8.67  Cu(OH)2
        Cu2(OH)3NO3      -4.95    4.30    9.25  Cu2(OH)3NO3
        Cu2SO4          -23.90  -25.85   -1.95  Cu2SO4
        Cu3(PO4)2       -10.98  -47.83  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -12.71  -47.83  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -3.05  -14.55  -11.50  CuCO3
        CuF             -10.71  -15.62   -4.91  CuF
        CuF2            -19.56  -18.44    1.12  CuF2
        CuF2:2H2O       -13.89  -18.44   -4.55  CuF2:2H2O
        Cumetal          -6.73  -15.49   -8.76  Cu
        CuOCuSO4        -14.83   -4.53   10.30  CuOCuSO4
        Cupricferrite    14.32   20.31    5.99  CuFe2O4
        Cuprite          -2.87   -4.27   -1.41  Cu2O
        Cuprousferrite   12.67    3.75   -8.92  CuFeO2
        CuSO4           -15.99  -13.05    2.94  CuSO4
        Diaspore          1.97    8.84    6.87  AlOOH
        Dolomite(disordered)  -0.38  -16.92  -16.54  CaMg(CO3)2
        Dolomite(ordered)   0.17  -16.92  -17.09  CaMg(CO3)2
        Epsomite         -5.23   -7.35   -2.13  MgSO4:7H2O
        FCO3Apatite      21.27  -93.13 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
```

```
Fe(OH)2           -7.99    5.57   13.56  Fe(OH)2
Fe(OH)2.7Cl.3      5.17    2.13   -3.04  Fe(OH)2.7Cl.3
Fe2(SO4)3        -49.21  -52.95   -3.73  Fe2(SO4)3
Fe3(OH)8          -2.87   17.35   20.22  Fe3(OH)8
Ferrihydrite       2.70    5.89    3.19  Fe(OH)3
Fluorite          -1.46  -11.96  -10.50  CaF2
Gibbsite           0.55    8.84    8.29  Al(OH)3
Goethite           5.40    5.89    0.49  FeOOH
Goslarite         -8.88  -10.89   -2.01  ZnSO4:7H2O
Greenalite       -11.27    9.54   20.81  Fe3Si2O5(OH)4
Gypsum            -1.96   -6.57   -4.61  CaSO4:2H2O
H-Jarosite       -13.38  -25.48  -12.10  (H3O)Fe3(SO4)2(OH)6
Halite            -7.64   -6.04    1.60  NaCl
Halloysite         0.94   10.51    9.57  Al2Si2O5(OH)4
Hausmannite        0.46   61.49   61.03  Mn3O4
Hematite          13.20   11.78   -1.42  Fe2O3
Hercynite          0.37   23.26   22.89  FeAl2O4
Hinsdalite       -19.10  -21.60   -2.50  PbAl3PO4SO4(OH)6
Huntite           -4.65  -34.62  -29.97  CaMg3(CO3)4
Hydrocerrusite     3.07  -15.70  -18.77  Pb3(OH)2(CO3)2
Hydromagnesite   -12.41  -21.18   -8.77  Mg5(CO3)4(OH)2:4H2O
Hydroxylapatite    9.25  -35.08  -44.33  Ca5(PO4)3OH
Hydroxylpyromorphite    3.44  -59.35  -62.79  Pb5(PO4)3OH
K-Alum           -22.24  -27.41   -5.17  KAl(SO4)2:12H2O
K-Jarosite        -3.78  -18.58  -14.80  KFe3(SO4)2(OH)6
Kaolinite          3.08   10.51    7.43  Al2Si2O5(OH)4
Langite           -4.97   12.52   17.49  Cu4(OH)6SO4:H2O
Larnakite         -0.84   -1.28   -0.43  PbO:PbSO4
Laurionite        -3.00   -2.38    0.62  PbOHCl
Lepidocrocite      4.52    5.89    1.37  FeOOH
Lime             -17.70   15.00   32.70  CaO
Litharge          -2.54   10.15   12.69  PbO
Maghemite          5.40   11.78    6.39  Fe2O3
Magnesioferrite    9.15   26.01   16.86  Fe2MgO4
Magnesite         -1.39   -8.85   -7.46  MgCO3
Magnetite         13.95   17.35    3.40  Fe3O4
Malachite         -0.72   -6.03   -5.31  Cu2(OH)2CO3
Manganite         -0.39   24.95   25.34  MnOOH
Massicot          -2.74   10.15   12.89  PbO
Matlockite        -6.89  -15.86   -8.97  PbClF
Melanothallite   -22.80  -16.54    6.26  CuCl2
Melanterite      -13.80  -16.00   -2.21  FeSO4:7H2O
Mg(OH)2(active)   -4.57   14.23   18.79  Mg(OH)2
Mg3(PO4)2         -7.44  -30.72  -23.28  Mg3(PO4)2
MgF2              -4.61  -12.74   -8.13  MgF2
MgHPO4:3H2O       -4.30  -22.48  -18.18  MgHPO4:3H2O
Minium           -16.37   57.15   73.52  Pb3O4
Mirabilite        -7.48   -8.59   -1.11  Na2SO4:10H2O
Mn2(SO4)3        -59.83  -65.54   -5.71  Mn2(SO4)3
Mn3(PO4)2        -14.79  -38.61  -23.83  Mn3(PO4)2
MnCl2:4H2O       -16.18  -13.47    2.72  MnCl2:4H2O
MnHPO4             0.30  -25.10  -25.40  MnHPO4
MnSO4            -12.56   -9.98    2.58  MnSO4
Monteponite       -6.65    8.45   15.10  CdO
Morenosite        -8.12  -10.27   -2.14  NiSO4:7H2O
Na-Jarosite       -7.79  -18.99  -11.20  NaFe3(SO4)2(OH)6
Nantokite         -7.94  -14.67   -6.73  CuCl
Natron            -8.78  -10.09   -1.31  Na2CO3:10H2O
Nesquehonite      -4.18   -8.85   -4.67  MgCO3:3H2O
Ni(OH)2           -1.49   11.31   12.79  Ni(OH)2
Ni3(PO4)2         -8.18  -39.48  -31.30  Ni3(PO4)2
Ni4(OH)6SO4       -8.34   23.66   32.00  Ni4(OH)6SO4
NiCO3             -4.90  -11.77   -6.87  NiCO3
Nsutite           -4.56   12.95   17.50  MnO2
O2(g)            -29.69   53.40   83.09  O2
Otavite           -2.62  -14.62  -12.00  CdCO3
Pb(OH)2            2.00   10.15    8.15  Pb(OH)2
Pb10(OH)6O(CO3)6  -28.20  -36.96   -8.76  Pb10(OH)6O(CO3)6
```

```
        Pb2(OH)3Cl       -1.02    7.77    8.79  Pb2(OH)3Cl
        Pb2O(OH)2        -5.89   20.30   26.19  Pb2O(OH)2
        Pb2O3           -14.04   47.00   61.04  Pb2O3
        Pb2OCO3          -2.22   -2.78   -0.56  Pb2OCO3
        Pb3(PO4)2         0.58  -42.95  -43.53  Pb3(PO4)2
        Pb3O2CO3         -3.65    7.37   11.02  Pb3O2CO3
        Pb3O2SO4         -1.81    8.87   10.69  Pb3O2SO4
        Pb4(OH)6SO4      -2.08   19.02   21.10  Pb4(OH)6SO4
        Pb4O3SO4         -2.85   19.02   21.88  Pb4O3SO4
        PbF2             -9.37  -16.81   -7.44  PbF2
        PbHPO4           -2.75  -26.55  -23.81  PbHPO4
        Pbmetal         -20.80  -16.55    4.25  Pb
        PbO:0.3H2O       -2.83   10.15   12.98  PbO:0.33H2O
        Periclase        -7.36   14.23   21.58  MgO
        Phosgenite       -8.03  -27.84  -19.81  PbCl2:PbCO3
        Plattnerite     -12.75   36.85   49.60  PbO2
        Plumbgummite     -3.93  -36.72  -32.79  PbAl3(PO4)2(OH)5:H2O
        Portlandite      -7.80   15.00   22.80  Ca(OH)2
        Pyrochroite      -3.60   11.60   15.19  Mn(OH)2
        Pyrolusite       -3.08   38.30   41.38  MnO2
        Pyromorphite     12.55  -71.88  -84.43  Pb5(PO4)3Cl
        Quartz            0.41   -3.59   -4.00  SiO2
        Retgersite       -8.23  -10.27   -2.04  NiSO4:6H2O
        Rhodochrosite    -0.90  -11.48  -10.58  MnCO3
        Sepiolite         1.93   17.69   15.76  Mg2Si3O7.5OH:3H2O
        Sepiolite(A)     -1.09   17.69   18.78  Mg2Si3O7.5OH:3H2O
        Siderite         -7.26  -17.50  -10.24  FeCO3
        SiO2(am-gel)     -0.88   -3.59   -2.71  SiO2
        SiO2(am-ppt)     -0.85   -3.59   -2.74  SiO2
        Smithsonite      -2.39  -12.39  -10.00  ZnCO3
        Spinel           -4.93   31.91   36.85  MgAl2O4
        Strengite        -4.41  -30.81  -26.40  FePO4:2H2O
        Tenorite          0.88    8.52    7.64  CuO
        Thenardite       -8.91   -8.59    0.32  Na2SO4
        Thermonatrite   -10.73  -10.09    0.64  Na2CO3:H2O
        Tsumebite         1.91   -7.88   -9.79  Pb2CuPO4(OH)3:3H2O
        Vivianite       -20.68  -56.68  -36.00  Fe3(PO4)2:8H2O
        Zincite          -0.65   10.69   11.33  ZnO
        Zincosite       -14.82  -10.89    3.93  ZnSO4
        Zn(NO3)2:6H2O   -18.13  -14.81    3.32  Zn(NO3)2:6H2O
        Zn(OH)2          -1.51   10.69   12.20  Zn(OH)2
        Zn(OH)2(am)      -1.79   10.69   12.47  Zn(OH)2
        Zn(OH)2(beta)    -1.07   10.69   11.75  Zn(OH)2
        Zn(OH)2(epsilon)  -0.85   10.69   11.53  Zn(OH)2
        Zn(OH)2(gamma)   -1.05   10.69   11.73  Zn(OH)2
        Zn2(OH)2SO4      -7.71   -0.21    7.50  Zn2(OH)2SO4
        Zn2(OH)3Cl       -6.35    8.84   15.19  Zn2(OH)3Cl
        Zn3(PO4)2:4H2O   -5.93  -41.35  -35.42  Zn3(PO4)2:4H2O
        Zn3O(SO4)2      -30.01  -11.10   18.91  Zn3O(SO4)2
        Zn4(OH)6SO4      -7.24   21.16   28.40  Zn4(OH)6SO4
        Zn5(OH)8Cl2     -10.14   28.36   38.50  Zn5(OH)8Cl2
        ZnCl2           -21.43  -14.38    7.05  ZnCl2
        ZnCO3:1H2O       -2.13  -12.39  -10.26  ZnCO3:1H2O
        ZnF2            -15.75  -16.28   -0.53  ZnF2
        Znmetal         -41.80  -16.01   25.79  Zn
        ZnO(active)      -0.50   10.69   11.19  ZnO
        ZnSO4:1H2O      -10.25  -10.89   -0.64  ZnSO4:1H2O

Initial solution 3-FA 120 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Al               3.634e-005  3.634e-005
        C(4)             6.602e-004  6.602e-004
        Ca               3.325e-004  3.325e-004
        Cd               8.900e-011  8.900e-011
```

```
        Cl               7.538e-004  7.538e-004
        Cu               1.417e-007  1.417e-007
        F                8.215e-005  8.215e-005
        Fe               8.958e-007  8.958e-007
        K                3.275e-003  3.275e-003
        Mg               1.235e-004  1.235e-004
        Mn               1.275e-007  1.275e-007
        N(-3)            2.143e-006  2.143e-006
        N(5)             4.607e-004  4.607e-004
        Na               1.871e-003  1.871e-003
        Ni               1.705e-007  1.705e-007
        P                7.074e-006  7.074e-006
        Pb               1.835e-006  1.835e-006
        S(6)             2.270e-003  2.270e-003
        Si               3.097e-004  3.097e-004
        Zn               1.530e-007  1.530e-007

----------------------------Description of solution----------------------------

                                       pH  =   9.500
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  8.794e-003
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.091e-003
                       Total CO2 (mol/kg)  =  6.602e-004
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  = -7.598e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -6.14
                               Iterations  =  10
                                  Total H  = 1.110155e+002
                                  Total O  = 5.552073e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           3.3542      0.1984

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                   Molality    Activity  Molality  Activity    Gamma

   OH-                   3.516e-005  3.184e-005    -4.454    -4.497    -0.043
   H+                    3.486e-010  3.162e-010    -9.458    -9.500    -0.042
   H2O                   5.551e+001  9.998e-001     1.744    -0.000     0.000
Al              3.634e-005
   Al(OH)4-              3.633e-005  3.299e-005    -4.440    -4.482    -0.042
   Al(OH)3               8.230e-009  8.230e-009    -8.085    -8.085     0.000
   Al(OH)2+              1.424e-011  1.296e-011   -10.847   -10.888    -0.041
   AlOH+2                7.471e-016  5.123e-016   -15.127   -15.290    -0.164
   AlF2+                 3.830e-016  3.485e-016   -15.417   -15.458    -0.041
   AlF3                  3.237e-016  3.237e-016   -15.490   -15.490     0.000
   AlF+2                 1.731e-017  1.187e-017   -16.762   -16.926    -0.164
   AlF4-                 1.318e-017  1.196e-017   -16.880   -16.922    -0.042
   AlSO4+                2.001e-019  1.817e-019   -18.699   -18.741    -0.042
   Al+3                  3.868e-020  1.609e-020   -19.412   -19.793    -0.381
   Al(SO4)2-             3.119e-021  2.832e-021   -20.506   -20.548    -0.042
C(4)            6.602e-004
   HCO3-                 5.255e-004  4.782e-004    -3.279    -3.320    -0.041
   CO3-2                 1.047e-004  7.090e-005    -3.980    -4.149    -0.169
   CaCO3                 1.917e-005  1.917e-005    -4.717    -4.717     0.000
   MgCO3                 3.978e-006  3.978e-006    -5.400    -5.400     0.000
   NaCO3-                2.440e-006  2.220e-006    -5.613    -5.654    -0.041
   CaHCO3+               1.667e-006  1.519e-006    -5.778    -5.818    -0.040
   PbCO3                 8.574e-007  8.574e-007    -6.067    -6.067     0.000
   NaHCO3                4.523e-007  4.523e-007    -6.345    -6.345     0.000
```

```
   MgHCO3+             3.641e-007  3.301e-007    -6.439    -6.481    -0.043
   H2CO3               3.401e-007  3.401e-007    -6.468    -6.468     0.000
   Pb(CO3)2-2          2.722e-007  1.753e-007    -6.565    -6.756    -0.191
   NiCO3               7.539e-008  7.539e-008    -7.123    -7.123     0.000
   CuCO3               4.413e-008  4.413e-008    -7.355    -7.355     0.000
   ZnCO3               2.194e-008  2.194e-008    -7.659    -7.659     0.000
   Cu(CO3)2-2          1.308e-008  8.422e-009    -7.884    -8.075    -0.191
   NiHCO3+             1.876e-009  1.680e-009    -8.727    -8.775    -0.048
   PbHCO3+             1.596e-009  1.430e-009    -8.797    -8.845    -0.048
   MnHCO3+             6.989e-010  6.354e-010    -9.156    -9.197    -0.041
   ZnHCO3+             9.076e-011  8.131e-011   -10.042   -10.090    -0.048
   CdCO3               3.533e-011  3.533e-011   -10.452   -10.452     0.000
   CuHCO3+             3.561e-012  3.190e-012   -11.448   -11.496    -0.048
   Cd(CO3)2-2          2.883e-012  1.857e-012   -11.540   -11.731    -0.191
   CdHCO3+             2.657e-014  2.380e-014   -13.576   -13.623    -0.048
   FeHCO3+             1.706e-016  1.555e-016   -15.768   -15.808    -0.040
Ca                3.325e-004
   Ca+2                2.519e-004  1.706e-004    -3.599    -3.768    -0.169
   CaSO4               5.685e-005  5.685e-005    -4.245    -4.245     0.000
   CaCO3               1.917e-005  1.917e-005    -4.717    -4.717     0.000
   CaPO4-              2.157e-006  1.963e-006    -5.666    -5.707    -0.041
   CaHCO3+             1.667e-006  1.519e-006    -5.778    -5.818    -0.040
   CaNO3+              2.515e-007  2.254e-007    -6.599    -6.647    -0.048
   CaHPO4              2.332e-007  2.332e-007    -6.632    -6.632     0.000
   CaF+                1.511e-007  1.373e-007    -6.821    -6.862    -0.041
   CaOH+               1.189e-007  1.084e-007    -6.925    -6.965    -0.040
   CaNH3+2             4.399e-010  2.834e-010    -9.357    -9.548    -0.191
   CaH2PO4+            6.263e-011  5.699e-011   -10.203   -10.244    -0.041
   Ca(NH3)2+2          2.311e-016  1.488e-016   -15.636   -15.827    -0.191
Cd                8.900e-011
   CdCO3               3.533e-011  3.533e-011   -10.452   -10.452     0.000
   Cd+2                3.228e-011  2.186e-011   -10.491   -10.660    -0.169
   CdSO4               7.454e-012  7.454e-012   -11.128   -11.128     0.000
   CdOH+               6.171e-012  5.528e-012   -11.210   -11.257    -0.048
   Cd(CO3)2-2          2.883e-012  1.857e-012   -11.540   -11.731    -0.191
   CdOHCl              1.864e-012  1.864e-012   -11.729   -11.729     0.000
   CdCl+               1.593e-012  1.428e-012   -11.798   -11.845    -0.048
   Cd(OH)2             1.110e-012  1.110e-012   -11.954   -11.954     0.000
   Cd(SO4)2-2          2.271e-013  1.463e-013   -12.644   -12.835    -0.191
   CdNO3+              3.223e-014  2.888e-014   -13.492   -13.539    -0.048
   CdF+                2.853e-014  2.556e-014   -13.545   -13.593    -0.048
   CdHCO3+             2.657e-014  2.380e-014   -13.576   -13.623    -0.048
   CdCl2               4.069e-015  4.069e-015   -14.391   -14.391     0.000
   Cd(OH)3-            2.411e-015  2.160e-015   -14.618   -14.666    -0.048
   Cd(NO3)2            6.045e-018  6.045e-018   -17.219   -17.219     0.000
   CdF2                3.761e-018  3.761e-018   -17.425   -17.425     0.000
   CdCl3-              1.960e-018  1.756e-018   -17.708   -17.756    -0.048
   Cd(OH)4-2           1.747e-020  1.126e-020   -19.758   -19.949    -0.191
   Cd2OH+3             1.630e-021  6.057e-022   -20.788   -21.218    -0.430
Cl                7.538e-004
   Cl-                 7.538e-004  6.838e-004    -3.123    -3.165    -0.042
   ZnOHCl              3.849e-010  3.849e-010    -9.415    -9.415     0.000
   PbCl+               1.089e-010  9.760e-011    -9.963   -10.011    -0.048
   MnCl+               6.305e-011  5.732e-011   -10.200   -10.242    -0.041
   NiCl+               5.566e-011  4.986e-011   -10.254   -10.302    -0.048
   ZnCl+               1.018e-011  9.235e-012   -10.992   -11.035    -0.043
   CuCl                4.457e-012  4.457e-012   -11.351   -11.351     0.000
   CdOHCl              1.864e-012  1.864e-012   -11.729   -11.729     0.000
   CdCl+               1.593e-012  1.428e-012   -11.798   -11.845    -0.048
   CuCl2-              7.022e-013  6.367e-013   -12.154   -12.196    -0.043
   PbCl2               2.981e-013  2.981e-013   -12.526   -12.526     0.000
   CuCl+               1.263e-013  1.146e-013   -12.898   -12.941    -0.043
   MnCl2               5.536e-014  5.536e-014   -13.257   -13.257     0.000
   ZnCl2               1.001e-014  1.001e-014   -14.000   -14.000     0.000
   CdCl2               4.069e-015  4.069e-015   -14.391   -14.391     0.000
   NiCl2               1.717e-016  1.717e-016   -15.765   -15.765     0.000
   CuCl3-2             1.363e-016  9.309e-017   -15.866   -16.031    -0.166
   PbCl3-              9.059e-017  8.115e-017   -16.043   -16.091    -0.048
```

```
   CuCl2                 2.716e-017  2.716e-017   -16.566   -16.566     0.000
   MnCl3-                1.147e-017  1.043e-017   -16.940   -16.982    -0.041
   ZnCl3-                5.995e-018  5.436e-018   -17.222   -17.265    -0.043
   CdCl3-                1.960e-018  1.756e-018   -17.708   -17.756    -0.048
   PbCl4-2               3.938e-020  2.536e-020   -19.405   -19.596    -0.191
   ZnCl4-2               2.721e-021  1.859e-021   -20.565   -20.731    -0.166
   CuCl3-                1.912e-022  1.733e-022   -21.719   -21.761    -0.043
   FeCl+2                7.252e-025  4.953e-025   -24.140   -24.305    -0.166
   FeCl2+                1.664e-027  1.513e-027   -26.779   -26.820    -0.041
   CuCl4-2               8.697e-028  5.940e-028   -27.061   -27.226    -0.166
   FeCl3                 1.035e-031  1.035e-031   -30.985   -30.985     0.000
Cu(1)           1.094e-011
   Cu+                   5.780e-012  5.178e-012   -11.238   -11.286    -0.048
   CuCl                  4.457e-012  4.457e-012   -11.351   -11.351     0.000
   CuCl2-                7.022e-013  6.367e-013   -12.154   -12.196    -0.043
   CuCl3-2               1.363e-016  9.309e-017   -15.866   -16.031    -0.166
Cu(2)           1.417e-007
   Cu(OH)2               6.761e-008  6.761e-008    -7.170    -7.170     0.000
   CuCO3                 4.413e-008  4.413e-008    -7.355    -7.355     0.000
   Cu(CO3)2-2            1.308e-008  8.422e-009    -7.884    -8.075    -0.191
   CuOH+                 1.174e-008  1.064e-008    -7.930    -7.973    -0.043
   Cu(OH)3-              4.928e-009  4.415e-009    -8.307    -8.355    -0.048
   Cu+2                  1.561e-010  1.057e-010    -9.807    -9.976    -0.169
   CuSO4                 3.523e-011  3.523e-011   -10.453   -10.453     0.000
   Cu2(OH)2+2            4.417e-012  2.845e-012   -11.355   -11.546    -0.191
   CuHCO3+               3.561e-012  3.190e-012   -11.448   -11.496    -0.048
   CuNH3+2               2.216e-012  1.427e-012   -11.654   -11.845    -0.191
   Cu(OH)4-2             1.717e-012  1.106e-012   -11.765   -11.956    -0.191
   CuF+                  5.492e-013  4.920e-013   -12.260   -12.308    -0.048
   CuNO3+                1.559e-013  1.396e-013   -12.807   -12.855    -0.048
   CuCl+                 1.263e-013  1.146e-013   -12.898   -12.941    -0.043
   CuCl2                 2.716e-017  2.716e-017   -16.566   -16.566     0.000
   Cu(NO3)2              7.343e-018  7.343e-018   -17.134   -17.134     0.000
   CuCl3-                1.912e-022  1.733e-022   -21.719   -21.761    -0.043
   CuCl4-2               8.697e-028  5.940e-028   -27.061   -27.226    -0.166
F               8.215e-005
   F-                    8.131e-005  7.376e-005    -4.090    -4.132    -0.042
   MgF+                  6.148e-007  5.582e-007    -6.211    -6.253    -0.042
   CaF+                  1.511e-007  1.373e-007    -6.821    -6.862    -0.041
   NaF                   7.827e-008  7.827e-008    -7.106    -7.106     0.000
   MnF+                  2.151e-010  1.955e-010    -9.667    -9.709    -0.041
   NiF+                  5.894e-011  5.281e-011   -10.230   -10.277    -0.048
   HF                    3.450e-011  3.450e-011   -10.462   -10.462     0.000
   PbF+                  2.334e-011  2.091e-011   -10.632   -10.680    -0.048
   ZnF+                  8.832e-012  7.913e-012   -11.054   -11.102    -0.048
   CuF+                  5.492e-013  4.920e-013   -12.260   -12.308    -0.048
   PbF2                  3.035e-014  3.035e-014   -13.518   -13.518     0.000
   CdF+                  2.853e-014  2.556e-014   -13.545   -13.593    -0.048
   HF2-                  1.068e-014  9.675e-015   -13.971   -14.014    -0.043
   AlF2+                 3.830e-016  3.485e-016   -15.417   -15.458    -0.041
   AlF3                  3.237e-016  3.237e-016   -15.490   -15.490     0.000
   AlF+2                 1.731e-017  1.187e-017   -16.762   -16.926    -0.164
   AlF4-                 1.318e-017  1.196e-017   -16.880   -16.922    -0.042
   PbF3-                 4.740e-018  4.246e-018   -17.324   -17.372    -0.048
   CdF2                  3.761e-018  3.761e-018   -17.425   -17.425     0.000
   FeF2+                 4.212e-021  3.829e-021   -20.375   -20.417    -0.041
   H2F2                  3.189e-021  3.189e-021   -20.496   -20.496     0.000
   FeF+2                 2.840e-021  1.940e-021   -20.547   -20.712    -0.166
   FeF3                  3.985e-022  3.985e-022   -21.400   -21.400     0.000
   PbF4-2                2.327e-022  1.499e-022   -21.633   -21.824    -0.191
   SiF6-2                7.362e-037  5.028e-037   -36.133   -36.299    -0.166
Fe(2)           9.578e-014
   Fe+2                  4.009e-014  2.582e-014   -13.397   -13.588    -0.191
   FeOH+                 3.600e-014  3.273e-014   -13.444   -13.485    -0.041
   FeSO4                 9.220e-015  9.220e-015   -14.035   -14.035     0.000
   Fe(OH)3-              9.166e-015  8.332e-015   -14.038   -14.079    -0.041
   Fe(OH)2               8.276e-016  8.276e-016   -15.082   -15.082     0.000
   FeHPO4                3.075e-016  3.075e-016   -15.512   -15.512     0.000
```

```
   FeHCO3+               1.706e-016  1.555e-016   -15.768   -15.808    -0.040
   FeH2PO4+              2.122e-019  1.931e-019   -18.673   -18.714    -0.041
Fe(3)           8.958e-007
   Fe(OH)4-              6.802e-007  6.190e-007    -6.167    -6.208    -0.041
   Fe(OH)3               2.088e-007  2.088e-007    -6.680    -6.680     0.000
   Fe(OH)2+              6.711e-009  6.107e-009    -8.173    -8.214    -0.041
   FeOH+2                7.219e-016  4.931e-016   -15.142   -15.307    -0.166
   FeHPO4+               6.513e-019  5.927e-019   -18.186   -18.227    -0.041
   FeF2+                 4.212e-021  3.829e-021   -20.375   -20.417    -0.041
   FeF+2                 2.840e-021  1.940e-021   -20.547   -20.712    -0.166
   FeSO4+                4.306e-022  3.915e-022   -21.366   -21.407    -0.041
   FeF3                  3.985e-022  3.985e-022   -21.400   -21.400     0.000
   Fe+3                  5.766e-023  2.399e-023   -22.239   -22.620    -0.381
   Fe(SO4)2-             1.359e-023  1.218e-023   -22.867   -22.915    -0.048
   FeCl+2                7.252e-025  4.953e-025   -24.140   -24.305    -0.166
   FeNO3+2               1.556e-025  1.002e-025   -24.808   -24.999    -0.191
   FeH2PO4+2             9.911e-027  6.797e-027   -26.004   -26.168    -0.164
   FeCl2+                1.664e-027  1.513e-027   -26.779   -26.820    -0.041
   Fe2(OH)2+4            4.677e-029  8.051e-030   -28.330   -29.094    -0.764
   FeCl3                 1.035e-031  1.035e-031   -30.985   -30.985     0.000
   Fe3(OH)4+5            1.111e-035  7.107e-037   -34.954   -36.148    -1.194
H(0)            1.413e-030
   H2                    7.065e-031  7.079e-031   -30.151   -30.150     0.001
K               3.275e-003
   K+                    3.242e-003  2.941e-003    -2.489    -2.531    -0.042
   KSO4-                 3.328e-005  3.029e-005    -4.478    -4.519    -0.041
   KHPO4-                7.333e-008  6.673e-008    -7.135    -7.176    -0.041
Mg              1.235e-004
   Mg+2                  9.960e-005  6.745e-005    -4.002    -4.171    -0.169
   MgSO4                 1.785e-005  1.785e-005    -4.748    -4.748     0.000
   MgCO3                 3.978e-006  3.978e-006    -5.400    -5.400     0.000
   MgOH+                 9.370e-007  8.549e-007    -6.028    -6.068    -0.040
   MgF+                  6.148e-007  5.582e-007    -6.211    -6.253    -0.042
   MgHCO3+               3.641e-007  3.301e-007    -6.439    -6.481    -0.043
   MgHPO4                1.273e-007  1.273e-007    -6.895    -6.895     0.000
   MgPO4-                1.333e-008  1.213e-008    -7.875    -7.916    -0.041
   MgH2PO4+              5.332e-011  4.852e-011   -10.273   -10.314    -0.041
Mn(2)           1.275e-007
   Mn+2                  1.034e-007  6.658e-008    -6.986    -7.177    -0.191
   MnSO4                 1.722e-008  1.722e-008    -7.764    -7.764     0.000
   MnOH+                 5.857e-009  5.325e-009    -8.232    -8.274    -0.041
   MnHCO3+               6.989e-010  6.354e-010    -9.156    -9.197    -0.041
   MnF+                  2.151e-010  1.955e-010    -9.667    -9.709    -0.041
   MnCl+                 6.305e-011  5.732e-011   -10.200   -10.242    -0.041
   MnNO3+                4.921e-011  4.408e-011   -10.308   -10.356    -0.048
   MnCl2                 5.536e-014  5.536e-014   -13.257   -13.257     0.000
   Mn(NO3)2              4.625e-014  4.625e-014   -13.335   -13.335     0.000
   Mn(OH)3-              3.669e-014  3.335e-014   -13.435   -13.477    -0.041
   MnCl3-                1.147e-017  1.043e-017   -16.940   -16.982    -0.041
   Mn(OH)4-2             5.019e-018  3.428e-018   -17.299   -17.465    -0.166
Mn(3)           7.149e-029
   Mn+3                  7.149e-029  2.974e-029   -28.146   -28.527    -0.381
Mn(6)           3.687e-034
   MnO4-2                3.687e-034  2.518e-034   -33.433   -33.599    -0.166
Mn(7)           1.182e-039
   MnO4-                 1.182e-039  1.069e-039   -38.927   -38.971    -0.044
N(-3)           2.143e-006
   NH3                   1.319e-006  1.319e-006    -5.880    -5.880     0.000
   NH4+                  8.105e-007  7.318e-007    -6.091    -6.136    -0.044
   NH4SO4-               1.255e-008  1.141e-008    -7.901    -7.943    -0.041
   CaNH3+2               4.399e-010  2.834e-010    -9.357    -9.548    -0.191
   NiNH3+2               3.135e-011  2.020e-011   -10.504   -10.695    -0.191
   CuNH3+2               2.216e-012  1.427e-012   -11.654   -11.845    -0.191
   Ni(NH3)2+2            5.980e-015  3.852e-015   -14.223   -14.414    -0.191
   Ca(NH3)2+2            2.311e-016  1.488e-016   -15.636   -15.827    -0.191
N(5)            4.607e-004
   NO3-                  4.605e-004  4.177e-004    -3.337    -3.379    -0.042
   CaNO3+                2.515e-007  2.254e-007    -6.599    -6.647    -0.048
```

