Extraction of heavy metals from contaminated clay soils

Citation for published version (APA):
Tuin, B. J. W. (1989). *Extraction of heavy metals from contaminated clay soils*. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Universiteit Eindhoven.
https://doi.org/10.6100/IR314307

DOI:
10.6100/IR314307

Document status and date:
Published: 01/01/1989

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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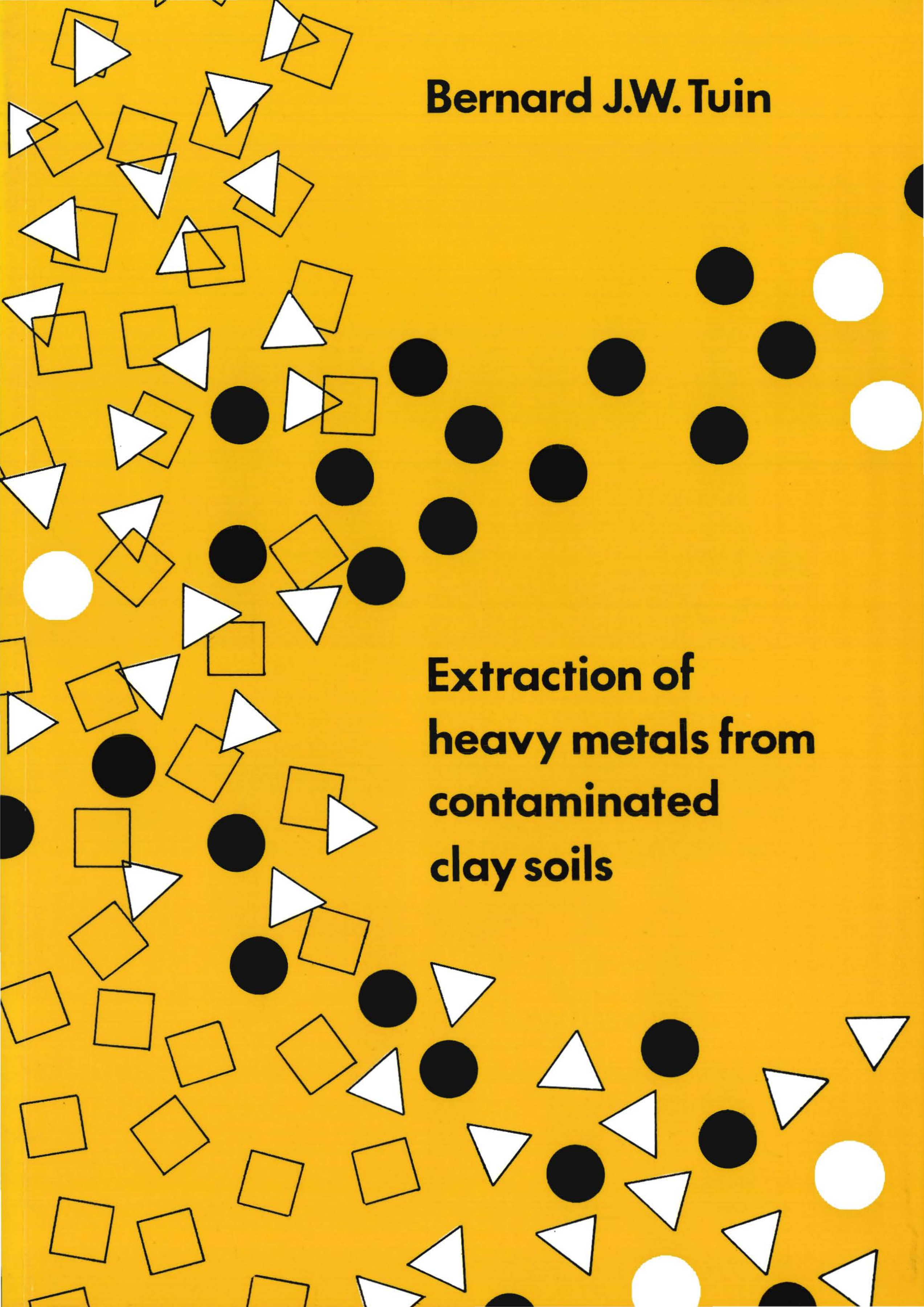

Bernard J.W. Tuin

Extraction of heavy metals from contaminated clay soils

EXTRACTION OF HEAVY METALS FROM CONTAMINATED CLAY SOILS

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE TECHNISCHE UNIVERSITEIT EINDHOVEN,
OP GEZAG VAN DE RECTOR MAGNIFICUS,
PROF.IR. M. TELS, VOOR EEN COMMISSIE
AANGEWEZEN DOOR HET COLLEGE VAN DEKANEN
IN HET OPENBAAR TE VERDEDIGEN OP
VRIJDAG 1 SEPTEMBER 1989 OM 16.00 UUR

DOOR

BERNARD JAN WILLEM TUIN

GEBOREN TE HOOGEVEEN

Dit proefschrift is goedgekeurd door de promotoren:
Prof.Ir. M. Tels
Prof.Dr. U. Förstner

In de herinnering
aan m'n lieve moeder

Verantwoording

Het onderzoek beschreven in dit proefschrift werd uitgevoerd in overleg met en met financiële ondersteuning van de Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek TNO, hoofdgroep Maatschappelijke Technologie. Naast de promotoren werd het onderzoek gedurende de eerste twee jaren tevens begeleid door Dr. Ir. M.M.G. Senden. Vanuit TNO werd het onderzoek begeleid door Dr. Ir. W.H. Rulkens.

Een belangrijk deel van het experimentele werk werd uitgevoerd door de volgende TUE afstudeerders: Leon Smeets, Tom van de Mast, John Heynen, Pieter Nonhebel, Frank van Dijck, Ivo van Boekhold, Erik Brink, Marc Pruijn, Ton van der Putten en Erica Suijkerbuijk. Verder werden metingen en analyses mede verricht door de stagiaires Rian Wouters, Joris Braspenning, Peter van Poppel en Miranda Baayens. Assistentie bij de AAS-analyses werd gegeven door mevr. A. Elemans.

Technische ondersteuning bij ontwerp, bouw en reparatie van de apparatuur werd verleend door Chris Luyk en op elektronisch vlak door Paul Peeters en Ton Boelaars. Secretariële hulp werd gegeven door Anniek van Bemmelen. Het omslag werd ontworpen door Tanja Algra (Bureau Karakter, Delft).

Bernard Tuin
Eindhoven, 1 september 1989

Curriculum vitae

Bernard Jan Willem Tuin werd geboren in 1958 te Hoogeveen. In 1976 behaalde hij in dezelfde plaats het V.W.O. diploma aan het Menso Alting College. Daarna begon hij de studie scheikunde aan de Rijksuniversiteit te Groningen, waar hij vanaf 1979 de afstudeerrichting Technische Scheikunde heeft gevolgd. Zijn afstudeerwerk over kolenasproduktie in een gefluïdiseerd bed verrichtte hij o.l.v. prof.ir. S. Stemerding. Na het behalen van het ingenieursexamen met lof in 1983 vertrok hij voor ca. anderhalf jaar naar de Verenigde Staten. In die periode behaalde hij zijn Master of Science degree aan de Vanderbilt University te Nashville, Tennessee. Tevens werkte hij gedurende enige tijd bij het ingenieursbureau A.W.A.R.E. Terug in Nederland trad hij in 1985 in dienst als wetenschappelijk assistent bij de vakgroep Fysische Technologie van de Technische Universiteit te Eindhoven. Hier heeft hij het onderzoek naar de extractie van zware metalen uit verontreinigde kleigronden uitgevoerd onder leiding van prof.ir. M. Tels. Na de afronding van dit onderzoek zal hij werkzaam zijn als research medewerker bij Akzo Research Laboratories te Arnhem.

SAMENVATTING

Het afgelopen decennium zijn veel gevallen van bodemverontreiniging geconstateerd bijvoorbeeld op (illegale) stortplaatsen en voormalige industrieterreinen. Bodemsanering is veelal gewenst om verdere verspreiding van de verontreiniging en gevaar voor volksgezondheid of milieu te voorkomen.

Het doel van deze studie is de extractie van zware metalen uit kleigronden of uit de fractie kleine deeltjes (d < 50 µm) van andere gronden te onderzoeken en continue reinigingsmethoden te ontwikkelen voor met zware metalen verontreinigde kleigronden.

Voor het reinigen van zand- en leem-gronden bestaan reeds installaties op grote schaal. Het reinigen van zware metalen uit de fijne fractie van een grond vormt (nog) een probleem omdat deze fractie (die het grootste deel van de kleimineralen, bodemoxiden en organisch materiaal bevat) een grote adsorptie capaciteit bezit voor zware metalen en de metalen ook relatief sterk bindt. Kleine deeltjes zijn bovendien moeilijker te hanteren in procesinstallaties.

Een extractieproces bestaat in het algemeen uit vier hoofdonderdelen:

1. voorbehandeling van de verontreinigde grond;
2. extractie van de verontreiniging uit de grond;
3. scheiding van grond en extractiemiddel;
4. reiniging en zo mogelijk recirculeren van het extractiemiddel.

In dit onderzoek ligt de nadruk op de tweede processtap en is ook enige aandacht geschonken aan onderdeel 3.

Extractie experimenten zijn eerst batch gewijs uitgevoerd op laboratorium schaal. Het extractiegedrag van de volgende zes metalen is gemeten: cadmium, chroom, koper, nikkel, lood en zink. Er is gemeten aan vijf kunstmatig verontreinigde kleigronden en aan twee gronden afkomstig van verontreinigde terreinen in de provincie Utrecht ("praktijkgronden"). Als extractiemiddelen zijn anorganische zuren en een complexvormer getest. De invloed van diverse parameters op de percentages verwijderd metaal is bepaald.

Metalen in de kunstmatig verontreinigde gronden worden slechts in geringe mate meer verwijderd als de extractiemiddel-grond gewichtsverhouding tijdens de extractie verhoogd wordt. Een veel grotere verbetering in het extractierendement wordt bereikt door de concentratie van het extractiemiddel

zoutzuur (HCl) te vergroten. De extractiepercentages uit de "praktijkgronden" Sophia en Melchior liggen in dezelfde grootte orde voor de volgende drie omstandigheden: drievoudige extractie (3x30 minuten) in 0.1 N HCl, 24 uur extractie in 0.1 N HCl en 30 minuten extractie in 2 N HCl (alle bij een vloeistof-grond verhouding van ca. 20). De extraheerbaarheid van de zes metalen neemt af in de volgorde:

Cd > Pb > Cu > Zn > Ni > Cr.

Voor bovengenoemde condities liggen de extractierendementen voor Cd, Cu, Pb en Zn tussen 80 en 90%. Het percentage is hoger naarmate de oorspronkelijke metaalconcentratie groter is. Dit verband is het sterkst voor Ni en Zn. De restconcentraties metaal in de kleigrond liggen nog boven of net onder de "B-waarde" uit de Interimwet Bodemsanering. Nikkel extractie percentages variëren van 45 tot 80% waarmee de restconcentratie in de Sophia "praktijkgrond" zelfs nog boven de C-waarde uitkomt. Chroom is nauwelijks extraheerbaar met zuur: het maximale extractie percentage is 50% (na 30 minuten extractie in 2 N HCl).

Het extractierendement in 0.1 N HCl kan nauwelijks verder verbeterd worden zoals blijkt uit de resultaten van de derde stap van de drievoudige extractie en van een extractie van 30 minuten plus 24 uur. Het bovengenoemde rendement in 2 N HCl kan verbeterd worden door het toepassen van meer extractiestappen. Deze vervolgstappen kunnen wellicht met kleinere zuur concentraties uitgevoerd worden. Hoewel een concentratie groter dan 0.1 N HCl nodig is om de "A-waarde" te bereiken, is het nog onbekend welke minimale concentratie vereist is bij het toepassen van een aantal extractiestappen.

Het gebruik van sterke zuren verhoogt de kosten van het extractieproces. Verder is een ernstig nadeel dat het bodemmateriaal zelf ook sterk wordt aangetast. Ongeveer 10 gew.% van het vaste materiaal van de "praktijkgronden" lost al op in 0.1 N HCl na 30 minuten.

Als 0.1 M EDTA wordt gebruikt in plaats van 0.1 N HCl, worden even grote of hogere extractierendementen gemeten voor de metalen in de kunstmatig verontreinigde kleigronden. Een pH lager dan 4 is vereist voor een succesvolle EDTA extractie. Hoewel met een 0.1 M EDTA oplossing recent aangebrachte metaalionen dus goed verwijderd kunnen worden, is dit niet het geval voor de metalen in de "praktijkgronden". Hier zijn alleen voor Cd -en in mindere mate voor Pb- dezelfde of grotere extractiepercentages als in 0.1 N HCl gemeten. Een nadeel van EDTA is de veel hogere prijs dan die van HCl.

De grootste verwijdering van chroom uit de "praktijkgronden" is bereikt na een extractie in 0.46 M natriumhypochloriet oplossing gebufferd op pH=8.5 en verhit tot ca. 80°C gedurende de eerste vijf minuten. Uit de kunstmatig verontreinigde gronden valt chroom gemakkelijker te extraheren (met een 0.046 M NaClO oplossing en zonder te verhitten). De oplosbaarheid van chroomverbindingen kan sterk afhangen van de ouderdom, hetgeen de reden kan zijn voor het verschil in extraheerbaarheid tussen de twee soorten verontreinigde gronden. Hoewel tijdens de extractie slechts korte tijd verhit hoeft te worden, is dit een kostbare operatie. Andere problemen zijn het corrosieve karakter van de hete suspensie en het NaClO verbruik door organisch materiaal in de bodem. Het is daaropm waarschijnlijk eenvoudiger en goedkoper een meervoudige extractie bij kamertemperatuur uit te voeren. In ieder geval maakt de aanwezigheid van chroom een extra behandeling naast zure extractie noodzakelijk en werkt daardoor kostenverhogend. In principe biedt de oxidatieve extractie met NaClO goede mogelijkheden.

Een sequentiële extractie analyse volgens Tessier e.a. is uitgevoerd. Deze techniek is toegepast om de verdeling van metalen over fracties in de bodem te vergelijken voor en na een extractieve reiniging. Vijf operationeel gedefinieerde fracties waarin metalen aanwezig kunnen zijn worden in de grond onderscheiden:

F1. "Uitwisselbaar" ($MgCl_2$ extraheerbaar)
F2. "Gebonden aan carbonaten"
F3. "Gebonden aan ijzer- of mangaan-oxiden"
F4. "Gebonden aan organisch materiaal of sulfides"
F5. "Restfractie"

In de kunstmatig met één of meer metalen verontreinigde gronden is 80-90% van het metaal aanwezig in de fracties F1, F2 en F3 van de Tessier-analyse. Twee uitzonderingen zijn gemeten: gronden die alleen met Ni of Cr verontreinigd zijn. Van Ni is 6-25% aanwezig in de "restfractie". Nikkel ionen zouden gebonden kunnen zijn aan meer inwendig gelegen bindingsplaatsen in de kleigronden.

De verdeling van de metalen in de "praktijkgronden" wijkt af van die in de kunstmatig verontreinigde gronden. De "uitwisselbare" fractie is erg gering en de fracties F4 en F5 bevatten een groter deel van de metalen. Het verschil in extraheerbaarheid in HCl van metalen uit de twee soorten verontreinigde gronden valt terug te voeren op dit verschil in verdeling. De labielere fracties F1, F2 en F3 die de belangrijkste opvang capaciteit vormen voor recent aangebrachte metalen, worden gemakkelijker door HCl geëxtraheerd dan de "restfractie" F5.

Het verwijderingsrendement behaald met HCl of EDTA uit een fractie wordt allereerst bepaald door het type bindingsplaats en minder door soort metaal of metaalconcentratie. Extractie van metalen uit de fracties met 0.1 N HCl of 0.1 M EDTA wordt in het algemeen moeilijker in de volgorde:

'CO_3' < 'Fe/Mn-Ox' < 'Org/Sulf' < 'Restfractie'

Extractie uit de "restfractie" is met name moeilijker dan uit de overige fracties: voor de helft van alle experimenten wordt een verwijderingsrendement uit deze fractie gemeten van minder dan 33%. Na een drievoudige behandeling met 0.1 N HCl zijn de metaalconcentraties in de "restfractie" van de "praktijkgronden" nog gelijk aan 1-5x de A-waarde uit de Interimwet Bodemsanering. Dit restant metaal zal moeilijk te verwijderen zijn zonder de grond zelf sterk aan te tasten en zonder hoge kosten. De metalen in deze fractie zijn het minst mobiel. De noodzaak voor een verdere reiniging zou daarom nader onderzocht moeten worden en naast het totaal metaalgehalte ook gebaseerd moeten worden op de mobiliteit en biologische beschikbaarheid van de metalen na reiniging.

De extractiesnelheid van vier metalen (Cu, Ni, Pb en Zn) uit kunstmatig verontreinigde gronden en uit de "praktijkgronden" is gemeten. Voor de laatsten is onder twee condities gemeten: in een volledig gemengde (homogene) klei suspensie en in een bezinkende geflocculeerde klei suspensie waar de menging veel minder intens is. Deze proefomstandigheden komen overeen met de twee types continue processen die zijn bestudeerd.

Twee verschillende types extractiecurves in de tijd zijn gevonden: het eerste patroon bestaat uit een zeer snelle extractie gevolgd door een veel langzamer extractie; het tweede patroom is een regelmatig afnemende kleiconcentratie in de tijd met een extractiesnelheid die ligt tussen de zeer snelle en de langzame extractie. De extractie van de vier metalen uit de "praktijkgronden" verloopt in het algemeen langzamer dan die uit de kunstmatig verontreinigde gronden. Het verschil in extractierendement komt tot uitdrukking in verschillende hoeveelheden van het totale metaalgehalte die volgens de snelle of langzame extractie verlopen.

Het verschil in extractiesnelheid tussen de condities "volledig gemengde" en "bezinkende geflocculeerde" kleisuspensie is klein in de meeste gevallen en kan alleen aan het begin van het extractieproces vastgesteld worden.

Een model is ontwikkeld dat de extractiesnelheid bij constante pH en temperatuur beschrijft met behulp van twee processen met verschillende snelheidsconstantes. Deze processen zijn: een snelle, irreversibele reactie van de eerste orde in de metaalconcentratie in de klei en een langzame, reversibele eerste orde reactie. Dit "twee-reactie model" beschrijft de metaal concentratie curves over een periode van 24 uur met een relatieve fout kleiner dan 20%. Een eenduidig verband tussen de fractie die langzaam reageert en de metaalverdeling volgens de sequentiële extractie analyse is niet aanwezig.

De invloed van de temperatuur op de extractiesnelheid is bepaald tussen 5 en 80°C voor de extractie van nikkel uit kunstmatig verontreinigde Winsum kleigrond onder condities van volledige menging. Het duidelijkste effect is een afname van uiteindelijk bereikte metaalconcentratie in de klei met toenemende temperatuur. Berekende waarden voor de aktiveringsenergie (bij benadering, gezien de experimentele fout) zijn klein en duiden op een extractie van Ni uit Winsum kleigrond in 0.1 N HCl die gelimiteerd is door diffusie in de poreuze kleideeltjes. De verontreinigingen in de "praktijkgronden" zijn ouder en grotere hoeveelheden worden aangetroffen in de "restfractie". Bovendien zijn deze verontreinigingen niet noodzakelijkerwijs als oplosbaar metaalzout in het milieu gebracht. Chemische reactie limitaties zijn daarom waarschijnlijker voor de extractie van de metalen uit de "praktijkgronden".

Een continu laboratoriumschaal procesinstallatie is gebouwd waarin de extractie van zware metalen uit de "praktijkgronden" met 0.1 N HCl op drie manieren getest is: extractie in twee continue geroerde tankreactors (CSTR), extractie in een tegenstroom zeefplatenkolom en extractie in een combinatie van geroerde tank en kolom. Kleigrond en extractiemiddel zijn in deze installatie continu gescheiden door flocculatie - sedimentatie. Een gecombineerde precipitatie plus flocculatie is gekozen om het extractiemiddel te ontdoen van zware metalen.

Om de fijne kleideeltjes in een tegenstroomkolom te kunnen hanteren is de vorming van aggregaten noodzakelijk. Daartoe wordt de kleisuspensie geflocculeerd vóór invoer in de kolom. Zeefplaten zijn op een as gemonteerd en kunnen geroteerd of op en neer bewogen worden (of beide) in een gewenste frequentie om daarmee de verblijftijd van de kleideeltjes in de kolom te beïnvloeden. De rotatie is niet continu maar is een draai over een hoek van ca. 50• en terug. Aantal en type zeefplaten kunnen worden gevarieerd.

De metaalconcentraties in de kleigronden na extractie in één van de drie continue procesuitvoeringen, liggen niet op het niveau van de "A- waarde" uit de Interimwet Bodemsanering. De concentraties aan Cr, Ni, en Zn in Sophia grond en Zn in Melchior grond zijn nog duidelijk te hoog. In de tegenstroomkolom worden hogere extractie rendementen behaald dan in het CSTR proces maar de verschillen zijn gering. De verschillen zijn groter bij vergelijking van kolom en CSTR als tweede processtap na een eerste extractie in een CSTR. Het volgende proces lijkt goede mogelijkheden te bieden: eerst extractie in een CSTR gevolgd door een verdere extractie in de tegenstroomkolom. De verblijftijd in de CSTR kan kort zijn (15 - 30 minuten), de verblijftijd in de kolom dient zo lang mogelijk te zijn. Hoewel de tegenstroomkolom ook hogere rendementen geeft als eerste deel van het proces, is een CSTR gemakkelijker te bedrijven en zeer geschikt om het eerste snelle deel van de extractie in uit te voeren. Het moeilijker te verwijderen metaal kan dan verwijderd worden in de kolom, eventueel bij een grotere concentratie extractiemiddel dan in de CSTR. Lange verblijftijden in de kolom zijn noodzakelijk voor metalen zoals Ni waar de langzame extractie overheerst.

Op dit moment is het nog niet zinvol de totale kosten te schatten van een extractieproces zoals hier beschreven. Het is echter duidelijk dat de kosten van de chemicaliën belangrijk zijn. De mogelijkheden voor recycling van het extractiemiddel dienen daarom verder nagegaan te worden. Deze bepalen ook de keuze voor de wijze waarop het vierde procesonderdeel (reiniging van het extractiemiddel) uitgevoerd zal moeten worden.

De continue extractie processen zijn ook modelmatig beschreven. Hiertoe is het kinetiek model gecombineerd met (experimentele) gegevens over het hydrodynamisch gedrag van vloeistof en vaste fase in de continue procesapparatuur.

In de CSTR is aangenomen dat kleigrond en extractiemiddel volledig gemengd zijn (homogene suspensie) op basis van verblijftijdspreiding experimenten uitgevoerd in de vloeistoffase. De extractierendementen kunnen met het model voorspeld worden met een fout van 15% absoluut als de pH-waarde tijdens de extractie goed overeenkomt met die tijdens de kinetiek experimenten. Het model laat zien dat slechts een geringe verbetering in het extractierendement behaald kan worden door de suspensie tussen de twee extractors verder te ontwateren. Dit betekent dat de teruggaande reactie in het model (re-adsorptie) niet erg belangrijk is.

De verblijftijdspreiding van zowel geflocculeerde kleideeltjes als extractiemiddel is gemeten in de tegenstroomkolom. De gemiddelde verblijftijd van de kleigrond ligt tussen 13 en 25 minuten. De longitudinale menging in de vaste fase kan beschreven worden met een Peclet getal tussen 9 en 16 en de vloeistoffase kan bij benadering beschreven worden door propstroom.

Het propstroom met axiale dispersie model is gebruikt voor de modellering van de stromen in de kolom. Samen met de kinetische vergelijkingen voorspelt het kolommodel lagere extractierendementen dan gemeten. Ten dele wordt dit veroorzaakt door iets lagere pH-waardes tijdens de kolomextracties dan in de kinetiekexperimenten. Het model laat zien dat de verwijdering van metalen uit de klei beperkt wordt door de langzame model reactie. Variatie van parameters met het model leert dat alleen door grotere kolomlengtes of een grotere massa klei in de kolom de extractierendementen in geringe mate te verbeteren zijn. Deze veranderingen veroorzaken beide grotere verblijftijden van de kleigrond in de kolom, hetgeen de voornaamste reden is voor de kleine verbetering. Het effect van de procesvoering in tegenstroom is gering omdat de terugreactie nauwelijks van belang is. Het extractierendement na korte tijd wordt bepaald door het snelle deel van de extractie. Een meestroomproces zou dus ongeveer dezelfde resultaten te zien geven. Het tegenstroomproces biedt toch extra voordelen omdat kleigrond en extractiemiddel gescheiden moeten worden na de extractie. De metaalconcentratie in de achterblijvende, aanhangende vloeistof aan de kleigrond is duidelijk lager bij procesvoering in tegenstroom dan bij die in meestroom of CSTR.

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SUMMARY AND CONCLUSION

Many old industrial areas and waste disposal sites are contaminated to such an extent that remedial action is required to prevent further environmental pollution.

The purpose of this study is to investigate the extraction of heavy metals from clay soils or the small-particle-size fractions (d < 50 µm) of other soils to develop possible (continuous) treatment processes for heavy metal contaminated clay soils.

Commercial scale plants are already operational for the decontamination of sandy or loamy soils. Cleaning of clay soils or fractions of other soils that contain the small particles is still a problem mainly because the fine-grained material (which contains the largest proportions of clay minerals, hydrous oxides and organic matter) has a high adsorption capacity for heavy metals and strong metal-substrate interactions occur. The smaller grain sizes are also more difficult to handle in a process installation.

Generally, an extraction process consists of four basic parts:

1. pretreatment of the contaminated soil;
2. extraction of the pollutant from the soil;
3. separation of the cleaned clay soil particles from the liquid phase;
4. cleaning and/or recycling of the extracting agent.

In this research project emphasis is on the second part and some attention is paid to the third part.

Extraction experiments are performed batch wise on a small scale first. The extraction behaviour is measured of six heavy metals (cadmium, copper, chromium, nickel, lead and zinc) from five artificially polluted clay soils and from two soils originating from contaminated sites. Both mineral acids and complexing agents are tested as possible extractants. The influence of several parameters on the heavy metal removal percentages is determined.

Metals from the soils that are artificially polluted in a previous adsorption experiment are only extracted to a slightly greater extent if the liquid-to-soil ratio (L/S) is increased. Higher concentrations of the extractant hydrochloric acid HCl can improve the removal efficiency much more than variations in L/S. Extraction efficiencies from the waste site soils Sophia and Melchior are in the same range for the following three conditions: a threefold 30 minutes extraction in 0.1 N HCl, a 24 hours extraction in 0.1 N

HCl and a 30 minutes extraction in 2 N HCl (all performed at L/S ≈ 20). The extractability of the six heavy metals from these soils decreases more or less in the order:

Cd > Pb > Cu > Zn > Ni > Cr

For the three conditions mentioned above extraction efficiencies are found between 80-90% for Cd, Cu Pb and Zn. Removal percentages are higher if initial metal concentrations are higher. This dependency is strongest for nickel and zinc. The remaining metal concentrations in the soils are, however, just below or above the 'B-level' of the Dutch Soil Clean-Up Interim Act. Nickel removal efficiencies vary from 45-80% which causes a remaining Ni concentration in the Sophia waste site soil above the 'C-level'. Chromium can hardly be extracted with the acid treatment: the maximum extraction percentage is 50% (after 30 minutes 2 N HCl extraction).

The extraction results after any 0.1 N HCl treatment can only be improved further to a negligible extent which appears from the results of the third step of the threefold extraction and from those of an extraction of 30 minutes + 24 hours. The extraction efficiencies in 2 N HCl can probably be improved further by applying more extraction steps. It should be investigated if these subsequent extractions may be performed with smaller acid concentrations. Although a concentration greater than 0.1 N HCl is required to reach the A-levels, it is not clear yet which acid concentration will be satisfactory.

The use of very strong acids has some severe drawbacks. In the first place the costs of the extraction process will generally rise. Secondly, the use of a more concentrated acid solution will cause severe 'damage' to the soil structure itself. About 10 wt.% of the solid material of the waste site soils dissolves already in 0.1 N HCl after 30 minutes.

The use of 0.1 M EDTA instead of 0.1 N HCl in a twofold extraction results in greater metal removal efficiencies from the artificially polluted clay soils. A successful extraction in EDTA requires a suspension pH of 4 or less. Although an 0.1 M EDTA solution is equally or more successful in removing recently adsorbed metal ions, this is not the case for the 'real' waste site soils. For the waste site soils only Cd and to a smaller extent Pb have relatively equal or greater removal percentages in EDTA solutions compared to those found in HCl solutions. A drawback of the use of EDTA is its much higher price than HCl.

The greatest Cr removal from the waste site soils (70-85%) in this study is measured in a 0.46 M sodium hypochlorite solution at pH=8.5 that is heated to about 80 °C for 5 minutes and is allowed to cool subsequently. Chromium can be extracted from artificially polluted soils far more easy (in 0.046 M NaClO and without heating). Solubility of chromium compounds can depend strongly on its age which may be the reason for the great difference in extractability between the Cr in the two types of soils. Although the suspension or extractant needs to be heated only for a short period, this is an expensive operation. Other problems are the corrosiveness of the hot solution and the NaClO consumption by organic material in the soil. It is therefore probably easier and cheaper to use multiple NaClO extractions at room temperature. Anyway, the presence of chromium in a contaminated clay soil requires an alternative treatment to HCl extraction. Oxidizing chemicals, like NaClO, offer good possibilities but will always raise the costs of total treatment.

A sequential extraction procedure according to Tessier et al. is carried out. This procedure is applied to compare the distribution of the metals over fractions of the contaminated soils before and after an extractive cleaning. Five -operationally defined- metal fractions in the soil are differentiated by this technique:

F1. 'Exchangeable' ($MgCl_2$ extractable) (Exch)
F2. 'Bound to carbonates' (CO_3)
F3. 'Bound to iron and manganese oxides' (Fe/Mn-Ox)
F4. 'Bound to organic matter or sulfides' (Org/Sulf)
F5. 'Residual'

When the clay soils are polluted artificially with one or more metals, approximately 80-90% of the total metal content is present in the more labile phases of the soils, the fractions F1, F2 and F3 of the Tessier-analysis. Two exceptions were noted: soils that are polluted with Ni only or with Cr only. Six to 25% of total Ni content is determined in the 'residual' fraction. Nickel ions might have diffused to more interior sites in the clay soils.

The metal distribution in the two waste site soils is quite different from that in the artificially polluted soils. The 'exchangeable' fraction is very small while the 'org/sulf' and 'residual' fractions contain larger fractions of metals. The main reason for the smaller removal efficiencies of the metals from the two waste site soils in 0.1 N HCl compared to those from the artificially polluted soils is this more abundant presence of the metals in the 'org/sulf' and especially the 'residual' fraction. The more labile fractions F1, F2 and F3, which are the most important metal sinks in the (freshly) artificially polluted soils, are more easily attacked by mineral acids like HCl than the 'residual' fraction F5.

The removal efficiency in HCl or EDTA from a fraction is determined in the first place by the type of site and less by the type of metal or the metal concentration. Extraction of metals from the 'soil fractions' with 0.1 N HCl or 0.1 M EDTA becomes more difficult in the order:

'CO_3' < 'Fe/Mn-Ox' < 'Org/Sulf' < 'Residual'

Extraction from the 'residual' fraction in particular is much harder than from the other three: 50% of the experiments shows a metal extraction efficiency less than 33% from this 'soil fraction'. After threefold 0.1 N HCl treatment the metal concentrations in only the 'residual' fraction range from 1-5x the A-levels. Removing this rest pollution will be difficult without drastic destruction of soil components. Treatment costs will also rise considerably. Metals in fraction F5 tend to be less mobile. The necessity of further treatment might therefore be related to the mobility or bio-availability of the metals after cleaning and restoration of the clay soil as well as to the total metal content.

The rate of the extraction of four heavy metals (Cu, Ni, Pb and Zn) from artificially polluted and waste site clay soils is determined in a 0.1 N HCl solution. For the waste site soils it is studied under two different conditions: vigorous mixing of the clay soil suspension and settling of a flocculated clay soil suspension. The conditions correspond to the two types of continuous processes that are tested.

Basically two different kinetic patterns are found: the first pattern shows a very rapid extraction followed by a much slower extraction, the second pattern consists of a regularly decreasing clay soil concentration with an extraction rate that is intermediate between those of the very rapid and the slow extraction. The extraction of the four metals from the two waste site soils proceeds generally slower than that from the artificially polluted soils. The differences in extraction efficiencies are described mainly in terms of different proportions of total metal content that react according to the fast or slow extraction process.

The differences in extraction rate between 'vigorously mixed' and 'settling floc' kinetics are small in many cases and can only be measured in the first phase of the extraction process.

A model is developed that describes the rate of extraction at a constant pH and at a constant temperature by two processes with different rate constants. These processes are a fast, irreversible reaction that is first-order in the metal concentration in the clay and a slow, reversible first-order reaction.

This 'two-reaction model' describes the metal concentration curves over a time period of 24 hours with an error less than 20%. A general relationship cannot be found between the fraction that reacts slowly or quickly and the metal distribution according to the sequential extraction procedure.

The influence of the temperature on the extraction rate is measured over a range of 5 to 80°C for Ni extraction from an artificially polluted Winsum clay soil under vigorous mixing conditions. The most evident effect is a decrease in final metal concentration in the clay soil with higher temperature. Calculated values for the energy of activation (although rough values due to the large experimental error) are small and suggest that the extraction process of Ni from Winsum clay soil in 0.1 N HCl is rate-limited by a diffusion process in the porous soil particles. The contaminations in the waste site soils are much older and greater metal contents are found in the 'residual' fraction. Moreover, metal contaminations are not brought necessarily into the environment as a soluble ionic species. Chemical reaction limitations seem more probable in the case of 'real' waste site clay soils.

A laboratory scale continuous installation is built in which the extraction of metals from two contaminated waste site clay soils by a 0.1 N HCl solution is studied in three different experimental set-ups: two continuous stirred tank reactors, a countercurrent sieve-plate column and a combination of one tank reactor and the countercurrent column. Clay soil suspension and extractant are separated by means of flocculation and sedimentation in this continuous set-up. A combined precipitation and flocculation unit is chosen in the test installation to remove heavy metals from the liquid phase.

Operation in the countercurrent column requires aggregates of the very small clay particles to prevent elutriation of the clay over the top of the column. Therefore a flocculation unit precedes the column and flocculated clay is fed to the column. Sieve-plates are mounted on an axis and can be rotated and/or moved up and down pneumatically at desired frequencies to influence the residence time of the clay soil flocs in the column. The rotation is not continuously but the axis turns each time over approx. an angle of 50° forwards and the next time backwards. The number and type of the sieve-plates can be varied.

Metal concentrations in the clay soil after continuous extraction in the different set-ups are not yet in the range of maximum tolerable A-levels. Especially Cr, Ni and Zn concentrations are still too high in Sophia waste site soil and Zn concentration in Melchior waste site soil. The countercurrent process shows higher efficiencies in removing the metal than the CSTR process but the difference is only small. The superiority of the countercurrent process over the CSTR is more evident in the second extraction step than in the first. The following type of cleaning process seems to be promising based on the experiments performed: first an extraction in a stirred tank followed by a further second extraction in a countercurrent column. Residence time in the CSTR can be short (15-30 minutes) while residence time in the column should be as long as possible. Although the countercurrent column showed also greater extraction efficiencies in the first step of the process, the CSTR can be operated more easily and is very well suited for the first rapid part of the extraction process. Metal fractions that are more difficult to extract can then be treated in the column with stronger acid solutions if necessary. Long residence times in the column are required for pollutants like Ni where slow extraction processes are predominant.

Although it is still too early to estimate total costs of the processes described here, it is clear that the costs of chemicals will be an important factor. Recycling of the extractant should therefore be investigated. This will also determine the choice of a method for the fourth part of the process (the cleaning of the extractant).

The continuous extraction processes are described by a model. The kinetic model (see above) is therefore combined with (experimental) information about the hydrodynamic behaviour of the liquid and soil phase in the continuous apparatuses.

The clay soil and the extractant are assumed to be perfectly mixed in the stirred tanks, based on residence time distribution experiments performed in the liquid phase in these tanks. The extraction percentages can be predicted with the model within 15% absolute error if the pH-value in the extractor is the same as in the kinetics experiments. The model shows that only a small improvement can be expected from a further thickening between the extractors. This result indicates that the backward (re-adsorption) reaction in the model is not very important.

The residence time distribution of flocculated clay soil and extractant in the countercurrent column are determined experimentally. The mean residence time of clay soil ranges from 13 to 25 minutes. The mixing conditions in the solid phase can be described by a Peclet number between 9 and 16 and the liquid phase can be approximated by plug flow. The plug flow with axial dispersion model is chosen to describe the flows in the column.

Combined with the kinetic expressions the model predicts in most cases extraction efficiencies that are smaller than the ones calculated from the measured concentrations. This is partly due to the lower pH values in the column compared to those in the kinetic experiments. The model results show that the removal of metals from the clay is limited by the slow, reversible extraction reaction. Variation of parameters in the model shows that extraction efficiencies in the countercurrent column can only be improved slightly by larger column lengths or greater solids hold-up. Both these factors cause longer residence times which are the main reason for a further decrease in the remaining metal concentration in the clay. The effect of countercurrent operation itself is actually small because the backward reaction is hardly important. The extraction efficiency after a short period is dominated by the fast reaction. Cocurrent operation would thus give about the same result in most cases. Countercurrent operation is still preferable because clay soil and extractant have to be separated after the extraction. Clay soil and liquid cannot be separated completely without thermal treatment. In countercurrent operation the amount of metal ions in the liquid adhering to the soil is much further reduced than in cocurrent or CSTR operation.

LIST OF SYMBOLS

a	specific surface	(m^{-1})
c	concentration	$(mol.m^{-3})$ or (ppm)
d	particle size diameter	(m)
d	rest metal concentration in clay soil	$(mol.m^{-3})$ or (ppm)
D	tube diameter	(m)
D	axial dispersion coefficient	$(m^2.sec^{-1})$
ds	dry matter content of suspension	$(wt.\%)$
E	extraction efficiency	$(\%)$
E_a	free energy of activation	$(kJ.mol^{-1})$
h	(column) height	(m)
H	total column height	(m)
ΔH°	standard reaction enthalpy	$(kJ.mol^{-1})$
k	first order reaction rate constant	(min^{-1})
k_{fd}	mass transfer coefficient	(min^{-1})
K_{eq}	equilibrium constant	$(-)$
L	mass flow of liquid	$(kg.sec^{-1})$
L/S	liquid to solid weight ratio	$(-)$
m	equilibrium constant	$(-)$
M	mass of liquid or solid	(kg)
N	number of tanks in series	$(-)$
Pe	Peclet number	$(-)$
R	gas constant	$(kJ.mol^{-1})$
$-R_a$	rate of reaction (1)	$(mol.sec^{-1})$ or $(ppm.min^{-1})$
$-R_b$	rate of reaction (2)	$(mol.sec^{-1})$ or $(ppm.min^{-1})$
Re	Reynolds number	$(-)$
S	mass flow of solids	$(kg.sec^{-1})$
t	time	(sec)
T	absolute temperature	(K)
v	average velocity	$(m.sec^{-1})$
V_ℓ	settling velocity of interface	$(m.sec^{-1})$

GREEK SYMBOLS

α_0	distribution parameter between two extraction reactions	$(-)$

ε	void fraction	(-)
σ	standard deviation of residence time distribution	(sec)
σ^2	variance of residence time distribution	(sec^2)
τ	mean residence time	(sec)

SUBSCRIPTS

a	according to reaction (1), see Chapter 4
b	according to reaction (2), see Chapter 4
b	bottom
e	extraction (extractant)
eq	at equilibrium
f(ℓ)	film
i	in
k	clay
l(ℓ)	liquid (extractant)
max	maximum
min	minimum
t	top
u	out
0	initial, at time zero
1	(*i.a.*) after one extraction
2	(*i.a.*) after two extractions, etc.

ABBREVIATIONS

Bu	Burum clay soil
Ma	Maas clay soil
Rn	Rhine clay soil
Wa	Waal clay soil
Wi	Winsum clay soil
Rn-1	Rhine clay soil polluted with one metal
Rn-3 etc.	Rhine clay soil polluted with three metals etc.
So	Sophia waste site clay soil
Mel	Melchior waste site clay soil
Exch	'Exchangeable' fraction of Tessier sequential extraction procedure (see Chapter 3)
CO	'Carbonate' fraction
Fe/Mn-Ox	'Iron and manganese oxide' fraction
Org/Sulf	'Organic and sulfidic' fraction
Res	'Residual' fraction

Chapter 1

INTRODUCTION

Due to activities in the past many old industrial areas and dumping sites are contaminated to such an extent that remedial action is required to prevent further environmental pollution. Surveys undertaken in five countries (Denmark, Germany, France, Netherlands and UK) indicated a number of about 8900 of such sites requiring immediate treatment *(1)*. They represent an area of 185,000 ha or 0.2 % of the total land area in these countries. A further 13,800 sites in three countries were designated as potentially contaminated. Common pollutants found are a large variety of hydrocarbons (aliphatic, aromatic, chlorinated; pesticides, dyes), cyanides and heavy metals. Public concern was growing about this subject (see Figure 1.1) and was also expressed in legislation (for example the Soil Clean-Up Interim Act *(2)* in the Netherlands). To examine the degree of contamination indicative levels of pollutants were designated like the A-, B- and C-levels (see Table 1.1). The A-level has been derived from the natural background concentrations measured in a large variety of soils that were considered to be not polluted. Remedial actions should generally be aimed at reducing the contaminant concentration to this A-value. A reference value for a clean 'standard' soil type was introduced later *(2)*. It differentiates for the soil type by including the organic matter and clay content in calculation of the 'clean-soil' level.

Thermal, biological and extractive cleaning methods have been developed to remove pollutants from different types of soils *(3)*. Various methods have been proposed for treating heavy metal pollution in soils or sludges. A very simple but still costly method is digging out the soil and deposition on a controlled 'hazardous' waste-site as was done for nickel and cadmium wastes from the soil of an abandoned battery factory *(4)*. Natural clay layers are sometimes used to prevent further dispersion of the contaminants at the bottom side of such controlled deposits. Clay liners can, however, be affected by acidic seepage water from the deposit *(5,6)*. An example of a thermal method is sintering that was used to fix chromium and other heavy metals present in tannery sludge *(7)* or in metal plating sludge *(8)*. Accumulation of heavy metals in earthworms was measured in polluted soils *(9,10)* which led to speculations about biological clean-up methods. A partial and slow removal of heavy metals was reached through the addition of zeolites to strongly contaminated soils *(11)*. Ion exchangers seemed suitable for removing the exchangeable fraction of metals

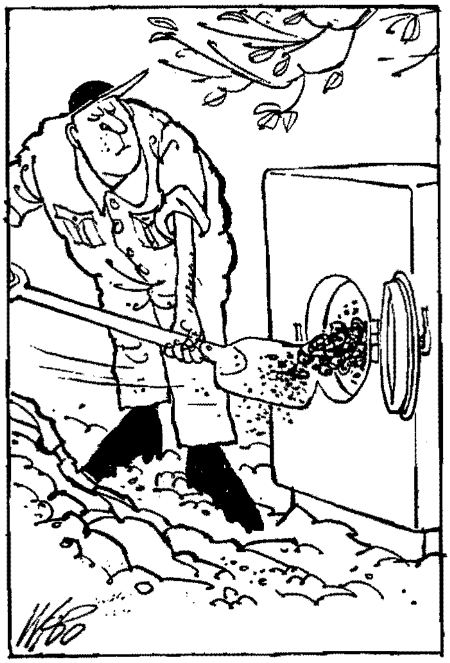

Figure.1.1. *Growing public concern about soil pollution expressed in newspaper cartoon (reproduction with permission)*

from Rhine sediment but selectivity should be further improved *(12)*.

The most widely applied and investigated cleaning techniques for heavy metals are based on extraction. Commercial scale plants are already operational for the decontamination of sandy or loamy soils *(13)*. Pollutants are removed with water based extractants in varying degrees of success. Cleaning of clay soils or fractions of soils with the smallest particles is still a problem mainly because the fine-grained material (which contains the largest proportions of clay minerals, hydrous oxides and organic matter) has a high adsorption capacity for heavy metals and strong metal-substrate interactions occur. The smaller grain sizes are more difficult to handle and normally end up in the uncleaned residual process stream in the existing treatment facilities. This material is still disposed of as chemical waste.

The purpose of this study is to investigate the extraction of heavy metals from clay soils or the small-particle-size fractions (d < 50 μm) of soils to develop possible (continuous) treatment processes for heavy metal contaminated clay soils.

Extraction can be defined here as the release and transport of a contaminant from a solid phase (soil or sludge) to a liquid phase (extracting

Table 1.1.
INDICATIVE A-, B- AND C-LEVELS FROM THE DUTCH SOIL CLEAN-UP INTERIM ACT AND NATURAL BACKGROUND CONCENTRATIONS FOR SIX HEAVY METALS (in ppm)

Metal	A-level[1]	B-level[2]	C-level[3]	Background concentration[4]
Cd(Cadmium)	1	5	20	0.05 - 1.8
Cr(Chromium)	100	250	800	11 - 17
Cu(Copper)	50	100	500	0.83 - 50
Ni(Nickel)	50	100	500	0.5 - 47
Pb(Lead)	50	150	600	3.1 - 200
Zn(Zinc)	200	500	3000	6.4 - 189

[1] Reference value based on natural background values
[2] Assessment value above which more thorough investigations are necessary
[3] Assessment value above which soil sanitation should be investigated
[4] From Edelman et al. *(34)*

agent, extractant). The mechanism of this transfer can be (a combination of) dispersion or dissolution of the soil substrate in the liquid phase with accompanying dissolution of the associated metal, ion exchange or a chemical reaction of the metal or metal compound itself (like chelation). Extractive cleaning can be used in-situ (without digging out the soil) as was shown for a cadmium polluted dune *(14)*. This method is however limited to permeable soils and cannot be applied easily for clay soils. If applicable it is very attractive because soil excavation is rather expensive. Extraction of excavated soils or of dredged sludges is performed with various cleaning agents. In most commercial operating plants water is used with some additives like detergents or dispersion agents *(13)*. A number of authors proposed the use of mineral acids: for example, Shimogawa et al. *(15)* used 0.5-5% sulfuric acid to remove zinc, cadmium, copper and iron; Müller *(16)* applied hydrochloric acid to dredged sludges and Calmano and Förstner *(17)* treated contaminated harbour sludges with a combination of dissolved sulfur dioxide and bacteria.

Generally, an extraction process consists of four basic parts:

1. pretreatment of the contaminated soil;
2. extraction of the pollutant from the soil;
3. separation of the cleaned clay soil particles from the liquid phase;
4. cleaning and/or recycling of the extracting agent.

In this research project emphasis is on the second part and some attention has been paid to the third part. Pretreatment methods basically fractionate the soil into a coarse and a fine fraction. Sieving and hydrocyclonation are commonly used techniques. Hydrocyclonation was also used in this work to 'produce' a clay soil suspension of desired mean particle diameter. In most cases the fraction 'fines' contained larger concentrations of contaminants than the coarse fraction. In this way fractionation can also be applied as a cleaning route *(13,18,19)*. Methods for removing heavy metals from a liquid waste stream (part 4) are well-known from waste water treatment technology *(20,21)* and are not a part of this study. Cleaning and recycling of the extractant are nevertheless essential points in the development of an economical feasible overall process. Electrodeposition, membrane, ion-exchange or bacterial processes seem to offer opportunities.

The extraction of the pollutants from the soil is the main subject of this study. Only clay soils or the fraction of other soils with a particle diameter below approximately 50 μm were investigated because this fraction is generally the most polluted and the most difficult to clean. Both mineral acids and complexing agents were investigated because these extractants seem to be the most successful agents for removing a wide range of heavy metals as has been discussed extensively in literature (see section 2.4). The extraction behaviour is measured of six heavy metals (cadmium, copper, chromium, nickel, lead and zinc) from five artificially polluted clay soils and from two soils originating from contaminated sites.

Extraction experiments were performed first batch wise on a small scale. The influence of several factors, like pH, number of extractions, liquid to solid ratio, was determined (see Chapter 2). To get some more insight in the behaviour of the various metals a sequential extraction procedure was carried out. By this technique the metals in the soil are classified into different retention modes (like exchangeable, bound to organics etc.). The metal distributions in the clay soils before and after the extractive cleaning were described by means of this experimental fractionation technique (see Chapter 3). The kinetics of the extraction play an important role in the cleaning process. Kinetics were measured under different experimental conditions and described by a mathematical model consisting of two parallel desorption reactions (see Chapter 4). Based on the batch results a continuous laboratory test installation was built. Continuous extraction of a flocculated settling clay suspension in a countercurrent sieve-plate column was tested in this installation. Other cleaning routes viz. extraction in continuous stirred tank reactors in series and a combination of tank and column were also investigated. Clay soil suspension and extractant were separated by means of flocculation and sedimentation in this continuous set-up. A combined precipitation and flocculation unit was chosen in the test installation to remove heavy metals from the liquid phase. Flocculation experiments and continuous extraction experiments are described in Chapter 5. The kinetic model developed in Chapter 4 was combined with information about the hydrodynamic behaviour of the clay soil and extractant in the continuous apparatus (from residence time distribution experiments). It is then possible to model the continuous extraction processes (see Chapter 6).

Part of the experimental work and the results given here were described earlier in internal reports and in conference papers *(22-33)*.

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Chapter 2

BATCH EXTRACTION OF HEAVY METALS FROM CONTAMINATED CLAY SOILS

2.1. INTRODUCTION

In this chapter batch extraction experiments will be discussed. Many authors have studied the extraction or desorption of metal ions from various kinds of soils. A lot of work has been done, especially in the field of plant nutrition and agriculture, on the subject of adsorption and desorption of metal ions under pH and redox conditions that are close to natural soil conditions *(e.g. 1)*. More recently, adsorption and desorption research on soil components is also being carried out from an environmental point of view. Leaching of metal ions to the ground water system is of interest, in particular the leaching by acid rain *(e.g. 2-5)*. The ground water system is the most important way of transport of toxic materials to plants or the public water supplies. Desorption or extraction is also being studied by some authors in order to clean heavy metal contaminated soils *(6-11)*. A number of extracting agents are known for various metals: inorganic and organic acids, complexing agents like EDTA and DTPA, salt solutions with competing ions like Ca^{2+}, oxidizing and reducing species *(6-22)*. In case of extractive cleaning conditions can be quite different from natural soil conditions. As a consequence, the soil properties can also change drastically under this heavy 'attack'.

The aim of the batch extractions is to determine the metal removal efficiencies with several extractants under varying conditions. Both inorganic acids and complexing agents were tested because these extractants seem to be the most promising for removing a wide range of heavy metals. Combinations of acid solutions, chelating and metal salt solutions were also investigated. Because Cr could hardly be extracted by hydrochloric acid, oxidizing solutions were tested for the removal of Cr.

We have studied two groups of contaminated soils in this project:

1. five artificially polluted clay soils;
2. two 'clay' soils from a depot of contaminated soils that were excavated from former industrial sites (waste site soils).

These seven soils will be described in more detail in Section 2.2. It is quite common to use artificially polluted clay soils, isolated soil components or synthetically prepared substrates in adsorption or desorption studies *(12,* *14, 15, 23, 24)*. There may, however exist considerable differences between the artificial and the 'real' pollution and the way it is present in the soil. It is therefore important to know how the clay soils are polluted. The adsorption of the metal ions on the five originally 'clean' clay soils will be discussed briefly in Section 2.3.

We restrict ourselves to clay soils or the fraction of loamy or sandy soils that has a particle size below approx. 50 μm. Treatment methods and facilities exist already for sandy soils (see Chapter 1).

The extraction of only six metal ions is measured: cadmium, chromium, copper, nickel, lead and zinc. More pollutants like arsenic and tin, are present in the waste site soils; a few extraction results with these other metals are shown in Appendix II.2.

The results of the different extracting agents will be discussed in the remainder of this chapter: extraction with hydrochloric acid in Section 2.4, extraction with a complexing agent (EDTA), metal salt solutions and combinations of EDTA and hydrochloric acid in Section 2.5 and Cr extraction with sodium hypochlorite as an oxidizing agent in Section 2.6. Finally, results are compared and discussed in Section 2.7.

2.2. CHARACTERIZATION OF THE SOIL MATERIALS

Seven different soils were used in the extraction experiments. Five of these were originally 'clean' clay soils and were artificially polluted by adsorption of metal ions (the adsorption experiments are described in Section 2.3). The five soils were top layers from different areas in the Netherlands. Three of them were taken from river areas (Rhine, Waal and Maas clay soils), and the other two from sea clay deposits (Winsum and Burum soils).

The two waste site soils (Sophia and Melchior) were taken from a (temporary) depot of contaminated soils that were excavated from former industrial sites. The Melchior pollution was caused by a metal plating industry approximately 30-60 years ago. Sophia soil is a mixture of sludge and soil from a ditch contaminated mainly by an enamel industry. The Melchior soil was excavated in 1982 and the Sophia soil in 1986.

The seven soils have a varying clay content (weight fraction of particles < 2μm). The originally clean soils contain at least 30 wt.% clay (see Table 2.1). Therefore, the complete soil was used in the batch extraction experiments (and in the soil characterization too). The waste site soils contain a much smaller clay fraction. Because the objective is to study only the extraction from the fine-grained material of soils, it is necessary to fractionate the two waste site soils. Therefore, the waste site soils were sieved or hydrocyclonated. The result of this pretreatment was a size fraction of particles smaller than approx. 60 µm that was used in the extraction experiments (see also Fig. 5.3. in Chapter 5).

Table 2.1.
SOME PROPERTIES OF FIVE (NON-POLLUTED) DUTCH CLAY SOILS USED IN THIS STUDY

Name of the soil (Abbreviation)	Rhine (Rn)	Waal (Wa)	Burum (Bu)	Maas (Ma)	Winsum (Wi)
Fraction clay (wt.% < 2 µm)	42	32	36	34	50
Fraction < 20 µm (wt.%)	85	62	57	64	70
d-50 [1] (µm)	3.4	11	10	9.5	1.9
Density (10^3 kg/m^3)	2.60	2.58	2.59	2.55	2.49
Specific surface [2] (m^2/gram)	112	71	113	94	132
CEC (meq/100 gram) [3]	22.8	16.3	17.6	21.8	22.6
pH-H_2O (-)	7.6	7.6	7.7	6.8	7.3
Carbonate content [4] (wt.% as $CaCO_3$)	10.1	8.0	2.8	0.0	0.0
Organic carbon content [5] (wt.% as C)	0.52	0.74	0.49	0.60	0.65
Free Fe-Ox (DCB) (wt.% as Fe)	1.16	1.07	0.69	1.79	1.12
Soil code on Dutch soil map	Rn95A	Rn15A	Mn85C	Rd90C	kMn68C

[1] Weight mean particle diameter;
[2] Determined by water adsorption;
[3] CEC=cation exchange capacity, determined by BaCl2/Mg^{2+} exchange;
[4] Determined volumetrically by modified procedure of Scheibler;
[5] Determined by oxidation with dichromate.

Some properties of the five clean clay soils that affect the sorption behaviour were determined (see Table 2.1). The soils were dried at 110 °C and crushed in a 2 mm jaw crusher before characterization. The drying in particular may have changed some of the natural clay soil properties. Lehmann and Harter reported that the Cu adsorption by air-dried and oven-dried soils differed relatively little from adsorption by field-moist soil *(25)*. Bartlett

(26) warned for the use of so-called 'lab dirt' (a dried, pulverized, sieved and stored soil) in studying soil chemistry. In this study extrapolation of the results from the 'lab-soils' to soils under field conditions is not of particular interest. Extraction conditions are extreme compared to the natural soil environment.

