

**Chemical Speciation and Behaviour
of Cyanide
in Contaminated Soils**

CENTRALE LANDBOUWCATALOGUS



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Chemical Speciation and Behaviour of Cyanide in Contaminated Soils

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in de landbouw- en milieuwetenschappen
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Stellingen

1. De in de literatuur vermelde microbiologische omzetting van ijzercyanide-complexen naar vrij cyanide kan ook verklaard worden door spontane dissociatie van ijzercyanide-complexen bij de door de micro-organismen veroorzaakte lage pH en redoxpotentiaal.

K.L. Cherryholmes, W.J. Cornils, D.B. McDonald and R.C. Splinter (1985). Biological degradation of complex iron cyanides in natural aquatic systems. *In* R.D. Cardwell, R. Purdy and R.C. Bahner (eds.) Proceedings of the 7th symposium on Aquatic Toxicology and Hazard Assessment, ASTM Technical Publications no. 854, Philadelphia, 502-511.

Dit proefschrift.

2. Het belang van kinetiek in de chemische speciatie van cyanide kon voordat het in dit proefschrift beschreven onderzoek was uitgevoerd al worden afgeleid uit het zeer grote verschil in humane toxiciteit tussen oraal opgenomen vrij cyanide en ijzercyanide-complexen.

R.H. Dreisbach and W.O. Robertson (1986). Handbook of Poisoning. Appleton & Lange, Norwalk, Connecticut USA.

Dit proefschrift.

3. Het maken van een goede evaluatie van de risico's van bodemverontreiniging met cyanide is niet mogelijk zonder onderscheid te maken tussen cyanide in de vrije vorm en ijzercyanide-complexen.

Dit proefschrift.

4. Indien de toxische werking van cyanide voornamelijk berust op een snelle evenwichtsreactie met het ijzeratoom in het enzym cytochroom-oxidase, is het niet verwonderlijk dat blootstelling aan concentraties lager dan een tiende van de acuut lethale concentratie, zelfs gedurende langere tijd, geen negatieve effecten veroorzaakt.

5. Consumptie van cyanide kan de gezondheid positief beïnvloeden.

Naar aanleiding van het toevoegen van Berlijns blauw aan veevoer om opname van radioactief cesium hieruit te voorkomen.

6. Indien de voorgestelde norm voor het maximaal toelaatbare cyanidegehalte van een Nederlandse bodem zou worden toegepast op dagelijkse voeding in de tropen zou menig bord met tapioca gesaneerd dienen te worden.

A.J.A. Essers and M.J.R. Nout (1989). The safety of dark, moulded cassava flour compared with white - A comparison of traditionally dried cassava pieces in North East Mozambique. *Trop. Sci.* 29, 261-268.

R. van den Berg en J.M. Roels (1991). Beoordeling van risico's voor mens en milieu bij blootstelling aan bodemverontreiniging, integratie van deelaspecten. Rapport nr. 725201007, RIVM, Bilthoven.

7. **Gevallen van bodemverontreiniging met ijzercyanide-complexen kunnen in het algemeen beter gekarakteriseerd worden met de term "chemische blindgangers" dan met de populaire term "chemische tijdbommen".**
8. **Het beoordelen van de risico's voor uitloging van stoffen uit afvalstoffen op basis van de voorgeschreven uitloogtesten, is een riskante zaak.**
Ontwerp-bouwstoffenbesluit bodem- en oppervlaktewater-bescherming, De Staatscourant (1991) 121, 28-47.
9. **Het in een publicatie vermelden, zoals vaak gebeurt, van de naam van een gebruikt chemisch-evenwichtprogramma, terwijl een beschrijving van de gebruikte evenwichten wordt weggelaten, doet onrecht aan het relatieve belang van beide zaken voor de berekende resultaten.**
10. **Omdat een wetenschappelijke carrière voor een belangrijk deel bestaat uit het mondeling en schriftelijk overdragen van informatie, verdient onderwijs op dit gebied een belangrijke plaats in een academische studie.**
11. **Indien bij een computerprogramma functionele specificaties ontbreken, is het niet mogelijk om aan te tonen dat dit programma al dan niet goed werkt.**
12. **Naarmate de "intelligentie" van machines zich ontwikkelt, zullen de mechanismen die hieraan ten grondslag liggen geleidelijk aan samenvallen met de mechanismen die aan menselijke intelligentie ten grondslag liggen.**
D.E. Hofstadter (1979). Gödel, Escher, Bach. Basic Books, New York.
T.J. Sejnowski and P.S. Churchland (1992). Silicon Brains. Byte 17(10), 137-146.
13. **Naast bepaalde soorten micro-organismen zijn ook sommige mensen in staat om enige tijd voornamelijk van cyanide te leven.**
C.J. Knowles (1976). Micro-organisms and Cyanide. Bact. Rev. 40, 652-680.
Dit proefschrift.
14. **There's no need to be afraid of Prussian blue.**
Naar aanleiding van het schilderij met de titel:
"Who's afraid of red yellow and blue III" van B. Newman.

Stellingen behorende bij het proefschrift "Chemical speciation and behaviour of cyanide in contaminated soils", Hans Meeussen, Wageningen, 30 oktober 1992.

Abstract

Meeussen, J.C.L., 1992. Chemical Speciation and Behaviour of Cyanide in Contaminated Soils. Doctoral thesis, Wageningen Agricultural University, Wageningen, The Netherlands. 133 pages.

Cyanide is present as a contaminant of the soil on several hundred (former) industrial sites in the Netherlands. The risk for the occurrence of adverse effects on human health and the environment strongly depends on the chemical form in which cyanide is present and on the behaviour of this cyanide in soils.

The research reported in this thesis aimed to elucidate the predominant forms of cyanide in contaminated soils and the main processes which govern the behaviour of this cyanide. First an automated method of chemical analysis was developed which differentiates the two main forms of cyanide: free cyanide and hexacyanoferrate, and corrects for the presence of thiocyanate. Using this method it was established that the groundwater on former gasworks sites only contains hexacyanoferrate, although this form of cyanide is not thermodynamically stable. The decomposition kinetics of hexacyanoferrate to free cyanide were studied. In daylight complete decomposition appears to proceed within hours. In the dark it proceeds very slowly, with a half-life of hexacyanoferrate ranging from years to hundreds of years, depending on pH and redox potential. These findings were used to improve the separation of free cyanide, hexacyanoferrate and thiocyanate in chemical analysis.

The behaviour of hexacyanoferrate in soils was found to be dominated by the precipitation and dissolution of Prussian blue, a mineral occurring in several chemical forms. The exact composition and the solubility product of this mineral were determined, which enabled calculation of hexacyanoferrate concentrations in equilibrium with Prussian blue as a function of pH and redox potential. Calculations revealed that the solubility of Prussian blue ranges from completely soluble in soils with a pH > ca. 6.5 to slightly soluble in more acid soils. This causes a large difference between the mobility of cyanide in alkaline and in acid soils which was also observed in the field situation.

Additional index words: Hexacyanoferrate, Decomposition Kinetics, Prussian blue, Solubility, Determination, Speciation, Analysis

*Aan Nelleke,
Vader en Moeder,
Guus, Joosje, Victor,
Liesbeth, Steef, Inés en Vincent.*

*Wat er gebeurt met de aarde,
gebeurt met de kinderen van de aarde.
Als een man op de grond spuwt,
spuwt hij op zichzelf.*

Dit weten wij:

de aarde behoort niet aan de mens.

De mens behoort aan de aarde.

Dit weten wij:

*alles hangt samen als het bloed dat
een familie bindt.*

Alles hangt met alles samen.

Seattle, opperhoofd der Dwamish, 1854.

Woord Vooraf

Dit proefschrift zou er niet zijn geweest zonder de bijdragen van de mensen waarmee ik tijdens het onderzoek heb samengewerkt en "samengewoond". Ik wil deze plaats dan ook graag gebruiken om deze mensen te bedanken.

In de eerste plaats wil ik Wendy Lukassen bedanken. Zij heeft op een enthousiaste manier het hele experimentele gedeelte van dit onderzoek uitgevoerd. Door haar inzet en betrokkenheid hierbij is het gelukt om in betrekkelijk korte tijd een meetmethode voor de verschillende cyanidevormen te ontwikkelen, die onmisbaar was voor het verdere onderzoek.

Ook zonder Meindert Keizer zou het cyanide-onderzoek niet geworden zijn wat het nu is. Om te beginnen heeft hij het onderzoek naar het gedrag van cyanide in het verleden aangezwengeld, het voorstel voor dit onderzoek geschreven en later de rol van dagelijks begeleider op zich genomen. Daarnaast heeft hij er ook voor gezorgd dat het chemisch evenwicht-model, een belangrijk stuk gereedschap in dit onderzoek, operationeel is geworden. Ik wil hem hierbij bedanken voor de prettige samenwerking, voor het feit dat hij werkelijk op elk moment voor hulp klaar stond, en voor het vele, niet altijd even dankbare, (corrigeer-) werk dat hij tijdens het onderzoek verricht heeft.

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Erwin Temminghoff en Ivo Novozamsky wil ik bedanken voor hun assistentie op analytisch gebied, Simon Maasland voor het supersnelle timmer- en draaiwerk ("Hup daar is Simon met de waterpomptang") en discussies over oude auto's, electronica en voorzetrampen, en Erik Heij voor het leveren van tips en reserve-onderdelen voor de analyse-apparatuur. Kees Koenders wil ik bedanken voor al het extra regelwerk dat bij zo'n derde-geldstroomproject komt kijken.

Naast Rob Braam en Gerrit Boer, die in het kader van een afstudeervak aan dit onderzoek hebben meegewerkt, wil ik verder mijn "lotgenoten" Sandra Boekhold, Maarten Nederlof en Han de Wit bedanken voor hun bijdragen in wetenschappelijke, maar vooral ook in sociale zin. Verder bedank ik Sandra speciaal voor het rookvrij houden van onze kamer.

Ook alle andere medewerkers van de vakgroep Bodemkunde en Plantevoeding bedank ik voor hun bijdragen aan dit onderzoek en aan een gezellig verblijf op de vakgroep.

Ten slotte wil ik Nelleke bedanken, die me op sleeptouw nam wanneer ik het wat minder zag zitten (ook vaak op de fiets met wind tegen, of hardlopend door het Renkumse bos), en er voor zorgde dat ik geen computer-ogen kreeg.

Hans Meeussen
Renkum, augustus 1992.

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Chapter 1

General Introduction

General Introduction

In this chapter several important properties of cyanide are described, including the occurrence of cyanide in different chemical species, the toxicity of these species, and the presence of cyanide in the environment due to natural and industrial sources. The main aims of this research and the outline of the thesis are given in the final section of this chapter.

Chemical speciation of cyanide

Cyanide occurs in many diverse organic and inorganic forms which have in common that they all contain a cyano group ($-C \equiv N$) as part of their molecule. Based on their physicochemical properties these forms can be classified in four different groups (1):

- (1) *Free cyanides*, $HCN(aq)$, $HCN(g)$ and CN^-
(volatile and toxic).
- (2) *Simple cyanides*, like KCN or $AgCN$,
(of which KCN readily dissolves in water to form CN^-
and K^+ , and $AgCN$ is only slightly soluble).
- (3) *Complex cyanides*, like $Fe(CN)_6^{3-}$, $Co(CN)_6^{2-}$ and $Zn(CN)_4^{2-}$
(dissociation to free cyanide depends on kinetic and
thermodynamic stability, $Fe(CN)_6^{3-}$ and $Co(CN)_6^{2-}$
are more stable than $Zn(CN)_4^{2-}$).
- (4) *Organic cyanides*, or nitriles,
(cyanohydrins, cyanogenic glucosides etc.).

Of these groups the free cyanides are considered to be the toxic species (2). The toxicity of the other groups mainly depends on the possibility of dissociation to free cyanide and varies from equally as toxic as free cyanide (e.g. simple cyanides like KCN) to slightly toxic (e.g. the stable metal cyanide complexes like the hexacyanoferrates $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$). In the case of the organic cyanides the possibility of releasing free cyanide under certain

conditions strongly depends on the type of molecules and on the way the cyanide is bound. This varies widely between the different types of organic cyanides, and therefore their toxicity cannot be generalized (2).

Cyanide toxicity

The toxicity of cyanide is doubtlessly its best known property. It is caused by the tendency of cyanide to form complexes with the metal ions present in enzymes. Formation of such complexes prevents further functioning of the enzyme involved. An example of an enzyme sensitive to this complexation is cytochrome oxidase, which plays a key role in the oxidative phosphorylation (the source of energy for cells) in a wide range of organisms, from plants to mammals. Blocking of this enzyme by cyanide immediately kills the cells involved, which causes cyanide to be toxic for most organisms (3).

Cyanide is known to be one of the most rapidly acting poisons in mammals (4). In the free form it can be adsorbed by the skin as well as by inhalation. The acute toxicity of cyanide for human beings is relatively high, with an immediate lethal dose for an adult person of ca. 1-2 mg/kg (3,4). However, because all higher plants and animals have the capacity to metabolize sub-lethal doses of cyanide, it is possible for them to ingest doses of cyanide only slightly less than the lethal dose over extended periods of time without adverse effects (4).

Natural sources of cyanide

Cyanides are introduced into the environment from several natural sources. They are produced by a wide variety of micro-organisms including fungi, bacteria, actinomycetes and algae (5). Furthermore, over 800 species of plants are known to synthesize cyanide, mainly in the form of cyanogenic glucosides (6). Well known examples of such plants are sorghum and Lima beans, and especially in their kernels: cherry, apple, peach and apricot. Due to these sources cyanide occurs naturally in low concentrations in soils and water, and in plants as well.

Apart from the "outdoor" environment cyanide is also naturally present in the blood of mammals. Concentrations found in human blood vary from ca. 75 $\mu\text{g l}^{-1}$ (non-smokers) to 175 $\mu\text{g l}^{-1}$ (smokers) (7).

Fate of cyanide in the environment

Because many species of bacteria, fungi, algae and also of plants are able to utilize cyanide and degrade it to harmless substances like CO_2 , NO_3^- , SCN^- and OCN^- (8,9), cyanides do not persist or accumulate in soils under natural

conditions. The relatively small amounts of cyanide produced by various organisms are readily attacked by soil organisms, which use cyanide as a source for carbon or nitrogen or both (5).

Anthropogenic sources of cyanide

Doubtlessly the oldest application of cyanide is as a dye, in the form of Prussian blue ($\text{Fe}_4\text{Fe}(\text{CN})_6)_3$). It is still used in paint and ink in this way. Prussian blue gave cyanide (deduced from the Greek word for blue) its name because none of the other cyanide species is blue (10). A more important application nowadays is its use as a complexing agent in several industrial processes like electroplating, extraction of precious metal ores and processing of photographic material (2). The cyanide-bearing wastewater of the industries involved has frequently caused contamination of the soil. In the Netherlands especially the sites of electroplating industries are often contaminated with cyanide (11).

Another important process in which cyanide was involved, although as a waste product this time, was the production of coal gas. This gas was produced by the destructive distillation of coal and consisted mainly of H_2 , CH_4 and CO . Gas for domestic use was produced in this way in local gas works from the middle of the last century until the 1960s. The use of this coal gas declined with the increasing availability of natural gas. It contained up to 0.15% $\text{HCN}(\text{g})$ which was formed from nitrogen-bearing substances in the coal during the distillation. Prior to distribution of this gas the $\text{HCN}(\text{g})$ was removed. This was done by filtration through iron-bearing soil material, the so-called bog ore, which was found in the north-eastern part of the Netherlands. The cyanide reacted with the iron in this material to form Prussian blue. When the material was saturated with cyanide, it contained up to 10-15% of cyanide. In the beginning it was sold as a raw material for the dyeing industries. But due to the abundance of the material most of it probably ended as waste material discarded nearby the gas plants.

Due to these activities, there are 234 so-called former gasworks sites present in the Netherlands which, without exception, are seriously contaminated with cyanide in the form of Prussian blue (11). The situation in the Netherlands might well reflect the situations in many other industrialized countries, as illustrated by the 152 seriously cyanide-contaminated gasworks sites found by an inventory made in New York State, USA (12).

Chemical determination of cyanide

In this research considerable attention has been paid to the chemical determination of cyanide and, in particular, to the differentiation between

different types of cyanide or the chemical speciation of cyanide. The chemical speciation of cyanide is especially important because of the different properties shown by the existing species.

Classically free cyanide is determined spectro-photometrically after a manual acidic distillation procedure. Differentiation between species, especially between free and complex cyanide, was made by applying different distillation conditions (different pH), and comparing the results. However, because the transition of complex to free cyanide depends strongly on kinetics and irradiation with light, as will be discussed later, the measurements were time consuming and the results inaccurate and not very reproducible. In order to determine total cyanide concentrations, complexed cyanide has to be decomposed under fairly rigorous conditions. However, these conditions can also cause the decomposition of free cyanide or even the formation of free cyanide from of nitrogen-bearing substances. Existing methods of analysis therefore had serious drawbacks and could not be applied successfully for our purpose.

Aim and outline of this thesis

The major aim of this research was to elucidate the main aspects of the chemical behaviour of cyanide in soils, in order to enable better evaluation of the possible hazards caused by the hundreds of contaminated soil sites.

The first step in this research was to obtain information about the chemical speciation of dissolved cyanide. This was especially important because of the different toxic, chemical and physical properties of the species involved. A method of analysis was developed to study the speciation of dissolved cyanide (chapter 2). It enables differentiation between the most important cyanide species, the results of which are presented in chapter 3. Using the new insights gained especially in the dissociation kinetics of hexacyanoferrate (or iron cyanide complexes), an improved method was developed for the separation of free cyanide from thiocyanate and hexacyanoferrate prior to chemical analysis (chapter 4).

In chapter 5 the interaction between hexacyanoferrate and the soil solid phase was found to be governed by equilibrium with a mineral phase. In chapter 6 the composition and the solubility product of this mineral (Prussian blue) are determined. In chapter 7 the mobility of cyanide in the field is compared with the assumed mobility based on equilibrium with Prussian blue. Finally, in chapter 8 the results of this research are evaluated with respect to their possible implications for environmental policy.

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**Spectrophotometric Determination of Total
Cyanide, Iron Cyanide Complexes, Free Cyanide
and Thiocyanate in Water by a Continuous-flow
System**

The Analyst 114, 959-964 (1989)

with Erwin J.M. Temminghoff,
Meindert G. Keizer and
Ivo Novozamsky

Spectrophotometric Determination of Total Cyanide, Iron Cyanide Complexes, Free Cyanide and Thiocyanate in Water by a Continuous-flow System

A combination of three automated determinations, has been developed to determine total cyanide, free cyanide [i.e., $\text{HCN}(\text{aq}) + \text{CN}^-$], iron cyanide complexes and thiocyanate. The methods are based on a continuous flow technique, combined with spectrophotometric detection, and have a detection limit of $0.6 \mu\text{g l}^{-1}$. The distinction between iron cyanide complexes and free cyanide plus thiocyanate is made by UV irradiation and distillation with citric acid. The distinction between free cyanide and thiocyanate was made by masking free cyanide with formaldehyde. Rapid and complete recovery of iron-cyanide complexes was obtained; the interference by nitrate was minimised. Shielding samples from diffuse daylight appeared to be necessary to prevent rapid photolysis of the iron cyanide complexes.

Keywords: *Cyanide determination; hexacyanoferrate determination; thiocyanate determination; continuous flow technique; spectrophotometry*

Introduction

The differences in toxicity and environmental behaviour between free cyanide [i.e., $\text{HCN}(\text{aq}) + \text{CN}^-$], iron cyanide complexes [$\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$] and thiocyanate make it desirable to distinguish these species analytically.

Small amounts of cyanide are usually determined after distillation by spectrophotometric methods based on a method first described by Aldridge¹. In this method the CN^- ion is first halogenated (with bromine) whereafter it reacts with a mixture of pyridine and benzidine to form a strongly coloured polymethine dye. Modifications of this method are based mainly on the replacement of pyridine, benzidine or bromine with less toxic equivalents. The most important modifications are the use of isonicotinic acid instead of pyridine², the replacement of benzidine by pyrazolone³ or barbituric acid⁴ and the replacement of bromine by chloramine-T. Some of these methods are used in continuous-flow systems^{5,6}.

The rate of cyanide recovery from iron cyanide complexes after distillation depends on distillation conditions. The distinction between these complexes and free cyanide is made by varying these conditions so that in one instance only free cyanide and in the other both free cyanide and iron cyanide complexes are decomposed and distilled. This strategy is followed in both manual and automated methods.

In the manual procedures, which are used as standards^{7,8}, the total decomposition of iron cyanide complexes is achieved by prolonged boiling of samples under acid conditions. Different acid mixtures such as HCl, H₃PO₄/H₃PO₂ or H₂SO₄, sometimes with addition of MgCl₂ or Cu₂Cl₂ are used^{4,7,8}.

Milder distillation conditions (e.g., pH 4 and room temperature) are employed in order to minimise decomposition of these complexes. Further, dissociation of iron cyanide complexes is reduced by enhancing formation of their precipitates by adding zinc or lead salts^{9,10}.

Results of these methods show that it is difficult to distil over all the free cyanide without partly decomposing the iron cyanide complexes and that to obtain complete recovery of iron cyanide complexes a time-consuming distillation under vigorous circumstances is needed. These circumstances can however, cause decomposition of thiocyanate, which is not distilled, to yield cyanide.

In the automated method proposed by Goulden *et al.*⁵ the decomposition of iron cyanide complexes is accelerated by the use of UV irradiation. Decomposition thus proceeds much faster, but is, under the experimental conditions, not complete⁴. Moreover with this treatment also thiocyanate is decomposed to yield cyanide and sulphide. Without UV irradiation, not only free cyanide but also about 20% of the iron cyanide complexes are distilled. These results make accurate determination of the amounts of free cyanide and iron cyanide complexes impossible.

The aim of this work was to develop an automated method without the drawbacks mentioned above. For this purpose three independent determinations were optimised. (A) The total concentration of cyanide plus thiocyanate was determined spectrophotometrically by a modification of Aldridge's method after destruction of the sample with UV irradiation and subsequent distillation with citric acid at pH 3.8. (B) The concentration of free cyanide plus thiocyanate was determined with the same spectrophotometrical method but without previous UV irradiation and distillation. (C) The thiocyanate concentration was determined with method B after masking free cyanide with

formaldehyde. From the results of these three methods it was possible to calculate the total concentration of cyanide (A - C), and the distribution of free cyanide (B - C) and iron cyanide complexes (A - B).