```
   MnNO3+                 4.921e-011  4.408e-011   -10.308   -10.356    -0.048
   NiNO3+                 3.338e-011  2.991e-011   -10.476   -10.524    -0.048
   PbNO3+                 2.775e-011  2.486e-011   -10.557   -10.605    -0.048
   ZnNO3+                 6.297e-012  5.641e-012   -11.201   -11.249    -0.048
   CuNO3+                 1.559e-013  1.396e-013   -12.807   -12.855    -0.048
   Mn(NO3)2               4.625e-014  4.625e-014   -13.335   -13.335     0.000
   CdNO3+                 3.223e-014  2.888e-014   -13.492   -13.539    -0.048
   Pb(NO3)2               1.763e-014  1.763e-014   -13.754   -13.754     0.000
   Zn(NO3)2               4.702e-016  4.702e-016   -15.328   -15.328     0.000
   Cu(NO3)2               7.343e-018  7.343e-018   -17.134   -17.134     0.000
   Cd(NO3)2               6.045e-018  6.045e-018   -17.219   -17.219     0.000
   FeNO3+2                1.556e-025  1.002e-025   -24.808   -24.999    -0.191
Na                1.871e-003
   Na+                    1.854e-003  1.682e-003    -2.732    -2.774    -0.042
   NaSO4-                 1.444e-005  1.314e-005    -4.841    -4.882    -0.041
   NaCO3-                 2.440e-006  2.220e-006    -5.613    -5.654    -0.041
   NaHCO3                 4.523e-007  4.523e-007    -6.345    -6.345     0.000
   NaF                    7.827e-008  7.827e-008    -7.106    -7.106     0.000
   NaHPO4-                6.494e-008  5.910e-008    -7.187    -7.228    -0.041
Ni                1.705e-007
   NiCO3                  7.539e-008  7.539e-008    -7.123    -7.123     0.000
   Ni+2                   4.209e-008  2.850e-008    -7.376    -7.545    -0.169
   Ni(OH)2                2.889e-008  2.889e-008    -7.539    -7.539     0.000
   NiOH+                  1.275e-008  1.142e-008    -7.894    -7.942    -0.048
   NiSO4                  8.272e-009  8.272e-009    -8.082    -8.082     0.000
   NiHCO3+                1.876e-009  1.680e-009    -8.727    -8.775    -0.048
   Ni(OH)3-               1.027e-009  9.197e-010    -8.989    -9.036    -0.048
   NiF+                   5.894e-011  5.281e-011   -10.230   -10.277    -0.048
   NiCl+                  5.566e-011  4.986e-011   -10.254   -10.302    -0.048
   NiNO3+                 3.338e-011  2.991e-011   -10.476   -10.524    -0.048
   NiNH3+2                3.135e-011  2.020e-011   -10.504   -10.695    -0.191
   Ni(SO4)2-2             6.186e-013  3.984e-013   -12.209   -12.400    -0.191
   Ni(NH3)2+2             5.980e-015  3.852e-015   -14.223   -14.414    -0.191
   NiCl2                  1.717e-016  1.717e-016   -15.765   -15.765     0.000
O(0)              2.018e-032
   O2                     1.009e-032  1.011e-032   -31.996   -31.995     0.001
P                 7.074e-006
   HPO4-2                 4.379e-006  2.991e-006    -5.359    -5.524    -0.166
   CaPO4-                 2.157e-006  1.963e-006    -5.666    -5.707    -0.041
   CaHPO4                 2.332e-007  2.332e-007    -6.632    -6.632     0.000
   MgHPO4                 1.273e-007  1.273e-007    -6.895    -6.895     0.000
   KHPO4-                 7.333e-008  6.673e-008    -7.135    -7.176    -0.041
   NaHPO4-                6.494e-008  5.910e-008    -7.187    -7.228    -0.041
   H2PO4-                 1.640e-008  1.492e-008    -7.785    -7.826    -0.041
   MgPO4-                 1.333e-008  1.213e-008    -7.875    -7.916    -0.041
   PO4-3                  9.588e-009  3.989e-009    -8.018    -8.399    -0.381
   CaH2PO4+               6.263e-011  5.699e-011   -10.203   -10.244    -0.041
   MgH2PO4+               5.332e-011  4.852e-011   -10.273   -10.314    -0.041
   H3PO4                  6.635e-016  6.635e-016   -15.178   -15.178     0.000
   FeHPO4                 3.075e-016  3.075e-016   -15.512   -15.512     0.000
   FeHPO4+                6.513e-019  5.927e-019   -18.186   -18.227    -0.041
   FeH2PO4+               2.122e-019  1.931e-019   -18.673   -18.714    -0.041
   FeH2PO4+2              9.911e-027  6.797e-027   -26.004   -26.168    -0.164
Pb                1.835e-006
   PbCO3                  8.574e-007  8.574e-007    -6.067    -6.067     0.000
   PbOH+                  3.591e-007  3.217e-007    -6.445    -6.493    -0.048
   Pb(OH)2                3.239e-007  3.239e-007    -6.490    -6.490     0.000
   Pb(CO3)2-2             2.722e-007  1.753e-007    -6.565    -6.756    -0.191
   Pb(OH)3-               1.151e-008  1.031e-008    -7.939    -7.987    -0.048
   Pb+2                   5.941e-009  4.023e-009    -8.226    -8.395    -0.169
   PbSO4                  2.866e-009  2.866e-009    -8.543    -8.543     0.000
   PbHCO3+                1.596e-009  1.430e-009    -8.797    -8.845    -0.048
   Pb(OH)4-2              1.248e-010  8.040e-011    -9.904   -10.095    -0.191
   PbCl+                  1.089e-010  9.760e-011    -9.963   -10.011    -0.048
   Pb(SO4)2-2             3.900e-011  2.512e-011   -10.409   -10.600    -0.191
   PbNO3+                 2.775e-011  2.486e-011   -10.557   -10.605    -0.048
   PbF+                   2.334e-011  2.091e-011   -10.632   -10.680    -0.048
   Pb3(OH)4+2             1.307e-011  8.421e-012   -10.884   -11.075    -0.191
```

```
   PbCl2                 2.981e-013  2.981e-013   -12.526   -12.526     0.000
   Pb2OH+3               5.519e-014  2.051e-014   -13.258   -13.688    -0.430
   PbF2                  3.035e-014  3.035e-014   -13.518   -13.518     0.000
   Pb(NO3)2              1.763e-014  1.763e-014   -13.754   -13.754     0.000
   Pb4(OH)4+4            1.563e-015  2.691e-016   -14.806   -15.570    -0.764
   PbCl3-                9.059e-017  8.115e-017   -16.043   -16.091    -0.048
   PbF3-                 4.740e-018  4.246e-018   -17.324   -17.372    -0.048
   PbCl4-2               3.938e-020  2.536e-020   -19.405   -19.596    -0.191
   PbF4-2                2.327e-022  1.499e-022   -21.633   -21.824    -0.191
S(6)            2.270e-003
   SO4-2                 2.148e-003  1.455e-003    -2.668    -2.837    -0.169
   CaSO4                 5.685e-005  5.685e-005    -4.245    -4.245     0.000
   KSO4-                 3.328e-005  3.029e-005    -4.478    -4.519    -0.041
   MgSO4                 1.785e-005  1.785e-005    -4.748    -4.748     0.000
   NaSO4-                1.444e-005  1.314e-005    -4.841    -4.882    -0.041
   MnSO4                 1.722e-008  1.722e-008    -7.764    -7.764     0.000
   NH4SO4-               1.255e-008  1.141e-008    -7.901    -7.943    -0.041
   NiSO4                 8.272e-009  8.272e-009    -8.082    -8.082     0.000
   PbSO4                 2.866e-009  2.866e-009    -8.543    -8.543     0.000
   ZnSO4                 1.711e-009  1.711e-009    -8.767    -8.767     0.000
   HSO4-                 4.951e-011  4.495e-011   -10.305   -10.347    -0.042
   Pb(SO4)2-2            3.900e-011  2.512e-011   -10.409   -10.600    -0.191
   CuSO4                 3.523e-011  3.523e-011   -10.453   -10.453     0.000
   Zn(SO4)2-2            3.365e-011  2.168e-011   -10.473   -10.664    -0.191
   CdSO4                 7.454e-012  7.454e-012   -11.128   -11.128     0.000
   Ni(SO4)2-2            6.186e-013  3.984e-013   -12.209   -12.400    -0.191
   Cd(SO4)2-2            2.271e-013  1.463e-013   -12.644   -12.835    -0.191
   FeSO4                 9.220e-015  9.220e-015   -14.035   -14.035     0.000
   AlSO4+                2.001e-019  1.817e-019   -18.699   -18.741    -0.042
   Al(SO4)2-             3.119e-021  2.832e-021   -20.506   -20.548    -0.042
   FeSO4+                4.306e-022  3.915e-022   -21.366   -21.407    -0.041
   Fe(SO4)2-             1.359e-023  1.218e-023   -22.867   -22.915    -0.048
Si              3.097e-004
   H4SiO4                2.058e-004  2.062e-004    -3.687    -3.686     0.001
   H3SiO4-               1.039e-004  9.424e-005    -3.983    -4.026    -0.043
   H2SiO4-2              2.742e-008  1.880e-008    -7.562    -7.726    -0.164
   SiF6-2                7.362e-037  5.028e-037   -36.133   -36.299    -0.166
Zn              1.530e-007
   Zn(OH)2               8.637e-008  8.637e-008    -7.064    -7.064     0.000
   ZnCO3                 2.194e-008  2.194e-008    -7.659    -7.659     0.000
   ZnOH+                 1.911e-008  1.712e-008    -7.719    -7.767    -0.048
   Zn(OH)3-              1.538e-008  1.378e-008    -7.813    -7.861    -0.048
   Zn+2                  7.939e-009  5.377e-009    -8.100    -8.269    -0.169
   ZnSO4                 1.711e-009  1.711e-009    -8.767    -8.767     0.000
   ZnOHCl                3.849e-010  3.849e-010    -9.415    -9.415     0.000
   ZnHCO3+               9.076e-011  8.131e-011   -10.042   -10.090    -0.048
   Zn(SO4)2-2            3.365e-011  2.168e-011   -10.473   -10.664    -0.191
   Zn(OH)4-2             2.712e-011  1.747e-011   -10.567   -10.758    -0.191
   ZnCl+                 1.018e-011  9.235e-012   -10.992   -11.035    -0.043
   ZnF+                  8.832e-012  7.913e-012   -11.054   -11.102    -0.048
   ZnNO3+                6.297e-012  5.641e-012   -11.201   -11.249    -0.048
   ZnCl2                 1.001e-014  1.001e-014   -14.000   -14.000     0.000
   Zn(NO3)2              4.702e-016  4.702e-016   -15.328   -15.328     0.000
   ZnCl3-                5.995e-018  5.436e-018   -17.222   -17.265    -0.043
   ZnCl4-2               2.721e-021  1.859e-021   -20.565   -20.731    -0.166

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -2.09    8.71   10.80  Al(OH)3
        Al2O3            -2.24   17.41   19.65  Al2O3
        Al4(OH)10SO4     -9.71   12.99   22.70  Al4(OH)10SO4
        AlOHSO4          -9.90  -13.13   -3.23  AlOHSO4
        Alunite          -9.19  -10.59   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -3.44  -11.23   -7.79  PbSO4
        Anhydrite        -2.25   -6.61   -4.36  CaSO4
        Antlerite        -3.55    5.23    8.79  Cu3(OH)4SO4
```

```
        Aragonite         0.38   -7.92   -8.30  CaCO3
        Artinite         -3.09    6.51    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -2.01    5.38    7.39  Cu2(OH)3Cl
        Azurite          -2.32  -19.23  -16.91  Cu3(OH)2(CO3)2
        Bianchite        -9.34  -11.11   -1.76  ZnSO4:6H2O
        Birnessite       -4.62   13.47   18.09  MnO2
        Bixbyite          0.59   -0.05   -0.64  Mn2O3
        Boehmite          0.13    8.71    8.58  AlOOH
        Brochantite      -0.96   14.26   15.22  Cu4(OH)6SO4
        Brucite          -2.02   14.83   16.84  Mg(OH)2
        Bunsenite        -0.99   11.45   12.45  NiO
        Ca3(PO4)2(beta)   0.82  -28.10  -28.92  Ca3(PO4)2
        Ca4H(PO4)3:3H2O  -2.69  -49.77  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -2.39  -21.67  -19.27  CaHPO4
        CaHPO4:2H2O      -2.67  -21.67  -19.00  CaHPO4:2H2O
        Calcite           0.56   -7.92   -8.48  CaCO3
        Cd(OH)2          -5.30    8.34   13.64  Cd(OH)2
        Cd(OH)2(am)      -5.39    8.34   13.73  Cd(OH)2
        Cd3(OH)2(SO4)2  -25.37  -18.66    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -19.38    3.18   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -16.18  -48.78  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -16.88   11.52   28.40  Cd4(OH)6SO4
        CdCl2           -16.33  -16.99   -0.66  CdCl2
        CdCl2:1H2O      -15.30  -16.99   -1.69  CdCl2:1H2O
        CdCl2:2.5H2O    -15.08  -16.99   -1.91  CdCl2:2.5H2O
        CdF2            -17.71  -18.92   -1.21  CdF2
        Cdmetal(alpha)  -32.18  -18.66   13.51  Cd
        Cdmetal(gamma)  -32.28  -18.66   13.62  Cd
        CdOHCl           -7.86   -4.33    3.54  CdOHCl
        CdSO4           -13.33  -13.50   -0.17  CdSO4
        CdSO4:1H2O      -11.77  -13.50   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -11.62  -13.50   -1.87  CdSO4:2.67H2O
        Cerrusite         0.59  -12.54  -13.13  PbCO3
        CH4(g)          -90.10 -131.15  -41.05  CH4
        Chalcanthite    -10.17  -12.81   -2.64  CuSO4:5H2O
        Chalcedony       -0.14   -3.69   -3.55  SiO2
        Chrysotile        4.92   37.12   32.20  Mg3Si2O5(OH)4
        CO2(g)           -5.00  -23.15  -18.15  CO2
        Cotunnite        -9.95  -14.73   -4.78  PbCl2
        Cristobalite     -0.34   -3.69   -3.35  SiO2
        Cryolite        -19.07  -52.91  -33.84  Na3AlF6
        Cu(OH)2           0.35    9.02    8.67  Cu(OH)2
        Cu2(OH)3NO3      -4.08    5.17    9.25  Cu2(OH)3NO3
        Cu2SO4          -23.46  -25.41   -1.95  Cu2SO4
        Cu3(PO4)2        -9.88  -46.73  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -11.61  -46.73  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -2.63  -14.13  -11.50  CuCO3
        CuF             -10.51  -15.42   -4.91  CuF
        CuF2            -19.36  -18.24    1.12  CuF2
        CuF2:2H2O       -13.69  -18.24   -4.55  CuF2:2H2O
        Cumetal          -6.53  -15.29   -8.76  Cu
        CuOCuSO4        -14.09   -3.79   10.30  CuOCuSO4
        Cupricferrite    14.80   20.78    5.99  CuFe2O4
        Cuprite          -2.17   -3.57   -1.41  Cu2O
        Cuprousferrite   13.01    4.09   -8.92  CuFeO2
        CuSO4           -15.75  -12.81    2.94  CuSO4
        Diaspore          1.83    8.71    6.87  AlOOH
        Dolomite(disordered)   0.30  -16.24  -16.54  CaMg(CO3)2
        Dolomite(ordered)   0.85  -16.24  -17.09  CaMg(CO3)2
        Epsomite         -4.88   -7.01   -2.13  MgSO4:7H2O
        FCO3Apatite      22.15  -92.25 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
        Fe(OH)2          -8.15    5.41   13.56  Fe(OH)2
        Fe(OH)2.7Cl.3     5.12    2.08   -3.04  Fe(OH)2.7Cl.3
        Fe2(SO4)3       -50.02  -53.75   -3.73  Fe2(SO4)3
        Fe3(OH)8         -3.05   17.17   20.22  Fe3(OH)8
        Ferrihydrite      2.69    5.88    3.19  Fe(OH)3
        Fluorite         -1.53  -12.03  -10.50  CaF2
```

```
Gibbsite          0.42    8.71    8.29  Al(OH)3
Goethite          5.39    5.88    0.49  FeOOH
Goslarite        -9.10  -11.11   -2.01  ZnSO4:7H2O
Greenalite      -11.95    8.86   20.81  Fe3Si2O5(OH)4
Gypsum           -2.00   -6.61   -4.61  CaSO4:2H2O
H-Jarosite      -13.94  -26.04  -12.10  (H3O)Fe3(SO4)2(OH)6
Halite           -7.54   -5.94    1.60  NaCl
Halloysite        0.47   10.04    9.57  Al2Si2O5(OH)4
Hausmannite       1.44   62.47   61.03  Mn3O4
Hematite         13.18   11.76   -1.42  Fe2O3
Hercynite        -0.07   22.82   22.89  FeAl2O4
Hinsdalite      -19.51  -22.01   -2.50  PbAl3PO4SO4(OH)6
Huntite          -2.91  -32.88  -29.97  CaMg3(CO3)4
Hydrocerrusite    4.29  -14.49  -18.77  Pb3(OH)2(CO3)2
Hydromagnesite   -9.69  -18.45   -8.77  Mg5(CO3)4(OH)2:4H2O
Hydroxylapatite   9.80  -34.54  -44.33  Ca5(PO4)3OH
Hydroxylpyromorphite   5.12  -57.67  -62.79  Pb5(PO4)3OH
K-Alum          -22.83  -28.00   -5.17  KAl(SO4)2:12H2O
K-Jarosite       -4.27  -19.07  -14.80  KFe3(SO4)2(OH)6
Kaolinite         2.61   10.04    7.43  Al2Si2O5(OH)4
Langite          -3.23   14.26   17.49  Cu4(OH)6SO4:H2O
Larnakite        -0.19   -0.63   -0.43  PbO:PbSO4
Laurionite       -2.68   -2.06    0.62  PbOHCl
Lepidocrocite     4.51    5.88    1.37  FeOOH
Lime            -17.47   15.23   32.70  CaO
Litharge         -2.09   10.60   12.69  PbO
Maghemite         5.37   11.76    6.39  Fe2O3
Magnesioferrite   9.73   26.59   16.86  Fe2MgO4
Magnesite        -0.86   -8.32   -7.46  MgCO3
Magnetite        13.77   17.17    3.40  Fe3O4
Malachite         0.20   -5.10   -5.31  Cu2(OH)2CO3
Manganite        -0.02   25.32   25.34  MnOOH
Massicot         -2.29   10.60   12.89  PbO
Matlockite       -6.72  -15.69   -8.97  PbClF
Melanothallite  -22.56  -16.31    6.26  CuCl2
Melanterite     -14.22  -16.43   -2.21  FeSO4:7H2O
Mg(OH)2(active)  -3.97   14.83   18.79  Mg(OH)2
Mg3(PO4)2        -6.03  -29.31  -23.28  Mg3(PO4)2
MgF2             -4.31  -12.44   -8.13  MgF2
MgHPO4:3H2O      -3.90  -22.07  -18.18  MgHPO4:3H2O
Minium          -14.71   58.81   73.52  Pb3O4
Mirabilite       -7.27   -8.39   -1.11  Na2SO4:10H2O
Mn2(SO4)3       -59.85  -65.57   -5.71  Mn2(SO4)3
Mn3(PO4)2       -14.50  -38.33  -23.83  Mn3(PO4)2
MnCl2:4H2O      -16.22  -13.51    2.72  MnCl2:4H2O
MnHPO4            0.32  -25.08  -25.40  MnHPO4
MnSO4           -12.60  -10.01    2.58  MnSO4
Monteponite      -6.76    8.34   15.10  CdO
Morenosite       -8.24  -10.38   -2.14  NiSO4:7H2O
Na-Jarosite      -8.11  -19.31  -11.20  NaFe3(SO4)2(OH)6
Nantokite        -7.72  -14.45   -6.73  CuCl
Natron           -8.39   -9.70   -1.31  Na2CO3:10H2O
Nesquehonite     -3.65   -8.32   -4.67  MgCO3:3H2O
Ni(OH)2          -1.34   11.45   12.79  Ni(OH)2
Ni3(PO4)2        -8.13  -39.43  -31.30  Ni3(PO4)2
Ni4(OH)6SO4      -8.02   23.98   32.00  Ni4(OH)6SO4
NiCO3            -4.82  -11.69   -6.87  NiCO3
Nsutite          -4.03   13.47   17.50  MnO2
O2(g)           -29.09   54.00   83.09  O2
Otavite          -2.81  -14.81  -12.00  CdCO3
Pb(OH)2           2.45   10.60    8.15  Pb(OH)2
Pb10(OH)6O(CO3)6 -24.09  -32.85   -8.76  Pb10(OH)6O(CO3)6
Pb2(OH)3Cl       -0.25    8.54    8.79  Pb2(OH)3Cl
Pb2O(OH)2        -4.98   21.21   26.19  Pb2O(OH)2
Pb2O3           -12.83   48.21   61.04  Pb2O3
Pb2OCO3          -1.38   -1.94   -0.56  Pb2OCO3
Pb3(PO4)2         1.55  -41.98  -43.53  Pb3(PO4)2
Pb3O2CO3         -2.36    8.66   11.02  Pb3O2CO3
```

```
        Pb3O2SO4         -0.71    9.98   10.69  Pb3O2SO4
        Pb4(OH)6SO4      -0.52   20.58   21.10  Pb4(OH)6SO4
        Pb4O3SO4         -1.30   20.58   21.88  Pb4O3SO4
        PbF2             -9.22  -16.66   -7.44  PbF2
        PbHPO4           -2.49  -26.29  -23.81  PbHPO4
        Pbmetal         -20.64  -16.40    4.25  Pb
        PbO:0.3H2O       -2.38   10.60   12.98  PbO:0.33H2O
        Periclase        -6.76   14.83   21.58  MgO
        Phosgenite       -7.46  -27.27  -19.81  PbCl2:PbCO3
        Plattnerite     -12.00   37.60   49.60  PbO2
        Plumbgummite     -4.28  -37.07  -32.79  PbAl3(PO4)2(OH)5:H2O
        Portlandite      -7.57   15.23   22.80  Ca(OH)2
        Pyrochroite      -3.37   11.82   15.19  Mn(OH)2
        Pyrolusite       -2.56   38.82   41.38  MnO2
        Pyromorphite     14.09  -70.34  -84.43  Pb5(PO4)3Cl
        Quartz            0.31   -3.69   -4.00  SiO2
        Retgersite       -8.34  -10.38   -2.04  NiSO4:6H2O
        Rhodochrosite    -0.75  -11.33  -10.58  MnCO3
        Sepiolite         2.84   18.60   15.76  Mg2Si3O7.5OH:3H2O
        Sepiolite(A)     -0.18   18.60   18.78  Mg2Si3O7.5OH:3H2O
        Siderite         -7.50  -17.74  -10.24  FeCO3
        SiO2(am-gel)     -0.98   -3.69   -2.71  SiO2
        SiO2(am-ppt)     -0.95   -3.69   -2.74  SiO2
        Smithsonite      -2.42  -12.42  -10.00  ZnCO3
        Spinel           -4.61   32.24   36.85  MgAl2O4
        Strengite        -4.62  -31.02  -26.40  FePO4:2H2O
        Tenorite          1.38    9.02    7.64  CuO
        Thenardite       -8.71   -8.39    0.32  Na2SO4
        Thermonatrite   -10.33   -9.70    0.64  Na2CO3:H2O
        Tsumebite         3.12   -6.67   -9.79  Pb2CuPO4(OH)3:3H2O
        Vivianite       -21.56  -57.56  -36.00  Fe3(PO4)2:8H2O
        Zincite          -0.60   10.73   11.33  ZnO
        Zincosite       -15.04  -11.11    3.93  ZnSO4
        Zn(NO3)2:6H2O   -18.34  -15.03    3.32  Zn(NO3)2:6H2O
        Zn(OH)2          -1.47   10.73   12.20  Zn(OH)2
        Zn(OH)2(am)      -1.74   10.73   12.47  Zn(OH)2
        Zn(OH)2(beta)    -1.02   10.73   11.75  Zn(OH)2
        Zn(OH)2(epsilon)  -0.80   10.73   11.53  Zn(OH)2
        Zn(OH)2(gamma)   -1.00   10.73   11.73  Zn(OH)2
        Zn2(OH)2SO4      -7.88   -0.38    7.50  Zn2(OH)2SO4
        Zn2(OH)3Cl       -6.40    8.80   15.19  Zn2(OH)3Cl
        Zn3(PO4)2:4H2O   -6.19  -41.61  -35.42  Zn3(PO4)2:4H2O
        Zn3O(SO4)2      -30.40  -11.48   18.91  Zn3O(SO4)2
        Zn4(OH)6SO4      -7.32   21.08   28.40  Zn4(OH)6SO4
        Zn5(OH)8Cl2     -10.18   28.32   38.50  Zn5(OH)8Cl2
        ZnCl2           -21.65  -14.60    7.05  ZnCl2
        ZnCO3:1H2O       -2.16  -12.42  -10.26  ZnCO3:1H2O
        ZnF2            -16.00  -16.53   -0.53  ZnF2
        Znmetal         -42.06  -16.27   25.79  Zn
        ZnO(active)      -0.46   10.73   11.19  ZnO
        ZnSO4:1H2O      -10.47  -11.11   -0.64  ZnSO4:1H2O

Initial solution 4-FA 300 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Al               2.225e-006  2.225e-006
        C(4)             1.139e-003  1.139e-003
        Ca               7.338e-004  7.338e-004
        Cd               2.671e-010  2.671e-010
        Cl               1.135e-003  1.135e-003
        Cu               2.834e-007  2.834e-007
        F                1.396e-004  1.396e-004
        Fe               1.075e-006  1.075e-006
        K                5.016e-003  5.016e-003
        Mg               1.647e-006  1.647e-006
```

```
        Mn               1.821e-008  1.821e-008
        N(-3)            5.001e-006  5.001e-006
        N(5)             5.808e-004  5.808e-004
        Na               2.725e-003  2.725e-003
        Ni               1.705e-007  1.705e-007
        P                1.486e-006  1.486e-006
        Pb               5.312e-007  5.312e-007
        S(6)             2.135e-003  2.135e-003
        Si               5.106e-004  5.106e-004
        Zn               1.530e-007  1.530e-007

----------------------------Description of solution----------------------------

                                       pH  =  10.200
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  1.121e-002
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.368e-003
                       Total CO2 (mol/kg)  =  1.139e-003
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  7.321e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   4.43
                               Iterations  =  11
                                  Total H  = 1.110160e+002
                                  Total O  = 5.552278e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           2.5128      0.1486

----------------------------Distribution of species----------------------------

                                                    Log       Log         Log 
   Species                   Molality    Activity  Molality  Activity       Gamma

   OH-                   1.782e-004  1.596e-004    -3.749    -3.797    -0.048
   H+                    7.032e-011  6.310e-011   -10.153   -10.200    -0.047
   H2O                   5.551e+001  9.998e-001     1.744    -0.000     0.000
Al              2.225e-006
   Al(OH)4-              2.225e-006  1.999e-006    -5.653    -5.699    -0.047
   Al(OH)3               9.950e-011  9.950e-011   -10.002   -10.002     0.000
   Al(OH)2+              3.470e-014  3.125e-014   -13.460   -13.505    -0.045
   AlOH+2                3.747e-019  2.466e-019   -18.426   -18.608    -0.182
   AlF3                  1.500e-019  1.500e-019   -18.824   -18.824     0.000
   AlF2+                 1.061e-019  9.559e-020   -18.974   -19.020    -0.045
   AlF4-                 1.043e-020  9.370e-021   -19.982   -20.028    -0.047
   AlF+2                 2.927e-021  1.927e-021   -20.534   -20.715    -0.182
   AlSO4+                1.715e-023  1.540e-023   -22.766   -22.812    -0.047
   Al+3                  4.098e-024  1.546e-024   -23.387   -23.811    -0.423
   Al(SO4)2-             2.359e-025  2.119e-025   -24.627   -24.674    -0.047
C(4)            1.139e-003
   CO3-2                 4.890e-004  3.170e-004    -3.311    -3.499    -0.188
   HCO3-                 4.737e-004  4.266e-004    -3.325    -3.370    -0.045
   CaCO3                 1.563e-004  1.563e-004    -3.806    -3.806     0.000
   NaCO3-                1.582e-005  1.425e-005    -4.801    -4.846    -0.045
   CaHCO3+               2.739e-006  2.472e-006    -5.562    -5.607    -0.045
   NaHCO3                5.790e-007  5.790e-007    -6.237    -6.237     0.000
   MgCO3                 2.038e-007  2.038e-007    -6.691    -6.691     0.000
   Pb(CO3)2-2            1.449e-007  8.817e-008    -6.839    -7.055    -0.216
   PbCO3                 9.644e-008  9.644e-008    -7.016    -7.016     0.000
   H2CO3                 6.054e-008  6.054e-008    -7.218    -7.218     0.000
   NiCO3                 4.381e-008  4.381e-008    -7.358    -7.358     0.000
   Cu(CO3)2-2            2.740e-008  1.667e-008    -7.562    -7.778    -0.216
   CuCO3                 1.954e-008  1.954e-008    -7.709    -7.709     0.000
   MgHCO3+               3.763e-009  3.374e-009    -8.424    -8.472    -0.047
```