Soil properties of the two waste site soils were measured for the complete soil sample and for a specified sieve fraction (Table 2.2). These soils were dried at the air. The sieve fractions can be considered to be representative of the waste site soil fractions used in the extraction experiments.

Table 2.2.
SOME PROPERTIES OF TWO WASTE SITE SOILS FROM TEMPORARY DEPOSITS

Name of the soil Particle size fraction	Sophia <100 μm	Sophia Total	Melchior <100 μm	Melchior Total
Fraction Clay (wt.% < 2 μm)	34	18	29	8
Fraction < 20 μm (wt.%)	79	43	65	18
d-50 (μm)	4	90	8	>80
Density (10^3 kg/m)	-	2.38	-	2.41
Specific surface (m^2/gram)	129	70	152	69
pH-H_2O (-)	7.4	-	7.6	-
Carbonate content (wt.% as $CaCO_3$)	6.9	4.2	4.3	1.8
Organic carbon content (wt.% as C)	5.47	3.52	6.45	2.67

A chemical analysis of the seven soils was made after destruction of the soil by a digestion procedure. This procedure is a hydrofluoric acid decomposition technique and is described in Appendix II.1. All metal concentrations in the clay throughout this study were measured by atomic absorption spectrophotometry (AAS) after application of this destruction. The total main element composition of the soils is given in Appendix II.2.

X-ray diffraction measurements showed that the clay minerals of the clean clay soils consist of a mixture of (mainly) illite and a small amount of kaolinite.

2.3. PREPARATION OF ARTIFICIALLY POLLUTED CLAY SOILS: ADSORPTION EXPERIMENTS

2.3.1. Introduction

A large number of variables complicates the study of the extractive behaviour of contaminants from a soil. Moreover, a special problem is caused by the nature of the starting materials: a polluted soil can be very inhomogeneous in composition and in degree and age of the contamination.

For this reason, extraction of artificially polluted soils was measured first. Differences exist between the artificially contaminated soils and the 'real' waste site soils. In the next sections the method of contaminating the clean soils by adsorption experiments is described and the results of the adsorption experiments are given. A tremendous number of adsorption studies have been published in the literature *(24, 27-32)*. Many authors have searched for a relation between soil properties and metal adsorption. Such correlations are of limited value only and can hardly ever be generalized to many soil-metal combinations. Therefore only the most remarkable results of the adsorption experiments will be discussed below. This information can be helpful in comparing the extraction results of the two types of soil.

2.3.2. Experimental methods: adsorption

The artificially polluted soils were prepared in the following way: a certain amount of air dried clay soil was ground in a mortar for 1-2 minutes. A metal salt solution was added to the ground clay soil in a glass beaker. The soil to solution weight ratio was normally 1:20 and in some cases 1:10 or 1:5. The beaker was covered with polyethylene and the suspension was stirred with a glass stirrer for 24 hours to establish equilibrium.

The pH was recorded. The temperature was kept at 22 ± 2 °C in all experiments. The suspension was centrifuged (for 15 minutes at 8800*g or for 45 minutes at 2000*g) after the end of the 24 hours period. The wet clay soil was dried in ambient air or in an oven at 50 °C. The dry matter content was measured. Total metal concentration in the supernatant liquid was measured by atomic absorption spectrometry (AAS). The total metal concentration in the clay was also determined after decomposition of the solid material (see Section 2.2).

Four types of artificially polluted clay soils were prepared: soils contaminated with one, three, five or six different heavy metals. The metals are: cadmium, chromium (III), copper, nickel, lead and zinc. Depending on the desired concentration in the soil, the composition and concentration of the metal salt solution varied in the adsorption experiments.

Nitrate salts of the metals were used, except the chloride salt in the case of chromium (III). All chemicals were reagent grade.

The conditions of some of the adsorption experiments were slightly different from those given above. This will be noted where relevant.

2.3.3. Results and discussion of adsorption experiments

If only one metal ion was adsorbed to one of the five clay soils, two types of adsorption isotherms were observed. The first type did not show a maximum in the amount of metal adsorbed: even in case of the highest initial liquid concentration approx. 100 % of the metal ions were adsorbed on the clay soil. The other type of adsorption approached saturation with increasing concentration and could be described by a Langmuir equation.

The adsorption to the non-calcareous clay soils Winsum and Maas follows the Langmuir behaviour in all cases, except for Cd-adsorption (the Cd concentrations applied are relatively low because of the lower natural background level). The other three clay soils adsorb less than 100 % of the metal only in the cases of Ni and Zn. The zinc saturation is not very surprising because the concentrations applied are much higher than those of the other metals.

These results show that the carbonate content of the clay soil strongly affects the adsorption capacity of these soils. Several other authors have found a positive relation between metal adsorption and carbonate content of the soil *(33-36)*. Carbonate causes (at least) two effects:

1. the possibility of heavy metal-carbonate precipitates;
2. buffering the slightly acidic metal solution during the adsorption.

The suspension pH in the different adsorption experiments depended on the initial metal concentration in the liquid and on the specific metal clay combination. A lower adsorption percentage was measured for experiments with lower pH values (see Figure 2.1). This observation is in accordance with the so-called ‘pH-adsorption-edge’, a rather steep decrease in adsorption over a small pH-trajectory *(23, 27, 37-40)*. The pH-value where the ‘adsorption-edge’ began decreased in the order: Ni > Cu > Cr.

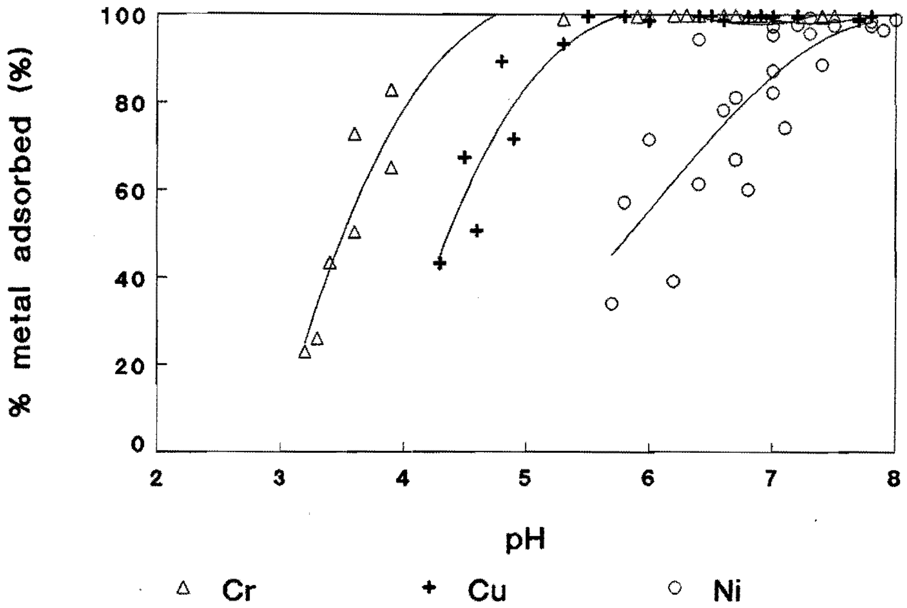

Figure 2.1. *Percentage Cr, Cu and Ni adsorbed to five originally clean clay soils from solutions with different initial metal concentrations as a function of pH value in suspension after 24 hours adsorption.*

This type of pH-dependence occurs especially with oxide or hydroxylic surface groups and suggests the importance of adsorption to Fe- and Mn-oxide and organic surface coatings. Sequential extraction measurements confirm these findings (see Chapter 3).

The metal ions competed for the adsorption sites in the experiments where 3, 5 or 6 different metals were present in the solution. Such experiment series were carried out with Rhine and Winsum clay soils. The different amounts of each metal adsorbed indicated an order of preference of the clay soil for the metal ions (original metal concentrations in the liquid were equal on a molar basis). Table 2.3 shows some of these experimental affinity sequences for Rhine and Winsum clay soils and some comparable data from the literature. Considering the different experimental conditions, the sequences are rather consistent. The preference is approximately in decreasing order:

chromium > lead ≥ copper > zinc > nickel > cadmium

Another interesting feature is the change in the position of Cu in the affinity sequences of the clay soils Rn-5a to d and Wi-5a to d (see Table 2.3). Copper shifts to a lower ranking as the initial solution concentration decreases. This effect may be due to a more specific (and strong) Zn- and Ni-adsorption than Cu-adsorption. This was confirmed by the extraction results (see Section 2.4).

Table 2.3.
METAL CLAY SELECTIVITY ORDERS

Clay Soil	Initial solution conc. (mmol/l)	Lit	Selectivity Order
Rn-3	8	-	Pb ≈ Cu > Zn
Wi-3	8	-	Pb > Cu > Zn
Rn-6	2.5-5	-	Cr ≥ Cu ≥ Pb > Zn > Ni > Cd
Wi-6 *	2.5-5	-	Cr > Pb ≥ Cu > Zn > Ni > Cd
Rn-5a	4	-	Pb > Cu > Zn > Ni
Rn-5b	0.8	-	Pb > Zn > Cu > Ni
Rn-5c	0.4	-	Pb > Zn > Cu > Ni
Rn-5d	0.2	-	Pb ≈ Zn > Ni ≥ Cu
Wi-5a	4	-	Pb > Cu > Zn > Ni
Wi-5b	0.8	-	Pb > Cu > Zn > Ni
Wi-5c	0.4	-	Pb > Zn > Cu > Ni
Wi-5d	0.2	-	Pb > Zn > Ni > Cu
Illite	0.083	*28*	Zn > Pb > Cu > Cd
Illite	-	*29*	Cu ≥ Pb > Zn > Cd
Winsum	-	*41*	Pb > Cu > Zn > Cd
Kaolinite	-	*42*	Cr > Cu > Pb > Ni > Zn

* Cd results are left out because of deviating initial solution conc.
Nomenclature:
Rn (Wi) = Rhine (Winsum) clay soil
-3 = clay soil artificially polluted with Cu, Pb and Zn
-5 = clay soil artificially polluted with Cd,Cu,Ni,Pb and Zn (a,b,c,d: different initial metal concentrations)
-6 = clay soil artificially polluted with Cd,Cr,Cu,Ni,Pb and Zn

Finally, the equilibration time for adsorption was 24 hours in all experiments. Some authors have measured that adsorption processes continued for days, even weeks *(43,44)*, but others concluded that equilibrium was reached within several to 24 hours *(45-47)*. The adsorption seems to be a two step process: a very rapid adsorption of the bulk of the metal followed by a slower adsorption (which may be to the more interior sites of the adsorbent). The 24 hours equilibration period is probably much shorter than the time of exposure in the waste site soils. This difference is one possible reason for deviating extractive behaviour of the two types of contaminated soils.

2.4. BATCH EXTRACTION EXPERIMENTS IN HYDROCHLORIC ACID

2.4.1. Introduction.

It is well known that hydrochloric acid is a fairly good extracting agent for metal ions from various kinds of soils. Table 2.4 shows a survey of the use of inorganic acids to extract metals from soils. A review of this literature will be given in the section Discussion. At this point it should be mentioned that besides an undesirable, but maybe inevitable change in soil properties, higher acid strengths cause higher costs of the extraction process. We have restricted the acid concentrations to an upper limit of 0.1 N HCl in this study except for one exploratory experiment.

The general purpose of the batch experiments with hydrochloric acid is to determine what final metal concentrations in the artificially contaminated and in the waste site clay soils can be reached under different conditions. The effect of the following variables on the extraction results was measured:

-hydrochloric acid concentration;
-soil to solution ratio;
-number of extractions;
-extraction time (see also Chapter 4).

Extractions were carried out with both artificially and originally contaminated soils. Metal combinations and metal concentrations were varied in the artificially polluted soils.

Table 2.4.
LITERATURE SURVEY OF EXTRACTIONS WITH INORGANIC ACIDS

First Author *(literature)*	Soil[1]	Extractant[2], time, L/S, temp	Extraction results (Percentage metal removed[3])					
			Cd	Cr	Cu	Ni	Pb	Zn
Aitang	Various	2N HNO_3, 18°C	-	-	30-60	4-20	-	10-30
(48)		2h, L/S=10 100°C	-	-	50-100	40-70	-	50-80
Andersson	Heavy	2N HNO_3, 2h	86	57	85	65	85	69
(49)	clay	L/S=10, 100°C (*)[4]	92	66	88	73	88	84
Assink	Various	0.1N HCl, 1x30m	30-100	1	30-50	-	10-60	50
(6)	sandy and	0.1N HCl, 3x30m	65-100	20	40-90	-	20-90	75
	loamy	0.3N HCl, 3x30m	-	1	-	-	90	-
		all: L/S=5						
Aualiitia	Estuarine	0.45N HCl,	60	-	40-100	-	60-100	-
(24)	sediments	0.45N HNO_3,	60	-	70-90	-	40-100	-
		both 24h, L/S=2000						
Baghdady	Various	0.5N HNO_3	77	3	-	8	54	-
(21)								
Brüne	Various	2N HCl, 1h,	100	15-20	75	15-20	100	30
(50)		L/S=10						
Chatterjee	Smectite	0.067N H_2SO_4, (*)	-	-	92-95	-	-	-
(51)		30m, L/S=1, 60-70°C						
Farrah	Illite	0.1N HNO_3, (*)	90-95	-	70-85	-	70-85	70-85
(12)	Kaolinite	0.1N HNO_3, (*)	70-85	-	70-85	-	100	90-95
		both 24h, L/S=2000						
Harter	Acidic	0.01N HCl, (*)	-	-	80-90	70-80	80-90	>90
(14)		1h, L/S=100						
Kaplunova	Various	0.1N HCl	-	-	≈100	-	-	≈100
(16)								
Kiekens	Calcareous	0.1N HNO_3,	74	-	30	-	42	14
(41)	heavy clay	0.5N HNO_3, both	74	-	44	-	54	18
		30m, L/S=5						
Müller	Dredged	0.3N HCl,	92-96	-	92	87	-	88
(7)	sludge	15m, L/S=3						

Table 2.4. (continued)
LITERATURE SURVEY OF EXTRACTIONS WITH INORGANIC ACIDS

First Author *(literature)*	Soil^1	Extractant^2, time, L/S, temp		Extraction results (Percentage metal removed^3)					
				Cd	Cr	Cu	Ni	Pb	Zn
Randall *(8)*	Clay loam	0.25N HCl	12h, L/S= 20	-	-	-	-	71	21
		1N HCl		-	-	-	-	74	31
		4N HCl		-	-	-	-	79	41
		4N HNO_3		-	-	-	-	78	35
Rietz *(22)*	Various	0.1N HCl	2h, L/S= 10	85	-	-	-	40-70	60-65
		0.1N HNO_3		80-85	-	-	-	65-85	60-65
		0.5N HNO_3		85-90	-	-	-	85	70
Staiger *(10)*	Various	1N HCl, 1h, L/S=2.5		100	-	40	-	90	20
		1.5N HNO_3, 30m L/S=10, 100°C		100	-	90	-	100	75
Tyler *(15)*	Fine loamy	0.1N HCl, 12h, L/S=1	(*)	67	-	27	50	-	-

Notes: 1) only some general indication is given.
2) time: m=minutes, h=hours, d=days; L/S=liquid to soil weight ratio; temp=temperature during extraction: room temp. except where mentioned.
3) percentages can be average from results with various soils.
4) (*) indicates extractions with artificially polluted soils.

2.4.2. Experimental methods: batch extraction

Artificially polluted and waste site clay soils were extracted in batch experiments. The general procedure in these extraction experiments is as follows.

An amount of air dried clay soil (2-20 g) was put into a glass beaker, the extraction cell. (Figure 2.2). At time zero a hydrochloric acid (HCl) solution was pipetted into the beaker and the suspension was mixed by means of a glass stirrer. The suspension was stirred for 1/2 or 1 hour at room temperature. The pH was recorded and controlled at a constant set-point value by addition of a HCl solution of the appropriate concentration from a burette. In most cases the pH was kept constant at 1.0 by adding 1 N HCl solution. The initial soil to solution weight ratio was 1:20, but this ratio could change slightly during

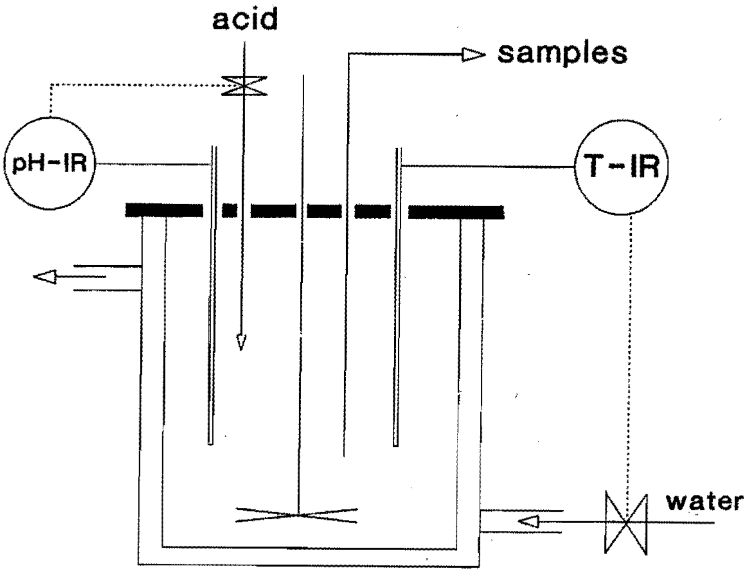

Figure 2.2. *Extraction cell for batch extractions.*

the experiment due to acid addition. After the 1/2 or 1 hour period, the suspension was centrifuged and samples were taken from the supernatant liquid and the clay material.

A second and third extraction were performed subsequently with the collected clay material after centrifugation. These experiments were carried out with a fresh amount of HCl solution and were similar to the first extraction. The clay soil was dried at the air after the centrifugation in some cases. If wet material was used in the second or third extraction, the dry matter content of the centrifuged clay soil was measured. The second and third extraction of the clay soils that were polluted artificially with only one metal were carried out in centrifugal tubes on a shaking-machine instead of in the extraction cell. The pH could not be controlled in this case but it changed only slightly from 1.0 to 1.1.

Samples of liquid and clay were taken after each extraction. The liquid samples were analysed directly by AAS. The clay samples were analysed by AAS after digestion of the solid material (see Appendix II.1).

This procedure is the general one for the batch extraction experiments. Some conditions were varied depending on the specific extraction experiment (for example, extraction time, acid concentration, number of extractions, drying after centrifugation). This will be noted where relevant.

2.4.3. Experiment series with HCl

The following batch extraction experiment series were carried out with hydrochloric acid solutions:

A - extraction of Cd, Cr, Cu, Ni, Pb, and Zn, from Rn, Wa, Bu, Ma and Wi clay soils, that were polluted artificially with only one metal.
Conditions: three extractions in 0.1 N HCl solution, air-drying after the first extraction; first extraction 1 h in a stirred beaker; 2nd and 3d step 1/2 h on a shaking-machine.
Results: Appendix II.3, Table II.3.1.

B - extraction of Cu, Pb and Zn from Rn and Wi clay soils, that were each polluted artificially with these three metals (indicated by Rn-3 and Wi-3).
Conditions: two extractions in 0.1 N HCl solution, both steps 1 h in a stirred beaker.
Results: Appendix II.3, Table II.3.2.

C - extraction of Cd, Cr, Cu, Ni, Pb, and Zn from Rn and Wi clay soils, that were each polluted artificially with six metals (indicated by Rn-6 and Wi-6). Conditions: same as series B
Results: Appendix II.3, Table II.3.2.

D - extraction of Cd, Cu, Ni, Pb, and Zn from four Rn and Wi clay soils, that were each polluted artificially to four different concentrations with these five metals (indicated by Rn-5a, Rn-5b, Rn-5c, Rn-5d, Wi-5a etc).
Conditions: three extractions in 0.1 N HCl solution, no drying after the 1st and 2nd extraction, all three steps had an extraction time of 1/2 h. and were carried out in stirred beakers.
Results: Appendix II.3, Table II.3.3.

E - extraction of Cd, Cr, Cu, Ni, Pb, and Zn from the two waste site soils Sophia and Melchior.
Conditions: same as series D
Results: Table 2.5.

F - extraction of Cu from artificially polluted Rn and Wi soils .
Conditions: extraction at six different HCl concentrations; extraction time: 1 h.
Results : Appendix II.3, Table II.3.4.

G - extraction of Cu and Ni from Wi and Rn clay soil respectively .
Conditions: extraction at four different soil to solution weight ratios; extraction time: 1 h
Results: Appendix II.3, Table II.3.5.

All extraction experiments were performed in duplicate, except the experiments of series A, F, and G. The clay concentrations in the tables are the mean values of the duplicate experiments.

2.4.4. Calculations and experimental errors

Both the metal concentration in the extraction solution after the experiment, C_ℓ, and in the clay, C_k, were measured in most cases. The metal concentration in the clay can be calculated from the liquid concentration by a metal balance over the liquid and solid phase:

$$C_{k1} = (M_{k0}*C_{k0} + M_{\ell 0}*C_{\ell 0} - M_{\ell 1}*C_{\ell 1}) / M_{k1} \tag{2.1}$$

where:
C_{k1} = metal concentration in the clay after 1 extraction (mg metal/kg clay)
C_{k0} = initial metal concentration in the clay (mg metal/kg clay)
$C_{\ell 1}$ = metal concentration in extraction solution (mg metal/kg liq)
$C_{\ell 0}$ = initial metal concentration in the extractant (mg metal/kg liq)
M_{k0} = initial mass of clay (kg)
$M_{\ell 0}$ = initial mass of extractant (kg)
M_{k1} = mass of clay after 1 extraction (kg)
$M_{\ell 1}$ = mass of extraction liquid after 1 extraction (kg)

Note that in this calculation the weight of 1 ml liquid or solution is taken to be 1 g. The error made by this assumption is generally less than 1 % and can be neglected when compared to other errors.

The calculated value for C_{k1} can be compared to the clay concentration measured directly after the extraction (which is called ‘the decomposition value’). The same holds for the situation after a second, third etc. extraction step. In these cases, a correction is necessary for the metal concentration in the clay at the beginning of the extraction due to the adhering liquid from the previous extraction.

Part of the clay material dissolves into the solution (especially in the case of clay soils high in carbonate content). This effect is taken into account by the difference in M_{k0} en M_{k1}. A number of separate measurements was performed to determine the dissolution of the solid material.

The values for the clay concentration given in this study are the ‘decomposition’ - values. The calculated clay concentrations are unreliable when the extraction percentage is very high. In such a case, two numbers of the same order of magnitude are subtracted in equation 2.1, which causes a large error in the result. When the amount of metal removed is small, the calculated value is used as a control value for the ‘decomposition’ value.

The experimental error in the metal concentration in the clay determined through decomposition is approximately the same as the experimental error in an atomic absorption spectrometry measurement. The standard solutions used for this analysis are the same as the neutralized hydrofluoric acid solution (see Appendix II.1) to exclude matrix effects. The standard solutions were not corrected for the presence of other heavy metals. The effect of these other metals on the AAS-signal is very small compared to the effect of the digesting solution. This was checked for the presence of iron ions in the digesting liquid. The experimental error of the AAS-measurements was not the same in all cases, because of different dilutions, varying sensitivities of the six metals etc. The relative error was generally estimated as 3-5%.

The relative error in the metal concentration in the clay is thus also 3-5%. This error can be greater in some cases depending on the sampling procedure before the AAS-measurement.

A special case is the analysis of Cd. The decomposition procedure causes a dilution of the concentration by a factor of approx. 400. The detection limit for Cd ions in solution is approx 0.02 ppm in the AAS-apparatus that was used. Clay concentrations smaller than 8 ppm Cd could not be determined by the decomposition procedure. Cd concentrations must then be calculated by use of equation 2.1. Results calculated in this way have a greater relative error than concentrations in the clay that are measured directly.

2.4.5. Results of extraction with hydrochloric acid

The extraction of metals strongly depends on the pH of the hydrochloric acid solution. This is in accordance with the findings in the literature as shown in Table 2.4. The impact of the acid strength is illustrated by Figure 2.3, where the results of experiment series F are plotted. The increase in extraction percentage with decreasing pH value is rather steep for Rn-Cu, and much more constant for Wi-Cu. The carbonate content of the Rhine clay probably causes this difference.

The liquid-to-solid ratio (extractant to clay weight ratio) seems to influence the removal efficiency much less than the pH does, as follows from Figure 2.4. The effect of L/S could be described by a logarithmic relationship.

Metal concentrations of the artificially polluted clay soils could be much more reduced by applying more than one extraction (see Appendix II.3). A threefold 0.1 N HCl extraction was performed with clay soils that were polluted with only one metal (experiment series A). Total extraction results were more than 90% for Cu, Pb and Zn and even >99% for Cd. The concentrations in the clay varied from 1-5x the natural background levels after the three

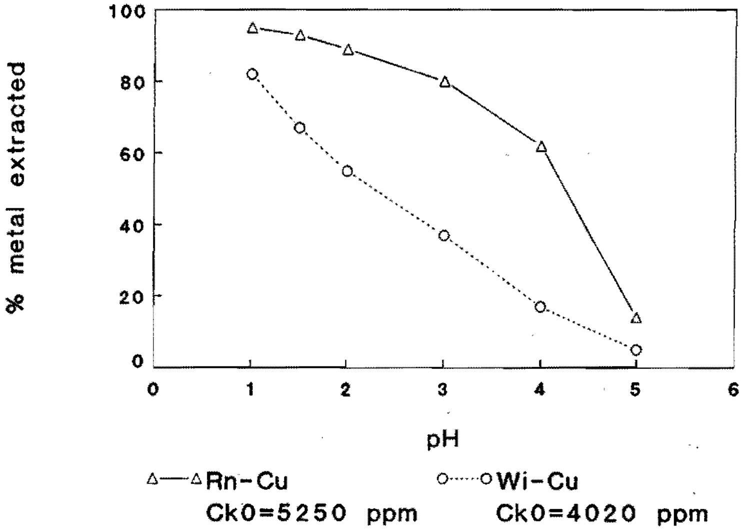

Figure 2.3. *Removal efficiencies of Copper from artificially polluted Rhine and Winsum clay soils after 1 h extraction in HCl at different constant pH values (C_{k0}=initial metal concentration in clay soil).*

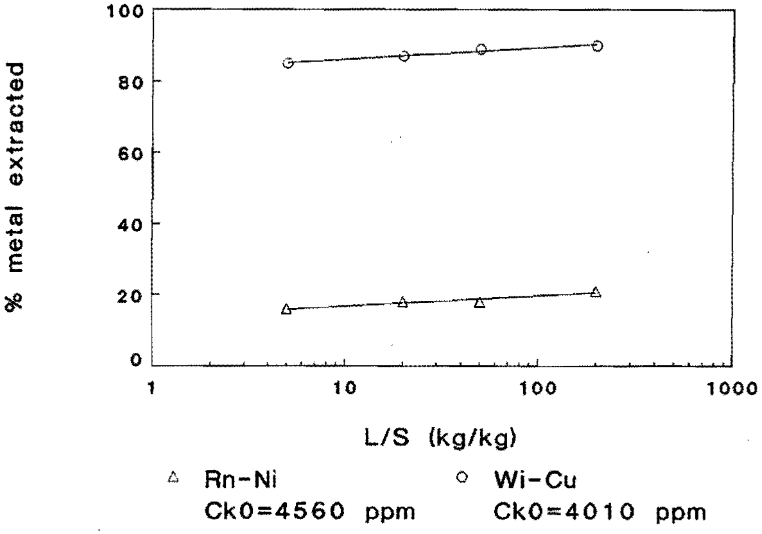

Figure 2.4. *Removal efficiencies of Nickel from artificially polluted Rhine clay soil and Copper from Winsum clay soil after 1 h extraction in 0.1 N HCl at different solution to soil weight ratios (L/S). (C_{k0}=initial metal concentration in clay soil).*

extractions. Nickel extraction percentages ranged from 70 to 90% but chromium could hardly be extracted (<25%).

When three, five or six metals were initially adsorbed to Rhine and Winsum clay (Rn-3, Rn-5, Rn-6 and Wi-3, Wi-5 and Wi-6 clay soils), the removal efficiencies of the two- and threefold extraction were smaller (see Appendix II.3 and Figure 2.5).

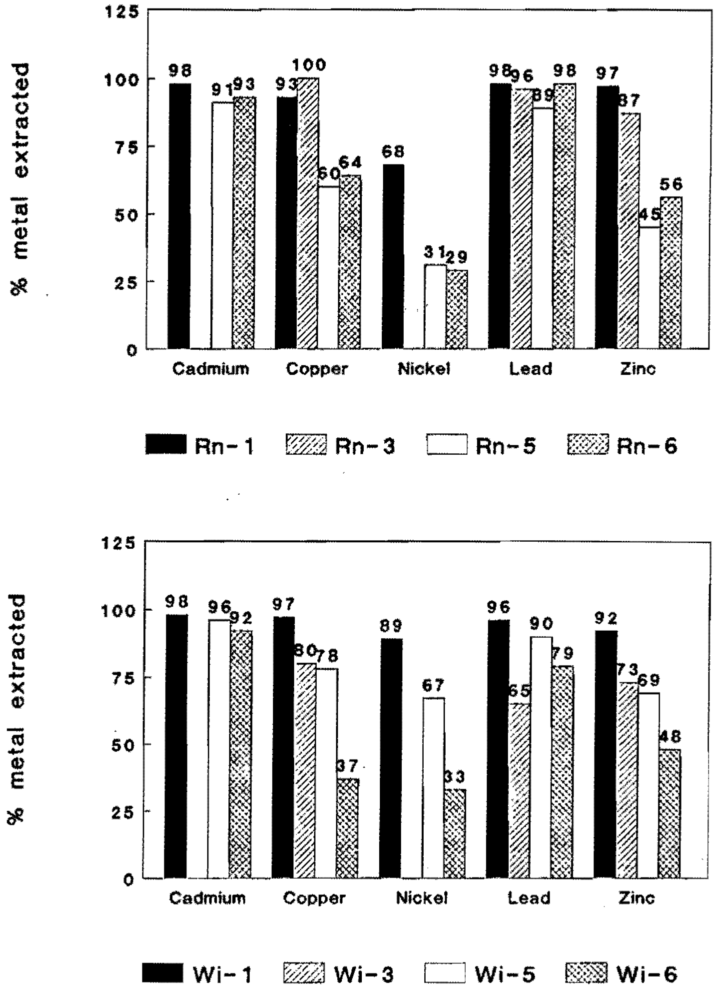

Figure 2.5. *Removal efficiencies of six metals from clay soils that were artificially polluted with 1, 3, 5 or 6 metals at a time. Efficiencies after twofold 0.5 h. extraction in 0.1 N HCl.*
TOP: *Rhine clay soils (Rn-1, Rn-3, Rn-5, Rn-6);*
BOTTOM: *Winsum clay soils (Wi-1, Wi-3, Wi-5, Wi-6).*

The decrease is especially clear for the metals Cu, Ni and Zn. The explanation for the constantly large Pb extraction efficiency could very well be the relatively high concentration of Pb that was adsorbed to the clays in the situation with 3, 5 and 6 competing ions. The amounts of Cu, Ni and Zn adsorbed became smaller because of this competition. The clay soil Rn-3 deviated from this pattern: Cu and Zn concentrations were approximately the same as in Rn-6, but removal efficiencies were much higher from the clay soil Rn-3 (see Figure 2.5).

Extractable proportions of metals thus generally decrease with decreasing initial concentration. This conclusion is illustrated by the results of experiment series D (see Figure 2.6). The effect is strongest for Ni and Zn which show more or less the same dependency on C_{ko}.

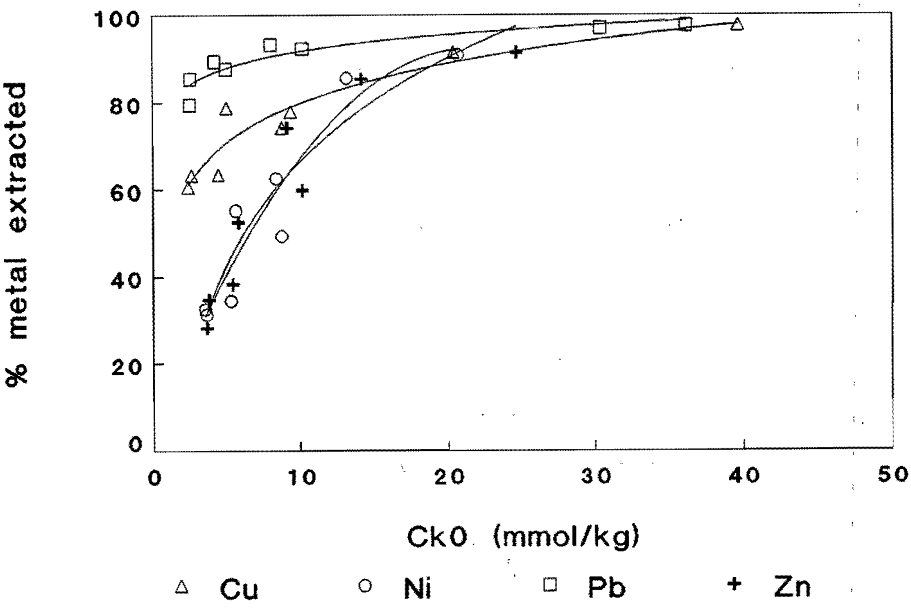

Figure 2.6. *Effect of varying initial metal concentrations on metal removal efficiencies after threefold 0.5 h. extraction in 0.1 N HCl from Rhine and Winsum clay soils that were artificially polluted with five metals.* C_{k0}*=initial metal concentration in clay soil.*

How do the waste site soils compare to the artificially polluted clay soils? The percentages of metal removed in a threefold 0.1 N HCl extraction were generally smaller (see Table 2.5): extraction percentages varied from 63-92% for Cd, Cu, Ni, Pb and Zn and were less than 10% for Cr.

Table 2.5.
METAL CONCENTRATIONS IN THE TWO WASTE SITE SOILS SOPHIA AND MELCHIOR AFTER THREEFOLD EXTRACTION WITH 0.1 N HCl

Clay Soil	Metal	C_{k0} (ppm)	C_{k1} (ppm)	C_{k2} (ppm)	C_{k3} (ppm)	E_1 (%)	E_2 (%)	E_3 (%)	E_{total} (%)
Sophia	Cd	16	3	3	2	81	0	33	88
	Cr	588	563	542	550	4	4	-	7
	Cu	2158	254	214	180	88	16	16	92
	Ni	2100	863	587	493	59	32	16	77
	Pb	428	162	116	88	62	28	24	79
	Zn	1185	404	312	292	66	23	6	75
Melchior	Cd	16	4	4	4	75	0	0	75
	Cr	190	174	171	204	8	2	-	-
	Cu	892	310	211	191	65	32	10	79
	Ni	495	215	156	161	57	27	-	68
	Pb	1826	427	310	261	77	27	16	86
	Zn	5350	834	715	704	84	14	2	87

C_{k0} = initial metal concentration in the clay (mg metal/kg clay)
$C_{k1(2,3)}$ = metal concentration in the clay after 1st (2nd, 3d) extraction (mg metal/kg clay)
$E_{1(2,3,total)}$ = percentage metal removed in 1st (2nd, 3d, all three) extractions (%)

When we express the results of the waste site soils as a function of initial concentration and compare them to Figure 2.6, the removal efficiencies are, however, surprisingly good! Only Zn and Ni from Sophia and Zn from Melchior were extracted significantly less than the same metal ions from Rn-5 and Wi-5. Probably, these Zn and Ni ions are bound to other types of sites in the waste site soils than in Rn-5 and Wi-5. The sequential extraction procedure indicated higher portions of Zn and Ni in the 'residual' fraction (this will be discussed in Chapter 3).

Other samples of Sophia and Melchior clay soils were extracted with 0.1 N HCl in the combined EDTA experiment series (see Section 2.5) and in kinetic studies (see Chapter 4). Initial concentrations were different in these other samples and generally smaller extraction percentages were measured after half an hour (see Table 2.6). C_{k0} of series II and III agreed reasonably well and so did the removal percentages after 30 minutes. E values of II and III (30m) were smaller than in series I which could be explained in some cases by lower C_{k0} values (e.g. Mel-Cu and Mel-Ni) but the reverse phenomenon was met as well. So, differences between metal speciation in the soil are likely to exist, even if total metal concentrations are comparable.

Table 2.6.
METAL EXTRACTIONS FROM SOPHIA AND MELCHIOR WASTE SITE CLAY SOILS IN 0.1 N HCl SOLUTION WITH DIFFERENT EXTRACTION TIMES

Clay soil-metal	C_{k0} (ppm) I	C_{k0} (ppm) II	C_{k0} (ppm) III	Extraction percentages (%)					$C_{k,end}$ (ppm)
				E(I) 30m	E(II) 30m	E(III) 30m	E(III) 24h	E(III) 30m+24h	
So-Cd	16	30	27	81	52	67	83	-	-
Cr	588	1016	994	4	8	0	23	-	-
Cu	2158	3300	3553	88	73	77	93	94	216
Ni	2100	3380	3455	59	23	19	78	83	582
Pb	428	634	739	62	52	50	68	77	171
Zn	1185	1832	1923	66	51	51	80	84	313
Mel-Cd	16	24	24	75	50	67	72	-	-
Cr	190	161	163	8	0	0	4	-	-
Cu	892	383	409	65	36	46	64	68	130
Ni	495	208	207	57	30	28	45	52	100
Pb	1826	1984	2378	77	56	66	79	85	353
Zn	5350	9412	9760	84	75	80	90	90	982

Notes: C_{k0}=initial metal concentration in the clay
$C_{k,end}$=metal concentration after two step (30m+24h) extraction
E=percentage metal removed by extraction
So=Sophia clay soil, Mel=Melchior clay soil
I=results from Table 2.5, II=results from first step of combined EDTA extractions, III=results from kinetics experiments.
30m(24h)=extraction percentage after 30 minutes (24 hours) extraction
30m+24h=extraction percentage after first extraction of 30 minutes followed by second extraction of 24 hours

It is interesting to compare the effect of more than one extraction to that of a longer extraction time. Threefold extraction clearly gives greater removal percentages than one single extraction as can be seen from Table 2.5 and it gives comparable results to 24h or 30m+24h extraction (see Table 2.6). Two exceptions occur: Mel-Cu and Mel-Ni, which are very probable due to the more than twice as big C_{k0} values in series I compared to series III.

The final metal concentrations reached by threefold extraction and 30m+24h extraction were in the same range even though initial concentrations differed (compare Table 2.5 and 2.6).

One extraction experiment series was performed with a stronger acid solution (2 N), although the extraction process will become considerably more expensive in this way. Table 2.7 shows the results of a single 30 minutes extraction in 2 N HCl. The improvement relative to 0.1 N HCl is very clear, but required A-levels are not reached in a single step.

Table 2.7.
EXTRACTION RESULTS FROM WASTE SITE SOILS IN 2 N HCl

Clay soil- Metal	C_{k0} (ppm)	$C_{k,end}$ (ppm)	E_1(30 min) (%)
Sophia -Cd	16	-	-
Cr	937	472	49
Cu	3977	685	83
Ni	4016	935	77
Pb	730	90	88
Zn	2108	505	76
Melchior-Cd	16	-	-
Cr	145	128	12
Cu	439	140	68
Ni	224	119	47
Pb	2446	200	92
Zn	10150	1090	89

2.5. COMBINATIONS OF EXTRACTING AGENTS

2.5.1. The complexing agent EDTA

The results of the extractions in hydrochloric acid have made it clear that the metal concentrations after extraction are still too high in many cases. Other chemicals or combinations of different extractants will be discussed in this section. A number of experimental extraction series were performed with the complexing agent EDTA (ethylene diamine tetra acetic acid) and with combinations of EDTA and HCl. Complexants like DTPA and NTA were also frequently reported as extractants *(6, 11, 12, 18)*. We have chosen EDTA as a sort of representative of the group of organic chelating agents. EDTA forms very stable complexes in aqueous solution with the six heavy metal ions in this study. The complexation constants range from 10^{16} to 10^{19} *(51)*. Although EDTA is a rather expensive reagent, it offers good possibilities to be recuperated and to be recycled *(52)*. Table 2.8 gives a summary of some extraction results with EDTA found in literature.

Concentration and pH effects were examined in this study by several experimental extraction series performed with EDTA. The experimental procedures and calculations are basically the same as those used for the batch extractions in HCl (see Section 2.4.2 and 2.4.4). One important difference is that the concentration of EDTA was not kept constant during the experiment.

Table 2.8.
LITERATURE SURVEY OF EXTRACTIONS WITH EDTA

First Author *(literature)*	Soil[1]	EDTA conc., time[2] L/S, pH	Extraction results (Percentage metal removed[3]) Cd	 Cr	 Cu	 Ni	 Pb	 Zn
Baghdady *(21)*	Various	0.5 M in NH_4Ac/ HAc, pH=4.65	64	0.3	-	4.5	34	-
Bowman *(13)*	Heavy clay	1.7E-04 M, 2 weeks, L/S=1	-	-	-	5	-	-
Farrah	Illite	1.0E-03 M, (*)[4]	100	-	100	-	100	100
(12)	Kaolinite	1.0E-03 M, (*)	100	-	100	-	100	100
		both 24h, L/S=2000						
Khan *(53)*	Clay	0.05 M, 30m, L/S=5	20-62	-	-	-	20-52	-
Sanders *(18)*	Silty clay loam	12h, L/S=5, pH=7	-	-	35-76	12-51	-	23-63
Rietz *(22)*	Various	0.02 M in NH_4Ac, 2h, L/S=5, pH=4.14	90-95	-	-	-	75-95	55-60
		0.05 M, 2h, L/S=5, pH=4.36	80	-	-	-	85	50-65
Staiger *(10)*	Various	0.025 M, 1h, L/S=2.5	80	-	30	-	60	8

Notes: 1) only some general indication is given.
2) time: m=minutes, h=hours, d=days; L/S=liquid to soil weight ratio;
3) percentages can be average from results with various soils.
4) (*) indicates extractions with artificially polluted soils.

2.5.2. Results of the EDTA extractions

Extractions with an EDTA solution were performed at four different EDTA concentrations with four types of artificially polluted clay soils (Rn-3, Wi-3, Rn-6, Wi-6). The EDTA concentration varied from 0.005 M to 0.1 M. Results of twofold extractions with these solutions are given in Appendix II.4, Tables II.4.1 to II.4.4. The Cr, Cu, Ni and Zn removal generally increased as the EDTA concentration of the extracting solution increased (see Fig. 2.7). Cd and Pb showed an increasing extraction percentage for the Rhine clay only, not for the Winsum clay (Rn-3 and Wi-3 behaved analogously).

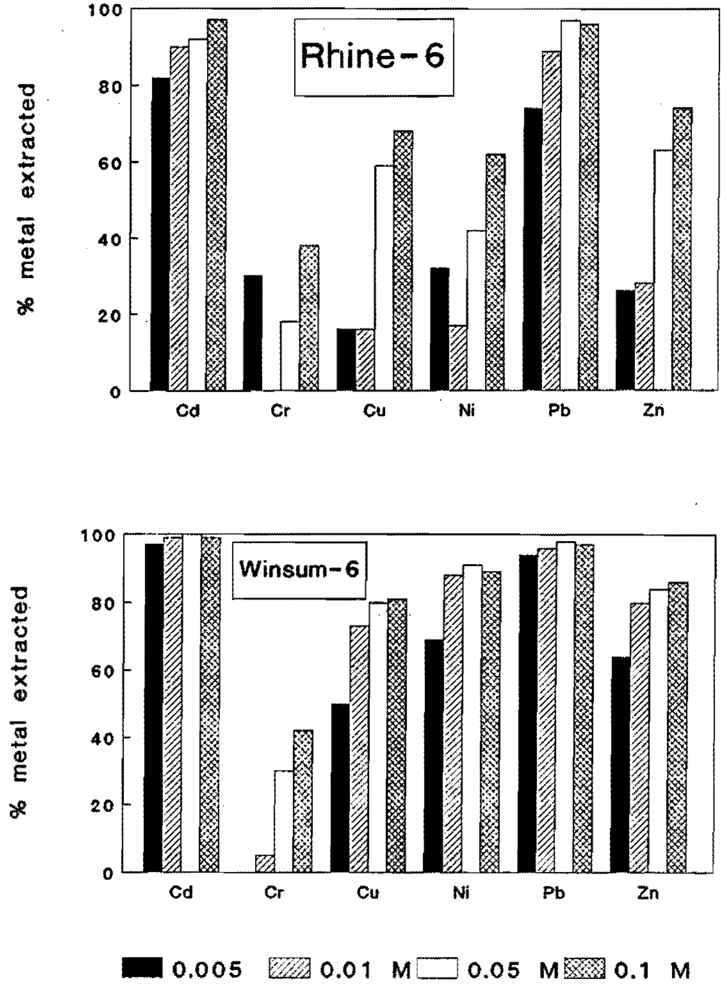

Figure 2.7. *Effect of EDTA concentration on removal efficiencies of six metals from clay soils that were artificially polluted with six metals. Efficiencies after two times 1/2 h extraction in EDTA solution (except 0.005 M solution: 1 h + 1/2 h). EDTA concentrations given under figure.*
TOP: *Rhine clay soil;* BOTTOM: *Winsum clay soil.*

It can be seen from Fig. 2.7 that improvement cannot be expected from an increase of EDTA concentration above 0.1 M for extraction from Wi-6: an extraction limit seems to be approached. The removal of Cr, Cu, Ni and Zn from Rn-6 might still become greater.

Rhine and Winsum clay soils behaved rather differently. Going from 0.01 M to 0.05 M EDTA, Rhine clay soil showed a very strong increase in metal release. This can be explained by the pH values during the experiment:

EDTA concentration:	0.005 M	0.01 M	0.05 M	0.1 M
pH of Rn-6 suspension:	7.5	6.5	4.5	4.5
pH of Wi-6 suspension:	3.5	3.5	3.5	4.0

Rhine is a calcareous clay soil and buffers the slightly acidic EDTA solution. As discussed in Section 2.4.1, the extraction percentage generally rises when the pH-value drops. The higher EDTA concentration has very clearly a positive effect on the extraction from Winsum clay soil; the results from Rhine clay are however influenced by two changing parameters. To check the influence of the pH, extraction in an acidified 0.005 M EDTA-solution was also measured. Results are given in Appendix II.4, Table II.4.5 and are illustrated for Rn-6 and Wi-6 in Fig. 2.8.

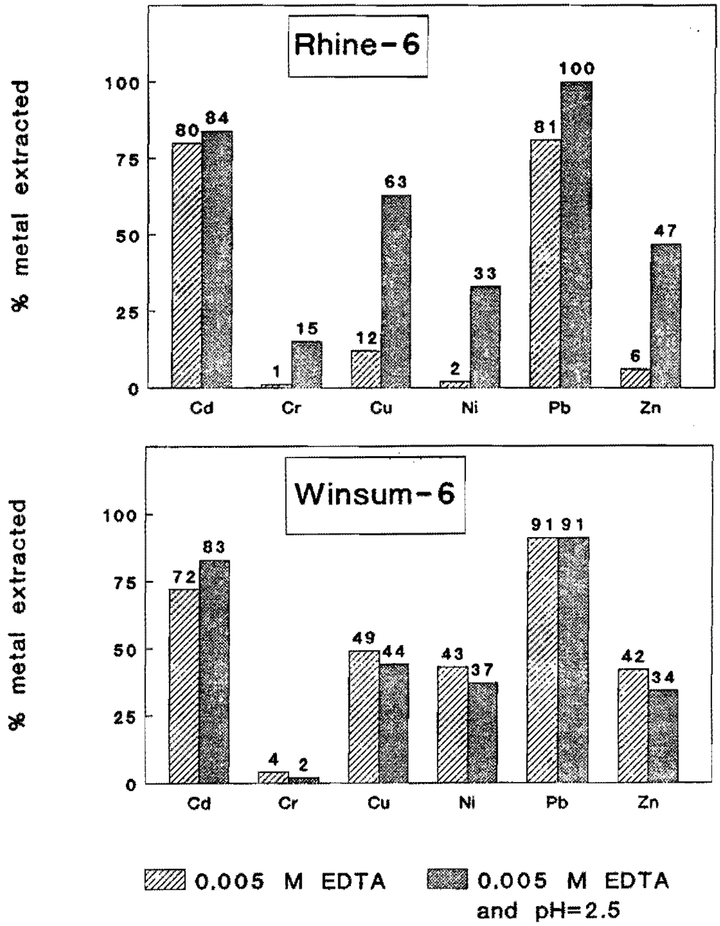

Figure 2.8. *Effect of fixing pH at constant value 2.5 on removal efficiencies of metals in 0.005 M EDTA solution from clay soils that were artificially polluted with 6 metals.* TOP: *Rhine clay soil;* BOTTOM: *Winsum clay soil.*

When the pH was fixed at a value of 2.5, all six metals were removed to a greater extent from the Rhine clay (see Fig. 2.8); the effect on Winsum clay soil was only small. At a low EDTA concentration the extraction can be improved very much by adding acid to the solution. The metal concentrations in the clay after treatment were in the range of the 'A-levels' in the case where the greatest removal percentages were measured (a threefold 0.1 M EDTA extraction, see Appendix II.4, Table II.4.4). Cu, Ni and Zn concentrations in Rn-6 and Cr concentrations in each clay soil were still above 'A-levels'.

The combination of HCl and EDTA solutions was therefore investigated in separate extraction steps. The sequence of applying the two extractants was compared for the four clay soils Rn-3, Wi-3, Rn-6 and Wi-6 (see Appendix II.4, Tables II.4.6 and II.4.7). Strongest effects were measured for the Rhine clay soils, as illustrated by the example of Rn-6 in Figure 2.9.

Extraction percentages were much higher if 0.1 N HCl was applied before 0.005 M EDTA than in the reverse procedure. The acidity of the EDTA extraction is the main cause for this difference: pH during the EDTA extraction was 3.0-3.5 versus 4.5-8.2 when EDTA was applied after and before HCl treatment respectively.

The results of this type of extraction could be further improved by using a higher EDTA concentration in the second extraction. Results of 0.1 N HCl extraction followed by 0.1 M EDTA extraction are given in Appendix II.4, Table II.4.8. The use of 0.1 M instead of 0.005 M EDTA after a 0.1 N HCl extraction is compared in Figure 2.10 for Wi-6.

The 0.1 M solution improved the extraction significantly for four of the six metals. Concentrations in Wi-6 after extraction were comparable to those after threefold 0.1 M EDTA extraction and were quite satisfactory, except for Cr concentration. Rhine clay soil showed about the same behaviour. Cu, Ni and Zn concentrations in Rn-6 were now reduced compared to the threefold 0.1 M EDTA extraction, although more extraction steps would be necessary to reach the background levels.

Finally, the HCl-EDTA combination that gave the greatest removal with the artificially polluted clay soils, was also used to clean the two waste site soils: extraction with 0.1 M HCl (1/2 h) followed by 1/2 or 1 hour extraction with 0.1 M EDTA (see Table 2.7 and Appendix II.4, Table II.4.9). The metal extraction percentages were smaller from the waste site soils than those from the artificially polluted clay soils.

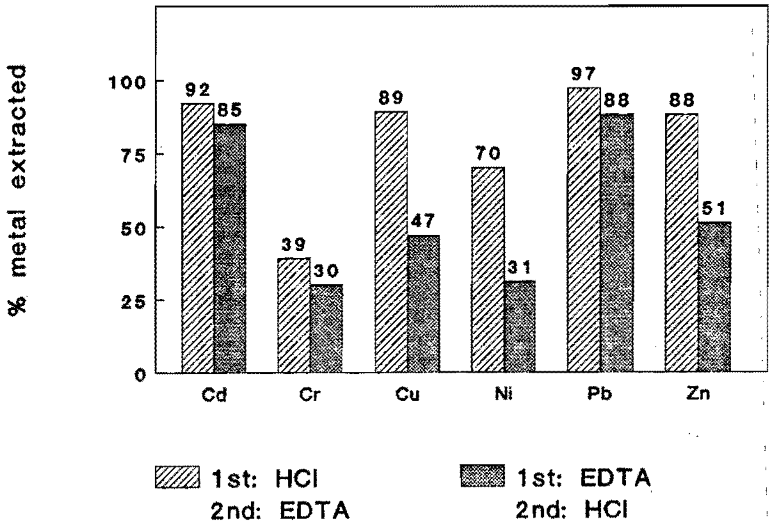

Figure 2.9. *Effect of different sequences of two applied extractants (0.1 N HCl and 0.005 M EDTA) on metal removal efficiencies from Rhine clay soil that was artificially polluted with 6 metals.*

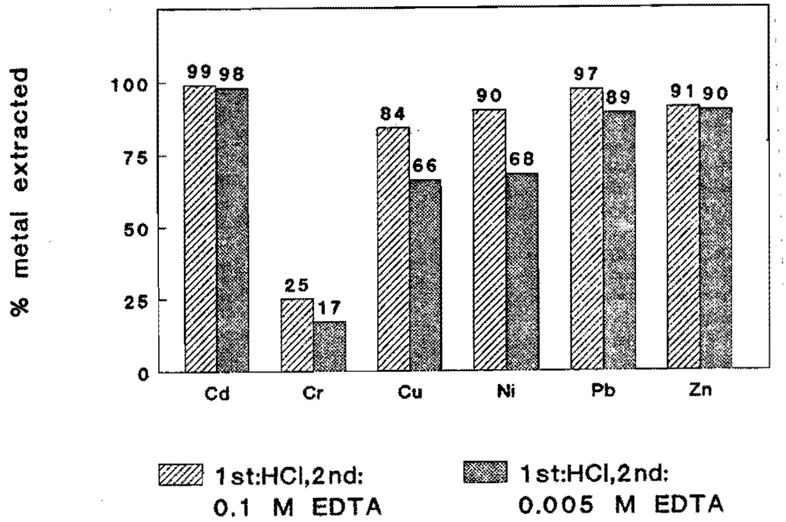

Figure 2.10. *Comparison of 0.1 M and 0.005 M EDTA in the second extraction step (after a 1/2 h extraction in 0.1 N HCl): effect on metal removal efficiencies from Winsum clay soil that was artificially polluted with 6 metals.*

Table 2.9.
METAL CONCENTRATIONS IN THE TWO WASTE SITE SOILS SOPHIA AND MELCHIOR AFTER TWOFOLD EXTRACTION: 1/2 h 0.1 N HCl AND 1/2 h 0.1 M EDTA

Clay	Metal	C_{k0} (ppm)	C_{k1} (ppm)	C_{k2} (ppm)	E_1 (%)	E_2 (%)	E_{total} (%)
Sophia	Cd	30	15	13	50	13	57
	Cr	1016	852	885	16	-	13
	Cu	3300	896	442	73	51	87
	Ni	3380	2543	1831	25	28	46
	Pb	634	306	118	52	61	81
	Zn	1832	922	694	50	25	62
Melchior	Cd	24	12	10	50	17	58
	Cr	161	153	148	5	3	8
	Cu	383	265	121	31	54	68
	Ni	208	143	126	31	12	39
	Pb	1984	933	265	53	72	87
	Zn	9412	2406	1348	74	44	86

2.5.3. Metal salt solutions as competing ions in 2nd extraction step

In some experiments removal percentages were found to be greater when ordinary tap water was used instead of deionized or distilled water. The tap water contained about 40 ppm Ca and 6 ppm Mg. The improvement was probably due to exchange effects between the ions. These effects play an important role in adsorption and desorption processes. Actually, adsorption or desorption of cations to or from a soil are in many cases ion exchange reactions. Metal salt solutions have also been used as extracting agents *(12, 18, 22, 54)*.

We tried to improve the extraction results by using calcium chloride or magnesium chloride solutions in the second extraction step (after a first extraction of 30 minutes with 0.1 N HCl). Some results from these extractions are compared to results with other extracting agents in the second step (see Table 2.10).

Copper could be removed to a greater extent from the artificially polluted clay soils if $CaCl_2$ or $MgCl_2$ was added to the 0.1 N HCl solution in the second extraction. Results were in the same range as those from extraction with 0.1 M EDTA.

Table 2.10.