Experimental

Apparatus

A Skalar 5101 continuous-flow system, equipped with an UV irradiation unit, a closed distillation system and a spectrophotometric detector was used. The sampling rate was 22 samples per hour and the sample to wash ratio was 1:1. Other conditions were as follows: UV irradiation time, approximately 3 min; chlorination time, 1.5 min; and colour development time, approximately 2.5 min at 40 °C.

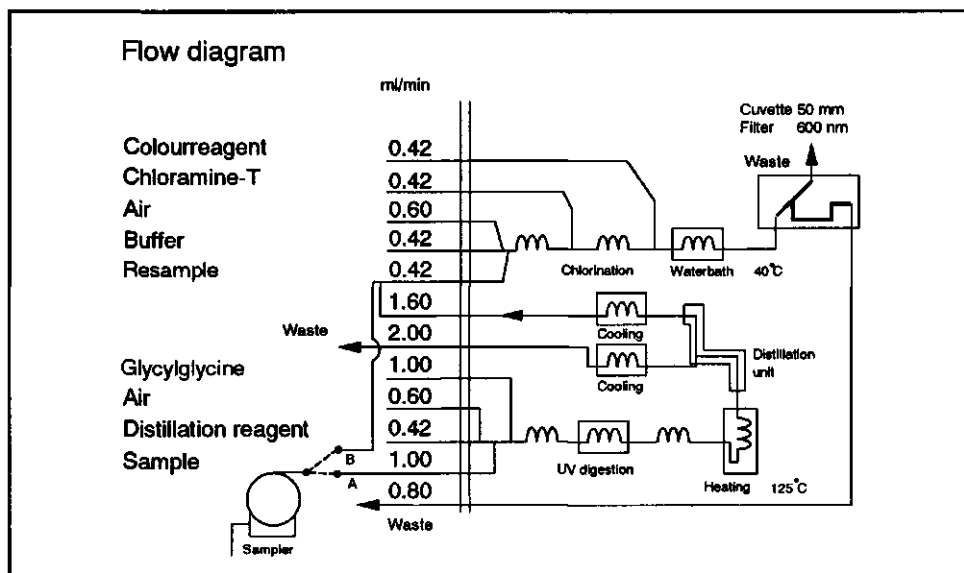


Figure 1. Schematic representation of the apparatus used

Reagents

All chemicals used were of analytical-reagent grade.

Distillation reagent

Dissolve 42.02 g of citric acid in 600 ml of water. Add 200 ml of 1 M sodium hydroxide and dilute to 1000 ml. Add 259.5 ml of 0.1 M hydrochloric acid to 240.5 ml of this solution. Correct pH to 3.8 if necessary with 1 M sodium hydroxide or hydrochloric acid. Add 1.08 ml of concentrated (12 M) hydrochloric acid. The extra amount acid will compensate for the amount hydroxide in samples at pH 12.

Glycylglycine solution

Dissolve 40.0 g of glycylglycine in 100 ml of water. Dilute this solution to 1000 ml with water.

Buffer solution (pH 5.2)

Dissolve 2.3 g of sodium hydroxide in 500 ml of water. Add 20.5 g of potassium hydrogen phthalate in this solution and make up to 1000 ml with water. Adjust the pH if necessary to 5.2 with 1 M sodium hydroxide or hydrochloric acid. Add 1 ml of wetting agent (brij 35, Skalar chemicals) shortly before use. (After addition of wetting agent, the solution is only stable for about 2 d).

Chloramine-T solution

Dissolve 2.0 g of chloramine-T in 100 ml of water and dilute to 1000 ml with water.

Colour reagent

Dissolve 8.8 g of sodium hydroxide in 500 ml of water. To this solution add 16.8 g of 1,3-dimethyl barbituric acid and 13.6 g of isonicotinic acid and dilute to 1000 ml with water. Correct pH if necessary to 5.2 with 1 M sodium hydroxide or hydrochloric acid.

Formaldehyde reagent

Dilute 10 ml of 37% formaldehyde to 100 ml with water.

Standard solutions

Stock solutions of potassium cyanide, potassium hexacyanoferrate(III), potassium hexacyanoferrate(II) and potassium thiocyanate, containing 1000 mg l⁻¹ of cyanide were prepared in 0.01 M sodium hydroxide solution. The concentrations of these solutions were checked by measuring the potassium concentrations. From these solutions, mixtures with different ratios of the above

mentioned cyanide species were prepared. Standard cyanide solutions were made from the potassium cyanide solution in the concentration range 25-200 $\mu\text{g l}^{-1}$ in 0.01 M sodium hydroxide. These solutions were analysed to establish a calibration graph for each of the three methods.

All reagents except the buffer reagent are stable for at least 1 week when stored at 5 °C and shielded from light.

Procedure

To determine the concentration of total cyanide, free cyanide, iron cyanide complexes and thiocyanate in a sample, three independent determinations are necessary. (A) The total concentration of cyanide plus thiocyanate is measured after UV irradiation and distillation. The sample must be inserted at position A (Fig. 1) of the apparatus. (B) The concentration of free cyanide plus thiocyanate is measured without previous distillation and UV destruction. The sample must be inserted at position B (Fig. 1). (C) The concentration of thiocyanate is measured with method B after masking free cyanide with formaldehyde. This is performed by adding 50 μl 3.7% formaldehyde to a 10-ml sample and either leaving the sample overnight or heating it for 15 min at 50 °C.

With all three methods the samples, at pH 12, are measured against standard solutions of potassium cyanide. It is important to shield samples for light, not only during storage, but also during all treatments prior to the determination. In this work the automatic sampler was covered with a black plastic hood.

Results and Discussion

Spectrophotometric determination of cyanide and thiocyanate

The spectrophotometric method used here is basically the same as proposed by Nagashima². The two major differences are the use of 1,3-dimethyl barbituric acid instead of barbituric acid, and the use of a 0.1 M phthalate instead of a 1 M phosphate buffer. 1,3-Dimethyl barbituric acid has previously been used in combination with pyridine¹¹ and appears to give good results in combination with less toxic isonicotinic acid.

The absorption spectrum of the complex formed by the reaction of cyanide with 1,3-dimethyl barbituric acid has a maximum at 600 nm. Colour development is faster and more intensive than with barbituric acid (fig. 2), resulting in a faster, more sensitive determination.

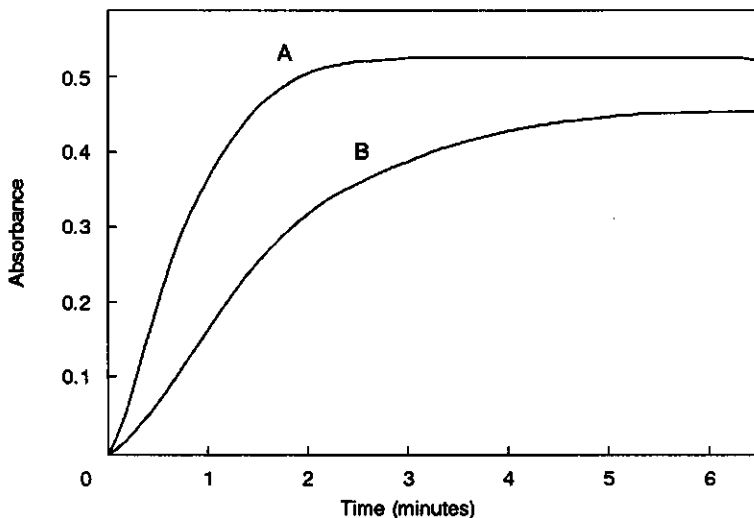


Figure 2. Rate of colour development of $100 \mu\text{g l}^{-1} \text{CN}^-$ with A, 1,3-dimethyl barbituric acid and B, barbituric acid

To prevent loss of HCN(aq) and to optimise the reaction between formaldehyde and free cyanide, as described below, the pH of samples must be adjusted to 12. However, for our purpose the rate of the chlorination reaction for CN^- and SCN^- should be the same: this the situation at pH values below 5.2¹², whereas at higher values the reaction rate for thiocyanate is lower than for cyanide resulting in a lower sensitivity for the former. To maintain this pH with a phosphate buffer, a high concentration (1 M) is used². A phosphate buffer, however, is not very efficient at this pH and, further, we have found that precipitates are sometimes formed. Therefore, other buffer systems were tried; phtalate was chosen as the most suitable, and it was capable of maintaining pH 5.2 at a concentration of 0.1 M.

Masking free cyanide with formaldehyde

In order to measure only thiocyanate with method C, free cyanide was masked with formaldehyde⁷ in samples adjusted to pH 12. In practice 50 μl 3.7% formaldehyde are sufficient to cover concentrations up to 250 $\mu\text{g l}^{-1}$ cyanide in 10 ml, without any effect on the concentration of thiocyanate measured.

Distillation

The effects of temperature and pH on the distillation were investigated. Results for the temperature dependence are shown in Fig. 3. The adverse effect of a higher temperature is due to the influence of dilution caused by the extra amount of water that is distilled. At 125 °C slightly more fluid is distilled than needed by re-sampling for the spectrophotometric measurement. Under the conditions used, cyanide is quantitatively distilled below pH 6.

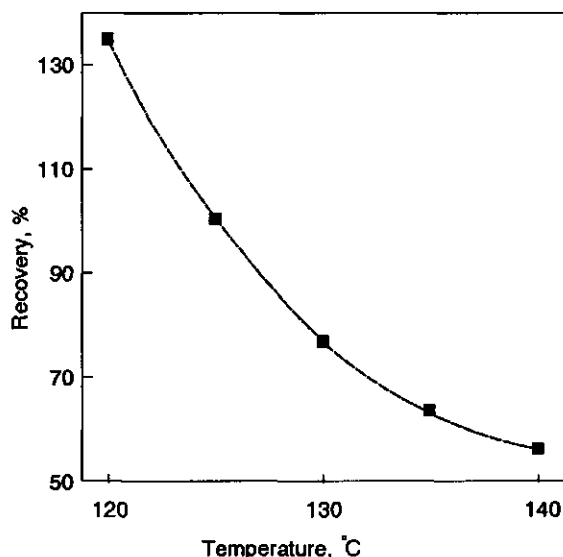


Figure 3. Effect of distillation temperature on cyanide recovery. Recoveries of 100 $\mu\text{g l}^{-1}$ CN⁻, added as KCN, were compared with recovery at 125 °C (100%)

Decomposition of iron cyanide complexes

For total cyanide determination iron cyanide complexes must be decomposed before distillation. In the method described by Goulden *et al.*⁵ UV irradiation in combination with a pH of less than 1 is used for this purpose. According to

Prober *et al.*⁶ who used the same method, this decomposition appears not to be complete under the specified conditions. These findings are confirmed by our results with this method, which gave recoveries of iron cyanide complexes of about 85% (Table 1).

However, the total decomposition of these complexes appeared to be possible under less vigorous circumstances, according to the results of the following experiment. It has been reported^{8,13}, that samples containing iron cyanide complexes placed in direct sunlight, undergo photolysis at a measurable rate. In order to determine the storage conditions, the rate of photodecomposition in diffuse daylight (laboratory conditions) had to be quantified. For this, samples containing 100 $\mu\text{g CN l}^{-1}$ as hexacyanoferrate(III) were adjusted to pH 12 (the usual practice during storage and pre-treatment for analysis), and exposed to diffuse daylight. Free cyanide was then measured after various times (Fig. 4). After 4 days the iron cyanide complexes were decomposed completely. The initial decomposition rate at this pH equals ca. 2.5% per hour. This complete decomposition could have been caused by the lowering of the activities of Fe^{2+} and Fe^{3+} by hydrolysis. The observed variation in reaction rate might be due to small differences exposure to light. The decomposition appeared not to be reversible to a measurable extent after 4 days.

Table 1. Recovery of iron cyanide complexes and interference of nitrate on the distillation according to Goulden *et al.*⁵

Sample	Concentration of cyanide added ($\mu\text{g l}^{-1} \text{CN}$)	Concentration of cyanide measured ($\mu\text{g l}^{-1} \text{CN}$)
68 $\mu\text{g l}^{-1} \text{Fe}(\text{CN})_6$	50	42
136 $\mu\text{g l}^{-1} \text{Fe}(\text{CN})_6$	100	86
203 $\mu\text{g l}^{-1} \text{Fe}(\text{CN})_6$	150	127
271 $\mu\text{g l}^{-1} \text{Fe}(\text{CN})_6$	200	169
50 $\text{mg l}^{-1} \text{NO}_3^-$ + 100 mg l^{-1} humic acid	0	10
50 $\text{mg l}^{-1} \text{NO}_3^-$ + 50 g l^{-1} citrate	0	45

The results of this experiment were used to ascertain the optimum conditions for the automated determination. It is however, not possible to obtain complete decomposition of iron cyanide complexes, by simply bringing the sample at pH 12 during UV irradiation, because at pH values above *ca.* 4, UV irradiation destroys the cyanide⁴. An alternative way of achieving low Fe activities below pH 4, is the addition of complexing agents. Citrate has been used for this purpose, because of its good solubility, its stability under UV irradiation and the high stability of its iron complexes at low pH. At pH 3.8, a concentration of 13 g l⁻¹, citrate improved the decomposition of iron cyanide complexes exposed to UV irradiation. This decomposition was found to be complete when 16 g l⁻¹ of citrate, or more, were present in the distillation reagent.

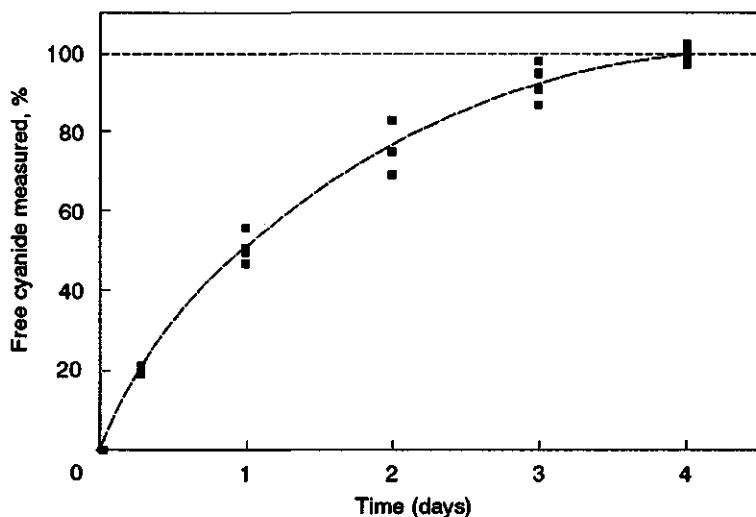


Figure 4. Rate of photodecomposition of 100 $\mu\text{g l}^{-1}$ of the iron cyanide complexes in diffuse daylight at pH 12

Recoveries

Samples containing different mixtures of cyanide species were analysed by the three methods (Table 2). The results obtained with method A show an equal recovery for all three cyanide species within 2%. The results of method B show an equal sensitivity for thiocyanate and free cyanide. Iron cyanide complexes give a response less than 2% when stored dark at pH 12. The results of method C show that the masking free cyanide with formaldehyde is very complete without influencing the sensitivity for thiocyanate.

Table 2. Recoveries obtained for the various cyanide species with the different methods

Cyanide added/ $\mu\text{g l}^{-1}$			Cyanide detected/ $\mu\text{g l}^{-1}$			Cyanide calculated/ $\mu\text{g l}^{-1}$		
Species			Method			Total	Free	$\text{Fe}(\text{CN})_6$
CN	$\text{Fe}(\text{CN})_6$	SCN	A	B	C	A-C	B-C	A-B
50			50	51	0	50	51	-1
100			99	100	1	98	99	-1
200			203	198	1	202	198	4
	30		29	1	0	28	1	28
	50		50	2	0	50	2	48
	100		98	2	1	97	1	97
	200		195	1	0	195	1	195
		30	31	33	32	-1	1	-2
		50	53	54	52	1	2	-1
		100	98	104	105	-7	-1	-7
		200	198	204	206	-6	-2	-8
50	50	50	152	103	53	99	50	49
	50	50	101	53	52	49	1	48
50		50	103	101	52	51	49	2
50	50		102	52	0	102	52	50
	30	100	127	105	104	23	1	23
30		100	127	131	104	23	27	-4
30	100		131	30	0	131	30	1
100	30		131	103	0	131		28
							103	

Interferences

Although the influence of most interfering substances is less after distillation, the UV irradiation used in method A, causes other substances to interfere. Ultraviolet irradiation will cause oxidation of organic substances by nitrate and nitrite to yield cyanide. In this method citrate is present as a potential reducing agent. Without precautions 5 mg l^{-1} nitrate will therefore give a response equal to that of 0.1 mg l^{-1} cyanide. Under the same experimental conditions, nitrite gives a response of about 20 times that of nitrate. This could be an indication that nitrite is the reactive species.

Table 3. Levels of interference for various substances with 100 $\mu\text{g l}^{-1}$ of cyanide

		Cyanide measured/ $\mu\text{g l}^{-1}$		
Interfering substance	Added as	Amount added/mg l^{-1}	Method	
			A	B and C
SO_4^{2-}	Na_2SO_4	1	100	
		10	99	
		100	97	
		1000	98	
SO_3^{2-}	Na_2SO_3	1	96	94
		10	59	10
S^{2-}	Na_2S	1	101	100
		5	103	99
		10	107	101
		15	110	102
		100	129	
NO_2^-	NaNO_2	1	100	100
		5	107	99
		10	112	99
		25	132	102
NO_3^-	NaNO_3	1	100	100
		10	101	101
		100	104	100
		1000	114	99
CO_3^{2-}	Na_2CO_3	1	101	
		10	104	
		100	125	
		1000	206	
Ca^{2+}	CaCl_2	1	100	99
		10	100	101
		100	100	100
		1000	103	102
Humic acid		100	102	101
		1000	105	

The formation of cyanide does not only occur under the conditions proposed here, but also under those used by Goulden *et al.*⁵ where nitrate and an organic substance (citrate, humic acid) are added (Table 1).

If nitrite is indeed the reactive form, nitrate as and nitrite interference could be reduced by masking nitrite. The addition of sulfamic acid, as described by Csikai and Barnhard¹⁰, is not possible because sulfamic acid is destroyed under UV irradiation to yield cyanide. Therefore, an alternative approach was required. The addition of glycyglycine, a substance able to form diazo compounds after reaction with nitrite, was tried. It was found that 17 g l⁻¹ glycyglycine, added before UV irradiation, reduced the response for 50 mg l⁻¹ nitrate to less than that for 0.005 mg l⁻¹ cyanide. The interference from 5 mg l⁻¹ of nitrite was reduced from a response equivalent to 2 mg l⁻¹ cyanide to a response equivalent to only 0.007 mg l⁻¹ of cyanide.

In addition to nitrate - nitrite, the total cyanide method is also relatively sensitive for interference by sulphite and carbonate (Table 3). However, this was not a problem, analysing soil solutions.

The colorimetric reaction between cyanogen chloride and isonicotinate is a relative specific reaction which is subject to very few interferences¹⁴. The results of testing the influence of the most common substances on the measurement of 100 µg l⁻¹ CN⁻ are shown in Table 3. Because none of the interfering substances reacted with formaldehyde, the results for method B and C are equivalent. Sulphide, a known interferent in this method, gives no interference up to 5 mg l⁻¹, and a positive interference over the range 10-100 mg l⁻¹.

Analytical performance

The detection limit (LOD), defined as 3 times the uncertainty (standard deviation) of ten measurements of the analytical blank with the proposed system was found to be 0.6 µg l⁻¹ CN⁻. The quantification limit, defined as ten times the standard deviation of the analytical blank, was 2 µg l⁻¹ of cyanide.

Repeatability, obtained from ten replicate analyses of a solution containing 100 µg l⁻¹ cyanide, was 1%. The absorbance appeared to be proportional to the concentration in the range 1-250 µg l⁻¹ of cyanide.

The distillation in method A and the presence of formaldehyde in method C had no influence on the sensitivity or on the standard deviation of the measurements. The analytical performance of the three methods therefore is equal.

Conclusions

The automated method proposed here, allows accurate determination of low cyanide concentrations, and can readily distinguish between free cyanide,

thiocyanate and iron cyanide complexes. The combination of UV irradiation and citric acid as the complexing agent results in rapid and complete decomposition of iron cyanide complexes.

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Chapter 3

**Chemical Stability and Decomposition Rate of
Iron Cyanide Complexes in Soil Solutions.**

Environmental Science & Technology 26(3), 511-516 (1992)

with Meindert G. Keizer and
Frans A.M. de Haan

The Chemical Stability and Decomposition Rate of Iron Cyanide Complexes in Soil Solutions.

In order to improve the assessment of the bioavailability and behaviour of cyanide in the environment, the speciation of dissolved cyanide was studied under pH and redox conditions relevant to soil and groundwater environments. The partition of cyanide over free cyanide [HCN(aq) + CN⁻] and iron cyanide complexes [or hexacyanoferrates, e. g. Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻] at thermodynamic equilibrium was calculated as a function of pH and redox potential. These calculations show that the free cyanide form will predominate at chemical equilibrium in the soil. In groundwater from sites contaminated with cyanide, however, only complexed cyanide was found, indicating that the speciation of cyanide is determined not by chemical equilibrium but by decomposition kinetics. In daylight, iron cyanide complexes appeared to decompose rapidly (ca. 8%/h). In the dark the rate of decomposition appeared to be much slower and was proportional to the fraction of hexacyanoferrate present as HFe(CN)₆³⁻ and H₂Fe(CN)₆²⁻. The decomposition rates of both species were determined as a function of temperature and used to model decomposition kinetics. Good predictions were made of decomposition rates under various pH and redox conditions.

Introduction

Cyanide is a highly toxic chemical which commonly occurs as an industrial contaminant of soils. Although cyanide is produced in small amounts by many different organisms (1), it reaches toxic levels in the environment solely because of human activities. Cyanide is used in several industrial processes because of its ability to form stable complexes with a range of metals. It was and still is used for this purpose in the mining industry, the metallurgical industry and the photographic industry. It used to be produced in large quantities in coal gasification plants where it was removed as an unwanted component from the gas produced. The soil on the sites of such industries is commonly contaminated with cyanide.

The threat to human health and the environment posed by such locations greatly depends on the toxicity of cyanide and on its physicochemical behaviour, both of which are strongly related to its chemical speciation. The distribution over free cyanide [HCN(aq) and CN⁻] and iron cyanide complexes [or hexacyanoferrates, e.g. Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻] is especially important. In its free form cyanide can be volatile [HCN(g)], is biodegradable (2,3), and is much

more toxic than cyanide complexed with iron. The complexed forms will interact more with the soil solid phase because of their ionic nature and their ability to precipitate. This may have a great impact on transport rates in soils.