```
   ZnCO3                 3.443e-009  3.443e-009    -8.463    -8.463     0.000
   NiHCO3+               2.206e-010  1.948e-010    -9.656    -9.710    -0.054
   CdCO3                 1.257e-010  1.257e-010    -9.900    -9.900     0.000
   MnHCO3+               7.383e-011  6.642e-011   -10.132   -10.178    -0.046
   Cd(CO3)2-2            4.856e-011  2.955e-011   -10.314   -10.529    -0.216
   PbHCO3+               3.632e-011  3.208e-011   -10.440   -10.494    -0.054
   ZnHCO3+               2.883e-012  2.546e-012   -11.540   -11.594    -0.054
   CuHCO3+               3.191e-013  2.818e-013   -12.496   -12.550    -0.054
   CdHCO3+               1.914e-014  1.690e-014   -13.718   -13.772    -0.054
   FeHCO3+               3.593e-019  3.242e-019   -18.445   -18.489    -0.045
Ca              7.338e-004
   Ca+2                  4.799e-004  3.111e-004    -3.319    -3.507    -0.188
   CaCO3                 1.563e-004  1.563e-004    -3.806    -3.806     0.000
   CaSO4                 9.150e-005  9.150e-005    -4.039    -4.039     0.000
   CaHCO3+               2.739e-006  2.472e-006    -5.562    -5.607    -0.045
   CaPO4-                1.176e-006  1.059e-006    -5.930    -5.975    -0.045
   CaOH+                 1.098e-006  9.904e-007    -5.960    -6.004    -0.045
   CaNO3+                5.800e-007  5.122e-007    -6.237    -6.291    -0.054
   CaF+                  4.705e-007  4.232e-007    -6.327    -6.373    -0.046
   CaHPO4                2.511e-008  2.511e-008    -7.600    -7.600     0.000
   CaNH3+2               2.858e-009  1.739e-009    -8.544    -8.760    -0.216
   CaH2PO4+              1.359e-012  1.224e-012   -11.867   -11.912    -0.045
   Ca(NH3)2+2            5.051e-015  3.073e-015   -14.297   -14.512    -0.216
Cd              2.671e-010
   CdCO3                 1.257e-010  1.257e-010    -9.900    -9.900     0.000
   Cd(CO3)2-2            4.856e-011  2.955e-011   -10.314   -10.529    -0.216
   Cd+2                  2.684e-011  1.740e-011   -10.571   -10.759    -0.188
   CdOH+                 2.497e-011  2.206e-011   -10.603   -10.656    -0.054
   Cd(OH)2               2.220e-011  2.220e-011   -10.654   -10.654     0.000
   CdOHCl                1.107e-011  1.107e-011   -10.956   -10.956     0.000
   CdSO4                 5.237e-012  5.237e-012   -11.281   -11.281     0.000
   CdCl+                 1.916e-012  1.692e-012   -11.718   -11.772    -0.054
   Cd(OH)3-              2.451e-013  2.164e-013   -12.611   -12.665    -0.054
   Cd(SO4)2-2            1.490e-013  9.070e-014   -12.827   -13.042    -0.216
   CdF+                  3.893e-014  3.438e-014   -13.410   -13.464    -0.054
   CdNO3+                3.244e-014  2.865e-014   -13.489   -13.543    -0.054
   CdHCO3+               1.914e-014  1.690e-014   -13.718   -13.772    -0.054
   CdCl2                 7.182e-015  7.182e-015   -14.144   -14.144     0.000
   Cd(OH)4-2             9.289e-018  5.652e-018   -17.032   -17.248    -0.216
   CdF2                  8.550e-018  8.550e-018   -17.068   -17.068     0.000
   Cd(NO3)2              7.477e-018  7.477e-018   -17.126   -17.126     0.000
   CdCl3-                5.224e-018  4.614e-018   -17.282   -17.336    -0.054
   Cd2OH+3               5.883e-021  1.924e-021   -20.230   -20.716    -0.485
Cl              1.135e-003
   Cl-                   1.135e-003  1.018e-003    -2.945    -2.992    -0.047
   ZnOHCl                1.008e-010  1.008e-010    -9.996    -9.996     0.000
   MnCl+                 1.112e-011  1.000e-011   -10.954   -11.000    -0.046
   CdOHCl                1.107e-011  1.107e-011   -10.956   -10.956     0.000
   NiCl+                 1.093e-011  9.650e-012   -10.962   -11.015    -0.054
   PbCl+                 4.139e-012  3.656e-012   -11.383   -11.437    -0.054
   CdCl+                 1.916e-012  1.692e-012   -11.718   -11.772    -0.054
   CuCl                  6.572e-013  6.572e-013   -12.182   -12.182     0.000
   ZnCl+                 5.383e-013  4.827e-013   -12.269   -12.316    -0.047
   CuCl2-                1.559e-013  1.398e-013   -12.807   -12.854    -0.047
   CuCl+                 1.884e-014  1.689e-014   -13.725   -13.772    -0.047
   PbCl2                 1.663e-014  1.663e-014   -13.779   -13.779     0.000
   MnCl2                 1.438e-014  1.438e-014   -13.842   -13.842     0.000
   CdCl2                 7.182e-015  7.182e-015   -14.144   -14.144     0.000
   ZnCl2                 7.789e-016  7.789e-016   -15.109   -15.109     0.000
   NiCl2                 4.947e-017  4.947e-017   -16.306   -16.306     0.000
   CuCl3-2               4.646e-017  3.043e-017   -16.333   -16.517    -0.184
   PbCl3-                7.630e-018  6.739e-018   -17.117   -17.171    -0.054
   CuCl2                 5.964e-018  5.964e-018   -17.224   -17.224     0.000
   CdCl3-                5.224e-018  4.614e-018   -17.282   -17.336    -0.054
   MnCl3-                4.483e-018  4.033e-018   -17.348   -17.394    -0.046
   ZnCl3-                7.024e-019  6.299e-019   -18.153   -18.201    -0.047
   PbCl4-2               5.154e-021  3.136e-021   -20.288   -20.504    -0.216
   ZnCl4-2               4.896e-022  3.207e-022   -21.310   -21.494    -0.184
```

```
   CuCl3-              6.319e-023  5.667e-023   -22.199   -22.247    -0.047
   FeCl+2              2.632e-027  1.724e-027   -26.580   -26.763    -0.184
   CuCl4-2             4.415e-028  2.891e-028   -27.355   -27.539    -0.184
   FeCl2+              8.715e-030  7.840e-030   -29.060   -29.106    -0.046
   FeCl3               7.982e-034  7.982e-034   -33.098   -33.098     0.000
Cu(1)             1.394e-012
   CuCl                6.572e-013  6.572e-013   -12.182   -12.182     0.000
   Cu+                 5.806e-013  5.128e-013   -12.236   -12.290    -0.054
   CuCl2-              1.559e-013  1.398e-013   -12.807   -12.854    -0.047
   CuCl3-2             4.646e-017  3.043e-017   -16.333   -16.517    -0.184
Cu(2)             2.834e-007
   Cu(OH)2             1.682e-007  1.682e-007    -6.774    -6.774     0.000
   Cu(OH)3-            6.231e-008  5.503e-008    -7.205    -7.259    -0.054
   Cu(CO3)2-2          2.740e-008  1.667e-008    -7.562    -7.778    -0.216
   CuCO3               1.954e-008  1.954e-008    -7.709    -7.709     0.000
   CuOH+               5.891e-009  5.282e-009    -8.230    -8.277    -0.047
   Cu(OH)4-2           1.136e-010  6.911e-011    -9.945   -10.160    -0.216
   Cu+2                1.615e-011  1.047e-011   -10.792   -10.980    -0.188
   CuSO4               3.079e-012  3.079e-012   -11.512   -11.512     0.000
   Cu2(OH)2+2          1.152e-012  7.009e-013   -11.939   -12.154    -0.216
   CuNH3+2             7.816e-013  4.756e-013   -12.107   -12.323    -0.216
   CuHCO3+             3.191e-013  2.818e-013   -12.496   -12.550    -0.054
   CuF+                9.322e-014  8.233e-014   -13.030   -13.084    -0.054
   CuNO3+              1.952e-014  1.724e-014   -13.710   -13.764    -0.054
   CuCl+               1.884e-014  1.689e-014   -13.725   -13.772    -0.047
   CuCl2               5.964e-018  5.964e-018   -17.224   -17.224     0.000
   Cu(NO3)2            1.130e-018  1.130e-018   -17.947   -17.947     0.000
   CuCl3-              6.319e-023  5.667e-023   -22.199   -22.247    -0.047
   CuCl4-2             4.415e-028  2.891e-028   -27.355   -27.539    -0.184
F                 1.396e-004
   F-                  1.389e-004  1.246e-004    -3.857    -3.904    -0.047
   CaF+                4.705e-007  4.232e-007    -6.327    -6.373    -0.046
   NaF                 1.898e-007  1.898e-007    -6.722    -6.722     0.000
   MgF+                1.203e-008  1.081e-008    -7.920    -7.966    -0.047
   MnF+                4.303e-011  3.871e-011   -10.366   -10.412    -0.046
   NiF+                1.313e-011  1.160e-011   -10.882   -10.936    -0.054
   HF                  1.163e-011  1.163e-011   -10.934   -10.934     0.000
   PbF+                1.006e-012  8.889e-013   -11.997   -12.051    -0.054
   ZnF+                5.314e-013  4.694e-013   -12.275   -12.328    -0.054
   CuF+                9.322e-014  8.233e-014   -13.030   -13.084    -0.054
   CdF+                3.893e-014  3.438e-014   -13.410   -13.464    -0.054
   HF2-                6.157e-015  5.512e-015   -14.211   -14.259    -0.048
   PbF2                2.180e-015  2.180e-015   -14.661   -14.661     0.000
   CdF2                8.550e-018  8.550e-018   -17.068   -17.068     0.000
   PbF3-               5.836e-019  5.154e-019   -18.234   -18.288    -0.054
   AlF3                1.500e-019  1.500e-019   -18.824   -18.824     0.000
   AlF2+               1.061e-019  9.559e-020   -18.974   -19.020    -0.045
   AlF4-               1.043e-020  9.370e-021   -19.982   -20.028    -0.047
   AlF+2               2.927e-021  1.927e-021   -20.534   -20.715    -0.182
   H2F2                3.625e-022  3.625e-022   -21.441   -21.441     0.000
   PbF4-2              5.053e-023  3.075e-023   -22.296   -22.512    -0.216
   FeF2+               2.841e-023  2.556e-023   -22.547   -22.592    -0.046
   FeF+2               1.170e-023  7.662e-024   -22.932   -23.116    -0.184
   FeF3                4.494e-024  4.494e-024   -23.347   -23.347     0.000
   SiF6-2              1.974e-038  1.293e-038   -37.705   -37.888    -0.184
Fe(2)             3.318e-015
   Fe(OH)3-            2.725e-015  2.451e-015   -14.565   -14.611    -0.046
   FeOH+               4.261e-016  3.834e-016   -15.370   -15.416    -0.046
   Fe+2                9.918e-017  6.035e-017   -16.004   -16.219    -0.216
   Fe(OH)2             4.859e-017  4.859e-017   -16.313   -16.313     0.000
   FeSO4               1.902e-017  1.902e-017   -16.721   -16.721     0.000
   FeHCO3+             3.593e-019  3.242e-019   -18.445   -18.489    -0.045
   FeHPO4              4.243e-020  4.243e-020   -19.372   -19.372     0.000
   FeH2PO4+            5.903e-024  5.317e-024   -23.229   -23.274    -0.045
Fe(3)             1.075e-006
   Fe(OH)4-            1.013e-006  9.126e-007    -5.994    -6.040    -0.045
   Fe(OH)3             6.143e-008  6.143e-008    -7.212    -7.212     0.000
   Fe(OH)2+            3.980e-010  3.585e-010    -9.400    -9.445    -0.045
```

```
   FeOH+2            8.818e-018  5.776e-018   -17.055   -17.238    -0.184
   FeHPO4+           9.080e-023  8.179e-023   -22.042   -22.087    -0.045
   FeF2+             2.841e-023  2.556e-023   -22.547   -22.592    -0.046
   FeF+2             1.170e-023  7.662e-024   -22.932   -23.116    -0.184
   FeF3              4.494e-024  4.494e-024   -23.347   -23.347     0.000
   FeSO4+            8.977e-025  8.076e-025   -24.047   -24.093    -0.046
   Fe+3              1.487e-025  5.607e-026   -24.828   -25.251    -0.423
   Fe(SO4)2-         2.510e-026  2.217e-026   -25.600   -25.654    -0.054
   FeCl+2            2.632e-027  1.724e-027   -26.580   -26.763    -0.184
   FeNO3+2           4.797e-028  2.919e-028   -27.319   -27.535    -0.216
   FeCl2+            8.715e-030  7.840e-030   -29.060   -29.106    -0.046
   FeH2PO4+2         2.843e-031  1.871e-031   -30.546   -30.728    -0.182
   Fe2(OH)2+4        8.056e-033  1.105e-033   -32.094   -32.957    -0.863
   FeCl3             7.982e-034  7.982e-034   -33.098   -33.098     0.000
   Fe3(OH)4+5        1.277e-040  0.000e+000   -39.894   -41.242    -1.348
H(0)            5.622e-032
   H2                2.811e-032  2.818e-032   -31.551   -31.550     0.001
K               5.016e-003
   K+                4.971e-003  4.461e-003    -2.304    -2.351    -0.047
   KSO4-             4.501e-005  4.054e-005    -4.347    -4.392    -0.045
   KHPO4-            6.634e-009  5.975e-009    -8.178    -8.224    -0.045
Mg              1.647e-006
   Mg+2              1.192e-006  7.729e-007    -5.924    -6.112    -0.188
   MgCO3             2.038e-007  2.038e-007    -6.691    -6.691     0.000
   MgSO4             1.806e-007  1.806e-007    -6.743    -6.743     0.000
   MgOH+             5.433e-008  4.909e-008    -7.265    -7.309    -0.044
   MgF+              1.203e-008  1.081e-008    -7.920    -7.966    -0.047
   MgHCO3+           3.763e-009  3.374e-009    -8.424    -8.472    -0.047
   MgHPO4            8.612e-011  8.612e-011   -10.065   -10.065     0.000
   MgPO4-            4.566e-011  4.112e-011   -10.340   -10.386    -0.045
   MgH2PO4+          7.271e-015  6.549e-015   -14.138   -14.184    -0.045
Mn(2)           1.821e-008
   Mn+2              1.282e-008  7.802e-009    -7.892    -8.108    -0.216
   MnOH+             3.476e-009  3.127e-009    -8.459    -8.505    -0.046
   MnSO4             1.781e-009  1.781e-009    -8.749    -8.749     0.000
   MnHCO3+           7.383e-011  6.642e-011   -10.132   -10.178    -0.046
   MnF+              4.303e-011  3.871e-011   -10.366   -10.412    -0.046
   MnCl+             1.112e-011  1.000e-011   -10.954   -11.000    -0.046
   MnNO3+            7.289e-012  6.438e-012   -11.137   -11.191    -0.054
   Mn(OH)3-          5.468e-013  4.919e-013   -12.262   -12.308    -0.046
   MnCl2             1.438e-014  1.438e-014   -13.842   -13.842     0.000
   Mn(NO3)2          8.420e-015  8.420e-015   -14.075   -14.075     0.000
   Mn(OH)4-2         3.869e-016  2.534e-016   -15.412   -15.596    -0.184
   MnCl3-            4.483e-018  4.033e-018   -17.348   -17.394    -0.046
Mn(3)           9.241e-030
   Mn+3              9.241e-030  3.485e-030   -29.034   -29.458    -0.423
Mn(6)           1.793e-029
   MnO4-2            1.793e-029  1.174e-029   -28.746   -28.930    -0.184
Mn(7)           5.580e-035
   MnO4-             5.580e-035  4.986e-035   -34.253   -34.302    -0.049
N(-3)           5.001e-006
   NH3               4.440e-006  4.440e-006    -5.353    -5.353     0.000
   NH4+              5.508e-007  4.913e-007    -6.259    -6.309    -0.050
   NH4SO4-           7.512e-009  6.758e-009    -8.124    -8.170    -0.046
   CaNH3+2           2.858e-009  1.739e-009    -8.544    -8.760    -0.216
   NiNH3+2           1.451e-011  8.832e-012   -10.838   -11.054    -0.216
   CuNH3+2           7.816e-013  4.756e-013   -12.107   -12.323    -0.216
   Ni(NH3)2+2        9.314e-015  5.668e-015   -14.031   -14.247    -0.216
   Ca(NH3)2+2        5.051e-015  3.073e-015   -14.297   -14.512    -0.216
N(5)            5.808e-004
   NO3-              5.802e-004  5.206e-004    -3.236    -3.283    -0.047
   CaNO3+            5.800e-007  5.122e-007    -6.237    -6.291    -0.054
   MnNO3+            7.289e-012  6.438e-012   -11.137   -11.191    -0.054
   NiNO3+            5.485e-012  4.845e-012   -11.261   -11.315    -0.054
   PbNO3+            8.824e-013  7.794e-013   -12.054   -12.108    -0.054
   ZnNO3+            2.795e-013  2.468e-013   -12.554   -12.608    -0.054
   CdNO3+            3.244e-014  2.865e-014   -13.489   -13.543    -0.054
   CuNO3+            1.952e-014  1.724e-014   -13.710   -13.764    -0.054
```

```
   Mn(NO3)2             8.420e-015  8.420e-015   -14.075   -14.075     0.000
   Pb(NO3)2             6.891e-016  6.891e-016   -15.162   -15.162     0.000
   Zn(NO3)2             2.564e-017  2.564e-017   -16.591   -16.591     0.000
   Cd(NO3)2             7.477e-018  7.477e-018   -17.126   -17.126     0.000
   Cu(NO3)2             1.130e-018  1.130e-018   -17.947   -17.947     0.000
   FeNO3+2              4.797e-028  2.919e-028   -27.319   -27.535    -0.216
Na                2.725e-003
   Na+                  2.690e-003  2.413e-003    -2.570    -2.617    -0.047
   NaSO4-               1.847e-005  1.664e-005    -4.733    -4.779    -0.045
   NaCO3-               1.582e-005  1.425e-005    -4.801    -4.846    -0.045
   NaHCO3               5.790e-007  5.790e-007    -6.237    -6.237     0.000
   NaF                  1.898e-007  1.898e-007    -6.722    -6.722     0.000
   NaHPO4-              5.559e-009  5.007e-009    -8.255    -8.300    -0.045
Ni                1.705e-007
   Ni(OH)2              9.430e-008  9.430e-008    -7.025    -7.025     0.000
   NiCO3                4.381e-008  4.381e-008    -7.358    -7.358     0.000
   Ni(OH)3-             1.703e-008  1.505e-008    -7.769    -7.823    -0.054
   NiOH+                8.425e-009  7.441e-009    -8.074    -8.128    -0.054
   Ni+2                 5.714e-009  3.704e-009    -8.243    -8.431    -0.188
   NiSO4                9.488e-010  9.488e-010    -9.023    -9.023     0.000
   NiHCO3+              2.206e-010  1.948e-010    -9.656    -9.710    -0.054
   NiNH3+2              1.451e-011  8.832e-012   -10.838   -11.054    -0.216
   NiF+                 1.313e-011  1.160e-011   -10.882   -10.936    -0.054
   NiCl+                1.093e-011  9.650e-012   -10.962   -11.015    -0.054
   NiNO3+               5.485e-012  4.845e-012   -11.261   -11.315    -0.054
   Ni(SO4)2-2           6.628e-014  4.033e-014   -13.179   -13.394    -0.216
   Ni(NH3)2+2           9.314e-015  5.668e-015   -14.031   -14.247    -0.216
   NiCl2                4.947e-017  4.947e-017   -16.306   -16.306     0.000
O(0)              1.272e-029
   O2                   6.362e-030  6.378e-030   -29.196   -29.195     0.001
P                 1.486e-006
   CaPO4-               1.176e-006  1.059e-006    -5.930    -5.975    -0.045
   HPO4-2               2.696e-007  1.766e-007    -6.569    -6.753    -0.184
   CaHPO4               2.511e-008  2.511e-008    -7.600    -7.600     0.000
   KHPO4-               6.634e-009  5.975e-009    -8.178    -8.224    -0.045
   NaHPO4-              5.559e-009  5.007e-009    -8.255    -8.300    -0.045
   PO4-3                3.129e-009  1.180e-009    -8.505    -8.928    -0.423
   H2PO4-               1.952e-010  1.758e-010    -9.710    -9.755    -0.045
   MgHPO4               8.612e-011  8.612e-011   -10.065   -10.065     0.000
   MgPO4-               4.566e-011  4.112e-011   -10.340   -10.386    -0.045
   CaH2PO4+             1.359e-012  1.224e-012   -11.867   -11.912    -0.045
   MgH2PO4+             7.271e-015  6.549e-015   -14.138   -14.184    -0.045
   H3PO4                1.559e-018  1.559e-018   -17.807   -17.807     0.000
   FeHPO4               4.243e-020  4.243e-020   -19.372   -19.372     0.000
   FeHPO4+              9.080e-023  8.179e-023   -22.042   -22.087    -0.045
   FeH2PO4+             5.903e-024  5.317e-024   -23.229   -23.274    -0.045
   FeH2PO4+2            2.843e-031  1.871e-031   -30.546   -30.728    -0.182
Pb                5.312e-007
   Pb(OH)2              2.046e-007  2.046e-007    -6.689    -6.689     0.000
   Pb(CO3)2-2           1.449e-007  8.817e-008    -6.839    -7.055    -0.216
   PbCO3                9.644e-008  9.644e-008    -7.016    -7.016     0.000
   PbOH+                4.592e-008  4.056e-008    -7.338    -7.392    -0.054
   Pb(OH)3-             3.697e-008  3.265e-008    -7.432    -7.486    -0.054
   Pb(OH)4-2            2.097e-009  1.276e-009    -8.678    -8.894    -0.216
   Pb+2                 1.561e-010  1.012e-010    -9.807    -9.995    -0.188
   PbSO4                6.363e-011  6.363e-011   -10.196   -10.196     0.000
   PbHCO3+              3.632e-011  3.208e-011   -10.440   -10.494    -0.054
   PbCl+                4.139e-012  3.656e-012   -11.383   -11.437    -0.054
   PbF+                 1.006e-012  8.889e-013   -11.997   -12.051    -0.054
   PbNO3+               8.824e-013  7.794e-013   -12.054   -12.108    -0.054
   Pb(SO4)2-2           8.089e-013  4.922e-013   -12.092   -12.308    -0.216
   Pb3(OH)4+2           1.390e-013  8.456e-014   -12.857   -13.073    -0.216
   PbCl2                1.663e-014  1.663e-014   -13.779   -13.779     0.000
   PbF2                 2.180e-015  2.180e-015   -14.661   -14.661     0.000
   Pb(NO3)2             6.891e-016  6.891e-016   -15.162   -15.162     0.000
   Pb2OH+3              1.989e-016  6.506e-017   -15.701   -16.187    -0.485
   PbCl3-               7.630e-018  6.739e-018   -17.117   -17.171    -0.054
   PbF3-                5.836e-019  5.154e-019   -18.234   -18.288    -0.054
```

```
   Pb4(OH)4+4            4.958e-019  6.798e-020   -18.305   -19.168    -0.863
   PbCl4-2               5.154e-021  3.136e-021   -20.288   -20.504    -0.216
   PbF4-2                5.053e-023  3.075e-023   -22.296   -22.512    -0.216
S(6)            2.135e-003
   SO4-2                 1.980e-003  1.284e-003    -2.703    -2.892    -0.188
   CaSO4                 9.150e-005  9.150e-005    -4.039    -4.039     0.000
   KSO4-                 4.501e-005  4.054e-005    -4.347    -4.392    -0.045
   NaSO4-                1.847e-005  1.664e-005    -4.733    -4.779    -0.045
   MgSO4                 1.806e-007  1.806e-007    -6.743    -6.743     0.000
   NH4SO4-               7.512e-009  6.758e-009    -8.124    -8.170    -0.046
   MnSO4                 1.781e-009  1.781e-009    -8.749    -8.749     0.000
   NiSO4                 9.488e-010  9.488e-010    -9.023    -9.023     0.000
   PbSO4                 6.363e-011  6.363e-011   -10.196   -10.196     0.000
   ZnSO4                 5.301e-011  5.301e-011   -10.276   -10.276     0.000
   HSO4-                 8.813e-012  7.916e-012   -11.055   -11.102    -0.047
   CdSO4                 5.237e-012  5.237e-012   -11.281   -11.281     0.000
   CuSO4                 3.079e-012  3.079e-012   -11.512   -11.512     0.000
   Zn(SO4)2-2            9.740e-013  5.927e-013   -12.011   -12.227    -0.216
   Pb(SO4)2-2            8.089e-013  4.922e-013   -12.092   -12.308    -0.216
   Cd(SO4)2-2            1.490e-013  9.070e-014   -12.827   -13.042    -0.216
   Ni(SO4)2-2            6.628e-014  4.033e-014   -13.179   -13.394    -0.216
   FeSO4                 1.902e-017  1.902e-017   -16.721   -16.721     0.000
   AlSO4+                1.715e-023  1.540e-023   -22.766   -22.812    -0.047
   FeSO4+                8.977e-025  8.076e-025   -24.047   -24.093    -0.046
   Al(SO4)2-             2.359e-025  2.119e-025   -24.627   -24.674    -0.047
   Fe(SO4)2-             2.510e-026  2.217e-026   -25.600   -25.654    -0.054
Si              5.106e-004
   H3SiO4-               3.669e-004  3.290e-004    -3.435    -3.483    -0.047
   H4SiO4                1.432e-004  1.436e-004    -3.844    -3.843     0.001
   H2SiO4-2              4.998e-007  3.290e-007    -6.301    -6.483    -0.182
   SiF6-2                1.974e-038  1.293e-038   -37.705   -37.888    -0.184
Zn              1.530e-007
   Zn(OH)2               7.615e-008  7.615e-008    -7.118    -7.118     0.000
   Zn(OH)3-              6.894e-008  6.089e-008    -7.162    -7.215    -0.054
   ZnCO3                 3.443e-009  3.443e-009    -8.463    -8.463     0.000
   ZnOH+                 3.409e-009  3.011e-009    -8.467    -8.521    -0.054
   Zn(OH)4-2             6.356e-010  3.868e-010    -9.197    -9.413    -0.216
   Zn+2                  2.911e-010  1.887e-010    -9.536    -9.724    -0.188
   ZnOHCl                1.008e-010  1.008e-010    -9.996    -9.996     0.000
   ZnSO4                 5.301e-011  5.301e-011   -10.276   -10.276     0.000
   ZnHCO3+               2.883e-012  2.546e-012   -11.540   -11.594    -0.054
   Zn(SO4)2-2            9.740e-013  5.927e-013   -12.011   -12.227    -0.216
   ZnCl+                 5.383e-013  4.827e-013   -12.269   -12.316    -0.047
   ZnF+                  5.314e-013  4.694e-013   -12.275   -12.328    -0.054
   ZnNO3+                2.795e-013  2.468e-013   -12.554   -12.608    -0.054
   ZnCl2                 7.789e-016  7.789e-016   -15.109   -15.109     0.000
   Zn(NO3)2              2.564e-017  2.564e-017   -16.591   -16.591     0.000
   ZnCl3-                7.024e-019  6.299e-019   -18.153   -18.201    -0.047
   ZnCl4-2               4.896e-022  3.207e-022   -21.310   -21.494    -0.184

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -4.01    6.79   10.80  Al(OH)3
        Al2O3            -6.07   13.58   19.65  Al2O3
        Al4(OH)10SO4    -18.84    3.86   22.70  Al4(OH)10SO4
        AlOHSO4         -13.27  -16.50   -3.23  AlOHSO4
        Alunite         -16.97  -18.37   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -5.10  -12.89   -7.79  PbSO4
        Anhydrite        -2.04   -6.40   -4.36  CaSO4
        Antlerite        -3.82    4.97    8.79  Cu3(OH)4SO4
        Aragonite         1.29   -7.01   -8.30  CaCO3
        Artinite         -4.92    4.68    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -1.74    5.65    7.39  Cu2(OH)3Cl
        Azurite          -2.63  -19.54  -16.91  Cu3(OH)2(CO3)2
        Bianchite       -10.85  -12.62   -1.76  ZnSO4:6H2O
        Birnessite       -2.75   15.34   18.09  MnO2
```