COMPARISON OF DIFFERENT EXTRACTANTS IN A SECOND STEP EXTRACTION AFTER A FIRST 30 MINUTES EXTRACTION WITH 0.1 N HCl

Clay Soil -	Metal	Second step extractant 0.1 N HCl	0.1 M EDTA	0.1 N HCl + 0.1 M $CaCl_2$	0.1 N HCl + 0.1 M $MgCl_2$
		-------	Extraction percentage (%)		--------
Rhine -	Cu	49	65^{*}_{*}	63	60
Winsum -	Cu	62**	68***	80	70
Sophia -	Cr	4	-	3	10
	Cu	16	51	19	20
	Ni	32	28	15	16
	Pb	28	61	37	35
	Zn	23	25	13	10
Melchior -	Cr	2	3	0	5
	Cu	32	54	23	21
	Ni	27	12	14	16
	Pb	27	72	54	47
	Zn	14	44	22	20

Notes: *)results of extraction from Rn-6 and Wi-6 (no data available for Rn-1 and Wi-1).

**)initial metal concentrations are different for 0.1 N HCl 2nd step extraction from Sophia and Melchior soils (see Table 2.5).

***)data from Table 2.9.

The effect of $CaCl_2$ or $MgCl_2$ on the extraction from the waste site soils was much smaller or even negative compared to the use of HCl alone. The exact influence is difficult to examine due to the different initial metal concentrations. Pb extraction only seemed to be improved by the metal salt additions. Extraction results with 0.1 M EDTA in the 2nd step were clearly better than those with a combination of HCl and $CaCl_2$ or $MgCl_2$. The extraction with the metal salts added to HCl was therefore not explored any further. Extraction percentages with metal salts without 0.1 N HCl in the 2nd extraction were always smaller than those with HCl. Metal salts were thus not applied in the rest of this study.

2.6. CHROMIUM EXTRACTION WITH SODIUM HYPOCHLORITE SOLUTIONS

2.6.1. Introduction

The proportions of extracted chromium were very moderate as was shown in the previous sections. More Cr was extracted by a 0.1 M EDTA solution than by 0.1 N HCl but removal efficiencies were still too small for both the artificially polluted clay soils as well as the waste site soils. These observations agreed well with literature values reported for Cr removal (see Tables 2.4 and 2.9).

A number of other extracting agents (oxalic acid, sodium dithionite citrate, hydroxylammonium-hydrochloride, phosphate solutions) were also not successful in removing Cr. If the Cr in the soil is present as Cr(III), an oxidizing agent might be a good choice as an extractant. The Cr(VI) species is known to be much more mobile in soils, although it can be reduced (back) to Cr(III) by the organic material in the soil *(55)*. We tested therefore both sodium hypochlorite (NaClO) and hydrogen peroxide (H_2O_2) solutions.

In the rest of this section results are given for the extraction of Cr with NaClO. NaClO was preferred to H_2O_2 because of the (sometimes slightly) greater removal and because of the decomposition reactions of H_2O_2 that decreased its effectiveness.

2.6.2. Experimental methods: NaClO extractions

The extraction experiments were basically performed in the same way as the HCl extractions (see Section 2.4.2). A NaClO solution was added as extracting agent and the pH was kept constant by HCl and/or NaOH addition from two titrators. First series of experiments were carried out to determine the optimum pH and NaClO concentration with artificially polluted soils. The effect of multiple extraction steps was tested at the optimum conditions subsequently.

The Cr was very hard to extract from the waste site soils. Higher NaClO concentrations were necessary. Pretreatment by 0.1 N HCl extraction and extraction at higher temperatures were also studied to a limited extent for these soils. The temperature was raised by heating the open extraction cell over a gas-burner until a temperature of about 80 °C was reached. Heating was stopped and the solution was left to cool during the rest of the extraction.

2.6.3. Results of oxidative chromium extractions

Chromium is usually present in a soil in the trivalent state. If the soil was originally polluted by Cr(VI), this ion will probably have been reduced to Cr^{3+} by the organic material of the soil *(56, 57)*. Chromium (III) forms chromium hydroxides and ultimately the very insoluble chromium oxide, Cr_2O_3. The possible formation of polymeric chromium hydroxy complexes as described by Larkworthy et al. *(58)* reduces the solubility even more.

The oxidation reaction of chromium by a hypochlorite solution is in an acidic environment:

$$2Cr^{3+} + 3HClO + 4H_2O \rightleftarrows Cr_2O_7^{\ 2-} + 3Cl^{\ -} + 11H^{\ +}$$

and in a basic environment:

$$2Cr(OH)_3 + 3ClO^- + 4OH^- \rightleftarrows 2CrO_4^{\ 2-} + 3Cl^- + 5H_2O$$

The standard reaction potentials of the Cr^{3+} oxidation are +0.16 and +1.06 V under acidic and basic conditions respectively. Basic conditions are therefore favoured thermodynamically but kinetic limitations can also play a role. Possible decomposition of hypochloric acid is another reason to perform the oxidation in an alkaline environment.

In the first experiment series Cr was extracted from Rhine clay at four different NaClO concentrations ranging from 0.009 M to 0.46 M (see Fig. 2.11). Chromium removal was greatest for the two intermediate concentrations. The 0.46 M NaClO solution seemed to be ineffective because of the high pH-value during this extraction. The oxidation reaction consumed hydroxylic ions and the pH decreased during the reaction, as illustrated in Fig. 2.12.

When we compare Figures 2.11 and 2.12, an acceleration of the Cr-extraction can be observed at the time when the pH starts to drop. The experiment with the 0.46 M NaClO solution did not reach this favourable pH-range. The concentration of the 0.009 M solution was probably too small for an efficient extraction.

The influence of the pH was investigated in another experiment series where Cr was extracted from Rhine clay at three different pH-values (see Fig. 2.13). In these experiments the clay was extracted with a 0.046 M NaClO solution and the suspension was kept at a constant pH-value by titrating with a NaOH solution only. (This explains the change in pH of the third experiment from 10 to 8.3). Extraction at a constant pH = 8.3 produced the highest Cr

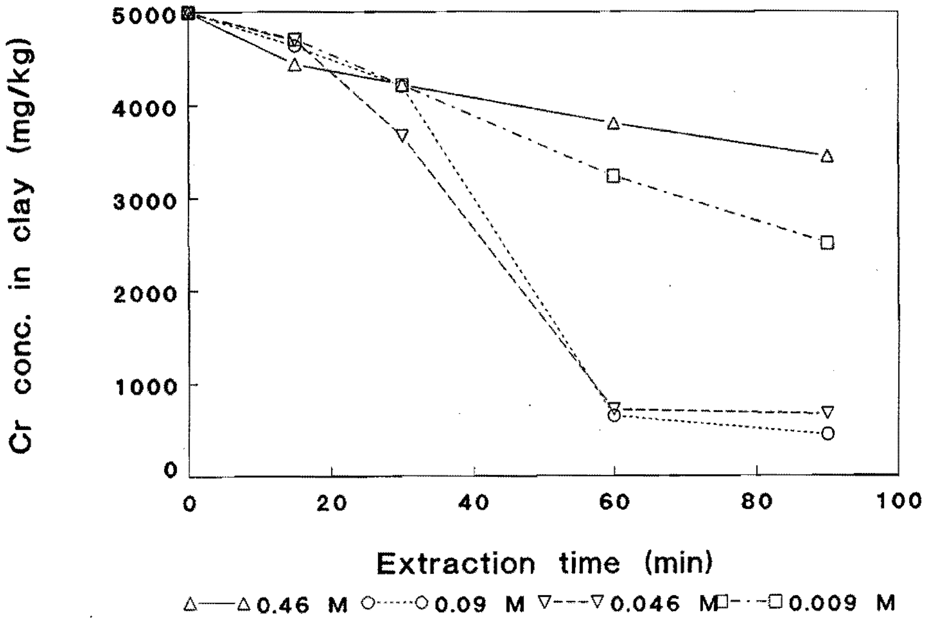

Figure 2.11. *Chromium concentration in clay soil versus time for extraction from artificially polluted Rhine clay soil with four different NaClO solutions (0.46 M, 0.09 M, 0.046 M, 0.009 M).*

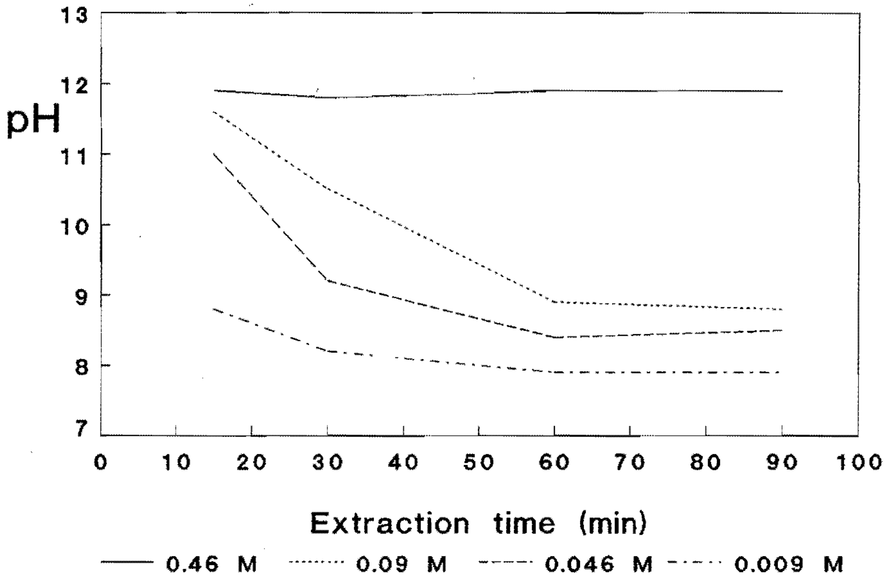

Figure 2.12. *pH changes during chromium extraction experiments from artificially polluted Rhine clay soil with four different NaClO solutions (see also Figure 2.11).*

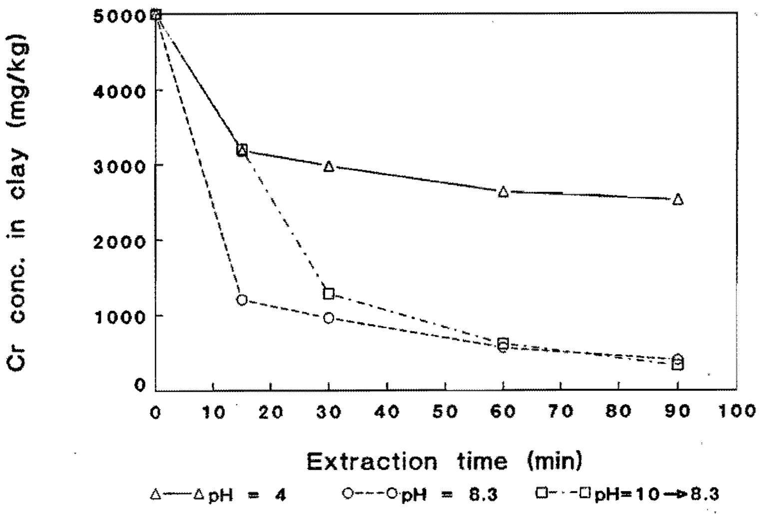

Figure 2.13. *Chromium extraction from artificially polluted Rhine clay soil in 0.046 M NaClO at three different pH values (two fixed, one changing).*

removal (92% after 1 h). Extraction at pH = 4 was not successful. The experiment with an initial pH = 10 showed a decrease in pH to the optimum value around 8 after approx. 15 minutes. At this point a further decrease of the Cr concentration in the clay was observed. With some delay an extraction result was reached comparable to that in the first experiment. Therefore, chromium can be well extracted from the artificially polluted Rhine clay soil by 0.046 M NaClO at pH ≈ 8.5. A threefold extraction under these conditions was applied to each of the five originally clean clay soils. Results are given in Table 2.11. Although the total extraction percentages ranged from 74 to 99%, the chromium concentration in the clay was still too high with respect to the required 'A-levels' in four out of five cases.

Table 2.11.
CHROMIUM CONCENTRATIONS IN ARTIFICIALLY POLLUTED CLAY SOILS AFTER THREEFOLD EXTRACTION WITH 0.046 M NaClO AT pH=8

	C_{k0}	C_{k1}	C_{k2}	C_{k3}	% metal removed in extraction			
					1	2	3	total
Clay	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(%)	(%)	(%)
Rhine	5000	700	161	41	86	77	74	99
Waal	5000	1000	370	220	80	63	40	96
Burum	4365	1615	1227	1120	63	24	9	74
Maas	3800	1180	720	554	69	39	23	85
Winsum	4000	680	306	226	83	55	26	95

Results could be further improved by a heat-treatment, which we practised only for the extraction from the two waste site soils.

A survey of the Cr-extractions from the waste site soils is given in Table 2.12. Extraction with 0.046 M NaClO was not successful. Efficiencies were much bigger when a ten times stronger NaClO solution was used at the same constant pH: 52% removal from Sophia with a twofold extraction. Metal-chromate compounds may precipitate during the Cr-extraction (e.g. $Pb(CrO_4)_2$) and may influence the extraction result in a negative way. Removal of other metals by a preceding HCl extraction could prevent this precipitation to a large extent. The effect of a previous HCl treatment on the Cr-extraction was measured. Only experiments where the Cr-extraction was carried out with NaClO plus heat treatment were available for comparison: in this case the 0.1 N HCl pretreatment seemed to have very little effect.

Table 2.12.
EXTRACTION OF CHROMIUM FROM TWO WASTE SITE SOILS

Clay	C_{k0} (ppm)	First Extractant	C_{k1} (ppm)	E_1 (%)	Second Extractant	C_{k2} (ppm)	E_2 (%)	E_{total} (%)
Sophia	1020	NaClO/10	1020	0	-	-	-	-
Sophia	1020	NaClO +ΔT	307	70	-	-	-	-
Sophia	1020	NaClO	580	43	NaClO	493	15	52
Sophia	1020	HCl	720	29	NaClO + ΔT	170	77	83
Melchior	160	NaClO/10	1600	0	-	-	-	-
Melchior	160	NaClO +ΔT	96	40	-	-	-	-
Melchior	215	HCl	205	4	NaClO	155	25	28
Melchior	215	HCl	205	4	2x NaClO	126	36	39
Melchior	215	HCl	205	4	NaClO + ΔT	123	40	43

Notes: NaClO is 0.46 M NaClO solution at constant pH=8.5
NaClO/10 is 0.046 M NaClO solution at constant pH=8.5
ΔT is temperature elevated to ≈ 80 °C
HCl is 0.1 N HCl solution kept at constant pH=1.0

The heat treatment itself improved the extraction strongly: from 43 to 70% removal for Sophia soil and from 25 to 40% for Melchior soil. The oxidation reaction was accelerated by the higher temperature. Applying two instead of one NaClO extraction increased the extraction percentage from 25 to 36% for Melchior. The greatest chromium removal was thus obtained by using a 0.46 M NaClO solution that was heated to about 80 °C.

2.7. DISCUSSION OF EXTRACTION RESULTS

The removal efficiencies vary widely between the six metals and the different soils, but some conclusions can be drawn.

Variation of L/S

Metals from the soils that are artificially polluted in a previous adsorption experiment are only extracted to a slightly greater extent if the liquid-to-soil ratio (L/S) is increased (see Figure 2.4). Steneker et al. *(59)* measured also flat logarithmic relations between leaching percentages of metals and L/S for harbour sludge at pH=4. Côté *(60)* pointed to a shift in suspension pH and subsequent leaching behaviour that could occur when L/S was varied. In this study the pH is fixed and such effects cannot play a role. Using L/S=2000, Farrah and Pickering found a relatively high metal release from artificially polluted clay minerals compared to other authors (see Table 2.4, *(12)*). When estuarine sediments were extracted under the same conditions, removal percentages were however smaller *(24)*. The ratio L/S was not varied in batch experiments of this study with the waste site soils. Extractions in the continuous installation showed little improvement in metal removal when greater L/S values were used (see Chapter 5). Variations of L/S values in model calculations confirmed this trend (see Chapter 6). So, the smaller liquid metal concentrations at higher L/S values cause hardly any shift in the metal distribution between liquid and solid phase. Part of the metal pollution is probably bound more strongly to soil components and it is not influenced by the smaller metal concentration in solution. Increasing L/S offers therefore no opportunity to improve the extraction efficiency very much.

Effect of acid strength

Higher acid concentrations of the extractant can improve the removal efficiency much more than variations in L/S. The pH-influence on soils artificially polluted with Cu can be seen in Figure 2.3. The effect on the waste site soils is also very clear when the extraction percentages in 0.1 N and 2 N HCl are compared (see Tables 2.6 and 2.7). From the literature survey about inorganic acids extraction (see Table 2.4) it appears also that greater acid strengths lead to a greater extraction percentage for the same metal-soil combination although the improvement is only small in some cases *(41, 48)*. Many authors found stronger metal release with hydrochloric than with nitric acid *(8, 48)*. Formation of soluble metal-chloride complexes may contribute to the better extraction results with HCl.

The use of very strong acids has some severe drawbacks. In the first place the costs of the extraction process will generally rise. The chemicals costs should be minimized by recuperating as much of the extractant (acid solution) as possible (see also Section 5.9). Part of the acid will however always be consumed in the extraction (by dissolution reactions). Secondly, the use of a more concentrated acid solution can cause severe ‘damage’ to the soil structure itself. Müller *(7)* reported that 20% of the total solid material dissolved in approx. 0.3 N acid solution during extraction. Randall et al. *(8)* stated that acid concentrations of 1.4 N and greater could be used without silicate matrix damage. The change in free iron concentration indicated that the surface coatings of the soil matrix were probably severely attacked and dissolved. In this study 8-11 wt.% of the solid material of the two waste site soils Sophia and Melchior was dissolved in 0.1 N HCl after 30 minutes and about 13-14 wt.% after 24 h. The calcareous Rhine clay soil was dissolved for 10-13 wt.% after 1/2 h in 0.1 N HCl while only 3-5 wt.% of the Winsum soil was dissolved. These amounts are expected to be greater when 2 N HCl is used.

The changes in main element composition before and after extractive cleaning (see Appendix II.2) indicate that hardly any Si or Al is dissolved in 0.1 N HCl. Large decreases occur in the concentrations of Fe, Ca and Mn. It suggests that mainly Fe- and Mn-coatings and carbonates of the soil are dissolved leaving the alumino-silicate matrix relatively unchanged. Extraction in 0.3 N HCl conducted by Malo *(61)* indicated also that trace elements followed the dissolution of Fe and Mn and not that of Si or Al. At higher temperatures or in stronger solutions HCl can react with more crystalline compounds or residual minerals like clays. (Experimental data about the change in main element composition was not available with the 2 N HCl treatment here.) Part of the organic material in the soil is also dissolved or dispersed in the acid solution *(1)*.

Assuming that the clay soil could be cleaned to the desired maximum tolerable metal concentrations (‘A-levels’), these changes in the soil material would still severely limit the possible use of the cleaned soil.

Extractability of the six metals

A threefold extraction with 0.1 N HCl is generally not sufficient to reach the ‘natural background’ metal concentrations in clay soils that are polluted artificially with only one metal (see Appendix II.3). Removal efficiencies become even smaller when the soils are polluted with more than one metal.

Metals are generally removed to a smaller extent from 'real' contaminated soils as can be seen from Table 2.4. The literature data indicated by (*) in Table 2.4 are studies with artificially polluted soils and these show somewhat greater removal efficiencies than the studies with 'real' contaminations. Extraction efficiencies from the waste site soils Sophia and Melchior are compared for three different conditions in Table 2.13. The removal percentages are in the same range for a threefold 30 minutes extraction in 0.1 N HCl, for a 24 hours extraction in 0.1 N HCl and for a 30 minutes extraction in 2 N HCl (all performed at L/S≈20).

Table 2.13
COMPARISON OF METAL EXTRACTIONS FROM WASTE SITE SOILS IN HCl

Clay soil-metal	C_{k0} (ppm) I	C_{k0} (ppm) II	C_{k0} (ppm) III	$C_{k,end}$ (ppm) I	$C_{k,end}$ (ppm) II	$C_{k,end}$ (ppm) III	E(I) 3x30m 0.1N (%)	E(II) 24h 0.1N (%)	E(III) 30min 2N (%)
So-Cd	16	27	16	2	4	-	88	83	-
Cr	588	994	937	550	765	472	7	23	49
Cu	2158	3553	3977	180	250	685	92	93	83
Ni	2100	3455	4016	493	760	935	77	78	77
Pb	428	739	730	88	235	90	79	68	88
Zn	1185	1923	2108	292	385	505	75	80	76
Mel-Cd	16	24	16	4	7	-	75	72	-
Cr	190	163	145	204	155	128	-	4	12
Cu	892	409	439	191	147	140	79	64	68
Ni	495	207	224	161	114	119	68	45	47
Pb	1826	2378	2446	261	500	200	86	79	92
Zn	5350	9760	10150	704	975	1090	87	90	89

Notes: C_{k0}=initial metal concentration in the clay
$C_{k,end}$=metal concentration after extraction under given conditions
E=percentage metal removed by extraction
So=Sophia clay soil, Mel=Melchior clay soil
Extraction conditions:
I = three times 30 minutes extraction in 0.1 N HCl
II = single 24 h extraction in 0.1 N HCl
III = single 30 minutes extraction in 2 N HCl

The results of extractions with conditions I and II can only be improved further to a small extent. This limit of metal extractability in 0.1 N HCl is clear when we look at the extraction percentage of the third step for condition I (see Table 2.5) and when we compare the results of II with the twofold extraction of 30 minutes + 24 hours (see Table 2.6). Since the required A-levels are not yet reached in any of the 0.1 N HCl extractions, other extraction conditions should be applied. The 2 N HCl extraction produced a much greater metal removal than the 0.1 N extraction under the same conditions (30 minutes, L/S=20) as can be seen from Tables 2.6 and 2.7. The increase in extraction percentage is greater than the difference measured by Randall *(22)* for Pb and Zn between extraction in 0.25 N and 4 N HCl (see also Table 2.4). The strongly varying results in Table 2.4. found at the same pH and for the same metal could be due to differences in the chemical form of the metal contamination and the soil type.

The extraction results of III (30 min. in 2 N HCl) can probably be improved further by applying a second and third extraction steps. It should be investigated if these subsequent extractions may be performed with smaller acid concentrations. Although a concentration greater than 0.1 N HCl is required to reach the A-levels, it is not clear yet which acid concentrations will be satisfactory. Intermediate concentrations between 0.1 N and 2 N should therefore be tested.

Adsorption of metals to clay soils can continue for weeks before equilibrium is reached *(43, 44)*. If the reverse process cannot be accelerated enough by chemical means (high acid strength) or by the process conditions (number of extraction steps), treatment in a process installation becomes impossible. The kinetic experiments (see Chapter 4) indicated that the rate of extraction in 0.1 N HCl was limited by a very slow reaction. It is not known how the rate of extraction is influenced by the acid concentration. The kinetics at varying acid concentrations should be investigated to find the limitations and possibilities of the extraction process at higher acid strengths.

The sequential extraction applied to the waste site soils (see Chapter 3), showed that the metals were mainly present in the 'residual' fraction after threefold extractive cleaning in 0.1 N HCl. This raises the question if it is necessary to remove the metals in this fraction completely (see Section 3.4 for a further discussion).

Individual metals

The extractability of the six heavy metals from the waste site soils decreases more or less in the order:

Cd > Pb > Cu > Zn > Ni > Cr

Assink *(6)* and Brüne *(50)* also measured a small removal for Cr (see Table 2.4). Chromium results are discussed below. Brüne *(50)* and Harter *(14)* also reported lower extraction percentages for Ni compared to Cu, Pb and Zn. The Ni might be bound to other sites than the other metals. For the artificially polluted clay soils sequential extraction measurements (see Chapter 3) proved greater Ni contents in the residual fractions.

Effect of initial concentrations

The clay soils that were artificially polluted with 3, 5 or 6 metals adsorbed less Cu, Ni and Zn due to the competition with the other metals than the soils that were polluted with only one metal. Removal percentages of Cu, Ni and Zn were smaller than those of Cd and Pb (see Figure 2.5). A relatively greater part of the amounts of Cu, Ni and Zn could have been bound to more specific adsorption sites (and be less extractable). Benjamin and Leckie pointed to the existence of multiple adsorption sites *(62)*. A number of other authors distinguished between specific and non-specific sorption sites *(1, 46, 63-66)*. Only a small fraction of total available sites can bind metals strongly (so-called 'high-energy sites'). The average binding energy decreases as lower energy sites are gradually filled *(67)*. If each metal has its own, specific high-energy sites, this would explain the decreasing extraction percentages of Cu, Ni and Zn compared to those of Pb. The reduction in extraction efficiencies (Pb < Cu < Zn < Ni) is just the opposite of the adsorption selectivity range noticed in Section 2.3.3. If more metal is adsorbed, a higher percentage can thus be extracted.

This effect is clearly illustrated by Figure 2.6. Ni and Zn extraction percentages depend stronger on the initial concentration than those of Cu and Pb. The results suggest that greater proportions of Ni and Zn are bound specific (stronger) to these clay soils than of Cu or Pb. The Pb removal efficiency is always higher than 80% even at a low initial Pb concentration. Probably, Pb is not bound very strongly to these clays. The unhydrated Pb-ion has greatest ionic radius of the metals studied here *(68)*:

metal ion	Cd^{2+}	Cr^{3+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
crystal ionic radius (Å)	0.97	0.63	0.72	0.69	1.20	0.74

Helios-Rybicka and Förstner *(69)* reported the possible adsorption of metals with an appropriate ionic diameter to more interior sites of three-layer clay minerals like illite or smectite. Cu, Ni and Zn could be bound to interlayer sites or substitute Fe- or Mg-ions which are of similar size (0.74 Å and 0.66 Å respectively, *(68)*). Tiller et al. *(70)* mentioned greater affinity for

Ni than for Cd or Zn shown by clay fractions dominated by kaolinite. These diffusion-type adsorptions are slow, but can become important after longer time. Pb and Cd ions are too big while the fact that Cr is in the trivalent state might make certain sites unavailable for this ion. For Pb, this explanation is confirmed by Padmanabham *(71)* who measured a marked hysteresis in desorption from goethite of ‘specifically’ adsorbed Cu, Zn and Co but not of Pb. He attributed the absence of specific adsorption of Pb to the large size of this ion.

Another factor is chloride complex formation. Pb and Cd form relatively stable chloride complexes *(72)*, which favour the removal of these metals. The stability constants of chloride complexes are however small compared to those of other complexes.

The effect of the initial concentrations is less evident for the two waste site soils. Table 2.6 showed results after 30 minutes extraction in 0.1 N HCl for two waste site soil samples with different initial Cu and Ni concentrations. Removal from Melchior waste site soil is greater if initial concentration is greater but the Sophia soil behaves just opposite. It is possible that metals are present in different chemical forms in the two samples. In case of the artificially polluted soils the method of polluting the soils was always the same and metal speciation is expected to be more uniform.

Extraction with EDTA

A comparison between the extractability of metals in hydrochloric acid and EDTA can only be made if the same polluted soil and the same extraction conditions are being used. Baghdady *(21)* and Staiger *(10)* measured greater percentages metal removed by inorganic acids than by buffered EDTA solutions (see the literature survey of EDTA extractions in Table 2.8). On the other hand, Rietz *(22)* found greater removal efficiencies for Cd and Pb in EDTA solutions, but smaller for Zn. Norvell *(11)* reported twice as large removal of Cu, Ni and Zn with 0.1 N HCl than with five different complexing agents (one of them being 0.005 M EDTA at pH=5.3); the amount of Cd extracted was about the same with HCl and with EDTA. Farrah *(12)* determined greater removal with EDTA than with HCl in the case of artificially contaminated clay minerals. The same was found in this study: extraction percentages from artificially polluted Rhine and Winsum soils were greater in 2x 1/2 h 0.1 M EDTA than in 2x 1/2 h 0.1 N HCl (compare Tables II.3.2 and II.4.4 in the Appendices). A successful extraction in EDTA required a pH of 4 or less.

An 0.1 M EDTA solution seems therefore to be more successful in removing recently adsorbed metal ions (as in the situation of the artificially polluted clay soils) than a 0.1 N inorganic acid solution. The literature mentioned above indicates that this is not the case for 'real' waste site soils with the exception of Cd and to a smaller extent of Pb, for which removal percentages are relatively large in EDTA solutions. The high Cd and Pb extraction percentages might be explained by their ionic radius (see above). These ions are probably bound to more exterior sites and can be reached by the EDTA more easily. Reasons for the different ranking of EDTA and HCl for the two types of soil might be the effect of aging and the presence of insoluble forms of metals. In the waste site soils metals might have reached more interior binding sites of minerals and can be covered by surface coatings or they may have exchanged with ions in the primary mineral lattice *(69, 70)*. Metals may also form less soluble oxide or hydroxylic complexes due to aging *(58, 73)*. The results of the sequential extraction analysis point also to differences in the distribution over chemical forms in which the metals are present in the soil (see Chapter 3). The waste site soils contained a larger proportion of metals in the 'residual' fraction than the artificially polluted soils.

The use of 0.1 N HCl and 0.1 M EDTA in a second extraction step after 30 minutes 0.1 N HCl treatment was compared in Table 2.10. Except for Sophia-Pb, Melchior-Pb and -Zn, the 0.1 N HCl-0.1 M EDTA extraction gave smaller total removal efficiencies than a twofold 0.1 N HCl extraction (compare Table 2.5). Chelation reactions of the metals (directly or indirectly by preventing re-adsorption through metal complexation in the liquid phase) seem thus less effective than the dissolution and exchange reactions of H^+ in most cases studied here. It is important to note, however, that the experiments were performed with different samples of the waste site soils. Initial concentrations and extraction results of the first HCl step differed. Comparison of total extraction efficiency is difficult; when we look at the removal in the second extraction only, then Cu, Pb - and to a smaller extent Zn - results are better in 0.1 M EDTA than in 0.1 N HCl. Therefore, at least for Cu, Pb and Zn the use of EDTA in a second extraction seems promising and should be investigated further.

Chromium extraction

A reason for the poor removal results of Cr might be the rather immobile species Cr^{3+} that can be present as an oxide compound. Crystalline Cr_2O_3 is very insoluble in inorganic acids, in many cases even at high temperatures

(74). The solubility of chromium(III)hydroxide hydrates (Cr_2O_3.aq, $Cr(OH)_3$.aq, $Cr(OH)_3$) in hydrochloric acid depends on the acid strength and on the age of the hydrate *(74)*. We measured already differences in Cr removal between a 1 month old contamination and a 7 month old one.

A survey of the Cr-extractions from the waste site soils was given in Table 2.12. The greatest Cr removal (70-85%) in this study was measured in a 0.46 M NaClO solution at pH=8.5 that was heated to about 80 °C and was allowed to cool subsequently. Andersson *(49)* found also a large Cr extraction in 2 N HNO_3 at 100 °C compared to the smaller removal at room temperature reported by other authors (see Table 2.4). In oxidative extractions a large part of the hypochlorite can be reduced by the organic material which will raise the costs of cleaning. Although the suspension or extractant needs to be heated only for a short period (approx. 5 minutes), this is an expensive operation. Another problem will be caused by the corrosiveness of the hot solution. It is therefore probably easier and cheaper to use multiple NaClO extractions at room temperature.

Anyway, the presence of chromium in a contaminated clay soil requires an alternative treatment to HCl extraction. Oxidizing chemicals, like NaClO, offer good possibilities but will always raise the costs of total treatment.

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Chapter 3

SEQUENTIAL EXTRACTION ANALYSIS

3.1. INTRODUCTION

Heavy metals may be associated with soil components in several different ways. Pickering *(1)* for example distinguished the following 'retention modes' for metals in soils and sediments:

- ion exchange sites
- surface adsorption
- precipitated (as carbonates, sulfides, hydroxides)
- co-precipitated on amorphous hydrous oxides (of Fe, Mn or Al)
- coordinated to organics
- occluded in crystalline hydrous oxides
- lattice components

Selective chemical extraction techniques have been widely applied to investigate metal distributions over types of bonds. Reviews of such techniques were given by Pickering *(1)*, Lake et al. *(2)*, Salomons and Förstner *(3)* and Kersten and Förstner *(4)*. Sometimes a number of single chemical extractions is used, often a procedure consisting of a number of successively applied leaching steps.

In this study we have employed the sequential extraction procedure according to Tessier et al.*(5)*. Five metal fractions in the soil are differentiated by this technique:

1. 'Exchangeable' ($MgCl_2$ extractable)
2. 'Bound to carbonates'
3. 'Bound to iron and manganese oxides'
4. 'Bound to organic matter or sulfides'
5. 'Residual'

Sulfidic metal associations were added to the interpretation of the fourth step of the Tessier procedure, because the H_2O_2 treatment does not differentiate between organic and sulfidic associations *(4,6)*. This five step procedure was applied to the contaminated soils before and after an extractive cleaning (by one of the methods described in the preceding chapter). The main purpose of the sequential extraction analysis is to compare the distribution of the metals before and after the extractive cleaning. Secondly, information about the soil fraction in which the metals are still present after cleaning may help to judge the necessity of and possible methods for further treatment.

Many authors have emphasized the limitations and difficulties of sequential extraction techniques *(1-8)*. Some fundamental questions about the assumptions underlying any sequential extraction procedure were raised by Martin et al. *(7)*. They measured matrix effects produced by the different soil components and element dependent results in individual soil components. Besides these basic questions a lot of operational problems exist: the applied reagents are not as selective as is sometimes suggested; overlap and incompleteness occur; soil samples and the indigenous metal speciation can change due to the reagent. Other shortcomings arise from the use of specific chemicals. The sequence in which a given set of reagents is employed also influences extraction results. Especially the order in which reagents for organic matter and for the easily/moderately reducible fraction (Fe/Mn-oxides) should be applied is a subject of controversy *(4,6)*.

Great caution is therefore required in interpreting the results of any sequential extraction technique. The distribution into well-defined physical-chemical forms cannot simply be determined. The names of the metal fractions in the speciation procedures suggest an unrealistic selectivity. For example, metals associated with iron oxides can be present in exchangeable forms, co-precipitated with amorphous oxides or occluded in more crystalline forms like goethite *(4)*. An analogous reasoning holds for the different types of interactions that exist for metals bound to organic material. The metal fractions measured by sequential extraction techniques are thus very clearly operationally defined metal-soil fractions. It is however still possible to get more information and insight about the metal behaviour than from only total metal concentration measurements. Results in this study will be compared mainly to measurements made with the Tessier procedure or slightly modified versions of it and will be used only to determine metal behaviour qualitatively.

3.2. EXPERIMENTAL METHODS

The clay soils were extracted according to the sequential extraction procedure given by Tessier et al.*(5)*. The procedure was changed slightly to make the destruction of the soil in the final step comparable to the results used in other parts of this study. The decomposition described in Appendix

II.1 was substituted for Tessier's step 5. Five different metal fractions were subsequently extracted by the following reagents and under the following conditions (a more detailed description is given in *(5)*):

1. Exchangeable metal ions: extraction for 1 hour at room temperature with 1 M $MgCl_2$ solution (pH=7) under continuous agitation.
2. Metals bound to carbonates: extraction for 5 hours at room temperature with 1 M NaOAc solution adjusted to pH=5 by means of HOAc under continuous agitation.
3. Metals bound to iron and manganese oxides: extraction for 6 hours with 0.04 M $NH_2OH.HCl$ in 25% (v/v) acetic acid (pH=2) at a temperature of 96 °C. The suspension was stirred occasionally.
4. Metals bound to organic matter: extraction for 2 hours with 0.02 M HNO_3 in 30 % H_2O_2 at a temperature of 85 °C under intermittent agitation. After cooling 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added to prevent re-adsorption.
5. Residual metals: the residual material was digested by hydrofluoric acid and aqua regia according to the procedure given in Appendix II.1.

Metal concentrations were determined after each step by AAS. Standards were adjusted to correct for matrix effects in solution. Samples were washed with distilled water between each step. Corrections were made for metal concentrations in washing and adhering liquids.

Three experiment series were performed with this sequential extraction procedure:

A - five clay soils each artificially polluted by one of the metals Cd, Cr, Cu, Ni, Pb or Zn were cleaned by a threefold extraction with 0.1 N HCl (see Section 2.4). The distribution of each metal ion before and after a *single* 0.1 N HCl extraction was determined.

B - two clay soils (Rhine and Winsum) each artificially polluted by three or six of the metals Cd, Cr, Cu, Ni, Pb or Zn were cleaned by a twofold extraction with 0.1 M EDTA (see Section 2.5). The distribution of each metal ion before and after this twofold cleaning was determined.

C - the two waste site soils (Sophia and Melchior) were extracted three times in 0.1 N HCl (see Section 2.4). The distribution of each metal ion before and after this threefold cleaning was determined.

Experiment series B and C were carried out in duplicate, the experiments of series A only once. Average concentrations were calculated. The sum of the five fractions was compared to the total metal concentration measured directly in the clay soil. These values were generally within approx. 10% of each other.

3.3. RESULTS

The metal concentrations measured in the sequential extraction experiment series A, B and C are given in Appendix III, Tables III.1, III.2 and III.3 respectively. In this section we will describe the distribution of the metals in the (artificially) polluted soils first. Then we will compare the metal speciation of these soils before and after extractive cleaning. The five metal fractions from the Tessier procedure are abbreviated as: F1 or 'Exch' (exchangeable metals), F2 or 'CO_3' (carbonate fraction), F3 or 'Fe/Mn-Ox' (bound to Fe/Mn oxides), F4 or 'Org/Sulf' (bound to organic matter or sulfidic metal associations), F5 or 'Res' (residual metals).

Sequential extraction analysis of polluted clay soils

The sequential extraction analysis of the clay soils that were artificially polluted with only one metal (experiment series A) shows that the largest amount of metal ions is present in the first three fractions according to the procedure of Tessier ('exchangeable', 'carbonates', 'Fe/Mn-oxides').

The distributions of Ni and Cr in the clay soils before cleaning differ from those of Cd, Cu, Pb and Zn: more Ni and Cr is present in F4 and the percentage in the residual fraction F5 is much higher for Ni than for the other metals (see Rn-1 and Wi-1 clay soils in Fig. 3.1). The distribution of Pb in Rn-1 and Wi-1 is given as an example of the distribution of the metals Cd, Cu, Pb and Zn. The speciation of Cd, Cu, Pb and Zn is more or less the same: these metals are mainly present in the first three fractions. Cadmium concentrations were generally highest in F1 whereas Cu, Pb and Zn showed maxima in F2 and F3. Exceptions were the non calcareous soils Maas and Winsum, where Pb and Zn were observed mainly in the 'Exch' fraction.

If a clay soil was artificially polluted by 3 or 6 metals (abbreviated as Rn-3 or Rn-6 etc., Rn for Rhine and Wi for Winsum clay soil), only minor changes occurred in the distributions of the individual metals. Comparison of Rn-1, Rn-3 and Rn-6 (or Wi-1, Wi-3 and Wi-6) is difficult because of different total metal concentrations. The most clear phenomenon seems to be a shift from metals 'bound to carbonates' to 'bound to Fe/Mn-oxides' when more metals are present. The presence of Pb in particular caused a shift of Cu and Zn from F2 to F3 fractions. The amount of metal present in the fraction determined in step 2 of the Tessier procedure appeared to be limited by a maximum. Rhine clay contained never more than approximately 60 mmol metal/kg clay in the F2 fraction and Winsum never more than approximately 17 mmol/kg.

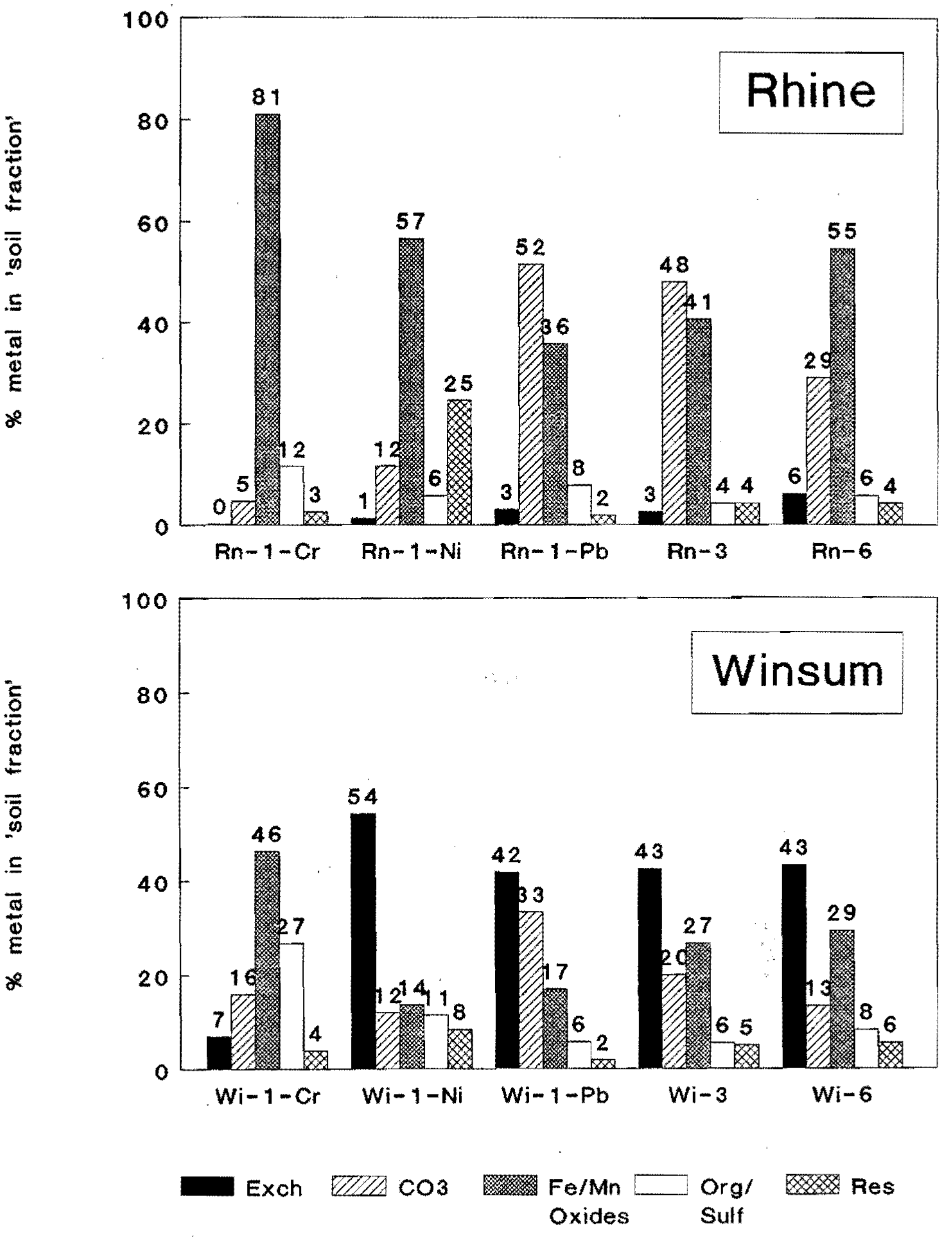

Figure 3.1. *Distribution (%) of metals in clay soils that were artificially polluted with one metal (Cr, Ni or Pb), three metals (Cu, Pb and Zn) or six metals (Cd, Cr, Cu, Ni, Pb and Zn). Distribution is of sum of metals, if more than one metal is present. 'Soil fractions': see text.* TOP: *Rhine clay soils;* BOTTOM: *Winsum clay soils.*

The removal percentage of Cu and Zn decreased much more compared to that of Pb, going from 0.1 N HCl extractive cleaning of Rn-1 (Wi-1) to that of Rn-6 (Wi-6) (see Section 2.4). The shift of Cu and Zn to fraction F3 might have contributed to this decrease.

The distribution of the sum of the three or six metals was calculated for Rhine (-3 and -6) and Winsum (-3 and -6) clay soils and is also represented in Fig. 3.1. It reflects the distributions of the composing metals and is dominated by the fractions F2 and F3 for the Rhine clay soils and by F1 and F3 for the Winsum clay soils.

The sequential extraction analysis of the waste site soils, Sophia and Melchior, showed some remarkable differences from that of the artificially polluted soils. Hardly any metal was present as exchangeable metal and much larger amounts of metal were present in the fractions F4 and F5 (see Figure 3.2):

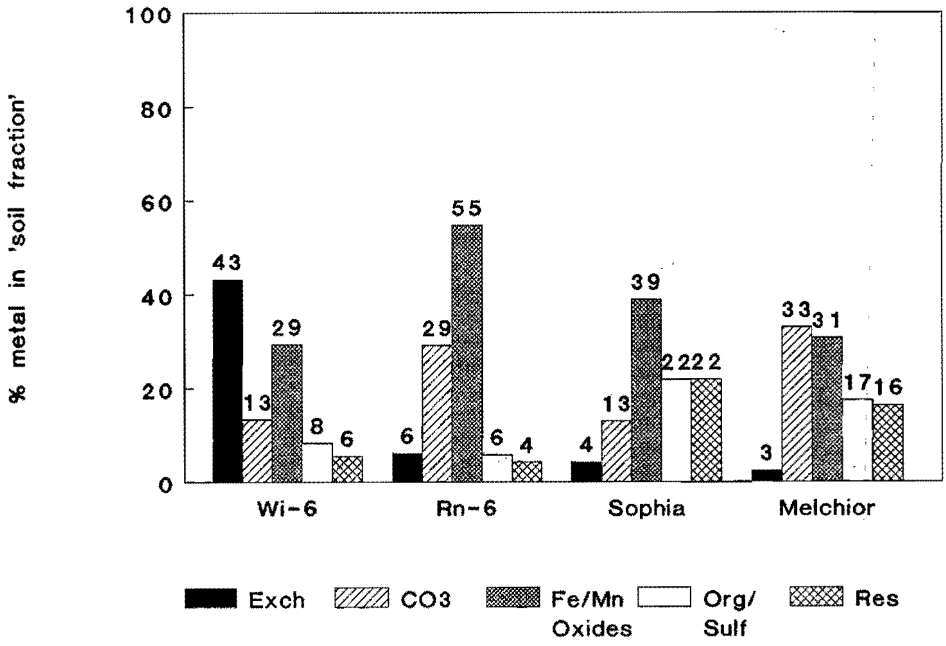

Figure 3.2. *Distribution (%) of sum of six metals (Cd, Cr, Cu, Ni, Pb and Zn) in artificially polluted Winsum and Rhine clay soils (Wi-6 and Rn-6) and in two waste site soils Sophia and Melchior.*

The two waste site soils originate from quite different industrial activities: Sophia from an enamel factory and Melchior from a metal plating industry. The metal speciations are however similar. For example, in both soils Cu is bound mainly to the 'org/sulf' fraction, only Zn is observed to a notable extent in the 'exch' fraction etc. Metals seem to be bound preferentially to specific types of sites, in spite of a quite different history.

This preference can be expressed as a 'selectivity ratio'. We calculated the ratio of the percentage of an individual metal in a specific fraction to the percentage of the same metal in the total clay soil. If this ratio equals 1 for each of the five Tessier fractions, the metal concerned shows no preference to one of the five 'soil fractions'. The calculated 'selectivity ratios' are given in Table 3.1.

The ratios indicate a clear preference of Cd for the 'exchangeable' fraction, of Cr and Pb for the 'residual' fraction and of Cu for the 'organic/ sulfidic' fraction. Nickel and zinc are distributed more evenly over the five fractions. Only small deviations in the preferences exist between the two soils (for example, the Zn-preference for the 'exchangeable' fraction in Sophia soil).

Table 3.1.
SELECTIVITY RATIOS OF METALS FOR SOIL FRACTIONS ACCORDING TO THE SEQUENTIAL EXTRACTION PROCEDURE OF TESSIER

Clay soil	Metal	Selectivity ratio in fraction: Exch F1	CO_3 F2	Fe/Mn-Ox F3	Org/Sulf F4	Res F5
Sophia	Cd	4.9	1.5	0.7	0.2	1.3
	Cr	0.0	0.1	0.8	0.6	2.4
	Cu	0.3	1.4	0.5	2.5	0.4
	Ni	0.5	0.7	1.4	0.5	1.0
	Pb	0.3	0.2	0.6	0.4	2.9
	Zn	3.8	1.8	1.1	0.2	0.6
Melchior	Cd	10.2	0.7	0.6	0.2	2.0
	Cr	0.1	0.1	1.0	1.8	2.3
	Cu	0.2	0.2	0.3	4.0	1.0
	Ni	1.0	0.3	1.4	1.3	1.3
	Pb	0.2	0.5	1.0	0.9	2.4
	Zn	1.3	1.4	1.1	0.3	0.7

Comparison of distribution before and after extractive cleaning

The Cd, Cu, Pb and Zn distributions of the artificially polluted clay soils after 0.1 N HCl extractive cleaning show that 90-99% of the metals in F1, F2 and F3 were removed by the single extraction. Removal from F4 and F5 was less complete (varying from 10-95%). The influence of these fractions on the total removal efficiency is strongest for Ni (see Figure 3.3). In Figures 3.3-3.7

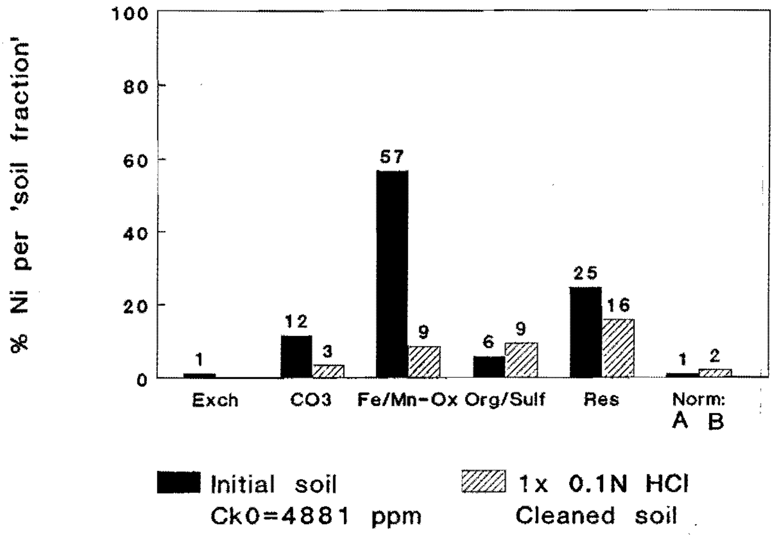

Figure 3.3. *Nickel distribution (%) in artificially polluted Rhine clay soil before and after extractive cleaning in 0.1 N HCl for 1 hour. % is based on initial metal concentration C_{k0} before cleaning. Norm: see text.*

the A- and B- maximum permissible metal concentration levels (see Chapter 1) are indicated by the bars 'Norm A and B'. The values are expressed as a percentage of the initial metal concentration in the clay (C_{k0}). The metal contents *after* extractive cleaning are also represented as a percentage of the initial metal concentration, i.e. *before* cleaning, for reasons of comparison.

Although hardly any Cr could be extracted by 0.1 N HCl (see Section 2.4), the fractionation of the Cr in the clay soils has changed during the extractive cleaning (see the example of Waal-1-Cr in Figure 3.4). Generally less Cr was determined in F3 and more Cr in F1 and F2 (and in some cases in F4) after HCl extraction than before. Although Cr was not extracted, it apparently becomes more mobile.

The treatment with 2x 0.1 M EDTA extracted metals to roughly the same degree from the five fractions as the single HCl treatment did. The results of experiment series B showed highest removal percentages for metals in F2 and F3 and smaller values for metals in F4 and F5. An example of this experiment series is given in Figure 3.5, where the distribution of Ni in Rn-6 is displayed.

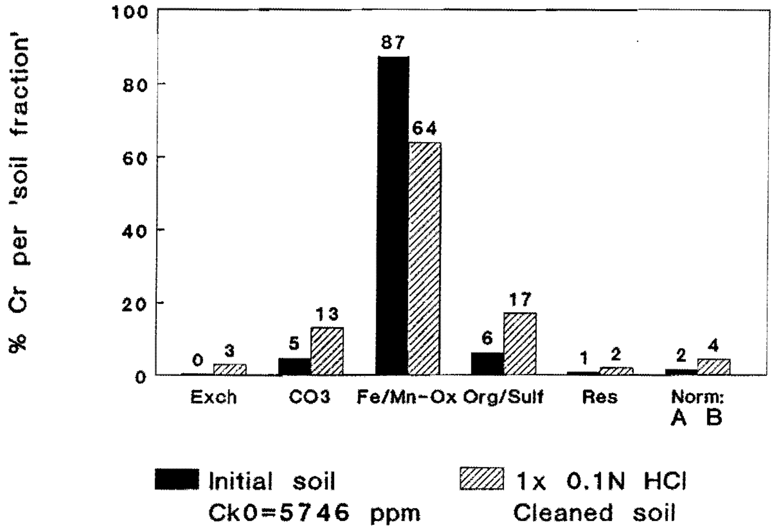

Figure 3.4. *Chromium distribution (%) in artificially polluted Waal clay soil before and after extractive cleaning in 0.1 N HCl for 1 hour. % is based on initial metal concentration* C_{k0} *before cleaning. Norm: see text.*

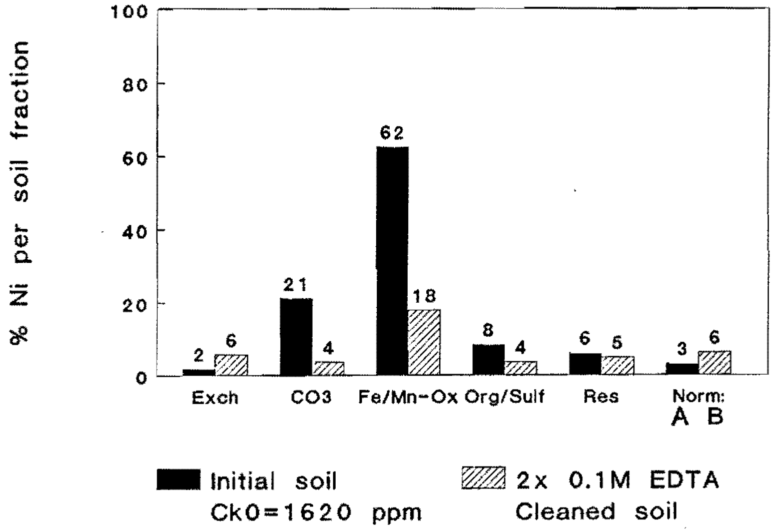

Figure 3.5. *Nickel distribution (%) in Rhine clay soil that was artificially polluted with six metals before and after twofold extractive cleaning (in 0.1 M EDTA for 2 x 30 minutes). % is based on initial metal concentration* C_{k0} *before cleaning. Norm: see text.*

The distributions in the two waste site soils before and after 3x 0.1 N HCl treatment are illustrated by Figures 3.6 and 3.7.

Metals present in the 'carbonate' and 'Fe-Mn-oxides' fractions were almost completely extracted by the 0.1 N HCl solution: 90-99 % of the metals could be removed (with the exception of Cr). Basically, this is the same behaviour as was seen for the artificially polluted clay soils.

Ni and Zn were poorly extracted from the organic fraction (54-71%); Cd, Cu and Pb fairly well (85-93%). Cu and Ni were removed more from the 'organic' fraction in the waste site soils than in the artificially polluted soils; just the opposite is true for Zn. For Cu, this is probably due to the high concentration, which causes the occupation of relatively more 'low-energy' binding sites *(19)*. Except for Pb and Cd, all metals were only removed to a very low degree from the residual fraction (32-57%).

The removal efficiencies from specific fractions are generally in the same range for the waste site soils as for the artificially polluted soils. The extraction percentage might increase if the concentration of the pollutant is higher as was suggested above for the Cu extraction (see also Section 2.4). When the removal percentage in threefold 0.1 N HCl extractive cleaning per fraction is plotted as a function of the initial metal concentration in that specific fraction, C_{k0}, a relationship could not be found.

The results of the sequential extraction analyses are discussed in the next section.