Cyanide is mainly disposed of in the form of dissolved iron cyanide complexes or iron cyanide minerals [e. g. $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$]. In the Netherlands, hundreds of former gasworks sites are contaminated with large amounts of iron cyanide minerals which cause high concentrations of cyanide in the groundwater. The partition of dissolved cyanide over the free and the complexed form is in the first place determined by the thermodynamic and kinetic stability of iron cyanide complexes. These complexes are generally considered to be extraordinarily stable and are even called kinetically inert (4). To be able to determine the cyanide chemically these complexes have to be broken down. The usual techniques are irradiation with ultraviolet light or a treatment with boiling acid (5-7). Less rigorous, but much slower, ways to decompose these complexes are illumination with visible light or the recently reported microbiologically mediated decomposition (8). However, no data are available about the thermodynamic stability or spontaneous decomposition rates of these complexes under pH and redox conditions found in soils [pH ranging from ca. 3.5 in acidic to ca. 8.5 in alkaline soils and pe ranging from ca. -4 in reduced to ca. 12 in oxidized soils (9)].

Available calculations of the thermodynamic stability of iron cyanide complexes in industrial waste water show that this stability greatly depends on the pH and the total cyanide concentration (10). Tauchnitz et al. looked at cyanide concentrations of 0.75-6 M, which are much higher than those found in contaminated groundwater. They ignored the effect of the redox potential. Therefore their results cannot be used to represent the speciation of cyanide in soil solutions.

Our initial aim was to elucidate the thermodynamic stability of iron cyanide complexes under the pH and redox conditions found in soils, and to find out how this stability is affected by changes in these parameters. To do this, we calculated the chemical equilibrium situation for different values of these parameters. But the results of these calculations did not agree with the speciation of cyanide we measured in samples of groundwater from contaminated sites. This suggests that cyanide speciation is not governed by thermodynamic equilibrium but by the kinetics of the slow decomposition of iron cyanide complexes. We decided to pursue this line of research further and to quantify the decomposition rate of iron cyanide complexes as a function of the major soil parameters (i.e., the pH, the pe and the temperature) that determine that rate.

Experimental Section

Chemical equilibrium calculations

A computer model based on MINEQL (11) was used to calculate the cyanide and hexacyanoferrate speciation in aqueous solutions. The input required consists of: total amounts or activities of the components involved, relevant expressions for the chemical equilibria of the species concerned with their equilibrium constants and the ionic strength. The selected components are: CN^- , Fe^{3+} , H^+ , Ca^{2+} , K^+ and e^- . The equilibrium constants used were selected from the literature and listed in table I. All equilibria listed in this table were used to calculate the speciation of cyanide. The Fe^{3+} activity was assumed to be controlled by equilibrium with solid $\text{Fe}(\text{OH})_3$ (reaction 15). $\text{Ca}(\text{t}) = 5 \text{ mM}$; and $\text{K}(\text{t}), 1 \text{ mM}$. Calculations were done at an ionic strength of 0.01 M with different concentrations of $\text{CN}(\text{t})$ and activities of e^- and H^+ .

The speciation of hexacyanoferrate, assuming no decomposition of these complexes into Fe^{3+} and CN^- was calculated with $\text{Fe}(\text{CN})_6^{3-}$, H^+ , Ca^{2+} , K^+ , and e^- as components. For that purpose the equations involving $\text{Fe}(\text{CN})_6$ complexes (reactions 2-14, table I) were modified in accordance with reaction 3. In this case reactions 1, 2 and 15 are irrelevant. The speciation of hexacyanoferrate was calculated using different values for $\text{Fe}(\text{CN})_6(\text{t})$, $\text{Ca}(\text{t})$, $\text{K}(\text{t})$, p_e , pH and ionic strength. (See Results and Discussion).

Determination of cyanide speciation in contaminated groundwater

At three locations in the Netherlands (A-C) contaminated with cyanide compounds the speciation of cyanide in the groundwater was measured. Samples were taken from bore holes with a suction pump and immediately stored in black bottles to protect them from light. All bore holes were emptied the day before sampling. Oxidation of the samples was minimized by filling the sample bottles completely and by carrying out the measurements within 1 day after sampling. The samples were analysed for E_h (redox potential) and pH , and after filtration over a $0.45\text{-}\mu\text{m}$ filter for $\text{Fe}(\text{t})$, $\text{CN}(\text{t})$, and free cyanide.

Decomposition Experiments

The rate and mechanism of the decomposition of iron cyanide complexes were studied by measuring the amounts of free cyanide in $\text{K}_4\text{Fe}(\text{CN})_6$ solutions formed after different reaction times. In order to estimate the permissible illumination time during sample treatment, the decomposition rate in diffuse daylight was determined first (experiment A). The other experiments were done in the dark at a combination of different pH and different redox conditions

(experiment B), at different temperatures (experiment C) and on addition of calcium and potassium (experiment D). All experiments were done on unbuffered solutions to prevent the added chemicals from affecting the decomposition rates.

Because all decomposition experiments were carried out under conditions far from thermodynamic equilibrium (low pH, low CN^- activity), the measured decomposition rates were not biased by reverse reactions. The redox potentials measured in the hexacyanoferrate solutions were probably accurate because they resemble the composition of a ZoBell's solution (12), which is used as a redox standard solution because of the fast redox equilibrium between $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$.

Experimental conditions:

Experiment A: diffuse daylight, pH 12 (0.01 M NaOH), 1.28×10^{-6} M $\text{K}_4\text{Fe}(\text{CN})_6$, reaction time 0-5 h.

Experiment B: dark, pH varying between 2 and 7 (HCl addition), 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$, reaction time 0-240 h.

Experiment C: dark, pH 1 and 3, (HCl addition), temp. 25.5, 19.8 and 13.6 °C, 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$, reaction time 0-140 h.

Experiment D: dark, pH 1 and 3, (HCl addition), 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$, 0.1 M CaCl_2 , 0.1 M KCl, reaction time 0-140 h.

In all experiments the total cyanide concentration, the free cyanide concentration, the pH and the E_h were measured. The effect of light on the decomposition rate in experiments B - D was minimized by the use of black plastic bottles.

Experiment C was done to quantify the temperature dependence of the decomposition rate (k) which can be described by the Arrhenius equation:

$$\ln k = -(E_a/RT) + \ln A \quad (1)$$

with A the preexponential factor, E_a the activation energy, R the gas constant and T the temperature (K). Without discussing the physical meaning of E_a or A it is evident that according to this equation $\ln k$ should be linear with $1/T$. A linear plot of measured values of $\ln k$ against $1/T$ therefore allows k to be determined at different temperatures.

Chemical analysis

The concentrations of free and total cyanide were determined with an automated spectrophotometrical method (7). Photolysis of iron cyanide

complexes during cyanide determination was prevented by covering the automatic analyser with a black plastic hood. Total iron concentrations were determined with a flame atomic absorption spectrophotometer. Redox potentials were determined with a platinum + calomel reference electrode.

Results and Discussion

Thermodynamic equilibrium calculations

As a first step in assessing the stability of iron cyanide complexes in soil solutions, their thermodynamic stability under soil conditions was calculated. This thermodynamic stability does not provide information about the rate at which the equilibrium situation is reached, therefore the calculated equilibrium may differ considerably from the actual situation, especially when slow reactions are involved. Nevertheless, these calculations do give information

Table I. Chemical equilibrium reactions and formation constants (log K°) used to calculate cyanide speciation

Reaction		log K°	ref.
1) $\text{Fe}^{3+} + \text{e}^-$	\rightleftharpoons	Fe^{2+}	13.0 (9)
2) $\text{H}^+ + \text{CN}^-$	\rightleftharpoons	$\text{HCN}_{(aq)}$	9.2 (13)
3) $\text{Fe}^{3+} + 6\text{CN}^-$	\rightleftharpoons	$\text{Fe}(\text{CN})_6^{3-}$	43.9 (14)
4) $\text{Fe}^{3+} + 6\text{CN}^- + \text{Ca}^{2+}$	\rightleftharpoons	$\text{CaFe}(\text{CN})_6$	46.5 (15)
5) $\text{Fe}^{3+} + 6\text{CN}^- + \text{K}^+$	\rightleftharpoons	$\text{KFe}(\text{CN})_6^{2-}$	45.4 (16)
6) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^-$	\rightleftharpoons	$\text{Fe}(\text{CN})_6^{4-}$	49.9 (14)
7) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{H}^+$	\rightleftharpoons	$\text{HFe}(\text{CN})_6^{3-}$	54.3 (17)
8) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + 2\text{H}^+$	\rightleftharpoons	$\text{H}_2\text{Fe}(\text{CN})_6^{2-}$	56.7 (17)
9) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{Ca}^{2+}$	\rightleftharpoons	$\text{CaFe}(\text{CN})_6^{2-}$	54.0 (17)
10) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + 2\text{Ca}^{2+}$	\rightleftharpoons	$\text{Ca}_2\text{Fe}(\text{CN})_6^0$	55.3 (17)
11) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{Ca}^{2+} + \text{H}^+$	\rightleftharpoons	$\text{CaHFe}(\text{CN})_6$	57.0 (17)
12) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{K}^+$	\rightleftharpoons	$\text{KFe}(\text{CN})_6^{3-}$	52.4 (17)
13) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + 2\text{K}^+$	\rightleftharpoons	$\text{K}_2\text{Fe}(\text{CN})_6^{2-}$	53.3 (17)
14) $\text{Fe}^{3+} + 6\text{CN}^- + \text{e}^- + \text{K}^+ + \text{H}^+$	\rightleftharpoons	$\text{KHFe}(\text{CN})_6^{2-}$	55.7 (17)
15) $\text{Fe}(\text{OH})_3(\text{s}) \text{ soil} + 3\text{H}^+$	\rightleftharpoons	Fe^{3+}	2.7 (9)

about the direction in which the reactions will proceed to reach equilibrium in the long term. The chemical reactions involved in the formation and dissociation of iron cyanide complexes as used in the calculations are listed in Table I.

The results of the calculations of chemical equilibrium are shown in Figure 1. In this figure a division is made between the area where most of the cyanide (> 50 %) is present as hexacyanoferrate and the area where most of the cyanide is present as free cyanide. The boundary between these areas, as indicated by the dashed lines, has been calculated at three different concentrations of total cyanide and plotted as a function of pH and redox potential ($E_h = 0.059$ pe). It is clear that the pH, the redox potential and also the total cyanide concentration all have a substantial effect on this partition. The pH influences the activity of the constituents of iron cyanide complexes, CN^- (reactions 7,8,11,14, Table I) and Fe^{3+} (reactions 2 and 15, Table I).

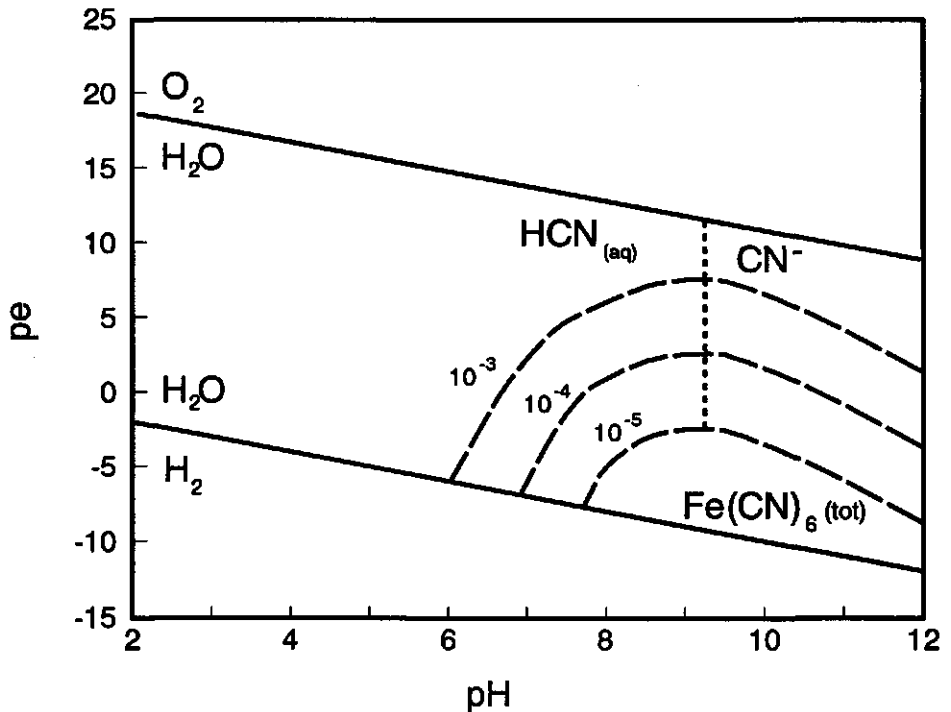


Figure 1. The predominance of cyanide species in solution as a function of pH, pe and total cyanide concentration (10^{-3} M, 10^{-4} M, 10^{-5} M) in equilibrium with solid $\text{Fe}(\text{OH})_3$, as calculated with the equations listed in table I. In the area indicated with $\text{Fe}(\text{CN})_6$ cyanide is predominantly present in one or more of the complexed species, in the remaining area it is predominantly present in the free forms. $\text{Ca}(\text{t})=5$ mM, $\text{K}(\text{t})=1$ mM, ionic strength = 0.01 M.

The redox potential (stabilizing iron cyanide complexes at lower pe levels) has an effect because below $pe = 6$ iron cyanide complexes are mainly present in the reduced form ($Fe(CN)_6^{4-}$) which according to reaction 6 (Table I) is more stable at low pe levels. The fraction of cyanide in complexed form is also greatly influenced by the total cyanide concentration. This is because there is more than one cyanide ion in one iron cyanide complex (reaction 3, Table I).

When the conditions (with respect to pH, redox potential and total cyanide concentration) under which complexed cyanide is thermodynamically stable are compared, with conditions occurring in soils, it appears that these complexes are stable neither in oxidized soils nor in soils with a pH below ca. 7. Only in reduced (anaerobic) soils at a pH higher than ca. 8 and with more than ca. $1 \cdot 10^{-4}$ M total cyanide present, cyanide is stable in the complexed form. Such conditions however are extreme for natural soils. This implies that in most soils complexed cyanide will tend to decompose to toxic free cyanide.

Furthermore, the equilibrium calculations show that even under the conditions where complexed cyanide is stable, free cyanide is still present (always more than ca $3 \cdot 10^{-6}$ M). Thus, even under optimal conditions the stability of iron cyanide complexes is not sufficient to reduce free cyanide concentrations to sub-toxic levels.

Cyanide speciation in contaminated groundwater

In order to compare the calculated speciation of cyanide with the actual speciation, the speciation of cyanide was measured in the groundwater from several former gasworks sites. The results show that in all cases the contribution of free cyanide to the total cyanide concentration is negligible (Table II). From the observed ratio of total dissolved cyanide to dissolved iron (about 6 in all cases) it can be concluded that virtually all cyanide is complexed with iron. Clearly this disagrees completely with the calculated speciation of cyanide under the conditions measured. This disparity cannot be attributed to the measured redox potentials being incorrect because of oxidation during sampling or to the inaccuracy of p_e measurements. However it might be a result of very slow decomposition rate of iron cyanide complexes. If so, the speciation of cyanide is determined by decomposition kinetics rather than by chemical equilibrium.

Table II. Measured pH, p_e , Fe(t) and cyanide speciation in contaminated groundwater at three locations in the Netherlands (A - C)

Location no	pH	p_e	Total Cyanide conc.(M)	Free Cyanide conc. (M)	Iron conc. (M)	CN/Fe
A1	7.1	7.3	6.7×10^{-5}	0.5×10^{-6}	1.1×10^{-4}	6.1
A2	7.0	7.7	1.1×10^{-4}	0.5×10^{-6}	2.0×10^{-5}	5.5
A3	7.6	7.3	1.0×10^{-4}	0.5×10^{-6}	1.6×10^{-5}	6.3
B1	5.9	8.5	4.4×10^{-4}	3.1×10^{-6}	7.2×10^{-5}	6.1
B2	5.6	8.8	3.6×10^{-4}	2.6×10^{-6}	6.1×10^{-5}	5.9
B3	6.4	8.2	3.3×10^{-4}	2.1×10^{-6}	5.4×10^{-5}	6.1
C1	7.3	8.1	3.4×10^{-4}	5.7×10^{-6}	5.5×10^{-5}	6.2
C2	5.9	6.5	1.8×10^{-4}	5.1×10^{-6}	3.1×10^{-5}	5.8

Decomposition experiments

The first decomposition experiment (A) was done simply to estimate how rapidly iron cyanide complexes decompose in diffuse daylight. We already knew that iron cyanide complexes decompose in direct sunlight or ultraviolet light. The results of experiment A show that complexed cyanide also decomposes behind glass windows not exposed to direct sunlight (Figure 2). The initial rate of this

reaction was measured to be ca. 8%/h. This rate will probably depend on parameters like temperature, light intensity and wavelength. But it is clear that already short illumination times may affect measurements of low concentrations of free cyanide in solutions containing iron cyanide. Therefore in subsequent experiments we treated the samples in the dark.

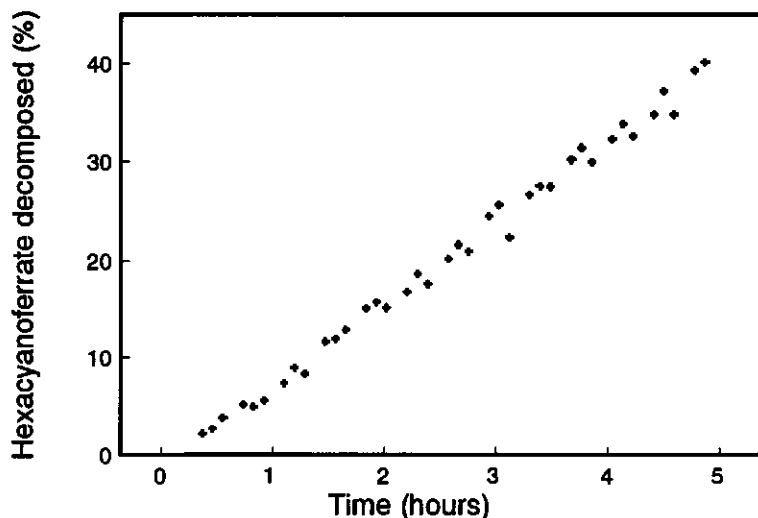


Figure 2. Percentage of the total amount of cyanide, added as iron cyanide complexes, decomposed to free cyanide as a result of exposure to diffuse daylight in a 1.28×10^{-6} M $K_4Fe(CN)_6$ solution at pH 12 (Experiment A).

The results of experiment B presented in figure 3 show that iron cyanide complexes do indeed decompose in the dark. The rate of this decomposition appears to be inversely related to the pH. During the experiments the decomposition rates were not constant (Figure 3a). This is partly because the pH increased greatly in the solutions with an initial pH of 3.8 and 4.2 (Figure 3b).

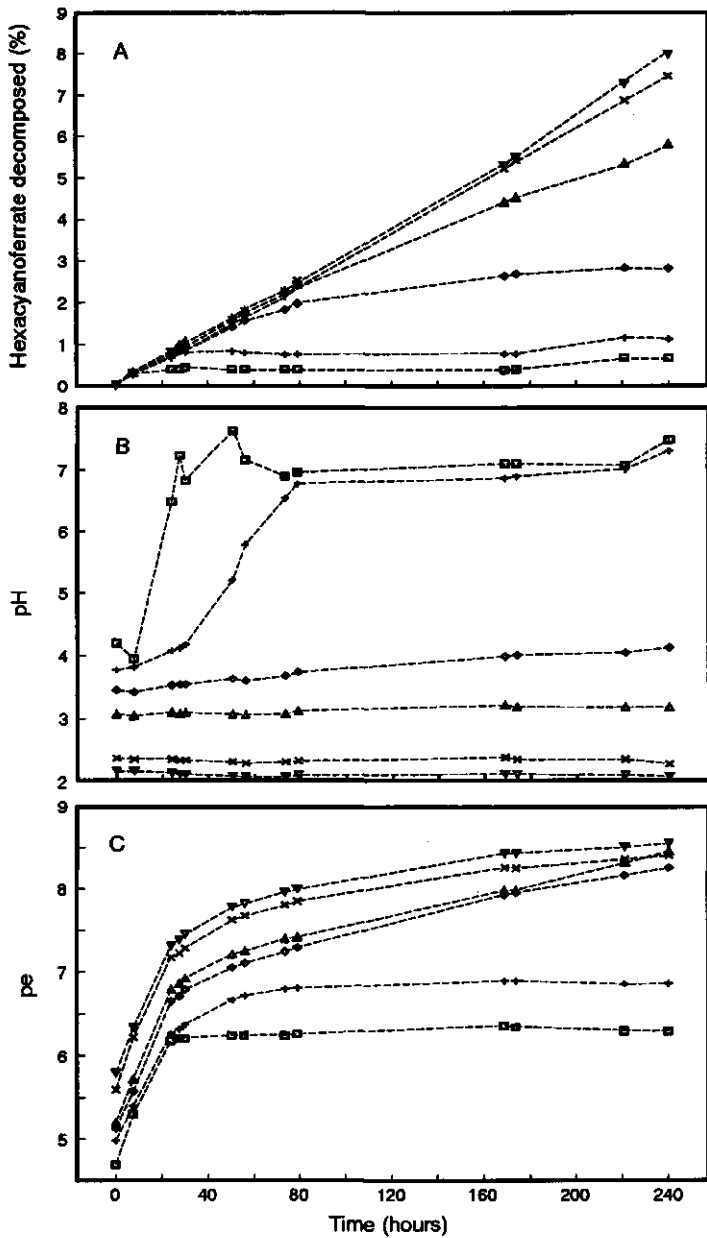


Figure 3. Composition of solutions during experiment B. Percentage of the total amount of cyanide, added as iron cyanide complexes, decomposed to free cyanide (a), pH (b) and pe (c) as a function of reaction time. Initial pH of solution $\square = 2.1$, $+$ = 2.3, $\diamond = 3.1$, $\triangle = 3.4$, $\times = 3.8$, $\nabla = 4.2$.