```
        Bixbyite          2.93    2.28   -0.64  Mn2O3
        Boehmite         -1.79    6.79    8.58  AlOOH
        Brochantite      -0.83   14.39   15.22  Cu4(OH)6SO4
        Brucite          -2.56   14.29   16.84  Mg(OH)2
        Bunsenite        -0.48   11.97   12.45  NiO
        Ca3(PO4)2(beta)   0.54  -28.38  -28.92  Ca3(PO4)2
        Ca4H(PO4)3:3H2O  -3.93  -51.01  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -3.36  -22.64  -19.27  CaHPO4
        CaHPO4:2H2O      -3.64  -22.64  -19.00  CaHPO4:2H2O
        Calcite           1.47   -7.01   -8.48  CaCO3
        Cd(OH)2          -4.00    9.64   13.64  Cd(OH)2
        Cd(OH)2(am)      -4.09    9.64   13.73  Cd(OH)2
        Cd3(OH)2(SO4)2  -24.37  -17.66    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -16.93    5.63   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -17.53  -50.13  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -13.13   15.27   28.40  Cd4(OH)6SO4
        CdCl2           -16.08  -16.74   -0.66  CdCl2
        CdCl2:1H2O      -15.05  -16.74   -1.69  CdCl2:1H2O
        CdCl2:2.5H2O    -14.83  -16.74   -1.91  CdCl2:2.5H2O
        CdF2            -17.36  -18.57   -1.21  CdF2
        Cdmetal(alpha)  -32.27  -18.76   13.51  Cd
        Cdmetal(gamma)  -32.38  -18.76   13.62  Cd
        CdOHCl           -7.09   -3.55    3.54  CdOHCl
        CdSO4           -13.48  -13.65   -0.17  CdSO4
        CdSO4:1H2O      -11.92  -13.65   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -11.78  -13.65   -1.87  CdSO4:2.67H2O
        Cerrusite        -0.36  -13.49  -13.13  PbCO3
        CH4(g)          -96.45 -137.50  -41.05  CH4
        Chalcanthite    -11.23  -13.87   -2.64  CuSO4:5H2O
        Chalcedony       -0.29   -3.84   -3.55  SiO2
        Chrysotile        2.98   35.18   32.20  Mg3Si2O5(OH)4
        CO2(g)           -5.75  -23.90  -18.15  CO2
        Cotunnite       -11.20  -15.98   -4.78  PbCl2
        Cristobalite     -0.49   -3.84   -3.35  SiO2
        Cryolite        -21.25  -55.09  -33.84  Na3AlF6
        Cu(OH)2           0.75    9.42    8.67  Cu(OH)2
        Cu2(OH)3NO3      -3.89    5.36    9.25  Cu2(OH)3NO3
        Cu2SO4          -25.52  -27.47   -1.95  Cu2SO4
        Cu3(PO4)2       -13.95  -50.80  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -15.68  -50.80  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -2.98  -14.48  -11.50  CuCO3
        CuF             -11.29  -16.19   -4.91  CuF
        CuF2            -19.90  -18.79    1.12  CuF2
        CuF2:2H2O       -14.24  -18.79   -4.55  CuF2:2H2O
        Cumetal          -7.53  -16.29   -8.76  Cu
        CuOCuSO4        -14.75   -4.45   10.30  CuOCuSO4
        Cupricferrite    14.13   20.12    5.99  CuFe2O4
        Cuprite          -2.77   -4.18   -1.41  Cu2O
        Cuprousferrite   12.18    3.26   -8.92  CuFeO2
        CuSO4           -16.81  -13.87    2.94  CuSO4
        Diaspore         -0.08    6.79    6.87  AlOOH
        Dolomite(disordered)  -0.08  -16.62  -16.54  CaMg(CO3)2
        Dolomite(ordered)   0.47  -16.62  -17.09  CaMg(CO3)2
        Epsomite         -6.88   -9.00   -2.13  MgSO4:7H2O
        FCO3Apatite      23.17  -91.23 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
        Fe(OH)2          -9.38    4.18   13.56  Fe(OH)2
        Fe(OH)2.7Cl.3     4.43    1.39   -3.04  Fe(OH)2.7Cl.3
        Fe2(SO4)3       -55.44  -59.18   -3.73  Fe2(SO4)3
        Fe3(OH)8         -5.34   14.88   20.22  Fe3(OH)8
        Ferrihydrite      2.16    5.35    3.19  Fe(OH)3
        Fluorite         -0.82  -11.32  -10.50  CaF2
        Gibbsite         -1.50    6.79    8.29  Al(OH)3
        Goethite          4.86    5.35    0.49  FeOOH
        Goslarite       -10.61  -12.62   -2.01  ZnSO4:7H2O
        Greenalite      -15.95    4.86   20.81  Fe3Si2O5(OH)4
        Gypsum           -1.79   -6.40   -4.61  CaSO4:2H2O
        H-Jarosite      -18.44  -30.54  -12.10  (H3O)Fe3(SO4)2(OH)6
```

```
Halite            -7.21   -5.61    1.60  NaCl
Halloysite        -3.68    5.89    9.57  Al2Si2O5(OH)4
Hausmannite        4.25   65.28   61.03  Mn3O4
Hematite          12.12   10.70   -1.42  Fe2O3
Hercynite         -5.13   17.76   22.89  FeAl2O4
Hinsdalite       -29.55  -32.05   -2.50  PbAl3PO4SO4(OH)6
Huntite           -5.87  -35.84  -29.97  CaMg3(CO3)4
Hydrocerrusite     2.19  -16.58  -18.77  Pb3(OH)2(CO3)2
Hydromagnesite   -15.39  -24.16   -8.77  Mg5(CO3)4(OH)2:4H2O
Hydroxylapatite   10.21  -34.12  -44.33  Ca5(PO4)3OH
Hydroxylpyromorphite  -3.77  -66.56  -62.79  Pb5(PO4)3OH
K-Alum           -26.78  -31.95   -5.17  KAl(SO4)2:12H2O
K-Jarosite        -7.89  -22.69  -14.80  KFe3(SO4)2(OH)6
Kaolinite         -1.54    5.89    7.43  Al2Si2O5(OH)4
Langite           -3.10   14.39   17.49  Cu4(OH)6SO4:H2O
Larnakite         -2.05   -2.48   -0.43  PbO:PbSO4
Laurionite        -3.41   -2.79    0.62  PbOHCl
Lepidocrocite      3.98    5.35    1.37  FeOOH
Lime             -15.81   16.89   32.70  CaO
Litharge          -2.29   10.41   12.69  PbO
Maghemite          4.31   10.70    6.39  Fe2O3
Magnesioferrite    8.13   24.99   16.86  Fe2MgO4
Magnesite         -2.15   -9.61   -7.46  MgCO3
Magnetite         11.47   14.88    3.40  Fe3O4
Malachite          0.25   -5.06   -5.31  Cu2(OH)2CO3
Manganite          1.15   26.49   25.34  MnOOH
Massicot          -2.49   10.41   12.89  PbO
Matlockite        -7.92  -16.89   -8.97  PbClF
Melanothallite   -23.22  -16.96    6.26  CuCl2
Melanterite      -16.90  -19.11   -2.21  FeSO4:7H2O
Mg(OH)2(active)   -4.51   14.29   18.79  Mg(OH)2
Mg3(PO4)2        -12.91  -36.19  -23.28  Mg3(PO4)2
MgF2              -5.79  -13.92   -8.13  MgF2
MgHPO4:3H2O       -7.07  -25.24  -18.18  MgHPO4:3H2O
Minium           -13.91   59.62   73.52  Pb3O4
Mirabilite        -7.01   -8.13   -1.11  Na2SO4:10H2O
Mn2(SO4)3        -61.88  -67.59   -5.71  Mn2(SO4)3
Mn3(PO4)2        -18.35  -42.18  -23.83  Mn3(PO4)2
MnCl2:4H2O       -16.81  -14.09    2.72  MnCl2:4H2O
MnHPO4            -1.84  -27.24  -25.40  MnHPO4
MnSO4            -13.58  -11.00    2.58  MnSO4
Monteponite       -5.46    9.64   15.10  CdO
Morenosite        -9.18  -11.32   -2.14  NiSO4:7H2O
Na-Jarosite      -11.75  -22.95  -11.20  NaFe3(SO4)2(OH)6
Nantokite         -8.55  -15.28   -6.73  CuCl
Natron            -7.42   -8.73   -1.31  Na2CO3:10H2O
Nesquehonite      -4.94   -9.61   -4.67  MgCO3:3H2O
Ni(OH)2           -0.83   11.97   12.79  Ni(OH)2
Ni3(PO4)2        -11.85  -43.15  -31.30  Ni3(PO4)2
Ni4(OH)6SO4       -7.42   24.58   32.00  Ni4(OH)6SO4
NiCO3             -5.06  -11.93   -6.87  NiCO3
Nsutite           -2.16   15.34   17.50  MnO2
O2(g)            -26.29   56.80   83.09  O2
Otavite           -2.26  -14.26  -12.00  CdCO3
Pb(OH)2            2.25   10.40    8.15  Pb(OH)2
Pb10(OH)6O(CO3)6 -30.58  -39.34   -8.76  Pb10(OH)6O(CO3)6
Pb2(OH)3Cl        -1.18    7.62    8.79  Pb2(OH)3Cl
Pb2O(OH)2         -5.38   20.81   26.19  Pb2O(OH)2
Pb2O3            -11.83   49.21   61.04  Pb2O3
Pb2OCO3           -2.53   -3.09   -0.56  Pb2OCO3
Pb3(PO4)2         -4.31  -47.84  -43.53  Pb3(PO4)2
Pb3O2CO3          -3.70    7.32   11.02  Pb3O2CO3
Pb3O2SO4          -2.76    7.92   10.69  Pb3O2SO4
Pb4(OH)6SO4       -2.77   18.33   21.10  Pb4(OH)6SO4
Pb4O3SO4          -3.55   18.33   21.88  Pb4O3SO4
PbF2             -10.36  -17.80   -7.44  PbF2
PbHPO4            -5.32  -29.12  -23.81  PbHPO4
Pbmetal          -22.24  -17.99    4.25  Pb
```

```
        PbO:0.3H2O       -2.57   10.41   12.98  PbO:0.33H2O
        Periclase        -7.30   14.29   21.58  MgO
        Phosgenite       -9.66  -29.47  -19.81  PbCl2:PbCO3
        Plattnerite     -10.80   38.80   49.60  PbO2
        Plumbgummite    -15.49  -48.28  -32.79  PbAl3(PO4)2(OH)5:H2O
        Portlandite      -5.91   16.89   22.80  Ca(OH)2
        Pyrochroite      -2.90   12.29   15.19  Mn(OH)2
        Pyrolusite       -0.69   40.69   41.38  MnO2
        Pyromorphite      4.68  -79.75  -84.43  Pb5(PO4)3Cl
        Quartz            0.16   -3.84   -4.00  SiO2
        Retgersite       -9.28  -11.32   -2.04  NiSO4:6H2O
        Rhodochrosite    -1.03  -11.61  -10.58  MnCO3
        Sepiolite         1.29   17.05   15.76  Mg2Si3O7.5OH:3H2O
        Sepiolite(A)     -1.73   17.05   18.78  Mg2Si3O7.5OH:3H2O
        Siderite         -9.48  -19.72  -10.24  FeCO3
        SiO2(am-gel)     -1.13   -3.84   -2.71  SiO2
        SiO2(am-ppt)     -1.10   -3.84   -2.74  SiO2
        Smithsonite      -3.22  -13.22  -10.00  ZnCO3
        Spinel           -8.98   27.87   36.85  MgAl2O4
        Strengite        -7.78  -34.18  -26.40  FePO4:2H2O
        Tenorite          1.78    9.42    7.64  CuO
        Thenardite       -8.45   -8.13    0.32  Na2SO4
        Thermonatrite    -9.37   -8.73    0.64  Na2CO3:H2O
        Tsumebite         0.49   -9.30   -9.79  Pb2CuPO4(OH)3:3H2O
        Vivianite       -30.51  -66.51  -36.00  Fe3(PO4)2:8H2O
        Zincite          -0.66   10.68   11.33  ZnO
        Zincosite       -16.55  -12.62    3.93  ZnSO4
        Zn(NO3)2:6H2O   -19.61  -16.29    3.32  Zn(NO3)2:6H2O
        Zn(OH)2          -1.52   10.68   12.20  Zn(OH)2
        Zn(OH)2(am)      -1.80   10.68   12.47  Zn(OH)2
        Zn(OH)2(beta)    -1.08   10.68   11.75  Zn(OH)2
        Zn(OH)2(epsilon)  -0.86   10.68   11.53  Zn(OH)2
        Zn(OH)2(gamma)   -1.06   10.68   11.73  Zn(OH)2
        Zn2(OH)2SO4      -9.44   -1.94    7.50  Zn2(OH)2SO4
        Zn2(OH)3Cl       -7.03    8.16   15.19  Zn2(OH)3Cl
        Zn3(PO4)2:4H2O  -11.61  -47.03  -35.42  Zn3(PO4)2:4H2O
        Zn3O(SO4)2      -33.47  -14.56   18.91  Zn3O(SO4)2
        Zn4(OH)6SO4      -8.99   19.41   28.40  Zn4(OH)6SO4
        Zn5(OH)8Cl2     -11.51   26.99   38.50  Zn5(OH)8Cl2
        ZnCl2           -22.76  -15.71    7.05  ZnCl2
        ZnCO3:1H2O       -2.96  -13.22  -10.26  ZnCO3:1H2O
        ZnF2            -17.00  -17.53   -0.53  ZnF2
        Znmetal         -43.51  -17.72   25.79  Zn
        ZnO(active)      -0.51   10.68   11.19  ZnO
        ZnSO4:1H2O      -11.98  -12.62   -0.64  ZnSO4:1H2O

Initial solution 5-FA 800 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Al               1.113e-006  1.113e-006
        C(4)             2.118e-003  2.118e-003
        Ca               1.910e-003  1.910e-003
        Cd               4.452e-010  4.452e-010
        Cl               1.138e-003  1.138e-003
        Cu               1.103e-007  1.103e-007
        F                1.470e-004  1.470e-004
        Fe               1.613e-006  1.613e-006
        K                6.144e-003  6.144e-003
        Mg               1.647e-006  1.647e-006
        Mn               1.822e-009  1.822e-009
        N(-3)            6.431e-006  6.431e-006
        N(5)             9.111e-004  9.111e-004
        Na               4.223e-003  4.223e-003
        Ni               1.705e-007  1.705e-007
        P                1.777e-006  1.777e-006
```

```
        Pb                5.797e-007  5.797e-007
        S(6)              2.178e-003  2.178e-003
        Si                1.445e-003  1.445e-003
        Zn                1.531e-007  1.531e-007

----------------------------Description of solution----------------------------

                                       pH  =  10.300
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  1.509e-002
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.954e-003
                       Total CO2 (mol/kg)  =  2.118e-003
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  2.698e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  12.06
                               Iterations  =  11
                                  Total H  = 1.110192e+002
                                  Total O  = 5.553066e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           2.4091      0.1425

----------------------------Distribution of species----------------------------

                                                            Log       Log         Log
   Species                   Molality    Activity  Molality  Activity       Gamma

   OH-                     2.279e-004  2.008e-004    -3.642    -3.697      -0.055
   H+                      5.668e-011  5.012e-011   -10.247   -10.300      -0.053
   H2O                     5.551e+001  9.997e-001     1.744    -0.000       0.000
Al                1.113e-006
   Al(OH)4-                1.113e-006  9.851e-007    -5.954    -6.007      -0.053
   Al(OH)3                 3.896e-011  3.896e-011   -10.409   -10.409       0.000
   Al(OH)2+                1.094e-014  9.722e-015   -13.961   -14.012      -0.051
   AlOH+2                  9.782e-020  6.094e-020   -19.010   -19.215      -0.206
   AlF3                    3.244e-020  3.244e-020   -19.489   -19.489       0.000
   AlF2+                   2.253e-020  2.002e-020   -19.647   -19.699      -0.051
   AlF4-                   2.364e-021  2.093e-021   -20.626   -20.679      -0.053
   AlF+2                   6.270e-022  3.906e-022   -21.203   -21.408      -0.206
   AlSO4+                  3.116e-024  2.758e-024   -23.506   -23.559      -0.053
   Al+3                    9.179e-025  3.034e-025   -24.037   -24.518      -0.481
   Al(SO4)2-               3.910e-026  3.461e-026   -25.408   -25.461      -0.053
C(4)              2.118e-003
   CO3-2                   8.590e-004  5.252e-004    -3.066    -3.280      -0.214
   HCO3-                   6.320e-004  5.615e-004    -3.199    -3.251      -0.051
   CaCO3                   5.763e-004  5.763e-004    -3.239    -3.239       0.000
   NaCO3-                  4.045e-005  3.594e-005    -4.393    -4.444      -0.051
   CaHCO3+                 8.129e-006  7.239e-006    -5.090    -5.140      -0.050
   NaHCO3                  1.160e-006  1.160e-006    -5.935    -5.935       0.000
   MgCO3                   3.001e-007  3.001e-007    -6.523    -6.523       0.000
   Pb(CO3)2-2              2.367e-007  1.330e-007    -6.626    -6.876      -0.250
   PbCO3                   8.780e-008  8.780e-008    -7.056    -7.056       0.000
   H2CO3                   6.329e-008  6.329e-008    -7.199    -7.199       0.000
   NiCO3                   4.505e-008  4.505e-008    -7.346    -7.346       0.000
   Cu(CO3)2-2              1.744e-008  9.801e-009    -7.758    -8.009      -0.250
   CuCO3                   6.933e-009  6.933e-009    -8.159    -8.159       0.000
   MgHCO3+                 4.468e-009  3.947e-009    -8.350    -8.404      -0.054
   ZnCO3                   3.196e-009  3.196e-009    -8.495    -8.495       0.000
   CdCO3                   1.975e-010  1.975e-010    -9.704    -9.704       0.000
   NiHCO3+                 1.838e-010  1.592e-010    -9.736    -9.798      -0.063
   Cd(CO3)2-2              1.368e-010  7.690e-011    -9.864   -10.114      -0.250
   PbHCO3+                 2.680e-011  2.320e-011   -10.572   -10.634      -0.063
   MnHCO3+                 8.926e-012  7.918e-012   -11.049   -11.101      -0.052
```

```
   ZnHCO3+             2.168e-012  1.877e-012   -11.664   -11.726    -0.063
   CuHCO3+             9.173e-014  7.942e-014   -13.038   -13.100    -0.063
   CdHCO3+             2.436e-014  2.109e-014   -13.613   -13.676    -0.063
   FeHCO3+             2.860e-019  2.546e-019   -18.544   -18.594    -0.050
Ca              1.910e-003
   Ca+2                1.132e-003  6.924e-004    -2.946    -3.160    -0.214
   CaCO3               5.763e-004  5.763e-004    -3.239    -3.239     0.000
   CaSO4               1.857e-004  1.857e-004    -3.731    -3.731     0.000
   CaHCO3+             8.129e-006  7.239e-006    -5.090    -5.140    -0.050
   CaOH+               3.116e-006  2.774e-006    -5.506    -5.557    -0.050
   CaNO3+              2.033e-006  1.760e-006    -5.692    -5.754    -0.063
   CaPO4-              1.603e-006  1.424e-006    -5.795    -5.846    -0.051
   CaF+                1.097e-006  9.728e-007    -5.960    -6.012    -0.052
   CaHPO4              2.683e-008  2.683e-008    -7.571    -7.571     0.000
   CaNH3+2             9.043e-009  5.082e-009    -8.044    -8.294    -0.250
   CaH2PO4+            1.169e-012  1.039e-012   -11.932   -11.983    -0.051
   Ca(NH3)2+2          2.099e-014  1.180e-014   -13.678   -13.928    -0.250
Cd              4.452e-010
   CdCO3               1.975e-010  1.975e-010    -9.704    -9.704     0.000
   Cd(CO3)2-2          1.368e-010  7.690e-011    -9.864   -10.114    -0.250
   Cd(OH)2             3.335e-011  3.335e-011   -10.477   -10.477     0.000
   CdOH+               3.040e-011  2.632e-011   -10.517   -10.580    -0.063
   Cd+2                2.698e-011  1.650e-011   -10.569   -10.783    -0.214
   CdOHCl              1.306e-011  1.306e-011   -10.884   -10.884     0.000
   CdSO4               4.529e-012  4.529e-012   -11.344   -11.344     0.000
   CdCl+               1.831e-012  1.585e-012   -11.737   -11.800    -0.063
   Cd(OH)3-            4.727e-013  4.092e-013   -12.325   -12.388    -0.063
   Cd(SO4)2-2          1.273e-013  7.154e-014   -12.895   -13.145    -0.250
   CdNO3+              4.843e-014  4.194e-014   -13.315   -13.377    -0.063
   CdF+                3.887e-014  3.366e-014   -13.410   -13.473    -0.063
   CdHCO3+             2.436e-014  2.109e-014   -13.613   -13.676    -0.063
   CdCl2               6.647e-015  6.647e-015   -14.177   -14.177     0.000
   Cd(OH)4-2           2.394e-017  1.345e-017   -16.621   -16.871    -0.250
   Cd(NO3)2            1.690e-017  1.690e-017   -16.772   -16.772     0.000
   CdF2                8.645e-018  8.645e-018   -17.063   -17.063     0.000
   CdCl3-              4.874e-018  4.220e-018   -17.312   -17.375    -0.063
   Cd2OH+3             7.958e-021  2.176e-021   -20.099   -20.662    -0.563
Cl              1.138e-003
   Cl-                 1.138e-003  1.006e-003    -2.944    -2.997    -0.053
   ZnOHCl              7.025e-011  7.025e-011   -10.153   -10.153     0.000
   CdOHCl              1.306e-011  1.306e-011   -10.884   -10.884     0.000
   NiCl+               6.835e-012  5.918e-012   -11.165   -11.228    -0.063
   PbCl+               2.293e-012  1.985e-012   -11.640   -11.702    -0.063
   CdCl+               1.831e-012  1.585e-012   -11.737   -11.800    -0.063
   MnCl+               1.009e-012  8.951e-013   -11.996   -12.048    -0.052
   ZnCl+               3.025e-013  2.672e-013   -12.519   -12.573    -0.054
   CuCl                1.391e-013  1.391e-013   -12.857   -12.857     0.000
   CuCl2-              3.309e-014  2.923e-014   -13.480   -13.534    -0.054
   PbCl2               8.921e-015  8.921e-015   -14.050   -14.050     0.000
   CdCl2               6.647e-015  6.647e-015   -14.177   -14.177     0.000
   CuCl+               4.046e-015  3.574e-015   -14.393   -14.447    -0.054
   MnCl2               1.272e-015  1.272e-015   -14.895   -14.895     0.000
   ZnCl2               4.260e-016  4.260e-016   -15.371   -15.371     0.000
   NiCl2               2.998e-017  2.998e-017   -16.523   -16.523     0.000
   CuCl3-2             1.016e-017  6.287e-018   -16.993   -17.202    -0.208
   CdCl3-              4.874e-018  4.220e-018   -17.312   -17.375    -0.063
   PbCl3-              4.127e-018  3.573e-018   -17.384   -17.447    -0.063
   CuCl2               1.247e-018  1.247e-018   -17.904   -17.904     0.000
   MnCl3-              3.974e-019  3.525e-019   -18.401   -18.453    -0.052
   ZnCl3-              3.854e-019  3.405e-019   -18.414   -18.468    -0.054
   PbCl4-2             2.924e-021  1.643e-021   -20.534   -20.784    -0.250
   ZnCl4-2             2.767e-022  1.713e-022   -21.558   -21.766    -0.208
   CuCl3-              1.325e-023  1.171e-023   -22.878   -22.932    -0.054
   FeCl+2              1.642e-027  1.017e-027   -26.785   -26.993    -0.208
   CuCl4-2             9.535e-029  5.903e-029   -28.021   -28.229    -0.208
   FeCl2+              5.151e-030  4.569e-030   -29.288   -29.340    -0.052
   FeCl3               4.597e-034  4.597e-034   -33.338   -33.338     0.000
Cu(1)           2.990e-013
```

```
   CuCl                  1.391e-013  1.391e-013   -12.857   -12.857     0.000
   Cu+                   1.268e-013  1.098e-013   -12.897   -12.959    -0.063
   CuCl2-                3.309e-014  2.923e-014   -13.480   -13.534    -0.054
   CuCl3-2               1.016e-017  6.287e-018   -16.993   -17.202    -0.208
Cu(2)           1.103e-007
   Cu(OH)2               5.705e-008  5.705e-008    -7.244    -7.244     0.000
   Cu(OH)3-              2.715e-008  2.350e-008    -7.566    -7.629    -0.063
   Cu(CO3)2-2            1.744e-008  9.801e-009    -7.758    -8.009    -0.250
   CuCO3                 6.933e-009  6.933e-009    -8.159    -8.159     0.000
   CuOH+                 1.612e-009  1.424e-009    -8.793    -8.847    -0.054
   Cu(OH)4-2             6.611e-011  3.715e-011   -10.180   -10.430    -0.250
   Cu+2                  3.666e-012  2.242e-012   -11.436   -11.649    -0.214
   CuSO4                 6.014e-013  6.014e-013   -12.221   -12.221     0.000
   CuNH3+2               2.380e-013  1.337e-013   -12.623   -12.874    -0.250
   CuHCO3+               9.173e-014  7.942e-014   -13.038   -13.100    -0.063
   Cu2(OH)2+2            9.060e-014  5.092e-014   -13.043   -13.293    -0.250
   CuF+                  2.103e-014  1.821e-014   -13.677   -13.740    -0.063
   CuNO3+                6.581e-015  5.698e-015   -14.182   -14.244    -0.063
   CuCl+                 4.046e-015  3.574e-015   -14.393   -14.447    -0.054
   CuCl2                 1.247e-018  1.247e-018   -17.904   -17.904     0.000
   Cu(NO3)2              5.767e-019  5.767e-019   -18.239   -18.239     0.000
   CuCl3-                1.325e-023  1.171e-023   -22.878   -22.932    -0.054
   CuCl4-2               9.535e-029  5.903e-029   -28.021   -28.229    -0.208
F               1.470e-004
   F-                    1.456e-004  1.287e-004    -3.837    -3.890    -0.053
   CaF+                  1.097e-006  9.728e-007    -5.960    -6.012    -0.052
   NaF                   2.984e-007  2.984e-007    -6.525    -6.525     0.000
   MgF+                  1.121e-008  9.921e-009    -7.950    -8.003    -0.053
   HF                    9.543e-012  9.543e-012   -11.020   -11.020     0.000
   NiF+                  8.587e-012  7.435e-012   -11.066   -11.129    -0.063
   MnF+                  4.083e-012  3.622e-012   -11.389   -11.441    -0.052
   PbF+                  5.826e-013  5.045e-013   -12.235   -12.297    -0.063
   ZnF+                  3.136e-013  2.716e-013   -12.504   -12.566    -0.063
   CdF+                  3.887e-014  3.366e-014   -13.410   -13.473    -0.063
   CuF+                  2.103e-014  1.821e-014   -13.677   -13.740    -0.063
   HF2-                  5.299e-015  4.671e-015   -14.276   -14.331    -0.055
   PbF2                  1.278e-015  1.278e-015   -14.893   -14.893     0.000
   CdF2                  8.645e-018  8.645e-018   -17.063   -17.063     0.000
   PbF3-                 3.604e-019  3.120e-019   -18.443   -18.506    -0.063
   AlF3                  3.244e-020  3.244e-020   -19.489   -19.489     0.000
   AlF2+                 2.253e-020  2.002e-020   -19.647   -19.699    -0.051
   AlF4-                 2.364e-021  2.093e-021   -20.626   -20.679    -0.053
   AlF+2                 6.270e-022  3.906e-022   -21.203   -21.408    -0.206
   H2F2                  2.440e-022  2.440e-022   -21.613   -21.613     0.000
   PbF4-2                3.421e-023  1.923e-023   -22.466   -22.716    -0.250
   FeF2+                 1.834e-023  1.627e-023   -22.736   -22.789    -0.052
   FeF+2                 7.630e-024  4.723e-024   -23.117   -23.326    -0.208
   FeF3                  2.955e-024  2.955e-024   -23.529   -23.529     0.000
   SiF6-2                2.381e-038  1.474e-038   -37.623   -37.831    -0.208
Fe(2)           3.735e-015
   Fe(OH)3-              3.290e-015  2.918e-015   -14.483   -14.535    -0.052
   FeOH+                 3.247e-016  2.880e-016   -15.489   -15.541    -0.052
   Fe+2                  6.410e-017  3.602e-017   -16.193   -16.443    -0.250
   Fe(OH)2               4.595e-017  4.595e-017   -16.338   -16.338     0.000
   FeSO4                 1.036e-017  1.036e-017   -16.985   -16.985     0.000
   FeHCO3+               2.860e-019  2.546e-019   -18.544   -18.594    -0.050
   FeHPO4                1.216e-020  1.216e-020   -19.915   -19.915     0.000
   FeH2PO4+              1.362e-024  1.210e-024   -23.866   -23.917    -0.051
Fe(3)           1.613e-006
   Fe(OH)4-              1.539e-006  1.368e-006    -5.813    -5.864    -0.051
   Fe(OH)3               7.314e-008  7.314e-008    -7.136    -7.136     0.000
   Fe(OH)2+              3.816e-010  3.391e-010    -9.418    -9.470    -0.051
   FeOH+2                7.010e-018  4.339e-018   -17.154   -17.363    -0.208
   FeHPO4+               2.638e-023  2.343e-023   -22.579   -22.630    -0.051
   FeF2+                 1.834e-023  1.627e-023   -22.736   -22.789    -0.052
   FeF+2                 7.630e-024  4.723e-024   -23.117   -23.326    -0.208
   FeF3                  2.955e-024  2.955e-024   -23.529   -23.529     0.000
   FeSO4+                4.957e-025  4.397e-025   -24.305   -24.357    -0.052
```