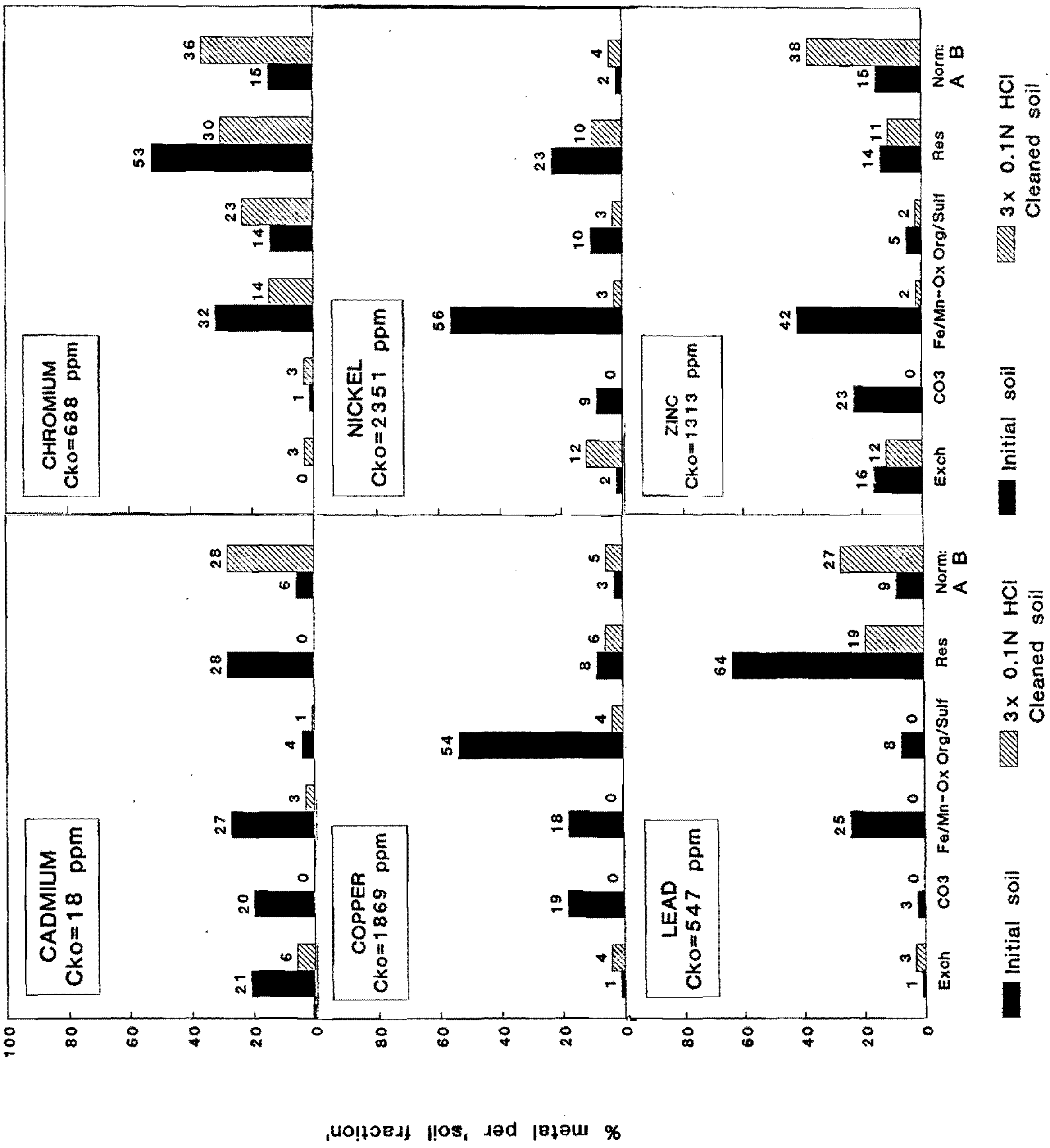

Figure 3.6. *Distribution (%) of Cd, Cr, Cu, Ni, Pb and Zn in Sophia waste site clay soil before and after threefold extractive cleaning (in 0.1 N HCl for 3 x 30 minutes). % is based on initial metal concentration C_{k0} before cleaning. 'Soil fraction' and 'Norm': see text.*

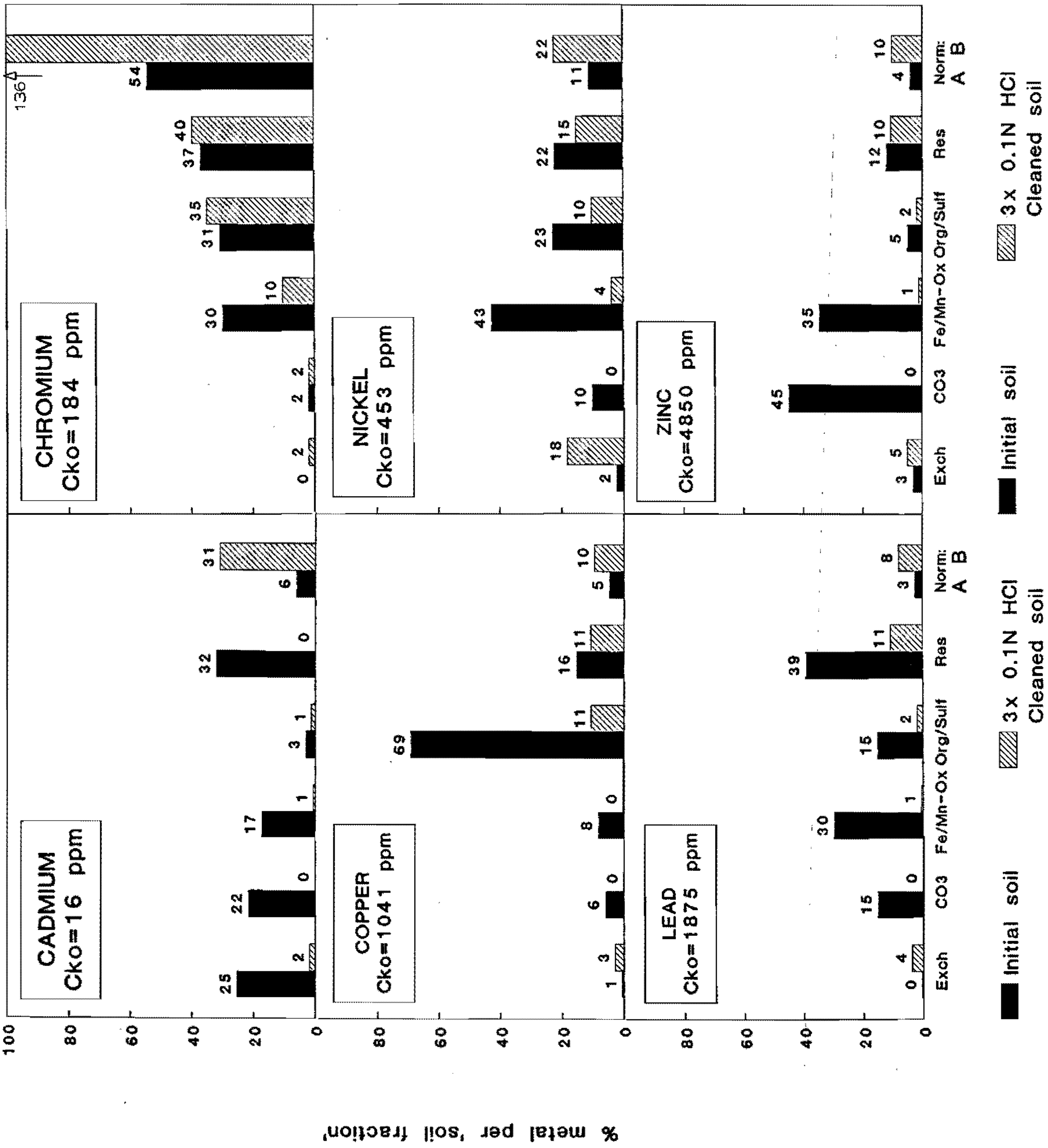

Figure 3.7. *Distribution (%) of Cd, Cr, Cu, Ni, Pb and Zn in Melchior waste site clay soil before and after threefold extractive cleaning (in 0.1 N HCl for 3 x 30 minutes). % is based on initial metal concentration C_{k0} before cleaning. 'Soil fraction' and 'Norm': see text.*

3.4. DISCUSSION

Speciation in polluted soils

Although problems arise in comparing the metal speciation in different soil samples *(1,4,6,7)*, it is possible to find some qualitative trends in the results given in Section 3.3.

When the clay soils were polluted artificially with one or more metals, approximately 80-90% of the total metal content was present in the fractions F1, F2 and F3 of the Tessier-analysis. This importance of the more labile phases of soils and sediments for metals from anthropogenic sources was also indicated by Förstner *(9)*. Two exceptions were noted: soils that were polluted only with Ni or only with Cr (see Appendix III). Six to 25% of total Ni content was determined in the 'residual' fraction. Nickel ions might have diffused to more interior sites in the porous clay soil particles. Experiments by Helios-Rybicka *(10)* showed that this is especially the case for the three-layer clay minerals, like illite, which is the main clay mineral component of the five clay soils used here. Six to 27% of total Cr was measured in the 'organic/sulfidic' fraction F4. Chromium was applied to the clay soils as the trivalent ion Cr(III). Insoluble Cr(III) compounds or co-precipates might have been formed. Oxidation reactions occur in the determination of fraction F4 that could oxidize Cr(III) to Cr(VI). The hexavalent chromium is known to be much more mobile (see also Section 2.6) and can thus be detected in fraction F4.

The metal distribution in the two waste site soils is quite different from that in the artificially polluted soils (see Figure 3.2). The 'exchangeable' metal fraction is very small while the 'org/sulf' and 'residual' fractions contain more metal. Possibly, exchangeable metal species have shifted to other binding sites or have already been washed out by the rain and transported to the ground-water system. The latter may also hold for part of the metals in the 'weakly adsorbed' fraction F2 due to leaching by (acid) rain. The organic matter content of Sophia and Melchior soils is much greater than that of the other five soils (see Section 2.2) and might explain the greater metal content in F4.

Looking at the distributions of the individual metals in the two waste site soils, several preferences of individual metals to specific fractions were noticed (see Table 3.1). The similarity between the two soils is striking and a further resemblance of some interactions can be seen in the literature. High percentages of Cd in the 'exchangeable' fraction were also found by Xian *(11)*, Gibson and Farmer *(12)*, Hickey and Kittrick *(13)* and Kuo et al.*(14)*. Several other authors *(8,11-14)* showed that the 'organic' fraction contained the largest amount of Cu. A high amount of Pb in the 'residual' fraction was also measured by Förstner et al.*(9)* (>50 %) in Rhine sediments, while Gibson and Farmer *(12)* found an average of only 17 % in the 'residual' fraction of 90 urban soil samples. Different sources of Pb contamination may be the cause. The high Pb content was attributed to atmospheric dust particles *(9)*.

Extractability and speciation

The differences in speciation between waste site soils and artificially polluted soils have important consequences for the extractive cleaning of the soils. The more labile fractions F1, F2 and F3, which are the most important metal sinks in the (freshly) artificially polluted soils, are more easily attacked by mineral acids like HCl than the 'residual' fraction F5. The removal efficiency from a fraction seems to be determined in the first place by the type of site and less by the type of metal or the metal concentration. For example, different metals were extracted to the same degree from 'CO_3' and 'Fe/Mn-Ox' fractions. Only chromium is an exception. Pb and Cd are exceptions for the small removal percentages from the 'Residual' fraction.

The influence of the kind of fraction can be expressed by the cumulative distribution of 0.1 N HCl removal percentages. It must be noted that the removal percentages in 0.1 N HCl per soil fraction could only be calculated under the assumption that re-adsorption would not occur. The metal content in fraction F1 is greater after extractive cleaning than before (see Figures 3.6 and 3.7). So, re-adsorption of metals to the 'exchangeable' fraction is evident. Kersten and Förstner *(4)* mentioned the possible increase in surface area for fine grained material on removal of coating materials. We measured larger specific surface areas of the clay soils after extractive cleaning than before. The number of 'exchangeable' surface sites seems thus to increase due to the extractive cleaning. The change in Cr distribution mentioned before (see Figure 3.4) indicates that re-adsorption to other soil fractions than F1 is also possible. The cumulative distribution functions were calculated for the different soil fractions of the Tessier analysis with the HCl results (experiment series A and C) and with the EDTA results (experiment series B). See Figure 3.8 and 3.9.

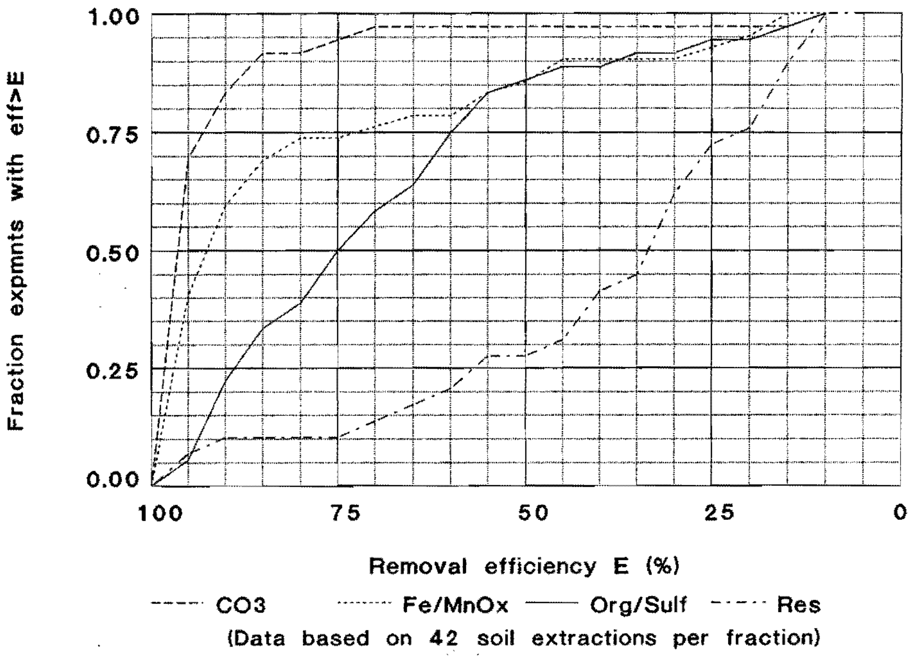

Figure 3.8. *Extractability by 0.1 N HCl of metals present in the different sequential extraction analysis fractions according to the procedure of Tessier Cumulative distribution of metal removal efficiencies from 42 experiments.*

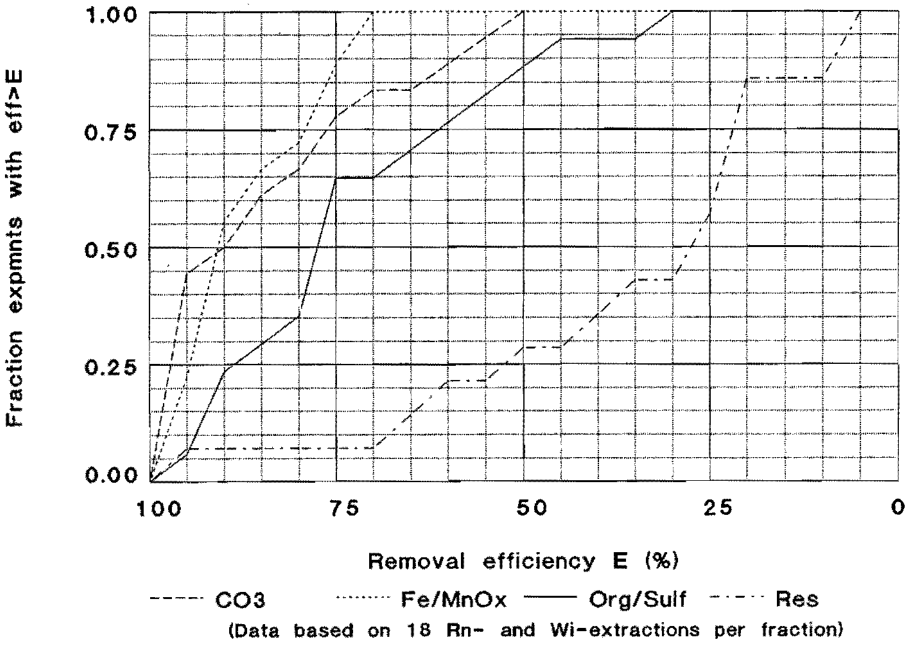

Figure 3.9. *Extractability by 0.1 M EDTA of metals present in the different sequential extraction analysis fractions according to the procedure of Tessier Cumulative distribution of metal removal efficiencies from 18 experiments.*

Although the extraction results of the six metals are taken together, the four fractions clearly behave in a distinct way. It is evident that extraction with 0.1 N HCl or 0.1 M EDTA becomes more difficult in the order:

'CO_3' < 'Fe/Mn-Ox' < 'Org/Sulf' < 'Residual'

Extraction from the 'Res' fraction in particular is much harder than from the other three: 50 % of the experiments shows a metal extraction efficiency less than 33% for HCl and even less than 27% for EDTA. Removal efficiencies are only slightly smaller for EDTA as compared to those for HCl. The main reason for the smaller removal results of the metals from the two waste site soils in 0.1 N HCl compared to those from the artificially polluted soils is the more abundant presence of the metals in the 'Org/Sulf' and especially the 'Residual' fraction (as illustrated by the distributions in Figure 3.2).

In this way the sequential extraction gives important information about the results that can be expected in extractive cleaning with 0.1 N HCl. Threefold 0.1 N HCl extraction gave a removal percentage of roughly:

(100 - % metal in 'residual' fraction)

except for Cr and Pb (compare Table 2.5 in Chapter 2). It must be noted that this expression is just a description. The actual fraction that was not removed in the HCl treatment was also found partly in other fractions than the 'residual' fraction.

Often a classification between metals in soils and sediments is made corresponding to the metal source: lithogenic or anthropogenic *(1,4,6)*. Lithogenic metals are assumed to be bound in crystal lattices and anthropogenic metals are due to human activities (like environmental pollution) and are not lattice-held. The sequential extraction analysis results of the two waste site soils in this study show that anthropogenic metals also end up in the 'residual' fraction. This could be due to two reasons. Originally the metals might have been present in the more labile fractions (like surface exchange sites, carbonates, amorphous hydrous oxides and part of the organic matter). These metal reservoirs seem to play the most important role at the time of first metal-soil contact, as shown by the results of the artificially polluted soils. In a later phase the metals could have been transformed or transported to less extractable forms, for example by means of aging of the amorphous (hydr)oxides *(15)*, formation of very insoluble poly-oxides *(16,17)* or slow diffusion to more interior lattice sites *(10)*. The other explanation for the presence of anthropogenic metals in the 'residual' fraction could be the chemical form in which the metal was brought into the environment (e.g. as a very insoluble compound or as an insoluble metalloid). Finally, it should be noted that experimental errors can also occur. Martin et al.*(7)* pointed to the possibility of an overestimation of the metal content in the 'residual' fraction due to the formation of insoluble residues in the preceding extractions.

Whatever the reason may be, once the 'residual' fraction has become an important metal reservoir (i.e. when the metal content is much bigger than the total background value), extractive cleaning by HCl or EDTA becomes more difficult. Although part of the metals in the 'residual' fraction could be removed from the waste site soils by threefold 0.1 N HCl treatment, only Pb and Cd showed large removal efficiencies (70-80%, see Appendix III). The greater ionic radii of Pb and Cd may have prevented diffusion to more interior (lattice-) binding sites. After treatment the metal concentrations in only the 'residual' fraction range from 1-5x the background A-level (see Chapter 1).

The question should thus be raised if soils containing such levels in the 'residual' fraction after threefold 0.1 N HCl cleaning should be treated any further. Removing the rest pollution will be difficult without drastic destruction of soil components. Treatment costs will also rise considerably. The necessity of further treatment might be related to the bio-availability of the metals after cleaning and restoration of the clay soil. Under natural soil conditions a pH<3 will hardly ever occur. The metals in the residual fraction are probably least bio-available. Tessier et al.*(18)* showed a significant relationship between trace metal concentrations in mollusks and the sum of the amount of trace metals in the first three sequential extraction fractions. Other authors also assumed decreasing bio-availability of metals going from the first to the last sequential extraction fraction *(12,13)*. Pickering *(6)*, Kersten and Förstner *(4)* and Martin et al. *(7)* all point, however, to the difficulties and the variabilities in the relationships between extraction studies and metal uptakes by plants or organisms. A solution may be found in the combination of two maximum permissible levels as proposed recently in the Swiss 'Ordinance on the Tolerable Heavy Metal Content in Soils' *(4)*. One level is based on the total metal content (HNO_3-soluble) and the other on the bio-available metal content ($NaNO_3$-soluble). Such an approach would also account for element specific behaviour like the relatively great removal efficiencies of the Cd and Pb from the 'residual' fraction.

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Chapter 4

KINETICS OF EXTRACTION

4.1. INTRODUCTION

The rate of the extraction of heavy metals from contaminated soils is a very important quantity in soil cleaning. It is one of the factors that determines the required size of extraction apparatus and in this way it influences the total costs of the operation.

Sparks *(1)* reviewed adsorption and desorption kinetics in soil systems. Desorption kinetics of plant nutrients, like nitrogen, phosphorus and potassium, have been studied extensively. Heavy metal kinetics in soils, and desorption kinetics especially, have been investigated to a limited extent only *(2-7)*. In most research work heavy metals were desorbed in a chemical environment close to field soil conditions or in a solution that was indicative of plant-uptake.

In this study extraction takes place in quite another chemical environment. We have studied the rate of the extraction of four heavy metals (Cu, Ni, Pb and Zn) from artificially polluted and waste site clay soils in a 0.1 N HCl solution. Information about the kinetics of the extraction is used in three ways. In the first place the kinetic experiments may lead to a better understanding of the process of extraction and its rate limitations. Secondly, we have described the kinetics in a model that can be used to calculate the extraction efficiency under various conditions. The model describes the rate of extraction at a constant pH and at a constant temperature by an effective rate equation. Finally, the contaminated clay soils were also extracted in a continuous test installation (see Chapter 5); the kinetic model will be applied to predict extraction results in this installation (see Chapter 6).

Kinetic experiments were performed with artificially polluted clay soils and waste site clay soils. The extraction rate of metals from the waste site soils was studied under two different conditions: vigorous mixing of the clay soil suspension and settling of a flocculated clay soil suspension. The conditions correspond to the two types of continuous processes that will be tested (see Chapter 5): extraction of clay in a continuous stirred tank reactor and of flocculated clay soil in a countercurrent column (where flocculation is required to make countercurrent contact possible). The influence of the temperature on the extraction rate was measured for Ni-extraction from artificially polluted Winsum soil under vigorous mixing conditions. To be able to model the kinetic data, separate experiments were carried out to determine the equilibrium metal distributions between clay soil and extractant.

In the rest of this chapter we will derive the 'two-reactions model' first (Section 4.2). Experimental methods and calculation methods will be given in Section 4.3. Experimental results and application of the model will be presented in Section 4.4. A final summarizing discussion will follow in Section 4.5.

4.2. TWO-REACTIONS MODEL

A number of different models have been applied to describe the extraction of various ions from soils *(1)*. Griffin et al. *(2,8)* used a first order rate equation to describe phosphate and boron desorption:

$$-R_d = k(c_k - c_{keq})$$

where: $-R_d$ = desorption extraction rate
c_k = ion concentration in the soil
c_{keq} = ion concentration in the soil at equilibrium soil-solution distribution
k = rate constant

They found, however, that the desorption data could be fitted by two or three different slopes. Griffin and Burau *(2)* postulated therefore two or three corresponding pseudo first-order reactions. The different first-order reactions were ascribed to the desorption of ions from two discrete types of binding sites. Jardine and Sparks *(9)* and Jopony and Young *(5)* described the desorption of potassium and copper by such multiple first-order equations. The first two authors attributed the fast desorption to K^+ bound to external surface sites of the (in)organic phases of the soil and the slow desorption to K^+ bound to less accessible sites of organic matter and interlayer sites of the 2:1 clay minerals.

Extraction can also be described in terms of the models that pass current in modeling heterogeneously catalytic processes. Both the clay soil and many heterogeneous catalysts have a porous structure in common. Soil components are however reactants during the extraction process in a strong acidic environment as opposed to catalysts. This suggests an analogy between gas-solid reactions and the extraction process and it suggests the use of models like the Shrinking-Core-Model *(10)*. It is, however, difficult to describe the complete kinetic behaviour of all the soil types and the four metals by only one type of process or reaction. Many processes can play a role in the very heterogeneous soil-extractant system. Moreover, the experimental information is too limited to determine all possible mechanisms separately. It is necessary to use effective ('lumped parameters') extraction rate equations.

In this study we have found basically two different kinetic patterns for the extraction of heavy metals from soils in a 0.1 N HCl solution (see Figure 4.1).

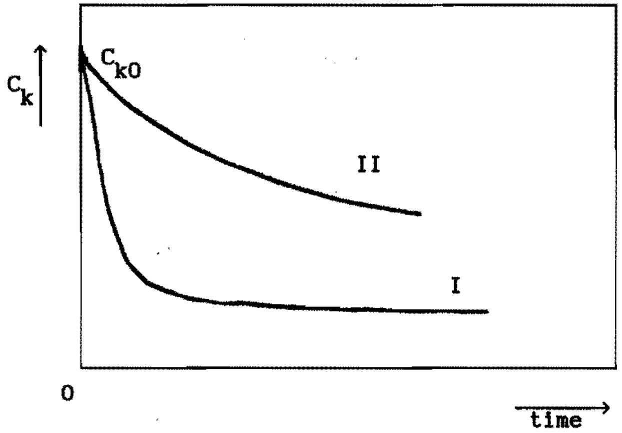

Figure 4.1. *Schematic representation of the two different extraction patterns in time (I and II: see text).* C_k*=metal concentration in clay soil.*

The first pattern showed a very rapid extraction followed by a much slower extraction, the second pattern consisted of a regularly decreasing clay soil concentration with an extraction rate that was intermediate between those of the very rapid and the slow extraction. A multiple reactions model seemed to be well suited to describe both types of curves with different parameter values for the two types of curves.

A distinction in differently reacting metal-soil sites is supported by the division of adsorbed metal species into specifically and non-specifically bound metals. A large number of authors have reported these two categories as a useful - although operationally defined - tool in indicating different metal behaviour *(4,11-15)*. Other authors *(16-18)* differentiate between metals from anthropogenic and lithogenic sources (see Section 3.4). Anthropogenic metals are supposed to be non-lattice held. As discussed in Chapter 3, the more labile fractions of a soil (as distinguished, for example, by a sequential extraction procedure) are the most important reservoirs for metals in recently polluted clay soils. Older contaminations, like the metals in the two waste site soils in this study, also end up in the 'residual' fraction of the sequential extraction analysis.

So, although various classifications are possible, it seems reasonable to distinguish two main categories in the description of the extraction rate: a fast and a slow reaction. Both model reactions can be considered to encompass each a number of actual processes occurring in the real soil-extractant system. The experimental approach limits, however, the description of the extraction rate in a more sophisticated way.

We have tried to model the extraction of heavy metals from soils by a 0.1 N HCl solution at constant pH and temperature by the two simultaneous reactions (1) and (2):

$$\text{(1)}\quad \begin{array}{l} \mathrm{Surf_1\text{-}O^-\text{-}Me^{2+}} + \mathrm{H^+} \xrightarrow{k_1} \mathrm{Surf\text{-}O\text{-}\ H} + \mathrm{Me^{2+}} \\ \text{or:}\quad \begin{array}{c} \mathrm{Me(CO_3)} \\ \mathrm{Me(OH)_2} \\ \text{etc.} \end{array} + 2\ \mathrm{H^+} \xrightarrow{k_1} \mathrm{Me^{2+}} + \ldots \end{array}$$

$$\text{(2)}\quad \mathrm{Surf_2\text{-}O^-\text{-}Me^{2+}} + \mathrm{H^+} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathrm{Surf\text{-}O\text{-}\ H} + \mathrm{Me^{2+}}$$

where: $\mathrm{Surf_1\text{-}O^-}$ - = active surface binding site (type 1)
$\mathrm{Surf_2\text{-}O^-}$ - = active surface binding site (type 2)
k_1, k_2, k_3 = reaction rate constants

Reaction (1) is fast compared to the forward reaction of (2) (i.e. $k_1 > k_2$) and it is irreversible. It represents the exchange of metals bound to surface sites and the dissolution of soluble metal compounds (carbonate-, and amorphous Fe- and Mn-oxide associated metals). We assumed that a large number of the sites involved in this reaction were destroyed by the strong acidic 'attack'. Part of this reaction is in principle reversible. The $[H^+]$ is, however, so much greater than $[Me^{2+}]$ that we considered the re-adsorption of heavy metal ions to these sites to be negligible. Reaction (2) is slower and the reaction is reversible. It can be thought to describe the exchange of metals bound to more interior (lattice-)sites and the extraction of metals occluded in or precipitated as compounds that do not dissolve easily in 0.1 N HCl at room temperature. In contrast to the multiple reactions models mentioned earlier *(1,2,9)* the two reactions are coupled. So, metal ions in solution formed by reaction **(1)** can also re-adsorb to the soil according to the backward reaction of **(2)**.

Both forward reactions are pseudo first-order, $[H^+]$ is kept constant during the extraction. The backward reaction is also considered to be pseudo first-order, mainly for sake of simplicity. The concentration of empty sites cannot be measured during the extraction. Extraction of an individual metal was assumed to be independent of the presence of other metals.

Besides the reaction-rate constants, k_1, k_2 and k_3, we need another parameter to describe the fractions of total heavy metal content that react according to reaction **(1)** and **(2)**. We assumed that a fraction α_0 reacted slowly (reaction **(2)**) and a fraction $(1-\alpha_0)$ quickly (reaction **(1)**).

The mathematical rate-expressions for the two reactions are then:

$$-R_a = k_1 . c_{ka} \tag{4.1}$$

$$-R_b = k_2 . c_{kb} - k_3 . c_\ell \tag{4.2}$$

where:
- $-R_a$ = rate of extraction according to reactions **(1)**
- $-R_b$ = rate of extraction according to reaction **(2)**
- k_1, k_2 = reaction rate constants (1/sec)
- k_3 = reaction rate constant (1/sec*kg liquid/kg clay soil)
- c_{ka} = heavy metal concentration in clay soil that reacts according to reactions **(1)**
- c_{kb} = heavy metal concentration in clay soil that reacts according to reaction **(2)**
- c_ℓ = heavy metal concentration in extraction liquid

If the initial total heavy metal concentration in the clay is c_{k0}, then α_0 is the fourth parameter:

$$c_{ka0} = (1-\alpha_0) . c_{k0}$$

$$c_{kb0} = \alpha_0 . c_{k0}$$

Note that α_0 is defined in terms at t=0 only. Now the kinetic model contains four parameters: k_1, k_2, k_3 and α_0.

The ratio k_3/k_2 was determined in separate equilibrium experiments. The 'real' chemical equilibrium between clay soil and extracting agent is difficult to determine experimentally. In some experiments a very slow extraction was still going on even after 24 hours. Bowman et al. *(7)* also measured very slow desorption reactions (that lasted many days) of Ni in an EDTA solution. Lion et al. *(6)* found Cd desorption going on at pH = 5.5 after 96 hours. We assumed that a quasi-equilibrium was reached after 24 hours extraction in 0.1 N HCl. Concentration changes 1-3 hours after this period were generally within the experimental error.

At the quasi-equilibrium $(-R_b)=0$ and $c_{ka,eq}=0$, so:

$$k_3 = \frac{k_2 \cdot c_{kb,eq}}{c_{\ell,eq}} \tag{4.3}$$

where: $c_{kb,eq}$ = total heavy metal concentration in clay soil after 24 h. extraction in 0.1 N HCl

$c_{\ell,eq}$ = heavy metal concentration in extraction liquid after 24 h. extraction in 0.1 N HCl

We adopted a linear equilibrium relationship:

$$c_{kb,eq} = m.c_{\ell,eq} + d \tag{4.4}$$

The term m is a quasi-equilibrium constant that depends on the pH value in the extraction process and the term d can be considered as a residual heavy metal concentration that cannot be removed by the 0.1 N HCl solution. Hysteresis between adsorption and desorption reactions confirms the possible existence of such a residual (not extractable) metal concentration. It must be noted that this linear equilibrium relationship is an assumption which might not be valid over the complete concentration ranges in the extraction process. Non-linear relations can also exist.

Equations (4.3) and (4.4) give:

$$k_3 = k_2 \cdot \left(m + \frac{d}{c_{\ell,eq}} \right) = m_1 . k_2 \tag{4.5}$$

We will now apply the two rate equations (4.1) and (4.2) to two experimental batch extractions.

4.2.1. Batch extraction in case of vigorous mixing

In the batch kinetic experiments the clay soil suspension was stirred vigorously. Conditions are supposed to be the same for all clay soil particles. The continuity equation can be applied to the batch system: the changes of metal concentrations, $-\frac{dC}{dt}ka$ and $-\frac{dC}{dt}kb$, are set equal to the rate equations (4.1) and (4.2). The initial conditions are:

$$t = 0: \; c_{ka}\,(0) = c_{ka0} = (1-\alpha_0).c_{k0}$$

$$c_{kb}\,(0) = c_{kb0} = \alpha_0 . c_{k0}$$

$$c_{\ell}\,(0) = c_{\ell 0}$$

The mass balance of heavy metal in the system is:

$$M_{k0}.c_{k0} + M_{\ell 0}.c_{\ell 0} = M_k(t).\left[\, c_{ka}(t) + c_{kb}(t) \,\right] + M_{\ell}(t).c_{\ell}(t) \qquad (4.6)$$

where: M_{k0}= mass of clay soil at time t=0
$M_k(t)$ =mass of clay soil at time t
$M_{\ell 0}$= mass of liquid at time t=0
$M_{\ell}(t)$ =mass of liquid at time t

In the beginning of the batch experiment the change per unit time in $M_k(t)$ and $M_{\ell}(t)$ was greatest: part of the clay soil dissolved and HCl solution was added to maintain a constant pH = 1. After this initial period the soil to solution ratio was about constant (only suspension samples were taken). We approximate the soil to solution ratio therefore by:

$$\frac{M_k(t)}{M_{\ell}(t)} \approx \text{constant} = \left(\frac{M_k}{M_{\ell}}\right)_{\text{mean}}$$

Integration of the continuity equation for the batch extraction of metal that reacts according to equation (4.1) gives:

$$c_{ka} = (1-\alpha_0).c_{k0}.e^{-k_1 . t} \qquad (4.7)$$

Combining this solution and the mass balance, we can write $c_{\ell}(t)$ in terms of $c_{kb}(t)$ and t and integrate the second continuity equation:

$$c_{kb} = \alpha_0 \cdot c_{k0} \cdot e^{-k_2 \cdot A \cdot t} + \frac{k_3\left[\frac{M_k}{M_\ell} \cdot c_{k0} + c_{\ell 0}\right]}{k_2 \cdot A} * \left(1 - e^{-k_2 \cdot A \cdot t}\right) +$$

$$+ \frac{k_3 \cdot \frac{M_k}{M_\ell}(1-\alpha_0) . C_{k0}}{k_2 \cdot A - k_1} * \left(e^{-k_2 \cdot A \cdot t} - e^{-k_1 \cdot t}\right) \qquad (4.8)$$

where: $A = 1 + \frac{M_k}{M_\ell} \cdot \frac{k_3}{k_2}$

The total metal concentration in the clay as a function of time is the sum of expressions (4.7) and (4.8). Rearranging and substituting the equilibrium relationship (4.5) into the term A, gives:

$$c_k(t) = c_{k0} * \left(\frac{k_2-k_1}{k_2A-k_1}\right) * \left\{ \left[\alpha_0 + \frac{k_1(1-1/A)}{k_2-k_1}\right] e^{-k_2At} + [1-\alpha_0]e^{-k_1t} \right\} +$$

$$+ (1-1/A)c_{k0} + (1-1/A)\frac{M_\ell}{M_k} \cdot c_{\ell 0}\left(1 - e^{-k_2At}\right) \qquad (4.9)$$

where: $A = 1 + \frac{M_k}{M_\ell} \cdot \frac{k_3}{k_2} = 1 + \frac{M_k}{M_\ell} \cdot m_1$

The three parameters k_1, k_2 and α_0 can be determined by fitting the data points $(t, c_k(t))$ to this equation. This was done by means of a computer programme that determines the minimum of a sum of squares of the function:

$$\sum_{i=1}^{N} (C^i_{k,\text{observed}} - C^i_{k,\text{calculated}})^2$$

where: N = total number of data points

4.2.2. Batch extraction in case of settling flocculated clay suspensions

Extraction of heavy metals from clay was also performed in a countercurrent column. The clay soil suspension was flocculated upstream of the inlet and flocculated clay soil aggregates settled in the column (see Chapter 5).

Because of these different extraction conditions to the vigorously mixed situation, we measured the kinetics of the batch extraction also under hydrodynamic conditions similar to those in the countercurrent extraction. Measured extraction rates were generally smaller in the latter case.

We have modeled this new situation (so-called 'floc-kinetics') by adding a mass-transfer step to the two-reactions model. A liquid film was assumed to exist between the individual particles of the floc. The concentration profile around a floc can then be visualized in the way shown in Figure 4.2.

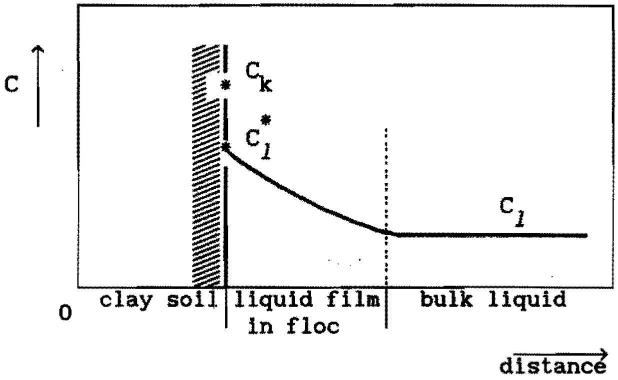

Figure 4.2. *Concentration profiles around a flocculated clay soil particle under settling conditions.*
C_k =*metal concentration in clay soil particle;*
C_ℓ =*metal concentration in liquid film in and around floc;*
C_ℓ =*metal concentration in bulk extraction solution.*

The rate of mass transfer between the liquid film (concentration c_ℓ) and the bulk liquid (concentration c_ℓ) can be described by:

$$+\ \Phi_{Me} = k_{fd} \cdot a\left(c_\ell^*(t) - c_\ell(t)\right) \qquad (4.10)$$

where: $c_\ell^*(t)$ = bulk liquid concentration in equilibrium with liquid film concentration $c_\ell(t)$ (ppm)
k_{fd} = overall mass transfer coefficient related to the bulk liquid phase (m/sec)
a = specific surface area for mass transfer (m^2/m^3)
Φ_{Me} = metal flux through liquid film in floc (ppm/sec)

Equations (4.1), (4.2) and (4.10) together describe the floc kinetics. Equation (4.2) has to be rewritten in terms of c_ℓ for the case of floc kinetics:

$$-\ R_b = k_2 \cdot c_{kb} - k_3 \cdot c_\ell \qquad (4.2^*)$$

An extra necessary equation is the equilibrium relationship between film and bulk liquid. Flocculant and (metal) ion concentrations are different in these two aqueous solutions. Surface charge of the clay soil particles may cause a difference in electrical potential. It is assumed that these conditions do not influence the equilibrium metal concentrations. The distribution at equilibrium is then given by the simple expression:

$$c_{\ell}^{*} = m_2 \cdot c_{\ell}$$

where: m_2 = 1 (kg film liquid/kg bulk liquid).
Now we make the following assumptions:

1. the extraction rate constants k_1 and k_2 are the same as in the situation of the - vigorous mixing - batch kinetics;
2. the value of α_0 is not influenced by the flocculation and is equal to the value in vigorous mixing kinetics. In reality it is very probable that surface properties of soil particles change due to flocculation;
3. the quasi-equilibrium constant m_1 is the same for the two kinetic conditions (if pH-value is the same in the extraction);
4. the liquid film concentration is in a stationary state, i.e. $(dc_{\ell}/dt) \approx 0$. This assumption is very clearly not valid at the beginning of the extraction process. It becomes more probable in a later phase.

The last assumption was made to reduce the model to a problem with three concentration variables. The rate of change of film concentration is given by:

$$\frac{dc_{\ell}}{dt} = k_1 \cdot c_{ka} \cdot \frac{M_k}{M_{\ell}} + k_2 \cdot c_{kb} \cdot \frac{M_k}{M_{\ell}} - k_3 \cdot c_{\ell} \cdot \frac{M_k}{M_{\ell}} - k_{fd} \cdot a \cdot \left(c_{\ell}^{*} - c_{\ell}\right) \frac{M_{\ell}}{M_{\ell}}$$

where: M_{ℓ} = mass of film liquid
*(Note that the units of k_3 are now (1/sec * kg film liquid/kg clay) and not as in the case of vigorous mixing: (1/sec * kg bulk liquid/kg clay)).*

Setting (dc_{ℓ}/dt) = 0 gives:

$$c_{\ell} = \frac{k_1 \cdot c_{ka} + k_2 \cdot c_{kb} + k_{fd} \cdot a \cdot c_{\ell} \cdot \frac{M_{\ell}}{M_k}}{k_3 + k_{fd} \cdot a \cdot m_2 \cdot \frac{M_{\ell}}{M_k}} \qquad (4.11)$$

The total mass balance of the system is now:

$$M_{k0}\cdot c_{k0} + M_{\boldsymbol{\ell}0}\cdot c_{\boldsymbol{\ell}0} + M_{\ell 0}\cdot c_{k0} = M_k(t)\left[c_{ka}(t) + c_{kb}(t)\right] +$$

$$+ M_{\boldsymbol{\ell}}(t).c_{\boldsymbol{\ell}}(t) + M_{\ell}(t).c_{\ell}(t) \qquad (4.6^*)$$

where: $M_{\boldsymbol{\ell}0}$ = mass of film liquid at time t = 0
$c_{\boldsymbol{\ell}0}$ = metal concentration in film liquid at time t = 0

We approximated the mass ratios again by their average values, i.e.:

$$\frac{M_k(t)}{M_{\boldsymbol{\ell}}(t)} \approx \text{constant} = \left(\frac{M_k}{M_{\boldsymbol{\ell}}}\right)_{avg}$$

$$\frac{M_k(t)}{M_{\ell}(t)} \approx \text{constant} = \left(\frac{M_k}{M_{\ell}}\right)_{avg}$$

Following an analogous procedure as in the previous section, we find an expression for $c_k(t)$:

$$c_k(t) = \left[\frac{c_{k0}\cdot\left(\frac{m_2}{m_1}\cdot\frac{M_\ell}{M_k} + \frac{1}{m_1}\cdot\frac{M_{\boldsymbol{\ell}}}{M_k}\right)}{\left(\frac{m_2}{m_1}\cdot\frac{M_\ell}{M_k} + \frac{1}{m_1}\cdot\frac{M_{\boldsymbol{\ell}}}{M_k}\right)\cdot\left(1 - \frac{k_1}{k_2}\right) + \left(1 - \frac{k_1}{k_{fd}\cdot a}\right)}\right] *$$

$$* \left\{(1-\alpha_0)\left(1 - \frac{k_1}{k_2}\right)e^{-k_1\cdot t} + \right.$$

$$\left. + \frac{\alpha_0\left(1 - \frac{1}{\alpha_0} + \frac{m_2}{m_1}\cdot\frac{M_\ell}{M_k} + \frac{1}{m_1}\cdot\frac{M_{\boldsymbol{\ell}}}{M_k}\right)\left(1 - \frac{k_1}{k_2}\right) + \left(1 - \frac{k_1}{k_{fd}\cdot a}\right)}{\left(1 + \frac{m_2}{m_1}\cdot\frac{M_\ell}{M_k} + \frac{1}{m_1}\cdot\frac{M_{\boldsymbol{\ell}}}{M_k}\right)} * e^{-P^{\ddagger}.t}\right\} +$$

$$+ \frac{c_{k0}}{\left(1 + \frac{m_2}{m_1}\cdot\frac{M_\ell}{M_k} + \frac{1}{m_1}\cdot\frac{M_{\boldsymbol{\ell}}}{M_k}\right)} \qquad (4.12)$$

where: $$P^{\ddagger} = \frac{\left(1 + \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k} + \frac{1}{m_1} \cdot \frac{M_{\mathscr{f}}}{M_k}\right)}{\left(\frac{1}{k_{fd} \cdot a} + \frac{1}{k_2} \cdot \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k} + \frac{1}{k_2} \cdot \frac{1}{m_1} \cdot \frac{M_{\mathscr{f}}}{M_k}\right)}$$

In equation (4.12) only the sum of $M_{\mathscr{f}}$ and M_{ℓ} is known, not the individual values. Because it seems probable that $M_{\mathscr{f}} << M_{\ell}$, we approximate:

$$\frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k} + \frac{1}{m_1} \cdot \frac{M_{\mathscr{f}}}{M_k} \approx \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}$$

($m_2 = 1$, see before).
Equation (4.12) can then be simplified to (4.13):

$$c_k(t) = \left[\frac{c_{k0} \cdot \left(\frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}\right)}{\frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k} \cdot \left(1 - \frac{k_1}{k_2}\right) + \left(1 - \frac{k_1}{k_{fd} \cdot a}\right)}\right] * \left\{(1-\alpha_0)\left(1 - \frac{k_1}{k_2}\right) e^{-k_1 \cdot t} + \right.$$

$$\left. + \frac{\alpha_0 \left(1 - \frac{1}{\alpha_0} + \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}\right)\left(1 - \frac{k_1}{k_2}\right) + \left(1 - \frac{k_1}{k_{fd} \cdot a}\right)}{\left(1 + \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}\right)} * e^{-P \cdot t}\right\} +$$

$$+ \frac{c_{k0}}{\left(1 + \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}\right)} \tag{4.13}$$

where: $$P = \frac{\left(1 + \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}\right)}{\left(\frac{1}{k_{fd} \cdot a} + \frac{1}{k_2} \cdot \frac{m_2}{m_1} \cdot \frac{M_{\ell}}{M_k}\right)}$$

The product $k_{fd} \cdot a$ can now be determined by fitting the data points of the floc kinetics experiments, (t, $c_k(t)$), to this equation. This was done again by calculating the minimum of a sum of squares of the differences between measured and calculated c_k values (see Section 4.2.1). The values of k_1, k_2 and α_0 determined from the mixed kinetics experiments were used as input for the computer programme used to calculate the parameter $k_{fd}.a$.

4.3. EXPERIMENTAL METHODS

The general procedure in the kinetic experiments with vigorous mixing was as follows:
an amount of dried or moist clay soil (10 - 20 g) was put into a glass beaker, the extraction cell (see Figure 2.2 in Chapter 2). At time zero a 0.1 N HCl solution was pipetted into the beaker and the suspension was mixed mechanically by a glass stirrer. The pH was recorded and controlled at a constant set-point value of pH=1 by adding a 1 N HCl solution from a burette. The initial soil to solution weight ratio was 1:20, but this ratio changed slightly due to acid addition and dissolution of soil components.

Samples of the suspension were taken with a 10 ml plastic syringe or with a plastic pipette-tip and were weighed. The sample was filtered through a 0.45 µm membrane filter in a 'Swinnex' filter set-up. The time required for sampling, weighing and phase separation was 10-20 seconds. Metal concentrations in the samples were analysed by AAS. After the extraction the suspension was centrifuged and clay samples were taken. The clay soil was decomposed according to the procedure given in Appendix II.1. Metal concentrations in the liquid were determined by AAS.

Nickel extraction from Winsum soil was measured at different temperatures (5, 20, 40, 60 and 80°C). In these experiments the HCl solution was put in the extraction cell first and equilibrated at the required temperature by hot or cold water pumped through the jacket around the cell. The standardization of the pH-meter was adjusted to the temperature concerned. Vapour was trapped in a refluxing condenser on top of the lid of the extraction cell. The jacket water temperature was kept constant by a thermostat. Separate experiments showed that the temperature in the cell closely followed the jacket temperature. At time zero air-dried Winsum clay soil was put into the extraction cell. The course of the rest of the experiment is analogous to that carried out at room temperature.

The kinetic experiments lasted 3-4 hours in case of the artificially polluted soils. Extraction of metals from the waste site soils and of Ni from Winsum clay soil at room temperature was prolonged to 24 hours. The metal concentrations in clay and liquid at 24 hours gave one data point of the quasi-equilibrium relationship (see equation 4.5). We needed a second point to determine this linear expression. Separate equilibrium experiments were therefore performed with the two waste site soils, Sophia and Melchior. These experiments consisted of 30 minutes extraction in 0.1 N HCl followed by a second step extraction in 0.1 N HCl of 24 hours. The extractions were carried out analogous to the kinetic experiments but samples of suspension were obtained only at the end of the experiment.

The kinetics of the extraction from a flocculated clay suspension under settling conditions were studied in a slowly turning batch reactor (to prevent break-up of the clay aggregates). The general procedure was as follows: a clay soil suspension (dry matter content approx. 5 wt.%) was flocculated by the anionic polyamide A100 (see Chapter 5) in a dose of about 450 mg flocculant/kg dry clay soil. After settling of the flocs the supernatant liquid was decanted and samples were taken from the flocculated clay soil to determine metal and dry matter content. An amount of approx. 50 g of moist flocculated clay suspension was put into the turn-over reactor and at time zero such an amount of 0.15 N HCl was added, that the soil-to-solution ratio was approximately 1:20. The turn-over reactor was a closed jar clamped to a stirrer at an angle of 45° with the vertical. Turning on the stirrer produced an upside-down motion of the reactor and caused the clay flocs to fall gently through the solution. The velocity of the rotation decreased gradually from 1 revolution per 1/2 minute to 1 revolution per 5 minutes. At regular time intervals the jar was opened and samples of the liquid were taken, filtered and weighed. The pH was checked and if necessary adjusted to pH=1. In some experiments flocculated clay samples were also taken to determine the metal concentration in the liquid around the flocs. After approximately 4 hours the experiment was stopped and the suspension was centrifuged. The metal concentration in the clay soil was analysed.

The floc-kinetics experiments were only carried out with the two waste site soils. All kinetics experiments were at least performed in duplicate.

The metal concentration in the clay soil as a function of time was calculated from a mass balance for the metal in the system. The change in mass of clay soil and liquid in the extraction cell was caused by four factors:

- volatilization of components due to decomposition of soil material in the acidic environment (CO_2, H_2S, etc.);
- HCl solution added to maintain a constant pH;
- sampling;
- evaporation.

The effect of the first factor was determined in separate experiments. The 2nd and 3rd factor were measured during the kinetic experiment. The last factor was checked for in the kinetic experiment and could generally be neglected in the calculation procedure. It is then possible to start the calculation of the metal concentration at either end of the extraction: from the metal concentration in the clay before the extraction or from the value determined at the end. If we calculated $c_{k,t}$ from $c_{k,t-1}$ (the first method) we applied the formula:

$$c_{k,t} = \Big(M_{k,t-1} \cdot c_{k,t-1} + M_{\ell,t-1} \cdot c_{\ell,t-1} - M_{\ell,t} \cdot c_{\ell,t} + M_{M,t-1} \cdot ds_{t-1} \cdot c_{k,t-1} + \\ + M_{M,t-1} \cdot (1-ds)_{t-1} \cdot c_{\ell,t-1} \Big) \Big/ M_{k,t} \qquad (4.14)$$

where: t = time
$t-1$ = time at which last sample was taken before time t
$c_{k,t}$ = metal concentration in clay at time t
$c_{\ell,t}$ = metal concentration in liquid at time t
$M_{k,t}$ = mass of clay soil at time t
$M_{\ell,t}$ = mass of liquid at time t
ds_{t-1} = dry matter content of extraction cell and sample at t-1
$M_{M,t-1}$ = mass of sample taken at time t-1

In case we started the calculation from the metal concentration in the clay after the experiment, we expressed $c_{k,t-1}$ as a function of $c_{k,t}$ and used the equation:

$$c_{k,t-1} = \Big(M_{k,t} \cdot c_{k,t} + M_{\ell,t} \cdot c_{\ell,t} - M_{\ell,t-1} \cdot c_{\ell,t-1} + \\ + M_{M,t-1} \cdot (1-ds_{t-1}) \cdot c_{\ell,t-1} \Big) \Big/ \Big(M_{k,t-1} - M_{M,t-1} \cdot ds_{t-1} \Big) \qquad (4.15)$$

Which calculation procedure was chosen depended mainly on the accuracy of the initial and final metal concentration in the clay soil. Values calculated by equations (4.14) and (4.15) were generally within 5% of each other.

4.4. RESULTS

4.4.1. Vigorous mixing kinetics

Two waste site soils and seven artificially polluted clay soils were subjected to the vigorous mixing kinetics study. The waste site soils were analysed for Cu, Ni, Pb and Zn and the other soils only for the single metal species they contained. The metal concentrations as a function of extraction time are given in Appendix IV.1.

As mentioned in Section 4.2 we found basically two different kinetic patterns for the extraction of heavy metals from clay soils in a 0.1 N HCl solution (see Fig. 4.1). Typical examples of these patterns are the extraction of Cu from Maas clay soil (Fig. 4.3a) and that of Ni from Rhine clay soil (Fig. 4.3b). The other five artificially polluted clay soils, Rhine-Pb, Winsum-Cu, Winsum-Ni, Winsum-Pb and Winsum-Zn, showed concentration curves similar to that of Maas-Cu.

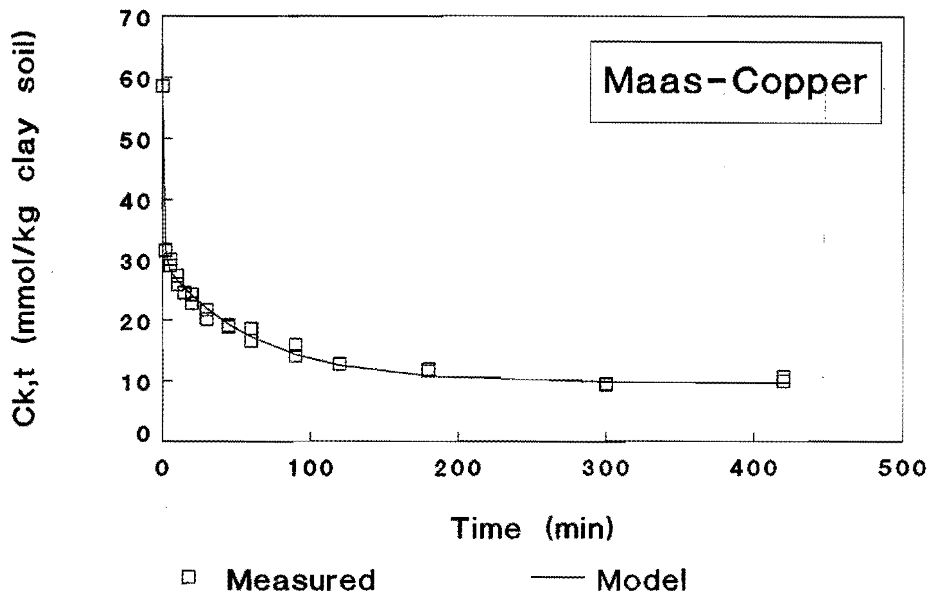

Figure 4.3.a *Copper concentration $C_{k,t}$ in artificially polluted Maas clay soil during extraction in 0.1 N HCl versus extraction time. Lines through data points are calculated with two-reactions model for vigorous mixing.*

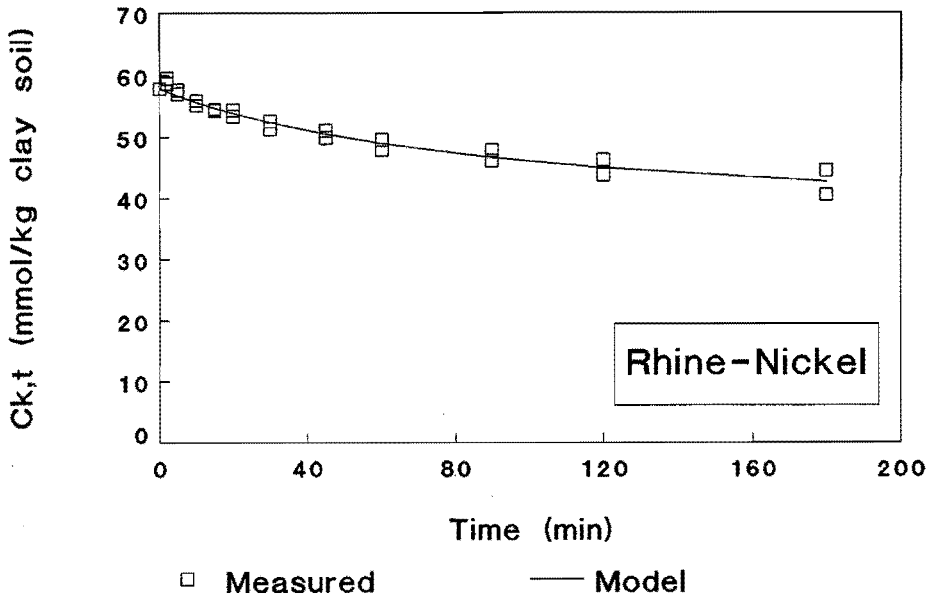

Figure 4.3.b *Nickel concentration* $C_{k,t}$ *in artificially polluted Rhine clay soil during extraction in 0.1 N HCl versus extraction time. Lines through data points are calculated with two-reactions model for vigorous mixing.*

The extraction of the four metals from the two waste site soils proceeded generally slower than that from the artificially polluted soils, as can be seen from Figures 4.4 and 4.5.