Decomposition rates however also decreased in solutions with a constant pH and increasing p_e (Figure 3c). A possible explanation for this behaviour is that only hexacyanoferrate species present at low pH and low p_e decompose. In that case, the overall decomposition rate of hexacyanoferrate will depend on the fraction present in such a "labile" form. To test this hypothesis the distribution of hexacyanoferrate over different species was calculated and the measured decomposition rate was compared with the concentration of the different species present. Figure 4 shows the results of the calculation of the distribution of $\text{Fe}(\text{CN})_6(t)$ over several complexes depending on the pH. The calculations assumed the conditions prevailing in experiment B: $p_e = 4$; $\text{Fe}(\text{CN})_6(t) = 1 \text{ mM}$; $\text{K}(t) = 4 \text{ mM}$; ionic strength = 0.03 M.

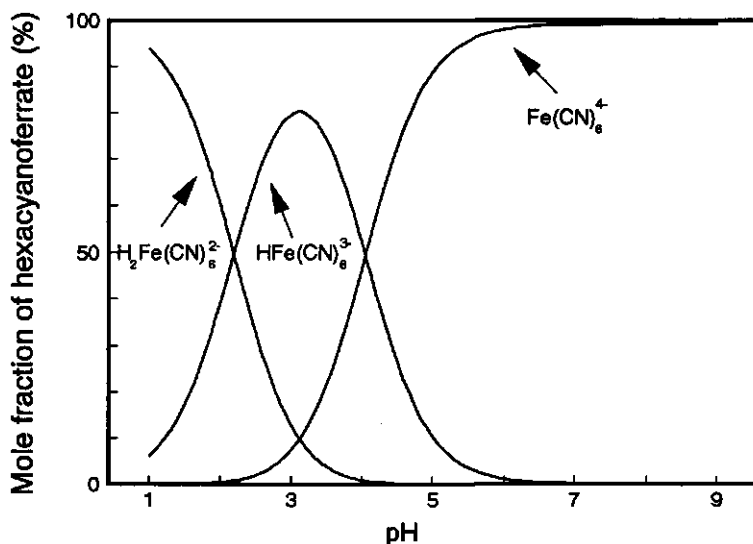


Figure 4. Distribution of $\text{Fe}(\text{CN})_6^{4-}$ over different species in a 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solution at $p_e < 5$ as a function of the pH.

The two iron cyanide species whose concentrations depend on pH and p_e in such a way that they can explain the reaction rate (more abundant at lower pH and redox potential) are $\text{HFe}(\text{CN})_6^{3-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ (Figure 4). The reaction rates measured at pH 2 and 3 indicate that both species must contribute to the decomposition. If this were not the case, the decomposition rate at pH 2 would be very different from the rate measured at pH 3 (Figure 3).

The individual decomposition rates of $\text{HFe}(\text{CN})_6^{3-}$ (k_1) and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ (k_2) can be estimated from the decomposition measured at pH 1 and 3 (exp. C).

Because the decomposition rate at pH 1 is lower than at pH 3 this experiment also shows clearly that the decomposition rate is not simply proportional to the pH. We determined the temperature dependence of both decomposition rates by measuring the decomposition rate at different temperatures. During that experiment the decomposition rates measured remained constant (Figure 5). This is probably because of the low pH and the fact that in all cases the p_e remained below 5. The constant pH is caused by the large buffer capacity of the solutions, while oxidation is probably prevented by less frequent sampling.

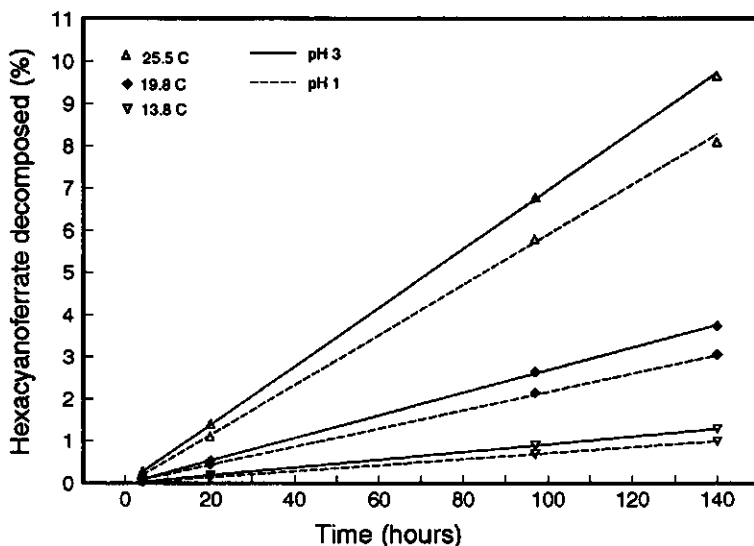


Figure 5. Degree of decomposition of iron cyanide complexes in a 1 mM $K_4Fe(CN)_6$ solution at $p_e < 5$ as a function of time at different temperature and pH (experiment C).

According to the speciation calculations (Figure 4) at pH 1 [95% $H_2Fe(CN)_6$ + 5% $HFe(CN)_6$] and at pH 3 [10% $H_2Fe(CN)_6$ + 80% $HFe(CN)_6$] the overall decomposition rate (k) would be:

$$k_{(pH\ 1)} = 0.05 k_1 + 0.95 k_2 \quad (2)$$

$$k_{(pH\ 3)} = 0.80 k_1 + 0.10 k_2 \quad (3)$$

The individual molar decomposition rates of $\text{H}_2\text{Fe}(\text{CN})_6$ and $\text{HFe}(\text{CN})_6$ at different temperatures can now be calculated from the measured overall decomposition rates (Table III).

Table III. Temperature dependence of the calculated dissociation rate of $\text{HFe}(\text{CN})_6^{3-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$

T, °C	Dissociation rate ($\text{mol}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	
	$\text{HFe}(\text{CN})_6^{3-}$	$\text{H}_2\text{Fe}(\text{CN})_6^{2-}$
25.5	2.22×10^{-7}	1.59×10^{-7}
19.8	8.61×10^{-8}	5.92×10^{-8}
13.6	2.96×10^{-8}	1.93×10^{-8}

For both reactions the decrease in the concentration of hexacyanoferrate during the reaction time is relatively small (max 10%) and so we ignored it.

The Arrhenius plot of $\ln k$ ($\text{mol}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) against the inverse temperature shows good linear relationships in both cases (Figure 6):

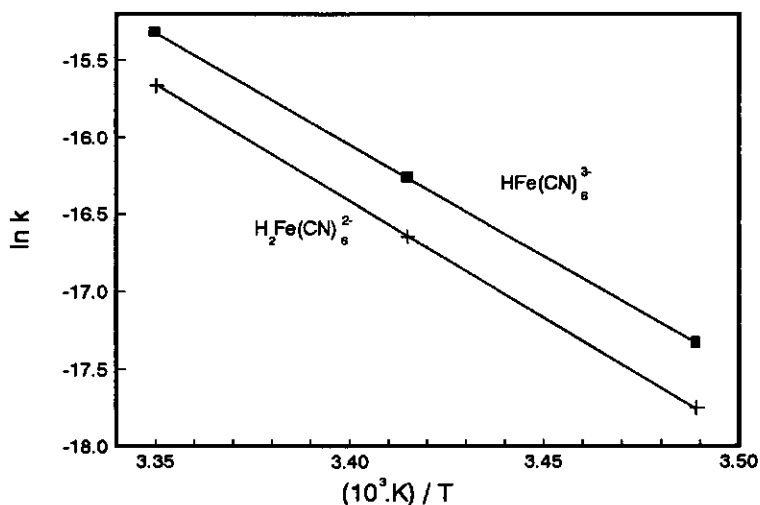


Figure 6. Arrhenius plot of the decomposition of $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ and $\text{HFe}(\text{CN})_6^{3-}$ in a 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solution at $p\text{e} = 4$.



$$\ln k = -14462(1/T) + 33.13 \quad (4)$$



$$\ln k = -15129(1/T) + 35.03 \quad (5)$$

The speciation of iron cyanide complexes is determined not only by the *pe* and pH but also by complexation with calcium or potassium (Table I, reactions 9-14). The formation of such complexes can affect the concentration of the dissociating species and in that way alter the overall decomposition rate. But our decomposition experiments in which extra calcium or potassium was added (experiment D) showed that these ions have no influence on the decomposition rate, although according to the calculations, when the pH is 3 virtually all the HFe(CN)_6^{3-} is converted to KFe(CN)_6^{2-} or CaHFe(CN)_6^- . Apparently, the metal ions associated with the HFe(CN)_6^{3-} complex do not affect the stability of this complex whereas an extra proton ($\text{H}_2\text{Fe(CN)}_6^{2-}$) does.

Calculation of decomposition rates

The decomposition model based on the results of experiment C was tested by calculating the concentrations of free cyanide in experiment B. The decomposition rate between two measurements was calculated using the *pe* and pH values at the moment of the first measurement. The results of these calculations (Figure 7), show that the predicted concentrations of free cyanide formed correspond very well with the concentrations determined experimentally. The pH and *pe* conditions at which the decomposition rate decreases are predicted especially well. The results are, insofar as comparison is possible, in accordance with the more qualitative results of Kruse and Thibault (5) who found a much slower decomposition rate in hexacyanoferrate(III) than in hexacyanoferrate(II) solutions.

The decomposition rate model can be used to estimate the overall decomposition rate of iron cyanide complexes in soil solutions as determined by *pe*, pH and temperature. First the concentrations of HFe(CN)_6^{3-} and $\text{H}_2\text{Fe(CN)}_6^{2-}$ have to be calculated with a speciation model. Then these concentrations must be multiplied by the molar decomposition rates of both species at the temperature under consideration. These molar decomposition rates can be calculated with eqs 4 and 5. The maximum decomposition rates will be found at pH 3 under reduced conditions. When the pH is above 3 the

concentration of $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ will be less than 1% of the concentration of $\text{HFe}(\text{CN})_6^{3-}$. Its contribution to the overall decomposition rate under those conditions can therefore be ignored.

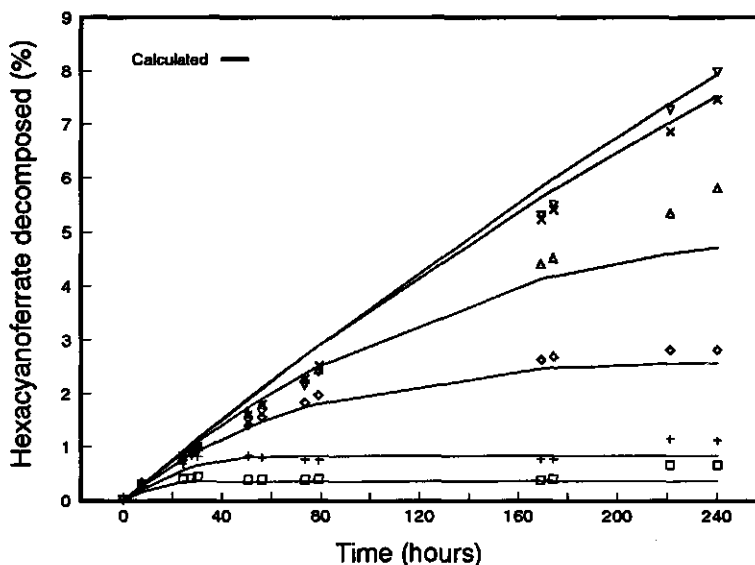


Figure 7. Calculated degree of decomposition of iron cyanide complexes during experiment B (solid lines) compared with the degree of decomposition measured (symbols).

Initial pH of solution □ = 2.1, + = 2.3, ◇ = 3.1, △ = 3.4, × = 3.8, ▽ = 4.2.

We used this model to find out how the half-life of iron cyanide complexes is affected by pH and p_e at 15 °C (Figure 8). A total hexacyanoferrate concentration of 1 mM and an ionic strength of 0.03 M were assumed. The results clearly show the effect of both p_e and pH on the calculated half-life, which varies from 1 year at pH 4 in a more or less reduced soil ($p_e=5$) to 1000 years at the same pH in an oxidized soil ($p_e=10$). The calculated half-lives will be the same at lower ionic strengths or lower hexacyanoferrate concentrations.

These model calculations should, however, be interpreted carefully. In the first place because E_h measurements in the environment have a limited accuracy. Furthermore, it is not certain that the decomposition reactions found still govern the decomposition at high values of pH and p_e . This is difficult to

verify experimentally. Decomposition might be enhanced by catalysts too. The model should therefore only be used for estimations, especially at slow decomposition rates.

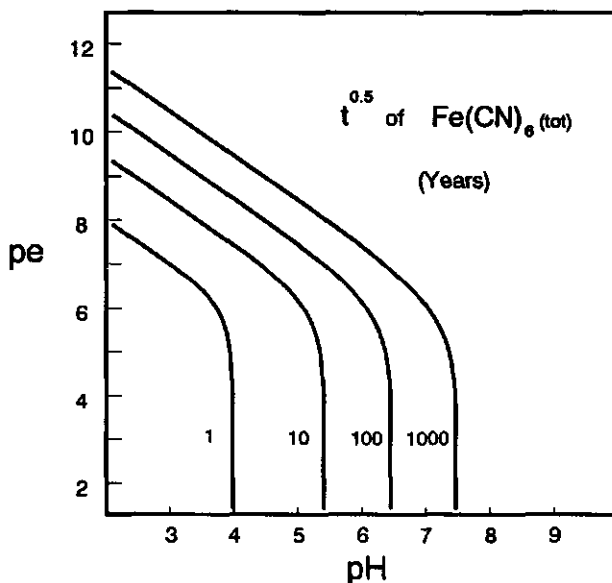


Figure 8. The half-life of iron cyanide complexes calculated with the decomposition model as a function of pH and pe in a 1 mmol $\text{K}_4\text{Fe}(\text{CN})_6$ solution at 15° C.

Hexacyanoferrate is thermodynamically unstable in groundwater as well as under the conditions applied in the experiments (figure 1). The rate of the formation reaction will therefore be very slow compared with the decomposition reaction. Alteration of the rate of the formation reaction (e. g. reduction of the iron activity by complexation) will therefore have no effect on the rate of decomposition. This implies that the decomposition rate of iron cyanide complexes in the environment will not be affected by the actual activities of Fe^{3+} or CN^- .

Microbiologically mediated decomposition of hexacyanoferrate

In addition to the thermal and the light enhanced decomposition of hexacyanoferrate discussed above, microbiologically mediated decomposition of these complexes has also been reported (8). Experiments done by Cherryholmes et al.(8) show that in the presence of microorganisms free

cyanide is formed in solutions containing hexacyanoferrate. They conclude that microorganisms must be responsible for this decomposition because it is not observed in sterile solutions at comparable pH levels. But the results of our work show that the thermal decomposition rate is also determined by the redox potential.

Cherryholmes et al. do not give exact redox potentials of the solutions they studied and therefore we were unable to calculate the thermal decomposition rate. But they did report "anoxic conditions" in the solutions with microbial activity, indicating low redox potentials. In contrast, their sterile solutions will have been more oxidized because they used hexacyanoferrate(III). This difference in redox potential could have caused the difference in decomposition rate. The decomposition rate they observed in the solutions inoculated with microorganisms is similar to the rate calculated with our model at a p_e below 5. This implies that the decomposition of iron cyanide complexes observed by Cherryholmes et al. is not necessarily directly induced by microbial activity but is probably indirectly caused by the influence of microbial activity on the redox potential. In this way, however, microbial activity can still accelerate the decomposition rate of iron cyanide complexes considerably.

Conclusions

Our calculations of thermodynamic equilibrium show that iron cyanide complexes are thermodynamically stable only under conditions which may be considered as rather extreme for soils and the environment: a relatively high pH combined with a low redox potential and a high total cyanide concentration. Iron cyanide complexes present in groundwater will therefore normally tend to dissociate to free cyanide. The speciation of cyanide we determined in groundwater indicates that this decomposition proceeds very slowly. Hence speciation of cyanide will be governed by decomposition kinetics rather than by chemical equilibrium.

The decomposition rate of iron cyanide complexes in the dark does indeed appear to be very slow. The rate of decomposition does not simply depend on the degree of disequilibrium, but on the fraction of hexacyanoferrate present as $\text{HFe}(\text{CN})_6^{3-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$. Complexed cyanide can decompose very rapidly when exposed to daylight. Therefore it is important that hexacyanoferrate is considered to be as toxic as free cyanide when exposure to light is likely to occur.

The biologically mediated decomposition of iron cyanide complexes to

HCN(aq) which was reported by Cherryholmes et al. (1985) can also be explained by the spontaneous thermal decomposition, as we have discussed above.

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**Determination of Total and Free Cyanide in Water
after Photodecomposition and Distillation.**

The Analyst 117, 1009-1012 (1992)

with Meindert G. Keizer and
Wendy D. Lukassen

Determination of Total and Free Cyanide in Water after Distillation

Improved analytical methods are described for the determination of total cyanide after separation from thiocyanate [SCN⁻] and free cyanide [CN⁻ + HCN(aq)] after separation from hexacyanoferrate [Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻] and thiocyanate in water by means of a standard continuous-flow system. Separation of total cyanide from thiocyanate is achieved by illumination of samples with visible light, preventing transition of SCN⁻ to CN⁻, prior to distillation. Separation of free cyanide from hexacyanoferrate and thiocyanate is performed by distillation of samples at pH 4 in a citrate buffer in the presence of Cu²⁺. Distillation under these conditions prevents decomposition of hexacyanoferrate and evaporation of thiocyanate as HSCN(g). Both methods combine the advantages of sample distillation with a high specificity for total and free cyanide respectively.

Keywords: Cyanide determination, hexacyanoferrate, thiocyanate, interference.

Introduction

Today, automated methods are commonly used for determination of cyanide¹⁻⁴. Compared to manual procedures these methods offer both better reproducibility and a more rapid determination. However, differences in toxicity between free cyanide [CN⁻ + HCN(aq)] and hexacyanoferrate [Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻], and the different nature of thiocyanate [SCN⁻] make improved differentiation between these species also desirable.

To accomplish decomposition of hexacyanoferrate within several minutes, all automated methods make use of ultraviolet (UV) irradiation. In the dark, as applied in the standard manual procedures, this is a very slow process needing several hours of rigorous treatment with strong acids at high temperatures^{5,6}. The introduction of UV irradiation for this purpose, however, also introduced the interference of thiocyanate, which is completely converted to cyanide by this treatment.

In order to separate cyanide from thiocyanate several methods are used¹⁻⁸. A useful difference between hexacyanoferrate and thiocyanate is the fact that hexacyanoferrate already dissociates under influence of visible light^{2,3,9} while thiocyanate requires UV radiation to decompose. One of the published methods makes use of these properties to differentiate between cyanide and thiocyanate². In this method, samples in a Pyrex glass tube, which permits only visible light to pass, are irradiated by an UV light source (500 watt). According

to our experience, irradiation with an 8 watt UV unit, which is normally used in automated analysis, was not successful in this respect. Therefore, illumination of samples with an ordinary fluorescent lamp to decompose hexacyanoferrate specifically was studied.

In order to determine free cyanide separately from hexacyanoferrate and thiocyanate, two methods are commonly used. Both use equivalent spectrophotometric methods which are sensitive to free cyanide and thiocyanate but not for hexacyanoferrates. The first method separates free cyanide from hexacyanoferrate and thiocyanate by distillation^{1,2}. The second method uses two measurements, one with and one without masking free cyanide³. The first measurement determines free cyanide plus thiocyanate, the second only the amount of thiocyanate. The concentration of free cyanide is then calculated from the difference between these measurements.

The advantages of the first method are that only one measurement is needed to determine the concentration of free cyanide in a sample and that the distillation removes interfering substances before the spectrometric determination. However, a serious disadvantage of this method is its sensitivity to interference by hexacyanoferrates, caused by the partial decomposition of these complexes during distillation.

The second method is virtually insensitive for hexacyanoferrates, provided that sample solutions are kept dark. However, these method omits the distillation and requires two measurements for the determination of free cyanide. As a result it suffers from the fact that the error in the free cyanide determination is influenced by the ratio of the cyanide to the thiocyanate concentration. A higher thiocyanate concentration causes larger errors in the determination of the free cyanide concentration.

The methods currently used to determine total cyanide and free cyanide therefore have serious drawbacks in their present form. Hence, the aim of the present work was to develop an improved method for the determination of total cyanide, in addition to a method for the determination of free cyanide, with the help of new insights into the dissociation kinetics of hexacyanoferrate¹⁰.

Experimental

Apparatus

A Skalar 5101 continuous-flow system equipped with a closed distillation unit and a spectrophotometric detector was used to determine cyanide concentrations in water samples. Apart from the addition of copper to the distillation

reagent and disregarding the UV-irradiation the composition of the system is identical with that used for the total cyanide determination described previously³. The main characteristics of this system are; distillation in 0.5 M citric acid at pH 4 and at 125° C, spectrophotometric determination of free cyanide after formation of a coloured complex with 1-3-dimethylbarbituric acid and isonicotinic acid.

Reagents

Standard solutions

Standard solutions of $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KSCN and KCN were prepared in 0.01 M NaOH and stored entirely in the dark. All chemicals used were of analytical-reagent grade.

Distillation reagent

Dissolve 11.0 g of citric acid in 200 cm³ of a 0.125 M sodium hydroxide solution. Add 50 cm³ of 1 M hydrochloric acid and 50 cm³ 0.5 M $CuSO_4$ and dilute to 500 cm³ with water. Adjust the pH to 4.0 if necessary with 1 M sodium hydroxide or hydrochloric acid. Use equal volumes of this reagent and sample during distillation.

Procedure for total cyanide determination

Three methods of sample illumination were compared in effectiveness for decomposition of complexed cyanide and thiocyanate. After illumination samples were analysed for free cyanide as described below.

- A: Illumination with the standard UV radiation source and replacement of the quartz coil with a Pyrex coil.
- B: Illumination with a 8 W fluorescent lamp (Philips type 32) in the continuous-flow system instead of the UV lamp.
- C: Illumination of the samples for several hours with a fluorescent lamp (Philips type 32) prior to analysis (1-170 h). No illumination was applied during analysis.
- D: No illumination applied at all, in order to show the pure thermal dissociation during distillation.

For all methods the pH of the samples during illumination was 12. The light source used in method C is a fluorescent lamp (Philips nr 32, 90 cm, 30 watt). The samples were illuminated in a glass (Pyrex) bottles. The solution height was 1 cm and the distance between the lamp and the bottom of the bottles was

3 cm. The bottles were closed with a plastic plug to avoid evaporation of the samples. The temperature of the solutions during illumination was approximately 45°C

Procedure for free cyanide determination

In order to determine free cyanide, samples were diluted 1 + 1 with the distillation reagent in the continuous-flow system. Distillation was carried out at pH 4.0 in the citrate buffer solution. After distillation, free cyanide was determined by spectrophotometry³. Alternative methods for determining free cyanide after distillation are also suitable. It is preferable to avoid the use of concentrated acid during distillation of cyanide because interference of thiocyanate due to evaporation of HSCN(g) may occur. Further, strong acid conditions enhance the possibility for oxidation of cyanide to CO₂ and NH₃ and also allow cyanide to be formed from nitrate/nitrite together with organic matter. In order to distil HCN(aq) quantitatively, a pH < 6 is sufficient³.