```
   Fe+3                 1.012e-025  3.346e-026   -24.995   -25.475    -0.481
   Fe(SO4)2-            1.271e-026  1.101e-026   -25.896   -25.958    -0.063
   FeCl+2               1.642e-027  1.017e-027   -26.785   -26.993    -0.208
   FeNO3+2              4.786e-028  2.690e-028   -27.320   -27.570    -0.250
   FeCl2+               5.151e-030  4.569e-030   -29.288   -29.340    -0.052
   FeH2PO4+2            6.837e-032  4.259e-032   -31.165   -31.371    -0.206
   Fe2(OH)2+4           6.251e-033  6.235e-034   -32.204   -33.205    -1.001
   FeCl3                4.597e-034  4.597e-034   -33.338   -33.338     0.000
   Fe3(OH)4+5           1.120e-040  0.000e+000   -39.951   -41.515    -1.564
H(0)            3.544e-032
   H2                   1.772e-032  1.778e-032   -31.752   -31.750     0.002
K               6.144e-003
   K+                   6.094e-003  5.388e-003    -2.215    -2.269    -0.053
   KSO4-                5.028e-005  4.467e-005    -4.299    -4.350    -0.051
   KHPO4-               3.900e-009  3.465e-009    -8.409    -8.460    -0.051
Mg              1.647e-006
   Mg+2                 1.123e-006  6.869e-007    -5.949    -6.163    -0.214
   MgCO3                3.001e-007  3.001e-007    -6.523    -6.523     0.000
   MgSO4                1.464e-007  1.464e-007    -6.835    -6.835     0.000
   MgOH+                6.156e-008  5.492e-008    -7.211    -7.260    -0.050
   MgF+                 1.121e-008  9.921e-009    -7.950    -8.003    -0.053
   MgHCO3+              4.468e-009  3.947e-009    -8.350    -8.404    -0.054
   MgHPO4               3.674e-011  3.674e-011   -10.435   -10.435     0.000
   MgPO4-               2.486e-011  2.209e-011   -10.604   -10.656    -0.051
   MgH2PO4+             2.498e-015  2.220e-015   -14.602   -14.654    -0.051
Mn(2)           1.822e-009
   Mn+2                 1.258e-009  7.067e-010    -8.900    -9.151    -0.250
   MnOH+                4.020e-010  3.565e-010    -9.396    -9.448    -0.052
   MnSO4                1.472e-010  1.472e-010    -9.832    -9.832     0.000
   MnHCO3+              8.926e-012  7.918e-012   -11.049   -11.101    -0.052
   MnF+                 4.083e-012  3.622e-012   -11.389   -11.441    -0.052
   MnNO3+               1.040e-012  9.004e-013   -11.983   -12.046    -0.063
   MnCl+                1.009e-012  8.951e-013   -11.996   -12.048    -0.052
   Mn(OH)3-             1.002e-013  8.888e-014   -12.999   -13.051    -0.052
   Mn(NO3)2             1.818e-015  1.818e-015   -14.740   -14.740     0.000
   MnCl2                1.272e-015  1.272e-015   -14.895   -14.895     0.000
   Mn(OH)4-2            9.310e-017  5.763e-017   -16.031   -16.239    -0.208
   MnCl3-               3.974e-019  3.525e-019   -18.401   -18.453    -0.052
Mn(3)           9.550e-031
   Mn+3                 9.550e-031  3.157e-031   -30.020   -30.501    -0.481
Mn(6)           1.084e-029
   MnO4-2               1.084e-029  6.709e-030   -28.965   -29.173    -0.208
Mn(7)           3.240e-035
   MnO4-                3.240e-035  2.849e-035   -34.490   -34.545    -0.056
N(-3)           6.431e-006
   NH3                  5.831e-006  5.831e-006    -5.234    -5.234     0.000
   NH4+                 5.842e-007  5.125e-007    -6.233    -6.290    -0.057
   CaNH3+2              9.043e-009  5.082e-009    -8.044    -8.294    -0.250
   NH4SO4-              7.251e-009  6.431e-009    -8.140    -8.192    -0.052
   NiNH3+2              1.281e-011  7.199e-012   -10.892   -11.143    -0.250
   CuNH3+2              2.380e-013  1.337e-013   -12.623   -12.874    -0.250
   Ca(NH3)2+2           2.099e-014  1.180e-014   -13.678   -13.928    -0.250
   Ni(NH3)2+2           1.080e-014  6.068e-015   -13.967   -14.217    -0.250
N(5)            9.111e-004
   NO3-                 9.091e-004  8.039e-004    -3.041    -3.095    -0.053
   CaNO3+               2.033e-006  1.760e-006    -5.692    -5.754    -0.063
   NiNO3+               5.362e-012  4.642e-012   -11.271   -11.333    -0.063
   MnNO3+               1.040e-012  9.004e-013   -11.983   -12.046    -0.063
   PbNO3+               7.637e-013  6.612e-013   -12.117   -12.180    -0.063
   ZnNO3+               2.466e-013  2.135e-013   -12.608   -12.671    -0.063
   CdNO3+               4.843e-014  4.194e-014   -13.315   -13.377    -0.063
   CuNO3+               6.581e-015  5.698e-015   -14.182   -14.244    -0.063
   Mn(NO3)2             1.818e-015  1.818e-015   -14.740   -14.740     0.000
   Pb(NO3)2             9.026e-016  9.026e-016   -15.044   -15.044     0.000
   Zn(NO3)2             3.424e-017  3.424e-017   -16.465   -16.465     0.000
   Cd(NO3)2             1.690e-017  1.690e-017   -16.772   -16.772     0.000
   Cu(NO3)2             5.767e-019  5.767e-019   -18.239   -18.239     0.000
   FeNO3+2              4.786e-028  2.690e-028   -27.320   -27.570    -0.250
```

```
Na              4.223e-003
   Na+                   4.155e-003  3.674e-003     -2.381     -2.435     -0.053
   NaCO3-                4.045e-005  3.594e-005     -4.393     -4.444     -0.051
   NaSO4-                2.601e-005  2.311e-005     -4.585     -4.636     -0.051
   NaHCO3                1.160e-006  1.160e-006     -5.935     -5.935      0.000
   NaF                   2.984e-007  2.984e-007     -6.525     -6.525      0.000
   NaHPO4-               4.119e-009  3.660e-009     -8.385     -8.437     -0.051
Ni              1.705e-007
   Ni(OH)2               9.274e-008  9.274e-008     -7.033     -7.033      0.000
   NiCO3                 4.505e-008  4.505e-008     -7.346     -7.346      0.000
   Ni(OH)3-              2.151e-008  1.863e-008     -7.667     -7.730     -0.063
   NiOH+                 6.714e-009  5.813e-009     -8.173     -8.236     -0.063
   Ni+2                  3.760e-009  2.299e-009     -8.425     -8.638     -0.214
   NiSO4                 5.372e-010  5.372e-010     -9.270     -9.270      0.000
   NiHCO3+               1.838e-010  1.592e-010     -9.736     -9.798     -0.063
   NiNH3+2               1.281e-011  7.199e-012    -10.892    -11.143     -0.250
   NiF+                  8.587e-012  7.435e-012    -11.066    -11.129     -0.063
   NiCl+                 6.835e-012  5.918e-012    -11.165    -11.228     -0.063
   NiNO3+                5.362e-012  4.642e-012    -11.271    -11.333     -0.063
   Ni(SO4)2-2            3.707e-014  2.083e-014    -13.431    -13.681     -0.250
   Ni(NH3)2+2            1.080e-014  6.068e-015    -13.967    -14.217     -0.250
   NiCl2                 2.998e-017  2.998e-017    -16.523    -16.523      0.000
O(0)            3.193e-029
   O2                    1.596e-029  1.602e-029    -28.797    -28.795      0.002
P               1.777e-006
   CaPO4-                1.603e-006  1.424e-006     -5.795     -5.846     -0.051
   HPO4-2                1.369e-007  8.478e-008     -6.863     -7.072     -0.208
   CaHPO4                2.683e-008  2.683e-008     -7.571     -7.571      0.000
   NaHPO4-               4.119e-009  3.660e-009     -8.385     -8.437     -0.051
   KHPO4-                3.900e-009  3.465e-009     -8.409     -8.460     -0.051
   PO4-3                 2.158e-009  7.133e-010     -8.666     -9.147     -0.481
   H2PO4-                7.545e-011  6.703e-011    -10.122    -10.174     -0.051
   MgHPO4                3.674e-011  3.674e-011    -10.435    -10.435      0.000
   MgPO4-                2.486e-011  2.209e-011    -10.604    -10.656     -0.051
   CaH2PO4+              1.169e-012  1.039e-012    -11.932    -11.983     -0.051
   MgH2PO4+              2.498e-015  2.220e-015    -14.602    -14.654     -0.051
   H3PO4                 4.724e-019  4.724e-019    -18.326    -18.326      0.000
   FeHPO4                1.216e-020  1.216e-020    -19.915    -19.915      0.000
   FeHPO4+               2.638e-023  2.343e-023    -22.579    -22.630     -0.051
   FeH2PO4+              1.362e-024  1.210e-024    -23.866    -23.917     -0.051
   FeH2PO4+2             6.837e-032  4.259e-032    -31.165    -31.371     -0.206
Pb              5.797e-007
   Pb(CO3)2-2            2.367e-007  1.330e-007     -6.626     -6.876     -0.250
   Pb(OH)2               1.782e-007  1.782e-007     -6.749     -6.749      0.000
   PbCO3                 8.780e-008  8.780e-008     -7.056     -7.056      0.000
   Pb(OH)3-              4.133e-008  3.579e-008     -7.384     -7.446     -0.063
   PbOH+                 3.240e-008  2.805e-008     -7.489     -7.552     -0.063
   Pb(OH)4-2             3.132e-009  1.760e-009     -8.504     -8.754     -0.250
   Pb+2                  9.095e-011  5.561e-011    -10.041    -10.255     -0.214
   PbSO4                 3.190e-011  3.190e-011    -10.496    -10.496      0.000
   PbHCO3+               2.680e-011  2.320e-011    -10.572    -10.634     -0.063
   PbCl+                 2.293e-012  1.985e-012    -11.640    -11.702     -0.063
   PbNO3+                7.637e-013  6.612e-013    -12.117    -12.180     -0.063
   PbF+                  5.826e-013  5.045e-013    -12.235    -12.297     -0.063
   Pb(SO4)2-2            4.005e-013  2.251e-013    -12.397    -12.648     -0.250
   Pb3(OH)4+2            6.268e-014  3.523e-014    -13.203    -13.453     -0.250
   PbCl2                 8.921e-015  8.921e-015    -14.050    -14.050      0.000
   PbF2                  1.278e-015  1.278e-015    -14.893    -14.893      0.000
   Pb(NO3)2              9.026e-016  9.026e-016    -15.044    -15.044      0.000
   Pb2OH+3               9.042e-017  2.473e-017    -16.044    -16.607     -0.563
   PbCl3-                4.127e-018  3.573e-018    -17.384    -17.447     -0.063
   PbF3-                 3.604e-019  3.120e-019    -18.443    -18.506     -0.063
   Pb4(OH)4+4            1.560e-019  1.556e-020    -18.807    -19.808     -1.001
   PbCl4-2               2.924e-021  1.643e-021    -20.534    -20.784     -0.250
   PbF4-2                3.421e-023  1.923e-023    -22.466    -22.716     -0.250
S(6)            2.178e-003
   SO4-2                 1.915e-003  1.171e-003     -2.718     -2.931     -0.214
   CaSO4                 1.857e-004  1.857e-004     -3.731     -3.731      0.000
```

```
   KSO4-                 5.028e-005  4.467e-005    -4.299    -4.350    -0.051
   NaSO4-                2.601e-005  2.311e-005    -4.585    -4.636    -0.051
   MgSO4                 1.464e-007  1.464e-007    -6.835    -6.835     0.000
   NH4SO4-               7.251e-009  6.431e-009    -8.140    -8.192    -0.052
   NiSO4                 5.372e-010  5.372e-010    -9.270    -9.270     0.000
   MnSO4                 1.472e-010  1.472e-010    -9.832    -9.832     0.000
   PbSO4                 3.190e-011  3.190e-011   -10.496   -10.496     0.000
   ZnSO4                 2.709e-011  2.709e-011   -10.567   -10.567     0.000
   HSO4-                 6.479e-012  5.736e-012   -11.188   -11.241    -0.053
   CdSO4                 4.529e-012  4.529e-012   -11.344   -11.344     0.000
   CuSO4                 6.014e-013  6.014e-013   -12.221   -12.221     0.000
   Zn(SO4)2-2            4.916e-013  2.763e-013   -12.308   -12.559    -0.250
   Pb(SO4)2-2            4.005e-013  2.251e-013   -12.397   -12.648    -0.250
   Cd(SO4)2-2            1.273e-013  7.154e-014   -12.895   -13.145    -0.250
   Ni(SO4)2-2            3.707e-014  2.083e-014   -13.431   -13.681    -0.250
   FeSO4                 1.036e-017  1.036e-017   -16.985   -16.985     0.000
   AlSO4+                3.116e-024  2.758e-024   -23.506   -23.559    -0.053
   FeSO4+                4.957e-025  4.397e-025   -24.305   -24.357    -0.052
   Al(SO4)2-             3.910e-026  3.461e-026   -25.408   -25.461    -0.053
   Fe(SO4)2-             1.271e-026  1.101e-026   -25.896   -25.958    -0.063
Si                1.445e-003
   H3SiO4-               1.106e-003  9.769e-004    -2.956    -3.010    -0.054
   H4SiO4                3.375e-004  3.387e-004    -3.472    -3.470     0.002
   H2SiO4-2              1.974e-006  1.230e-006    -5.705    -5.910    -0.206
   SiF6-2                2.381e-038  1.474e-038   -37.623   -37.831    -0.208
Zn                1.531e-007
   Zn(OH)3-              7.858e-008  6.804e-008    -7.105    -7.167    -0.063
   Zn(OH)2               6.759e-008  6.759e-008    -7.170    -7.170     0.000
   ZnCO3                 3.196e-009  3.196e-009    -8.495    -8.495     0.000
   ZnOH+                 2.453e-009  2.123e-009    -8.610    -8.673    -0.063
   Zn(OH)4-2             9.680e-010  5.440e-010    -9.014    -9.264    -0.250
   Zn+2                  1.729e-010  1.057e-010    -9.762    -9.976    -0.214
   ZnOHCl                7.025e-011  7.025e-011   -10.153   -10.153     0.000
   ZnSO4                 2.709e-011  2.709e-011   -10.567   -10.567     0.000
   ZnHCO3+               2.168e-012  1.877e-012   -11.664   -11.726    -0.063
   Zn(SO4)2-2            4.916e-013  2.763e-013   -12.308   -12.559    -0.250
   ZnF+                  3.136e-013  2.716e-013   -12.504   -12.566    -0.063
   ZnCl+                 3.025e-013  2.672e-013   -12.519   -12.573    -0.054
   ZnNO3+                2.466e-013  2.135e-013   -12.608   -12.671    -0.063
   ZnCl2                 4.260e-016  4.260e-016   -15.371   -15.371     0.000
   Zn(NO3)2              3.424e-017  3.424e-017   -16.465   -16.465     0.000
   ZnCl3-                3.854e-019  3.405e-019   -18.414   -18.468    -0.054
   ZnCl4-2               2.767e-022  1.713e-022   -21.558   -21.766    -0.208

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -4.42    6.38   10.80  Al(OH)3
        Al2O3            -6.89   12.76   19.65  Al2O3
        Al4(OH)10SO4    -20.70    2.00   22.70  Al4(OH)10SO4
        AlOHSO4         -13.92  -17.15   -3.23  AlOHSO4
        Alunite         -18.49  -19.89   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -5.40  -13.19   -7.79  PbSO4
        Anhydrite        -1.73   -6.09   -4.36  CaSO4
        Antlerite        -5.47    3.32    8.79  Cu3(OH)4SO4
        Aragonite         1.86   -6.44   -8.30  CaCO3
        Artinite         -4.61    4.99    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -2.79    4.60    7.39  Cu2(OH)3Cl
        Azurite          -4.00  -20.91  -16.91  Cu3(OH)2(CO3)2
        Bianchite       -11.14  -12.91   -1.76  ZnSO4:6H2O
        Birnessite       -3.39   14.70   18.09  MnO2
        Bixbyite          1.44    0.80   -0.64  Mn2O3
        Boehmite         -2.20    6.38    8.58  AlOOH
        Brochantite      -2.95   12.27   15.22  Cu4(OH)6SO4
        Brucite          -2.41   14.44   16.84  Mg(OH)2
        Bunsenite        -0.48   11.96   12.45  NiO
        Ca3(PO4)2(beta)   1.15  -27.77  -28.92  Ca3(PO4)2
```

```
        Ca4H(PO4)3:3H2O  -3.30  -50.38  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -3.33  -22.61  -19.27  CaHPO4
        CaHPO4:2H2O      -3.61  -22.61  -19.00  CaHPO4:2H2O
        Calcite           2.04   -6.44   -8.48  CaCO3
        Cd(OH)2          -3.83    9.82   13.64  Cd(OH)2
        Cd(OH)2(am)      -3.91    9.82   13.73  Cd(OH)2
        Cd3(OH)2(SO4)2  -24.32  -17.61    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -16.64    5.92   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -18.04  -50.64  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -12.66   15.74   28.40  Cd4(OH)6SO4
        CdCl2           -16.12  -16.78   -0.66  CdCl2
        CdCl2:1H2O      -15.08  -16.78   -1.69  CdCl2:1H2O
        CdCl2:2.5H2O    -14.86  -16.78   -1.91  CdCl2:2.5H2O
        CdF2            -17.35  -18.56   -1.21  CdF2
        Cdmetal(alpha)  -32.30  -18.78   13.51  Cd
        Cdmetal(gamma)  -32.40  -18.78   13.62  Cd
        CdOHCl           -7.02   -3.48    3.54  CdOHCl
        CdSO4           -13.54  -13.71   -0.17  CdSO4
        CdSO4:1H2O      -11.99  -13.71   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -11.84  -13.71   -1.87  CdSO4:2.67H2O
        Cerrusite        -0.40  -13.53  -13.13  PbCO3
        CH4(g)          -97.23 -138.28  -41.05  CH4
        Chalcanthite    -11.94  -14.58   -2.64  CuSO4:5H2O
        Chalcedony        0.08   -3.47   -3.55  SiO2
        Chrysotile        4.17   36.37   32.20  Mg3Si2O5(OH)4
        CO2(g)           -5.73  -23.88  -18.15  CO2
        Cotunnite       -11.47  -16.25   -4.78  PbCl2
        Cristobalite     -0.12   -3.47   -3.35  SiO2
        Cryolite        -21.32  -55.16  -33.84  Na3AlF6
        Cu(OH)2           0.28    8.95    8.67  Cu(OH)2
        Cu2(OH)3NO3      -4.75    4.51    9.25  Cu2(OH)3NO3
        Cu2SO4          -26.90  -28.85   -1.95  Cu2SO4
        Cu3(PO4)2       -16.39  -53.24  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -18.12  -53.24  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -3.43  -14.93  -11.50  CuCO3
        CuF             -11.94  -16.85   -4.91  CuF
        CuF2            -20.55  -19.43    1.12  CuF2
        CuF2:2H2O       -14.88  -19.43   -4.55  CuF2:2H2O
        Cumetal          -8.20  -16.96   -8.76  Cu
        CuOCuSO4        -15.93   -5.63   10.30  CuOCuSO4
        Cupricferrite    13.81   19.80    5.99  CuFe2O4
        Cuprite          -3.91   -5.32   -1.41  Cu2O
        Cuprousferrite   11.68    2.76   -8.92  CuFeO2
        CuSO4           -17.52  -14.58    2.94  CuSO4
        Diaspore         -0.49    6.38    6.87  AlOOH
        Dolomite(disordered)   0.66  -15.88  -16.54  CaMg(CO3)2
        Dolomite(ordered)   1.21  -15.88  -17.09  CaMg(CO3)2
        Epsomite         -6.97   -9.10   -2.13  MgSO4:7H2O
        FCO3Apatite      25.71  -88.69 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
        Fe(OH)2          -9.41    4.16   13.56  Fe(OH)2
        Fe(OH)2.7Cl.3     4.47    1.43   -3.04  Fe(OH)2.7Cl.3
        Fe2(SO4)3       -56.01  -59.75   -3.73  Fe2(SO4)3
        Fe3(OH)8         -5.22   15.00   20.22  Fe3(OH)8
        Ferrihydrite      2.23    5.42    3.19  Fe(OH)3
        Fluorite         -0.44  -10.94  -10.50  CaF2
        Gibbsite         -1.91    6.38    8.29  Al(OH)3
        Goethite          4.93    5.42    0.49  FeOOH
        Goslarite       -10.90  -12.91   -2.01  ZnSO4:7H2O
        Greenalite      -15.28    5.53   20.81  Fe3Si2O5(OH)4
        Gypsum           -1.48   -6.09   -4.61  CaSO4:2H2O
        H-Jarosite      -18.69  -30.79  -12.10  (H3O)Fe3(SO4)2(OH)6
        Halite           -7.03   -5.43    1.60  NaCl
        Halloysite       -3.75    5.82    9.57  Al2Si2O5(OH)4
        Hausmannite       1.92   62.95   61.03  Mn3O4
        Hematite         12.27   10.85   -1.42  Fe2O3
        Hercynite        -5.97   16.92   22.89  FeAl2O4
        Hinsdalite      -31.59  -34.09   -2.50  PbAl3PO4SO4(OH)6
```

```
Huntite          -4.80  -34.77  -29.97  CaMg3(CO3)4
Hydrocerrusite    2.05  -16.72  -18.77  Pb3(OH)2(CO3)2
Hydromagnesite  -14.57  -23.34   -8.77  Mg5(CO3)4(OH)2:4H2O
Hydroxylapatite  11.39  -32.94  -44.33  Ca5(PO4)3OH
Hydroxylpyromorphite  -5.62  -68.41  -62.79  Pb5(PO4)3OH
K-Alum          -27.48  -32.65   -5.17  KAl(SO4)2:12H2O
K-Jarosite       -7.96  -22.76  -14.80  KFe3(SO4)2(OH)6
Kaolinite        -1.61    5.82    7.43  Al2Si2O5(OH)4
Langite          -5.22   12.27   17.49  Cu4(OH)6SO4:H2O
Larnakite        -2.41   -2.84   -0.43  PbO:PbSO4
Laurionite       -3.58   -2.95    0.62  PbOHCl
Lepidocrocite     4.05    5.42    1.37  FeOOH
Lime            -15.26   17.44   32.70  CaO
Litharge         -2.35   10.35   12.69  PbO
Maghemite         4.46   10.85    6.39  Fe2O3
Magnesioferrite   8.43   25.29   16.86  Fe2MgO4
Magnesite        -1.98   -9.44   -7.46  MgCO3
Magnetite        11.60   15.01    3.40  Fe3O4
Malachite        -0.67   -5.98   -5.31  Cu2(OH)2CO3
Manganite         0.41   25.75   25.34  MnOOH
Massicot         -2.55   10.35   12.89  PbO
Matlockite       -8.17  -17.14   -8.97  PbClF
Melanothallite  -23.90  -17.64    6.26  CuCl2
Melanterite     -17.17  -19.38   -2.21  FeSO4:7H2O
Mg(OH)2(active)  -4.36   14.44   18.79  Mg(OH)2
Mg3(PO4)2       -13.50  -36.78  -23.28  Mg3(PO4)2
MgF2             -5.81  -13.94   -8.13  MgF2
MgHPO4:3H2O      -7.44  -25.61  -18.18  MgHPO4:3H2O
Minium          -13.89   59.63   73.52  Pb3O4
Mirabilite       -6.69   -7.80   -1.11  Na2SO4:10H2O
Mn2(SO4)3       -64.08  -69.80   -5.71  Mn2(SO4)3
Mn3(PO4)2       -21.92  -45.75  -23.83  Mn3(PO4)2
MnCl2:4H2O      -17.86  -15.15    2.72  MnCl2:4H2O
MnHPO4           -3.20  -28.60  -25.40  MnHPO4
MnSO4           -14.67  -12.08    2.58  MnSO4
Monteponite      -5.29    9.82   15.10  CdO
Morenosite       -9.43  -11.57   -2.14  NiSO4:7H2O
Na-Jarosite     -11.72  -22.92  -11.20  NaFe3(SO4)2(OH)6
Nantokite        -9.23  -15.96   -6.73  CuCl
Natron           -6.84   -8.15   -1.31  Na2CO3:10H2O
Nesquehonite     -4.77   -9.44   -4.67  MgCO3:3H2O
Ni(OH)2          -0.83   11.96   12.79  Ni(OH)2
Ni3(PO4)2       -12.91  -44.21  -31.30  Ni3(PO4)2
Ni4(OH)6SO4      -7.69   24.31   32.00  Ni4(OH)6SO4
NiCO3            -5.05  -11.92   -6.87  NiCO3
Nsutite          -2.81   14.70   17.50  MnO2
O2(g)           -25.89   57.20   83.09  O2
Otavite          -2.06  -14.06  -12.00  CdCO3
Pb(OH)2           2.19   10.34    8.15  Pb(OH)2
Pb10(OH)6O(CO3)6 -31.07  -39.83   -8.76  Pb10(OH)6O(CO3)6
Pb2(OH)3Cl       -1.40    7.39    8.79  Pb2(OH)3Cl
Pb2O(OH)2        -5.50   20.69   26.19  Pb2O(OH)2
Pb2O3           -11.75   49.29   61.04  Pb2O3
Pb2OCO3          -2.63   -3.19   -0.56  Pb2OCO3
Pb3(PO4)2        -5.53  -49.06  -43.53  Pb3(PO4)2
Pb3O2CO3         -3.86    7.16   11.02  Pb3O2CO3
Pb3O2SO4         -3.18    7.50   10.69  Pb3O2SO4
Pb4(OH)6SO4      -3.25   17.85   21.10  Pb4(OH)6SO4
Pb4O3SO4         -4.03   17.85   21.88  Pb4O3SO4
PbF2            -10.60  -18.04   -7.44  PbF2
PbHPO4           -5.90  -29.70  -23.81  PbHPO4
Pbmetal         -22.50  -18.25    4.25  Pb
PbO:0.3H2O       -2.64   10.34   12.98  PbO:0.33H2O
Periclase        -7.15   14.44   21.58  MgO
Phosgenite       -9.97  -29.78  -19.81  PbCl2:PbCO3
Plattnerite     -10.66   38.94   49.60  PbO2
Plumbgummite    -17.81  -50.60  -32.79  PbAl3(PO4)2(OH)5:H2O
Portlandite      -5.36   17.44   22.80  Ca(OH)2
```

```
        Pyrochroite      -3.75   11.45   15.19  Mn(OH)2
        Pyrolusite       -1.33   40.05   41.38  MnO2
        Pyromorphite      2.72  -81.71  -84.43  Pb5(PO4)3Cl
        Quartz            0.53   -3.47   -4.00  SiO2
        Retgersite       -9.53  -11.57   -2.04  NiSO4:6H2O
        Rhodochrosite    -1.85  -12.43  -10.58  MnCO3
        Sepiolite         2.70   18.46   15.76  Mg2Si3O7.5OH:3H2O
        Sepiolite(A)     -0.32   18.46   18.78  Mg2Si3O7.5OH:3H2O
        Siderite         -9.48  -19.72  -10.24  FeCO3
        SiO2(am-gel)     -0.76   -3.47   -2.71  SiO2
        SiO2(am-ppt)     -0.73   -3.47   -2.74  SiO2
        Smithsonite      -3.26  -13.26  -10.00  ZnCO3
        Spinel           -9.65   27.20   36.85  MgAl2O4
        Strengite        -8.22  -34.62  -26.40  FePO4:2H2O
        Tenorite          1.31    8.95    7.64  CuO
        Thenardite       -8.12   -7.80    0.32  Na2SO4
        Thermonatrite    -8.79   -8.15    0.64  Na2CO3:H2O
        Tsumebite        -0.62  -10.41   -9.79  Pb2CuPO4(OH)3:3H2O
        Vivianite       -31.62  -67.62  -36.00  Fe3(PO4)2:8H2O
        Zincite          -0.71   10.62   11.33  ZnO
        Zincosite       -16.84  -12.91    3.93  ZnSO4
        Zn(NO3)2:6H2O   -19.48  -16.17    3.32  Zn(NO3)2:6H2O
        Zn(OH)2          -1.58   10.62   12.20  Zn(OH)2
        Zn(OH)2(am)      -1.85   10.62   12.47  Zn(OH)2
        Zn(OH)2(beta)    -1.13   10.62   11.75  Zn(OH)2
        Zn(OH)2(epsilon)  -0.91   10.62   11.53  Zn(OH)2
        Zn(OH)2(gamma)   -1.11   10.62   11.73  Zn(OH)2
        Zn2(OH)2SO4      -9.78   -2.28    7.50  Zn2(OH)2SO4
        Zn2(OH)3Cl       -7.24    7.95   15.19  Zn2(OH)3Cl
        Zn3(PO4)2:4H2O  -12.80  -48.22  -35.42  Zn3(PO4)2:4H2O
        Zn3O(SO4)2      -34.10  -15.19   18.91  Zn3O(SO4)2
        Zn4(OH)6SO4      -9.44   18.96   28.40  Zn4(OH)6SO4
        Zn5(OH)8Cl2     -11.97   26.53   38.50  Zn5(OH)8Cl2
        ZnCl2           -23.02  -15.97    7.05  ZnCl2
        ZnCO3:1H2O       -3.00  -13.26  -10.26  ZnCO3:1H2O
        ZnF2            -17.22  -17.76   -0.53  ZnF2
        Znmetal         -43.76  -17.98   25.79  Zn
        ZnO(active)      -0.56   10.62   11.19  ZnO
        ZnSO4:1H2O      -12.27  -12.91   -0.64  ZnSO4:1H2O

Initial solution 6-FA 1304 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Al               7.420e-007  7.420e-007
        C(4)             2.969e-003  2.969e-003
        Ca               9.316e-004  9.316e-004
        Cd               8.905e-011  8.905e-011
        Cl               1.047e-003  1.047e-003
        Cu               3.150e-008  3.150e-008
        F                1.349e-004  1.349e-004
        Fe               8.962e-007  8.962e-007
        K                5.837e-003  5.837e-003
        Mg               1.236e-006  1.236e-006
        Mn               3.644e-009  3.644e-009
        N(-3)            1.000e-005  1.000e-005
        N(5)             9.054e-004  9.054e-004
        Na               4.398e-003  4.398e-003
        Ni               1.706e-007  1.706e-007
        P                1.777e-006  1.777e-006
        Pb               3.865e-007  3.865e-007
        S(6)             2.146e-003  2.146e-003
        Si               2.715e-003  2.715e-003
        Zn               1.531e-007  1.531e-007

----------------------------Description of solution----------------------------
```

```
                                       pH  =   9.320
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  1.366e-002
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  4.193e-003
                       Total CO2 (mol/kg)  =  2.969e-003
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  1.539e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   7.19
                               Iterations  =  11
                                  Total H  = 1.110264e+002
                                  Total O  = 5.553794e+001

---------------------------------Redox couples---------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)           3.5189      0.2082

----------------------------Distribution of species----------------------------

                                                   Log       Log         Log
   Species                   Molality    Activity  Molality  Activity     Gamma