The data of the mixed kinetics experiments were fitted to equation (4.9) of the two-reactions model, as discussed in Section 4.2.1. The metal concentrations calculated with the model are represented by the lines in Figures 4.3-4.5. The two-reactions model gives a good fit of the experimental data in all cases. The values of the model parameters m_1, k_1, k_2 and α_0 are given in Table 4.1.

The order of magnitude of the reaction rate constant of the fast irreversible reaction, k_1, is 1-2 min^{-1} for the metals from the artificially polluted clay soils with the extraction of Ni from Rhine clay as the only exception. The value of the quasi-equilibrium constant m_1 is much bigger in this last case.

The values of k_1 of the waste site soils are on the whole slightly less than those of the artificially polluted soils, while the values of k_2 are in the same range for both types of soils. The differences in extraction results seem to be described by the model mainly in terms of different values for m_1 and α_0. A great value for m_1 indicates that the removal percentage will be low in a single 0.1 N HCl extraction even after a long time. If the fraction $\alpha_0 \geq 0.5$, the main part of the metal in the clay reacts slowly and the quasi-equilibrium concentration is reached slowly (see Figures 4.3-4.5).

Table 4.1.
MODEL PARAMETERS OF TWO-REACTIONS MODEL FOR VIGOROUS MIXING KINETICS

Clay soil	Metal	m_1 ($L.kg^{-1}$)	k_1 (min^{-1})	k_2 (min^{-1})	α_0 (-)	AREPD[1] (%)
Maas	Cu	3.95	1.16	$1.3.10^{-2}$	0.51	3.9
Rhine	Ni	38.7	$3.3.10^{-2}$	$2.3.10^{-3}$	0.93	1.7
Rhine	Pb	2.01	1.63	$1.0.10^{-1}$	0.15	10.9
Winsum	Cu	1.49	1.06	$5.8.10^{-3}$	0.17	6.6
Winsum	Ni	4.95	2.16	$4.4.10^{-3}$	0.42	2.2
Winsum	Pb	2.12	2.65	$4.4.10^{-2}$	0.21	6.0
Winsum	Zn	2.34	1.39	$2.6.10^{-2}$	0.20	9.4
Sophia	Cu	1.64	1.54	$4.5.10^{-3}$	0.35	18.4
Sophia	Ni	6.59	$2.4.10^{-2}$	$1.9.10^{-3}$	0.77	8.7
Sophia	Pb	9.42	$9.9.10^{-2}$	$1.3.10^{-3}$	0.57	14.0
Sophia	Zn	5.06	$9.1.10^{-1}$	$2.8.10^{-3}$	0.64	9.1
Melchior	Cu	11.6	$1.2.10^{-1}$	$5.6.10^{-4}$	0.51	7.6
Melchior	Ni	22.0	1.05	$4.4.10^{-4}$	0.75	3.3
Melchior	Pb	5.14	$2.5.10^{-1}$	$6.6.10^{-4}$	0.34	22.1
Melchior	Zn	2.64	1.3	$4.3.10^{-3}$	0.28	17.4

1) AREPD = average relative error per data point

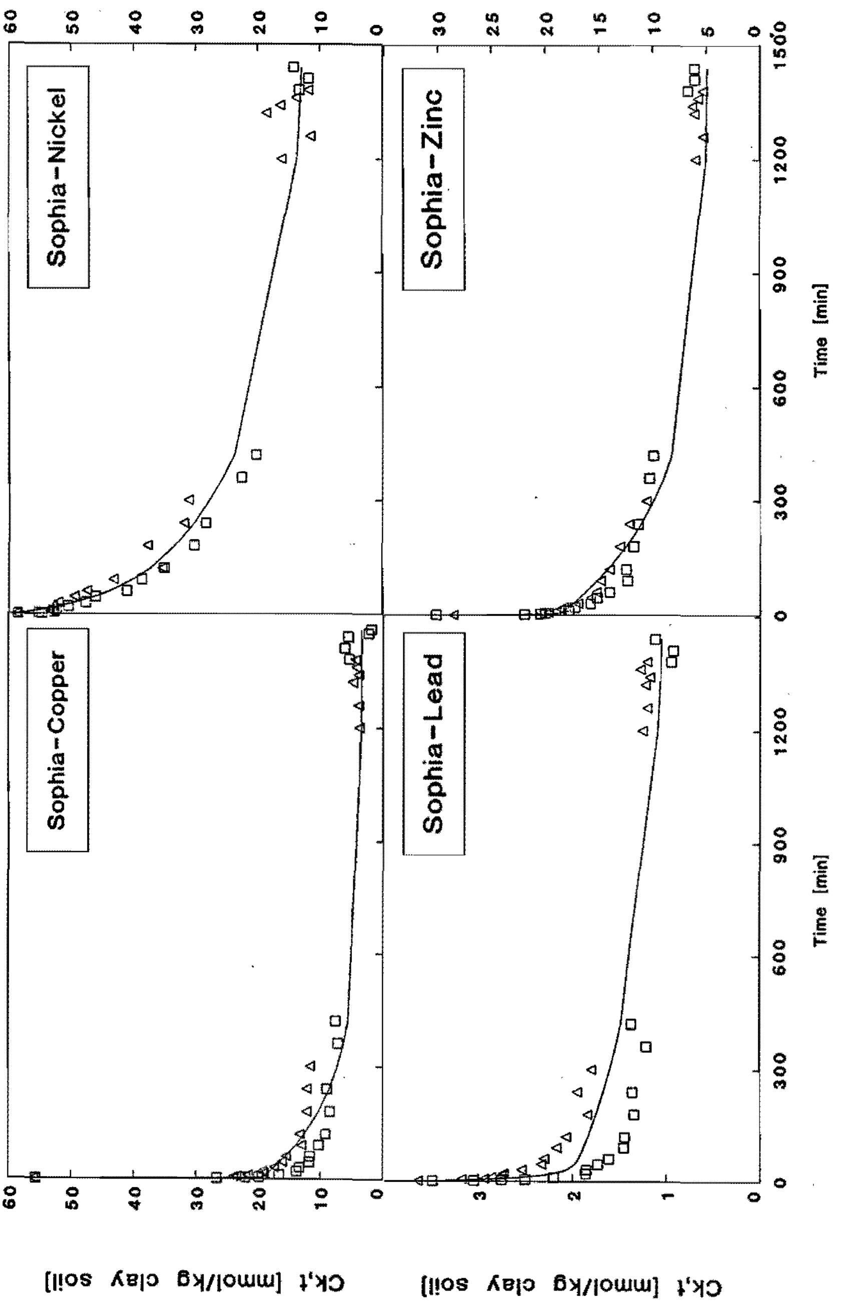

Figure 4.4. *Metal concentration $C_{k,t}$ in waste site clay soil Sophia during extraction in 0.1 N HCl versus extraction time. Extraction of Cu, Ni, Pb and Zn. Lines through data points are calculated with two-reactions model for vigorous mixing.*

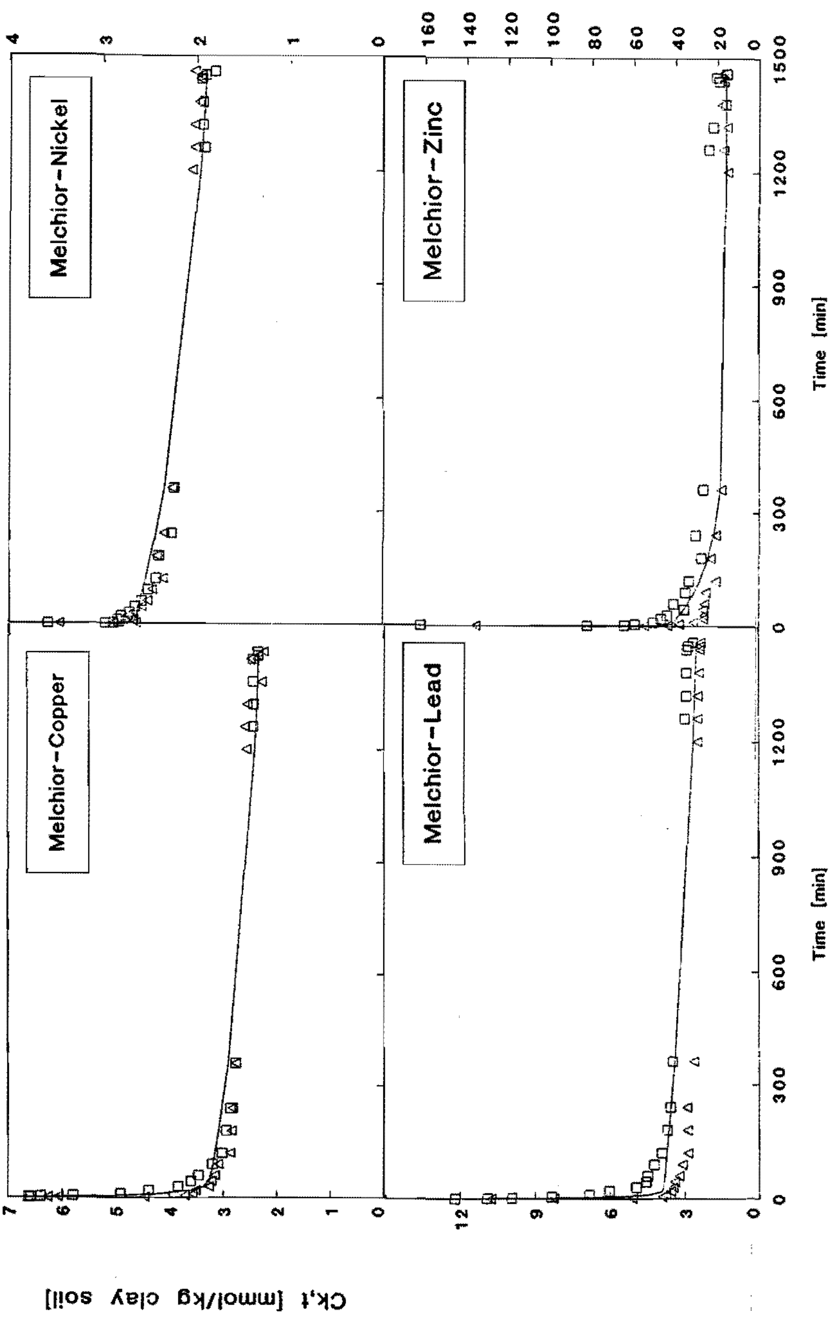

Figure 4.5. *Metal concentration $C_{k,t}$ in waste site clay soil Melchior during extraction in 0.1 N HCl versus extraction time. Extraction of Cu, Ni, Pb and Zn. Lines through data points are calculated with two-reactions model for vigorous mixing.*

4.4.2. Winsum-Ni kinetics at different temperatures

The kinetics of the extraction of Ni from Winsum clay soil were measured at five different temperatures: 5, 20, 40, 60 and 80 °C. Metal concentrations in the clay are given in Appendix IV.2 and are plotted in Fig. 4.6.

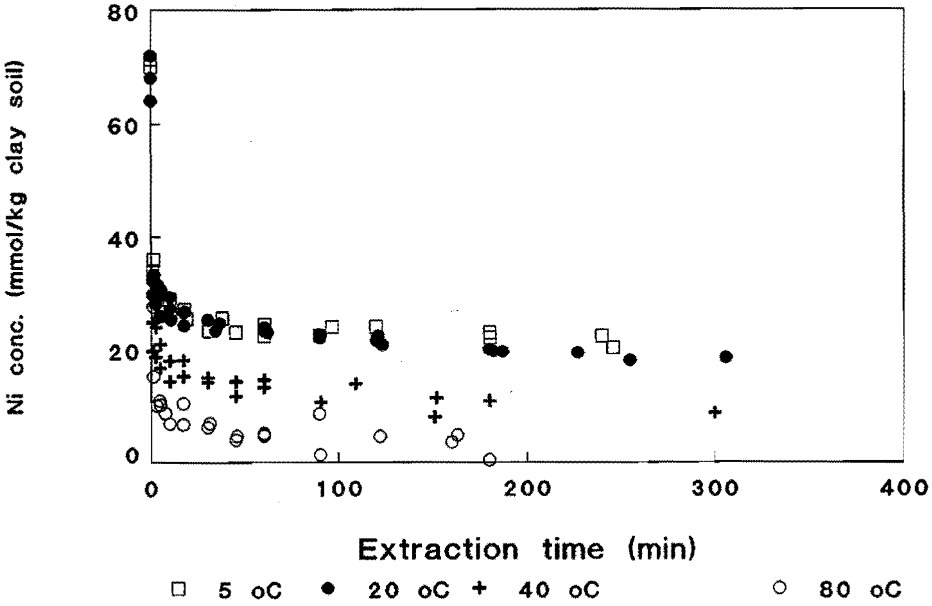

Figure 4.6. *Effect of temperature on extraction: Nickel concentration in artificially polluted Winsum clay soil during extraction in 0.1 N HCl at four different temperatures (5, 20, 40 and 80 °C) as a function of extraction time.*

It is clear that Ni removal efficiencies become greater at higher temperatures. Going from 5 to 20 °C the improvement in extraction result was only small but from 20 to 40 °C and higher temperatures a strong increase in extraction percentage resulted. The difference between extraction at 60 and 80 °C was small but data points were scattered at these temperatures. The temperature influence became evident, however, from the quasi-equilibrium values at the different temperatures.

The calculated model parameters are given in Table 4.2. Apparently, α_0 and m_1 depended more strongly on the temperature than k_1 and k_2. If m_1 is considered to be the equilibrium constant of the reversible extraction reaction (2) at a constant pH (see Section 4.2), we can calculate the enthalpy change of this reaction (2) from the Van 't Hoff relationship:

$$\frac{d(\ln K_{eq})}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (4.16)$$

where: K_{eq} = equilibrium constant
T = absolute temperature
R = gas constant
ΔH° = standard reaction enthalpy

A plot of ln m_1 versus 1/T (see Figure 4.7) gives the enthalpy of the extraction of Ni(II) in 0.1 N HCl as approximately 20 kJ/mol. Aitang and Häni *(19)* measured Ni extraction at four different temperatures in 2 N HNO_3. The ΔH° for Ni-extraction from their samples that contained ≥ 30 wt% clay could be estimated as 24-31 kJ/mol (using the same procedure as above). These values indicate the same type of temperature dependency for Ni extraction in an acidic environment.

Table 4.2.
MODEL PARAMETERS OF TWO-REACTIONS MODEL FOR Winsum-Ni KINETICS AT DIFFERENT TEMPERATURES

Exp.	Temperature (°C)	m_1 ($L.kg^{-1}$)	k_1 (min^{-1})	k_2 (min^{-1})	α_0 (-)	AREPD[1] (%)
51	5	9.24	2.33	$1.0.10^{-2}$	0.42	1.8
52	5	8.82	1.12	$1.4.10^{-2}$	0.39	2.2
21	20	6.72	2.33	$4.1.10^{-3}$	0.41	1.8
22	20	6.42	2.55	$6.5.10^{-3}$	0.40	2.6
23	20	7.43	1.55	$9.5.10^{-3}$	0.45	2.3
41	40	3.01	2.40	$1.4.10^{-2}$	0.27	4.9
42	40	3.01	2.30	$9.3.10^{-3}$	0.33	6.6
60	60	2.10	1.77	$6.4.10^{-3}$	0.18	17
81	80	1.54	0.97	$3.6.10^{-2}$	0.17	18
82	80	1.15	1.86	$3.1.10^{-2}$	0.17	13
21 (24h)	20	4.95	2.28	$2.9.10^{-3}$	0.41	2.1
22 (24h)	20	4.95	2.43	$4.1.10^{-3}$	0.40	3.2
23 (24h)	20	4.95	1.36	$4.6.10^{-3}$	0.44	3.8

1) AREPD = average relative error per data point

The m_1 values in Table 4.2 were extrapolated values from the kinetic curves with data points until 3-4 hours. Nickel extraction rate at 20°C was also measured for 24 hours. The value of m_1 was considerably smaller in this experiment (viz. 4.95 l/kg) than the extrapolated value at 20°C (viz. 6.4-7.4 l/kg, see Table 4.2). When the kinetics data at 20°C were modeled with this m_1 value, the parameters α_0 and k_1 hardly changed. But k_2 decreased and

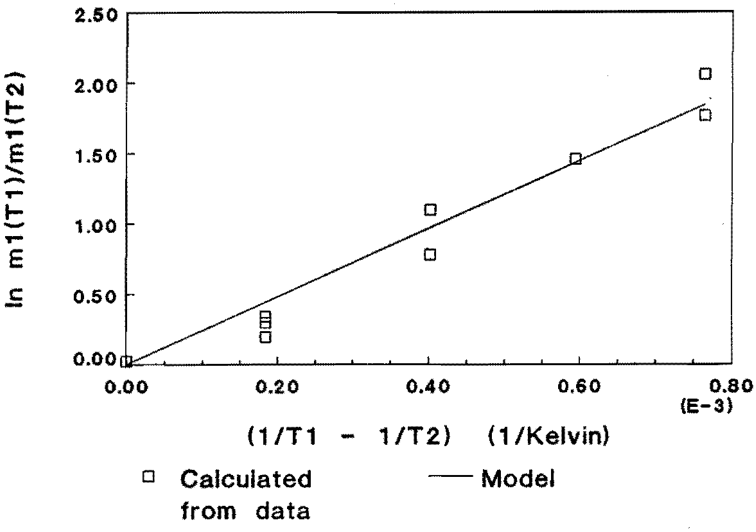

Figure 4.7. *Determination of enthalpy change of Nickel extraction from artificially polluted Winsum clay soil from plot of natural logarithm of 'quasi'-equilibrium constant m_1 versus absolute temperature T.*

appeared to be the most sensitive to changes in m_1 (as expected). So, to find a reliable value for k_2 it is important to follow the extraction for at least 24 hours.

The model calculations produced values for α_0 depending on the temperature. The fraction α_0 was, however, defined in terms at t=0 only (see Section 4.2) and should therefore be constant as well in time as in experiments performed at different temperatures. The kinetic parameters k_1 and k_2 were thus also calculated at a constant value of α_0. For this calculation it was assumed that α_0 was constant and was equal to the average value at 20°C ($\alpha_{0,avg}=0.42$). This fixed value of α_0 was used as input for the computer programme that calculated the new values for k_1 and k_2 (see Table 4.3).

Comparison of Table 4.2 and 4.3 shows that k_1 and k_2 depend much stronger on temperature when the value of α_0 is fixed in the calculations. It is evident from the error values at temperatures above 20°C, that the rate constants at these temperatures become increasingly inaccurate.

Table 4.3.

MODEL PARAMETERS OF TWO-REACTIONS MODEL FOR Winsum-Ni KINETICS AT A CONSTANT VALUE OF α_0 (α_0= 0.42 = average value at 20°C)[2]

Exp.	Temperature (°C)	k_1 (min^{-1})	k_2 (min^{-1})	AREPD[1] (%)
51	5	2.24	$9.5.10^{-3}$	2.5
52	5	1.21	$2.0.10^{-2}$	2.4
21	20	2.45	$4.4.10^{-3}$	2.4
22	20	2.86	$5.0.10^{-3}$	4.5
23	20	1.18	$3.8.10^{-3}$	4.2
41	40	6.39	$8.9.10^{-2}$	21
42	40	8.12	$2.4.10^{-2}$	15
60	60	7.88	$1.8.10^{-1}$	29
81	80	1.50	$2.2.10^{-1}$	24
82	80	6.38	$3.4.10^{-1}$	30

1) AREPD = average relative error per datapoint
2) m_1 values were the same as in Table 4.2.

To get information about the possible rate limitations of the extraction process, we determined the (free) energy of activation of the two rate processes described by the model. The reaction rate constants k_1 and k_2 depend on the temperature according to the equation:

$$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2} \qquad (4.17)$$

where: k = reaction rate constant
E_a = (free) energy of activation of the reaction

The energies of activation could only be estimated roughly from the average values of k_1 and k_2 at the five temperatures. We calculated from the integrated form of equation (4.17): $E_{a1} \cong 24$ kJ/mol and $E_{a2} \cong 41$ kJ/mol.

4.4.3. Floc-kinetics

The results of the kinetic experiments in the flocculated clay suspensions are given in Appendix IV.3. The extraction proceeded generally slower under 'floc' conditions than in the 'mixed' kinetics experiments. This delay was most evident from the extraction percentages just after the start of the kinetic experiment (see Table 4.4). Results were difficult to compare in cases where the initial metal concentrations in the waste site soils strongly differed.

Table 4.4.
COMPARISON OF EXTRACTION PERCENTAGES AND INITIAL CONCENTRATIONS OF WASTE SITE SOILS IN 'FLOC' AND 'MIXED' KINETICS

Clay soil	Metal	C_{ko} (mmol/kg) 'mixed'	C_{ko} (mmol/kg) 'floc'	E (%) after 15 min. 'mixed	E (%) after 15 min. 'floc'	E (%) after 30 min. 'mixed	E (%) after 30 min. 'floc'
Sophia	Cu	55.9	59.0	69	67	73	77
	Ni	58.9	42.5	11	6	15	11
	Pb	3.57	2.37	33	19	39	26
	Zn	29.4	20.2	38	33	44	41
Melchior	Cu	6.43	18.4	36	28	45	33
	Ni	3.53	11.4	22	24	24	28
	Pb	11.5	8.30	56	37	63	40
	Zn	149	77.2	74	72	76	78

Note: C_{k0}=initial metal concentration; E=extraction efficiency

Extraction percentages of Ni and to a smaller extent of Zn from Melchior and Cu from Sophia were greater for the floc-kinetics than for the mixed-kinetics. The deviations could be very well due to differences in initial metal concentrations, especially in the case of Melchior-Ni.

Typical examples of the difference in kinetic behaviour are shown by the extraction curves of Pb from Melchior soil and of Ni from Sophia soil for the two different experimental conditions (see Figure 4.8). It is clear that differences were small in some cases.

The experimental data points of the floc-kinetics until an extraction time of 60 minutes were fitted to equation (4.13). The values of k_1, k_2, α_0 and m_1 given in Table 4.1 were used as input for the computer programme with which the value for $k_{fd}.a$ was determined. The lines in Figure 4.8 are examples of the metal concentrations calculated by the model. The calculated $k_{fd}.a$ values are given in Table 4.5.

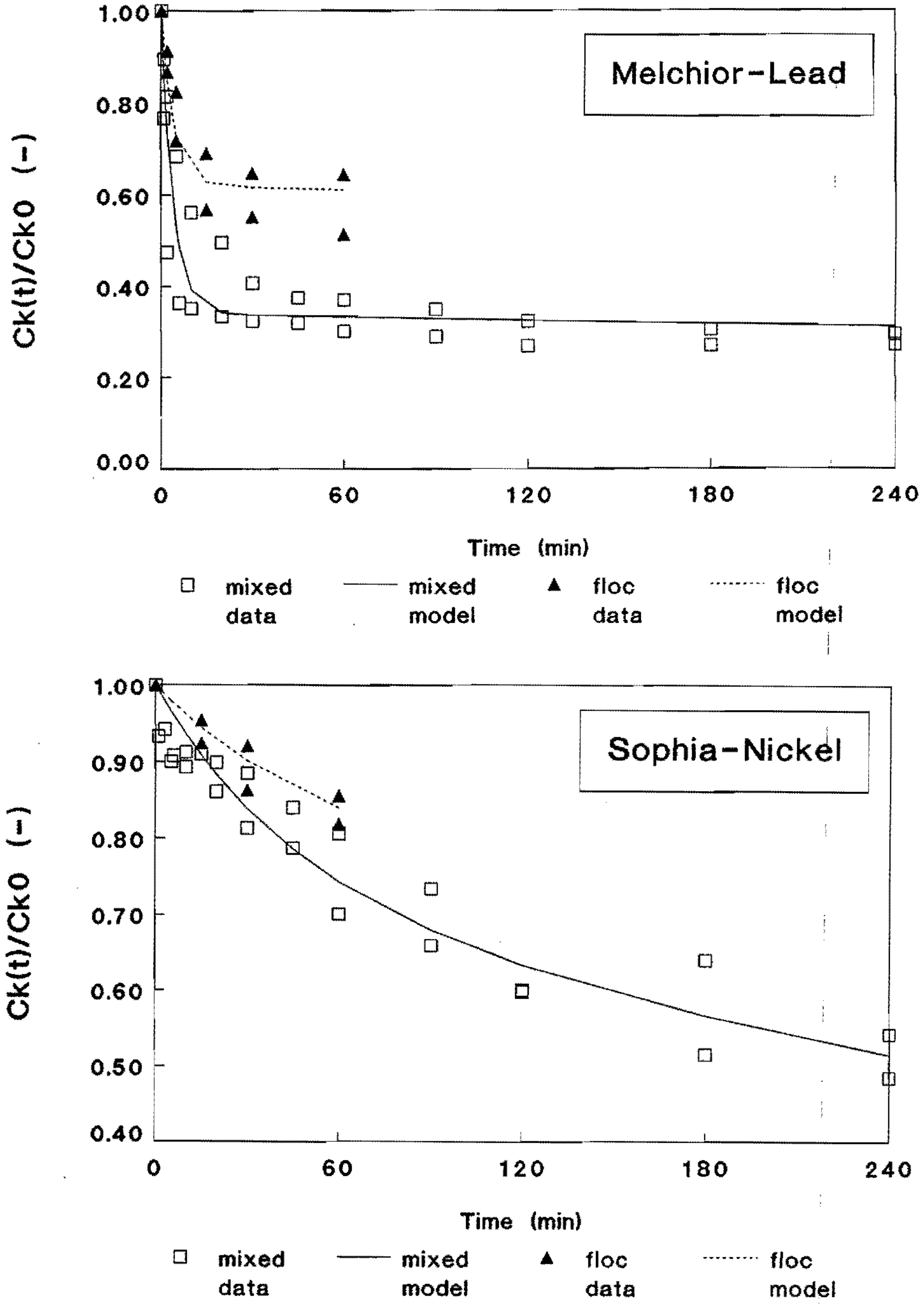

Figure 4.8. *Comparison of dimensionless metal concentration - time profiles during vigorous mixing kinetics ('mixed data') and floc kinetics ('floc data') extraction experiments. Lines ('mixed model' and 'floc model'): calculated with two-reactions model for the respective conditions.*
TOP: *Extraction of Pb from Melchior soil;*
BOTTOM: *Extraction of Ni from Sophia soil.*

Table 4.5.

PRODUCT OF MASS TRANSFER RATE COEFFICIENT AND SPECIFIC SURFACE DETERMINED FROM FLOC-KINETICS OF WASTE SITE CLAY SOILS

Clay soil	Metal	$k_{fd}.a$ (10^{-3} min^{-1})	AREPD (%)
Sophia	Cu	1.3	38
	Ni	0.95	3.8
	Pb	0.74	5.1
	Zn	2.1	13
Melchior	Cu	0.70	6.6
	Ni	2.7	10
	Pb	0.22	7.8
	Zn	2.3	32

The errors in the model values became very large for the combinations Sophia-Cu and Melchior-Zn. This agreed with their anomalous extraction behaviour (see Table 4.4). the fit for Melchior-Ni was not too bad. The $k_{fd}.a$ values lie in a close range from approximately 0.2 to $2*10^{-3}$ min^{-1} (approx. 5.10^{-5}-$10^{-6}sec^{-1}$).

4.5. DISCUSSION

Description of extraction by Two-Reactions Model

The fit of the data points by the two-reaction model (see Figures 4.3-4.5) shows that a reasonable rate description is possible by two processes with different rate constants. These processes are a fast, irreversible first-order reaction and a slow, reversible first order reaction. The model describes the metal concentration curves over a time period of 24 hours with a relative error less than 20%. The curves and the model parameters show that the individual metals can behave in quite a different way, as well in case of the artificially polluted soils as in case of the waste site soils. This complicates the cleaning of soils polluted with a number of metals in a single treatment.

The extraction rate of Ni out of Rhine clay soil deviated from that of the other metals in the artificially polluted clay soils. This might be explained by the much greater Ni content in the 'residual' fraction as was determined by the sequential extraction analysis (see Chapter 3).

It is interesting to see whether a relationship exists between α_0 and experimentally determined metal fractions in the clay, like the sequential extraction fractions discussed in Chapter 3. No general relationship seems to exist as can be seen from the values in Table 4.6 and as was checked by (multi)linear regression analyses. Only rough trends can be found like a relation between α_0 and the sum of the fractions 'Fe-MnOx' and 'Residual' for the metals Cu, Ni and Zn. The value of α_0 for Pb in the waste site soils appears to be a little less than the percentage in the 'Residual' fraction. Further experiments are, however, required to explore possible relationships in more depth.

Table 4.6.

SEQUENTIAL EXTRACTION DISTRIBUTION AND THE MODEL PARAMETER α_0

Clay	Metal		Percentage metal (%) in seq.extr.fraction:				
soil		α_0	Exch	CO_3	Fe-Mn-ox	Org/Sulf	Residual
Maas	Cu	0.51	0.04	0.29	0.57	0.05	0.05
Rhine	Ni	0.93	0.01	0.12	0.57	0.06	0.25
Rhine	Pb	0.15	0.03	0.52	0.36	0.08	0.02
Winsum	Cu	0.17	0.26	0.18	0.45	0.05	0.06
Winsum	Ni	0.42	0.54	0.12	0.14	0.11	0.08
Winsum	Pb	0.21	0.42	0.33	0.17	0.06	0.02
Winsum	Zn	0.20	0.47	0.28	0.17	0.05	0.03
Sophia	Cu	0.35	0.01	0.19	0.18	0.54	0.08
Sophia	Ni	0.77	0.02	0.09	0.56	0.10	0.23
Sophia	Pb	0.57	0.01	0.03	0.25	0.08	0.64
Sophia	Zn	0.64	0.16	0.23	0.42	0.05	0.14
Melchior	Cu	0.51	0.01	0.06	0.08	0.69	0.16
Melchior	Ni	0.75	0.02	0.10	0.43	0.23	0.22
Melchior	Pb	0.34	0.00	0.15	0.30	0.15	0.39
Melchior	Zn	0.28	0.03	0.45	0.35	0.05	0.12

The values of the model parameter k_1 are for the waste site soils in the same range (0.1-1 min^{-1}) as the 1st order rate constants measured for Cu extraction in EDTA by Jopony and Young *(5)*. These extraction rates are comparable to the order of magnitude of the fast rates of ion exchange or carbonate dissolution reactions.

The value of k_2 strongly depends on the value of the equilibrium constant m_1. For example, when m_1 values determined after 24 hours for Winsum-Nickel kinetics (see Table 4.2) were used instead of the extrapolated values after

3-4 hours, k_2 values decreased up to a factor 2 in the model calculations. For the waste site soils equilibrium constants were determined from 24 hours experiments. The very slow rate of the 2nd reaction and the fairly large fractions α_0 that react according to the slow process indicate that prolonged extraction times will hardly improve the metal removal efficiencies from the waste site soils in 0.1 N HCl. In continuous -commercial scale- apparatus such very long residence times are no longer economically feasible. It would be interesting, however, to investigate the removal efficiencies after very long periods (weeks, months) and under other hydrodynamic conditions to judge possibilities of in-situ treatment or heap leaching.

The differences in extraction rate between 'mixed' and 'floc' kinetics were small in many cases and could be measured only in the first phase of the extraction process (see Figure 4.8). These facts were confirmed by another set of floc-kinetic experiments where mixing was increased slightly by means of a higher turning frequency of the batch turn-over reactor. In this case differences between 'mixed' and 'floc' kinetic curves were generally smaller and in some cases no longer significant. Metal concentrations in the bulk liquid and in the liquid around the flocculated clay aggregates were also determined in these experiments. A concentration gradient between 'floc' and bulk liquid could be measured in a number of cases. It decreased with elapsed extraction time. It must be noted, however, that the sample with 'liquid around the flocculated clay' contained partly bulk liquid. But the temporary existence of a liquid film in and around the flocculated clay with a greater metal concentration appeared to be confirmed. It is probably due to the very rapid release of metals that occurred in some cases during the first few minutes of the extraction.

Temperature effects

The most evident temperature influence is a decrease with increasing temperature in final metal concentration in the clay soil that was reached in Winsum Ni kinetics (see Figure 4.6). This effect could be expressed as a decrease in the equilibrium value m_1 with temperature from which the standard enthalpy change 'of the Ni desorption reaction' was calculated. The actual reaction that takes place is, however, unknown and involves very likely a number of Ni-ions bound to different sites with different energies. The ΔH° value describes only the overall temperature effect on the complex of reactions involved in the equilibrium distribution.

The value of α_0 changed also with temperature (see Table 4.2). α_0 was considered to be a property of a specific polluted clay soil. It is however very well conceivable that at other temperatures the fraction of metal that can be extracted according to one of the two proposed reactions changes, for example due to a different solubility of soil components in acid.

The effect of temperature on the rate of the two proposed reactions of the model was expressed in the E_a values (see Section 4.5.2). Sparks *(1)* mentioned that liquid film-diffusion typically has an E_a value of 17 to 21 kJ/mol and diffusion in the pores of soil particles an E_a of 21 to 42 kJ/mol. Surface reactions have even much greater energies of activation (>100 kJ/mol). So, the calculated small E_a values (although rough values due to the large experimental error) suggest that the desorption process of Ni from Winsum clay soil in 0.1 N HCl is rate-limited by a diffusion process in the porous soil particles. The Ni was adsorbed to the Winsum clay soil as Ni^{2+} in a 24 h adsorption experiment. About 50% of the Ni was present in the 'exchangeable' fraction of the Winsum soil (see Table 4.6). It seems therefore probable that the Ni is not yet bound very strongly to the Winsum clay soil. The greatest E_a value (E_{a2}) could come from diffusion of Ni bound to more interior sites and the smaller E_{a1} value of diffusion of Ni bound to surface sites. More accurate data are, however, necessary to confirm this statement.

The contaminations in the waste site soils are much older and greater metal contents were measured in the 'residual' fraction. Metals were not brought necessarily into the environment as a soluble ionic species. Chemical reaction limitations seem much more probable in this case. Very insoluble compounds may have formed or metals may have become (lattice-)bound in a very stable way. It would be necessary to investigate the kinetics of the extraction of the metals from the waste site soils at different temperatures to examine the rate limitations for metals in these soils.

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Chapter 5

CONTINUOUS EXTRACTION PROCESSES

5.1. INTRODUCTION

Extraction was first tested with artificially polluted clay soils and two waste site soils in small scale batch experiments (see Chapters 2, 3 and 4). Based on the results of batch experiments possible treatment schemes were developed for a continuous extraction of metals from clay soils. A more limited study of solid-liquid separation methods was performed and flocculation was chosen as the method to separate the clay soil particles from the extractant after cleaning. Flocculation experiments and results are given in Section 5.4.

A laboratory scale continuous installation was then built in which different cleaning routes could be tested. This test installation is described in Section 5.2. Some introductory experiments were performed with artificially polluted clay soils in this installation. The extraction of metals from two contaminated waste site soils in 0.1 N HCl was then studied in three different experimental set-ups: in two continuous stirred tank reactors (see Section 5.5), in a counter current sieve-plate column (see Section 5.6) and in a combination of one tank reactor and the counter current column (see Section 5.7). So far extraction experiments have been performed only in 0.1-0.3 N HCl solutions. The results of these three different processing routes will be compared in Section 5.8. Some aspects of treatment costs are discussed briefly in Section 5.9.

5.2. TEST INSTALLATION FOR CONTINUOUS EXTRACTION

A laboratory scale continuous installation was built in which different extraction routes could be tested. Three basic process schemes were applied:

1. extraction in two stirred tank reactors each followed by a flocculation unit to separate clay soil and extractant (see Figure 5.1);
2. extraction in a counter current sieve-plate column preceded by a flocculation unit (see Figure 5.2);
3. extraction in a combination of one tank reactor and the countercurrent column.

The complete test installation was built from glass or PVC materials (except for the monel stirring rods of the two extractors) to prevent heavy metal dissolution due to corrosion which would disturb analyses. All pipes between the vessels were PVC-tubes and all pumps were variable flow peristaltic pumps. A minimum velocity of the clay suspension in the tubes was required to prevent settling which might obstruct the tubes. In most cases a suspension flow of 10 l/h appeared to be enough. Flows could be smaller when they were directed vertically downwards.

Process scheme 1 (Figure 5.1) is built from simpler equipment and can be operated more easily than the column process scheme. The clay soil was treated in this extraction process as follows: after pretreatment by a hydrocyclone unit (see Section 5.3) a clay soil suspension (dry matter content 3-10 wt.%) was pumped to the first extractor. This extractor was a continuous stirred glass tank (diameter 0.225 m) with four baffles. Suspension pH could be controlled by adding HCl. The suspension level was kept constant by a floating device which controlled the suspension inlet flow. The volume of the clay suspension in the tank could be adjusted to a value between 5 and 12 liters depending on the desired residence time of the clay in the extractor. The suspension was stirred with a propeller at approx. 750 rpm. Residence time distribution experiments showed that a liquid (without particles) in this vessel could be considered ideally mixed at a stirring speed of 580 rpm. To keep the soil particles homogeneously suspended a minimal stirring speed of 380 rpm and a dissipated power of 0.33 W were required for this vessel according to the correlations proposed by Zwietering *(1)*. We therefore assumed that the clay suspension was ideally mixed at the standard stirring speed of 750 rpm.

After the first extraction the clay suspension was pumped to flocculation unit 1. This unit consisted of two stirred vessels in series with an adjustable suspension volume of 0.75-1.5 l. A flocculant A100 solution (see Section 5.4) was added to the suspension in the first vessel under vigorously stirring (stirring speed ≈ 700 rpm). In the second vessel stirring was slower (approx. 300 rpm) and floc growth occurred. The flocculated clay soil suspension passed through an overflow to a sedimentation tank. The main separation of clay soil and extractant solution took place in this tank as the flocculated clay material settled. The sedimentation tank has a volume of approx. 10 l and a conical bottom part. A twisted stirrer (speed ≈1 rpm) was designed to prevent channeling and to promote the transport of the flocculated clay mass to the bottom outlet. The extractant flowed from the sedimentation

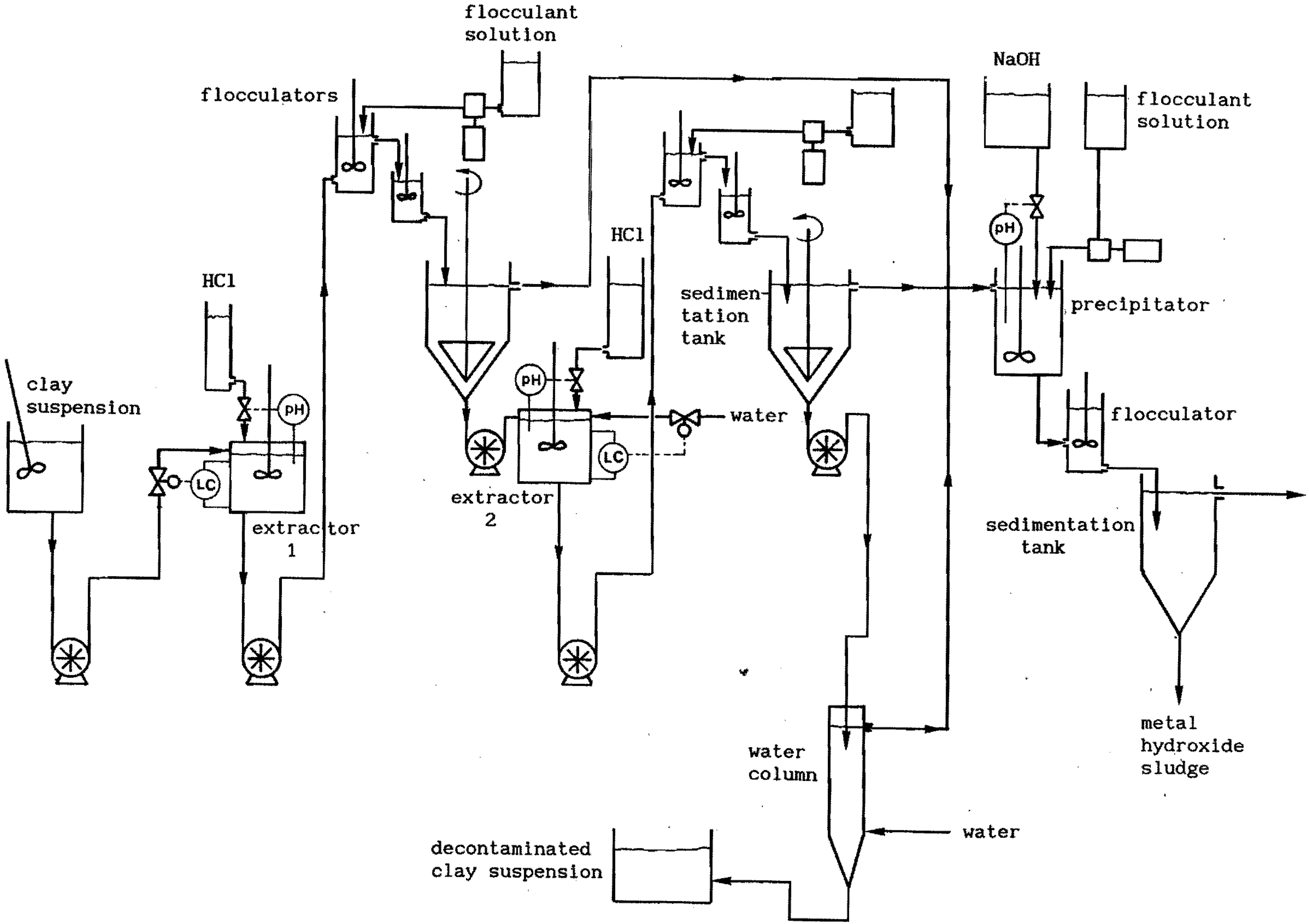

Figure 5.1. *Process scheme of continuous extraction in two stirred tank extractors in series.*

tank through an overflow to the precipitation unit where sodium hydroxide solution was added to precipitate the heavy and other metals. Flocculant was added to accelerate settling of the hydroxide precipitate. Eventually a hydroxide sludge remained at the end of the process as chemical waste that had to be disposed of.

The bottom discharge of the settling tank (dry matter content 7-25 wt.%) was transported to the second extractor. A second extraction and separation were now applied analogously to the first steps. Residence time and pH could be chosen independently. Make-up water was supplied to the second extractor to get the required dry matter content. The level-control of the second extractor was connected to this make-up water supply. Flocculant dosage in the second flocculation unit was generally smaller than in the first. After this second treatment the flocculated clay mass from sedimentation tank 2 could be washed with water in a small column or directly collected in a vessel.

The second extraction process scheme (see Figure 5.2) was chosen because operation in a countercurrent process is expected to be more effective than that in stirred tanks in series. Operation in the countercurrent column required aggregates of the very small clay particles to prevent elutriation of the clay over the top of the column. Therefore a flocculation unit as described above preceded the column and flocculated clay was fed to the column. Note that the flocculation took place under neutral conditions. The sedimentation rate of the aggregates was generally so fast that sieve-plates were required to increase the residence time of the clay soil flocs in the column. These sieve-plates were mounted on an axis and could be rotated and/or moved up and down pneumatically at desired frequencies. The rotation was not continuously but the axis turned each time over approx. an angle of 50° forwards and the next time backwards. The number and type of the sieve-plates could be varied. We have so far always used 18 sieve-plates placed at intervals of 0.1 m. The plate motions caused transport and mixing of the clay flocs. Residence time of the clay flocs in the column could be influenced in this way.

The extraction conditions and the hydrodynamics in the column are totally different from those in the stirred tank situation: the polluted clay soil was present as an aggregate and only a mild mixing was possible if the flocs were not to break up. Extraction of flocculated clay under these conditions was tested in a model compartment of the column with only a very slow agitation (see Chapter 4).

The countercurrent column is 3 m high and has an internal diameter of

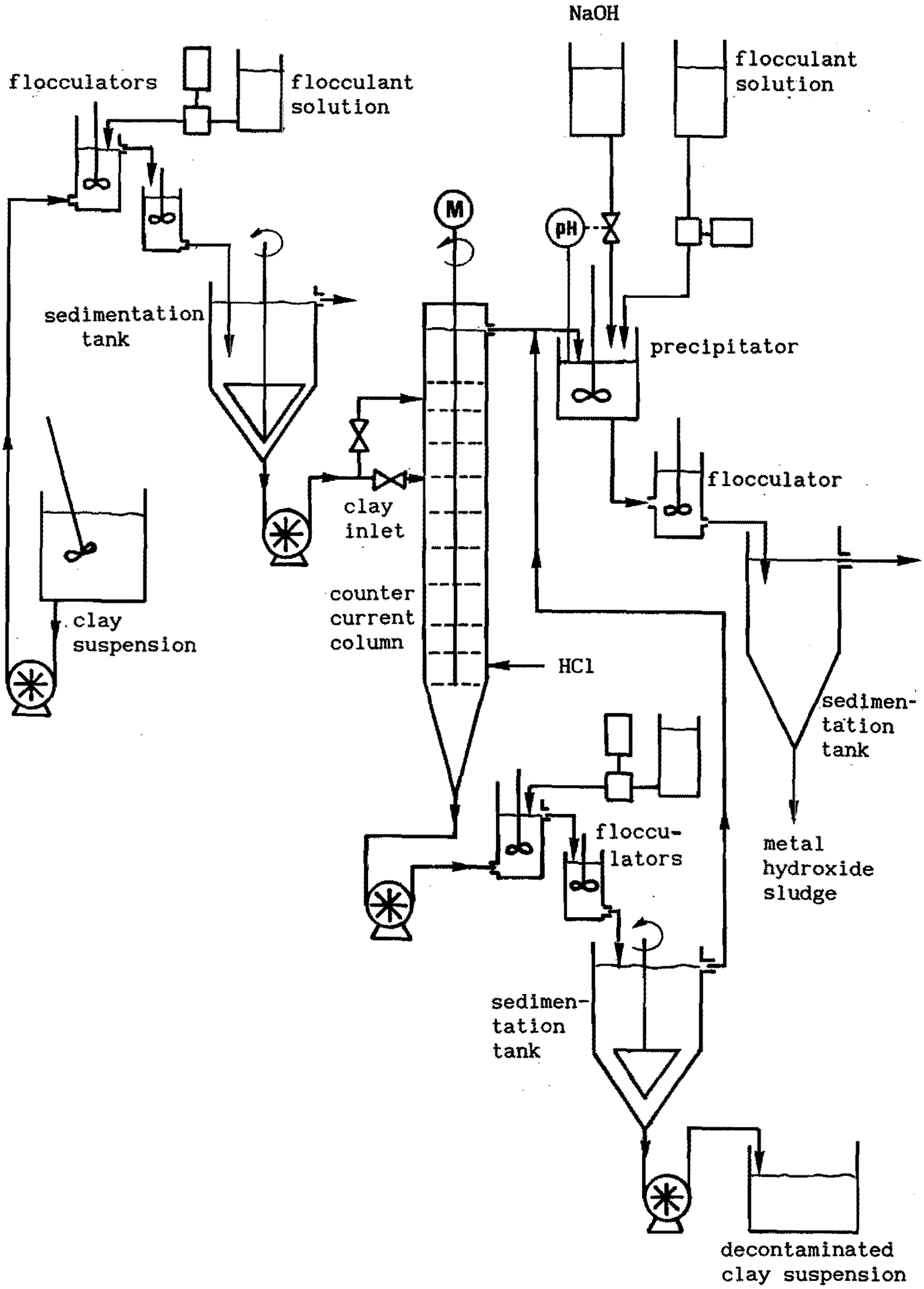

Figure 5.2. *Process scheme of continuous extraction in countercurrent sieve-plate column.*

0.10 m. It consists of glass elements separated by PVC elements that contain all the in- and outlets. The flocculated clay suspension can be pumped into the column at two heights which results in countercurrent zones with a heightof 1.37 or 1.82 m. Above the clay inlet a zone free of sieve-plates exists where entrained clay particles can settle again. Below the extractant inlet there is a conical part free of sieve-plates where the clay suspension can thicken. Sample taps and pH-electrodes are present in the PVC elements (i.e. at 0.455 m intervals). The extractant (HCl solution) was always pumped into the column at the inlet 0.70 m above the bottom. It flowed through the column and an overflow to the precipitation unit (see description above). Inevitably part of the HCl solution ended up in the suspension that was discharged through the bottom outlet. The flocculated clay suspension was thickened in the conical part, discharged through the bottom outlet of the column and pumped to a second flocculation sedimentation unit for further thickening. The clay soil was then collected in a vessel and the extractant overflow of the second sedimentation tank was led to the precipitation unit where it was treated in the usual way. Alternatively it was possible to wash the bottom discharge of the countercurrent column in a water column.

The third process scheme that was tested experimentally is a combination of a stirred tank reactor and the countercurrent column. The clay suspension was treated like the first extraction of process scheme 1. The flocculated clay soil flow from sedimentation tank 1 was now fed into the column (instead of into extractor 2). The same apparatus was used in this scheme as described in the two previous process routes (see Figures 5.1 and 5.2).

To obtain an effective extraction in treatment scheme 1 the extracted metals should not re-adsorb to the clay aggregates or form complexes with the flocculant in the flocculation unit. Experiments in stirred cells and in the continuous installation with Cu-polluted Maas-, Rhine- and Winsum-clay soil and Pb-polluted Winsum clay showed that the extraction result was not influenced by the subsequent flocculation. These experiments proved also that it was possible to break up the flocs and extract the clay further in a second stirred tank reactor. The effects of flocculation before extraction were also tested in batch experiments with Cu-polluted Rhine- and Winsum-clay soil. Extraction results in stirred cells were the same with and without preceding flocculation. Finally, it was possible to flocculate the clay material more than once: the clay suspension could be flocculated again after passing the second extractor or the countercurrent column.

5.3. EXPERIMENTAL PROCEDURES

A number of experimental methods and procedures were applied during an extraction experiment in the continuous test installation (independent of the process route that was used). These methods and procedures are described in this section.

Pretreatment of the clay soils

The two waste site soils, Sophia and Melchior, contained on the average only a fraction of 43 and 18 wt.% of total sample that had a particle size below 20 μm (see for the properties of these two soils Table 2.2 in Chapter 2). The smaller particles (d < 10 μm) are generally more polluted than the larger ones *(2-4)*. Because the aim is to study the extraction of metals from the most contaminated fraction of the soil only, it is necessary to fractionate the soils before the experiments. Fractionation was performed by separating the total clay suspension in a coarse and a fine fraction with a hydrocyclone of 25 mm diameter. The cut diameter of the hydrocyclonation *(5)* varied between 10-20 μm. The clay suspension that contained mainly fine particles (top flow from hydrocyclone) was used in the experiments. Examples of particle size distribution curves of the fines fraction are shown in Fig. 5.3. Large organic particles generally end up in the 'fines' fraction also due to their low density. This is important because these particles can be highly contaminated (see Chapter 3).

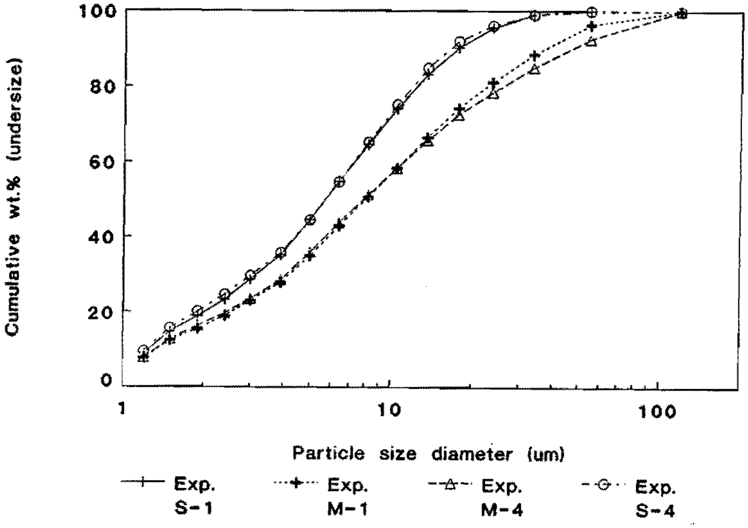

Figure 5.3. *Particle size distributions of clay soils that were extracted in experiments* S-1, M-1, S-4 *and* M-4.

Sampling and measurements in continuous experiments

After start-up the extraction process was run for a few hours before a stationary state was assumed to have been reached. During this first period all flows were checked and if necessary adjusted to the right values. The following types of samples were then taken during the stationary state:

1. suspension samples to measure total mass flow and (after evaporation at 100 °C) solids flow and dry matter content of the suspension;
2. suspension samples that were centrifuged for 15 minutes at 8800*g. Metal concentrations were determined in the solid material and in the supernatant liquid by atomic absorption spectrometry. (The solid material was dried and decomposed according to the procedure given in Appendix II.1). The liquid samples were acidified if necessary to prevent metal losses during storage;
3. suspension samples that were filtered through a "Swinnex" 0.45 µm filter set-up (see Chapter 4). Metal concentrations were determined in the filtered liquids by AAS.

During the experiment a number of variables were recorded continuously: pH-values in extractor 1 and 2 and at five different heights in the countercurrent column by means of pH-electrodes; 3 N HCl consumption by extractor 1 and 2 and 3 M NaOH consumption by the precipitation unit through pressure gage sensors; the volumetric flow rate through the outlet of the first sedimentation tank by means of a magnetic induction flow meter; the total cumulative volume that had passed through this same outlet; temperature.

The pH was measured intermittently in other solutions than mentioned above with a pH-stick. Water-flows to second extractor and wash-column could be measured by rotameters.

5.4. FLOCCULATION OF CLAY SOIL SUSPENSIONS

Solid-Liquid separation - Jar tests results

Separation of the suspension into a solid and a liquid phase is required after the extraction of the metals from the clay. Many methods are known for solid-liquid separation *(5)*. The small size of the clay particles makes simple sedimentation or filtration impracticable. Sedimentation can be accelerated by the use of a centrifugal field (as in a hydrocyclone) or by coagulation or flocculation of the particles to larger aggregates (flocs).