Determination of total cyanide and free cyanide in soil extracts

Both methods were applied to determine the concentration of total cyanide and free cyanide in soil extracts obtained by extraction of two contaminated soils. An amount of 5 g soil was heated with 100 cm³ 0.25 M NaOH on a boiling water bath (3 h). Subsequently the samples were filtered and analysed. Recovery of both methods for different cyanide species were measured by standard addition of K₄Fe(CN)₆, KCN, KSCN to the extracts.

Results and Discussion

Total cyanide determination

Recovery of different illumination methods for free cyanide, hexacyanoferrate and thiocyanate.

The purpose of these methods is to separate both free cyanide and hexacyanoferrate from thiocyanate. The results obtained with the different illumination methods are presented in Table 1. None of the methods appears to be sensitive for thiocyanate. Method A, however, shows almost no additional recovery of hexacyanoferrate compared with that for method D. Replacing the UV radiation source by an ordinary fluorescence light source of the same power (method B) improved this recovery significantly. Further improvement was obtained by applying a longer illumination time. This treatment was carried out

before the automated analyses. The degree of the dissociation was measured after different times and appeared to be complete after approximately 8 h. There was no difference between the recovery of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. In subsequent experiments an illumination time of approximately 16 h was applied.

Table 1. Recoveries (%) of different illumination methods for cyanide species and thiocyanate at a total CN concentration of $200 \mu g L^{-1}$.

Method	Species			
	KCN	$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	KSCN
A	100	12	21	<0.1
B	100	34	45	<0.1
C	100	100	100	<0.1
D	100	13	19	<0.1

Effect of $Fe(CN)_6$ concentration on recovery of method C

In order to evaluate the effect of higher $Fe(CN)_6$ concentrations on the effectiveness of decomposition of method C (16 h), the method was applied to samples in concentrations ranging from 200 to 2000 $\mu g/l$ CN as $Fe(CN)_6$. The results are shown in Table 2.

Table 2. Recovery of method C for $Fe(CN)_6$ at different total CN concentrations.

Fe(CN) ₆ Concentration ($\mu g l^{-1}$ as CN)		Recovery (%)
Added	Measured	
200	201	101
200	197	98
500	493	99
500	488	98
1000	963	96
1000	956	96
2000	1830	92
2000	1850	93

According to these results, decomposition of $\text{Fe}(\text{CN})_6$ is complete up to concentrations of 1000 $\mu\text{g/l}$ CN. Only for the highest concentration is a slight decrease in recovery observed, probably because the light intensity becomes a rate limiting factor at higher concentration levels.

Effect of prolonged illumination times on recovery of method C.

Because the CN^- ion is not stable at high pH's under influence of UV irradiation⁵, the effect of prolonged irradiation with visible light on cyanide was studied. Solutions containing 200 $\mu\text{g/l}$ CN were treated for several days according to method C. However, no significant decrease of the CN^- concentration was observed after 48 hours of illumination. Illumination for one week showed a decrease in recovery of approximately 15%, probably owing to a residual amount of UV light present in the light from the fluorescent lamp even after filtering by several glass layers.

Free cyanide determination

Recovery of free cyanide after distillation

The purpose of this determination is to separate free cyanide from hexacyanoferrate, thiocyanate and other interfering substances. In general, distillation

Table 3. Recovery of free cyanide determination for different cyanide species.

Cyanide added ($\mu\text{g l}^{-1}$)				Free cyanide measured ($\mu\text{g l}^{-1}$)
Species				
$\text{Fe}(\text{CN})_6^{3-}$	$\text{Fe}(\text{CN})_6^{4-}$	CN^-	SCN^-	
250	-			<1
-	250			<1
250	250			<1
250	250	50		49
250	250	100		102
250	250	200		203
-	-	-	1000	<1

is an effective way of removing interfering substances from sample solutions. The effectiveness of this treatment depends mainly on differences in volatility between free cyanide and the interfering substance. The volatility of cyanide is mainly determined by its chemical speciation, which in turn strongly depends on the pH. At high pH levels (>9), free cyanide is mainly present as non volatile CN^- ; at lower pH levels it is converted to $\text{HCN}(\text{aq})$, which is very volatile. Below pH 7, more than 99% of the free cyanide is present as $\text{HCN}(\text{aq})$. Further reduction of the pH therefore does not, therefore, significantly increase the amount of cyanide present as $\text{HCN}(\text{aq})$ and hence will not enhance the evaporation of cyanide.

Interference by thiocyanate

Thiocyanate could possibly interfere the cyanide determination when it evaporates as $\text{HSCN}(\text{g})$, although it is much less volatile than $\text{HCN}(\text{g})$. The HSCN is, however, a strong acid (pK about 1); therefore substantial concentrations of $\text{HSCN}(\text{aq})$ will only exist at a pH below 1. $\text{HSCN}(\text{aq})$ is far less volatile compared to $\text{HCN}(\text{aq})$, so even at low pH levels interference of HSCN will be minimal.

As can be deduced from results for illumination method D (Table 1) the normal distillation procedure at pH 4, without ultraviolet irradiation, effectively separates free cyanide from thiocyanate.

Interference by hexacyanoferrate

According to the results of method D (Table 1), distillation does not prevent significant interference of hexacyanoferrate, particularly by the reduced form. This interference is not caused by evaporation of hexacyanoferrate, but by partial decomposition of these complexes to free cyanide during distillation. This reaction is not governed by equilibrium but by decomposition kinetics. In the dark at room temperature this decomposition proceeds extremely slow. From earlier work it was found that, in addition to the temperature, the rate of this reaction is governed by pH and redox potential¹⁰. This is caused by the fact that the oxidized form of hexacyanoferrate ($\text{Fe}(\text{CN})_6^{3-}$) decomposes far more slowly than the reduced form ($\text{Fe}(\text{CN})_6^{4-}$), which agrees with the observed difference in interference between $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. The decomposition rate of hexacyanoferrate is furthermore proportional to the fraction of hexacyanoferrate present as $\text{HFe}(\text{CN})_6^{3-}$.

In order to minimize the decomposition of hexacyanoferrate, distillation should be carried out under oxidizing conditions. However, oxidation of free cyanide to cyanate may occur when oxidants that are too strong are applied for this purpose. A suitable oxidizing agent appeared to be Cu^{2+} which apparently is not able to oxidize free cyanide but still reacts sufficiently rapidly to oxidize $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$ when citrate is present (Table 3).

No interaction of copper with free cyanide is observed. Possible reactions are the formation of dicyan¹² or the formation of $\text{Cu}(\text{CN})_4^{2-}$ complexes¹³. However, at pH 4 and a total cyanide concentration of 10^{-5} M (=260 $\mu\text{g/l}$) the maximum activity of CN^- is approximately 10^{-10} M ($\text{pK of } \text{CN}^- + \text{H}^+ \leftrightarrow \text{HCN}(\text{aq}) = 9.2$). Considering the formation constant for $\text{Cu}(\text{CN})_4^{2-}$ of 10^{29} , it follows that substantial complexation of CN^- with Cu^{2+} will not occur in the distillation reagent, where the maximum Cu^{2+} activity is approximately 0.01 M.

Further, copper does not seem to catalyse the decomposition of hexacyanoferrates during the distillation as was observed by Mertens(1976)¹². Probably the reducing effect of added $\text{Sn}(\text{I})\text{Cl}$ caused the observed decomposition in his experiments.

Interference by sulfide

Apart from thiocyanate, another substance known to interfere with cyanide is sulfide^{3,5,6,12}. Sulfide interferes with the colorimetric determination, and cannot be removed by distillation because like free cyanide it is volatile [$\text{H}_2\text{S}(\text{g})$] at low

Table 4. Interference of sulfide on the free cyanide determination method

Sulfide added	Cyanide measured ($\mu\text{g l}^{-1}$)		
	blank	CN- 100 $\mu\text{g l}^{-1}$	$\text{Fe}(\text{CN})_6$ 500 $\mu\text{g l}^{-1}$
0	0	102	0
1	0	98	4
5	0	97	21
15	3	73	113
25	5	55	73

pH. The addition of copper, as proposed here, to decrease the interference of hexacyanoferrate might possibly also decrease interference of sulfide by

formation of CuS(s). The interference of sulfide on the determination of different species was studied. However, the results show that the presence of Cu²⁺ does not prevent sulfide interfering in the determination of free cyanide (Table 4). Furthermore, sulfide increases interference in the determination of free cyanide determination by Fe(CN)₆, probably by reducing Fe(CN)₆ to Fe(CN)₆⁴⁻.

Application of both methods to soil extracts

The results of the determination of total cyanide according to method C and free cyanide, according to the improved distillation method, in soil extracts, show clearly that thiocyanate does not interfere with either of the two methods (Table 5). Further, the method for total cyanide shows complete recovery of complexed cyanide after illumination, although samples are coloured by

Table 5. Determination of total and free cyanide in soil extracts.

Extract	Cyanide added/ $\mu\text{g l}^{-1}$			Cyanide measured/ $\mu\text{g l}^{-1}$	
	Species K ₄ Fe(CN) ₆	KCN	KSCN	Free	Total
A				<10	6690
B				<10	7340
A	4020			<10	10390
B	4020			<10	10940
A	8530			<10	14870
B	8530			<10	15580
A		1000		1030	7710
B		1000		1020	8440
A			1320	<10	6620
B			1320	<10	7460

dissolved organic matter making them less transparent. The free cyanide method shows good specificity for free cyanide when complexed cyanide is present. The small amounts of free cyanide detected show that the presence of organic matter does not decrease the effect of the added Cu²⁺. The use of less concentrated sodium hydroxide for the extraction of soil samples compared with standard extraction procedures results in less potentially interfering dissolved organic material and makes it easier to adjust samples to pH 11 - 12, which is necessary for chemical analysis.

Conclusions

The method described here for total cyanide allows direct measurement of total cyanide in samples containing high concentrations of thiocyanate. The simplicity of the procedure and the lack of need for special materials make it functional and easy to implement. Because there are no chemicals added during this treatment it will not have adverse effects on any method of determination of total cyanide used subsequently.

The distillation method proposed here for the determination of free cyanide allows direct measurement of free cyanide in samples containing thiocyanate and/or iron cyanide complexes. This method can be used prior to any method of free cyanide determination and requires little modification of existing distillation methods. The presence of copper in the distillation reagent has no influence on the sensitivity or accuracy for the determination of free cyanide. It combines the specificity for free cyanide in the direct method with the advantages of distillation, with regard to suppression of interference. However, addition of copper does not reduce interference by sulfide.

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The Solubility of Iron Cyanide Complexes in Soils

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The Solubility of Iron Cyanide Complexes in Soils

Soils contaminated with iron cyanide minerals and soils spiked with dissolved iron cyanide were leached in a column experiment and extracted at various pH's in batch experiments. The cyanide concentrations in the leachates and extracts appeared to be dependent on soil pH but were not related to the total cyanide content of the soils. The pH- $\text{Fe}(\text{CN})_6(\text{t})$ concentration relationships found in different soils were comparable to those found when dissolving pure mineral Prussian blue. This indicates that $\text{Fe}(\text{CN})_6$ concentrations in groundwater are most likely controlled by equilibrium with this mineral.

Introduction

In the Netherlands several hundreds of former gas work sites are contaminated with large amounts of iron cyanide minerals which cause high cyanide concentrations in the groundwater. The possible hazards caused by these sites for the environment and especially for human health depend strongly on the speciation of cyanide and on its behaviour in soils. In case of gas work sites, cyanide is predominantly present as iron cyanide complexes (e.g. $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$)(1), which are a relatively harmless form of cyanide(2). These complexes however do dissociate very fast when exposed to light to yield toxic free cyanide ($\text{HCN}(\text{aq})$ and CN^-). In groundwater dissociation also takes place because iron cyanide complexes are thermodynamically unstable under prevailing soil conditions(1). This thermal dissociation however proceeds extremely slow which causes complexed cyanide to persist as the dominant species in the groundwater. The behaviour of complexed cyanide therefore will dominate the overall behaviour of cyanide in soils.

Of this behaviour especially the partitioning of cyanide over the soil solution and the soil solid phase is important. This partitioning determines the concentration of $\text{Fe}(\text{CN})_6$ in the groundwater which is not only of interest from toxicological viewpoint, but also determines the transport rate of cyanide through the soil. The partitioning of cyanide can be governed by several processes e.g. by electrostatic sorption of the negatively charged iron cyanide ions on positively charged soil sites, or by precipitation/ dissolution of sparingly soluble minerals like $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ (Prussian blue)(3). All processes have their own characteristics, like dependence on pH, redox potential, reaction time, total

cyanide content of the soil, soil composition etc. Insight in the actual dominating process increases the possibility of relating cyanide behaviour to soil characteristics.

The aim of this study is to investigate if the behaviour of cyanide in various soils is governed by a solubility equilibrium with mineral cyanide. Comparing the blue colour of the contaminated soils with the colour of mineral Prussian blue easily leads to the presumption that Prussian blue must be present in those soils. This however does not guarantee that $\text{Fe}(\text{CN})_6$ concentrations in the soil solution are controlled by equilibrium with this mineral. This could for example be prevented by dissolution and/ or precipitation kinetics. Experiments are carried out to study these equilibria. In order to obtain information to what extent equilibria are affected by kinetics, pH, and total cyanide content of the soil, a column experiment is carried out with two soils from contaminated sites and two clean soils spiked with dissolved iron cyanide. To further study the influence of the pH on the equilibria, batch extraction experiments at different pH's were carried out with three contaminated soils and with one of the spiked soils. The results of this experiment were compared with the results of a similar extraction experiment with pure Prussian blue.

Experimental Section

Column experiments

Column experiments were carried out with two contaminated soils from former gas work sites (A and B) and two "artificially" contaminated soils (C and D). The artificially contaminated soils were prepared by adding 1 l 0.01 M $\text{K}_4\text{Fe}(\text{CN})_6$ solution to 300 g of the soil material. After three days the solutions were decanted, the moist soils were homogenised and mixed 1:1 with quartz. Of this mixture 250 g was used per column which had a diameter of 90 mm. The resulting thickness of the mixed soil layer in the columns was approximately 2.5 cm. Soils C and D are both sandy soils containing 378 and 173 mmol/kg ammonium oxalate extractable iron respectively, and have an original pH-KCl of 3.0 and 4.4. The addition of $\text{K}_4\text{Fe}(\text{CN})_6$ caused the pH of both soils to increase. One of the contaminated soils (A) was stored moist and was not dried before the experiment. The other soil (B) was stored air dried.

Of all soils the total cyanide content was determined in dried samples (Table 1). The columns were percolated with 0.01 M CaCl_2 at a rate of ca. 1 pore volume per day for ca. 3 weeks, and subsequently at a rate of ca. 0.2 pore volume for 2 weeks. Finally the columns were again percolated at 1 pore volume

per day for two weeks. In the effluents the $\text{Fe}(\text{CN})_6(t)$ concentration, pH, and redox potential (Eh) were determined. The percentage of cyanide leached from the columns is calculated from their initial cyanide contents and the cyanide concentrations in the effluents.

Batch experiments

The batch extraction experiments were carried out with samples of soils A, B, and D and with soil material from another contaminated site: E (containing 0.0132 mol/kg $\text{Fe}(\text{CN})_6$). The extractions were carried out by adding 80 ml of extraction solution to 20 g of air dried soil. The different pH's of the solutions were obtained by mixing 0.01 M CaCl_2 at different ratios with 0.03 M HCl or 0.03 M NaOH. Samples were rotated for 3 days at 5 RPM at 20° C. Soils A and B were also used in an experiment with an extraction time of 5 weeks. After extraction the solutions were filtered and in the filtrates pH, redox potential and $\text{Fe}(\text{CN})_6(t)$ concentration were determined.

The extraction (dissolution) of pure mineral Prussian blue was carried out using 2 g mineral instead of 20 g soil and by separating the solution from the solid material by centrifugation at 32600 g for 20 minutes.

Chemical determinations

Total cyanide determinations were carried out with an automated spectrophotometrical method(4), measurements of pH were made with a glass-calomel electrode and of Eh with a platinum-calomel electrode.

The total cyanide content of the soils was determined after extraction with NaOH. To 5 g of air dried soil 50 ml 0.3 M NaOH was added. This mixture was heated for 3 hours at 100° C on a boiling water bath. After cooling down the solution was diluted to 100 ml with demineralised water and analysed for total cyanide.

Results and Discussion

Column experiments

The results of the column experiments (Figure 1) show that in all cases within a limited amount of percolated pore volumes, a fairly stable total $\text{Fe}(\text{CN})_6$ concentration in the effluent is reached. The same can be observed for pH and pe ($E_h = 0.059 \text{ pe}$) values. Decreasing the percolation rate to one fifth (0.2 pore volumes per day) of the initial rate did not alter the $\text{Fe}(\text{CN})_6(t)$ concentration in any of the columns. Apparently the concentrations in the effluents are not governed by dissolution/desorption kinetics at the percolation rates applied.

Table 1. Total amount of cyanide initially present in soils and percentage leached during flow experiment.

Soil	Initial $\text{Fe}(\text{CN})_6$ content (mol/kg)	$\text{Fe}(\text{CN})_6$ leached (%)
A	0.0620	18
B	0.232	<1
C	0.0168	<1
D	0.0038	43

This indicates the existence of equilibrium between dissolved and precipitated or adsorbed cyanide. The higher initial $\text{Fe}(\text{CN})_6(t)$ concentrations in the effluents of especially columns A, B, and D are possibly due to the transport of cyanide associated with small particles which are washed from the columns in the initial stage of the experiment. It furthermore is noticeable that in soils A and D the $\text{Fe}(\text{CN})_6(t)$ concentrations of the effluents do not decrease although during the experiment a significant part of the cyanide initially present is leached from the column (Table 1). This implies that there is no relationship between the total amount cyanide present in these soils and the concentration of $\text{Fe}(\text{CN})_6(t)$ in the effluents.

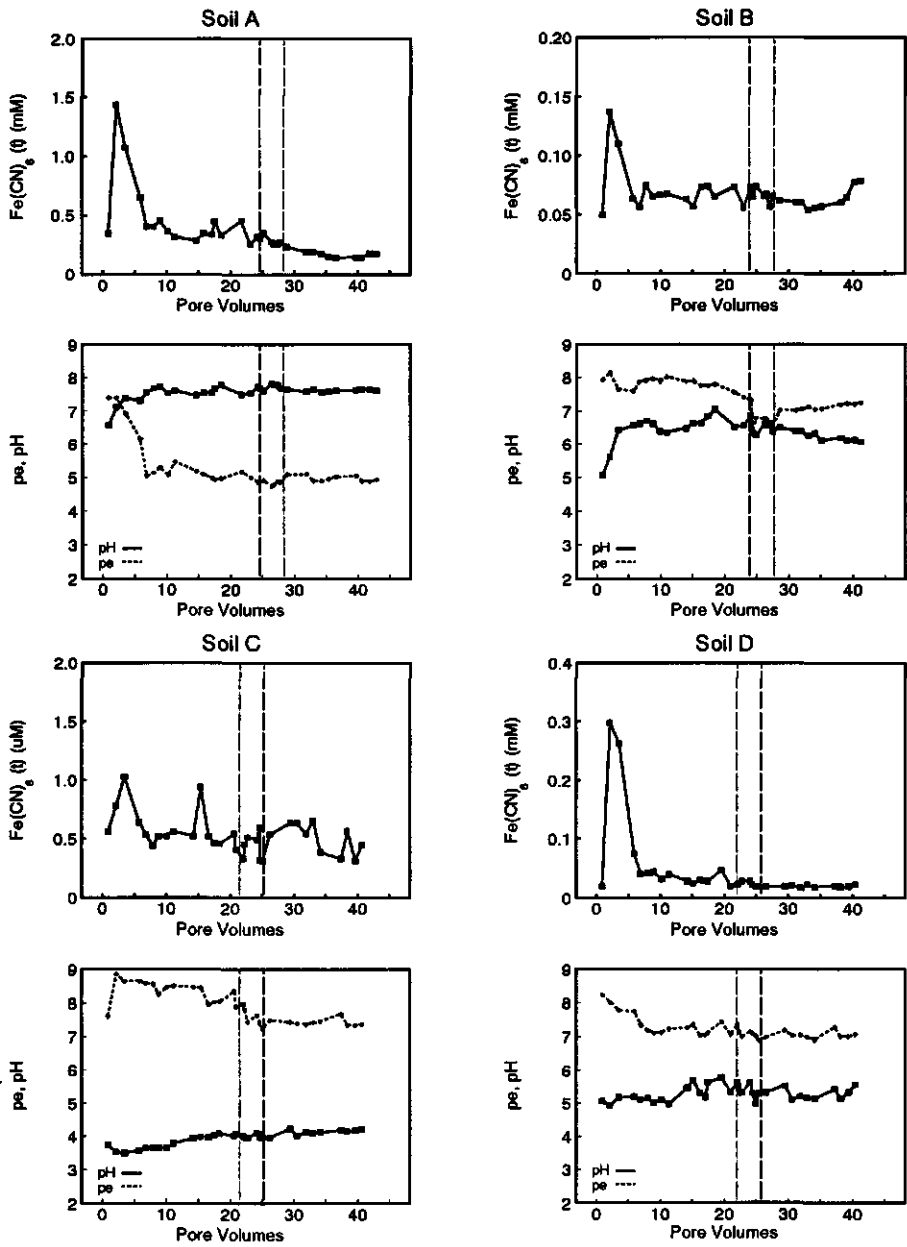


Figure 1. Concentrations $\text{Fe}(\text{CN})_6(t)$, pH and pe as measured in the effluents of the columns. The area between dotted lines indicates the period of reduced flow rate.

The composition of the effluents from the different columns shows that the $\text{Fe}(\text{CN})_6(t)$ concentration in these solutions is not related to the total amount of $\text{Fe}(\text{CN})_6$ present in the soil (Figure 2a), but appears to depend on the pH of the effluent (Figure 2b).