   OH-                   2.373e-005  2.103e-005    -4.625    -4.677    -0.052
   H+                    5.385e-010  4.786e-010    -9.269    -9.320    -0.051
   H2O                   5.551e+001  9.996e-001     1.744    -0.000     0.000
Al              7.420e-007
   Al(OH)4-              7.417e-007  6.599e-007    -6.130    -6.181    -0.051
   Al(OH)3               2.492e-010  2.492e-010    -9.603    -9.603     0.000
   Al(OH)2+              6.654e-013  5.940e-013   -12.177   -12.226    -0.049
   AlF3                  1.431e-016  1.431e-016   -15.844   -15.844     0.000
   AlF2+                 1.069e-016  9.545e-017   -15.971   -16.020    -0.049
   AlOH+2                5.600e-017  3.556e-017   -16.252   -16.449    -0.197
   AlF4-                 9.598e-018  8.539e-018   -17.018   -17.069    -0.051
   AlF+2                 3.171e-018  2.013e-018   -17.499   -17.696    -0.197
   AlSO4+                1.798e-020  1.600e-020   -19.745   -19.796    -0.051
   Al+3                  4.886e-021  1.691e-021   -20.311   -20.772    -0.461
   Al(SO4)2-             2.349e-022  2.090e-022   -21.629   -21.680    -0.051
C(4)            2.969e-003
   HCO3-                 2.444e-003  2.182e-003    -2.612    -2.661    -0.049
   CO3-2                 3.425e-004  2.137e-004    -3.465    -3.670    -0.205
   CaCO3                 1.388e-004  1.388e-004    -3.858    -3.858     0.000
   CaHCO3+               1.861e-005  1.665e-005    -4.730    -4.779    -0.048
   NaCO3-                1.722e-005  1.537e-005    -4.764    -4.813    -0.049
   NaHCO3                4.740e-006  4.740e-006    -5.324    -5.324     0.000
   H2CO3                 2.348e-006  2.348e-006    -5.629    -5.629     0.000
   Pb(CO3)2-2            1.854e-007  1.071e-007    -6.732    -6.970    -0.238
   PbCO3                 1.738e-007  1.738e-007    -6.760    -6.760     0.000
   NiCO3                 1.248e-007  1.248e-007    -6.904    -6.904     0.000
   MgCO3                 1.070e-007  1.070e-007    -6.971    -6.971     0.000
   ZnCO3                 7.654e-008  7.654e-008    -7.116    -7.116     0.000
   MgHCO3+               1.514e-008  1.344e-008    -7.820    -7.872    -0.052
   CuCO3                 1.376e-008  1.376e-008    -7.861    -7.861     0.000
   Cu(CO3)2-2            1.369e-008  7.915e-009    -7.863    -8.102    -0.238
   NiHCO3+               4.828e-009  4.210e-009    -8.316    -8.376    -0.060
   PbHCO3+               5.031e-010  4.387e-010    -9.298    -9.358    -0.060
   ZnHCO3+               4.925e-010  4.294e-010    -9.308    -9.367    -0.060
   MnHCO3+               8.625e-011  7.688e-011   -10.064   -10.114    -0.050
   CdCO3                 5.099e-011  5.099e-011   -10.293   -10.293     0.000
   Cd(CO3)2-2            1.398e-011  8.077e-012   -10.855   -11.093    -0.238
   CuHCO3+               1.727e-012  1.505e-012   -11.763   -11.822    -0.060
   CdHCO3+               5.964e-014  5.200e-014   -13.224   -13.284    -0.060
   FeHCO3+               3.639e-015  3.256e-015   -14.439   -14.487    -0.048
Ca              9.316e-004
   Ca+2                  6.569e-004  4.099e-004    -3.182    -3.387    -0.205
```

```
   CaCO3                 1.388e-004  1.388e-004    -3.858    -3.858     0.000
   CaSO4                 1.145e-004  1.145e-004    -3.941    -3.941     0.000
   CaHCO3+               1.861e-005  1.665e-005    -4.730    -4.779    -0.048
   CaNO3+                1.195e-006  1.042e-006    -5.923    -5.982    -0.060
   CaPO4-                6.812e-007  6.081e-007    -6.167    -6.216    -0.049
   CaF+                  5.976e-007  5.327e-007    -6.224    -6.274    -0.050
   CaOH+                 1.923e-007  1.720e-007    -6.716    -6.764    -0.048
   CaHPO4                1.094e-007  1.094e-007    -6.961    -6.961     0.000
   CaNH3+2               4.547e-009  2.628e-009    -8.342    -8.580    -0.238
   CaH2PO4+              4.532e-011  4.046e-011   -10.344   -10.393    -0.049
   Ca(NH3)2+2            9.219e-015  5.328e-015   -14.035   -14.273    -0.238
Cd              8.905e-011
   CdCO3                 5.099e-011  5.099e-011   -10.293   -10.293     0.000
   Cd+2                  1.678e-011  1.047e-011   -10.775   -10.980    -0.205
   Cd(CO3)2-2            1.398e-011  8.077e-012   -10.855   -11.093    -0.238
   CdSO4                 2.992e-012  2.992e-012   -11.524   -11.524     0.000
   CdOH+                 2.006e-012  1.749e-012   -11.698   -11.757    -0.060
   CdCl+                 1.068e-012  9.308e-013   -11.972   -12.031    -0.060
   CdOHCl                8.030e-013  8.030e-013   -12.095   -12.095     0.000
   Cd(OH)2               2.321e-013  2.321e-013   -12.634   -12.634     0.000
   Cd(SO4)2-2            8.512e-014  4.920e-014   -13.070   -13.308    -0.238
   CdHCO3+               5.964e-014  5.200e-014   -13.224   -13.284    -0.060
   CdNO3+                3.052e-014  2.661e-014   -13.515   -13.575    -0.060
   CdF+                  2.266e-014  1.976e-014   -13.645   -13.704    -0.060
   CdCl2                 3.612e-015  3.612e-015   -14.442   -14.442     0.000
   Cd(OH)3-              3.420e-016  2.982e-016   -15.466   -15.526    -0.060
   Cd(NO3)2              1.072e-017  1.072e-017   -16.970   -16.970     0.000
   CdF2                  4.694e-018  4.694e-018   -17.328   -17.328     0.000
   CdCl3-                2.434e-018  2.122e-018   -17.614   -17.673    -0.060
   Cd(OH)4-2             1.776e-021  1.026e-021   -20.751   -20.989    -0.238
   Cd2OH+3               3.151e-022  9.177e-023   -21.502   -22.037    -0.536
Cl              1.047e-003
   Cl-                   1.047e-003  9.310e-004    -2.980    -3.031    -0.051
   ZnOHCl                4.008e-010  4.008e-010    -9.397    -9.397     0.000
   NiCl+                 4.276e-011  3.728e-011   -10.369   -10.428    -0.060
   ZnCl+                 1.639e-011  1.456e-011   -10.785   -10.837    -0.052
   PbCl+                 1.025e-011  8.940e-012   -10.989   -11.049    -0.060
   MnCl+                 2.322e-012  2.070e-012   -11.634   -11.684    -0.050
   CdCl+                 1.068e-012  9.308e-013   -11.972   -12.031    -0.060
   CdOHCl                8.030e-013  8.030e-013   -12.095   -12.095     0.000
   CuCl                  6.278e-013  6.278e-013   -12.202   -12.202     0.000
   CuCl2-                1.375e-013  1.221e-013   -12.862   -12.913    -0.052
   PbCl2                 3.718e-014  3.718e-014   -13.430   -13.430     0.000
   ZnCl2                 2.148e-014  2.148e-014   -13.668   -13.668     0.000
   CuCl+                 1.817e-014  1.614e-014   -13.741   -13.792    -0.052
   CdCl2                 3.612e-015  3.612e-015   -14.442   -14.442     0.000
   MnCl2                 2.722e-015  2.722e-015   -14.565   -14.565     0.000
   NiCl2                 1.748e-016  1.748e-016   -15.758   -15.758     0.000
   CuCl3-2               3.850e-017  2.430e-017   -16.415   -16.614    -0.200
   ZnCl3-                1.789e-017  1.588e-017   -16.747   -16.799    -0.052
   PbCl3-                1.580e-017  1.378e-017   -16.801   -16.861    -0.060
   CuCl2                 5.209e-018  5.209e-018   -17.283   -17.283     0.000
   CdCl3-                2.434e-018  2.122e-018   -17.614   -17.673    -0.060
   MnCl3-                7.830e-019  6.979e-019   -18.106   -18.156    -0.050
   ZnCl4-2               1.171e-020  7.393e-021   -19.931   -20.131    -0.200
   PbCl4-2               1.014e-020  5.863e-021   -19.994   -20.232    -0.238
   CuCl3-                5.097e-023  4.526e-023   -22.293   -22.344    -0.052
   FeCl+2                4.904e-024  3.096e-024   -23.309   -23.509    -0.200
   FeCl2+                1.444e-026  1.287e-026   -25.840   -25.890    -0.050
   CuCl4-2               3.345e-028  2.112e-028   -27.476   -27.675    -0.200
   FeCl3                 1.199e-030  1.199e-030   -29.921   -29.921     0.000
Cu(1)           1.380e-012
   CuCl                  6.278e-013  6.278e-013   -12.202   -12.202     0.000
   Cu+                   6.144e-013  5.357e-013   -12.212   -12.271    -0.060
   CuCl2-                1.375e-013  1.221e-013   -12.862   -12.913    -0.052
   CuCl3-2               3.850e-017  2.430e-017   -16.415   -16.614    -0.200
Cu(2)           3.150e-008
   CuCO3                 1.376e-008  1.376e-008    -7.861    -7.861     0.000
```

```
   Cu(CO3)2-2            1.369e-008  7.915e-009    -7.863    -8.102    -0.238
   Cu(OH)2               3.052e-009  3.052e-009    -8.515    -8.515     0.000
   CuOH+                 8.191e-010  7.274e-010    -9.087    -9.138    -0.052
   Cu(OH)3-              1.510e-010  1.317e-010    -9.821    -9.881    -0.060
   Cu+2                  1.753e-011  1.094e-011   -10.756   -10.961    -0.205
   CuSO4                 3.054e-012  3.054e-012   -11.515   -11.515     0.000
   CuHCO3+               1.727e-012  1.505e-012   -11.763   -11.822    -0.060
   CuNH3+2               9.862e-013  5.700e-013   -12.006   -12.244    -0.238
   CuF+                  9.425e-014  8.217e-014   -13.026   -13.085    -0.060
   Cu(OH)4-2             3.771e-014  2.179e-014   -13.424   -13.662    -0.238
   CuNO3+                3.188e-014  2.780e-014   -13.496   -13.556    -0.060
   Cu2(OH)2+2            2.299e-014  1.329e-014   -13.638   -13.876    -0.238
   CuCl+                 1.817e-014  1.614e-014   -13.741   -13.792    -0.052
   CuCl2                 5.209e-018  5.209e-018   -17.283   -17.283     0.000
   Cu(NO3)2              2.812e-018  2.812e-018   -17.551   -17.551     0.000
   CuCl3-                5.097e-023  4.526e-023   -22.293   -22.344    -0.052
   CuCl4-2               3.345e-028  2.112e-028   -27.476   -27.675    -0.200
F                1.349e-004
   F-                    1.340e-004  1.191e-004    -3.873    -3.924    -0.051
   CaF+                  5.976e-007  5.327e-007    -6.224    -6.274    -0.050
   NaF                   2.903e-007  2.903e-007    -6.537    -6.537     0.000
   MgF+                  9.041e-009  8.044e-009    -8.044    -8.095    -0.051
   HF                    8.430e-011  8.430e-011   -10.074   -10.074     0.000
   NiF+                  5.370e-011  4.682e-011   -10.270   -10.330    -0.060
   ZnF+                  1.696e-011  1.479e-011   -10.771   -10.830    -0.060
   MnF+                  9.393e-012  8.373e-012   -11.027   -11.077    -0.050
   PbF+                  2.605e-012  2.271e-012   -11.584   -11.644    -0.060
   CuF+                  9.425e-014  8.217e-014   -13.026   -13.085    -0.060
   HF2-                  4.307e-014  3.817e-014   -13.366   -13.418    -0.052
   CdF+                  2.266e-014  1.976e-014   -13.645   -13.704    -0.060
   PbF2                  5.322e-015  5.322e-015   -14.274   -14.274     0.000
   AlF3                  1.431e-016  1.431e-016   -15.844   -15.844     0.000
   AlF2+                 1.069e-016  9.545e-017   -15.971   -16.020    -0.049
   AlF4-                 9.598e-018  8.539e-018   -17.018   -17.069    -0.051
   CdF2                  4.694e-018  4.694e-018   -17.328   -17.328     0.000
   AlF+2                 3.171e-018  2.013e-018   -17.499   -17.696    -0.197
   PbF3-                 1.379e-018  1.202e-018   -17.861   -17.920    -0.060
   FeF2+                 5.140e-020  4.582e-020   -19.289   -19.339    -0.050
   FeF+2                 2.278e-020  1.438e-020   -19.643   -19.842    -0.200
   H2F2                  1.904e-020  1.904e-020   -19.720   -19.720     0.000
   FeF3                  7.698e-021  7.698e-021   -20.114   -20.114     0.000
   PbF4-2                1.185e-022  6.851e-023   -21.926   -22.164    -0.238
   SiF6-2                7.296e-034  4.606e-034   -33.137   -33.337    -0.200
Fe(2)            3.699e-013
   Fe+2                  2.051e-013  1.185e-013   -12.688   -12.926    -0.238
   FeOH+                 1.113e-013  9.925e-014   -12.953   -13.003    -0.050
   FeSO4                 3.547e-014  3.547e-014   -13.450   -13.450     0.000
   Fe(OH)3-              1.237e-014  1.103e-014   -13.908   -13.958    -0.050
   FeHCO3+               3.639e-015  3.256e-015   -14.439   -14.487    -0.048
   Fe(OH)2               1.658e-015  1.658e-015   -14.780   -14.780     0.000
   FeHPO4                2.755e-016  2.755e-016   -15.560   -15.560     0.000
   FeH2PO4+              2.934e-019  2.619e-019   -18.533   -18.582    -0.049
Fe(3)            8.962e-007
   Fe(OH)4-              6.061e-007  5.411e-007    -6.217    -6.267    -0.049
   Fe(OH)3               2.763e-007  2.763e-007    -6.559    -6.559     0.000
   Fe(OH)2+              1.371e-008  1.223e-008    -7.863    -7.912    -0.049
   FeOH+2                2.369e-015  1.495e-015   -14.625   -14.825    -0.200
   FeHPO4+               5.950e-019  5.311e-019   -18.226   -18.275    -0.049
   FeF2+                 5.140e-020  4.582e-020   -19.289   -19.339    -0.050
   FeF+2                 2.278e-020  1.438e-020   -19.643   -19.842    -0.200
   FeF3                  7.698e-021  7.698e-021   -20.114   -20.114     0.000
   FeSO4+                1.690e-021  1.506e-021   -20.772   -20.822    -0.050
   Fe+3                  3.183e-022  1.101e-022   -21.497   -21.958    -0.461
   Fe(SO4)2-             4.502e-023  3.926e-023   -22.347   -22.406    -0.060
   FeCl+2                4.904e-024  3.096e-024   -23.309   -23.509    -0.200
   FeNO3+2               1.531e-024  8.850e-025   -23.815   -24.053    -0.238
   FeH2PO4+2             1.452e-026  9.219e-027   -25.838   -26.035    -0.197
   FeCl2+                1.444e-026  1.287e-026   -25.840   -25.890    -0.050
```

```
   Fe2(OH)2+4            6.636e-028  7.404e-029   -27.178   -28.131    -0.952
   FeCl3                 1.199e-030  1.199e-030   -29.921   -29.921     0.000
   Fe3(OH)4+5            4.029e-034  1.309e-035   -33.395   -34.883    -1.488
H(0)            3.233e-030
   H2                    1.617e-030  1.622e-030   -29.791   -29.790     0.001
K               5.837e-003
   K+                    5.787e-003  5.144e-003    -2.238    -2.289    -0.051
   KSO4-                 4.973e-005  4.439e-005    -4.303    -4.353    -0.049
   KHPO4-                2.552e-008  2.278e-008    -7.593    -7.642    -0.049
Mg              1.236e-006
   Mg+2                  9.649e-007  6.021e-007    -6.016    -6.220    -0.205
   MgSO4                 1.336e-007  1.336e-007    -6.874    -6.874     0.000
   MgCO3                 1.070e-007  1.070e-007    -6.971    -6.971     0.000
   MgHCO3+               1.514e-008  1.344e-008    -7.820    -7.872    -0.052
   MgF+                  9.041e-009  8.044e-009    -8.044    -8.095    -0.051
   MgOH+                 5.625e-009  5.041e-009    -8.250    -8.298    -0.048
   MgHPO4                2.218e-010  2.218e-010    -9.654    -9.654     0.000
   MgPO4-                1.564e-011  1.396e-011   -10.806   -10.855    -0.049
   MgH2PO4+              1.433e-013  1.280e-013   -12.844   -12.893    -0.049
Mn(2)           3.644e-009
   Mn+2                  3.056e-009  1.766e-009    -8.515    -8.753    -0.238
   MnSO4                 3.829e-010  3.829e-010    -9.417    -9.417     0.000
   MnOH+                 1.047e-010  9.330e-011    -9.980   -10.030    -0.050
   MnHCO3+               8.625e-011  7.688e-011   -10.064   -10.114    -0.050
   MnF+                  9.393e-012  8.373e-012   -11.027   -11.077    -0.050
   MnNO3+                2.580e-012  2.250e-012   -11.588   -11.648    -0.060
   MnCl+                 2.322e-012  2.070e-012   -11.634   -11.684    -0.050
   Mn(NO3)2              4.541e-015  4.541e-015   -14.343   -14.343     0.000
   MnCl2                 2.722e-015  2.722e-015   -14.565   -14.565     0.000
   Mn(OH)3-              2.861e-016  2.550e-016   -15.543   -15.593    -0.050
   MnCl3-                7.830e-019  6.979e-019   -18.106   -18.156    -0.050
   Mn(OH)4-2             2.743e-020  1.731e-020   -19.562   -19.762    -0.200
Mn(3)           2.280e-030
   Mn+3                  2.280e-030  7.889e-031   -29.642   -30.103    -0.461
Mn(6)           3.839e-037
   MnO4-2                3.839e-037  2.423e-037   -36.416   -36.616    -0.200
Mn(7)           0.000e+000
   MnO4-                 0.000e+000  0.000e+000   -41.934   -41.988    -0.053
N(-3)           1.000e-005
   NH3                   5.093e-006  5.093e-006    -5.293    -5.293     0.000
   NH4+                  4.845e-006  4.275e-006    -5.315    -5.369    -0.054
   NH4SO4-               6.265e-008  5.584e-008    -7.203    -7.253    -0.050
   CaNH3+2               4.547e-009  2.628e-009    -8.342    -8.580    -0.238
   NiNH3+2               7.407e-011  4.281e-011   -10.130   -10.368    -0.238
   CuNH3+2               9.862e-013  5.700e-013   -12.006   -12.244    -0.238
   Ni(NH3)2+2            5.453e-014  3.151e-014   -13.263   -13.502    -0.238
   Ca(NH3)2+2            9.219e-015  5.328e-015   -14.035   -14.273    -0.238
N(5)            9.054e-004
   NO3-                  9.042e-004  8.037e-004    -3.044    -3.095    -0.051
   CaNO3+                1.195e-006  1.042e-006    -5.923    -5.982    -0.060
   NiNO3+                3.624e-011  3.160e-011   -10.441   -10.500    -0.060
   ZnNO3+                1.441e-011  1.257e-011   -10.841   -10.901    -0.060
   PbNO3+                3.690e-012  3.217e-012   -11.433   -11.493    -0.060
   MnNO3+                2.580e-012  2.250e-012   -11.588   -11.648    -0.060
   CuNO3+                3.188e-014  2.780e-014   -13.496   -13.556    -0.060
   CdNO3+                3.052e-014  2.661e-014   -13.515   -13.575    -0.060
   Mn(NO3)2              4.541e-015  4.541e-015   -14.343   -14.343     0.000
   Pb(NO3)2              4.391e-015  4.391e-015   -14.357   -14.357     0.000
   Zn(NO3)2              2.015e-015  2.015e-015   -14.696   -14.696     0.000
   Cd(NO3)2              1.072e-017  1.072e-017   -16.970   -16.970     0.000
   Cu(NO3)2              2.812e-018  2.812e-018   -17.551   -17.551     0.000
   FeNO3+2               1.531e-024  8.850e-025   -23.815   -24.053    -0.238
Na              4.398e-003
   Na+                   4.347e-003  3.863e-003    -2.362    -2.413    -0.051
   NaSO4-                2.833e-005  2.529e-005    -4.548    -4.597    -0.049
   NaCO3-                1.722e-005  1.537e-005    -4.764    -4.813    -0.049
   NaHCO3                4.740e-006  4.740e-006    -5.324    -5.324     0.000
   NaF                   2.903e-007  2.903e-007    -6.537    -6.537     0.000
```

```
   NaHPO4-               2.969e-008  2.650e-008    -7.527    -7.577    -0.049
Ni              1.706e-007
   NiCO3                 1.248e-007  1.248e-007    -6.904    -6.904     0.000
   Ni+2                  2.509e-008  1.565e-008    -7.601    -7.805    -0.205
   Ni(OH)2               6.923e-009  6.923e-009    -8.160    -8.160     0.000
   NiHCO3+               4.828e-009  4.210e-009    -8.316    -8.376    -0.060
   NiOH+                 4.753e-009  4.144e-009    -8.323    -8.383    -0.060
   NiSO4                 3.807e-009  3.807e-009    -8.419    -8.419     0.000
   Ni(OH)3-              1.670e-010  1.456e-010    -9.777    -9.837    -0.060
   NiNH3+2               7.407e-011  4.281e-011   -10.130   -10.368    -0.238
   NiF+                  5.370e-011  4.682e-011   -10.270   -10.330    -0.060
   NiCl+                 4.276e-011  3.728e-011   -10.369   -10.428    -0.060
   NiNO3+                3.624e-011  3.160e-011   -10.441   -10.500    -0.060
   Ni(SO4)2-2            2.659e-013  1.537e-013   -12.575   -12.813    -0.238
   Ni(NH3)2+2            5.453e-014  3.151e-014   -13.263   -13.502    -0.238
   NiCl2                 1.748e-016  1.748e-016   -15.758   -15.758     0.000
O(0)            3.840e-033
   O2                    1.920e-033  1.926e-033   -32.717   -32.715     0.001
P               1.777e-006
   HPO4-2                9.249e-007  5.839e-007    -6.034    -6.234    -0.200
   CaPO4-                6.812e-007  6.081e-007    -6.167    -6.216    -0.049
   CaHPO4                1.094e-007  1.094e-007    -6.961    -6.961     0.000
   NaHPO4-               2.969e-008  2.650e-008    -7.527    -7.577    -0.049
   KHPO4-                2.552e-008  2.278e-008    -7.593    -7.642    -0.049
   H2PO4-                4.939e-009  4.409e-009    -8.306    -8.356    -0.049
   PO4-3                 1.487e-009  5.144e-010    -8.828    -9.289    -0.461
   MgHPO4                2.218e-010  2.218e-010    -9.654    -9.654     0.000
   CaH2PO4+              4.532e-011  4.046e-011   -10.344   -10.393    -0.049
   MgPO4-                1.564e-011  1.396e-011   -10.806   -10.855    -0.049
   MgH2PO4+              1.433e-013  1.280e-013   -12.844   -12.893    -0.049
   H3PO4                 2.967e-016  2.967e-016   -15.528   -15.528     0.000
   FeHPO4                2.755e-016  2.755e-016   -15.560   -15.560     0.000
   FeHPO4+               5.950e-019  5.311e-019   -18.226   -18.275    -0.049
   FeH2PO4+              2.934e-019  2.619e-019   -18.533   -18.582    -0.049
   FeH2PO4+2             1.452e-026  9.219e-027   -25.838   -26.035    -0.197
Pb              3.865e-007
   Pb(CO3)2-2            1.854e-007  1.071e-007    -6.732    -6.970    -0.238
   PbCO3                 1.738e-007  1.738e-007    -6.760    -6.760     0.000
   PbOH+                 1.640e-008  1.430e-008    -7.785    -7.845    -0.060
   Pb(OH)2               9.508e-009  9.508e-009    -8.022    -8.022     0.000
   PbHCO3+               5.031e-010  4.387e-010    -9.298    -9.358    -0.060
   Pb+2                  4.338e-010  2.706e-010    -9.363    -9.568    -0.205
   Pb(OH)3-              2.293e-010  2.000e-010    -9.640    -9.699    -0.060
   PbSO4                 1.616e-010  1.616e-010    -9.792    -9.792     0.000
   PbCl+                 1.025e-011  8.940e-012   -10.989   -11.049    -0.060
   PbNO3+                3.690e-012  3.217e-012   -11.433   -11.493    -0.060
   PbF+                  2.605e-012  2.271e-012   -11.584   -11.644    -0.060
   Pb(SO4)2-2            2.054e-012  1.187e-012   -11.687   -11.926    -0.238
   Pb(OH)4-2             1.782e-012  1.030e-012   -11.749   -11.987    -0.238
   PbCl2                 3.718e-014  3.718e-014   -13.430   -13.430     0.000
   PbF2                  5.322e-015  5.322e-015   -14.274   -14.274     0.000
   Pb(NO3)2              4.391e-015  4.391e-015   -14.357   -14.357     0.000
   Pb3(OH)4+2            8.447e-016  4.882e-016   -15.073   -15.311    -0.238
   Pb2OH+3               2.106e-016  6.133e-017   -15.677   -16.212    -0.536
   PbCl3-                1.580e-017  1.378e-017   -16.801   -16.861    -0.060
   PbF3-                 1.379e-018  1.202e-018   -17.861   -17.920    -0.060
   PbCl4-2               1.014e-020  5.863e-021   -19.994   -20.232    -0.238
   Pb4(OH)4+4            9.407e-021  1.049e-021   -20.027   -20.979    -0.952
   PbF4-2                1.185e-022  6.851e-023   -21.926   -22.164    -0.238
S(6)            2.146e-003
   SO4-2                 1.954e-003  1.219e-003    -2.709    -2.914    -0.205
   CaSO4                 1.145e-004  1.145e-004    -3.941    -3.941     0.000
   KSO4-                 4.973e-005  4.439e-005    -4.303    -4.353    -0.049
   NaSO4-                2.833e-005  2.529e-005    -4.548    -4.597    -0.049
   MgSO4                 1.336e-007  1.336e-007    -6.874    -6.874     0.000
   NH4SO4-               6.265e-008  5.584e-008    -7.203    -7.253    -0.050
   NiSO4                 3.807e-009  3.807e-009    -8.419    -8.419     0.000
   ZnSO4                 1.660e-009  1.660e-009    -8.780    -8.780     0.000
```

```
   MnSO4                 3.829e-010  3.829e-010    -9.417    -9.417     0.000
   PbSO4                 1.616e-010  1.616e-010    -9.792    -9.792     0.000
   HSO4-                 6.409e-011  5.702e-011   -10.193   -10.244    -0.051
   Zn(SO4)2-2            3.050e-011  1.763e-011   -10.516   -10.754    -0.238
   CuSO4                 3.054e-012  3.054e-012   -11.515   -11.515     0.000
   CdSO4                 2.992e-012  2.992e-012   -11.524   -11.524     0.000
   Pb(SO4)2-2            2.054e-012  1.187e-012   -11.687   -11.926    -0.238
   Ni(SO4)2-2            2.659e-013  1.537e-013   -12.575   -12.813    -0.238
   Cd(SO4)2-2            8.512e-014  4.920e-014   -13.070   -13.308    -0.238
   FeSO4                 3.547e-014  3.547e-014   -13.450   -13.450     0.000
   AlSO4+                1.798e-020  1.600e-020   -19.745   -19.796    -0.051
   FeSO4+                1.690e-021  1.506e-021   -20.772   -20.822    -0.050
   Al(SO4)2-             2.349e-022  2.090e-022   -21.629   -21.680    -0.051
   Fe(SO4)2-             4.502e-023  3.926e-023   -22.347   -22.406    -0.060
Si              2.715e-003
   H4SiO4                2.025e-003  2.031e-003    -2.694    -2.692     0.001
   H3SiO4-               6.907e-004  6.133e-004    -3.161    -3.212    -0.052
   H2SiO4-2              1.273e-007  8.086e-008    -6.895    -7.092    -0.197
   SiF6-2                7.296e-034  4.606e-034   -33.137   -33.337    -0.200
Zn              1.531e-007
   ZnCO3                 7.654e-008  7.654e-008    -7.116    -7.116     0.000
   Zn(OH)2               4.363e-008  4.363e-008    -7.360    -7.360     0.000
   ZnOH+                 1.501e-008  1.309e-008    -7.824    -7.883    -0.060
   Zn+2                  9.976e-009  6.225e-009    -8.001    -8.206    -0.205
   Zn(OH)3-              5.275e-009  4.599e-009    -8.278    -8.337    -0.060
   ZnSO4                 1.660e-009  1.660e-009    -8.780    -8.780     0.000
   ZnHCO3+               4.925e-010  4.294e-010    -9.308    -9.367    -0.060
   ZnOHCl                4.008e-010  4.008e-010    -9.397    -9.397     0.000
   Zn(SO4)2-2            3.050e-011  1.763e-011   -10.516   -10.754    -0.238
   ZnF+                  1.696e-011  1.479e-011   -10.771   -10.830    -0.060
   ZnCl+                 1.639e-011  1.456e-011   -10.785   -10.837    -0.052
   ZnNO3+                1.441e-011  1.257e-011   -10.841   -10.901    -0.060
   Zn(OH)4-2             6.662e-012  3.850e-012   -11.176   -11.414    -0.238
   ZnCl2                 2.148e-014  2.148e-014   -13.668   -13.668     0.000
   Zn(NO3)2              2.015e-015  2.015e-015   -14.696   -14.696     0.000
   ZnCl3-                1.789e-017  1.588e-017   -16.747   -16.799    -0.052
   ZnCl4-2               1.171e-020  7.393e-021   -19.931   -20.131    -0.200

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -3.61    7.19   10.80  Al(OH)3
        Al2O3            -5.28   14.38   19.65  Al2O3
        Al4(OH)10SO4    -15.50    7.20   22.70  Al4(OH)10SO4
        AlOHSO4         -11.14  -14.37   -3.23  AlOHSO4
        Alunite         -13.11  -14.51   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -4.69  -12.48   -7.79  PbSO4
        Anhydrite        -1.94   -6.30   -4.36  CaSO4
        Antlerite        -7.31    1.48    8.79  Cu3(OH)4SO4
        Aragonite         1.24   -7.06   -8.30  CaCO3
        Artinite         -7.07    2.53    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -4.38    3.01    7.39  Cu2(OH)3Cl
        Azurite          -4.68  -21.58  -16.91  Cu3(OH)2(CO3)2
        Bianchite        -9.36  -11.12   -1.76  ZnSO4:6H2O
        Birnessite       -6.91   11.18   18.09  MnO2
        Bixbyite         -3.64   -4.29   -0.64  Mn2O3
        Boehmite         -1.39    7.19    8.58  AlOOH
        Brochantite      -6.06    9.16   15.22  Cu4(OH)6SO4
        Brucite          -4.42   12.42   16.84  Mg(OH)2
        Bunsenite        -1.61   10.83   12.45  NiO
        Ca3(PO4)2(beta)   0.18  -28.74  -28.92  Ca3(PO4)2
        Ca4H(PO4)3:3H2O  -3.66  -50.74  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -2.72  -22.00  -19.27  CaHPO4
        CaHPO4:2H2O      -3.00  -22.00  -19.00  CaHPO4:2H2O
        Calcite           1.42   -7.06   -8.48  CaCO3
        Cd(OH)2          -5.98    7.66   13.64  Cd(OH)2
        Cd(OH)2(am)      -6.07    7.66   13.73  Cd(OH)2
```