We have tested these three methods. Hydrocyclones of 25 and 75 mm diameter

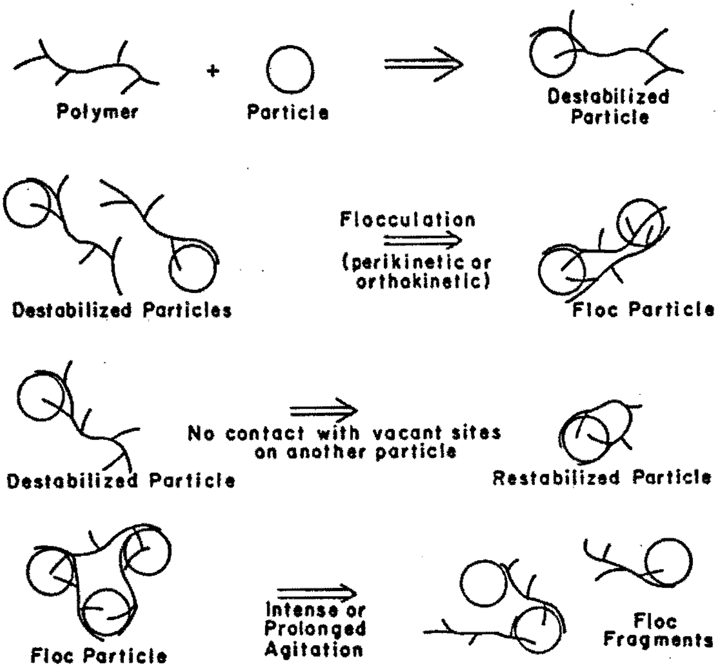

Figure 5.4. *Schematic representation of the bridging model for the destabilization of colloids by flocculants.*

were fed with clay suspensions of different dry matter content and at different inlet pressures. Complete separation of the clay from the liquid phase by means of a hydrocyclone was not possible. The experiments showed that hydrocyclones could be used to split up the soil suspension in a coarse and a fine fraction before the extraction process. This is very useful when the fraction below 30-50 μm is much stronger contaminated than the coarse fraction of a soil.

Two coagulants ($FeCl_3$ and $Al_2(SO_4)_3$ solutions) were tested. The liquid solid separation by coagulants was not successful.

Flocculation of the clay was studied in jar tests *(5-7)* and in settling rate experiments. Several polyelectrolytes ("Cyanamid" A-,C- and N-types and "Wisprofloc" starch derivatives) were used. The "Cyanamid" polyelectrolytes are anionic-, cationic- or nonionic polyacrylic acids or polyacrylic amides. Flocs are formed by soil particles being bound to the polymeric chains and by the bridging action of these polymers (see Figure 5.4).

The addition of polyelectrolytes caused a very good separation between the flocculated clay material and the hydrochloric acid solution. The optimum separation was defined as the condition for which a minimal dry matter content of the supernatant liquid was obtained in the jar test. The jar test consisted of 2 minutes of rapid stirring (200 rpm) during which the flocculant solution was added, followed by 5 minutes of slow agitation (50 rpm). A sample was taken after 1 minute sedimentation. The dry matter content of the supernatant was measured by the turbidity of the sample in a spectrofotometer. Each flocculant was tested in two suspensions of 2 wt.% clay in hydrochloric acid (pH=1 and pH=3). The flocculant was added as a 0.04 mg/l solution into the clay suspension.

The minimal dosage for an optimum separation was about the same for the three "Cyanamid" polyelectrolytes. Types A100 and N300 were the best flocculants and had an optimum dosage of 10-25 mg of flocculant/kg clay. Flocculation with the starch derivatives required a higher dosage, but these flocculants are cheaper. The optimum concentration resulted in a dry matter content in the supernatant liquid of less than 14 mg/l (detection limit).

The optimum flocculant dosage at pH=3 was slightly higher than that at pH=1. Faster sedimentation rates were also observed in a 0.1 N HCl solution (without flocculant) than in the corresponding neutral solutions. Probably, the H^+-ions already have a coagulating effect on the clay *(8)*. Protons can replace Al-ions present along the edges of clay minerals *(9)*. The Al^{3+} ions that are released promote flocculation of the clay.

Dry matter content of sediment

Besides flocculant dosage the dry matter content of the sediment is an important parameter. It determines the amount of extractant that adheres to the flocculated clay soil when it is pumped to the second extractor. This amount should be as small as possible to obtain the greatest extraction efficiency. Batch sedimentation experiments with 5 wt.% clay soil suspensions in 0.1 N HCl showed that the maximum dry matter contents in gravity thickening were 16 wt.% and 14 wt.% for Sophia and Melchior waste site soils respectively. This thickened solids concentration is fairly large compared to a number of large scale operational processes *(10)*. The dry matter content of the sediment depended on sedimentation time (see Figure 5.5). The maximum value was generally reached within approx. 45 minutes and depended on the height of the sediment layer (and thus on the initial dry matter content of the suspension and on the experiment vessel). Apparently, compression in the bottom part of the sediment took place under the influence of the weight of the overlying clay layer. Such compression is the second phase of the thickening process *(11)*.

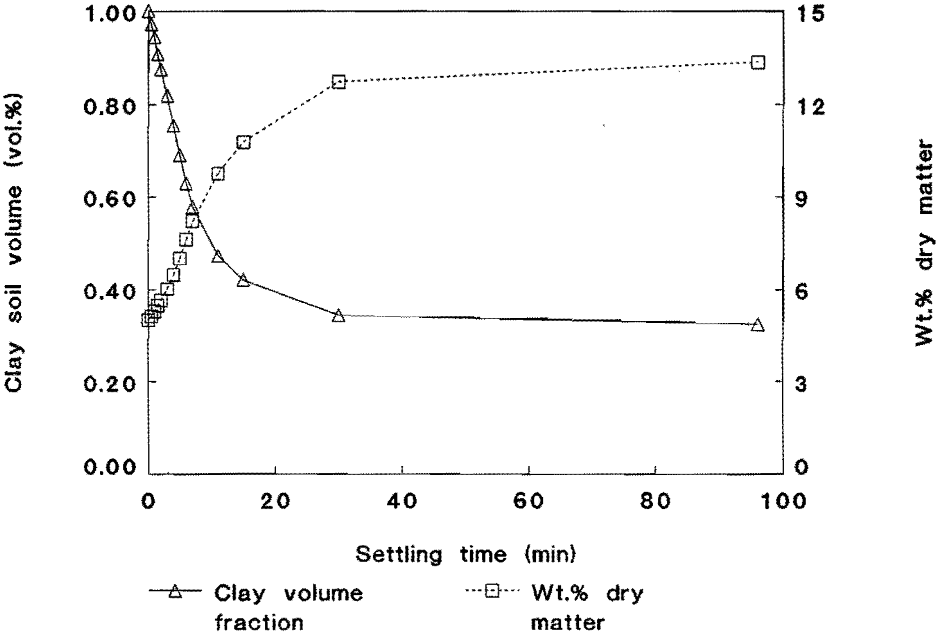

Figure 5.5. *Volume occupied by flocculated clay soil suspension (vol.%) and dry matter content of sediment (wt.% dry matter) as a function of settling time.*

The residence time of the flocculated clay soil in the sedimentation tanks of the continuous test installation should thus preferably be at least 45 minutes. Even then we cannot expect dry matter contents above approx. 15 wt.% with gravity thickening only.

Settling rates of flocculated clay suspensions

Another very important process variable is the settling rate of the flocculated clay soil particles. In the sedimentation tanks this rate should be large enough to make separation possible and in the countercurrent column it influences the residence time (and therefore extraction time!) of the clay particles. Experiments were performed to get information about the settling velocity of the interface, V_i *(11,12)*.

This V_i is not the real settling rate of the individual clay particles. In a flocculated clay suspension hindered settling occurs *(11,12)*. Settling of a swarm of particles is hindered by the displaced liquid that rises through the swarm. Due to this hindering a more or less sharp interface is created between the front of the falling swarm and the liquid above it. The rate at which this slurry/supernatant front is descending can be measured. V_i was measured in graduated cylinders for Sophia, Melchior and Rhine clay soil suspensions that were flocculated for a number of different conditions. Samples of flocculated clay were also taken from the continuous test installation during operation and values of V_i for these suspensions were also determined.

A summary of the results is given in Figure 5.6: the settling velocity of the interface which was measured in suspensions of varying initial dry matter content is plotted versus the applied flocculant dosage. Other flocculation conditions (like batch or continuous operation, time, stirring speed, type of soil) vary widely between the data points. Despite these differences two effects are evident: V_i increased strongly with decreasing initial dry matter content of the suspension. Secondly, V_i increased with increasing flocculant dosage. The latter effect was clearer at smaller solids concentrations. Another conclusion (not in the figure) was that V_i was generally somewhat larger for Rhine clay soil flocs than for Melchior and Sophia flocs. About the same V_i values were measured for these last two soils. The larger V_i at a higher flocculant dosage can be attributed to the formation of larger flocs. Floc size depends, however, also on variables like intensity and time of mixing during flocculation. Tomi and Bagster *(13)* concluded that an optimum concentration of flocculant existed at which floc size should be largest.

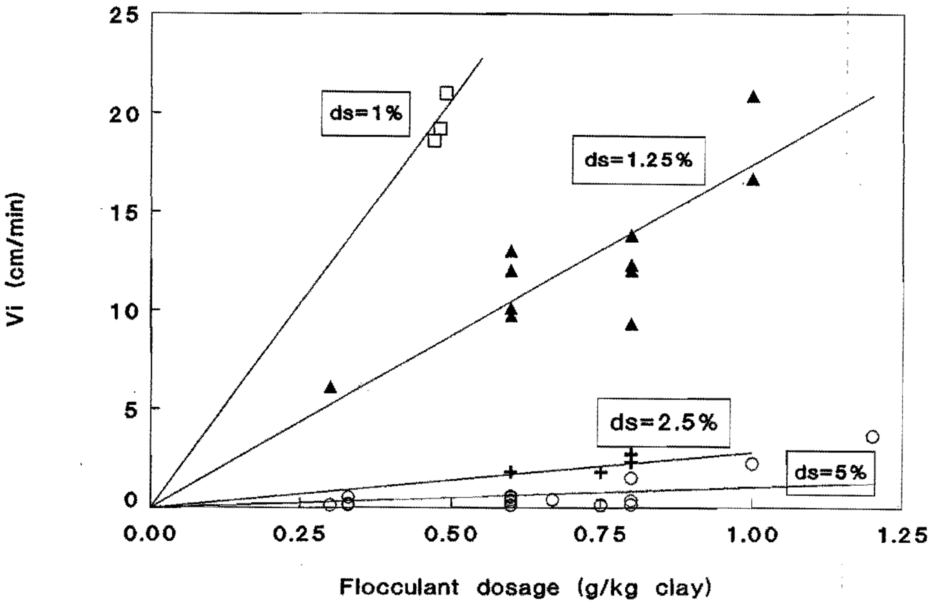

Figure 5.6. *Settling rate of interface between flocculated clay suspension and supernatant liquid (Vi) as a function of flocculant dosage. Experiments for four different initial solids concentrations in suspension (ds).*

With respect to the solid-liquid separation in the sedimentation tank a small flocculant dosage already produced settling rates that are large enough in the dilute upper region of the tank.

The smaller V_i values with increasing solids concentration can be explained by the effect of hindered settling. Richardson and Zaki *(12)* have derived correlations for hindered settling. The interface settling rate of uniform, spherical particles was given by the equation:

$$V_i = V_{io} \cdot \varepsilon^n \qquad (5.1)$$

where: V_i = settling rate of slurry-supernatant interface with respect to a fixed horizontal plane
V_{io} = V_i at infinite dilution
ε = void fraction (i.e. total volume fraction minus floc volume fraction)
n = parameter depending on $\frac{d}{D}$ and Re *(lit. 12)*
d = particle diameter
D = settling tube diameter
Re = Reynolds number

In this study flocculated particles were neither uniform nor spherical. Equation (5.1) can therefore only be applied to get a rough indication about the floc size and settling rates that are to be expected in the countercurrent column.

For the experimental conditions used, Re ≈ 3-30 and $\frac{d}{D} \approx 0.01$. The value of n in equation (5.1) thus varied from 3.3 to 4.1 (see equations in *(12)*). We determined the value of V_{io}, the dry matter content of the floc, $d.s._f$, and the floc diameter, d, according to the graphical procedure given by Michaels and Bolger *(11)*. This calculation was carried out for the data from the continuous flocculation of Rhine, Sophia and Melchior clay soils at a flocculant dosage of 0.5-0.8 g flocculant/kg dry clay soil. Results were:

V_{io} ≈ 40 - 45 cm/min
$d.s._f$ ≈ 4 - 5 wt.%
d ≈ 0.6 - 0.7 mm.

The value for $d.s._f$ is very small compared to the dry matter content of the flocculated material from the bottom of the sedimentation tank (which is about 10 to 15 wt.%). The value of d is fairly large compared to photographs taken of flocculated clay suspensions under a light-microscope (see Figure 5.7). Floc diameters of 0.1 - 0.3 mm were estimated for Melchior clay soil from these pictures. Although these two factors ($d.s._f$ and d) have opposite effects on V_{io}, it is expected that the calculated value of V_{io} is too large.

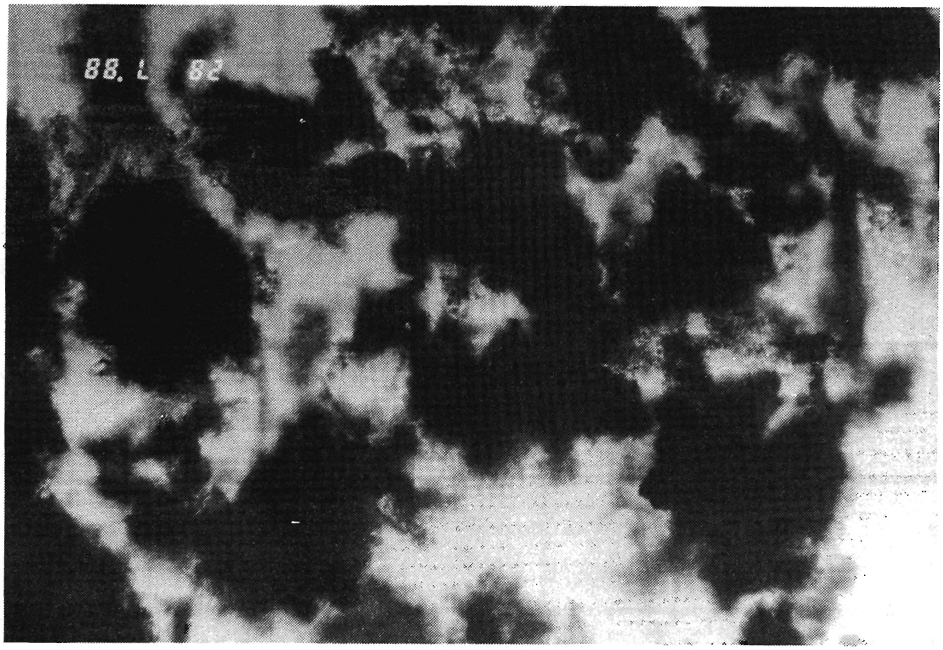

Figure 5.7. *Flocculated Melchior waste site clay soil suspension (0.6 g flocculant/kg clay soil) under light microscope (125x).*

In the countercurrent column residence times of flocculated Rhine clay soil were measured between 13 and 25 minutes (see Chapter 6). The distance between clay inlet and outlet was 2.06 m and sieve-plates were present in the column. A single aggregate (infinite dilution) with the properties as calculated above would have a settling time of about 5 minutes in the column without sieve-plates. Actually retardation will occur due to the sieve-plates and hindered settling. Residence times as given above are then plausible. The order of magnitude of the calculated V_{io}, $d.s._f$ and d-values thus seems right.

Further investigations are necessary to make more accurate calculations. It is worthwhile to search for relations between the flocculation conditions and clay soil properties on one hand and the settling rate of interface or flocculated aggregates on the other. This information would be useful for choosing the operating conditions in the extraction column.

Design of continuous flocculation unit

A flocculation unit was designed for the continuous installation. It consists of two stirred cells in series followed by a sedimentation vessel. The flocculant is added from a dilute solution in the first rapidly stirred cell. The second cell is used for floc growth and is moderately agitated. Stirring speed in the first vessel is 650-850 rpm and in the second one 300-350 rpm. Residence times were approx. 3.5 min. in the first cell and 5 (for Rhine clay) or 6.5 min. (for Sophia or Melchior soils) in the second cell. These values fall within the range given by Svarovsky *(5)* for optimum flocculation conditions (the product of the average velocity gradient G and the residence time τ should be between 10^4 and 10^5).

5.5 EXTRACTION RESULTS IN TWO STIRRED TANKS IN SERIES

The two waste site soils Sophia and Melchior were extracted in the stirred-tanks-in-series installation as described in Section 5.3 (see also Figure 5.1 for process scheme). During the experiments several sampling series were taken at regular time intervals. The results given in this section are average values of these series; outliers were discarded.

Many material balances can be made over (parts of) the total installation. A number of total material, solid material, metal ion, liquid and acid balances were calculated to examine the steady state behaviour of the total or a part of the installation. The balances generally agreed within about 10% of the values on either side. Metal ion balances showed sometimes deviations up to 30-40%. The experiment time (5-10 hours) is short for simulating a continuous process and fluctuations in the flows occur permanently due to intensive sampling and a lack of process control equipment in the laboratory set-up. A steady state was never reached completely. The balances were also used to calculate flows or metal concentrations at certain places in the installation where no measurements could be made.

Several characteristic quantities were calculated from the measurements and the balances. These quantities are given in Table 5.1 together with the most important process conditions of the two experiments S-1 and M-1.

The operational conditions for the two experiments were basically the same. The pH control of the first extractor was disturbed in experiment S-1 and as a consequence the HCl and NaOH consumption were very large. The chemicals consumption and the discharges are expressed per kg dry clay soil that was fed to the installation. These numbers are the average values over the total time of the experiment (5-10 hours). Especially the values for the discharges are rough numbers. 'Clean' clay soil is the suspension that was collected at the

Table 5.1.
PROCESS CONDITIONS AND MAIN CHARACTERISTICS OF CONTINUOUS EXTRACTION EXPERIMENTS IN TWO TANKS IN SERIES

Experiment		S(ophia)-1	M(elchior)-1
Process conditions:			
Clay soil flow to Ext.1 (kg/h)		0.34	0.59
Suspension flow to Ext.1 (kg/h)		6.4	9.8
Residence time:	in Ext.1 (min)	68	50
	in Ext.2 (min)	53	43
pH	in Ext.1	0.5 - 1.0	1.0
	in Ext.2	1.0	1.0
Chemicals consumption:			
HCl in Ext.1 (mol/kg)		16.40	4.13
in Ext.2 (mol/kg)		1.40	0.91
HCl, total	(mol/kg)	17.80	5.04
NaOH	(mol/kg)	12.80	2.38
Water	(kg/kg)	39.4	33.0
Flocculant	in FU 1 (g/kg)	0.40	0.56
	in FU 2 (g/kg)	0.14	0.26
	in Prec. Unit (g/kg)	0.11	0.09
Flocculant, total (g/kg)		0.65	0.91
Discharges:			
'Clean' clay soil (kg/kg)		0.79	0.59
Clay soil in samples (kg/kg)		0.03	0.03
Hydroxide sludge (kg/kg)		0.44	0.10
NaCl in sludge (kg/kg)		0.22	-
Acidity in clay soil (mol/kg)		6.3	4.6

Notes: 1) Abbreviations used are: Ext.1(2) = Extractor 1(2), FU 1(2) = Flocculation unit 1(2), Prec. Unit = Precipitation Unit
2) Per kg is always per kg dry clay soil fed to the installation
3) - means 'not determined'

end of the process. 'Hydroxide sludge' is the amount of solids collected from the precipitator. It was measured by evaporating the water from the settled wet sludge. The dry matter contained also sodium chloride. An indication of the amount of chemical waste that has to be disposed of is given by the amount of hydroxide sludge minus the amount of NaCl. The clay soil was still very acidic after treatment. The amount of residual acidity is given.

The extraction results of the experiments S-1 and M-1 are shown in Table 5.2. In the case of Melchior soil chromium concentrations were not measured because the initial Cr concentration was relatively low (160-200 ppm) and extraction in 0.1 N HCl was expected to be very limited (see Chapter 2).

Extraction percentages in the first extractor were higher for Sophia soil than for Melchior soil. Apart from differences in soil type and metal

Table 5.2.
EXTRACTION RESULTS OF METALS FROM THE THE WASTE SITE SOILS IN 0.1 N HCl
WITH TWO TANKS IN SERIES CONTINUOUS OPERATION

Experiment S-1:

Metal	C_{k0}(ppm)	C_{k1}(ppm)	E_1(%)	C_{k2}(ppm)	E_2(%)	E_{1+2}(%)
Cadmium	62	11	82	11	0	82
Chromium	861	646	25	512	21	41
Copper	3228	414	87	301	27	91
Nickel	3313	1576	52	990	37	70
Lead	688	200	71	159	21	77
Zinc	1882	603	68	500	17	73

Experiment M-1:

Metal	C_{k0}(ppm)	C_{k1}(ppm)	E_1(%)	C_{k2}(ppm)	E_2(%)	E_{1+2}(%)
Cadmium	22	<10	>55	<10	-	>55
Copper	449	238	47	240	0	47
Nickel	211	154	27	145	6	31
Lead	2703	940	65	884	6	67
Zinc	8060	1504	81	1472	2	82

Nomenclature:
C_{k0} =initial metal concentration in clay soil
$C_{k1(2)}$=metal concentration in clay after first (second) extractor
$E_{1(2)}$ =percentage metal extracted in first (second) stirred tank
E_{1+2} =total percentage metal extracted

concentrations this was due to the lower pH value (pH = 0.5-1.0). This can be seen from a comparison of the extraction results of Sophia soil in the first extractor to those in the combined CSTR-column experiment (see Section 5.7).

The extraction efficiency in the second extractor was much smaller than that in the first and it was much smaller for Melchior soil than for Sophia soil. The difference between the two soils might be caused by the low concentrations of Cu and Ni in Melchior soil after the first extraction; the explanation for Pb and Zn is still uncertain but the lower pH of the preceding extraction (extractor 1) might play a role.

5.6 EXTRACTION RESULTS IN COUNTERCURRENT SIEVE-PLATE COLUMN

Three continuous experiments were performed with each waste site soil in the countercurrent extraction column. The first aim of these experiments was to measure the effect of countercurrent operation on the extraction result. As was discussed in Section 5.2 conditions in the column were very different from

Table 5.3.
PROCESS CONDITIONS AND MAIN CHARACTERISTICS OF CONTINUOUS EXTRACTION EXPERIMENTS IN COUNTERCURRENT COLUMN

Experiment	S-2	S-3	M-2	M-3
Process conditions:				
Clay soil flow (kg/h)	0.49	a)0.64 b)0.53	0.55	a)0.35 b)0.35
Suspension flow (kg/h)	3.5	a)3.9 b)3.1	3.5	a)3.3 b)3.3
HCl solution flow (kg/h) 3)	15.2	a)13.5 b)13.1	14.0	a)13.6 b)13.8
Extractant concentration (mol/kg)	0.15	0.17	0.15	0.18
Average pH in column	1.3	0.9	1.4	0.8
Sieve-plate type in column	I	III	I	III
Frequency of sieve-plate movements				
turn (min^{-1})	2.9	a)3 b)0	2.9	a)3 b)3
stroke (min^{-1})	1.8	2	1.8	2
Countercurrent height (m)	1.37	a)1.37 b)1.37	1.37	a)1.37 b)1.82
Chemicals consumption:				
HCl in column (mol/kg)	5.7	4.2	4.4	5.4
NaOH (mol/kg)	4.0	2.5	2.0	3.3
Water (kg/kg) 3)	56	45	48	78
Flocculant in FU 1 (g/kg)	0.45	a)0.75 b)0.60	0.45	a)0.69 b)1.15
in FU 2 (g/kg)	0.015	0.015	0.015	0.015
in Prec. Unit (g/kg)	0.005	0.005	0.005	0.005
Flocculant, total (g/kg)	0.65	a)0.95 b)0.80	0.65	a)0.89 b)1.35
Discharges: 3)				
'Clean' clay soil (kg/kg)	0.77	0.80	0.80	0.62
Clay soil in samples (kg/kg)	0.03	0.03	0.03	0.03
Hydroxide sludge (kg/kg)	0.16	0.09	0.09	0.28
NaCl in sludge (kg/kg)	0.06	0.02	0.02	0.03

Notes: 1) Abbreviations used are: Ext.1 = Extractor 1, FU 1(2) = Flocculation unit 1(2), Prec. Unit = Precipitation Unit
2) Per kg is always per kg dry clay soil fed to the installation
3) Calculated from balances

those in the stirred tanks (and from those in the batch experiments discussed in Chapter 2). The floc-kinetics experiments have shown already that the initial extraction proceeded usually slower in a settling flocculated clay suspension than in a vigorously stirred clay suspension (see Chapter 4). The question is now what the metal extraction will be from a settling flocculated clay suspension in a countercurrent column ?

The main characteristics of the six experiments are given in Table 5.3 (for terminology see also Section 5.5). The most important differences between the experiments were variations in liquid-to-solid ratio, in pH and in movement and type of sieve-plate.

The main difference between the experiments S-2 and M-2 and the experiments S-3a, S-3b, M-3a and M-3b is the type of sieve-plates in the column. The characteristics of sieve-plate types I, II and III are given in Table 5.4. Sieve-plate type III has less open area and longer residence times of the clay suspension were expected. Type I has a relatively large open area around the edge and short-cuts may occur in the flow of the settling clay soil suspension. Especially at start-up short-cuts were observed with sieve-plate type I. Type II was used in the experiments with one stirred tank followed by the column (Section 5.7). Total open areas of type I and II are about the same, but the open area was concentrated in the holes for sieve-plate II.

Residence time distribution experiments were performed in the solid and the liquid phase with sieve-plate type II and III (see Chapter 6). The effect of different plates or plate motions on the mean residence time was small for a flocculated Rhine clay suspension. Liquid and solid flows vary also between the experiments. We assume that clay soil residence times are approximately the same for all the countercurrent column experiments, because not enough experimental information on the residence times is available.

Table 5.4
CHARACTERISTICS OF SIEVE PLATE TYPES

Sieve-plate type	I	II	III
Plate diameter (10^{-3} m)	90	98.5	98.5
Number of holes	24	36	18
Hole diameter (10^{-3} m)	5	7	5
Open area edge (10^{-4} m^2)*	14.92	2.34	2.34
Open area holes („)	4.71	13.85	3.53
Total open area („)	19.63	16.19	5.87

*The total column area is $78.54 \cdot 10^{-4}$ m^2

Remaining differences in process conditions are the pH in the column, the liquid-to-solid-ratio and the height of the countercurrent part of the column. Initial clay concentrations differed also considerably between the experiments with Melchior clay soil. The strength of the inlet HCl solution was chosen above 0.1 N because the pH was not controlled in the column. This resulted generally in a pH value close to 1.0 over the total height of the column.

Chemicals consumption and discharges were based again on total cumulative values and gave a rough indication only. In experiments M-3a and M-3b dry matter content of the hydrocyclonated suspension was fairly low which caused the large water consumption of this experiment. More clay soil was elutriated in these experiments resulting in a very high 'hydroxide' sludge discharge.

The countercurrent column is divided into three sections to describe the extraction results (see Fig. 5.8). The hydrodynamic behaviour of these three sections was already given in Section 5.2: the top part from the clay inlet to the overflow is a sort of disengaging zone for entrained clay particles. The dry matter content is very small and only a few sieve-plates are present. The middle part from the extractant inlet to the clay inlet is the countercurrent extraction zone which is agitated by the sieve-plates. The bottom conical part (free of sieve-plates) is a thickening zone for the clay suspension where cocurrent flow is dominating. Solid and liquid flows in the three zones are

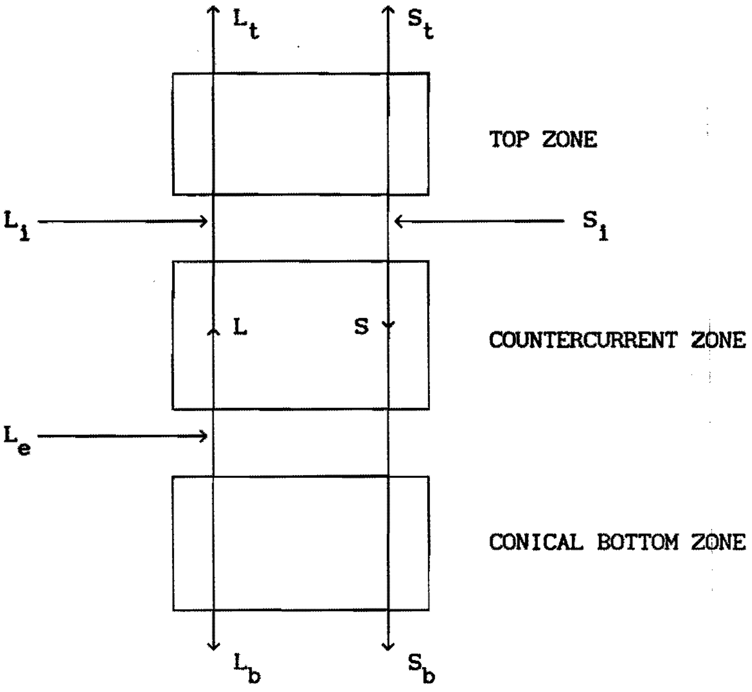

Figure 5.8. *Division of countercurrent sieve-plate column into three different hydrodynamic sections*

indicated in Fig. 5.8. Some metal concentrations in the clay soil and in the extractant at places where no measurements were carried out were calculated with the help of this flow scheme.

Extraction results of the countercurrent experiments are given in Tables 5.5 and 5.6. The extraction efficiencies of the countercurrent zone and the bottom zone were calculated from metal balances. Metal contents in the extractant were also measured over the height of the column. These results will be presented in Chapter 6 together with the model that describes the continuous extraction.

Extraction efficiencies were generally greater in experiments 3a and 3b than in experiments 2. This is very probable due to the lower pH-values in the column during the experiments 3a and 3b. A shorter clay residence time in the experiments 2 might have contributed too, but no information was available about the residence time in the column with sieve-plate type I. The nickel extraction efficiency from Melchior soil was smaller in experiments 3a and 3b. Initial Ni concentration was however much smaller in the experiments 3a and 3b than in experiment 2. Extraction efficiencies are greatest when initial metal concentrations are high except for Ni in Sophia soil. But even then the metal content after treatment is still too large to consider the clay soil as clean soil (see 'A,B,C-values' in Chapter 1). Nickel is the least extractable of the five metals. Especially in the experiments with Sophia clay soil Ni extraction efficiency increased in the bottom zone which can be seen from the difference in E-countercurrent zone and E-total. Prolonging the extraction time would therefore enhance the Ni-extraction efficiency from Sophia waste site soil.

The longer countercurrent zone in experiment M-3b compared to M-3a did not lead to greater extraction efficiencies. Results were the same considering the degree of accuracy of the continuous experiments. Comparison of results from these experiments was difficult due to problems with elutriated clay soil in experiment M-3a. These led to a smaller mass flow of solids through the bottom discharge, S_b, and to a bigger liquid-to-solid-ratio in the countercurrent zone. This effect might have compensated for the shorter countercurrent zone of experiment M-3a.

The different sieve-plate movements between experiments S-3a and S-3b did not affect the extraction efficiencies to a measurable extent.

Table 5.5. EXTRACTION RESULTS FROM SOPHIA WASTE SITE SOIL IN CONTINUOUS COUNTERCURRENT COLUMN EXPERIMENTS

EXPERIMENT S - 2

Mass flow (symbol) -	value (kg/h)	spot -	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
S_i	0.49	C_{ki}	22	3165	3127	590	1597
L_i	3.02	$C_{\ell i}$	-	-	-	-	-
S_t	-						
L_t	12.1	$C_{\ell t}$	0.6	103	26	12	31
S_b	0.48	C_{kb}	8	613	2465	265	732
L_b	6.08	$C_{\ell b}$	0.1	22	28	6.3	14
-	-	$C_{kb,calc}$	6	371	3196	210	666
-	-	$C_{k5,calc}$	8	811	2761	313	873

Extraction efficiencies	Cd	Cu	Ni	Pb	Zn
E-countercurrent zone (%)	64	74	12	47	45
E-total (%)	64	81	21	55	54

EXPERIMENT S - 3a

Mass flow (symbol) -	value (kg/h)	spot -	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
S_i	0.64	C_{ki}	28	3365	3409	648	1797
L_i	3.22	$C_{\ell i}$	0.05	0.49	0.38	0.11	0.25
S_t	0.10						
L_t	10.7	$C_{\ell t}$	0.94	138	35	14	47
S_b	0.48	C_{kb}	8	452	2166	194	752
L_b	6.06	$C_{\ell b}$	0.23	17	43	5.4	15
-	-	$C_{kb,calc}$	8	441	2460	343	751
-	-	$C_{k5,calc}$	9	625	2649	238	913

Extraction efficiencies	Cd	Cu	Ni	Pb	Zn
E-countercurrent zone (%)	68	81	22	63	49
E-total (%)	72	87	37	70	58

EXPERIMENT S - 3b

Mass flow (symbol) -	value (kg/h)	spot -	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
S_i	0.53	C_{ki}	26	3348	3311	645	1749
L_i	2.56	$C_{\ell i}$	0.02	0.28	0.18	0.09	0.14
S_t	0.08						
L_t	10.1	$C_{\ell t}$	0.86	123	34	17	42
S_b	0.46	C_{kb}	8	462	2133	206	769
L_b	5.48	$C_{\ell b}$	0.22	21	58	8.5	21
-	-	$C_{kb,calc}$	4	325	1835	171	548
-	-	$C_{k5,calc}$	9	655	2743	265	972

Extraction efficiencies	Cd	Cu	Ni	Pb	Zn
E-countercurrent zone (%)	65	80	17	59	44
E-total (%)	71	86	36	68	56

Table 5.6. EXTRACTION RESULTS FROM MELCHIOR WASTE SITE SOIL IN CONTINUOUS COUNTERCURRENT COLUMN EXPERIMENTS

EXPERIMENT M - 2

Mass flow			Metal concentrations				
(symbol) -	value (kg/h)	spot -	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
S_i	0.55	C_{ki}	24	1245	678	1855	5516
L_i	2.93	$C_{\ell i}$	-	-	-	-	-
S_t	-						
L_t	11.5	$C_{\ell t}$	0.6	40	12	63	200
S_b	0.55	C_{kb}	15	420	442	554	1317
L_b	5.42	$C_{\ell b}$	0.1	14	5.6	22	34
-	-	$C_{kb,calc}$	10	275	366	329	1019
-	-	$C_{k5,calc}$	15	491	484	656	1527

Extraction efficiencies	Cd	Cu	Ni	Pb	Zn
E-countercurrent zone (%)	38	61	29	65	72
E-total (%)	38	66	35	70	76

EXPERIMENT M - 3a

Mass flow			Metal concentrations				
(symbol) -	value (kg/h)	spot -	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
S_i	0.35	C_{ki}	20	416	274	2804	9480
L_i	2.96	$C_{\ell i}$	0.01	0.03	0.09	0.19	0.84
S_t	0.23						
L_t	13.3	$C_{\ell t}$	0.51	7.2	1.5	59	236
S_b	0.14	C_{kb}	6	82	227	334	1085
L_b	3.19	$C_{\ell b}$	5.5	0.52	0.33	2.0	8.8
-	-	$C_{kb,calc}$	-	-	-	-	-
-	-	$C_{k5,calc}$	-	87	233	367	1262

Extraction efficiencies	Cd	Cu	Ni	Pb	Zn
E-countercurrent zone (%)	-	79	15	87	87
E-total (%)	69	80	17	88	88

EXPERIMENT M - 3b

Mass flow			Metal concentrations				
(symbol) -	value (kg/h)	spot -	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
S_i	0.35	C_{ki}	20	424	269	2836	9507
L_i	2.93	$C_{\ell i}$	0.01	0.04	0.03	0.28	0.84
S_t	0.18						
L_t	12.3	$C_{\ell t}$	0.74	8.0	18	62	267
S_b	0.32	C_{kb}	6	100	241	318	1419
L_b	4.26	$C_{\ell b}$	-	0.48	0.33	1.7	7.9
-	-	$C_{kb,calc}$	-	-	-	-	-
-	-	$C_{k5,calc}$	-	102	245	335	1507

Extraction efficiencies	Cd	Cu	Ni	Pb	Zn
E-countercurrent zone (%)	-	76	9	88	84
E-total (%)	70	76	10	89	85

Notes with Tables 5.5 and 5.6:

1. Nomenclature:
   S_i = mass flow of solids into the column
   L_i = mass flow of liquid into the column
   S_t = mass flow of solids out of column through overflow (top)
   L_t = mass flow of liquid out of column through overflow (top)
   S_b = mass flow of solids out of column through bottom
   L_b = mass flow of liquid out of column through bottom
   C_{ki} = metal concentration in clay at clay suspension inlet
   $C_{\ell i}$ = metal concentration in liquid at clay suspension inlet
   $C_{\ell t}$ = metal concentration in liquid at top of the column
   C_{kb} = metal concentration in clay at bottom of the column
   $C_{\ell b}$ = metal concentration in liquid at bottom of the column
   $C_{kb,calc}$ = calculated metal concentration in clay at bottom of column
   $C_{k5,calc}$ = calculated metal concentration in clay at height of the extractant inlet

   (All mass flows in kg/h and all concentrations in ppm)
2. In case $C_{\ell i}$ was not measured it was assumed to be zero.
3. In case $C_{kb,calc}$ gave negative numbers, no values were given.
4. $C_{kt} = C_{ki}$ was assumed for calculation purposes.

5.7 EXTRACTION RESULTS IN ONE STIRRED TANK AND COUNTERCURRENT COLUMN IN SERIES

The third process scheme that was tested was a continuous set-up of one stirred tank and the countercurrent sieve-plate column in series. One experiment with each waste site clay soil was performed. Process conditions, main characteristics and extraction results are presented in Tables 5.7 and 5.8 analogous to those in the preceding sections.

Process conditions were more or less the same in the experiments S-4 and M-4. Residence time in the first extractor was prolonged for the Sophia waste site soil in order to approximate the extraction result of experiment S-1 where pH varied in extractor 1 (see Section 5.5). This did not succeed however. Sieve-plate type II (see Table 5.4) was used in both experiments and the sieve-plates were only turned (no stroke).

The extraction results will be compared to the results in the other process schemes in Section 5.8.

Table 5.7.

PROCESS CONDITIONS AND MAIN CHARACTERISTICS OF CONTINUOUS EXTRACTION EXPERIMENTS IN STIRRED TANK FOLLOWED BY COUNTERCURRENT COLUMN

Experiment	S(ophia)-4	M(elchior)-4
Process conditions:		
Clay soil flow to Ext.1 (kg/h)	0.48	0.64
Suspension flow to Ext.1 (kg/h)	7.7	10.0
Residence time: in Ext.1 (min)	85	49
pH in Ext.1	1.0	1.0
Normality of extractant to column (mol/kg)	0.1	0.1
Extractant flow to column (kg/h)	8.35	14.6
Sieve-plate type in column	II	II
Frequency of sieve-plate movements:		
turn (min^{-1})	3	3
stroke (min^{-1})	0	0
Chemicals consumption:		
HCl in Ext.1 (mol/kg)	3.41	2.75
in column (mol/kg)	2.32	2.29
HCl, total (mol/kg)	5.73	5.04
NaOH (mol/kg)	3.64	2.60
Water (kg/kg)	46.3	41.4
Flocculant in FU 1 (g/kg)	0.83	0.68
in FU 2 (g/kg)	0.15	0.11
in Prec. Unit (g/kg)	0.05	0.04
Flocculant, total (g/kg)	1.03	0.83
Discharges:		
'Clean' clay soil (kg/kg)	0.83	0.61
Clay soil in samples (kg/kg)	0.03	0.03
Hydroxide sludge (kg/kg)	0.31	0.11
NaCl in sludge (kg/kg)	0.11	0.04
Acidity in clay soil (mol/kg)	2.5	4.0

Notes: 1) Abbreviations used are: Ext.1 = Extractor 1, FU 1(2) = Flocculation unit 1(2), Prec. Unit = Precipitation Unit

2) Per kg is always per kg dry clay soil fed to the installation

Table 5.8.
EXTRACTION RESULTS FROM THE TWO WASTE SITE SOILS IN 0.1 N HCl
WITH OPERATION IN STIRRED TANK FOLLOWED BY COUNTERCURRENT COLUMN

Experiment S-4:

Metal	C_{k0}(ppm)	C_{k1}(ppm)	E_1(%)	C_{k2}(ppm)	E_2(%)	E_{1+2}(%)
Cadmium	28	<10	>65	10	0	64
Chromium	858	616	28	538	13	37
Copper	3372	786	77	470	40	86
Nickel	3440	2590	25	1905	26	45
Lead	642	434	32	257	41	60
Zinc	2091	1161	45	1047	10	50

Experiment M-4:

Metal	C_{k0}(ppm)	C_{k1}(ppm)	E_1(%)	C_{k2}(ppm)	E_2(%)	E_{1+2}(%)
Cadmium	19	<10	>47	<10	-	>47
Copper	559	318	43	158	50	72
Nickel	241	207	14	193	7	20
Lead	2946	1565	47	565	64	81
Zinc	7422	1662	78	1388	16	81

Nomenclature:
C_{k0} =initial metal concentration in clay soil
C_{k1} =metal concentration in clay after first extractor
C_{k2} =metal concentration in clay at countercurrent column outlet
E_1 =percentage metal extracted in first stirred tank
E_2 =percentage metal extracted in countercurrent column
E_{1+2} =total percentage metal extracted

5.8. COMPARISON OF THE THREE CONTINUOUS EXTRACTION PROCESS SCHEMES

The extraction results obtained in the three continuous processes are compared to each other and to some batch results that were already discussed in Section 2.5. Table 5.9 summarizes the obtained ranges of extraction efficiencies. Comparison of type of the continuous process is complicated by many different process conditions between the experiments. Especially pH differences are very significant because the extraction results strongly depend on the HCl concentration. Varying initial metal concentrations in the clay soil are also important. Cu, Ni and Zn initial concentrations in experiment M-2 deviated so strongly, that the extraction results are not considered.

Metal removal from Sophia waste-site soil was greatest in the experiment 2xCSTR (two stirred tanks in series) for each of the six metals. The reason, however, is probably not the type of process, but the low pH value of 0.5-1.0

Table 5.9.
COMPARISON OF CONTINUOUS AND BATCH EXTRACTION RESULTS IN APPROX. 0.1 N HCl FOR THE TWO WASTE SITE SOILS

Clay soil	Metal	Range of initial metal concentrations (ppm)	Total extraction efficiency (%) in:				
			column	2x CSTR	CSTR+ column	30 min* batch	30min+24h* batch
Sophia	Cd	20-60	64-72	82	64	52-67	-
	Cr	860-1020	-	41	37	0-8	-
	Cu	3170-3550	81-87	91	86	73-77	94
	Ni	3130-3460	21-37	70	45	19-23	83
	Pb	590-740	55-70	77	60	50-52	77
	Zn	1600-2090	54-58	73	50	51	84
Melchior	Cd	20-25	38-70	>55	>47	50-67	-
	Cr	160-190	-	-	-	0-8	-
	Cu	380-560	76-80	47	72	36-46	68
	Ni	210-270	10-17	31	20	28-30	52
	Pb	1830-2950	70-89	67	81	56-77	85
	Zn	7420-9760	85-88	82	81	75-80	90

*Results from table 2.6, 30m+24h = 30 minutes extraction followed by 24 h extraction, both in 0.1 N HCl.

during the first extraction of this experiment. This is indicated by a comparison of the extraction efficiencies in the second extractor to those in the countercurrent column as second step (experiment CSTR + column): Cu and Pb extraction percentages were higher in the column. Better proof can be found in the results of the Melchior experiments M-1 and M-4 that were both performed at pH = 1: extraction efficiencies were higher for all metals in case of the column as second process.

At first sight extraction efficiencies from Melchior (except Ni) seem to be greatest in the countercurrent column alone followed closely by the combination CSTR+column. But here again pH was lower for column experiments (0.8 versus 1.0) which probably explains this seemingly contradiction. Moreover, sieve-plate type III in column experiments M-3a and M-3b might have caused alonger clay residence time than sieve-plate II in the CSTR+column experiment.

The relative efficiency of the processes becomes more obvious when we compare results in the first extractor only with those in the countercurrent column. The removal efficiencies of the first extractor at pH=1 (given by the values of E_1 in Table 5.8) were smaller than or equal to the smallest values in the range of efficiencies of the column experiments (see Table 5.9). The smallest values in these ranges belonged generally to the column experiments with pH = 1.3-1.4. The extraction efficiency was thus clearly greater in the countercurrent column than in the CSTR, especially for the metals Cu, Pb and Zn. The Ni extraction seemed to be more determined by the pH than the type of process and Cd results were too inaccurate to draw conclusions. This behaviour was the same for both waste-site soils. Only Ni concentrations in Melchior clay soil were too small to observe pronounced differences.

The extraction efficiencies in the countercurrent column were also higher than those in the 30 minutes batch experiments which further supports the above conclusion. The differing Ni behaviour might be explained by its extraction kinetics (see Chapter 4). Only a small fraction of the Ni present in Sophia or Melchior clay soil could be extracted very rapidly in 0.1 N HCl. So, the mixing conditions (column or CSTR) have less influence on the extraction result of Ni than the extraction time. Extraction times in the CSTR are much longer than in the column. Improved nickel extraction results by longer extraction times are also illustrated by the results of the 30 min + 24 hours batch experiments (see Table 5.9).

To examine the efficiency of column and CSTR in the second part of the process, the experiments M-1 and M-4 can be compared (both at pH = 1). The extraction percentages (E_2 values in Tables 5.2 and 5.8) were higher in the case of the column (Ni results showed again the smallest difference). So, when the more easy extractable fraction of metal is removed, the countercurrent process shows higher efficiencies in removing the rest of the metal than the CSTR process, especially in the case of Cu, Pb and Zn. The superiority of the countercurrent process over the CSTR seemed to be more evident in the second extraction step than in the first. Another argument in the comparison between column and CSTR are the mean residence times. Although these were generally much longer in the CSTR (43-85 minutes) than in the column (10-30 minutes, estimated values), extraction efficiencies were generally greater in the column. Some further discussion about column and CSTR efficiencies will be given in Chapter 6.

Only a beginning has been made with the examination of different types of continuous extraction processes. The following type of cleaning process seems to be promising based on the few experiments performed: a first extraction in a stirred tank followed by a further second extraction in a countercurrent column. Residence time in the CSTR can be short (15-30 minutes) while residence time in the column should be as long as possible. Although the countercurrent column showed also greater extraction efficiencies in the first step of the process, the CSTR can be operated more easily and is very well suited for the first rapid part of the extraction process. Metal fractions that are more difficult to extract can then be treated in the column (with stronger acid solutions if necessary). Long residence times in the column are required for pollutants like Ni where slow extraction processes are predominant.

Metal concentrations in the clay soil after continuous extraction were not yet in the range of maximum tolerable 'A'-levels (see Chapter 1). Especially Cr, Ni and Zn concentrations are still too high in 'cleaned' Sophia waste site soil and Zn concentration in 'cleaned' Melchior waste site soil. Although the continuous extraction process is not yet operating optimally, it is not expected that these soils can be cleaned completely to 'A'-concentration levels by 0.1 N HCl treatment only. Further investigations are necessary to find possibilities for improving the extraction results. Some interesting directions for future research are: the use of greater HCl concentrations in the first or second extractor and/or the column (combined with recirculation of acid); the effect of flocculation conditions, sieve-plate types and sieve-plate motions on the clay residence time in the countercurrent column and on the extraction results; greater dry matter contents in the CSTR and the column; possibilities of extractant recycling.

5.9. TREATMENT COSTS

At this stage of the investigations it is still too early to estimate the costs of cleaning a waste-site clay soil in such a process as described in the preceding sections. A prerequisite for such a process is of course that the 'produced' soil can be considered 'clean' according to the requirements of the environmental laws or authorities. The process described here does not satisfy this condition at this moment. A detailed cost estimate is thus not meaningful. Only some aspects of the costs of the chemicals involved in treatment with 0.1 N HCl are discussed here. A more complete analysis would include at least the costs of: equipment and installation, excavation and transport of soil, soil analyses, disposal of residual metal sludge, labour.

As an example we calculated the costs of the amount of chemicals consumed in the experiments S-4 and M-4 (CSTR and column in series, see Table 5.7). The total costs add up to 200-300 Dfl/ton dry clay soil (see Table 5.10).

Table 5.10.
ESTIMATE OF COSTS OF CHEMICALS CONSUMED IN CONTINUOUS EXTRACTION (NO RECYCLING OF EXTRACTANT)

Chemicals consumption	Price (Dfl/ton)	Treatment costs (Dfl/ton dry soil)
5.0-5.7 mol HCl/kg soil	170*	95-110
0.8-1.0 g flocculant/kg soil	8600	7-9
2.6-3.6 mol NaOH/kg soil	450-700**	100-200

* 33 wt.% HCl solution
** 50 wt.% (technical) NaOH solution

This chemicals costs estimate is unrealistically high. In the first place NaOH would never be used in such a treatment on a commercial scale but $Ca(OH)_2$ or CaO instead. The latter chemical is about 10-20 times cheaper than NaOH on a mole base *(14)*. Secondly, complete neutralization of the HCl solution after one single treatment cycle is very inefficient. So, other methods to remove the metals from the extraction solution should be applied which make recycling of -at least part of- the HCl solution possible. This will reduce the costs of chemicals considerably.

When on the other hand stronger acid solutions are necessary to obtain required residual metal concentrations, costs of HCl will rise. The need for recycling the extractant solution becomes even more evident now. Complete recycling is never possible because part of the acid is consumed in the extraction process. This amount depends *i.a.* on the buffer capacity of the soil (especially the carbonate content is important). Another part of the acid solution is lost through liquid that adheres to the clay soil.

Some other aspects of the chemicals costs are: neutralization of the discharged clay soil and special chromium treatment. The clay soil is still very acidic after treatment. Before neutralizing a thickening process is recommended that results in greater dry matter contents than gravity thickening only. More HCl can thus be recycled and less base is necessary for neutralization of the cleaned soil. When a special other cleaning route is required for Cr (like the oxidative NaClO extraction discussed in Section 2.6) or for other pollutants that were not examined in this study, total chemical costs will increase further.

The high chemicals costs show that it is necessary to optimize the continuous extraction process not only with respect to the extraction results but also with respect to the costs. To some extent the latter can be done by choosing other methods for the fourth part of the extraction process (the cleaning of the extractant) which makes recycling possible. The total costs of the extraction process have to be compared to those of possible alternatives. However, alternative treatments, like thermal treatment or in-situ techniques, may often be not applicable in the case of heavy metal contaminated clay soils. A more extensive analysis of a contaminated site or pretreatment (e.g. separation in particle size fractions) may help to reduce the total amount of soil to be treated.

LITERATURE CHAPTER 5

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Chapter 6

MODELING CONTINUOUS EXTRACTION PROCESSES

6.1. INTRODUCTION

Extraction of heavy metals from contaminated waste site clay soils was performed in a continuous test installation (see Chapter 5). To describe the continuous extraction processes by a model, information is required about the extraction kinetics and about the hydrodynamic behaviour of clay soil and extractant in the various apparatuses. A model (two reaction model) was already developed to describe the kinetics of the extraction at a constant pH and temperature under two different mixing conditions (see Chapter 4).

This kinetic model is also used to describe the continuous extraction. The apparatus in which the clay soil was cleaned continuously was described in Section 5.2. The main elements are continuous stirred tank reactors and a countercurrent sieve-plate column. We have assumed that the clay soil and the extractant were perfectly mixed in the stirred tanks. This assumption was based on residence time distribution experiments performed in the liquid phase in these tanks and on the correlations of Zwietering *(3)*. The hydrodynamic behaviour of clay soil and extractant in the countercurrent column were determined experimentally. Residence time distribution experiments were carried out with two different types of sieve-plates and various sieve-plate movements. Methods and results are given in Section 6.2.

The extraction will be modeled for the two tanks in series process (see Section 6.3) and for the countercurrent process (see Section 6.4). The model description is limited to the main components of each continuous set-up. The extraction process did actually continue in other parts of the installation like the flocculation units and the sedimentation tanks. These parts were not described in the model.

The model will be used to determine the influence of several factors on the extraction results in the two continuous extraction processes.

6.2. RESIDENCE TIME DISTRIBUTION IN COUNTERCURRENT COLUMN

6.2.1. Theory

Mixing and residence time of the clay particles in the countercurrent column influence the extraction results. Mixing and mean residence time can be determined from residence time distribution (RTD) experiments *(1,2)*. In RTD-experiments an appropriate tracer is added to the inlet flow of solid or liquid phase and the tracer-response is measured at the outlet(s). The tracer must be inert and must have the same hydrodynamic behaviour as the phase that has to be characterized. We used Cu- or Cr- polluted clay soil as tracer for the unpolluted flocculated clay suspension and a NaCl solution as tracer for the liquid phase (see further Section 6.2.2).

A pulse injection is difficult to apply with a solid phase tracer. Density differences can cause problems in applying a pulse input to the liquid phase. Therefore, a step-input function was used for both the liquid and the solid phase.

The mean residence time, τ, can be found from the tracer-response curve to a positive step function ('step-up' function) by:

$$\tau = \int_0^\infty (1 - F(t)) \, dt \qquad (6.1)$$

where: τ = mean residence time
t = time
F(t) = normalized cumulative step response function

The variance, σ^2, or the standard deviation σ, of the step-response curve give information about the spread around the mean residence time. The variance of the response to a step input can be found by:

$$\sigma^2 = 2 * \int_0^\infty t * (1 - F(t)) \, dt - \tau^2 \qquad (6.2)$$

where: σ^2 = variance of step response curve

Analogous expressions exist for a negative step function ('step-down' experiment).

In the RTD experiments a sample was taken of the flocculated clay suspension every 3 minutes at the bottom outlet of the column. Sampling time was approx. 20 seconds. The values of τ and σ^2 were calculated from these discrete, instantaneous measurements by linear interpolation *(1)*. Expressions for τ and σ^2 for a step-up input are:

$$\tau = \frac{\sum_{i=1}^{n}\left\{ (2C_{max} - C_{i-1} - C_i) * (t_i - t_{i-1}) \right\}}{2(C_{max} - C_{min})} \qquad (6.3)$$

$$\sigma^2 = \frac{\sum_{i=1}^{n}\left\{ (2C_{max} - C_{i-1} - C_i) * (t_i - t_{i-1}) * (t_{i-1} + t_i) \right\}}{2(C_{max} - C_{min})} - \tau^2 \qquad (6.4)$$

and for a step-down input:

$$\tau = \frac{\sum_{i=1}^{n}\left\{ (C_i + C_{i-1} - 2C_{min}) * (t_i - t_{i-1}) \right\}}{2(C_{max} - C_{min})} \qquad (6.5)$$

$$\sigma^2 = \frac{\sum_{i=1}^{n}\left\{ (C_i + C_{i-1} - 2C_{min}) * (t_i - t_{i-1}) * (t_{i-1} + t_i) \right\}}{2(C_{max} - C_{min})} - \tau^2 \qquad (6.6)$$

where: C_i = tracer concentration at time i
C_{max} = maximum tracer concentration
C_{min} = minimum tracer concentration

The mixing conditions in the countercurrent column can now be described by the longitudinal dispersion model or the tanks-in-series model *(1,2)*. The dispersion model describes the flow in the column with an axial dispersion superimposed on a plug flow. This axial spreading is characterized by the axial dispersion coefficient D and the Peclet number $\frac{u.L}{D}$ where u is the velocity of the bulk flow in the longitudinal direction and L is a characteristic length, like the column height.