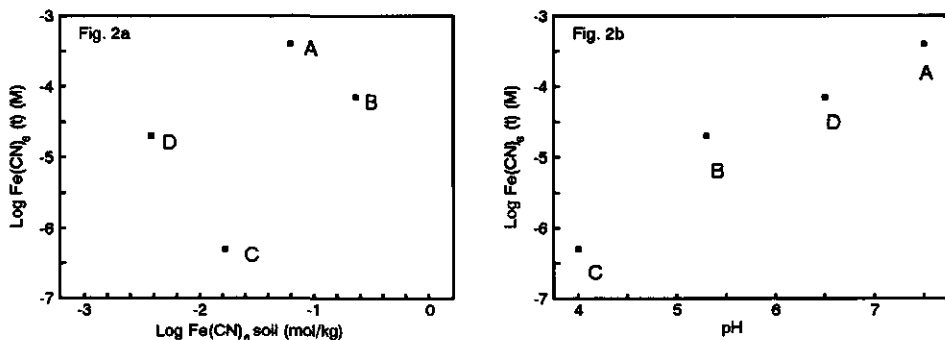


Figure 2. Dependence of $\text{Fe}(\text{CN})_6(t)$ concentrations in column effluents on total $\text{Fe}(\text{CN})_6$ content of soil (a) and on pH (b). The values shown represent the average composition of the effluents after the first ten percolated pore volumes.

Batch experiments

Contaminated soils

To further investigate the relationship between pH and $\text{Fe}(\text{CN})_6(t)$ in the soil solution, three contaminated soils (A, B and E) were extracted at various pH's. The results are shown in figure (3). As can be seen more or less linear relationships with equal slopes do exist between pH and $\log(\text{Fe}(\text{CN})_6(t))$ in the extracts of the different soils, suggesting equilibrium with a similar cyanide mineral. The deviation of linearity at higher pH's in case of soil A is caused by complete dissolution of the present cyanide mineral. Under those circumstances an increase of the pH does not result in an increase of the amount of dissolved $\text{Fe}(\text{CN})_6(t)$. In order to estimate the magnitude of the bias possibly caused by dissolution kinetics, this experiment was repeated with a reaction time of 5 weeks instead of 3 days using soils A and B. The obtained results however did not differ from the short time experiment indicating that an equilibrium situation is reached within 3 days.

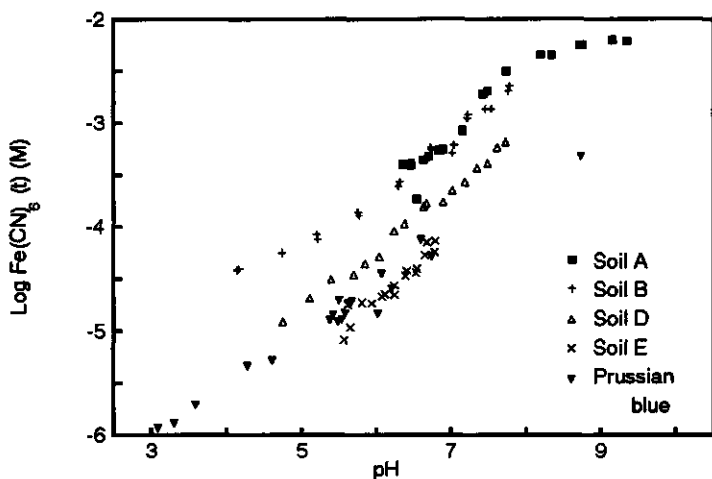


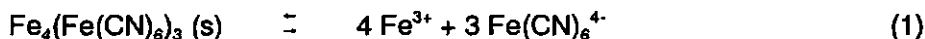
Figure 3. Dependence of $\log (\text{Fe}(\text{CN})_6(t))$ on pH in extracts of Prussian blue and of the soils used in the batch experiment.

Artificially contaminated soil

The results of the extraction of the artificially contaminated soil D (Figure 3) show a similar pH - $\log (\text{Fe}(\text{CN})_6(t))$ relationship as was found in the batch experiment with the contaminated soils (A and B). This indicates that cyanide-minerals present in contaminated soils, which might be formed at high temperatures during an industrial process, and the minerals formed by the reaction of dissolved $\text{Fe}(\text{CN})_6$ with soil material, might be of a similar type.

Prussian blue

A dissolution experiment carried out with the pure mineral Prussian blue (Figure 3) without soil material present, shows a pH - $\log (\text{Fe}(\text{CN})_6(t))$ relationship which is comparable to those found in the previous experiments with soils. This makes it very likely that the $\text{Fe}(\text{CN})_6$ concentrations in the soils are also governed by equilibrium with a Prussian blue ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) type mineral. At equilibrium the product of $(\text{Fe}^{3+})^4$ and $(\text{Fe}(\text{CN})_6^{4-})^3$ equals the solubility product of Prussian blue (equation 1).



Due to equilibrium with iron hydroxides like $\text{Fe}(\text{OH})_3(\text{s})$ or $\text{Fe}_3(\text{OH})_8(\text{s})$ the Fe^{3+} activity in soil solutions is pH dependent(5,6). An increase of the pH will cause the Fe^{3+} activity to drop. The $\text{Fe}(\text{CN})_6^{4-}$ activity will then be increased by

dissolution of some Prussian blue, which results in a higher $\text{Fe}(\text{CN})_6(t)$ concentration. Apart this pH effect the $\text{Fe}(\text{CN})_6(t)$ concentration is directly affected by complexation of $\text{Fe}(\text{CN})_6^{4-}$ with cations like Ca^{2+} , K^+ and Na^+ , and by oxidation of $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$. These reactions allow the $\text{Fe}(\text{CN})_6(t)$ concentration to be much higher than the $\text{Fe}(\text{CN})_6^{4-}$ activity. Therefore the total $\text{Fe}(\text{CN})_6(t)$ concentration at equilibrium with mineral Prussian blue not only depends on the solubility product of this mineral but also on pH, redox potential and concentrations of complexing cations. The solubility product of Prussian blue as reported in literature ($3.0 \cdot 10^{-41}$)(7,8), which was determined by measuring only the $\text{Fe}(\text{CN})_6(t)$ concentration without taking into account complexation or oxidation reactions is therefore probably incorrect.

Discussion

From the results of the experiments it can be concluded that $\text{Fe}(\text{CN})_6$ concentrations in soil solutions are controlled by equilibrium with a Prussian blue like $\text{Fe}(\text{CN})_6$ mineral. Via this equilibrium the pH to a large extent appears to dominate the $\text{Fe}(\text{CN})_6$ concentrations (Figure 2b). Remaining differences in solubility between different soils and pure Prussian blue (Figure 3) may have several reasons: different degrees of complexation of $\text{Fe}(\text{CN})_6$, slight differences in solubility of iron hydroxide minerals, different pH dependence of the Fe^{2+} activity due to pH dependent oxidation kinetics, and by variation in the solubility product of the $\text{Fe}(\text{CN})_6$ mineral due to variation in crystallinity and composition. More insight in the relative importance of each of these subjects will allow better estimation of the extent to which soil parameters affect $\text{Fe}(\text{CN})_6(t)$ concentrations in soil solutions.

Conclusions

- The total $\text{Fe}(\text{CN})_6$ concentration in solutions in equilibrium with cyanide containing soils does not depend on the total amount of cyanide present in these soils.
- Total cyanide contents of soils therefore are of limited use in assessing possible hazards of contaminated sites.
- $\text{Fe}(\text{CN})_6(t)$ concentrations in extracts of cyanide containing soils are to a large extent determined by the pH of the solution.
- Cyanide in originally as well as in artificially contaminated soils exhibits a $\text{Fe}(\text{CN})_6(t)$ dissolution behaviour comparable to that of pure Prussian blue.

- $\text{Fe}(\text{CN})_6(t)$ concentrations in soil solutions therefore are most likely controlled by equilibrium with a Prussian blue like mineral.

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**Dissolution Behaviour of Iron Cyanide
(Prussian Blue) in Contaminated Soils**

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Dissolution Behaviour of Iron Cyanide (Prussian Blue) in Contaminated Soils

The solubility of iron cyanide complexes $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ in soils was studied, to elucidate the possible hazards posed by soils contaminated with cyanide. Earlier work had indicated that these complexes probably precipitate as a form of Prussian blue, a mineral containing iron cyanide and iron. The composition and solubility product of this mineral were estimated from experiments in which it was precipitated from solutions containing $\text{Fe}(\text{CN})_6$ and iron chelated with EGTA, HEDTA, NTA, or citrate. The composition of the mineral was found to be $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$, its $\log K_{\text{sol}}$ was estimated to be ca. -84.5. These results were used to model the dissolution and precipitation behaviour of $\text{Fe}(\text{CN})_6$ in the soil. The model calculations do agree with experimental results and show that the solubility of Prussian blue strongly depends on the pH. Above a pH of ca. 6 it is very soluble allowing high cyanide concentrations in groundwater or soil solutions. Below this pH cyanide concentrations are reduced by precipitation of Prussian blue. Above a pH of ca. 4 cyanide concentrations in groundwater will still exceed the Dutch maximum tolerated level.

Introduction

In some of its chemical forms cyanide is an extremely toxic substance. It is commonly found as a soil contaminant on industrial sites. (In The Netherlands these are often sites of electroplating industries and the sites of former coal gasification plants.) These sites often contain large amounts of cyanide. The possible hazards for human health and the environment posed by such locations greatly depend on the toxicity of cyanide and on its physico-chemical behaviour. Both are strongly related to its chemical speciation. Cyanide in its free form ($\text{HCN}(\text{aq})$ and CN^-) can be volatile ($\text{HCN}(\text{g})$), is biodegradable and is much more toxic than cyanide complexed with iron $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ (1). On the sites of coal gasification plants cyanide was disposed of as iron cyanide complexes. In earlier work we found that although complexed cyanide is not thermodynamically stable under normal soil conditions, it remains the dominant cyanide species in soils because of its slow decomposition kinetics. However, when this complexed cyanide is exposed to light it rapidly decomposes to the free form (2). Therefore, complexed cyanide cannot be regarded as a safe form of cyanide.

The distribution of cyanide over the soil solution and the soil solid phase determines the concentration of cyanide in the soil solution and the transport rate of cyanide through the soil. During earlier work, in which we studied the leaching behaviour of cyanide from contaminated soils, we found that the distribution is probably governed by equilibrium with a iron cyanide mineral. A large part of the cyanide present in the soil solid phase was leached from soils at a nearly constant cyanide concentration in the leachate, indicating that the dissolved cyanide was in equilibrium with a mineral phase (3).

The composition and solubility product of such a mineral phase determine how concentrations of dissolved iron cyanide depend on parameters like pH and redox potential. Several $\text{Fe}(\text{CN})_6^{4-}$ minerals are known, containing metals like iron, zinc, copper, lead or manganese as cations, sometimes in combination with potassium (4). The mineral containing Fe^{3+} as cation is known as Prussian blue, an intense coloured substance, commonly used as a dye in paint and ink (5). The abundance of iron and the blue colour often found in soils contaminated with cyanide suggest that Prussian blue is present in soils. However, several different forms of this mineral exist, all containing $\text{Fe}(\text{CN})_6^{4-}$ and Fe^{3+} (6). In some forms part of the Fe^{3+} has been replaced by K^+ , resulting in $\text{KFeFe}(\text{CN})_6(\text{s})$. Other alkaline metals might behave similarly. The solubility product of only one of these forms ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$) has been determined ($\log K_{\text{sol}} = 10^{-40.6}$) (7). However, this value is defined as the product of total concentrations of the components iron and $\text{Fe}(\text{CN})_6^{4-}$ rather than as the product of their activities (8). Both Fe^{3+} and $\text{Fe}(\text{CN})_6^{4-}$ can oxidise, protonate, hydroxylate and form ion pairs, therefore this solubility product is dependent on pH and pe ($\text{pe} = 16.59 E_{\text{h}}$). Tananaev and his colleagues did not state at which pH and pe they determined this solubility product and therefore it is of little value and cannot be used to construct a solubility product expressed as activities. The solubility of the other forms of Prussian blue is unknown, so it is unclear which of these minerals will be stable in soils.

We set out to assess which form of Prussian blue is present in contaminated soils and to determine its solubility product. We estimated the composition and solubility product from an experiment in which Prussian blue was precipitated from solutions containing chelated iron and iron cyanide. The results were used to calculate total iron cyanide concentrations as a function of pH, assuming equilibrium with Prussian blue and amorphous $\text{Fe}(\text{OH})_3(\text{s})$. These calculated concentrations were compared with concentrations measured in solutions in equilibrium with pure Prussian blue and in equilibrium with contaminated soils.

Experimental Section

Determination of composition and solubility product of Prussian blue

To estimate the composition and the solubility product of Prussian blue we precipitated iron cyanide complexes from solutions containing nearly equal molar concentrations of chelated iron and $\text{Fe}(\text{CN})_6^{4-}$ at a range of pH values. The composition of the precipitated mineral was deduced from the amounts of iron and iron cyanide disappearing from solutions when Prussian blue precipitated. Because of the kinetic stability of iron cyanide ions, the iron present in these complexes will not take part in chemical reactions. Therefore, subtracting this amount of iron from the total amount of iron ($\text{Fe}(\text{t})$) yields the amount of reactive iron ($\text{Fe}(\text{t}^*)$, with $\text{Fe}(\text{t}^*) = \text{Fe}(\text{t}) - \text{Fe}(\text{CN})_6(\text{t})$). The solubility product was derived from the activities of the components present in the mineral for those solutions in which there was equilibrium between dissolved and precipitated iron cyanide.

The iron chelate solutions were made by dissolving 0.2 mM FeCl_3 in 2 mM solutions of the Na salts of EGTA, HEDTA, NTA, and citrate. The pH of these solutions was adjusted to ca. 5 with 0.1M HCl (max. 0.5 ml) to prevent precipitation of iron or cyanide. The solutions then were mixed 1:1 with a 0.2 mM solution of $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.02 M CaCl_2 (pH 7.4). From this solution 12 samples of 100 ml were taken and were adjusted to different pH values with 0.1 M HCl or 0.01 M NaOH. These samples were allowed to equilibrate for four days in the dark at 20°C. After equilibration the samples were analysed for pH and E_{h} , centrifuged for 20 minutes at 32600 g and the supernatants analysed for $\text{Fe}(\text{CN})_6(\text{t})$ and $\text{Fe}(\text{t})$.

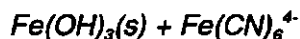
Equilibrium experiments with Prussian blue, suspended $\text{Fe}(\text{OH})_3(\text{s}) + \text{Fe}(\text{CN})_6^{4-}$ and contaminated soils

Total concentrations of iron cyanide in solutions in equilibrium with pure Prussian blue, suspended $\text{Fe}(\text{OH})_3(\text{s}) +$ dissolved $\text{Fe}(\text{CN})_6^{4-}$ and contaminated soils were determined at different pH values. For this purpose an amount of soil, solid Prussian blue or a suspension of $\text{Fe}(\text{OH})_3(\text{s})$ with $\text{K}_4\text{Fe}(\text{CN})_6$ was equilibrated for 7 days in the dark at 20° C in 0.01 M CaCl_2 on a rotary shaker. After 7 days of equilibration the suspensions were analysed for pH and E_{h} , centrifuged at 32600 g for 20 minutes, and analysed for $\text{Fe}(\text{CN})_6(\text{t})$.

Prussian blue

An amount of 0.1 g pure Prussian blue (Janssen Chimica Belgium), in the form of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$, was equilibrated for 7 days with 80 ml 0.01M CaCl_2 on a rotary

shaker in the dark at 20°C. The pH of the suspensions was adjusted before equilibration by adding of hydrochloric acid or sodium hydroxide solutions (max. 0.5 ml) to obtain a pH range from 2 to 9.



Fresh $\text{Fe(OH)}_3(\text{s})$ was prepared by adding a 0.1M sodium hydroxide solution to a 0.01M FeCl_3 solution. The resulting precipitate was collected on a paper filter and rinsed with water to remove the excess sodium hydroxide. The precipitate was suspended in a 0.01M CaCl_2 solution and divided among plastic bottles (50 ml each). The concentration of suspended $\text{Fe(OH)}_3(\text{s})$ in these bottles was ca. 0.02 M. The pH of the suspensions was adjusted by adding hydrochloric acid or sodium hydroxide (max. 0.5 ml), to obtain a pH range from 2 to 11. Then 50 ml 0.0013 M Fe(CN)_6^{4-} in 0.01M CaCl_2 was added to each bottle. As a result each bottle contained a solution of 100 ml $6.5 \cdot 10^{-4}$ M Fe(CN)_6^{4-} , 0.01M suspended $\text{Fe(OH)}_3(\text{s})$ and 0.01M CaCl_2 .

Soils

The soil samples used in the experiments were collected from various sites in the Netherlands contaminated with cyanide in solid or dissolved form by the activities of former gasworks. Before being used in the experiments the soils were air dried. Subsamples (20 g) of the test soils were equilibrated with 80 ml 0.01M CaCl_2 .

Analytical procedures

Total concentrations of iron cyanide [$\text{Fe(CN)}_6(\text{t})$] were measured by an automated spectrophotometric method (9). The pH of the samples was determined with a combined glass calomel electrode. Total iron concentrations in solutions were determined with a flame atomic absorption spectrometer. This ensures that the iron present in the iron cyanide complexes is also measured. The concentration of iron not complexed with cyanide ($=\text{Fe}(\text{t}^*)$) was obtained by subtracting the concentration of $\text{Fe(CN)}_6(\text{t})$ from the total concentration of iron measured ($\text{Fe}(\text{t})$). Redox potentials were determined with a platinum electrode and a calomel reference electrode.

Determination of total cyanide content of soil samples

The total amount of iron cyanide in the soil samples was determined as follows: 5 g of soil material was heated in 50 ml 0.25 M NaOH for 3 hours on a boiling water bath. The samples were then made up to 100 ml with water, filtered and analysed.

We used less concentrated NaOH than standard methods for this extraction because the pH of more dilute extracts is easier to adjust to the value of 12, necessary for the analysis. Furthermore, extraction at a lower pH causes less organic matter to dissolve, and thus reduces the interference of this material in the cyanide determination. We found no decrease in the efficacy of the extraction when we used more dilute NaOH. However, the weaker NaOH concentration allows the soils to have more influence on the pH of the extraction solution. Therefore, after extraction the pH of the solutions must be checked and if it is less than ca. 11, a stronger NaOH concentration must be applied.

Chemical equilibrium calculations

Chemical equilibrium was calculated with the ECOSAT computer program (10) for the following purposes:

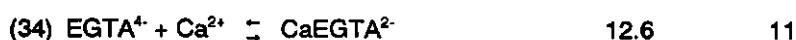
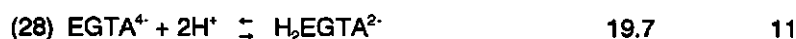
- A: to calculate the activities of Fe^{3+} , $\text{Fe}(\text{CN})_6^{3-}$ and e^- in the chelate experiments from the measured concentrations of dissolved $\text{Fe}(\text{CN})_6(t)$ and $\text{Fe}(t)$, the pH and p_e , and the added concentrations of chelate(t) (1 mM citrate, EGTA, NTA or HEDTA), $\text{Ca}(t) = 0.01\text{M}$, and ionic strength (I) = 0.03M. All equations listed in Table I were used, except for the reaction with Prussian blue (Table I, reaction 2). Equilibrium with amorphous $\text{Fe}(\text{OH})_3(s)$ (Table I, reaction 1) was assumed in cases where supersaturation of the solution with regard to this mineral would otherwise occur.
- B: to calculate the concentrations of dissolved $\text{Fe}(\text{CN})_6(t)$ and $\text{Fe}(t^*)$, and the p_e as a function of pH in the chelate experiments, assuming equilibrium with Prussian blue and amorphous $\text{Fe}(\text{OH})_3(s)$ at $I = 0.03\text{M}$. For these calculations the total amounts of $\text{Fe}(\text{CN})_6(t)$, $\text{Fe}(t^*)$, $e(t)$, chelate(t) were used, together with all equations given in Table I. The precise amounts of $\text{Fe}(\text{CN})_6(t)$ and $\text{Fe}(t^*)$ added were determined separately for each chelate from the measurements in those solutions where no precipitation had occurred. The total amount of electrons present ($e(t)$) was assumed to be equal to the amount of $\text{Fe}(\text{CN})_6^{4-}$ added.
- C: to calculate the concentration of dissolved $\text{Fe}(\text{CN})_6(t)$ in equilibrium with Prussian blue and amorphous $\text{Fe}(\text{OH})_3(s)$, as a function of pH. These calculations were done assuming excess of iron present (a ratio $\text{Fe}(t^*):\text{Fe}(\text{CN})_6(t)$ of 10:1), as will be the case in soils and in 0.01 M CaCl_2 , and $I = 0.03\text{M}$. The total amount of electrons ($e(t)$) was assumed to be equal to the amount of $\text{Fe}(\text{CN})_6(t)$ (10^{-2}M). For these calculations all equations from Table I were used, except for the chelate reactions.

Table I. Equilibrium reactions and constants used in the speciation calculations.