```
        Cd3(OH)2(SO4)2  -26.84  -20.13    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -21.13    1.43   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -18.92  -51.52  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -19.32    9.08   28.40  Cd4(OH)6SO4
        CdCl2           -16.38  -17.04   -0.66  CdCl2
        CdCl2:1H2O      -15.35  -17.04   -1.69  CdCl2:1H2O
        CdCl2:2.5H2O    -15.13  -17.04   -1.91  CdCl2:2.5H2O
        CdF2            -17.62  -18.83   -1.21  CdF2
        Cdmetal(alpha)  -32.49  -18.98   13.51  Cd
        Cdmetal(gamma)  -32.60  -18.98   13.62  Cd
        CdOHCl           -8.23   -4.69    3.54  CdOHCl
        CdSO4           -13.72  -13.89   -0.17  CdSO4
        CdSO4:1H2O      -12.17  -13.89   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -12.02  -13.89   -1.87  CdSO4:2.67H2O
        Cerrusite        -0.11  -13.24  -13.13  PbCO3
        CH4(g)          -87.82 -128.87  -41.05  CH4
        Chalcanthite    -11.24  -13.88   -2.64  CuSO4:5H2O
        Chalcedony        0.86   -2.69   -3.55  SiO2
        Chrysotile       -0.33   31.87   32.20  Mg3Si2O5(OH)4
        CO2(g)           -4.16  -22.31  -18.15  CO2
        Cotunnite       -10.85  -15.63   -4.78  PbCl2
        Cristobalite      0.66   -2.69   -3.35  SiO2
        Cryolite        -17.72  -51.56  -33.84  Na3AlF6
        Cu(OH)2          -1.00    7.68    8.67  Cu(OH)2
        Cu2(OH)3NO3      -6.31    2.94    9.25  Cu2(OH)3NO3
        Cu2SO4          -25.51  -27.46   -1.95  Cu2SO4
        Cu3(PO4)2       -14.61  -51.46  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -16.34  -51.46  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -3.13  -14.63  -11.50  CuCO3
        CuF             -11.29  -16.20   -4.91  CuF
        CuF2            -19.92  -18.81    1.12  CuF2
        CuF2:2H2O       -14.26  -18.81   -4.55  CuF2:2H2O
        Cumetal          -7.52  -16.27   -8.76  Cu
        CuOCuSO4        -16.50   -6.20   10.30  CuOCuSO4
        Cupricferrite    13.69   19.68    5.99  CuFe2O4
        Cuprite          -4.50   -5.90   -1.41  Cu2O
        Cuprousferrite   11.97    3.05   -8.92  CuFeO2
        CuSO4           -16.81  -13.88    2.94  CuSO4
        Diaspore          0.31    7.19    6.87  AlOOH
        Dolomite(disordered)  -0.41  -16.95  -16.54  CaMg(CO3)2
        Dolomite(ordered)   0.14  -16.95  -17.09  CaMg(CO3)2
        Epsomite         -7.01   -9.14   -2.13  MgSO4:7H2O
        FCO3Apatite      22.36  -92.04 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
        Fe(OH)2          -7.85    5.71   13.56  Fe(OH)2
        Fe(OH)2.7Cl.3     5.34    2.30   -3.04  Fe(OH)2.7Cl.3
        Fe2(SO4)3       -48.92  -52.66   -3.73  Fe2(SO4)3
        Fe3(OH)8         -2.51   17.72   20.22  Fe3(OH)8
        Ferrihydrite      2.81    6.00    3.19  Fe(OH)3
        Fluorite         -0.74  -11.24  -10.50  CaF2
        Gibbsite         -1.10    7.19    8.29  Al(OH)3
        Goethite          5.51    6.00    0.49  FeOOH
        Goslarite        -9.11  -11.12   -2.01  ZnSO4:7H2O
        Greenalite       -9.05   11.76   20.81  Fe3Si2O5(OH)4
        Gypsum           -1.69   -6.30   -4.61  CaSO4:2H2O
        H-Jarosite      -13.00  -25.10  -12.10  (H3O)Fe3(SO4)2(OH)6
        Halite           -7.05   -5.44    1.60  NaCl
        Halloysite       -0.58    8.99    9.57  Al2Si2O5(OH)4
        Hausmannite      -4.73   56.30   61.03  Mn3O4
        Hematite         13.42   12.00   -1.42  Fe2O3
        Hercynite        -2.80   20.09   22.89  FeAl2O4
        Hinsdalite      -25.67  -28.17   -2.50  PbAl3PO4SO4(OH)6
        Huntite          -6.76  -36.73  -29.97  CaMg3(CO3)4
        Hydrocerrusite    1.37  -17.40  -18.77  Pb3(OH)2(CO3)2
        Hydromagnesite  -18.38  -27.14   -8.77  Mg5(CO3)4(OH)2:4H2O
        Hydroxylapatite   8.85  -35.48  -44.33  Ca5(PO4)3OH
        Hydroxylpyromorphite  -3.59  -66.38  -62.79  Pb5(PO4)3OH
        K-Alum          -23.72  -28.89   -5.17  KAl(SO4)2:12H2O
```

```
K-Jarosite       -3.27  -18.07  -14.80  KFe3(SO4)2(OH)6
Kaolinite         1.56    8.99    7.43  Al2Si2O5(OH)4
Langite          -8.33    9.16   17.49  Cu4(OH)6SO4:H2O
Larnakite        -2.97   -3.41   -0.43  PbO:PbSO4
Laurionite       -3.90   -3.28    0.62  PbOHCl
Lepidocrocite     4.63    6.00    1.37  FeOOH
Lime            -17.45   15.25   32.70  CaO
Litharge         -3.62    9.07   12.69  PbO
Maghemite         5.62   12.00    6.39  Fe2O3
Magnesioferrite   7.56   24.42   16.86  Fe2MgO4
Magnesite        -2.43   -9.89   -7.46  MgCO3
Magnetite        14.31   17.72    3.40  Fe3O4
Malachite        -1.65   -6.95   -5.31  Cu2(OH)2CO3
Manganite        -2.13   23.21   25.34  MnOOH
Massicot         -3.82    9.07   12.89  PbO
Matlockite       -7.55  -16.52   -8.97  PbClF
Melanothallite  -23.28  -17.02    6.26  CuCl2
Melanterite     -13.63  -15.84   -2.21  FeSO4:7H2O
Mg(OH)2(active)  -6.37   12.42   18.79  Mg(OH)2
Mg3(PO4)2       -13.96  -37.24  -23.28  Mg3(PO4)2
MgF2             -5.94  -14.07   -8.13  MgF2
MgHPO4:3H2O      -6.65  -24.83  -18.18  MgHPO4:3H2O
Minium          -19.67   53.86   73.52  Pb3O4
Mirabilite       -6.63   -7.74   -1.11  Na2SO4:10H2O
Mn2(SO4)3       -63.24  -68.95   -5.71  Mn2(SO4)3
Mn3(PO4)2       -21.01  -44.84  -23.83  Mn3(PO4)2
MnCl2:4H2O      -17.53  -14.82    2.72  MnCl2:4H2O
MnHPO4           -1.96  -27.36  -25.40  MnHPO4
MnSO4           -14.25  -11.67    2.58  MnSO4
Monteponite      -7.44    7.66   15.10  CdO
Morenosite       -8.58  -10.72   -2.14  NiSO4:7H2O
Na-Jarosite      -7.00  -18.20  -11.20  NaFe3(SO4)2(OH)6
Nantokite        -8.57  -15.30   -6.73  CuCl
Natron           -7.19   -8.50   -1.31  Na2CO3:10H2O
Nesquehonite     -5.22   -9.89   -4.67  MgCO3:3H2O
Ni(OH)2          -1.96   10.83   12.79  Ni(OH)2
Ni3(PO4)2       -10.69  -41.99  -31.30  Ni3(PO4)2
Ni4(OH)6SO4     -10.22   21.78   32.00  Ni4(OH)6SO4
NiCO3            -4.61  -11.48   -6.87  NiCO3
Nsutite          -6.33   11.18   17.50  MnO2
O2(g)           -29.81   53.28   83.09  O2
Otavite          -2.65  -14.65  -12.00  CdCO3
Pb(OH)2           0.92    9.07    8.15  Pb(OH)2
Pb10(OH)6O(CO3)6 -34.38  -43.14   -8.76  Pb10(OH)6O(CO3)6
Pb2(OH)3Cl       -3.00    5.79    8.79  Pb2(OH)3Cl
Pb2O(OH)2        -8.04   18.14   26.19  Pb2O(OH)2
Pb2O3           -16.26   44.78   61.04  Pb2O3
Pb2OCO3          -3.61   -4.17   -0.56  Pb2OCO3
Pb3(PO4)2        -3.75  -47.28  -43.53  Pb3(PO4)2
Pb3O2CO3         -6.11    4.91   11.02  Pb3O2CO3
Pb3O2SO4         -5.02    5.66   10.69  Pb3O2SO4
Pb4(OH)6SO4      -6.37   14.73   21.10  Pb4(OH)6SO4
Pb4O3SO4         -7.14   14.74   21.88  Pb4O3SO4
PbF2             -9.98  -17.42   -7.44  PbF2
PbHPO4           -4.37  -28.18  -23.81  PbHPO4
Pbmetal         -21.81  -17.57    4.25  Pb
PbO:0.3H2O       -3.91    9.07   12.98  PbO:0.33H2O
Periclase        -9.16   12.42   21.58  MgO
Phosgenite       -9.06  -28.87  -19.81  PbCl2:PbCO3
Plattnerite     -13.89   35.71   49.60  PbO2
Plumbgummite    -11.07  -43.86  -32.79  PbAl3(PO4)2(OH)5:H2O
Portlandite      -7.55   15.25   22.80  Ca(OH)2
Pyrochroite      -5.31    9.89   15.19  Mn(OH)2
Pyrolusite       -4.85   36.53   41.38  MnO2
Pyromorphite      5.69  -78.74  -84.43  Pb5(PO4)3Cl
Quartz            1.31   -2.69   -4.00  SiO2
Retgersite       -8.68  -10.72   -2.04  NiSO4:6H2O
Rhodochrosite    -1.84  -12.42  -10.58  MnCO3
```

```
        Sepiolite          1.00   16.76   15.76  Mg2Si3O7.5OH:3H2O
        Sepiolite(A)      -2.02   16.76   18.78  Mg2Si3O7.5OH:3H2O
        Siderite          -6.36  -16.60  -10.24  FeCO3
        SiO2(am-gel)       0.02   -2.69   -2.71  SiO2
        SiO2(am-ppt)       0.05   -2.69   -2.74  SiO2
        Smithsonite       -1.88  -11.88  -10.00  ZnCO3
        Spinel           -10.05   26.80   36.85  MgAl2O4
        Strengite         -4.85  -31.25  -26.40  FePO4:2H2O
        Tenorite           0.03    7.68    7.64  CuO
        Thenardite        -8.06   -7.74    0.32  Na2SO4
        Thermonatrite     -9.13   -8.50    0.64  Na2CO3:H2O
        Tsumebite         -1.64  -11.43   -9.79  Pb2CuPO4(OH)3:3H2O
        Vivianite        -21.36  -57.36  -36.00  Fe3(PO4)2:8H2O
        Zincite           -0.90   10.43   11.33  ZnO
        Zincosite        -15.05  -11.12    3.93  ZnSO4
        Zn(NO3)2:6H2O    -17.71  -14.40    3.32  Zn(NO3)2:6H2O
        Zn(OH)2           -1.77   10.43   12.20  Zn(OH)2
        Zn(OH)2(am)       -2.04   10.43   12.47  Zn(OH)2
        Zn(OH)2(beta)     -1.32   10.43   11.75  Zn(OH)2
        Zn(OH)2(epsilon)  -1.10   10.43   11.53  Zn(OH)2
        Zn(OH)2(gamma)    -1.30   10.43   11.73  Zn(OH)2
        Zn2(OH)2SO4       -8.19   -0.69    7.50  Zn2(OH)2SO4
        Zn2(OH)3Cl        -6.67    8.52   15.19  Zn2(OH)3Cl
        Zn3(PO4)2:4H2O    -7.78  -43.20  -35.42  Zn3(PO4)2:4H2O
        Zn3O(SO4)2       -30.72  -11.81   18.91  Zn3O(SO4)2
        Zn4(OH)6SO4       -8.22   20.18   28.40  Zn4(OH)6SO4
        Zn5(OH)8Cl2      -11.03   27.47   38.50  Zn5(OH)8Cl2
        ZnCl2            -21.32  -14.27    7.05  ZnCl2
        ZnCO3:1H2O        -1.62  -11.88  -10.26  ZnCO3:1H2O
        ZnF2             -15.52  -16.05   -0.53  ZnF2
        Znmetal          -41.99  -16.21   25.79  Zn
        ZnO(active)       -0.75   10.43   11.19  ZnO
        ZnSO4:1H2O       -10.48  -11.12   -0.64  ZnSO4:1H2O

Initial solution 7-FA 1808 h.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Al                 7.420e-007  7.420e-007
        C(4)               3.553e-003  3.553e-003
        Ca                 1.276e-003  1.276e-003
        Cd                 8.905e-011  8.905e-011
        Cl                 1.019e-003  1.019e-003
        Cu                 3.151e-008  3.151e-008
        F                  1.328e-004  1.328e-004
        Fe                 1.075e-006  1.075e-006
        K                  5.863e-003  5.863e-003
        Mg                 1.647e-006  1.647e-006
        Mn                 1.822e-009  1.822e-009
        N(-3)              1.644e-005  1.644e-005
        N(5)               9.570e-004  9.570e-004
        Na                 4.964e-003  4.964e-003
        Ni                 1.706e-007  1.706e-007
        P                  2.747e-006  2.747e-006
        Pb                 4.348e-007  4.348e-007
        S(6)               2.292e-003  2.292e-003
        Si                 2.516e-003  2.516e-003
        Zn                 1.531e-007  1.531e-007

----------------------------Description of solution----------------------------

                                       pH  =   9.260
                                       pe  =   4.000
                        Activity of water  =   1.000
                           Ionic strength  =  1.487e-002
                       Mass of water (kg)  =  1.000e+000
```

```
                  Total alkalinity (eq/kg)  =  4.743e-003
                        Total CO2 (mol/kg)  =  3.553e-003
                       Temperature (deg C)  =  25.000
                   Electrical balance (eq)  =  1.964e-003
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   8.50
                                Iterations  =  10
                                   Total H  = 1.110262e+002
                                   Total O  = 5.553963e+001

--------------------------------Redox couples-------------------------------

        Redox couple             pe  Eh (volts)

        N(-3)/N(5)          3.5662      0.2110

---------------------------Distribution of species----------------------------

                                                     Log       Log         Log
   Species                 Molality    Activity  Molality  Activity       Gamma

   OH-                   2.076e-005  1.832e-005    -4.683    -4.737      -0.054
   H+                    6.210e-010  5.495e-010    -9.207    -9.260      -0.053
   H2O                   5.551e+001  9.996e-001     1.744    -0.000       0.000
Al               7.420e-007
   Al(OH)4-              7.417e-007  6.571e-007    -6.130    -6.182      -0.053
   Al(OH)3               2.850e-010  2.850e-010    -9.545    -9.545       0.000
   Al(OH)2+              8.770e-013  7.797e-013   -12.057   -12.108      -0.051
   AlF3                  2.320e-016  2.320e-016   -15.635   -15.635       0.000
   AlF2+                 1.779e-016  1.581e-016   -15.750   -15.801      -0.051
   AlOH+2                8.578e-017  5.359e-017   -16.067   -16.271      -0.204
   AlF4-                 1.529e-017  1.355e-017   -16.816   -16.868      -0.053
   AlF+2                 5.457e-018  3.409e-018   -17.263   -17.467      -0.204
   AlSO4+                3.224e-020  2.856e-020   -19.492   -19.544      -0.053
   Al+3                  8.790e-021  2.926e-021   -20.056   -20.534      -0.478
   Al(SO4)2-             4.343e-022  3.848e-022   -21.362   -21.415      -0.053
C(4)             3.553e-003
   HCO3-                 2.936e-003  2.610e-003    -2.532    -2.583      -0.051
   CO3-2                 3.631e-004  2.227e-004    -3.440    -3.652      -0.212
   CaCO3                 1.931e-004  1.931e-004    -3.714    -3.714       0.000
   CaHCO3+               2.984e-005  2.659e-005    -4.525    -4.575      -0.050
   NaCO3-                2.024e-005  1.800e-005    -4.694    -4.745      -0.051
   NaHCO3                6.370e-006  6.370e-006    -5.196    -5.196       0.000
   H2CO3                 3.226e-006  3.226e-006    -5.491    -5.491       0.000
   Pb(CO3)2-2            2.185e-007  1.233e-007    -6.661    -6.909      -0.248
   PbCO3                 1.920e-007  1.920e-007    -6.717    -6.717       0.000
   MgCO3                 1.454e-007  1.454e-007    -6.837    -6.837       0.000
   NiCO3                 1.267e-007  1.267e-007    -6.897    -6.897       0.000
   ZnCO3                 8.575e-008  8.575e-008    -7.067    -7.067       0.000
   MgHCO3+               2.372e-008  2.097e-008    -7.625    -7.678      -0.054
   Cu(CO3)2-2            1.466e-008  8.275e-009    -7.834    -8.082      -0.248
   CuCO3                 1.380e-008  1.380e-008    -7.860    -7.860       0.000
   NiHCO3+               5.662e-009  4.907e-009    -8.247    -8.309      -0.062
   PbHCO3+               6.418e-010  5.563e-010    -9.193    -9.255      -0.062
   ZnHCO3+               6.373e-010  5.524e-010    -9.196    -9.258      -0.062
   CdCO3                 5.104e-011  5.104e-011   -10.292   -10.292       0.000
   MnHCO3+               5.057e-011  4.489e-011   -10.296   -10.348      -0.052
   Cd(CO3)2-2            1.493e-011  8.426e-012   -10.826   -11.074      -0.248
   CuHCO3+               2.001e-012  1.734e-012   -11.699   -11.761      -0.062
   CdHCO3+               6.895e-014  5.976e-014   -13.161   -13.224      -0.062
   FeHCO3+               8.656e-015  7.713e-015   -14.063   -14.113      -0.050
Ca               1.276e-003
   Ca+2                  8.919e-004  5.470e-004    -3.050    -3.262      -0.212
   CaCO3                 1.931e-004  1.931e-004    -3.714    -3.714       0.000
   CaSO4                 1.576e-004  1.576e-004    -3.803    -3.803       0.000
   CaHCO3+               2.984e-005  2.659e-005    -4.525    -4.575      -0.050
   CaNO3+                1.687e-006  1.462e-006    -5.773    -5.835      -0.062
   CaPO4-                1.121e-006  9.968e-007    -5.950    -6.001      -0.051
   CaF+                  7.836e-007  6.956e-007    -6.106    -6.158      -0.052
```

```
   CaOH+                 2.243e-007  1.999e-007    -6.649    -6.699    -0.050
   CaHPO4                2.059e-007  2.059e-007    -6.686    -6.686     0.000
   CaNH3+2               9.489e-009  5.356e-009    -8.023    -8.271    -0.248
   CaH2PO4+              9.833e-011  8.742e-011   -10.007   -10.058    -0.051
   Ca(NH3)2+2            2.938e-014  1.658e-014   -13.532   -13.780    -0.248
Cd              8.905e-011
   CdCO3                 5.104e-011  5.104e-011   -10.292   -10.292     0.000
   Cd+2                  1.640e-011  1.006e-011   -10.785   -10.998    -0.212
   Cd(CO3)2-2            1.493e-011  8.426e-012   -10.826   -11.074    -0.248
   CdSO4                 2.964e-012  2.964e-012   -11.528   -11.528     0.000
   CdOH+                 1.688e-012  1.463e-012   -11.773   -11.835    -0.062
   CdCl+                 9.994e-013  8.662e-013   -12.000   -12.062    -0.062
   CdOHCl                6.508e-013  6.508e-013   -12.187   -12.187     0.000
   Cd(OH)2               1.691e-013  1.691e-013   -12.772   -12.772     0.000
   Cd(SO4)2-2            8.907e-014  5.027e-014   -13.050   -13.299    -0.248
   CdHCO3+               6.895e-014  5.976e-014   -13.161   -13.224    -0.062
   CdNO3+                3.101e-014  2.688e-014   -13.508   -13.571    -0.062
   CdF+                  2.142e-014  1.857e-014   -13.669   -13.731    -0.062
   CdCl2                 3.257e-015  3.257e-015   -14.487   -14.487     0.000
   Cd(OH)3-              2.183e-016  1.892e-016   -15.661   -15.723    -0.062
   Cd(NO3)2              1.139e-017  1.139e-017   -16.943   -16.943     0.000
   CdF2                  4.317e-018  4.317e-018   -17.365   -17.365     0.000
   CdCl3-                2.139e-018  1.854e-018   -17.670   -17.732    -0.062
   Cd(OH)4-2             1.005e-021  5.672e-022   -20.998   -21.246    -0.248
   Cd2OH+3               2.671e-022  7.373e-023   -21.573   -22.132    -0.559
Cl              1.019e-003
   Cl-                   1.019e-003  9.020e-004    -2.992    -3.045    -0.053
   ZnOHCl                3.636e-010  3.636e-010    -9.439    -9.439     0.000
   NiCl+                 4.060e-011  3.519e-011   -10.391   -10.454    -0.062
   ZnCl+                 1.715e-011  1.516e-011   -10.766   -10.819    -0.054
   PbCl+                 1.059e-011  9.179e-012   -10.975   -11.037    -0.062
   MnCl+                 1.103e-012  9.788e-013   -11.958   -12.009    -0.052
   CdCl+                 9.994e-013  8.662e-013   -12.000   -12.062    -0.062
   CdOHCl                6.508e-013  6.508e-013   -12.187   -12.187     0.000
   CuCl                  5.855e-013  5.855e-013   -12.232   -12.232     0.000
   CuCl2-                1.248e-013  1.103e-013   -12.904   -12.957    -0.054
   PbCl2                 3.698e-014  3.698e-014   -13.432   -13.432     0.000
   ZnCl2                 2.168e-014  2.168e-014   -13.664   -13.664     0.000
   CuCl+                 1.702e-014  1.505e-014   -13.769   -13.822    -0.054
   CdCl2                 3.257e-015  3.257e-015   -14.487   -14.487     0.000
   MnCl2                 1.247e-015  1.247e-015   -14.904   -14.904     0.000
   NiCl2                 1.598e-016  1.598e-016   -15.796   -15.796     0.000
   CuCl3-2               3.427e-017  2.128e-017   -16.465   -16.672    -0.207
   ZnCl3-                1.757e-017  1.553e-017   -16.755   -16.809    -0.054
   PbCl3-                1.532e-017  1.328e-017   -16.815   -16.877    -0.062
   CuCl2                 4.707e-018  4.707e-018   -17.327   -17.327     0.000
   CdCl3-                2.139e-018  1.854e-018   -17.670   -17.732    -0.062
   MnCl3-                3.490e-019  3.098e-019   -18.457   -18.509    -0.052
   ZnCl4-2               1.128e-020  7.005e-021   -19.948   -20.155    -0.207
   PbCl4-2               9.702e-021  5.476e-021   -20.013   -20.262    -0.248
   CuCl3-                4.482e-023  3.963e-023   -22.348   -22.402    -0.054
   FeCl+2                9.566e-024  5.940e-024   -23.019   -23.226    -0.207
   FeCl2+                2.696e-026  2.393e-026   -25.569   -25.621    -0.052
   CuCl4-2               2.885e-028  1.791e-028   -27.540   -27.747    -0.207
   FeCl3                 2.159e-030  2.159e-030   -29.666   -29.666     0.000
Cu(1)           1.305e-012
   Cu+                   5.949e-013  5.156e-013   -12.226   -12.288    -0.062
   CuCl                  5.855e-013  5.855e-013   -12.232   -12.232     0.000
   CuCl2-                1.248e-013  1.103e-013   -12.904   -12.957    -0.054
   CuCl3-2               3.427e-017  2.128e-017   -16.465   -16.672    -0.207
Cu(2)           3.150e-008
   Cu(CO3)2-2            1.466e-008  8.275e-009    -7.834    -8.082    -0.248
   CuCO3                 1.380e-008  1.380e-008    -7.860    -7.860     0.000
   Cu(OH)2               2.228e-009  2.228e-009    -8.652    -8.652     0.000
   CuOH+                 6.898e-010  6.098e-010    -9.161    -9.215    -0.054
   Cu(OH)3-              9.659e-011  8.372e-011   -10.015   -10.077    -0.062
   Cu+2                  1.717e-011  1.053e-011   -10.765   -10.978    -0.212
   CuSO4                 3.032e-012  3.032e-012   -11.518   -11.518     0.000
```

```
   CuHCO3+              2.001e-012  1.734e-012   -11.699   -11.761    -0.062
   CuNH3+2              1.485e-012  8.379e-013   -11.828   -12.077    -0.248
   CuF+                 8.929e-014  7.740e-014   -13.049   -13.111    -0.062
   CuNO3+               3.247e-014  2.814e-014   -13.489   -13.551    -0.062
   Cu(OH)4-2            2.138e-014  1.207e-014   -13.670   -13.918    -0.248
   CuCl+                1.702e-014  1.505e-014   -13.769   -13.822    -0.054
   Cu2(OH)2+2           1.655e-014  9.340e-015   -13.781   -14.030    -0.248
   CuCl2                4.707e-018  4.707e-018   -17.327   -17.327     0.000
   Cu(NO3)2             2.995e-018  2.995e-018   -17.524   -17.524     0.000
   CuCl3-               4.482e-023  3.963e-023   -22.348   -22.402    -0.054
   CuCl4-2              2.885e-028  1.791e-028   -27.540   -27.747    -0.207
F               1.328e-004
   F-                   1.317e-004  1.165e-004    -3.881    -3.934    -0.053
   CaF+                 7.836e-007  6.956e-007    -6.106    -6.158    -0.052
   NaF                  3.190e-007  3.190e-007    -6.496    -6.496     0.000
   MgF+                 1.159e-008  1.026e-008    -7.936    -7.989    -0.053
   HF                   9.471e-011  9.471e-011   -10.024   -10.024     0.000
   NiF+                 5.149e-011  4.463e-011   -10.288   -10.350    -0.062
   ZnF+                 1.795e-011  1.556e-011   -10.746   -10.808    -0.062
   MnF+                 4.504e-012  3.998e-012   -11.346   -11.398    -0.052
   PbF+                 2.717e-012  2.355e-012   -11.566   -11.628    -0.062
   CuF+                 8.929e-014  7.740e-014   -13.049   -13.111    -0.062
   HF2-                 4.756e-014  4.195e-014   -13.323   -13.377    -0.054
   CdF+                 2.142e-014  1.857e-014   -13.669   -13.731    -0.062
   PbF2                 5.400e-015  5.400e-015   -14.268   -14.268     0.000
   AlF3                 2.320e-016  2.320e-016   -15.635   -15.635     0.000
   AlF2+                1.779e-016  1.581e-016   -15.750   -15.801    -0.051
   AlF4-                1.529e-017  1.355e-017   -16.816   -16.868    -0.053
   AlF+2                5.457e-018  3.409e-018   -17.263   -17.467    -0.204
   CdF2                 4.317e-018  4.317e-018   -17.365   -17.365     0.000
   PbF3-                1.377e-018  1.193e-018   -17.861   -17.923    -0.062
   FeF2+                9.785e-020  8.686e-020   -19.009   -19.061    -0.052
   FeF+2                4.487e-020  2.786e-020   -19.348   -19.555    -0.207
   H2F2                 2.403e-020  2.403e-020   -19.619   -19.619     0.000
   FeF3                 1.428e-020  1.428e-020   -19.845   -19.845     0.000
   PbF4-2               1.179e-022  6.655e-023   -21.928   -22.177    -0.248
   SiF6-2               1.083e-033  6.725e-034   -32.965   -33.172    -0.207
Fe(2)           7.093e-013
   Fe+2                 4.159e-013  2.347e-013   -12.381   -12.629    -0.248
   FeOH+                1.928e-013  1.712e-013   -12.715   -12.767    -0.052
   FeSO4                7.244e-014  7.244e-014   -13.140   -13.140     0.000
   Fe(OH)3-             1.625e-014  1.442e-014   -13.789   -13.841    -0.052
   FeHCO3+              8.656e-015  7.713e-015   -14.063   -14.113    -0.050
   Fe(OH)2              2.490e-015  2.490e-015   -14.604   -14.604     0.000
   FeHPO4               7.694e-016  7.694e-016   -15.114   -15.114     0.000
   FeH2PO4+             9.446e-019  8.398e-019   -18.025   -18.076    -0.051
Fe(3)           1.075e-006
   Fe(OH)4-             6.934e-007  6.164e-007    -6.159    -6.210    -0.051
   Fe(OH)3              3.615e-007  3.615e-007    -6.442    -6.442     0.000
   Fe(OH)2+             2.067e-008  1.837e-008    -7.685    -7.736    -0.051
   FeOH+2               4.153e-015  2.579e-015   -14.382   -14.589    -0.207
   FeHPO4+              1.668e-018  1.483e-018   -17.778   -17.829    -0.051
   FeF2+                9.785e-020  8.686e-020   -19.009   -19.061    -0.052
   FeF+2                4.487e-020  2.786e-020   -19.348   -19.555    -0.207
   FeF3                 1.428e-020  1.428e-020   -19.845   -19.845     0.000
   FeSO4+               3.465e-021  3.076e-021   -20.460   -20.512    -0.052
   Fe+3                 6.551e-022  2.180e-022   -21.184   -21.661    -0.478
   Fe(SO4)2-            9.540e-023  8.269e-023   -22.020   -22.083    -0.062
   FeCl+2               9.566e-024  5.940e-024   -23.019   -23.226    -0.207
   FeNO3+2              3.266e-024  1.843e-024   -23.486   -23.734    -0.248
   FeH2PO4+2            4.731e-026  2.956e-026   -25.325   -25.529    -0.204
   FeCl2+               2.696e-026  2.393e-026   -25.569   -25.621    -0.052
   Fe2(OH)2+4           2.170e-027  2.202e-028   -26.664   -27.657    -0.994
   FeCl3                2.159e-030  2.159e-030   -29.666   -29.666     0.000
   Fe3(OH)4+5           2.087e-033  5.848e-035   -32.680   -34.233    -1.553
H(0)            4.261e-030
   H2                   2.131e-030  2.138e-030   -29.671   -29.670     0.001
K               5.863e-003
```