The countercurrent column can be considered as a vessel with closed boundary conditions when the boundaries are chosen as the clay inlet before the column and the bottom discharge below the conical part of the column. Inlet and outlet are small tubes where plug flow can be assumed. Some back-mixing from the zone above the clay inlet may occur but this is neglected. In this case the relationship between τ, σ^2 and the Pe-number is given by *(1)*:

$$\left(\frac{\sigma}{\tau}\right)^2 = \frac{2}{Pe} - \frac{2}{Pe^2} * \left(1 - e^{-Pe}\right) \qquad (6.7)$$

The Pe-number can thus be calculated from the experimentally determined τ and σ^2 values by solving equation 6.7.

Alternatively the flow pattern in the column can be described by a cascade of N perfectly mixed tanks. The number of mixed tanks, N, is given by:

$$\frac{1}{N} = \left(\frac{\sigma}{\tau}\right)^2 \qquad (6.8)$$

For small deviations from plug flow the Pe-number and N are related by:

$$Pe \approx 2 * (N - 0.5) \qquad (6.9)$$

The values of Pe and N are calculated for the various RTD experiments. The influence of different sieve-plate motions in the column on the flow pattern can thus be expressed in a single overall parameter. A simple comparison is possible in this way.

6.2.2. Experimental methods

The residence time distribution of a flocculated clay suspension and the liquid phase were measured in the continuous countercurrent sieve-plate column that was described in Section 5.2. The experimental installation for the RTD experiments is basically the same as that given in Figure 5.2. Differences in the set-up are: two flocculation units are needed for changing the feed from the initial flocculated clay suspension to the tracer flocculated clay suspension at the beginning of the step input. Two supplies of liquid solutions are also present (water and a NaCl solution).

The RTD experiments were performed with a flocculated Rhine clay soil suspension (approx. 0.5 g of flocculant A100/kg dry clay soil was used). The tracer was the same Rhine clay but artificially polluted with chromium or copper. The Cr or Cu was applied to the clay soil in adsorption experiments (see Section 2.3). It is necessary that the tracer is inert. Possible desorption from the tracer clay and successive adsorption to the non-polluted Rhine clay soil were checked in water and in NaCl solutions. The results of these batch experiments showed that less than 0.03% of Cr and less than 0.2%

of Cu were desorbed. So, even if 100% re-adsorption to the clean clay soil would occur, errors would be small. During the experiments suspension samples were taken at the bottom outlet of the countercurrent column (i.e. below the conical part of the column). The samples were dried and the clay soil was decomposed (according to the procedure given in Appendix II.1). Cu and Cr concentrations in the resulting solution were then measured by atomic absorption spectrometry (AAS). The Cu or Cr content was proportional to the tracer clay concentration in the sample.

It is not possible to use a HCl solution as the liquid phase in the RTD experiments. A considerable fraction of Cu and to a less extent of Cr would desorb. Ordinary tap water was chosen as the liquid phase and the clay suspension was flocculated before the column inlet in neutral conditions. Differences may therefore exist between the flocculated clay suspension and its settling pattern in the RTD experiments and those in the actual continuous extraction experiments.

The tracer for the liquid phase was a NaCl solution of 1 g/l. Liquid tracer concentrations were determined continuously by measuring the conductivity of the suspension at the bottom outlet and of the solution at the overflow of the column. The influence of the clay and the flocculant on the conductivity appeared to be negligible as was checked in separate batch experiments.

The RTD experiment itself was performed in the following way:
a flocculated Rhine clay soil suspension and water (or NaCl solution) were pumped into the column until a steady state could be assumed. During this period all liquid and suspension flows were measured and adjusted if necessary. At the beginning of the step input the clay inlet was switched to the other flocculation unit and the liquid inlet to the other solution. (In one experiment it was generally possible to switch back to the first flocculation unit several hours later). Every 3 minutes a suspension sample was taken at the bottom discharge of the column which lasted approx. 20 seconds. Sampling was started 30 minutes before the step input and was continued until 2-3 hours after the step input. Samples were dried, decomposed and analysed for Cu and Cr by AAS. Samples were also taken from the clay soil suspension that was fed to the flocculation units. The conductivity was measured continuously at the bottom and top outlet of the column by conductivity cells. Temperature of the suspension was permanently recorded with a resistance thermometer. Generally only one step-input for the liquid phase could be made in one experiment.

A special problem was caused by the conical bottom section of the column where the clay suspension was thickening. Due to instabilities the level of the layer of settled clay soil was not exactly constant. The suspension flow out of the bottom of the column was therefore varied to keep the sediment level more or less constant. The level and suspension flow rate were recorded so that corrections could be made in the response curve by estimating the residence time of the clay soil in the conical bottom section.

6.2.3 Results and discussion

Four RTD experiments were carried out with two different sieve-plate types in the column. These plate types were described in Section 5.6, Table 5.4. Type II has much more open space than type III. The sieve-plate movements were varied according to the frequencies given in Table 6.1. In the first experiments only Cu was used as a tracer, in the other experiments Cr as well. A step-up and a step-down input in the solid phase were always performed within one experiment.

Residence time distribution in the solid phase

Values of τ and σ^2 were calculated from the step-response curves with the linear interpolation method. Results are shown in Table 6.1. In case of pronounced 'tailing' the curve was cut off to determine σ^2. An example of a cumulative step response curve for the clay soil phase is given in Figure 6.1. The model parameters Pe and N were calculated from τ and σ^2 with equations 6.7 and 6.8.

In some experiments the solids flow to the column before and after the step-input differed due to varying dry matter contents of the clay in the sedimentation tanks. A weight factor was introduced to correct the tracer concentration in these cases. It was assumed that the hydrodynamic behaviour of the suspension in the column was not influenced by these variations.

The mean residence time in the four experiments ranged from 13.0 to 24.6 minutes. These values are plausible compared to the settling time of a single aggregate (floc) in the column without sieve-plates. In Section 5.4. this settling time was estimated as 5 minutes. Part of the 13-25 minutes the clay soil was passing through the bottom section of the column. The volume of

Table 6.1.

MEAN RESIDENCE TIME τ, STANDARD DEVIATION σ, MIXING MODEL PARAMETERS N AND Pe OF THE SOLID PHASE IN THE COUNTERCURRENT COLUMN UNDER VARYING CONDITIONS

Experiment conditions									
No.	Plate Type (-)	f_{stroke} (min^{-1})	f_{turn} (min^{-1})	Step-input	Tracer	τ (min)	σ (min)	N (-)	Pe (-)
1	II	0	6.8	Rn → RnCu	Cu	19.5	8.7	5.1	9
1	II	0	6.8	RnCu → Rn	Cu	19.2	8.1	5.6	10
2	II	0	1.4	RnCu → RnCr	Cu	13.0	7.0	3.5	6
2	II	0	1.4	RnCu → RnCr	Cr	16.0	6.3	6.4	12
2	II	0	1.4	RnCr → RnCu	Cu	15.7	7.3	4.6	8
2	II	0	1.4	RnCr → RnCu	Cr	15.9	6.8	5.5	10
3	II	8.9	0	RnCu → RnCr	Cu	23.0	8.9	6.7	12
3	II	8.9	0	RnCu → RnCr	Cr	23.8	5.3	21	39
3	II	8.9	0	RnCr → RnCu	Cu	24.6	9.4	6.8	13
3	II	8.9	0	RnCr → RnCu	Cr	18.9	7.0	7.3	14
4	III	2	3	RnCu → RnCr	Cu	21.7	7.4	8.7	16
4	III	2	3	RnCu → RnCr	Cr	22.9	7.4	9.5	18
4	III	2	3	RnCr → RnCu	Cu	23.8	8.2	8.5	16
4	III	2	3	RnCr → RnCu	Cr	22.5	8.7	6.8	12

Nomenclature: Rn = not polluted Rhine clay
RnCu = Rhine clay polluted with Cu as a tracer
RnCr = Rhine clay polluted with Cr as a tracer
f_{stroke} = frequency of stroke motion of sieve-plates
f_{turn} = frequency of turning motion of sieve-plates

sediment in the conical bottom section was not constant during the experiment. It is not known for which part differences in the measured τ values must be attributed to the change in volume of bottom sediment or to the experimentalvariations in sieve-plate type and movements. The latter conditions mainly affect the hydrodynamics of the clay in the countercurrent part of the column, hardly those in the bottom part (where no sieve-plates are present). It would be useful to measure the RTD in the bottom zone separately. This information being unavailable the same contribution from the bottom zone to the total mean residence time was assumed in the four experiments. The τ in the bottom section was estimated between 5 and 10 minutes.

Some trends can be seen in the τ and σ values. When sieve-plate type II was installed, a stroke of the plates caused a larger τ than a turn. This is in agreement with the visual observations of the larger amount of clay that was whirling up with a stroke than with a turn. In experiment 1 the turn frequency was larger and the residence time of the clay was longer than in experiment 2. This might indicate that the upward movement of the flocculated clay soil

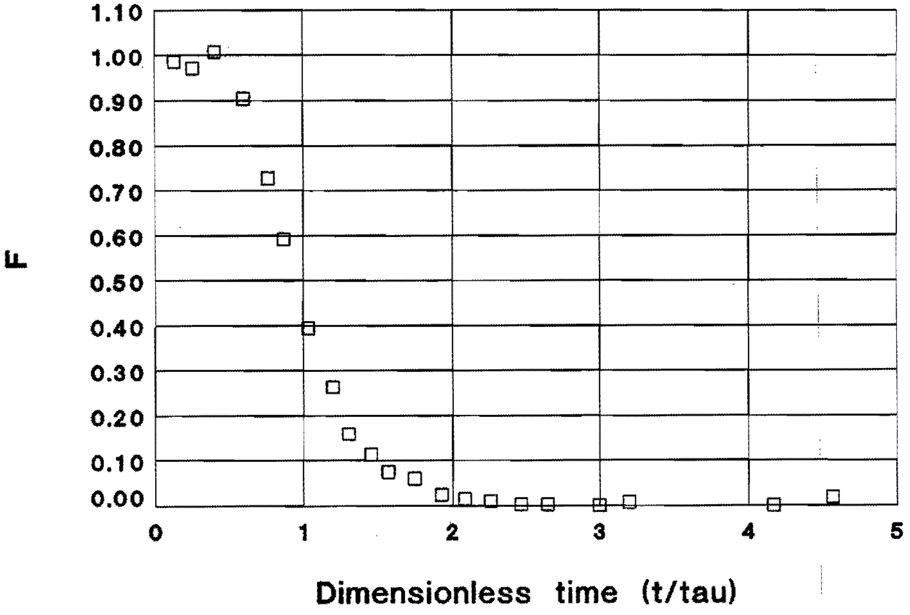

Figure 6.1. *Example of cumulative dimensionless response function F to step input function in clay soil suspension fed to countercurrent column (experiment no.2, Cu-tracer). tau=mean residence time.*

caused by the turn dominated the downward transport. Sieve-plate type III (with less open space than type II) *seemed* to increase τ relative to plate type II (results with same motion frequencies were not available).

Values of N can be compared to examine mixing in the different situations. Discarding outliers the average values for N were 5, 5, 7 and 9 for experiments 1 to 4 respectively. Surprisingly, the experiment with a sieve-plate stroke (no.3) showed less axial dispersion than the experiments with the rotation only (no. 1 and 2). The reason is not really clear but the difference in N is only small. The settling flocculated clay suspension itself has a large spread in floc sizes and thus in settling rates. This spread might be more reduced by the stronger mixing of a stroke than a turn. The more plug flow like behaviour with plate type III was expected considering the smaller open area of this plate. More floc particles can be stopped and gathered on the surface by plate type III than type II.

When an estimate for τ in the conical part was subtracted from the total τ, calculated N values for the countercurrent section were about 2-4. The suspension in the conical zone was however not really flowing as a plug but it showed spreading due to changes in the level of the sediment volume. At least part of the total σ was thus caused by the bottom section and values of N for the countercurrent zone were probably somewhat more than 2 to 4. Pe numbers of the countercurrent zone would then vary from 5 to 10.

Rhine clay soil was used in the RTD experiments but Sophia and Melchior waste site soils were extracted in the continuous installation. Rhine clay soil flocs have generally larger settling rates than the other two soils (see Section 5.4). Larger τ values should therefore be expected for Sophia and Melchior soils. On the other hand, the settling of the waste site soils took place in HCl and the acidic environment generally accelerated the sedimentation.

It should be clear that only a beginning has been made to describe the effect of various parameters on the residence time distribution of the flocculated clay soil in the countercurrent column. The experimental method has to be further improved: a better control of the inlet solids flow and of the sediment level in the conical bottom section are necessary. τ and σ^2 of the bottom part should be measured separately to obtain more reliable results for the countercurrent zone alone. In Chapter 5 long residence times were recommended for a more efficient extraction. Variations in sieve-plate type and motions so far showed only a small effect on τ and σ^2 in the RTD experiments. A higher stroke frequency with sieve-plate type III, other flocculation conditions, larger solids concentrations in the column and longer countercurrent zones are interesting directions for further RTD experiments. A greater number of sieve-plates in the column may also create longer residence times.

Residence time distribution in the liquid phase

The RTD of the extractant was also determined in four experiments. The NaCl step-input in the extractant was performed at one spot but the response was measured at two outlets: overflow and bottom. The possibility of liquid exchange between the zone above the extractant feed and below it, makes the two compartments open-closed systems. Each compartment was however treated like a closed-closed systems with a step-input proportional to its liquid flow for sake of simplicity. Values of τ and σ^2 were calculated from the response curves with the linear interpolation method. Results are given in Table 6.2 and examples of the curves are given in Figure 6.2.

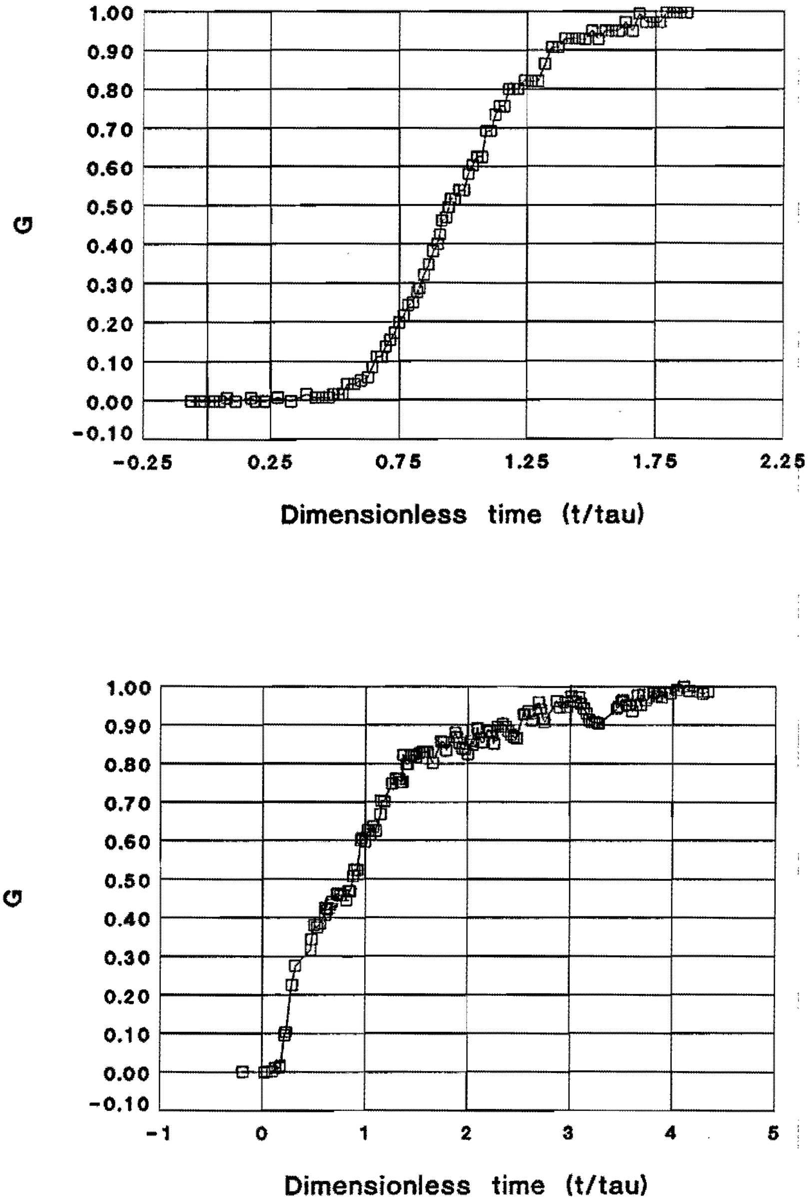

Figure 6.2. *Examples of dimensionless response functions G to step input function in extractant solution; TOP: response at overflow; BELOW: response at bottom discharge (experiment no.1).*

The value of τ for the zone above the extractant inlet ranged from 100-120 minutes and N varied from 10-13. A systematic influence of the different process conditions could not be noticed. The liquid flow in the countercurrent and top zone can therefore be approximated by plug flow in modeling.

Residence times in the bottom section varied from 30 to 40 minutes. σ^2 values were large indicating a fairly mixed system (N was small if a step-input from water to NaCl was carried out). This could be due to strong mixing between inlet extractant and the liquid flow coming with the clay from the countercurrent zone. A different type of extractant inlet nozzle (where the extractant is brought into the column with a velocity directed upwards) might reduce this mixing of the two flows and might also improve the countercurrent flow. Exchange of the extractant with liquid that adheres to the falling clay soil flocs is also a source of mixing for the liquid flow. Mixing was smaller if a step-input in the opposite direction was performed (from NaCl to water). This might be due to different densities of the two solutions.

Table 6.2.
MEAN RESIDENCE TIME τ, STANDARD DEVIATION σ, MIXING MODEL PARAMETERS N AND Pe OF THE LIQUID PHASE IN THE COUNTERCURRENT COLUMN UNDER VARYING CONDITIONS

Experiment No.	Step Input	Bottom Discharge τ (min)	σ (min)	N (-)	Pe (-)	Overflow τ (min)	σ (min)	N (-)	Pe (-)
1	$H_2O \rightarrow NaCl$	38	32	1.4	1.2	114	33	12	23
2	$H_2O \rightarrow NaCl$	41	26	2.4	3.5	120	38	10	19
3	$H_2O \rightarrow NaCl$	40	24	2.8	4.3	-	-	-	-
4	$H_2O \rightarrow NaCl$	-	-	-	-	100	30	11	21
4	$NaCl \rightarrow H_2O$	30	7.7	15	29	124	35	13	24

Note: see Table 6.1 for conditions of experiments 1 - 4

Variations in the response curves are also caused by the changing bottom suspension discharge to maintain the constant sediment level in the conical bottom part. During the second step-input from NaCl to water these changes in suspension discharge did not occur anymore which is probably the other reason besides the density differences for the more plug-flow like behaviour calculated from the negative step-input.

The many disturbances in the bottom part of the column make the RTD results for this section unreliable. They will not be used in any modeling.

6.3. MODELING EXTRACTION IN TWO CONTINUOUS STIRRED TANK REACTORS

6.3.1. Theory

To keep the clay soil particles homogeneously suspended in the stirred tanks of the continuous extraction installation a minimal stirring speed of approx. 380 rpm and a dissipated power of 0.33 W were required, according to the correlations of Zwietering *(3)*. RTD experiments showed that a liquid phase without particles could be considered ideally mixed at a stirring speed of 580 rpm. We therefore assumed that the clay suspension was ideally mixed at the actual stirring speed of 750 rpm.

The two-reactions model that was derived in Chapter 4, can be applied to calculate the extraction of metals from the clay soil in a continuous stirred tank extractor. The clay soil particles in the stirred tank extractor exhibit complete segregation, i.e. each individual particle keeps its identity. Extraction from an individual particle depends on its residence time in the tank and the kinetics. The two-reactions model describes the extraction as the sum of an irreversible first-order reaction and a reversible first-order reaction (see Chapter 4). It can be shown that the degree of segregation has no effect on the conversion for first-order reactions *(1)*. In the situation of extraction in continuous stirred tanks segregation does therefore not influence the sum of two independent first-order reactions. The two reactions in the model are, however, coupled which results in an order for the backward reaction differing from 1. Some effect of segregation could thus be expected. The backward reaction plays a minor role in the kinetics model. The effect of segregation was therefore neglected and the equations for homogeneously mixed fluids were used to describe the extraction in the stirred extractors.

To calculate the extraction results in the stirred tank extractors we used the following calculation procedure *(1,4)*. A material balance for any metal over a CSTR gives:

$$S_i \cdot c_{ki} - S_u \cdot c_{ku1} = -R_e \cdot M \qquad (6.10)$$

where: S_i = mass flow of clay soil into extractor
S_u = mass flow of clay soil out extractor
c_{ki} = metal concentration in clay flowing into extractor
c_{ku1} = metal concentration in clay flowing out extractor 1
M = mass of clay soil in extractor
$(-R_e)$= rate of extraction

If we assume $S_i \approx S_u$ then (6.10) can be written as:

$$-R_e = \frac{1}{\tau}\,(c_{ki} - c_{ku1}) \tag{6.11}$$

where: τ = (M/S) = mean residence time of clay soil in extractor.

The extraction rate is not known explicitly as a function of the concentration. Both the concentration and the extraction rate are known as a function of time (see Chapter 4):

$$c_k(t) = c_{k0} * \left(\frac{k_2-k_1}{k_2A-k_1}\right) * \left\{\left[\alpha_0 + \frac{k_1(1-1/A)}{k_2-k_1}\right] e^{-k_2At} + [1-\alpha_0]e^{-k_1t}\right\} +$$

$$+ (1-1/A)c_{k0} + (1-1/A)\,\frac{M_\ell}{M_k}\cdot c_{\ell 0}\left(1 - e^{-k_2At}\right) \tag{6.12}$$

where: $A = 1 + \frac{M_k}{M_\ell}\cdot\frac{k_3}{k_2} = 1 + \frac{M_k}{M_\ell}\cdot m_1$

The rate of extraction is given by:

$$-R_e(t) = c_{k0}\cdot\left(\frac{k_2-k_1}{k_2A-k_1}\right)\left\{\left[\alpha_0 + \frac{k_1(1-1/A)}{k_2-k_1}\right] k_2\,A\,e^{-k_2A.t} + k_1(1-\alpha_0)e^{-k_1t}\right\}$$

$$+ (1-1/A)\,\frac{M_\ell}{M_k}\,C_{\ell 0}\,k_2A\,e^{-k_2At} \tag{6.13}$$

Using the time t as parameter a plot of the reaction rate versus the concentration of metal in the clay can be constructed with equations (6.12) and (6.13). A graphical procedure can now be applied to solve the material balance (6.11) *(1,4)*: a line was drawn from the point $(-R_e)=0$, $c_k=c_{ki}$ with a slope $-\frac{1}{\tau}$. The point of intersection gives the value of c_{ku1}, i.e. the outlet concentration according to the model. The equations can also be solved numerically.

The same procedure can be applied to the second extractor. The graph of $(-R_e)$ versus c_k has to be redrawn due to different inlet conditions. In the first place the value of α_0, which gives the fraction of metal in the clay reacting according to the slow reversible reaction, has changed. In most cases α_0 is close to unity at the inlet of the second extractor. Secondly, the inlet liquid metal concentration is not equal to zero anymore and, finally, the liquid-to-solid ratio is generally somewhat different from that in the first extractor. These changes result in a lower extraction rate (at the same c_k value) for the second extractor.

6.3.2. Results and discussion

Two continuous experiments were performed in the two tanks in series set-up (experiments S-1 and M-1, see Section 5.5). The first extraction of the experiments S-4 and M-4 took also place in a stirred tank. The graphical procedure of the preceding section was applied to calculate the extraction results in the first extractor for these four experiments. In case of the experiments S-1 and M-1 results were also calculated for the second extractor.

Relevant process conditions of each experiment are shown in Table 6.3. Values are averages of each experiment; in some cases they are the average of the most representative data sets. Values of the kinetic constants were determined in Chapter 4 and were already given in Table 4.1.

Table 6.3.
PROCESS CONDITIONS FOR MODELING EXTRACTION IN ONE OR TWO CONTINUOUS STIRRED TANK REACTORS

Experiment*	S_{u1} (kg/h)	S_{u2} (kg/h)	L_{u1} (kg/h)	L_{u2} (kg/h)	τ_1 (min)	τ_2 (min)
S-1	0.35	0.68	6.17	10.6	74	44
M-1	0.59	0.49	9.19	9.36	50	48
S-4	0.47	-	7.23	-	84	-
M-4	0.61	-	9.14	-	46	-

*See for further description of experiments Chapter 5

Calculated outlet metal concentrations in the clay soil are compared to experimentally determined values in Table 6.4 for the Sophia (S) and Melchior (M) experiments. Figure 6.3 illustrates the calculation procedure for the extraction of Pb from Melchior soil. Deviations occur between measured outlet concentrations of extractor 1 and inlet concentrations of extractor 2. These were caused by the slight increase in pH-value between the two extractors, that may result in re-adsorption, or by the residence time in the flocculation unit and the sedimentation tank between the two extractors. The latter effect causes a further extraction *between* the two extractors.

Table 6.4.
COMPARISON OF MEASURED AND MODEL CONCENTRATIONS AND EXTRACTION EFFICIENCIES FOR CONTINUOUS EXTRACTION IN ONE OR TWO STIRRED TANK REACTORS

		First Extractor					*Second Extractor*				
		Measured values:			Model:		Measured values:			Model:	
Experiment	Metal	C_{ki1} (ppm)	C_{ku1} (ppm)	E_1 (%)	C_{ku1} (ppm)	E_1 (%)	C_{ki2} (ppm)	C_{ku2} (ppm)	E_2 (%)	C_{ku2} (ppm)	E_2 (%)
S-1	Cu	3228	419	87	1125	65	414	330	20	375	9
	Ni	3313	1554	53	2600	22	1576	1122	29	1500	5
	Pb	688	189	73	415	40	200	154	23	195	3
	Zn	1882	635	66	1180	37	603	565	6	565	6
S-4	Cu	3372	979	71	1180	65					
	Ni	3440	2707	21	2625	24					
	Pb	642	480	25	388	40					
	Zn	2091	1348	36	1328	36					
M-1	Cu	449	244	46	260	42	238	242	0	225	5
	Ni	211	150	29	159	25	154	150	3	153	1
	Pb	2703	788	70	1040	62	940	793	16	895	5
	Zn	8060	1522	81	2300	71	1504	1458	3	1295	14
M-4	Cu	559	362	35	325	42					
	Ni	241	208	14	182	24					
	Pb	2946	1569	47	1150	61					
	Zn	7422	1864	75	2150	71					

Nomenclature:
$C_{ki1(2)}$ = metal concentration in clay soil before first (second) extractor
$C_{ku1(2)}$ = metal concentration in clay soil after first (second) extractor
$E_{1(2)}$ = extraction efficiency of first (second) extractor

Calculated values for the first extractor agreed reasonably well with measured values in experiments M-1, S-4 and M-4. Differences in extraction percentages varied from 0-14% and were greatest for Pb. Much too low extraction percentages were predicted by the model for experiment S-1. The reason was already discussed in Chapter 5: pH value was between 0.5 and 1.0 during this experiment.

Model predictions for the second extractor were fairly good for experiment M-1 but poor for S-1. In experiment S-1 pH-deviations from 1 may have occurred which probably explains the poor model description. The model predicted the

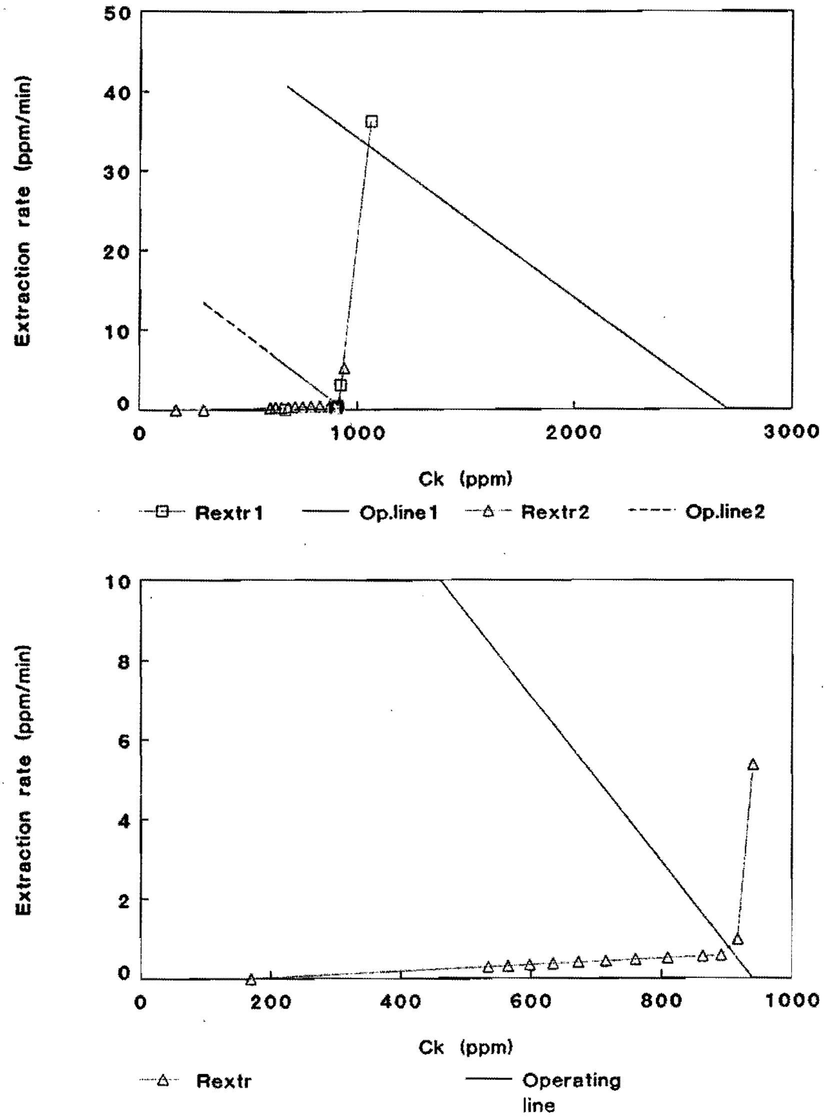

Figure 6.3. *Graphical construction for calculation of extraction efficiency of Pb from Melchior waste site clay soil in stirred tank reactors in series* TOP: *Two tanks in series;* BELOW: *Enlargement of construction for 2nd tank. Ck=Pb concentration in clay soil; Rextr1 (2)=extraction rate in tank 1 (2); Op.line1 (2)=metal balance for tank 1 (2).*

trend of hardly any extraction in the second extractor for experiment M-1.

We therefore conclude that it is possible to predict the extraction percentages with the model within 15% absolute error if the pH-value in the extractor is the same as in the kinetics experiments.

The influence of several parameters on the extraction efficiencies can be calculated with the model, for example the effect of a further dewatering between the two extractors. Further thickening of the clay soil suspension decreases the amount of adhering extractant that contains metal ions desorbed in the first extractor. Lowering the inlet liquid metal concentration in the second extractor might improve the extraction result. Model calculations with an inlet liquid concentration equal to zero show, however, only a very small decrease in outlet clay concentration (0-8%). Only a small improvement can thus be expected from a further thickening between the extractors. This result confirms the conclusion that the backward (re-adsorption) reaction is not very important.

Looking at the shape of the extraction rate versus metal concentration curve (see the example of Figure 6.3), a third extractor will contribute only to a small extent to the total extraction efficiency. The effect of the second extractor is already small in most cases. When very large residence times would be used (a very flat slope of the straight line in the plots), the contribution of second and further extractors would be enhanced. Batch or column operations are, however, more efficient when long residence times are required.

6.4. MODELING EXTRACTION IN THE COUNTERCURRENT SIEVE-PLATE COLUMN

6.4.1. Theory

To model the extraction process in the countercurrent column information about the kinetics (see Chapter 4) and about the hydrodynamic behaviour of the two phases is combined (see Section 6.2). Only the extraction in the countercurrent part of the column is modeled, the 'disengaging zone' at the top and the conical part at the bottom are not considered. A difficulty is that the RTD of the two phases was not measured separately for the countercurrent zone of the column but in combination with the conical bottom section. The mixing model parameters of the countercurrent part alone were estimated in Section 6.2 and these will be used. Parameters can easily be varied in the model to determine their impact on the extraction results.

To make a continuous variation of parameters possible we have chosen the plug flow with axial dispersion model. As discussed in Section 6.2 at least the liquid phase behaves close to plug flow. The extraction kinetics of a settling flocculated clay suspension were described by the two reaction model in combination with mass transfer from the liquid in and around the floc to the bulk liquid ('floc-kinetics', see Chapter 4). The conditions in the column were simulated in a batch extraction cell and the kinetic parameters were determined (see Section 4.4.3).

The continuity equation for a differential section of the column gives for metal in the solid phase:

$$D_s \frac{\partial^2 c_k}{\partial h^2} + v_s \frac{\partial c_k}{\partial h} - (-R_e) = \frac{\partial c_k}{\partial t} \tag{6.14}$$

and for metal in the liquid phase:

$$D_\ell \frac{\partial^2 c_\ell}{\partial h^2} - v_\ell \frac{\partial c_\ell}{\partial h} + (-R_e) \frac{\varepsilon_s}{1-\varepsilon_s} \frac{\rho_s}{\rho_\ell} = \frac{\partial c_\ell}{\partial t} \tag{6.15}$$

where: c_k = metal concentration in the clay soil
c_ℓ = metal concentration in the bulk liquid phase
h = column height (extractant inlet = 0)
t = time
$D_{s(\ell)}$ = axial dispersion coefficient of solid (liquid) phase
$v_{s(\ell)}$ = average velocity of solid (liquid) phase in downward (upward) direction
$-R_e$ = rate of extraction
ε_s = volume fraction of solid phase
$\rho_{s(\ell)}$ = density of solid (liquid) phase

We assume that a steady state is reached in the continuous extraction process. The right hand sides of equations (6.14) and (6.15) are thus equal to zero and the partial differential equations change into ordinary differential equations. The rate of extraction was described by the three differential equations (4.1), (4.2*) and (4.10) (that were discussed in Chapter 4):

$$- R_a = k_1 . c_{ka} \tag{6.16}$$

$$- R_b = k_2 . c_{kb} - k_3 . c_\ell \tag{6.17}$$

$$+ \Phi_{Me} = k_{fd} . a \; (m_2 . c_\ell - c_\ell) \tag{6.18}$$

where: c_{ka} = metal concentration in the clay reacting according to fast irreversible reaction
c_{kb} = metal concentration in the clay reacting according to slow reversible reaction
k_1, k_2, k_3 = reaction rate constants
$k_{fd}.a$ = product of mass transfer coefficient and specific surface for mass transfer
c_ℓ = liquid film concentration
m_2 = equilibrium constant
Φ_{Me} = metal flux through liquid film in floc

Just like the situation in the batch 'floc-kinetics' experiments, a steady state was assumed for c_ℓ: $(dc_\ell/dt) = 0$. This assumption gave an expression for c_ℓ (equation 4.11) that can be substituted in equations (6.17) and (6.18). When we split up the metal balance in the solid phase, (6.14), into c_{ka} and c_{kb} balances and substitute the rate expressions, we find the following set of two continuity equations for metal in the solid phase:

$$D_s \frac{d^2c_{ka}}{dh^2} + v_s \frac{dc_{ka}}{dh} - k_1.c_{ka} = 0 \tag{6.19}$$

$$D_s \frac{d^2c_{kb}}{dh^2} + v_s \frac{dc_{kb}}{dh} + \frac{k_1.k_B}{k_{fd}.a}.c_{ka} - k_B \frac{M_\ell}{M_k} . \frac{m_2}{m_1} . c_{kb} + k_B \frac{M_\ell}{M_k}.c_\ell = 0 \tag{6.20}$$

where: $k_B = \left\{ \dfrac{1}{k_{fd}.a} + \dfrac{M_\ell}{M_k} . \dfrac{m_2}{m_1} . \dfrac{1}{k_2} \right\}^{-1}$
$\dfrac{M_\ell}{M_k}$ = mass of bulk liquid per mass of clay soil in a column section
m_1, m_2 = equilibrium constants (see Chapter 4)

It was assumed that D_s and v_s were the same in (6.19) and in (6.20) and that M_ℓ/M_k has a constant value over the total height of the countercurrent part of the column. For the metal in the liquid phase we find the continuity equation (note that $k_{fd}.a$ is related to the bulk liquid!):

$$D_\ell \frac{d^2c_\ell}{dh^2} - v_\ell \frac{dc_\ell}{dh} + \frac{k_1.k_B}{k_2}.\frac{m_2}{m_1} c_{ka} + k_B.\frac{m_2}{m_1}.c_{kb} - k_B.c_\ell = 0 \tag{6.21}$$

The three continuity equations (6.19), (6.20) and (6.21) form a set of coupled, linear, ordinary differential equations of the second order. This set of equations can be solved if it is possible to decouple the system and if we can find appropriate boundary conditions. The decoupling can be done by a matrix method derived by Van Loon *(5)*. The system is then written as a matrix equation of the form:

$$\frac{d}{d\sigma}(X) = M \cdot X$$

where: X = vector of the type............$X = \begin{pmatrix} c_{ka} \\ c_{kb} \\ c_{\ell} \\ \frac{dc_{ka}}{d\sigma} \\ \frac{dc_{kb}}{d\sigma} \\ \frac{dc_{\ell}}{d\sigma} \end{pmatrix}$

M = (6x6) matrix of coefficients

σ = dimensionless column height variable ($\sigma = h/H$)

If six eigenvalues of the matrix M are not equal to zero, the system of equations can be decoupled by determining the eigenvalues and the matrix of eigenvectors. It is possible for this extraction problem. The calculations were performed with the help of a computer programme that used some matrix calculation routines from the NAG-library.

The first three boundary conditions for the system of equations can be found from mass balances at the clay soil inlet and extractant inlet of the column. Metal concentrations in the feed of the clay soil were measured (say c_{ki}). The inlet metal concentrations in the two differently reacting fractions can then be calculated with the help of the kinetic parameter α_0:

$$c_{kai} = (1-\alpha_0).c_{ki}$$

$$c_{kbi} = \alpha_0 . c_{ki}$$

The metal inlet concentration in the extractant was always zero. But the actual inlet flow into the countercurrent part of the column comes from the 'open end' of the countercurrent zone. We have therefore used the actual metal concentration of the liquid at h=0 in the mass balance.

The other three boundary conditions were given by the concentration profiles. We assumed flat concentration profiles in the clay soil at the bottom of the countercurrent zone. Since no clay soil was assumed to be present in the top of the column, extraction would not take place above the top of the countercurrent zone. We therefore assumed a maximum in the liquid concentration at h=H. In this way the boundary conditions can be written at the top of the column (h=H, σ=1) as:

$$c_{ka}(H) = c_{kai} - \frac{D_s}{v_s}\left(\frac{dc_{ka}}{dh}\right)_{h=H}$$

$$c_{kb}(H) = c_{kbi} - \frac{D_s}{v_s}\left(\frac{dc_{kb}}{dh}\right)_{h=H}$$

$$\left(\frac{dc_\ell}{dh}\right)_{h=H} = 0$$

and at the bottom of the countercurrent zone of the column (h=0, σ=0) as:

$$\left(\frac{dc_{ka}}{dh}\right)_{h=0} = 0$$

$$\left(\frac{dc_{kb}}{dh}\right)_{h=0} = 0$$

$$c_\ell(0) = c_{\ell 0} + \frac{D_\ell}{v_\ell}\left(\frac{dc_\ell}{dh}\right)_{h=0}$$

The values for v_s and v_ℓ in the above equations were calculated from the measured mass flow rates and solid and liquid hold-ups. The values for D_s and D_ℓ were calculated from estimated Peclet numbers as determined in Section 6.2.

6.4.2. Results and discussion

Metal concentrations in the extractant were measured at different heights in the countercurrent column during the continuous extraction experiments S-2, S-3, S-4 and M-2, M-3 and M-4 (see Chapter 5). Concentrations in the clay soil can be calculated at the different heights with the flow scheme given in Figure 5.8 and metal balances over solid and liquid phase together. Calculated values from metal balances were rather inaccurate because deviations of up to 30% occurred frequently in the metal balances. The inequalities can be explained by unsteady state behaviour and by the presence of clay soil in the top zone of the column where no solids and no extraction were assumed. The flow scheme of Figure 5.8 was also used to calculate the upward extractant flow L.

Relevant process conditions of the six experiments are given in Table 6.6. Values of the kinetic parameters used in the model equations were determined in the vigorous mixing- and floc-kinetics experiments (see Tables 4.1 and 4.5 in Chapter 4).

The differential equations (6.19), (6.20) and (6.21) were solved for the conditions given in Table 6.6. The flow in the liquid phase was approximated by plug-flow and a Pe-number of 20 was chosen. The Pe-number of the clay soil phase was first set at the value of 5 but was also varied to determine its influence.

Table 6.6.
PROCESS CONDITIONS OF CONTINUOUS COUNTERCURRENT EXTRACTION EXPERIMENTS USED IN MODELING

				Experiment*				
	S-2	S-3A	S-3B	S-4	M-2	M-3A	M-3B	M-4
Mass flows:								
S (10^{-3} kg/sec)	0.13	0.13	0.13	0.12	0.15	0.039	0.089	0.13
L (10^{-3} kg/sec)	2.52	2.09	2.10	1.53	2.38	2.89	2.66	1.29
Solids hold-up (wt.%)	1.0	1.5	1.5	1.5	1.5	1.0	1.0	1.5
Column height (m)	1.37	1.37	1.37	1.37	1.37	1.37	1.82	1.37
Inlet concentrations:								
c_{ki} (ppm) Cu	3165	3365	3348	786	1245	416	424	318
Ni	3127	3409	3311	2590	678	274	269	207
Pb	590	648	645	434	1855	2804	2836	1565
Zn	1597	1797	1749	1161	5516	9480	9508	1662
$c_{\ell o}$ (ppm) Cu	6.2	3.4	5.2	1.4	6.5	0.3	0.4	0.8
Ni	4.1	4.9	6.5	1.4	1.3	0.1	0.1	0.02
Pb	2.5	2.0	3.5	1.5	11.9	0.5	0.4	6.7
Zn	3.3	2.7	3.5	1.2	12.3	1.1	1.3	3.6

* See for further description of experiments Chapter 5.
In experiments S-4 and M-4 column was placed behind stirred tank extractor

Dimensionless concentration profiles for the extraction of copper from Sophia soil in experiment S-2 are shown in Figure 6.4. The picture illustrates some general trends that were observed for extraction of other metals and in other experiments as well. The concentration of Cu in the clay that reacted

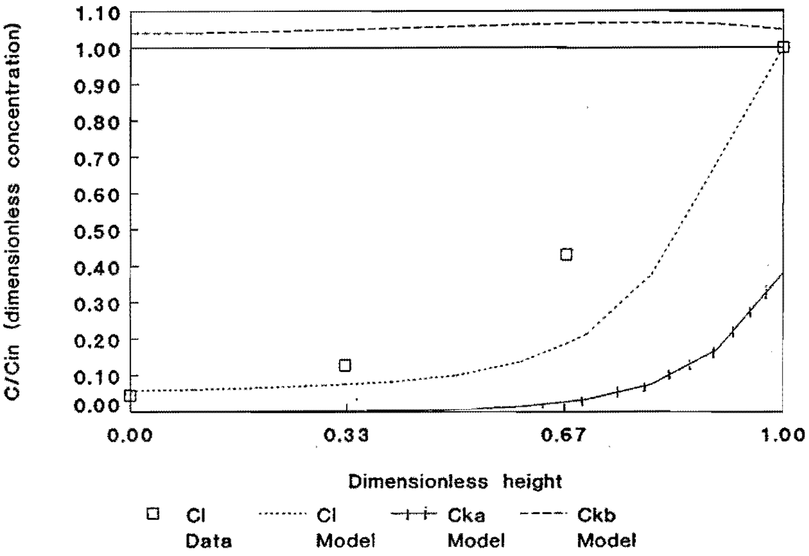

Figure 6.4. *Dimensionless metal concentration in liquid and solid phase for the extraction of Cu from Sophia waste site soil over the height of the column. C/Cin= dimensionless metal concentration in liquid or solid phase;* C_l, C_{ka}, C_{kb}*: see text.*

fast, c_{ka}, showed a sharp decrease resulting in a concentration close to zero at height 0. The only exceptions to this behaviour were the extraction of Ni from Sophia soil and of Cu from Melchior soil. The concentration of slow reacting metals, c_{kb}, increased in the top of the column followed by a small decrease at smaller heights. The net result was a small decrease or for some metals even an increase in c_{kb} over the total height of the column. This maximum in c_{kb} was caused by the low value of the product k_{fd}.a. Metal 'produced' by the fast reaction could not be transferred to the bulk liquid fast enough to prevent the backward re-adsorption reaction. The metal concentration in the extractant increased with the height of the column, the increase being more 'plug flow like' than the measured concentration profile.

Model concentrations in the clay at h=0 were in almost all cases larger than the values that could be calculated at height h=0 from a mass balance over the bottom section and the measured metal concentrations in the bottom outlet. Model concentrations in the liquid at height h=H were generally smaller than measured concentrations. The model predicted thus a lower extraction efficiency for the countercurrent zone than could be calculated from the measured values.

A lot of factors may cause these differences. An important parameter is the product k_{fd}.a that describes the rate of mass transfer from floc liquid to bulk liquid. The value of $k_{fd}.a$ was determined in a model compartment (see Chapter 4). The difference in extraction rate was small between the vigorously mixed and settling floc conditions and could only be measured in the beginning of the process. Mixing in the column was possibly stronger than in the batch turn-over reactor: the extractant was flowing through the flocs in the column, there were several in- and outlet streams in the column, samples were taken in the column. To test its influence, concentration profiles were also modeled with larger values of $k_{fd}.a$ (see Fig. 6.5).

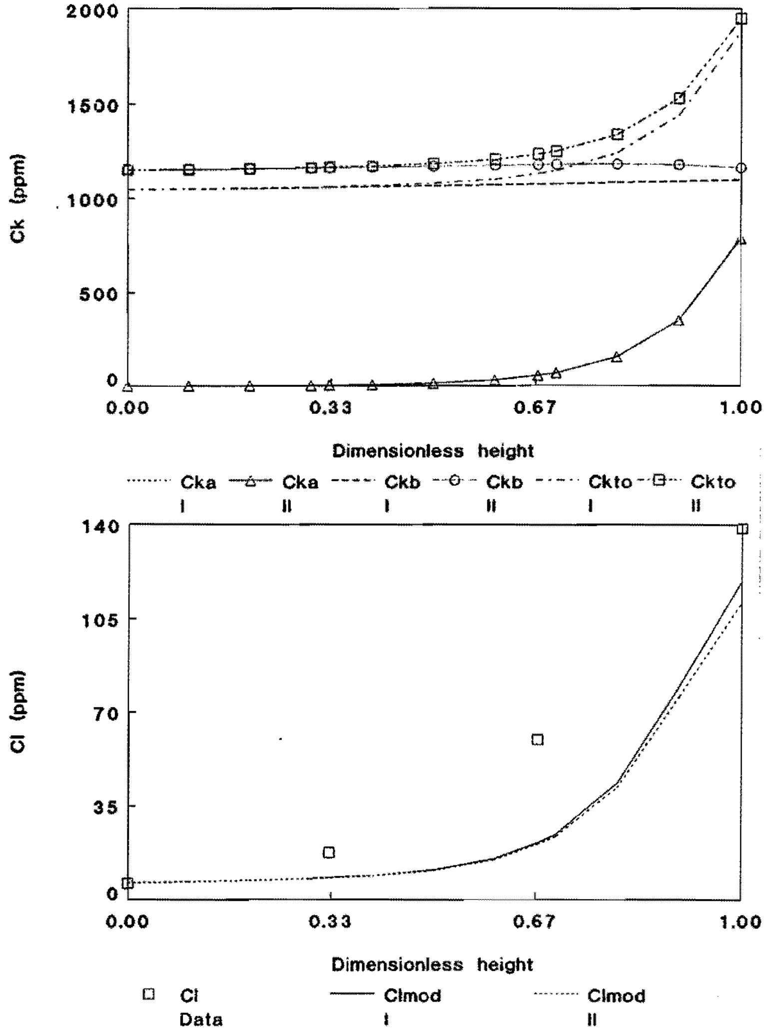

Figure 6.5. *Effect of different $k_{fd}a$ values on metal concentration profiles for the extraction of Cu from the waste site soil Sophia in countercurrent column operation. I: $k_{fd}a=10^{-3}$; II: $k_{fd}a=2.10^{-5}$ (min^{-1}). Ckto= total metal concentration in clay.*

TOP: *Profiles in clay soil phase;* BELOW: *Profiles in liquid phase.*

The example of the extraction of Cu from Sophia soil in Fig. 6.5 shows that a change in the value of $k_{fd}.a$ from $2.2*10^{-5}$ sec^{-1} (measured value) to $1.0*10^{-3}$ sec^{-1} changed the c_{kb} and c_{ℓ} profiles. As expected the c_{ka} values were not influenced by $k_{fd}.a$. The greater $k_{fd}.a$ values resulted generally in smaller total metal concentrations at the bottom of the column and the c_{kb} profiles did not show a maximum anymore.

In most cases predicted model extraction efficiencies with the greater $k_{fd}.a$ values were still smaller than the ones calculated from the measured concentrations (see Table 6.7). Model values agreed better with measured values for the experiments S-2 and M-2 than for the other experiments. This is probably due to the pH values in the column during the experiments: pH=1.3-1.4 for experiments 2 and pH=0.8-0.9 for experiments 3A and 3B. The kinetic parameters were determined for a constant pH=1. At this moment a more precise prediction cannot be expected considering the accuracy of all the experimental factors involved in the model. A large number of factors is also involved in the calculation of the extraction efficiencies from the measured concentrations.

Table 6.7.

EXTRACTION EFFICIENCIES OF COUNTERCURRENT ZONE: MODEL VALUES VERSUS VALUES CALCULATED FROM MEASURED CLAY SOIL AND LIQUID CONCENTRATIONS

Experiment		Extraction efficiency (%) for metal: Cu	Ni	Pb	Zn
S-2	E-model[1]	67	8	44	38
	E-measured[2]	74	12	47	45
S-3A	E-model	68	11	44	39
	E-measured	81	22	63	49
S-3B	E-model	68	12	44	39
	E-measured	80	17	59	44
M-2	E-model	40	25	63	74
	E-measured	61	29	65	72
M-3A	E-model	49	26	67	77
	E-measured	79	15	87	87
M-3B	E-model	46	26	66	75
	E-measured	76	9	88	84

[1] Model values were determined with process conditions from Table 6.6 but with $k_{fd}.a$ set equal to $1.0*10^{-3}$ sec^{-1}

[2] Measured values were calculated from mass balances and were given earlier in Tables 5.5 and 5.6 in Chapter 5.

It is, however, interesting to investigate possible methods for further improvement of the extraction efficiency with the model for the countercurrent column. The results have shown that the removal of metals from the clay was limited by the slow reversible reaction. The following parameters were varied to see if a further decrease of c_{kb} (or $c_{ka}+c_{kb}$) at column height h=0 was possible: S, L, solids hold-up, H, $c_{\ell o}$, Pe-numbers of solid and liquid phase.

The Pe-number of the solid phase, Pe_s, influenced the concentration profiles in the liquid and clay as illustrated by Figure 6.6 (extraction of Pb from Melchior soil).

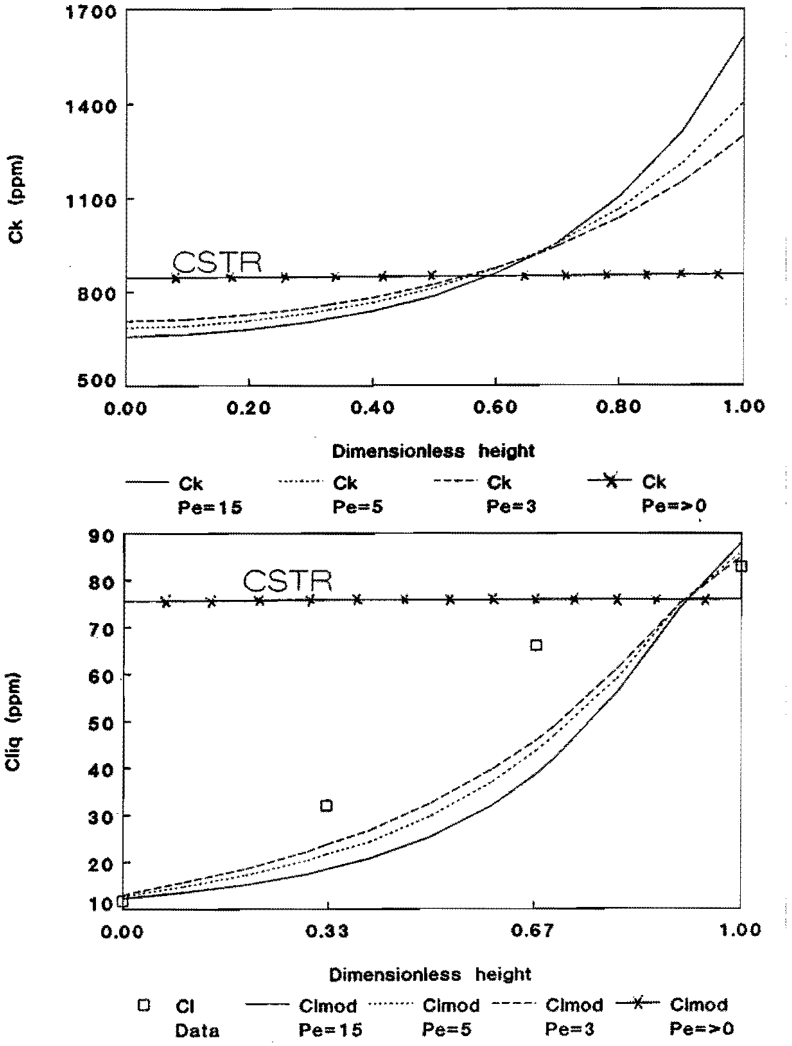

Figure 6.6. *Effect of different Pe numbers in the solid phase on metal concentration profiles for the extraction of Pb from Melchior waste site soil in countercurrent operation. TOP: Profiles of total metal concentration in clay soil; BELOW: Profile in liquid phase.*

Profiles became more 'plug flow like' with increasing Pe_s. The effect of Pe_s on the final extraction result was limited although significant. For comparison the model profiles for a CSTR ($Pe_s = Pe_\ell = 0$) are also given in the figures. Use of the countercurrent column instead of a CSTR raised the extraction efficiency for instance from 54% to 63% in case of Melchior-Pb.

Variation of the Pe-number of the liquid phase, Pe_ℓ, between 5 and 25 did not change the metal concentration in the clay. The calculated liquid profiles did change and were close to the measured profiles for Pe_ℓ=5 (see the examples of Melchior-Pb and Sophia-Zn in Figure 6.7).