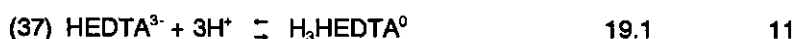
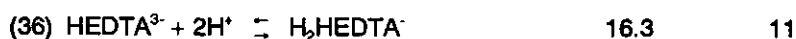
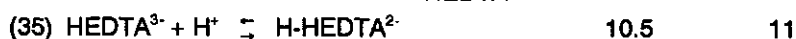
reaction	Log K°	ref
Minerals		
(1) $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Fe}^{3+}$	3.54	11
(2) $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3 \rightleftharpoons 4\text{Fe}^{3+} + 3\text{Fe}(\text{CN})_6^{3-} + 3\text{e}^-$	-84.5	(This study)
Iron hydroxo complexes		
(3) $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	13.0	11
(4) $\text{Fe}^{3+} - \text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_2^+$	6.3	11
(5) $\text{Fe}^{3+} - \text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_2^+$	-2.2	11
(6) $\text{Fe}^{3+} - 2\text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_2^+$	-5.7	11
(7) $\text{Fe}^{3+} - 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_2^0$	-3.0	11
(8) $\text{Fe}^{3+} - 3\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_3^-$	-19.0	11
(9) $\text{Fe}^{3+} - 3\text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_3^0$	-13.1	11
(10) $\text{Fe}^{3+} - 4\text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_4^-$	-21.6	11
Fe(CN)₆ complexes		
(11) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	-6.0	12
(12) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HFe}(\text{CN})_6^{3-}$	10.4	12
(13) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Fe}(\text{CN})_6^{2-}$	12.8	12
(14) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{3-}$	8.5	12
(15) $\text{Fe}(\text{CN})_6^{3-} + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{2-}$	1.5	12
(16) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaFe}(\text{CN})_6^{2-}$	10.1	12
(17) $\text{Fe}(\text{CN})_6^{3-} + \text{Ca}^{2+} \rightleftharpoons \text{CaFe}(\text{CN})_6^-$	2.6	12
Chelate complexes		
<i>Citrate</i>		
(19) $\text{Cit} + \text{H}^+ \rightleftharpoons \text{HCit}^{\ominus}$	6.4	8
(20) $\text{Cit} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Cit}^{2-}$	11.2	8
(21) $\text{Cit} + 3\text{H}^+ \rightleftharpoons \text{H}_3\text{Cit}$	14.3	8
(22) $\text{Cit} + \text{Fe}^{3+} \rightleftharpoons \text{FeCit}^-$	13.4	8
(23) $\text{Cit} + \text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{FeCit}^-$	18.7	8
(24) $\text{Cit} + \text{Fe}^{3+} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{FeHCit}$	23.0	8
(25) $2\text{Cit} + 2\text{Fe}^{3+} + 2\text{e}^- - 2\text{H}^+ \rightleftharpoons \text{Fe}_2\text{Cit}_2\text{OH}_2$	24.4	8



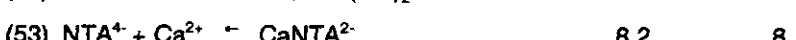
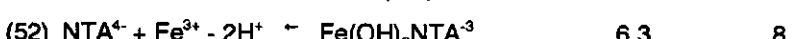
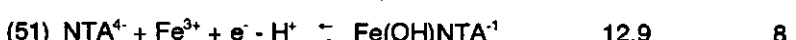
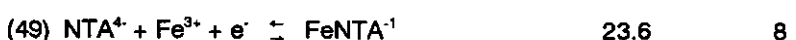
EGTA



HEDTA



NTA



Results and Discussion

Determination of the composition of Prussian blue

From the concentrations of dissolved iron cyanide and iron measured in the chelate experiments it appears that in all cases iron cyanide remains dissolved in the high pH range ($\text{pH} > \text{ca. } 6$, Figure 1). This is also the case for iron, except for the samples with EGTA and citrate where iron hydroxide precipitates at the highest pH values. The measured concentrations of dissolved cyanide and iron even appear to exceed the 0.1 mM added, but this is probably because of an inaccuracy in the added amounts. In the low pH range part of the cyanide and virtually all the iron precipitates (Table II). The pH at which cyanide starts to precipitate depends on which chelate is present. In the low pH range, iron is prevented from precipitating as hydroxide by the low activity of OH^- , combined with the low activity of Fe^{3+} resulting from complexation with the chelates.

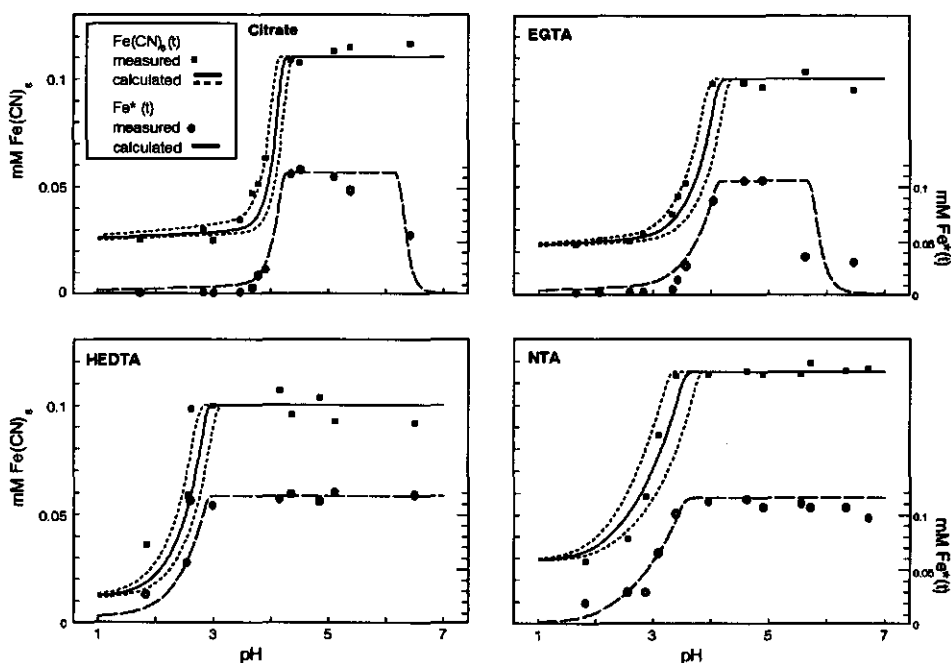


Figure 1. Concentrations of dissolved iron and complexed cyanide as a function of pH, measured and calculated according to method B using $\log K_{\text{sol}} = -84.5$ (solid line), -83.5 and -85.5 (dotted lines) for $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$.

Under those conditions iron can only be removed from solutions by precipitation of an iron cyanide mineral. This enables the composition of the precipitate to be estimated from the remaining concentrations of dissolved $\text{Fe}(\text{t}^*)$ and $\text{Fe}(\text{CN})_6(\text{t})$.

According to Figure 1 in the EGTA and citrate solutions in the low pH range, ca. one-quarter of the added iron cyanide remains dissolved. This indicates that the ratio between $\text{Fe}(\text{t}^*)$ and $\text{Fe}(\text{CN})_6(\text{t})$ in the precipitate must equal ca. 4:3, which agrees with the $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$ form of Prussian blue. Apparently the $\text{KFeFe}(\text{CN})_6(\text{s})$ form, in which the ratio between $\text{Fe}(\text{t}^*)$ and $\text{Fe}(\text{CN})_6(\text{t})$ equals 1:1, was not stable under the experimental conditions even though potassium was available. $\text{KFeFe}(\text{CN})_6(\text{s})$ might still be more stable than $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$ at high $(\text{K}^+):(\text{Fe}^{3+})$ ratios. However, the ratio $(\text{K}^+):(\text{Fe}^{3+})$ in our experiments was much greater than in natural soils, and therefore it is unlikely that $\text{KFeFe}(\text{CN})_6$ will form in such soils.

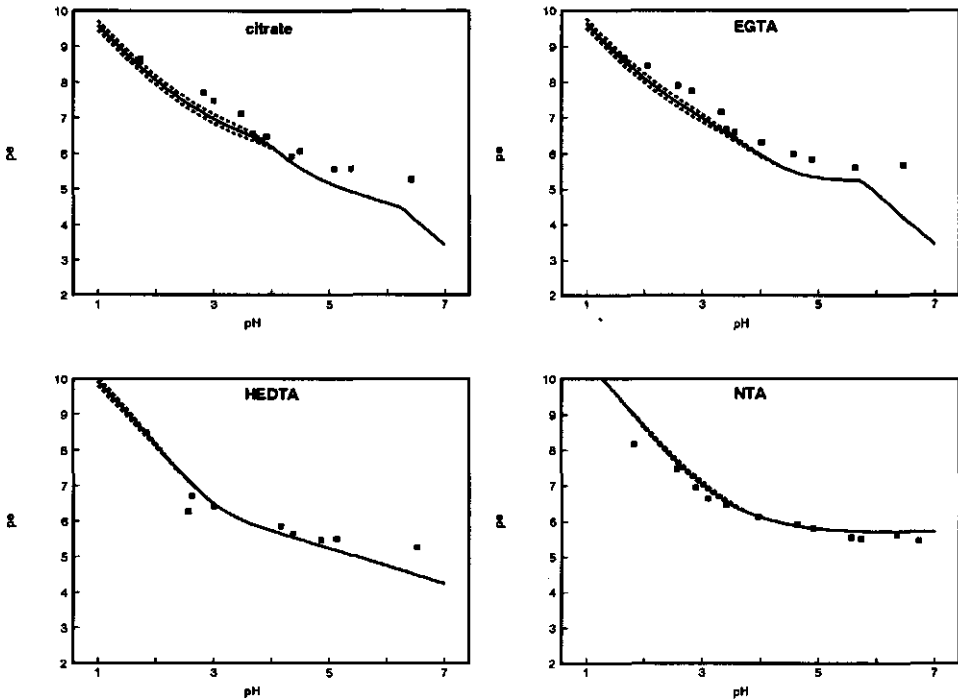


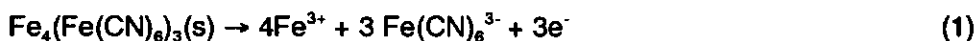
Figure 2. p_e as a function of pH, measured and calculated. Calculations according to method B, using $\log K_{\text{sol}} = -84.5$ (solid line), -83.5 and -85.5 (dotted lines) for $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$.

Determination of the solubility product of Prussian blue

The observed pH dependence of the precipitation of Prussian blue can be ascribed to the chelate ions and the $\text{Fe}(\text{CN})_6^{4-}$ ions competing for association with Fe^{3+} . Under conditions where $\text{Fe}(\text{CN})_6^{4-}$ has a greater affinity for iron than the chelate, Prussian blue will precipitate. Otherwise both iron cyanide and iron will remain dissolved.

Competition between protons and Fe^{3+} , causes the stability of the chelate iron complexes to be pH dependent. This implies that below a certain pH, Prussian blue will precipitate. This pH depends on the affinity of iron for the chelate used (fig 1).

The dissolution reaction of Prussian blue can be given as:



The ion activity product (IAP), which equals the solubility product K_{sol} when there is equilibrium is formulated as:

$$\text{IAP} = (\text{Fe}^{3+})^4 \times (\text{Fe}(\text{CN})_6^{3-})^3 \times (\text{e}^-)^3 \quad (2)$$

The solubility product of Prussian blue can now be estimated by calculating the activities of Fe^{3+} and $\text{Fe}(\text{CN})_6^{3-}$, according to method A, from the $\text{Fe}(\text{t}^*)$, $\text{Fe}(\text{CN})_6(\text{t})$, pH and pe measured in those solutions where there is equilibrium with precipitated Prussian blue. The results of these calculations are presented in Table II. The most reliable IAP values are those obtained from solutions where the $\text{Fe}(\text{CN})_6(\text{t})$ concentration has fallen because of precipitation, but where still detectable amounts of $\text{Fe}(\text{t}^*)$ are present. In the low pH ranges the concentrations of dissolved $\text{Fe}(\text{t}^*)$ cannot be determined very accurately because of the much higher concentrations of $\text{Fe}(\text{CN})_6(\text{t})$. Therefore, the calculated solubility products in the low pH range are not very precise. The most reliable values are asterisked in Table II.

Table II. Measured pH, pe, Fe(CN)₆(t) and Fe(t*) and calculated ion activity product (Fe³⁺)⁴ * (e)⁻³ * (Fe(CN)₆)³ in the chelate experiments.

pH	pe	Fe(CN) ₆ (t)	Fe(t*)	log IAP
CITRATE				
1.73	8.65	2.54 10 ⁻⁵	<1.00 10 ⁻⁷	>-90.3
2.83	7.70	3.01 10 ⁻⁵	<1.00 10 ⁻⁷	>-90.1
3.00	7.47	2.53 10 ⁻⁵	<1.00 10 ⁻⁷	>-90.7
3.47	7.11	3.48 10 ⁻⁵	<1.00 10 ⁻⁷	>-91.2
3.78	6.38	5.14 10 ⁻⁵	1.91 10 ⁻⁵	-83.9*
3.68	6.56	4.71 10 ⁻⁵	7.45 10 ⁻⁶	-84.7*
3.91	6.47	6.33 10 ⁻⁵	2.54 10 ⁻⁵	-84.3*
4.35	5.93	1.09 10 ⁻⁴	1.14 10 ⁻⁴	-86.0
4.50	6.07	1.08 10 ⁻⁴	1.18 10 ⁻⁴	-87.5
5.09	5.57	1.13 10 ⁻⁴	1.12 10 ⁻⁴	-92.6
5.38	5.58	1.15 10 ⁻⁴	9.94 10 ⁻⁵	-95.1
6.43	5.27	1.17 10 ⁻⁴	5.73 10 ⁻⁵	-102.3
HEDTA				
1.85	8.48	3.63 10 ⁻⁵	2.43 10 ⁻⁵	-82.3*
2.56	6.26	5.91 10 ⁻⁵	5.62 10 ⁻⁵	-85.3*
2.62	6.70	9.85 10 ⁻⁵	1.17 10 ⁻⁴	-82.9
3.00	6.41	1.00 10 ⁻⁴	1.11 10 ⁻⁴	-85.4
4.16	5.87	1.07 10 ⁻⁴	1.18 10 ⁻⁴	-94.0
4.37	5.66	9.61 10 ⁻⁵	1.23 10 ⁻⁴	-96.1
4.86	5.47	1.04 10 ⁻⁴	1.18 10 ⁻⁴	-101.1
5.13	5.51	9.30 10 ⁻⁵	1.26 10 ⁻⁴	-103.9
6.52	5.28	9.22 10 ⁻⁵	1.23 10 ⁻⁴	-117.0
8.81	5.09	9.65 10 ⁻⁵	1.12 10 ⁻⁴	-136.1
EGTA				
1.65	8.68	2.34 10 ⁻⁵	<1.00 10 ⁻⁷	>-90.6
2.06	8.46	2.56 10 ⁻⁵	<1.00 10 ⁻⁷	>-89.8
2.58	7.91	2.53 10 ⁻⁵	<1.00 10 ⁻⁷	>-90.4
2.82	7.75	2.83 10 ⁻⁵	<1.00 10 ⁻⁷	>-90.9
3.33	7.16	3.76 10 ⁻⁵	6.14 10 ⁻⁶	-86.1
3.42	6.68	4.60 10 ⁻⁵	1.54 10 ⁻⁵	-84.6*
3.56	6.60	5.20 10 ⁻⁵	2.86 10 ⁻⁵	-84.1*
4.03	6.32	9.80 10 ⁻⁵	8.74 10 ⁻⁵	-84.2
4.57	5.99	9.83 10 ⁻⁵	1.05 10 ⁻⁴	-87.7
4.89	5.84	9.63 10 ⁻⁵	1.06 10 ⁻⁴	-90.1
5.63	5.61	1.04 10 ⁻⁴	3.64 10 ⁻⁵	-97.7
6.47	5.68	9.51 10 ⁻⁵	3.14 10 ⁻⁵	-104.8

		NTA		
1.83	8.17	$2.88 \cdot 10^{-5}$	$1.84 \cdot 10^{-5}$	-83.2*
2.57	7.47	$3.93 \cdot 10^{-5}$	$2.94 \cdot 10^{-5}$	-84.7*
2.88	6.96	$5.88 \cdot 10^{-5}$	$2.87 \cdot 10^{-5}$	-85.5*
3.10	6.64	$8.67 \cdot 10^{-5}$	$6.52 \cdot 10^{-5}$	-84.3*
3.41	6.48	$1.14 \cdot 10^{-4}$	$1.02 \cdot 10^{-4}$	-84.2
3.96	6.14	$1.14 \cdot 10^{-4}$	$1.12 \cdot 10^{-4}$	-86.4
4.63	5.92	$1.16 \cdot 10^{-4}$	$1.14 \cdot 10^{-4}$	-90.5
4.91	5.81	$1.14 \cdot 10^{-4}$	$1.07 \cdot 10^{-4}$	-92.6
5.56	5.56	$1.14 \cdot 10^{-4}$	$1.11 \cdot 10^{-4}$	-97.4
5.73	5.51	$1.20 \cdot 10^{-4}$	$1.07 \cdot 10^{-4}$	-98.8
6.34	5.61	$1.16 \cdot 10^{-4}$	$1.07 \cdot 10^{-4}$	-103.7
6.73	5.46	$1.17 \cdot 10^{-4}$	$9.74 \cdot 10^{-5}$	-107.0

(* = Selected value)

There appears to be good agreement between the IAP values obtained with the different chelates. The log of the calculated solubility product appears to vary between -82.3 and -85.5 with a mean of -84.4 and a standard deviation of 0.83. We will henceforth use the rounded-off values of these Figures, -84.5 ± 1 , as an estimate of the $\log K_{\text{sol}}$ of Prussian blue.

We used this solubility product to model the precipitation behaviour of Prussian blue in the chelate experiments and then compared the results for $\text{Fe}(\text{CN})_6(\text{t})$, $\text{Fe}(\text{t}^*)$, and p_e calculated in this way (method B) with the measured values (Figures 1 and 2).

As can be seen, the $\text{Fe}(\text{CN})_6(\text{t})$ concentrations calculated with a solubility product of $10^{-84.5}$ largely agree with the measured concentrations. The sensitivity of the calculated results to variation in the estimated solubility product follows from Figures 1 and 2, where the results of calculations with solubility products of $10^{-83.5}$ and $10^{-85.5}$ are shown. The results show that the calculated concentrations are sensitive to small changes in the solubility product. However, the measured concentrations adequately accounted for by assuming a $\log K_{\text{sol}}$ of -84.5 ± 1 . The actual solubility product probably depends on the crystallinity of the precipitate, and therefore will change upon aging. Figure 1 gives the calculated and measured concentrations of $\text{Fe}(\text{t}^*)$ too. In the case of citrate and EGTA, iron is removed from the solutions in the high pH range by precipitation of iron hydroxide. This can also be observed in the calculated results.

In Figure 2 the calculated and measured p_e values are compared because this parameter is essential when modelling the precipitation behaviour of iron cyanide complexes. Determining the p_e by measuring E_h is generally not very accurate; however, in this case, because of the fast redox equilibrium between

$\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ the conditions in the experiments were relatively suitable for pe measurements. The results of the calculations appear to agree well with the measured results, especially in the low pH ranges where Prussian blue is present. This supports the validity of the modelled precipitation behaviour. In the pH range the measured pe values tend to be somewhat larger than calculated, probably because of some oxidation of the samples which was not taken into account in the calculations. In the high pH ranges the pe is not buffered by equilibrium with Prussian blue and even the oxidation of a very small part of the dissolved $\text{Fe}(\text{CN})_6^{4-}$ leads to an increase of the pe .

At first sight, the value of $10^{-84.5}$ found for the solubility product of Prussian blue differs greatly from the $10^{-40.6}$ reported in the literature (7). But as discussed earlier, these values are not directly comparable. A better comparison can be made when the new solubility product is used to calculate total concentrations of dissolved iron, iron cyanide and pe at different pH levels in equilibrium with Prussian blue. In this way a solubility product based on total concentrations can be calculated. This results in values ranging from $10^{-39.2}$ at pH 1 to $10^{-36.5}$ at pH 5, which are much more comparable with the value determined by Tananaev (7).

Dissolution and precipitation of Prussian blue in equilibrium with iron hydroxide

The solubility product of Prussian blue as estimated from the chelate experiments can now be used to model the dissolution and precipitation behaviour of Prussian blue when the activity of Fe^{3+} is governed by equilibrium with amorphous $\text{Fe}(\text{OH})_3(\text{s})$ (equation 1, Table I). This is probably the case when no chelates are present, and will more closely resemble the field situation.

We calculated in this way the total cyanide concentrations in equilibrium with Prussian blue according to method C as a function of pH. In Figure 3 the results of these calculations are presented together with the results of the equilibrium experiments with pure Prussian blue, $\text{Fe}(\text{OH})_3(\text{s}) + \text{Fe}(\text{CN})_6^{4-}$ and the contaminated soils.

Prussian blue

The total iron cyanide concentrations measured in equilibrium with Prussian blue appear to be close to the calculated concentrations. The strong tendency of Prussian blue to form colloids makes it difficult to separate precipitated Prussian blue from solutions, when relatively large amounts of solid Prussian blue are present, which was the case in this experiment. Incomplete separation results in the dissolved cyanide concentration being overestimated. This

probably caused the high concentrations we measured in some solutions in the low pH range. No results are available because for pH values above 6, the pH of the alkaline solutions decreased significantly, from ca. pH 9 to ca. pH 6, during equilibration.

Iron hydroxide + $Fe(CN)_6^{4-}$

In this experiment, in which solid Prussian blue is formed from dissolved $Fe(CN)_6^{4-}$ and suspended $Fe(OH)_3(s)$, equilibrium is approached from the opposite direction compared with the experiment in which Prussian blue is dissolved. If concentrations of dissolved iron cyanide were dominated by kinetic effects, e.g. in the case of slow dissolution or precipitation of Prussian blue or iron hydroxide, then the concentrations observed in both experiments would differ significantly from each other. But as shown in Figure 3 the results of both experiments are largely comparable. The remaining discrepancy with the Prussian blue experiment and with the calculated concentrations might still be attributed to kinetic effects (slow dissolution of iron hydroxide) or to the fact that the iron hydroxide present in this experiment is slightly less soluble than in the Prussian blue experiment or the calculations. Both phenomena would have the same effect.

In the pH range 6-8 the measured concentrations are lower than calculated. Some dissolved cyanide has disappeared although precipitation was not predicted. This cannot be attributed to kinetic effects, but is most likely the result of adsorption of $Fe(CN)_6^{4-}$ on the iron hydroxide. In the high pH range all iron cyanide remains dissolved, which agrees with the calculations.

Soils

The results of the measurements of pH, p_e and $CN(t)$ in the soil extracts and $CN(t)$ in the soils are presented in Table III. The largest amounts of cyanide are found in the more acidic soils. In contrast the highest concentrations of dissolved iron cyanide are found in the more alkaline extracts. According to Table III, only a small percentage (<1.5%) of the total amount of iron cyanide present in the acidic soils dissolves. The iron cyanide concentrations in the extracts of the soils in the low pH range are comparable with the concentrations observed in equilibrium with pure Prussian blue and also agree well with the calculated concentrations in this pH range. This indicates that Prussian blue is probably present in those soils and that iron cyanide concentrations are governed by equilibrium with Prussian blue and amorphous iron

Table III. Total cyanide content of the soils and results of the 0.01 M CaCl₂ extractions.