```
   K+                    5.812e-003  5.143e-003    -2.236    -2.289    -0.053
   KSO4-                 5.149e-005  4.578e-005    -4.288    -4.339    -0.051
   KHPO4-                3.613e-008  3.213e-008    -7.442    -7.493    -0.051
Mg              1.647e-006
   Mg+2                  1.280e-006  7.852e-007    -5.893    -6.105    -0.212
   MgSO4                 1.796e-007  1.796e-007    -6.746    -6.746     0.000
   MgCO3                 1.454e-007  1.454e-007    -6.837    -6.837     0.000
   MgHCO3+               2.372e-008  2.097e-008    -7.625    -7.678    -0.054
   MgF+                  1.159e-008  1.026e-008    -7.936    -7.989    -0.053
   MgOH+                 6.413e-009  5.725e-009    -8.193    -8.242    -0.049
   MgHPO4                4.079e-010  4.079e-010    -9.389    -9.389     0.000
   MgPO4-                2.516e-011  2.237e-011   -10.599   -10.650    -0.051
   MgH2PO4+              3.039e-013  2.702e-013   -12.517   -12.568    -0.051
Mn(2)           1.822e-009
   Mn+2                  1.527e-009  8.619e-010    -8.816    -9.065    -0.248
   MnSO4                 1.927e-010  1.927e-010    -9.715    -9.715     0.000
   MnHCO3+               5.057e-011  4.489e-011   -10.296   -10.348    -0.052
   MnOH+                 4.467e-011  3.966e-011   -10.350   -10.402    -0.052
   MnF+                  4.504e-012  3.998e-012   -11.346   -11.398    -0.052
   MnNO3+                1.332e-012  1.155e-012   -11.875   -11.937    -0.062
   MnCl+                 1.103e-012  9.788e-013   -11.958   -12.009    -0.052
   Mn(NO3)2              2.452e-015  2.452e-015   -14.610   -14.610     0.000
   MnCl2                 1.247e-015  1.247e-015   -14.904   -14.904     0.000
   Mn(OH)3-              9.263e-017  8.222e-017   -16.033   -16.085    -0.052
   MnCl3-                3.490e-019  3.098e-019   -18.457   -18.509    -0.052
   Mn(OH)4-2             7.831e-021  4.862e-021   -20.106   -20.313    -0.207
Mn(3)           1.157e-030
   Mn+3                  1.157e-030  3.850e-031   -29.937   -30.415    -0.478
Mn(6)           6.307e-038
   MnO4-2                6.307e-038  3.916e-038   -37.200   -37.407    -0.207
Mn(7)           0.000e+000
   MnO4-                 0.000e+000  0.000e+000   -42.724   -42.779    -0.055
N(-3)           1.644e-005
   NH4+                  8.537e-006  7.496e-006    -5.069    -5.125    -0.056
   NH3                   7.778e-006  7.778e-006    -5.109    -5.109     0.000
   NH4SO4-               1.138e-007  1.010e-007    -6.944    -6.996    -0.052
   CaNH3+2               9.489e-009  5.356e-009    -8.023    -8.271    -0.248
   NiNH3+2               1.128e-010  6.369e-011    -9.948   -10.196    -0.248
   CuNH3+2               1.485e-012  8.379e-013   -11.828   -12.077    -0.248
   Ni(NH3)2+2            1.269e-013  7.160e-014   -12.897   -13.145    -0.248
   Ca(NH3)2+2            2.938e-014  1.658e-014   -13.532   -13.780    -0.248
N(5)            9.570e-004
   NO3-                  9.553e-004  8.454e-004    -3.020    -3.073    -0.053
   CaNO3+                1.687e-006  1.462e-006    -5.773    -5.835    -0.062
   NiNO3+                3.736e-011  3.238e-011   -10.428   -10.490    -0.062
   ZnNO3+                1.639e-011  1.421e-011   -10.785   -10.847    -0.062
   PbNO3+                4.137e-012  3.586e-012   -11.383   -11.445    -0.062
   MnNO3+                1.332e-012  1.155e-012   -11.875   -11.937    -0.062
   CuNO3+                3.247e-014  2.814e-014   -13.489   -13.551    -0.062
   CdNO3+                3.101e-014  2.688e-014   -13.508   -13.571    -0.062
   Pb(NO3)2              5.148e-015  5.148e-015   -14.288   -14.288     0.000
   Mn(NO3)2              2.452e-015  2.452e-015   -14.610   -14.610     0.000
   Zn(NO3)2              2.397e-015  2.397e-015   -14.620   -14.620     0.000
   Cd(NO3)2              1.139e-017  1.139e-017   -16.943   -16.943     0.000
   Cu(NO3)2              2.995e-018  2.995e-018   -17.524   -17.524     0.000
   FeNO3+2               3.266e-024  1.843e-024   -23.486   -23.734    -0.248
Na              4.964e-003
   Na+                   4.904e-003  4.340e-003    -2.309    -2.363    -0.053
   NaSO4-                3.296e-005  2.930e-005    -4.482    -4.533    -0.051
   NaCO3-                2.024e-005  1.800e-005    -4.694    -4.745    -0.051
   NaHCO3                6.370e-006  6.370e-006    -5.196    -5.196     0.000
   NaF                   3.190e-007  3.190e-007    -6.496    -6.496     0.000
   NaHPO4-               4.722e-008  4.199e-008    -7.326    -7.377    -0.051
Ni              1.706e-007
   NiCO3                 1.267e-007  1.267e-007    -6.897    -6.897     0.000
   Ni+2                  2.486e-008  1.525e-008    -7.604    -7.817    -0.212
   NiHCO3+               5.662e-009  4.907e-009    -8.247    -8.309    -0.062
   Ni(OH)2               5.116e-009  5.116e-009    -8.291    -8.291     0.000
```

```
   NiOH+                 4.057e-009  3.516e-009    -8.392    -8.454    -0.062
   NiSO4                 3.826e-009  3.826e-009    -8.417    -8.417     0.000
   NiNH3+2               1.128e-010  6.369e-011    -9.948   -10.196    -0.248
   Ni(OH)3-              1.081e-010  9.370e-011    -9.966   -10.028    -0.062
   NiF+                  5.149e-011  4.463e-011   -10.288   -10.350    -0.062
   NiCl+                 4.060e-011  3.519e-011   -10.391   -10.454    -0.062
   NiNO3+                3.736e-011  3.238e-011   -10.428   -10.490    -0.062
   Ni(SO4)2-2            2.822e-013  1.593e-013   -12.549   -12.798    -0.248
   Ni(NH3)2+2            1.269e-013  7.160e-014   -12.897   -13.145    -0.248
   NiCl2                 1.598e-016  1.598e-016   -15.796   -15.796     0.000
O(0)            2.209e-033
   O2                    1.104e-033  1.108e-033   -32.957   -32.955     0.001
P               2.747e-006
   HPO4-2                1.326e-006  8.234e-007    -5.877    -6.084    -0.207
   CaPO4-                1.121e-006  9.968e-007    -5.950    -6.001    -0.051
   CaHPO4                2.059e-007  2.059e-007    -6.686    -6.686     0.000
   NaHPO4-               4.722e-008  4.199e-008    -7.326    -7.377    -0.051
   KHPO4-                3.613e-008  3.213e-008    -7.442    -7.493    -0.051
   H2PO4-                8.030e-009  7.139e-009    -8.095    -8.146    -0.051
   PO4-3                 1.898e-009  6.319e-010    -8.722    -9.199    -0.478
   MgHPO4                4.079e-010  4.079e-010    -9.389    -9.389     0.000
   CaH2PO4+              9.833e-011  8.742e-011   -10.007   -10.058    -0.051
   MgPO4-                2.516e-011  2.237e-011   -10.599   -10.650    -0.051
   MgH2PO4+              3.039e-013  2.702e-013   -12.517   -12.568    -0.051
   FeHPO4                7.694e-016  7.694e-016   -15.114   -15.114     0.000
   H3PO4                 5.516e-016  5.516e-016   -15.258   -15.258     0.000
   FeHPO4+               1.668e-018  1.483e-018   -17.778   -17.829    -0.051
   FeH2PO4+              9.446e-019  8.398e-019   -18.025   -18.076    -0.051
   FeH2PO4+2             4.731e-026  2.956e-026   -25.325   -25.529    -0.204
Pb              4.348e-007
   Pb(CO3)2-2            2.185e-007  1.233e-007    -6.661    -6.909    -0.248
   PbCO3                 1.920e-007  1.920e-007    -6.717    -6.717     0.000
   PbOH+                 1.522e-008  1.320e-008    -7.817    -7.880    -0.062
   Pb(OH)2               7.643e-009  7.643e-009    -8.117    -8.117     0.000
   PbHCO3+               6.418e-010  5.563e-010    -9.193    -9.255    -0.062
   Pb+2                  4.676e-010  2.868e-010    -9.330    -9.542    -0.212
   PbSO4                 1.766e-010  1.766e-010    -9.753    -9.753     0.000
   Pb(OH)3-              1.615e-010  1.400e-010    -9.792    -9.854    -0.062
   PbCl+                 1.059e-011  9.179e-012   -10.975   -11.037    -0.062
   PbNO3+                4.137e-012  3.586e-012   -11.383   -11.445    -0.062
   PbF+                  2.717e-012  2.355e-012   -11.566   -11.628    -0.062
   Pb(SO4)2-2            2.371e-012  1.338e-012   -11.625   -11.874    -0.248
   Pb(OH)4-2             1.113e-012  6.280e-013   -11.954   -12.202    -0.248
   PbCl2                 3.698e-014  3.698e-014   -13.432   -13.432     0.000
   PbF2                  5.400e-015  5.400e-015   -14.268   -14.268     0.000
   Pb(NO3)2              5.148e-015  5.148e-015   -14.288   -14.288     0.000
   Pb3(OH)4+2            5.923e-016  3.343e-016   -15.227   -15.476    -0.248
   Pb2OH+3               2.172e-016  5.998e-017   -15.663   -16.222    -0.559
   PbCl3-                1.532e-017  1.328e-017   -16.815   -16.877    -0.062
   PbF3-                 1.377e-018  1.193e-018   -17.861   -17.923    -0.062
   PbCl4-2               9.702e-021  5.476e-021   -20.013   -20.262    -0.248
   Pb4(OH)4+4            7.505e-021  7.615e-022   -20.125   -21.118    -0.994
   PbF4-2                1.179e-022  6.655e-023   -21.928   -22.177    -0.248
S(6)            2.292e-003
   SO4-2                 2.050e-003  1.257e-003    -2.688    -2.901    -0.212
   CaSO4                 1.576e-004  1.576e-004    -3.803    -3.803     0.000
   KSO4-                 5.149e-005  4.578e-005    -4.288    -4.339    -0.051
   NaSO4-                3.296e-005  2.930e-005    -4.482    -4.533    -0.051
   MgSO4                 1.796e-007  1.796e-007    -6.746    -6.746     0.000
   NH4SO4-               1.138e-007  1.010e-007    -6.944    -6.996    -0.052
   NiSO4                 3.826e-009  3.826e-009    -8.417    -8.417     0.000
   ZnSO4                 1.841e-009  1.841e-009    -8.735    -8.735     0.000
   MnSO4                 1.927e-010  1.927e-010    -9.715    -9.715     0.000
   PbSO4                 1.766e-010  1.766e-010    -9.753    -9.753     0.000
   HSO4-                 7.622e-011  6.752e-011   -10.118   -10.171    -0.053
   Zn(SO4)2-2            3.572e-011  2.016e-011   -10.447   -10.696    -0.248
   CuSO4                 3.032e-012  3.032e-012   -11.518   -11.518     0.000
   CdSO4                 2.964e-012  2.964e-012   -11.528   -11.528     0.000
```

```
   Pb(SO4)2-2            2.371e-012  1.338e-012   -11.625   -11.874    -0.248
   Ni(SO4)2-2            2.822e-013  1.593e-013   -12.549   -12.798    -0.248
   Cd(SO4)2-2            8.907e-014  5.027e-014   -13.050   -13.299    -0.248
   FeSO4                 7.244e-014  7.244e-014   -13.140   -13.140     0.000
   AlSO4+                3.224e-020  2.856e-020   -19.492   -19.544    -0.053
   FeSO4+                3.465e-021  3.076e-021   -20.460   -20.512    -0.052
   Al(SO4)2-             4.343e-022  3.848e-022   -21.362   -21.415    -0.053
   Fe(SO4)2-             9.540e-023  8.269e-023   -22.020   -22.083    -0.062
Si              2.516e-003
   H4SiO4                1.937e-003  1.944e-003    -2.713    -2.711     0.001
   H3SiO4-               5.784e-004  5.113e-004    -3.238    -3.291    -0.054
   H2SiO4-2              9.396e-008  5.871e-008    -7.027    -7.231    -0.204
   SiF6-2                1.083e-033  6.725e-034   -32.965   -33.172    -0.207
Zn              1.531e-007
   ZnCO3                 8.575e-008  8.575e-008    -7.067    -7.067     0.000
   Zn(OH)2               3.558e-008  3.558e-008    -7.449    -7.449     0.000
   ZnOH+                 1.414e-008  1.226e-008    -7.850    -7.912    -0.062
   Zn+2                  1.091e-008  6.692e-009    -7.962    -8.174    -0.212
   Zn(OH)3-              3.768e-009  3.266e-009    -8.424    -8.486    -0.062
   ZnSO4                 1.841e-009  1.841e-009    -8.735    -8.735     0.000
   ZnHCO3+               6.373e-010  5.524e-010    -9.196    -9.258    -0.062
   ZnOHCl                3.636e-010  3.636e-010    -9.439    -9.439     0.000
   Zn(SO4)2-2            3.572e-011  2.016e-011   -10.447   -10.696    -0.248
   ZnF+                  1.795e-011  1.556e-011   -10.746   -10.808    -0.062
   ZnCl+                 1.715e-011  1.516e-011   -10.766   -10.819    -0.054
   ZnNO3+                1.639e-011  1.421e-011   -10.785   -10.847    -0.062
   Zn(OH)4-2             4.220e-012  2.382e-012   -11.375   -11.623    -0.248
   ZnCl2                 2.168e-014  2.168e-014   -13.664   -13.664     0.000
   Zn(NO3)2              2.397e-015  2.397e-015   -14.620   -14.620     0.000
   ZnCl3-                1.757e-017  1.553e-017   -16.755   -16.809    -0.054
   ZnCl4-2               1.128e-020  7.005e-021   -19.948   -20.155    -0.207

------------------------------Saturation indices-------------------------------

        Phase               SI log IAP  log KT

        Al(OH)3(am)      -3.55    7.25   10.80  Al(OH)3
        Al2O3            -5.16   14.49   19.65  Al2O3
        Al4(OH)10SO4    -15.14    7.56   22.70  Al4(OH)10SO4
        AlOHSO4         -10.94  -14.17   -3.23  AlOHSO4
        Alunite         -12.73  -14.13   -1.40  KAl3(SO4)2(OH)6
        Anglesite        -4.65  -12.44   -7.79  PbSO4
        Anhydrite        -1.80   -6.16   -4.36  CaSO4
        Antlerite        -7.58    1.21    8.79  Cu3(OH)4SO4
        Aragonite         1.39   -6.91   -8.30  CaCO3
        Artinite         -6.94    2.66    9.60  MgCO3:Mg(OH)2:3H2O
        Atacamite        -4.61    2.78    7.39  Cu2(OH)3Cl
        Azurite          -4.81  -21.72  -16.91  Cu3(OH)2(CO3)2
        Bianchite        -9.31  -11.08   -1.76  ZnSO4:6H2O
        Birnessite       -7.47   10.63   18.09  MnO2
        Bixbyite         -4.63   -5.27   -0.64  Mn2O3
        Boehmite         -1.33    7.25    8.58  AlOOH
        Brochantite      -6.47    8.75   15.22  Cu4(OH)6SO4
        Brucite          -4.43   12.41   16.84  Mg(OH)2
        Bunsenite        -1.74   10.70   12.45  NiO
        Ca3(PO4)2(beta)   0.74  -28.18  -28.92  Ca3(PO4)2
        Ca4H(PO4)3:3H2O  -2.83  -49.91  -47.08  Ca4H(PO4)3:3H2O
        CaHPO4           -2.45  -21.72  -19.27  CaHPO4
        CaHPO4:2H2O      -2.73  -21.72  -19.00  CaHPO4:2H2O
        Calcite           1.57   -6.91   -8.48  CaCO3
        Cd(OH)2          -6.12    7.52   13.64  Cd(OH)2
        Cd(OH)2(am)      -6.21    7.52   13.73  Cd(OH)2
        Cd3(OH)2(SO4)2  -26.98  -20.27    6.71  Cd3(OH)2(SO4)2
        Cd3(OH)4SO4     -21.41    1.15   22.56  Cd3(OH)4SO4
        Cd3(PO4)2       -18.79  -51.39  -32.60  Cd3(PO4)2
        Cd4(OH)6SO4     -19.73    8.67   28.40  Cd4(OH)6SO4
        CdCl2           -16.43  -17.09   -0.66  CdCl2
        CdCl2:1H2O      -15.39  -17.09   -1.69  CdCl2:1H2O
```

```
        CdCl2:2.5H2O    -15.17  -17.09   -1.91  CdCl2:2.5H2O
        CdF2            -17.65  -18.86   -1.21  CdF2
        Cdmetal(alpha)  -32.51  -19.00   13.51  Cd
        Cdmetal(gamma)  -32.62  -19.00   13.62  Cd
        CdOHCl           -8.32   -4.78    3.54  CdOHCl
        CdSO4           -13.73  -13.90   -0.17  CdSO4
        CdSO4:1H2O      -12.17  -13.90   -1.73  CdSO4:1H2O
        CdSO4:2.67H2O   -12.03  -13.90   -1.87  CdSO4:2.67H2O
        Cerrusite        -0.06  -13.19  -13.13  PbCO3
        CH4(g)          -87.21 -128.25  -41.05  CH4
        Chalcanthite    -11.24  -13.88   -2.64  CuSO4:5H2O
        Chalcedony        0.84   -2.71   -3.55  SiO2
        Chrysotile       -0.38   31.82   32.20  Mg3Si2O5(OH)4
        CO2(g)           -4.03  -22.17  -18.15  CO2
        Cotunnite       -10.85  -15.63   -4.78  PbCl2
        Cristobalite      0.64   -2.71   -3.35  SiO2
        Cryolite        -17.38  -51.22  -33.84  Na3AlF6
        Cu(OH)2          -1.13    7.54    8.67  Cu(OH)2
        Cu2(OH)3NO3      -6.50    2.75    9.25  Cu2(OH)3NO3
        Cu2SO4          -25.53  -27.48   -1.95  Cu2SO4
        Cu3(PO4)2       -14.48  -51.33  -36.85  Cu3(PO4)2
        Cu3(PO4)2:3H2O  -16.21  -51.33  -35.12  Cu3(PO4)2:3H2O
        CuCO3            -3.13  -14.63  -11.50  CuCO3
        CuF             -11.32  -16.22   -4.91  CuF
        CuF2            -19.96  -18.84    1.12  CuF2
        CuF2:2H2O       -14.30  -18.85   -4.55  CuF2:2H2O
        Cumetal          -7.53  -16.29   -8.76  Cu
        CuOCuSO4        -16.64   -6.34   10.30  CuOCuSO4
        Cupricferrite    13.79   19.78    5.99  CuFe2O4
        Cuprite          -4.65   -6.06   -1.41  Cu2O
        Cuprousferrite   12.01    3.09   -8.92  CuFeO2
        CuSO4           -16.82  -13.88    2.94  CuSO4
        Diaspore          0.37    7.25    6.87  AlOOH
        Dolomite(disordered)  -0.13  -16.67  -16.54  CaMg(CO3)2
        Dolomite(ordered)   0.42  -16.67  -17.09  CaMg(CO3)2
        Epsomite         -6.88   -9.01   -2.13  MgSO4:7H2O
        FCO3Apatite      23.99  -90.41 -114.40
Ca9.316Na0.36Mg0.144(PO4)4.8(CO3)1.2F2.48
        Fe(OH)2          -7.67    5.89   13.56  Fe(OH)2
        Fe(OH)2.7Cl.3     5.47    2.43   -3.04  Fe(OH)2.7Cl.3
        Fe2(SO4)3       -48.29  -52.02   -3.73  Fe2(SO4)3
        Fe3(OH)8         -2.10   18.13   20.22  Fe3(OH)8
        Ferrihydrite      2.93    6.12    3.19  Fe(OH)3
        Fluorite         -0.63  -11.13  -10.50  CaF2
        Gibbsite         -1.05    7.25    8.29  Al(OH)3
        Goethite          5.63    6.12    0.49  FeOOH
        Goslarite        -9.06  -11.08   -2.01  ZnSO4:7H2O
        Greenalite       -8.56   12.25   20.81  Fe3Si2O5(OH)4
        Gypsum           -1.55   -6.16   -4.61  CaSO4:2H2O
        H-Jarosite      -12.39  -24.49  -12.10  (H3O)Fe3(SO4)2(OH)6
        Halite           -7.01   -5.41    1.60  NaCl
        Halloysite       -0.51    9.07    9.57  Al2Si2O5(OH)4
        Hausmannite      -6.14   54.89   61.03  Mn3O4
        Hematite         13.65   12.24   -1.42  Fe2O3
        Hercynite        -2.51   20.38   22.89  FeAl2O4
        Hinsdalite      -25.18  -27.68   -2.50  PbAl3PO4SO4(OH)6
        Huntite          -6.22  -36.19  -29.97  CaMg3(CO3)4
        Hydrocerrusite    1.36  -17.41  -18.77  Pb3(OH)2(CO3)2
        Hydromagnesite  -17.85  -26.62   -8.77  Mg5(CO3)4(OH)2:4H2O
        Hydroxylapatite   9.68  -34.65  -44.33  Ca5(PO4)3OH
        Hydroxylpyromorphite  -3.26  -66.05  -62.79  Pb5(PO4)3OH
        K-Alum          -23.46  -28.63   -5.17  KAl(SO4)2:12H2O
        K-Jarosite       -2.72  -17.52  -14.80  KFe3(SO4)2(OH)6
        Kaolinite         1.63    9.07    7.43  Al2Si2O5(OH)4
        Langite          -8.74    8.75   17.49  Cu4(OH)6SO4:H2O
        Larnakite        -3.03   -3.47   -0.43  PbO:PbSO4
        Laurionite       -3.95   -3.33    0.62  PbOHCl
        Lepidocrocite     4.75    6.12    1.37  FeOOH
```

```
Lime            -17.44   15.26   32.70  CaO
Litharge         -3.72    8.98   12.69  PbO
Maghemite         5.85   12.24    6.39  Fe2O3
Magnesioferrite   7.79   24.65   16.86  Fe2MgO4
Magnesite        -2.30   -9.76   -7.46  MgCO3
Magnetite        14.72   18.13    3.40  Fe3O4
Malachite        -1.78   -7.09   -5.31  Cu2(OH)2CO3
Manganite        -2.62   22.72   25.34  MnOOH
Massicot         -3.92    8.98   12.89  PbO
Matlockite       -7.55  -16.52   -8.97  PbClF
Melanothallite  -23.32  -17.07    6.26  CuCl2
Melanterite     -13.32  -15.53   -2.21  FeSO4:7H2O
Mg(OH)2(active)  -6.38   12.41   18.79  Mg(OH)2
Mg3(PO4)2       -13.43  -36.71  -23.28  Mg3(PO4)2
MgF2             -5.84  -13.97   -8.13  MgF2
MgHPO4:3H2O      -6.39  -24.56  -18.18  MgHPO4:3H2O
Minium          -20.07   53.45   73.52  Pb3O4
Mirabilite       -6.51   -7.63   -1.11  Na2SO4:10H2O
Mn2(SO4)3       -63.82  -69.53   -5.71  Mn2(SO4)3
Mn3(PO4)2       -21.77  -45.59  -23.83  Mn3(PO4)2
MnCl2:4H2O      -17.87  -15.15    2.72  MnCl2:4H2O
MnHPO4           -2.12  -27.52  -25.40  MnHPO4
MnSO4           -14.55  -11.97    2.58  MnSO4
Monteponite      -7.58    7.52   15.10  CdO
Morenosite       -8.57  -10.72   -2.14  NiSO4:7H2O
Na-Jarosite      -6.39  -17.59  -11.20  NaFe3(SO4)2(OH)6
Nantokite        -8.60  -15.33   -6.73  CuCl
Natron           -7.07   -8.38   -1.31  Na2CO3:10H2O
Nesquehonite     -5.09   -9.76   -4.67  MgCO3:3H2O
Ni(OH)2          -2.09   10.70   12.79  Ni(OH)2
Ni3(PO4)2       -10.55  -41.85  -31.30  Ni3(PO4)2
Ni4(OH)6SO4     -10.61   21.39   32.00  Ni4(OH)6SO4
NiCO3            -4.60  -11.47   -6.87  NiCO3
Nsutite          -6.88   10.63   17.50  MnO2
O2(g)           -30.05   53.04   83.09  O2
Otavite          -2.65  -14.65  -12.00  CdCO3
Pb(OH)2           0.83    8.98    8.15  Pb(OH)2
Pb10(OH)6O(CO3)6 -34.50  -43.26   -8.76  Pb10(OH)6O(CO3)6
Pb2(OH)3Cl       -3.14    5.65    8.79  Pb2(OH)3Cl
Pb2O(OH)2        -8.23   17.95   26.19  Pb2O(OH)2
Pb2O3           -16.57   44.47   61.04  Pb2O3
Pb2OCO3          -3.66   -4.22   -0.56  Pb2OCO3
Pb3(PO4)2        -3.50  -47.03  -43.53  Pb3(PO4)2
Pb3O2CO3         -6.26    4.76   11.02  Pb3O2CO3
Pb3O2SO4         -5.17    5.51   10.69  Pb3O2SO4
Pb4(OH)6SO4      -6.61   14.49   21.10  Pb4(OH)6SO4
Pb4O3SO4         -7.39   14.49   21.88  Pb4O3SO4
PbF2             -9.97  -17.41   -7.44  PbF2
PbHPO4           -4.20  -28.00  -23.81  PbHPO4
Pbmetal         -21.79  -17.54    4.25  Pb
PbO:0.3H2O       -4.00    8.98   12.98  PbO:0.33H2O
Periclase        -9.17   12.41   21.58  MgO
Phosgenite       -9.02  -28.83  -19.81  PbCl2:PbCO3
Plattnerite     -14.10   35.50   49.60  PbO2
Plumbgummite    -10.45  -43.24  -32.79  PbAl3(PO4)2(OH)5:H2O
Portlandite      -7.55   15.26   22.80  Ca(OH)2
Pyrochroite      -5.74    9.46   15.19  Mn(OH)2
Pyrolusite       -5.40   35.98   41.38  MnO2
Pyromorphite      6.08  -78.35  -84.43  Pb5(PO4)3Cl
Quartz            1.29   -2.71   -4.00  SiO2
Retgersite       -8.68  -10.72   -2.04  NiSO4:6H2O
Rhodochrosite    -2.14  -12.72  -10.58  MnCO3
Sepiolite         0.94   16.70   15.76  Mg2Si3O7.5OH:3H2O
Sepiolite(A)     -2.08   16.70   18.78  Mg2Si3O7.5OH:3H2O
Siderite         -6.04  -16.28  -10.24  FeCO3
SiO2(am-gel)     -0.00   -2.71   -2.71  SiO2
SiO2(am-ppt)      0.03   -2.71   -2.74  SiO2
Smithsonite      -1.83  -11.83  -10.00  ZnCO3
```

```
Spinel           -9.94   26.91   36.85  MgAl2O4
Strengite        -4.46  -30.86  -26.40  FePO4:2H2O
Tenorite         -0.10    7.54    7.64  CuO
Thenardite       -7.95   -7.63    0.32  Na2SO4
Thermonatrite    -9.01   -8.38    0.64  Na2CO3:H2O
Tsumebite        -1.69  -11.48   -9.79  Pb2CuPO4(OH)3:3H2O
Vivianite       -20.29  -56.29  -36.00  Fe3(PO4)2:8H2O
Zincite          -0.99   10.35   11.33  ZnO
Zincosite       -15.00  -11.08    3.93  ZnSO4
Zn(NO3)2:6H2O   -17.64  -14.32    3.32  Zn(NO3)2:6H2O
Zn(OH)2          -1.85   10.35   12.20  Zn(OH)2
Zn(OH)2(am)      -2.13   10.35   12.47  Zn(OH)2
Zn(OH)2(beta)    -1.41   10.35   11.75  Zn(OH)2
Zn(OH)2(epsilon)  -1.19   10.35   11.53  Zn(OH)2
Zn(OH)2(gamma)   -1.39   10.35   11.73  Zn(OH)2
Zn2(OH)2SO4      -8.23   -0.73    7.50  Zn2(OH)2SO4
Zn2(OH)3Cl       -6.81    8.39   15.19  Zn2(OH)3Cl
Zn3(PO4)2:4H2O   -7.50  -42.92  -35.42  Zn3(PO4)2:4H2O
Zn3O(SO4)2      -30.72  -11.80   18.91  Zn3O(SO4)2
Zn4(OH)6SO4      -8.44   19.96   28.40  Zn4(OH)6SO4
Zn5(OH)8Cl2     -11.38   27.12   38.50  Zn5(OH)8Cl2
ZnCl2           -21.31  -14.26    7.05  ZnCl2
ZnCO3:1H2O       -1.57  -11.83  -10.26  ZnCO3:1H2O
ZnF2            -15.51  -16.04   -0.53  ZnF2
Znmetal         -41.96  -16.17   25.79  Zn
ZnO(active)      -0.84   10.35   11.19  ZnO
ZnSO4:1H2O      -10.44  -11.08   -0.64  ZnSO4:1H2O
```