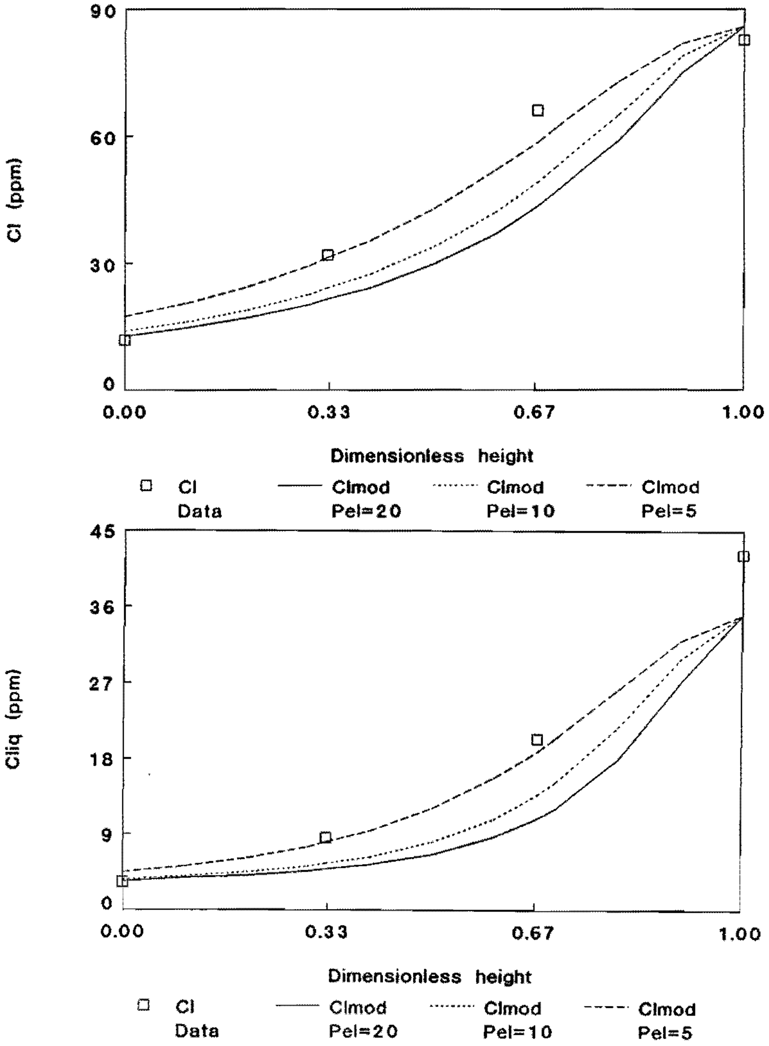

Figure 6.7. *Effect of different Pe numbers in the liquid phase on metal concentration profiles in the liquid phase; extraction in countercurrent column*
TOP: *Profiles for extraction of Pb from Melchior waste site soil;*
BELOW: *Profiles for extraction of Zn from Sophia soil.*

The behaviour of the extractant phase seemed thus further away from plug-flow than was concluded from the RTD experiments (described in Section 6.2). It is, however, in agreement with the possible reasons given above for the greater $k_{fd}.a$ values. Experiments under more accurate steady state conditions are necessary to draw more precise conclusions.

A greater solids hold-up in the column caused generally a small increase in extraction efficiency as can be seen from the Ni profiles calculated for experiment S-2 (see Figure 6.8).

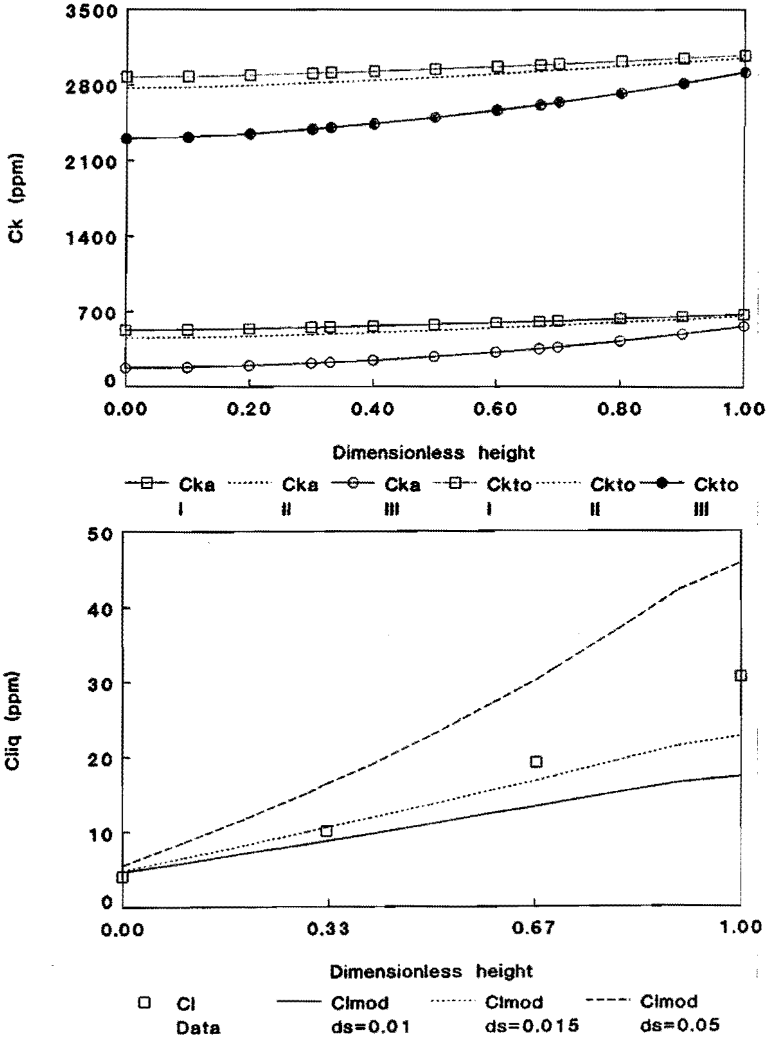

Figure 6.8. *Effect of different solid concentrations in column (ds) on metal concentration profiles for the extraction of Ni from Sophia waste site soil in countercurrent operation.* TOP: *Profiles of total metal concentration in clay soil and of Cka ;* BELOW: *Profiles in liquid phase.*
I: ds=0.01; II: ds=0.015; III: ds=0.05 wt.%

Both the liquid and solid phase concentrations were influenced. The main reason for the greater extraction efficiencies at higher dry matter content in the column is the longer mean residence time that is created. Improvements are only small. In reality the dry matter content in the column increased from the bottom to the top of the countercurrent zone. The highest solids concentrations were measured in the inlet compartment of the clay suspension especially in experiments with sieve-plate type III (experiments 3A and 3B). This effect has probably contributed to the slightly steeper decrease of the metal concentration in the liquid phase during the experiments 3A and 3B compared to those in experiments 2.

When the solids mass flow rate is increased at constant solids hold-up, the extraction efficiency decreases. In reality, these two parameters cannot be changed independently (which is by the way the case for more combinations of parameters). When an increase in S is accompanied by an increase of solids hold-up, the effect on the concentrations is rather small. Variations of L and $c_{\ell 0}$ hardly influence the extraction efficiency according to the model.

A greater column height caused a slightly greater removal of metals from the clay soils which depended on the metal-clay combination (see Figure 6.9). In experiment M-3B a column height of 1.33x the standard height (H=1.37 m) was tested. Hardly any difference in extraction efficiency could be measured which is in agreement with the findings of the model.

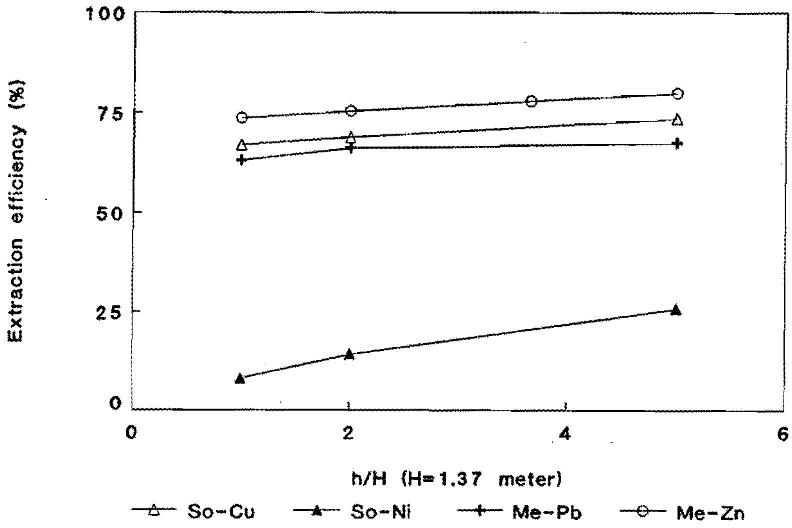

Figure 6.9. *Effect of column height (h/H) on extraction efficiency in counter current column operation for four different metal-soil combinations.*

Variations of parameters with the model showed that extraction efficiencies in the countercurrent column could only be a little bit improved by larger column lengths or greater solids hold-up. Both these factors cause longer residence times which are the main reason for a further decrease in C_k. The effect of countercurrent operation itself is actually small. Because the extraction efficiency is dominated by the fast reaction (described by C_{ka} in terms of the model), cocurrent operation would probably give about the same result. Countercurrent operation is still preferable because clay soil and extractant have to be separated after the extraction. Clay soil and liquid cannot be separated completely without thermal treatment. In countercurrent operation the amount of metal ions in the liquid adhering to the soil is much further reduced than in cocurrent operation.

The model predicted generally extraction efficiencies that were too small in case of the experiments S-4 and M-4 where the column was put in series with a stirred tank extractor. A problem in modeling this situation was the unknown value of α_0 at the clay suspension inlet. This is analogous to the situation at the inlet of the second extractor in the two tanks in series set-up. So, α could be estimated in the same way (see Section 6.3.1). This resulted in a value of α_0 close to unity for most cases and consequently in hardly any extraction in the column. The deviation between the model and measured values is unexplained but very interesting because the measured metal removal was better than calculated. Segregation of the clay soil particles in the first extractor could be of some influence. The value of α_0 at the beginning of the second process step would then be much smaller than unity for a number of particles. The big difference between the model fits for column as second process and second tank reactor stays yet unexplained. The backward reaction might be more important in the second extraction step than was assumed in the model. Investigation of the kinetics of extraction of a soil suspension coming out of the CSTR may give more information and is recommended.

The most powerful tool to get the necessary greater extraction efficiencies is a stronger acid solution. This appeared already from the extraction percentages in Table 6.7 although the numbers are obscured through the different initial metal concentrations in the clay in the various experiments. The extraction percentages of Table 6.7 can be fitted for each metal by a correlation of the type:

$$E = \text{constant} \;.\; (C_{ki})^p \;.\; (C_{H^+})^q \qquad (6.22)$$

where: E = extraction efficiency of countercurrent zone
C_{ki} = initial metal concentration in the clay soil
C_{H^+} = H^+- concentration in the column
p, q = constants

The constant p in equation (6.22) was metal dependent but q was the same for the four metals and was equal to 0.17±0.03. The variation in pH between the six experiments was small (pH ranged from 0.8 to 1.4). But the dependency on C_{H^+} can be compared to those for batch extraction experiments with Sophia and Melchior clay soil performed in 0.1 N and 2 N HCl (see Section 2.4). If the dependency would be the same, then the extraction efficiencies in 2 N HCl should relate to those in 0.1 N HCl as 1.65±0.15 : 1. It is true for extraction of Pb and Zn from Sophia soil and of Cu, Ni and Pb from Melchior soil. The ratio is smaller (about 1.2) for Sophia-Cu and Melchior-Zn and greater (about 3.7) for Sophia-Ni. The latter three combinations have the largest initial concentrations. Further experiments are necessary to determine the influence of pH.

Since higher acid strengths are the most promising way to clean the contaminated waste soils to the required maximum permissible A-levels (see Chapter 1), the relationship between extraction efficiency and H^+-concentration should be further investigated. Kinetics experiments are recommended at different constant H^+-concentrations (between 0.1 and 2 N). The kinetic model might then be extended to a model including the H^+-concentration. When greater acid strengths are used, more attention should also be paid to dissolution of the soil components itself and to the possibility of recycling the extractant as was discussed in Section 5.9.

LITERATURE CHAPTER 6

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APPENDICES

APPENDIX II.1

DECOMPOSITION METHOD OF CLAY SOIL

The method used in this study to decompose the clay soils is based on a method proposed by Vierveijzer et al. (Vierveijzer H.C. et al.; Analytical Methods for Soil; Institute for Soil Fertility, Haren, Netherlands, 1979).

Procedure:

1. A soil sample is ground in a mortar
2. About 250 mg of the sample is weighed precisely in a polyethylene bottle
3. The sample is moisturized with 0.7-1.0 ml 30% hydrogen peroxide solution The bottle is put in a oven at 50 °C for two hours.
4. 3.8 ml of a 1:3 (v/v) mixture of concentrated HNO_3 - HCl is added and 5 ml of concentrated hydrofluoric acid. The plastic bottle is closed and put in an oven at 50 °C for two hours.
5. After cooling 62.5 ml boric acid solution (37.5 gram per liter) is added and the solution is left to stand at least 5 hours.
6. The contents of the bottle are filled up quantitatively to 100 ml.
7. If the resulting solution contains still any solid material, it is filtered.

All chemicals were reagent grade.

APPENDIX II.2

TOTAL ELEMENT CONCENTRATIONS IN CLAY SOILS BEFORE AND AFTER EXTRACTIVE CLEANING

Clay Soil	Main Elements Concentration					
	Si (wt.%)	Fe (wt.%)	Al (wt.%)	Ca (wt.%)	Mg (wt.%)	K (wt.%)
Winsum	30.6	3.72	5.88	0.30	0.71	1.88
Winsum after 1/2 h cleaning in 0.1 N HCl	32.0	3.78	6.02	0.17	0.70	1.91
Rhine	26.5	3.69	6.54	3.91	1.25	2.05
Rhine after 1/2 h cleaning in 0.1 N HCl	29.0	4.01	7.26	0.43	1.06	2.25
Sophia waste site soil	18.8	9.91	6.16	2.36	0.83	1.51
Sophia after 24 h cleaning in 0.1 N HCl	22.4	6.59	6.72	0.46	0.82	1.71
Sophia waste site soil	18.4	9.52	5.89	2.35	0.80	1.39
Sophia after cleaning in 2 CSTR's (0.1 N HCl)	21.8	6.24	6.54	0.32	0.81	1.67
Melchior waste site soil	15.0	5.20	4.08	3.68	0.53	0.94
Melchior after 24 h cleaning in 0.1 N HCl	16.1	4.57	3.98	0.74	0.45	0.97
Melchior waste site soil	13.6	5.82	4.23	3.70	0.52	0.93
Melchior after cleaning in 2 CSTR's (0.1 N HCl)	14.9	5.43	4.02	0.33	0.41	0.94

	Main elements (continued)				
	Na (wt.%)	Mn (mg/kg)	Ti (mg/kg)	P (mg/kg)	S (mg/kg)
Winsum	0.56	518	2072	423	225
Winsum after 1/2 h cleaning in 0.1 N HCl	0.57	313	2071	325	252
Rhine	0.54	888	2285	941	120
Rhine after 1/2 h cleaning in 0.1 N HCl	0.57	486	2289	782	217
Sophia waste site soil	0.35	1442	1721	4509	3468
Sophia after 24 h cleaning in 0.1 N HCl	0.43	536	2384	3249	2317
Sophia waste site soil	0.35	1394	1710	4345	2273
Sophia after cleaning in 2 CSTR's (0.1 N HCl)	0.71	259	1920	2542	2494
Melchior waste site soil	0.49	1056	1392	2896	5236
Melchior after 24 h cleaning in 0.1 N HCl	0.49	313	1522	2551	5194
Melchior waste site soil	0.31	1046	1802	3154	4218
Melchior after cleaning in 2 CSTR's (0.1 N HCl)	0.34	290	1737	2814	4482

Clay Soil	Concentration of Minor Pollutants or Elements					
	Ba (mg/kg)	Be (mg/kg)	Co (mg/kg)	Li (mg/kg)	Mo (mg/kg)	Sn (mg/kg)
Winsum	274	2	5	48	8	12
Winsum after 1/2 h cleaning in 0.1 N HCl	275	2	7	48	6	15
Rhine	349	2	12	61	12	25
Rhine after 1/2 h cleaning in 0.1 N HCl	325	2	7	67	4	25
Sophia waste site soil	494	3	157	54	396	1377
Sophia after 24 h cleaning in 0.1 N HCl	451	2	79	63	421	1526
Sophia waste site soil	470	3	145	54	330	1290
Sophia after cleaning in 2 CSTR's (0.1 N HCl)	412	2	83	64	380	1320
Melchior waste site soil	896	2	20	39	11	140
Melchior after 24 h cleaning in 0.1 N HCl	910	1	15	41	11	139
Melchior waste site soil	1065	2	20	41	15	174
Melchior after cleaning in 2 CSTR's (0.1 N HCl)	975	2	12	41	16	164

Clay Soil	Concentration of Minor Pollutants or Elements (continued)			
	Sr (mg/kg)	V (mg/kg)	Y (mg/kg)	Zr (mg/kg)
Winsum	82	101	19	110
Winsum after 1/2 h cleaning in 0.1 N HCl	76	98	16	101
Rhine	161	93	25	118
Rhine after 1/2 h cleaning in 0.1 N HCl	83	90	14	118
Sophia waste site soil	124	109	22	90
Sophia after 24 h cleaning in 0.1 N HCl	81	87	11	105
Sophia waste site soil	122	102	22	88
Sophia after cleaning in 2 CSTR's (0.1 N HCl)	74	83	9	104
Melchior waste site soil	206	79	18	72
Melchior after 24 h cleaning in 0.1 N HCl	109	57	10	78
Melchior waste site soil	201	87	20	87
Melchior after cleaning in 2 CSTR's (0.1 N HCl)	88	62	11	77

APPENDIX II.3

EXTRACTION RESULTS IN DILUTE HYDROCHLORIC ACID

Experiment descriptions: see section 2.4.3 series A-F

Nomenclature: C_{k0} = initial metal concentration in clay soil (ppm)
$C_{k1(2,3)}$ = metal concentration in clay after 1st (2nd, 3d) extraction (ppm)
E1(2,3,total) = percentage metal removed in 1st (2nd, 3d or all) extractions (%)
Rn-3 (Wi-3) = Rhine (Winsum) clay soil artificially polluted with 3 metals (Cu,Pb,Zn)
Rn-5 (Wi-5) = Rhine (Winsum) clay soil artificially polluted with 5 metals (Cd,Cu,Ni,Pb,Zn)
Rn-6 (Wi-6) = Rhine (Winsum) clay soil artificially polluted with 6 metals (Cd,Cr,Cu,Ni,Pb,Zn)
Rn = Rhine clay soil
Wa = Waal clay soil
Bu = Burum clay soil
Ma = Maas clay soil
Wi = Winsum clay soil

Table II.3.1: see next page.

Table II.3.2. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with 0.1 N HCl (2 x 1 hour extraction)

Clay	Metal	C_{k0} (ppm)	C_{k1} (ppm)	C_{k2} (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2544	108	0	96	100	100
Rn-3	Pb	8325	792	299	90	62	96
Rn-3	Zn	2090	333	278	84	17	87
Wi-3	Cu	1848	550	363	70	34	80
Wi-3	Pb	7571	3014	2657	60	12	65
Wi-3	Zn	1346	494	359	63	27	73
Rn-6	Cd	1776	162	133	91	18	93
Rn-6	Cr	2080	1715	1710	18	0	18
Rn-6	Cu	2534	1245	902	51	28	64
Rn-6	Ni	1461	1158	1032	21	11	29
Rn-6	Pb	8329	693	187	92	73	98
Rn-6	Zn	2161	1230	941	43	23	56
Wi-6	Cd	1139	113	89	90	21	92
Wi-6	Cr	2024	2037	2088	-	-	-
Wi-6	Cu	1343	917	849	32	7	37
Wi-6	Ni	827	599	555	28	7	33
Wi-6	Pb	5449	1575	1125	71	29	79
Wi-6	Zn	924	574	478	38	17	48

Table II.3.1. Metal concentrations in artificially polluted clay soils after threefold extraction with 0.1 N HCl (3 x 30 minutes)

Metal		C_{k0}	C_{k1}	C_{k2}	C_{k3}	% metal removed in extraction			
	Clay	(ppm)	(ppm)	(ppm)	(ppm)	1 (%)	2 (%)	3 (%)	total (%)
Cd	Rn	111	10.4	2.4	1.2	91	77	50	99
	Wa	109	9.6	0.6	<0.1	91	94	–	>99
	Bu	113	9.5	2.3	1.5	92	76	35	99
	Ma	107	12.9	2.3	1.0	88	82	59	>99
	Wi	80	10.2	2.0	0.4	87	80	80	>99
Cr	Rn	5000	5400	5020	4900	–	7	2	2
	Wa	5280	5550	5380	5300	–	3	2	0
	Bu	5250	5370	5150	5080	–	4	2	3
	Ma	4000	3800	3280	3110	5	14	5	22
	Wi	3800	3680	3050	2860	3	17	6	25
Cu	Rn	5340	390	–	–	93	–	–	–
	Wa	5280	380	91	54	93	76	41	99
	Bu	5110	650	210	160	87	68	21	97
	Ma	3870	960	430	390	75	55	9	90
	Wi	4090	520	130	110	87	75	15	97
Ni	Rn	4590	3760	1490	1370	18	60	8	70
	Wa	4470	2960	1030	870	34	65	15	81
	Bu	4230	2420	680	560	43	72	18	87
	Ma	3890	1730	750	690	56	57	7	82
	Wi	3750	1550	400	340	59	74	16	91
Pb	Rn	5050	560	120	87	89	79	26	98
	Wa	4960	990	250	180	80	74	27	96
	Bu	4990	720	230	180	86	69	19	96
	Ma	4970	1260	310	240	75	76	21	95
	Wi	5030	750	200	170	85	73	15	96
Zn	Rn	5040	520	160	140	90	69	12	97
	Wa	5150	580	240	241	89	59	10	96
	Bu	4670	500	82	59	89	84	28	99
	Ma	3800	960	360	330	75	63	9	91
	Wi	4170	840	340	300	80	60	10	93

Table II.3.3. Metal concentrations in artificially polluted clay soils after threefold extraction with 0.1 M HCl. Effect of decreasing original metal concentration.

Metal Clay	C_{k0} (ppm)	C_{k1} (ppm)	C_{k2} (ppm)	C_{k3} (ppm)	% metal removed in extraction 1 (%)	2 (%)	3 (%)	total (%)
Cd Rn-5a	219	<6	<6	<6	98	-	-	>97
b	85	9	8	<6	90	11	-	>93
c	48	7	8	8	86	-	-	84
d	28	7	<6	<6	74	-	-	>79
Cu Rn-5a	2520	218	98	58	91	55	40	98
b	561	271	226	145	52	17	36	74
c	284	160	127	104	44	21	18	63
d	166	80	68	61	52	15	11	63
Ni Rn-5a	1214	211	107	110	83	49	-	91
b	516	358	355	262	31	1	26	49
c	312	260	220	205	17	16	7	34
d	213	170	157	147	21	7	7	31
Pb Rn-5a	7500	495	254	178	93	49	30	98
b	1674	287	186	112	83	35	40	93
c	873	207	121	92	76	42	24	89
d	530	149	111	77	72	25	31	86
Zn Rn-5a	1612	205	150	138	87	27	8	91
b	665	387	366	267	42	6	27	60
c	356	279	247	220	22	11	11	38
d	249	204	181	162	18	11	10	35
Cd Wi-5a	133	15	8	<6	88	51	-	>95
b	84	<6	<6	<6	96	-	-	>93
c	53	8	8	8	90	-	-	>85
d	32	8	<6	<6	92	-	-	>81
Cu Wi-5a	1295	274	172	110	79	37	36	92
b	598	196	131	132	67	33	0	78
c	320	121	77	68	62	36	12	79
d	152	75	64	60	51	15	6	61
Ni Wi-5a	775	179	138	111	77	23	19	86
b	494	215	165	185	56	23	-	63
c	332	184	161	149	45	12	8	55
d	207	141	145	140	32	-	4	33
Pb Wi-5a	6295	744	364	185	88	51	49	97
b	2112	413	220	161	80	47	27	92
c	1038	300	154	127	71	49	17	88
d	522	221	128	107	58	42	17	80
Zn Wi-5a	928	215	173	135	77	20	22	85
b	598	249	188	154	58	25	18	74
c	381	214	185	181	44	14	2	53
d	239	180	169	172	25	6	-	28

Table II.3.4. Extraction results at different pH values

pH	Clay concentration after extraction (ppm)		Extraction percentage (%)	
	Rn-Cu	Wi-Cu	Rn-Cu	Wi-Cu
1	259	718	95	82
1.5	389	1317	93	67
2	585	1823	89	55
3	1033	2526	80	37
4	1990	3336	62	17
5	4512	3825	14	5

Note: Original metal concentrations are: 5250 ppm for Rn-Cu
4020 ppm for Wi-Cu

Table II.3.5. Extraction results at different soil to solution ratios

Soil to solution ratio (wt/wt)	Clay concentration after extraction (ppm)		Extraction percentage (%)	
	Rn-Ni	Wi-Cu	Rn-Ni	Wi-Cu
1:5	3845	611	16	85
1:20	3764	518	18	87
1:50	3733	433	18	89
1:200	3579	404	21	90

Note: Original metal concentrations are: 4560 ppm for Rn-Ni
4010 ppm for Wi-Cu

APPENDIX II.4

EXTRACTION RESULTS IN DILUTE EDTA SOLUTIONS AND COMBINATIONS OF EDTA AND HYDROCHLORIC ACID

Experiment descriptions: see section 2.5.1 and 2.5.2.
Nomenclature: see Appendix II.3

Table II.4.1. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with 0.005 M EDTA (first extraction 1h, second 1/2 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2544	2580	2040	-	21	20
Rn-3	Pb	8325	3294	3164	60	4	62
Rn-3	Zn	2090	1980	1620	5	18	22
Wi-3	Cu	1848	1020	480	45	53	74
Wi-3	Pb	7571	1067	329	86	69	96
Wi-3	Zn	1346	710	310	47	56	77
Rn-6	Cd	1776	300	320	83	-	82
Rn-6	Cr	2080	1740	1490	16	14	28
Rn-6	Cu	2534	2850	2126	-	25	16
Rn-6	Ni	1461	1180	1053	19	11	28
Rn-6	Pb	8329	3551	2075	57	42	75
Rn-6	Zn	2161	2360	1640	-	31	24
Wi-6	Cd	1139	25	40	98	-	96
Wi-6	Cr	2024	2160	2980	-	-	-
Wi-6	Cu	1343	1280	670	5	48	50
Wi-6	Ni	827	580	275	30	53	67
Wi-6	Pb	5449	891	333	84	63	94
Wi-6	Zn	924	820	390	11	52	58

Table II.4.2. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with 0.01 M EDTA (both extractions 1/2 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2544	2163	1677	15	22	34
Rn-3	Pb	8325	2505	1124	70	55	86
Rn-3	Zn	2090	1786	1405	15	21	33
Wi-3	Cu	1848	849	401	54	53	78
Wi-3	Pb	7571	755	267	90	65	96
Wi-3	Zn	1346	500	341	63	32	75
Rn-6	Cd	1740	400	169	77	58	90
Rn-6	Cr	2420	2319	2440	4	-	-
Rn-6	Cu	2830	2632	2370	7	10	16
Rn-6	Ni	1620	1437	1342	11	7	17
Rn-6	Pb	7780	2443	863	69	65	89
Rn-6	Zn	2750	2206	1971	20	11	28
Wi-6	Cd	1020	60	10	94	84	99
Wi-6	Cr	2100	2103	1993	-	5	5
Wi-6	Cu	1385	694	374	50	46	73
Wi-6	Ni	810	149	97	82	35	88
Wi-6	Pb	4527	536	165	88	69	96
Wi-6	Zn	990	258	194	74	25	80

Table II.4.3. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with 0.05 M EDTA (both extractions 1/2 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2235	230	62	90	73	97
Rn-3	Pb	7479	640	131	91	79	98
Rn-3	Zn	1813	291	152	84	48	92
Wi-3	Cu	1221	226	35	81	84	97
Wi-3	Pb	5557	468	98	92	79	98
Wi-3	Zn	889	194	94	78	51	89
Rn-6	Cd	1740	396	140	77	65	92
Rn-6	Cr	2420	2082	1985	14	5	18
Rn-6	Cu	2830	1753	1147	38	35	59
Rn-6	Ni	1620	1291	948	20	27	42
Rn-6	Pb	7780	791	269	90	66	97
Rn-6	Zn	2750	1649	1027	40	38	63
Wi-6	Cd	1020	70	<10	93	>85	>99
Wi-6	Cr	2100	1839	1466	12	20	30
Wi-6	Cu	1385	666	276	89	81	98
Wi-6	Ni	810	159	69	80	57	91
Wi-6	Pb	4527	477	89	89	81	98
Wi-6	Zn	990	288	157	71	45	84

Table II.4.4. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after threefold extraction with 0.1 M EDTA (3 x 1/2 h)

Clay	Metal	C_{k0} (ppm)	C_{k1} (ppm)	C_{k2} (ppm)	C_{k3} (ppm)	E1 (%)	E2 (%)	E3 (%)	Etot (%)	E1+2 (%)
Rn-3	Cu	2544	849	317	190	67	63	40	93	8
Rn-3	Pb	8325	839	287	162	90	66	44	98	97
Rn-3	Zn	2090	729	307	200	65	58	35	90	85
Wi-3	Cu	1848	819	269	218	56	67	19	88	85
Wi-3	Pb	7571	683	202	139	91	70	31	98	97
Wi-3	Zn	1346	497	269	268	63	46	1	80	80
Rn-6	Cd	1740	265	49	49	85	81	0	97	97
Rn-6	Cr	2420	1785	1511	1376	26	15	9	43	38
Rn-6	Cu	2830	1648	909	531	42	45	42	81	68
Rn-6	Ni	1620	1059	612	403	35	42	34	75	62
Rn-6	Pb	7780	1128	277	138	85	75	50	98	96
Rn-6	Zn	2750	1472	721	501	46	51	30	82	74
Wi-6	Cd	1020	39	10	20	96	75	-	98	99
Wi-6	Cr	2100	1760	1226	994	16	30	19	53	42
Wi-6	Cu	1385	645	257	151	53	60	41	89	81
Wi-6	Ni	810	117	89	80	86	24	10	90	89
Wi-6	Pb	4527	489	119	90	89	76	24	98	97
Wi-6	Zn	990	254	138	110	74	46	20	89	86

Table II.4.5. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with an acidified 0.005 M EDTA solution, pH=2.5 (both extractions 1h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2544	959	755	62	21	70
Rn-3	Pb	8325	2930	1483	65	49	82
Rn-3	Zn	2090	600	344	71	43	84
Wi-3	Cu	1848	405	91	78	78	95
Wi-3	Pb	7571	829	112	89	86	99
Wi-3	Zn	1346	483	322	64	33	76
Rn-6	Cd	1776	429	290	76	32	84
Rn-6	Cr	2080	1812	1772	13	2	15
Rn-6	Cu	2534	1380	939	46	32	63
Rn-6	Ni	1461	1164	978	20	16	33
Rn-6	Pb	8329	676	<20	92	>97	>99
Rn-6	Zn	2161	1470	1146	32	22	47
Wi-6	Cd	1139	267	199	77	25	83
Wi-6	Cr	2024	2005	1978	1	1	2
Wi-6	Cu	1343	832	748	38	10	44
Wi-6	Ni	827	557	520	33	7	37
Wi-6	Pb	5449	931	509	83	45	91
Wi-6	Zn	924	662	610	28	8	34

Table II.4.6. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with firstly 0.1 M HCl and secondly 0.005 M EDTA (both extractions 1/2 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2544	-	125	-	-	95
Rn-3	Pb	8325	389	208	95	47	98
Rn-3	Zn	2090	-	122	-	-	94
Wi-3	Cu	1848	314	140	83	55	92
Wi-3	Pb	7571	914	273	88	70	96
Wi-3	Zn	1346	196	92	85	53	93
Rn-6	Cd	1776	232	47	87	80	97
Rn-6	Cr	2080	1306	1205	37	8	42
Rn-6	Cu	2534	970	343	62	65	86
Rn-6	Ni	1461	867	288	41	67	80
Rn-6	Pb	8329	609	307	93	50	96
Rn-6	Zn	2161	1013	272	53	73	87
Wi-6	Cd	1139	44	10	96	77	99
Wi-6	Cr	2024	1909	1291	6	32	36
Wi-6	Cu	1343	726	470	46	35	65
Wi-6	Ni	827	466	248	44	47	70
Wi-6	Pb	5449	678	283	88	58	95
Wi-6	Zn	924	340	189	63	44	80

Table II.4.7. Metal concentrations in Rhine and Winsum clay soil polluted with three and six metals after twofold extraction with firstly 0.005 M EDTA and secondly 0.1 M HCl (both extractions 1/2 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-3	Cu	2544	2229	165	12	93	94
Rn-3	Pb	8325	3706	251	55	93	97
Rn-3	Zn	2090	1821	165	13	91	92
Wi-3	Cu	1848	1110	601	40	46	67
Wi-3	Pb	7571	1210	260	84	79	97
Wi-3	Zn	1346	592	341	56	42	75
Rn-6	Cd	1776	661	92	63	86	95
Rn-6	Cr	2080	2079	1095	0	47	47
Rn-6	Cu	2534	2432	987	4	59	61
Rn-6	Ni	1461	1454	695	0	52	52
Rn-6	Pb	8329	3729	392	55	89	95
Rn-6	Zn	2161	2102	939	3	55	57
Wi-6	Cd	1139	67	43	94	36	96
Wi-6	Cr	2024	2000	60	1	97	97
Wi-6	Cu	1343	833	325	38	61	76
Wi-6	Ni	827	519	47	37	91	94
Wi-6	Pb	5449	795	211	85	73	96
Wi-6	Zn	924	477	189	48	60	80

Table II.4.8. Metal concentrations in Rhine and Winsum clay soil polluted with six metals after twofold extraction with firstly 0.1 M HCl and secondly 0.1 M EDTA (both extractions 1/2 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Rn-6	Cd	1740	130	10	93	92	99
Rn-6	Cr	2420	1295	1248	47	4	48
Rn-6	Cu	2830	1071	372	62	65	87
Rn-6	Ni	1620	720	328	56	54	80
Rn-6	Pb	7780	986	145	87	85	98
Rn-6	Zn	2750	988	251	64	75	91
Wi-6	Cd	1020	55	6	95	89	99
Wi-6	Cr	2100	1638	1565	22	4	25
Wi-6	Cu	1385	668	215	52	68	84
Wi-6	Ni	810	200	85	75	58	90
Wi-6	Pb	4527	919	118	80	87	97
Wi-6	Zn	990	284	88	71	69	91

Table II.4.9. Metal concentrations in the two waste site soils Sophia and Melchior after twofold extraction with firstly 0.1 M HCl and secondly 0.1 M EDTA (first extraction 1/2 h, second 1 h)

Clay	Metal	Ck0 (ppm)	Ck1 (ppm)	Ck2 (ppm)	E1 (%)	E2 (%)	Etotal (%)
Sophia	Cd	30	14	12	53	14	60
	Cr	1016	1008	1004	1	0	1
	Cu	3300	871	426	74	51	88
	Ni	3380	2677	1760	21	34	48
	Pb	634	307	96	52	69	85
	Zn	1832	890	613	51	31	67
Melchior	Cd	24	12	10	50	17	58
	Cr	161	169	163	–	–	–
	Cu	383	229	96	41	58	75
	Ni	208	147	134	30	9	36
	Pb	1984	809	234	60	72	88
	Zn	9412	2323	1363	76	41	86

APPENDIX III

SEQUENTIAL EXTRACTION ANALYSIS RESULTS

Nomenclature: Rn = Rhine clay soil Ma = Maas clay soil
Wa = Waal clay soil Wi = Winsumclay soil
Bu = Burum clay soil
Exch = 'Exchangeable' fraction of metals
Carb = Fraction of metals bound to carbonates (CO_3)
Fe/Mn-ox = Fraction of metals bound to iron and manganese oxides
Org = Fraction of metals bound to organics or present as sulfides
Res = Residual fraction
See section 3.2 for a more detailed description of fractions and experimental methods

Table III.1: see next page

Table III.2. Metal distribution (according to the sequential extraction procedure of Tessier) in Rhine and Winsum clay soils, artificially polluted with 3 or 6 metals, before and after twofold extraction by 0.1 M EDTA

		Original distribution of metal ions in polluted soil (mg metal/kg clay soil)						Metal distribution in clay after 2 x 1/2 hour extraction (cleaning) by 0.1 M EDTA					
		Metal:						Metal:					
Clay	Fraction	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
Rn-3	Exch	-	-	13	-	350	89	-	-	120	-	106	114
	Carb	-	-	1133	-	5761	983	-	-	29	-	22	31
	Fe/Mn-ox	-	-	1487	-	2285	1112	-	-	78	-	68	74
	Org	-	-	148	-	332	95	-	-	34	-	22	17
	Res	-	-	129	-	228	154	-	-	103	-	84	112
Rn-6	Exch	1224	1	3	29	301	14	19	139	230	89	106	167
	Carb	495	322	449	334	6160	583	7	119	102	57	22	66
	Fe/Mn-ox	195	1629	2034	981	2441	1499	26	106	452	281	60	344
	Org	8	172	194	131	329	137	2	226	71	57	16	64
	Res	5	140	100	95	200	135	0	102	132	76	67	123
Wi-3	Exch	-	-	415	-	4218	588	-	-	67	-	78	78
	Carb	-	-	364	-	1963	109	-	-	22	-	21	25
	Fe/Mn-ox	-	-	832	-	891	343	-	-	70	-	33	76
	Org	-	-	139	-	238	90	-	-	30	-	18	29
	Res	-	-	125	-	124	115	-	-	133	-	61	122
Wi-6	Exch	1034	34	492	580	3872	537	8	265	89	11	33	19
	Carb	610	230	108	25	904	32	0	106	31	3	9	13
	Fe/Mn-ox	10	1158	560	51	524	153	1	62	80	13	12	26
	Org	1	341	143	20	157	33	0	230	17	11	8	7
	Res	5	165	80	45	90	85	11	105	64	43	53	64

Table III.1. Metal distribution (according to the sequential extraction procedure of Tessier) in clay soils, artificially polluted with one metal, before and after cleaning by a single 0.1 N HCl extraction

		Original distribution of metal ions in polluted clay (mg metal/kg clay)					Metal distribution in clay after 1 hour extractive cleaning with 0.1 N HCl (mg metal/kg clay)				
		Clay soil:					Clay soil:				
Metal	Fraction	Rn	Wa	Bu	Ma	Wi	Rn	Wa	Bu	Ma	Wi
Cd	Exch	63	60	60	76	43	–	–	–	–	–
	Carb	45	27	25	12	18	1.0	1.3	0.8	1.3	1.0
	Fe/Mn-ox	27	23	14	19	16	0.6	1.3	0.4	1.4	0.6
	Org	1.5	1.3	1.7	1.7	1.4	0.4	0.6	0.2	0.7	0.2
	Res	9.9	10	8.7	9.9	8.8	–	–	–	–	–
Cr	Exch	12	25	29	233	280	277	168	62	466	564
	Carb	242	282	293	449	637	1060	814	331	628	701
	Fe/Mn-ox	4200	5020	2710	2240	1850	3390	3930	1390	1820	1370
	Org	599	363	383	430	1070	527	1060	996	750	690
	Res	133	57	79	205	156	114	124	139	229	129
Cu	Exch	15	27	28	118	1150	–	–	–	–	–
	Carb	3070	4630	3980	847	770	29	41	35	55	39
	Fe/Mn-ox	2250	981	238	1640	1970	61	119	119	174	97
	Org	163	116	122	149	223	55	26	29	45	62
	Res	188	130	115	148	246	68	7	96	100	104
Ni	Exch	67	407	339	2190	2120	–	–	–	–	–
	Carb	567	1040	1360	274	471	165	150	98	68	70
	Fe/Mn-ox	2770	2260	1490	451	535	416	570	294	221	239
	Org	281	430	611	226	449	455	359	270	163	239
	Res	1200	609	242	577	329	766	484	122	514	181
Pb	Exch	159	813	1410	2290	2300	–	–	–	–	–
	Carb	2700	4470	3160	1510	1830	30	124	49	64	49
	Fe/Mn-ox	1880	1500	1080	1470	933	45	138	47	152	50
	Org	407	213	280	327	319	16	80	18	48	21
	Res	100	90	160	160	108	67	126	114	175	110
Zn	Exch	125	294	420	1670	1850	–	–	–	–	–
	Carb	3540	4270	3640	417	1110	10	13	11	17	15
	Fe/Mn-ox	1480	718	699	987	650	33	38	20	61	39
	Org	106	49	109	130	193	10	11	8	26	17
	Res	167	176	128	200	99	118	105	95	167	123

Table III.3. Metal distribution (according to the sequential extraction procedure of Tessier) in the two waste site soils Sophia and Melchior before and after threefold extraction by 0.1 N HCl

		Original distribution of metal ions in polluted soil (mg metal/kg clay soil)						Metal distribution in clay after 3 x 1/2 hour extraction (cleaning) by 0.1 N HCl					
		Metal:						Metal:					
Clay	Fraction	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
Sophia	Exch	3.7	0.5	23	49	6.3	214	1.0	20	77	276	17	157
	Carb	3.5	8.7	346	201	15	300	0.0	21	0.2	2.7	1.0	0.6
	Fe/Mn-ox	4.8	220	337	1318	134	550	0.5	98	8.5	61	1.2	25
	Org	0.7	96	1005	245	42	68	0.1	159	68	70	2.0	26
	Res	5.0	363	158	539	349	181	0.0	208	105	231	106	146
Melchior	Exch	4.1	0.4	5.8	11	8.0	158	0.3	3.5	30	82	70	247
	Carb	3.5	3.7	64	46	286	2181	0.0	3.3	0.0	0.0	0.0	0.0
	Fe/Mn-ox	2.8	55	87	193	558	1678	0.1	19	3.1	17	10	59
	Org	0.5	57	721	103	287	245	0.2	64	111	46	36	88
	Res	5.2	68	163	100	736	587	0.0	73	112	68	201	505

APPENDIX IV.1
RESULTS OF VIGOROUS MIXING KINETICS EXPERIMENTS

Table IV.1.1. Metal concentrations in clay soils that were artificially polluted with one metal in kinetic extraction experiments (vigorous mixing) with 0.1 N HCl.
Ma=Maas clay soil; Rn=Rhine clay soil; Wi=Winsum clay soil.
Ck,t=metal concentration in clay at time t.

Time (min)	Ma-Cu Ck,t (mmol/kg)	Rn-Ni Ck,t (mmol/kg)	Rn-Pb Ck,t (mmol/kg)	Wi-Pb Ck,t (mmol/kg)	Wi-Zn Ck,t (mmol/kg)
0	58.62	57.91	25.44	24.23	55.84
2	31.74	58.73	4.06	4.70	16.38
2	31.52	59.55	4.52	5.00	10.85
5	30.12	57.08	3.11	4.25	10.28
5	29.07	57.67	3.16	4.28	11.34
10	27.37	55.15	2.85	4.51	8.86
10	25.97	55.95	2.45	4.00	10.28
15	24.63	54.54	3.06	3.46	9.03
15	24.52	54.35	2.67	3.83	9.44
20	24.24	54.39	2.37	3.06	7.97
20	22.79	53.31	2.57	3.45	9.45
30	21.73	52.53	2.05	2.59	7.39
30	20.22	51.32	2.17	2.93	8.86
45	18.96	51.05	2.20	2.57	6.26
45	19.18	49.89	1.91	2.82	8.49
60	18.63	49.55	1.77	2.36	6.13
60	16.60	47.96	2.01	2.70	7.08
90	15.90	47.83	2.27	2.04	5.57
90	14.13	46.14	1.80	2.82	7.48
120	12.85	46.24	1.82	2.15	5.95
120	12.77	43.88	2.05	2.19	6.87
180	11.92	44.46	2.16	2.26	6.65
180	11.61	40.50	2.02	2.39	5.34
300	9.35				
300	9.57				
420	10.70				
420	10.01				

Table IV.1.2. Metal concentrations in Sophia waste site clay soil during kinetic extraction experiments (vigorous mixing) with 0.1 N HCl.

Time [min]	Copper Ck-Cu(t) [mmol/kg]		Nickel Ck-Ni(t) [mmol/kg]		Lead Ck-Pb(t) [mmol/kg]		Zinc Ck-Zn(t) [mmol/kg]	
	exp.1	exp.2	exp.1	exp.2	exp.1	exp.2	exp.1	exp.2
0	55.92	55.92	59.00	58.70	3.65	3.49	28.61	30.21
1		26.76		54.79		3.05		21.98
3		22		55.32		2.75		20.51
5	23.97	19.84	53.10	52.87	3.18	2.5	20.41	20.05
6	23.46		53.59		2.94		19.75	
10	21.61	16.59	53.85	52.43	2.86	2.2	19.09	17.88
15	19.1		53.69		2.75		18.59	
20	19.3	13.8	53.04	50.54	2.73	1.86	18.35	17.3
30	17.42	13.32	52.22	47.74	2.54	1.85	17.03	15.83
45	16.17	11.79	49.57	46.20	2.33	1.73	15.8	15.2
60	15.49	11.64	47.56	41.13	2.3	1.61	15.29	14
90	13.03	10.18	43.29	38.70	2.17	1.45	14.85	12.34
120	13.27	9.12	35.40	35.08	2.07	1.44	14.03	12.46
180	12.18	8.41	37.78	30.25	1.84	1.34	13.08	11.78
240	12.14	8.87	31.98	28.45	1.95	1.36	12.22	11.38
300	11.62		31.22		1.8		10.64	
360		7.16		22.64		1.21		10.33
420		7.52		20.29		1.37		9.95
1200	3.75		16.22		1.25		6.04	
1260	3.84		11.52		1.2		5.3	
1320	4.75		18.60		1.22		6.1	
1340	3.87		16.38		1.17		6.31	
1360	4.2		13.76		1.27		5.78	
1380	4.41	5.29	11.85	13.26	1.2	0.94	5.35	6.72
1410		6.04		11.78		0.92		6.06
1440		5.43		14.17		1.11		6.1

Table IV.1.3. Metal concentrations in Melchior waste site clay soil during kinetic extraction experiments (vigorous mixing) with 0.1 N HCl.

Time [min]	Copper Ck-Cu(t) [mmol/kg]		Nickel Ck-Ni(t) [mmol/kg]		Lead Ck-Pb(t) [mmol/kg]		Zinc Ck-Zn(t) [mmol/kg]	
	exp.1	exp.2	exp.1	exp.2	exp.1	exp.2	exp.1	exp.2
0	6.27	6.58	3.47	3.59	10.76	12.19	136.11	162.51
1	6.07	6.62	2.9	2.98	8.25	10.91	55.26	82.66
2	4.46	6.40	2.65	2.89	5.1	9.92	44.19	64.96
5	5.8		2.83		8.33		59.84	
6	3.72		2.68		3.9		38.67	
10	3.57	4.91	2.69	2.85	3.77	6.83	31.86	51.02
20	3.52	4.39	2.74	2.81	3.58	6.03	26.96	47.25
30	3.27	3.84	2.68	2.72	3.47	4.95	26.58	44.3
45	3.22	3.60	2.59	2.66	3.42	4.55	26.98	36.15
60	3.16	3.46	2.53	2.59	3.23	4.49	26.33	41.18
90	3.09	3.20	2.48	2.52	3.1	4.23	25.62	35.57
120	2.87	3.02	2.37	2.44	2.88	3.92	20.82	33.82
180	2.84	2.94	2.43	2.41	2.89	3.7	23.2	27.85
240	2.82	2.86	2.36	2.28	2.91	3.56	20.93	30.73
360	2.76	2.76	2.27	2.25	2.63	3.47	18.25	27.14
1200	2.57		2.06		2.46		15.21	
1260	2.6	2.44	2.03	1.92	2.46	2.97	17.25	24.3
1320	2.55	2.43	2.03	1.94	2.45	2.91	15.56	22.2
1380	2.28	2.44	1.98	1.94	2.4	2.91	17.87	15.98
1440	2.48	2.44	1.97	1.95	2.36	2.89	17.07	19.37
1450	2.34	2.35	1.96	1.91	2.37	2.82	18.73	20.67
1460	2.24	2.35	2.03	1.81	2.34	2.64	17.5	15.45

APPENDIX IV.2
RESULTS OF WINSUM-Ni KINETICS AT FIVE DIFFERENT TEMPERATURES

Note: t=time; Ck(t)=Ni concentration in Winsum clay soil at time t.

Table IV.2.1. Results at 5 °C

t(min)	Ck(t) (mmol/kg)	t(min)	Ck(t) (mmol/kg)
0.00	70.10	0.00	71.41
1.40	35.91	1.00	33.96
7.00	26.73	3.00	30.91
10.30	26.30	5.00	29.60
18.70	25.44	10.00	28.96
30.80	23.35	17.60	27.11
45.00	23.06	37.70	25.49
60.00	22.34	60.20	24.39
90.00	22.51	96.60	23.94
180.40	22.12	120.00	24.02
246.00	20.30	180.20	22.98
		240.00	22.37

Table IV.2.3.Results at 60 °C

t(min)	Ck(t) (mmol/kg)
0.00	61.09
1.00	18.56
2.20	15.43
5.20	18.47
10.00	11.56
15.30	9.21
30.00	9.24
45.20	6.64
60.00	7.60
90.00	9.27
120.70	9.22
158.10	8.51

Table IV.2.2. Results at 20 °C

t(min)	Ck(t) (mmol/kg)	t(min)	Ck(t) (mmol/kg)	t(min)	Ck(t) (mmol/kg)
0.00	64.06	0.00	72.00	0.00	68.11
1.00	29.72	1.00	32.23	1.60	33.30
2.50	28.00	3.50	29.67	3.50	31.52
5.00	25.95	5.30	29.70	5.20	30.57
10.30	25.33	10.00	27.26	10.00	29.26
17.50	24.28	17.50	26.60	17.80	26.71
34.20	23.34	36.20	24.66	30.00	25.27
62.00	23.02	60.00	23.30	60.20	23.87
90.30	22.59	90.00	22.62	90.10	22.05
123.30	20.81	121.00	22.42	120.00	21.54
187.00	19.61	182.00	19.71	180.00	19.99
255.00	18.09	306.00	18.54	227.00	19.41

Table IV.2.4. Results at 40 °C

t(min)	Ck(t) (mmol/kg)	t(min)	Ck(t) (mmol/kg)
0.00	64.06	0.00	64.06
1.20	19.77	1.00	24.86
2.50	18.68	2.70	23.94
5.00	16.78	5.00	20.97
10.00	14.41	10.00	18.02
17.00	15.31	17.20	18.12
30.00	14.20	30.00	15.06
45.00	11.74	45.00	14.34
60.00	13.31	60.00	14.64
90.70	10.68	109.30	13.92
151.00	8.05	152.00	11.36
		180.00	10.87
		300.00	8.74

Table IV.2.5. Results at 80 °C

t(min)	Ck(t) (mmol/kg)	t(min)	Ck(t) (mmol/kg)
0.00	64.06	0.00	64.06
1.20	27.65	1.30	15.29
4.50	11.02	3.00	10.15
7.50	8.78	5.00	10.27
17.00	6.75	10.00	6.89
31.00	6.92	17.00	10.47
45.00	3.95	30.00	6.20
60.00	5.10	45.50	4.65
90.00	8.62	60.00	4.72
122.00	4.59	90.50	1.33
163.00	4.81	160.00	3.56
180.00	0.36		

APPENDIX IV.3
RESULTS OF FLOC KINETICS EXPERIMENTS WITH WASTE SITE SOILS IN 0.1 N HCl

t=time; Ck-Me(t)=concentration of metal Me in clay soil at time t.

Table IV.3.1. Results of floc kinetics of Sophia waste site soil

t (min)	Ck-Cu(t) (mmol/kg)	Ck-Ni(t) (mmol/kg)	Ck-Pb(t) (mmol/kg)	Ck-Zn(t) (mmol/kg)
0	59.04	42.51	2.37	20.18
2	53.27	45.08	2.47	19.54
5	39.29	43.46	2.19	16.96
15	21.40	39.29	1.86	13.67
30	13.92	36.68	1.68	11.64
60	12.62	34.79	1.61	10.98
2	51.74	45.82	2.52	19.04
5	34.61	43.94	2.34	16.17
15	17.51	40.58	1.97	13.40
30	13.53	39.13	1.84	12.17
60	11.84	36.37	1.74	11.17

Table IV.3.2. Results of floc kinetics of Melchior waste site soil

t (min)	Ck-Cu(t) (mmol/kg)	Ck-Ni(t) (mmol/kg)	Ck-Pb(t) (mmol/kg)	Ck-Zn(t) (mmol/kg)
0	18.38	11.43	8.3	77.2
2	17.69	10.69	7.20	52.70
5	15.34	9.56	5.95	35.00
15	12.36	8.47	4.70	18.90
30	11.47	8.09	4.57	16.72
60	9.96	7.26	4.24	16.85
2	18.10	11.06	7.57	56.83
5	16.76	10.27	6.84	44.02
15	14.21	9.01	5.72	24.24
30	13.09	8.26	5.36	17.72
60	12.65	7.57	5.33	-

STELLINGEN

behorende bij het proefschrift van B.J.W. Tuin

1. *Uit verouderde, verontreinigde kleigronden zijn zware metalen niet met zoutzuur te extraheren in een technologisch aantrekkelijke tijdsduur tot de zogenaamde referentiewaarde voor 'schone' grond, zonder een verregaande aantasting van het bodemmateriaal.*

   Dit proefschrift; Hoofdstuk 2.

2. *Hoewel de extractie van een recent aangebrachte nikkelverontreiniging door diffusie gelimiteerd lijkt, is reactie-limitatie aannemelijk voor extractie uit verouderde, verontreinigde kleigronden.*

   Dit proefschrift; Hoofdstuk 4.

3. *Gesuspendeerde kleideeltjes bezinken na flocculatie zódanig snel, dat extractie van metalen uit geflocculeerde kleideeltjes mogelijk is in een tegenstroomkolom op technische schaal.*

   Dit proefschrift; Hoofdstuk 5.

4. *Gezien de kinetiek van de extractie van zware metalen uit verontreinigde kleigronden, is het grootste voordeel van uitvoering van de extractie in een tegenstroomkolom, boven die in continue, geroerde vaten, de geringere concentratie metaalionen in de aanhangende vloeistof na extractie.*

   Dit proefschrift; Hoofdstuk 5 en 6.

5. *De normwaarde voor het zware-metaalgehalte van een gereinigde grond zou, behalve op het totaalgehalte, ook gebaseerd moeten zijn op een concentratie, die verband vertoont met mobiliteit of biologische beschikbaarheid van het metaal.*

   Dit proefschrift; Hoofdstuk 3.

6. *Kinetiekmodellen zoals de "Parabolic Diffusion Law" en de "Two-Constant Rate Equation", zijn niet geschikt om de kinetiek van de extractie van zware metalen uit verontreinigde kleigronden te beschrijven.*

   Sparks D.L.; Chapter 3 in: "Soil Physical Chemistry"; CRC Press, 1986.

7. *Onder invloed van waterstofsulfide (H_2S) in de omringende lucht treedt in een electrode systeem bestaande uit een koperprintplaat met een vloeistoffilm, kortsluiting op, die bij lage H_2S concentraties en lage potentiaalverschillen berust op de vorming van kopersulfide-dendrieten. Bij hogere concentraties en potentiaalverschillen berust zij echter op de vorming van zowel kopersulfide- als koper-dendrieten.*

   Steppan J.J. et al.; J.Electrochem.Soc. 132(11), 2567-2571, 1985.
   Tuin B.J.W.; M.S. Thesis, Vanderbilt University, Nashville; 1984.

8. *Flotatie uitgevoerd in een centrifugaalveld groter dan 100g, leidt tot hogere scheidingsefficiënties vanwege sterkere drainage van water uit schuim.*

   Miller J.D., Van Camp M.C.; Mining Eng., 34(11), 1575-1580, 1982.

9. *Bij modellering van aggregaatvorming kan de botsingsefficiëntie van aggregaten beter gelijkgesteld worden aan 1 dan aan de waarde, zoals berekend voor massieve bollen.*

   Higashitani R.O. et al.; J.Chem.Eng.Japan, 15(4), 299-304, 1982.
   Adler P.M.; J.Colloid Interface Sci., 81(2), 531-535, 1981.

10. *Het inzetten van "grote grazers", zoals Schotse Hooglanders, voor het onderhoud van wegbermen zou kunnen leiden tot een loodvergiftiging van deze dieren.*

11. *Het verbieden van een dankwoord in een proefschrift doet geen recht aan de wijze, waarop bijdragen van anderen aan een dergelijk werkstuk door een promovendus beleefd worden.*

12. *Na 1992 kan het aantal deelnemers aan allerlei Europese kampioenschappen fors verminderd worden.*