Soil	Fe(CN) ₆ (t) mg.Kg ⁻¹ as CN)	pH	pe (16.95 E _h)	Fe(CN) ₆ (t). in extracts (μMol.L ⁻¹)	Percentage of Fe(CN) ₆ (t) in extract.
A	204	4.0	9.9	0.97	0.3
B	4100	4.1	9.4	3.23	0.05
C	84	4.3	6.5	2.02	1.5
D	2090	5.2	8.8	8.08	0.2
E	1070	5.2	8.5	18.6	1.1
F	2110	5.2	8.8	12.4	0.4
G	20850	5.6	9.1	89.9	0.3
H	54	6.6	6.6	6.68	7.8
I	105	7.0	8.1	76.9	45.7
J	1182	7.0	7.6	62.0	3.3
K	34	7.3	8.5	2.59	4.8
L	81	7.3	9.3	60.0	46.5

hydroxide. In the extraction experiments this amorphous iron hydroxide is probably formed when Prussian blue dissolves. In soils in situ the solubility of iron might also be controlled by less soluble (hydr)oxides, resulting in a higher solubility of iron cyanide. When equilibrium of dissolved iron with Fe-soil ($\log K_{\text{sol}} = 2.7$ (11)) is assumed instead of equilibrium with amorphous iron, the solubility of cyanide increases tenfold at the same pH, or the same iron cyanide concentrations will be found at a pH ca. one-third of a unit lower than indicated in Figure 3.

A much larger part of the cyanide present dissolves in the soils in the higher pH range (3.3-47%) than in the more acidic soils. Nevertheless, it appears that iron cyanide does not dissolve completely, although this is predicted. Complete dissolution is probably prevented by dissolution kinetics which might play a more important role in the higher pH range, because a larger part of the present iron cyanide has to dissolve to reach equilibrium. Unlike the experiment with pure Prussian blue, the pH and pe are now buffered by the soil material present. Therefore, in this case fast equilibrium cannot be reached by a decrease of the pH caused by dissolution of Prussian blue.

Apart from dissolution kinetics, incomplete dissolution of iron cyanide in the alkaline soils could also be caused by the occurrence of iron cyanide in precipitates containing metals like Pb²⁺ or Zn²⁺ instead of Fe³⁺.

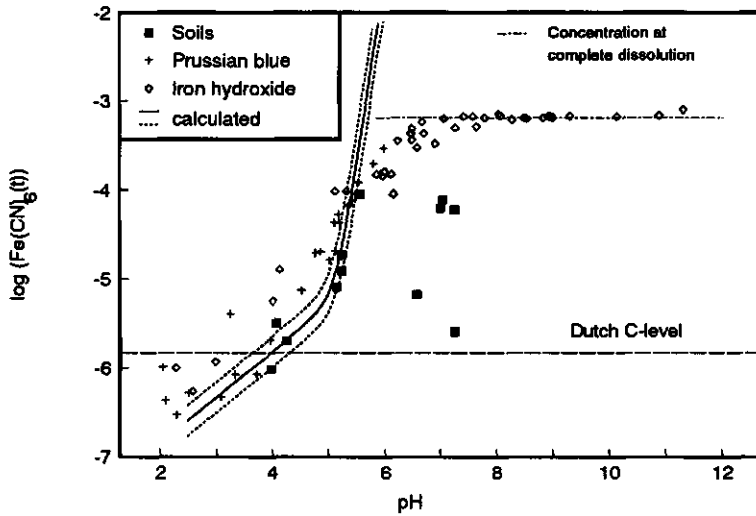


Figure 3. Concentrations of $\text{Fe}(\text{CN})_6(\text{t})$ as a function of pH in equilibrium with pure Prussian blue, $\text{Fe}(\text{OH})_3(\text{s}) + \text{Fe}(\text{CN})_6$, and contaminated soils, measured and calculated according to method C.

In the Netherlands, the concentration of iron cyanide in groundwater above which immediate remedial action is desired, the so-called C-level, is $200 \mu\text{gL}^{-1}$ as CN^- , which is equivalent to $1.28 \cdot 10^{-6} \text{ M Fe}(\text{CN})_6(\text{t})$ (13). From our results it can be concluded that when there is equilibrium with Prussian blue, this concentration is already exceeded above a pH of ca. 4 (Figure 3). This implies that all Prussian blue present has to be removed before concentrations will fall to a tolerated level.

Conclusions

- Concentrations of iron cyanide in soil solutions below a pH of ca. 6 are probably controlled by equilibrium with Prussian blue ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$).
- The solubility of this mineral and thus the mobility of cyanide in soils, will strongly depend on the pH and redox potential.
- The solubility product of Prussian blue expressed in activities of Fe^{3+} , e^- and $\text{Fe}(\text{CN})_6^{3-}$ is estimated to be $10^{-84.5}$.
- Although precipitation of Prussian blue occurs in acid soils, this does not prevent cyanide concentrations in groundwater exceeding the maximum levels tolerated in the Netherlands.

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Mobility of Cyanide on Contaminated Soil Sites

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Mobility of Cyanide on Contaminated Soil Sites

In the Netherlands more than 200 soil sites are seriously contaminated with cyanide, mainly in the form of iron cyanide complexes [$\text{Fe}(\text{CN})_6^{3-} + \text{Fe}(\text{CN})_6^{4-}$]. The mobility of this cyanide plays an important role in predicting the possible hazards for environment and human health. This mobility was investigated by evaluating available data on concentrations of cyanide occurring in groundwater on contaminated sites and by examination of four contaminated soil sites. On sites with alkaline soils (pH ca. 7.5), cyanide was found to be relatively mobile, whereas on sites with acidic soils (pH ca. 4) cyanide was relatively immobile. This agrees with the assumption that the behaviour of cyanide in these contaminated soils is largely governed by dissolution and precipitation of Prussian blue [$\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})$]. In acidic soils the concentration in the groundwater is in good agreement with equilibrium with this mineral, whereas in alkaline soils the concentration is determined by slow dissolution kinetics. Precipitation of Prussian blue in acidic soils does not prevent dissolved iron cyanide concentrations to exceed Dutch soil quality standards.

Introduction

Cyanide has been called one of nature's most toxic substances (Fuller, 1984). However, its toxicity strongly depends on the chemical form in which it is present. The free form [$\text{HCN}(\text{aq}) + \text{CN}^-$] is extremely toxic whereas iron cyanide complexes [$\text{Fe}(\text{CN})_6^{3-} + \text{Fe}(\text{CN})_6^{4-}$] are considered to be relatively harmless. Cyanide is often found as a soil contaminant on industrial sites, especially on the sites of former gasworks and of electroplating industries (Alessi et al., 1976). On the sites of former gasworks, of which there are 234 in the Netherlands, cyanide was mainly discharged as complexed cyanide present in mineral form in waste material. Leaching of this material after disposal causes contamination of the soil with iron cyanide complexes. This form of cyanide is not thermodynamically stable in soil solutions and tends to decompose to free cyanide. However, in the dark this proceeds extremely slowly which is illustrated by half-lives of complexed cyanide varying from years to hundreds of years depending on pH and redox potential (Meeussen et al., 1992a). This allows the complexed form to persist in soils and to govern the overall behaviour of cyanide. Exposure to daylight significantly increases the decomposition rate of these iron cyanide complexes. Complete decomposition then occurs within hours or days, depending on light intensity (Meeussen et al., 1989 & 1992a).

Therefore complexed cyanide cannot be regarded as a completely safe form of cyanide. The possible risks for negative effects on human health or the environment are strongly influenced by the physico-chemical behaviour of this cyanide in soils. Insight in this behaviour and how it is affected by soil parameters like pH and p_e enables better evaluation of those risks.

The behaviour of contaminants in soils is largely governed by the interaction between the dissolved contaminant and the soil solid phase. In case of contamination of soils with cyanide in the form of iron cyanide complexes this interaction is probably dominated by precipitation of Prussian blue, a precipitate of iron and iron cyanide $[\text{Fe}_4(\text{Fe}(\text{CN})_6)_3(\text{s})]$ (Meeussen et al., 1990). Although this mineral is normally considered to be rather insoluble, its solubility strongly depends on the pH and redox potential in the ranges found in soils. Using the solubility product of Prussian blue to calculate concentrations of dissolved iron cyanide in equilibrium with this mineral, it is possible to estimate the effect of the pH and redox potential on the mobility of cyanide in the soil.

In the Netherlands both soils with a pH around 7 and more acidic soils with a pH around 4 commonly occur. The more alkaline pH values are found in soils in the lower areas of the country which are primarily carbonate containing clay soils formed by sea and river sedimentation whereas the more acidic pH levels are found in sandy soils in the higher parts of the country. The difference in pH between those soil types is expected to cause a rather large difference in solubility of Prussian blue and in that way also a large difference in mobility of cyanide between those soil types.

The main objective of this study is to investigate the mobility of cyanide in the field as influenced by pH and redox potential, and to verify if the observed mobility can be explained to be governed by equilibrium with Prussian blue and the calculated solubility of this mineral.

We studied this mobility in field situations by evaluating available data on cyanide concentrations measured in groundwater on contaminated sites and by determining the distribution of cyanide in soil profiles on three contaminated sites with different pH levels.

Materials and methods

Calculation of dissolved iron cyanide concentrations in equilibrium with Prussian blue and iron (hydr)oxide

The solubility of iron cyanide in equilibrium with Prussian blue as a function of pH and p_e ($p_e = 16.95 E_h$) was calculated with the computer program ECOSAT

(Keizer, 1991). The chemical equilibria used as input for this program are listed in Table 1. Calculations are done at a total iron cyanide concentration ($\text{Fe}(\text{CN})_6(\text{t})$) of 0.1 M, a total iron concentration $\text{Fe}(\text{t}^*)$ of 1 M (with $\text{Fe}(\text{t}^*) = \text{Fe}(\text{t}) - \text{Fe}(\text{CN})_6(\text{t})$), $\text{Ca}(\text{t}) = 0.01$ M and a ionic strength of 0.03 M.

Table 1. Equilibrium reactions and constants used in the speclation calculations.

reaction	Log K°	reference
Minerals		
(1) $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Fe}^{3+}$	3.54	(Lindsay 1976)
(2) $\text{Fe}_3(\text{OH})_8(\text{s}) + 8\text{H}^+ \rightleftharpoons 3\text{Fe}^{3+} + \text{e}^- + 8\text{H}_2\text{O}$	4.63	(Lindsay 1976)
(3) $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3 \rightleftharpoons 4\text{Fe}^{3+} + 3\text{Fe}(\text{CN})_6^{3-} + 3\text{e}^-$	-84.5	(Meeussen 1992 b)
Iron hydroxo complexes		
(4) $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	13.0	(Lindsay 1976)
(5) $\text{Fe}^{3+} - \text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})^{2+}$	6.3	"
(6) $\text{Fe}^{3+} - \text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_2^+$	-2.2	"
(7) $\text{Fe}^{3+} - 2\text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_2^+$	-5.7	"
(8) $\text{Fe}^{3+} - 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_2^0$	-3.0	"
(9) $\text{Fe}^{3+} - 3\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_3^-$	-19.0	"
(10) $\text{Fe}^{3+} - 3\text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_3^0$	-13.1	"
(11) $\text{Fe}^{3+} - 4\text{H}^+ \rightleftharpoons \text{Fe}(\text{OH})_4^-$	-21.6	"
$\text{Fe}(\text{CN})_6$ complexes		
(12) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	-6.0	(Beck 1987)
(13) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HFe}(\text{CN})_6^{3-}$	10.4	"
(14) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{Fe}(\text{CN})_6^{2-}$	12.8	"
(15) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{3-}$	8.5	"
(16) $\text{Fe}(\text{CN})_6^{3-} + \text{K}^+ \rightleftharpoons \text{KFe}(\text{CN})_6^{2-}$	1.5	"
(17) $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaFe}(\text{CN})_6^{2-}$	10.1	"
(18) $\text{Fe}(\text{CN})_6^{3-} + \text{Ca}^{2+} \rightleftharpoons \text{CaFe}(\text{CN})_6^-$	2.6	"

Because of the very low decomposition rate of iron cyanide complexes in the dark these complexes are assumed not to decompose (Meeussen et al., 1992a). The calculations are done for pH values ranging from 3 to 8 and p_e values ranging from -6 to 18.

Evaluation of available data

In the Netherlands a large part of the contaminated soil sites has been investigated for the presence of potentially hazardous substances. As a result a lot of data exists on concentrations of cyanide present in soil and groundwater on former gasworks sites. Unfortunately, these data do not contain information about pH or p_e levels. However, the geographical location of the investigated sites enabled selection of two groups of 6 sites, one with presumably a pH below 5, and the other group with presumably a pH around 7.5. The 6 acidic sites are located on the higher sandy soils in the province of Gelderland, the 6 alkaline sites are located in the province of Zuid-Holland on carbonate containing clay soils. From each of these sites the two highest concentrations of total cyanide measured in the groundwater were selected. Total cyanide concentrations in these groundwater samples were in most cases measured according to the Dutch standard method (NEN 6489), which is based on a manual acidic distillation procedure followed by colorimetric determination of cyanide. The maximum total cyanide concentrations found in the contaminated soils vary between ca. 0.30 g.kg^{-1} to ca. 10.0 g.kg^{-1} . In most cases the distribution of this cyanide over a site is very heterogeneous which prevents the use of a "mean" cyanide concentration of the soil per site.

Investigation of contaminated soil sites

Additionally, we determined the distribution of cyanide in soil profiles on several contaminated sites, together with the pH and p_e . Initially we selected two sites on acidic soils (A,B) and two sites on more alkaline soil types (C,D). However, on one of the alkaline sites (D) the soil profile appeared to be recently disturbed by human activities, so it was impossible to relate the present spatial distribution of cyanide to its leaching behaviour. On the remaining three sites the soil was sampled at two locations located several meters from each other, at several depths until the groundwater level was reached.

In these soil samples the total cyanide ($\text{Fe}(\text{CN})_6(\text{t})$) content was determined by extracting 5 g of the samples with 50 ml of 0.25 M NaOH on a boiling water bath (3 h).

In order to estimate the concentrations of cyanide present in the soil solution under field conditions 20.0 g of the soil samples was equilibrated for five days

with 80 ml 0.01 M CaCl_2 . The extracts were analysed for pH, p_e and for total dissolved cyanide $\text{CN}(t)$.

Samples of the groundwater were obtained by centrifuging the deepest (water saturated) soil sample from each profile. In these samples also the total concentration of dissolved cyanide $\text{CN}(t)$ was measured.

The pH and p_e as measured in the soil extracts combined with the total cyanide content of the soil samples at different depths were used to calculate the concentration of dissolved iron cyanide in equilibrium with Prussian blue and iron (hydr)oxide. These calculations were done with the ECOSAT model at a ionic strength of 0.03 M, $\text{Ca}(t)=0.01$ M and $\text{Fe}(t^*)= 1$ M and the total amount of iron cyanide in the soil $(\text{Fe}(\text{CN})_6(t))$ as measured.

Chemical analysis

The total concentration of cyanide in all solutions was measured, after centrifugation for 20 minutes at 32600 g, by an automated spectrophotometric method (Meeussen et al., 1989). The pH of the solutions was determined with a combined glass/calomel electrode, redox potentials with a platinum electrode and a calomel reference electrode.

Results and Discussion

Calculation of dissolved iron cyanide concentrations in equilibrium with Prussian blue and iron (hydr)oxide

The calculated total concentration of dissolved iron cyanide in equilibrium with Prussian blue and $\text{Fe}(\text{OH})_3(s)$ is shown in figure 1 as a function of pH and p_e . The solid curves connect the points with equal total concentrations of dissolved iron cyanide complexes. The diagonal solid lines enclose the area where water is thermodynamically stable, the dotted circle roughly encloses the conditions occurring in natural soils (Lindsay, 1976).

From this figure it appears that although Prussian blue is known as only slightly soluble, this solubility strongly depends on both pH and redox potential. At pH levels higher than 6 the solubility of Prussian blue is higher than 0.01 M regardless of the p_e .

At the pH levels occurring in acidic soils the solubility of Prussian blue is much lower, which makes precipitation possible at much lower concentrations of dissolved iron cyanide complexes. In that case the total concentration of dissolved iron cyanide strongly depends on pH and p_e (Figure 1).

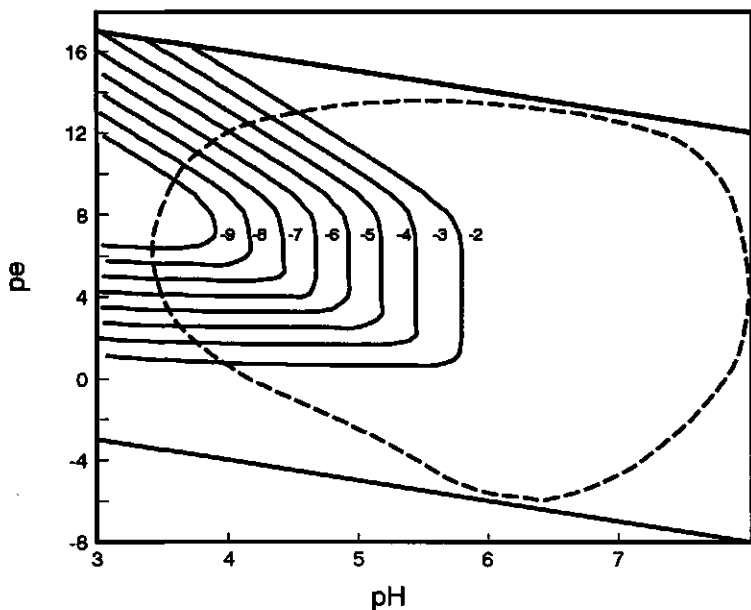
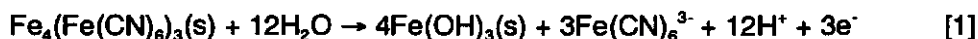


Figure 1. Calculated log of the $[\text{Fe}(\text{CN})_6(t)]$ concentration in mol.l^{-1} in equilibrium with Prussian blue and iron (hydr)oxide as a function of pH and pe.

In mildly reduced to oxidized soils (pH + pe ranging from ca. 11-18, Lindsay, 1976) the overall dissolution reaction in 0.01M CaCl_2 is:



This reaction causes the equilibrium total concentration of dissolved iron cyanide complexes to be proportional to $4 \text{ pH} - \text{pe}$, which implies that at a constant pe the iron cyanide concentration increases with a factor 10^4 with a one unit increase of the pH. On the other hand at a constant pH level the solubility of iron cyanide decreases with a factor 10 when the pe decreases one unit.

At lower redox potentials (pe < ca. 7), the overall dissolution reaction of Prussian blue in 0.01 M CaCl_2 becomes:



In this reaction no electrons are involved which makes the solubility of iron cyanide independent of the pe , as is shown by the vertical parts of the curves in figure 1.

Although it is not a very common combination in soils, a low redox potential combined with a low pH , considerably increases the solubility of iron. At dissolution of Prussian blue then no longer precipitation of iron (hydr)oxide occurs:



In this reaction no protons are produced or consumed which makes the solubility of Prussian blue independent of the pH , shown by the horizontal parts of the curves in figure 1. The remaining pe dependence is due to the produced electrons.

In general, when Prussian blue precipitates in soils iron (hydr)oxide is transformed into Prussian blue. In case of dissolution of Prussian blue iron hydroxide will be formed. Therefore, equilibrium concentrations of iron cyanide complexes do not only depend on the solubility of Prussian blue, but also on the solubility of the present iron (hydr)oxide.

According to the calculations it is most likely that precipitation of Prussian blue will not happen in alkaline soils at the iron cyanide concentrations found on contaminated soil sites (Figure 2). Therefore, iron cyanide complexes will be rather mobile in soils with a high pH and high cyanide concentrations can be expected in the groundwater.

In acidic soils precipitation of Prussian blue is very well possible according to the calculations. This will considerably decrease the concentrations in the groundwater and reduce the mobility of iron cyanide complexes in such soils.

Inventarisation of available data

The results of the inventarisation of the two highest total cyanide concentrations found in the groundwater on contaminated sites (all former gasworks sites) indeed reveal a large contrast between the sites located on the higher sandy soils with a presumable pH of ca. 4 and the sites located on the lower, most clay, soils with a pH of ca. 7 (Figure 2). Although the actual pH of the sites was not determined and may in some cases differ from the assumed pH level, and cyanide concentrations in the groundwater may also be influenced by different groundwater heights, different total amounts of cyanide present and different hydrological situations, the results are a strong indication for the existence of

large differences in concentrations of dissolved cyanide between the alkaline and the acidic sites. These results agree quantitatively with the results of the model calculations presented in figure 1.

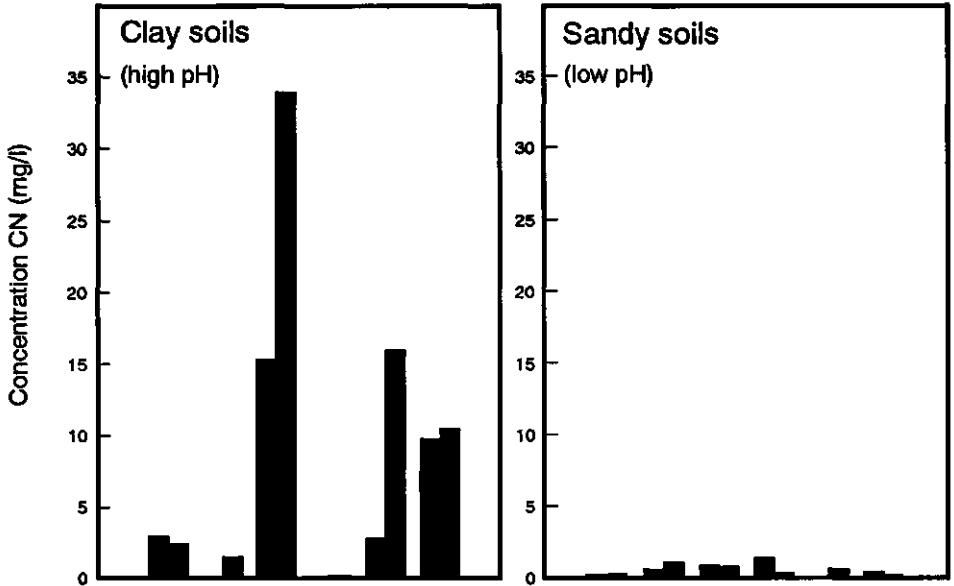


Figure 2. Two highest concentrations per site of total dissolved iron cyanide complexes found in the groundwater on 6 contaminated soil sites with a high pH (left), and 6 contaminated sites with a low pH (right).

Although the concentrations observed on the acidic sites are much lower than on the alkaline sites, they still exceed the Dutch quality standard for total cyanide concentrations in groundwater. At present this standard equals 0.2 mg.l^{-1} . Apparently the solubility of Prussian blue in acidic soils is not low enough to prevent unacceptable cyanide concentrations to occur in the groundwater. However, a new groundwater standard is proposed which allows a total cyanide concentration of 8 mg.l^{-1} . If this standard becomes effective it will probably only be exceeded in the groundwater of alkaline soil sites.

Investigation of contaminated sites

Acidic sites

The pH in the profiles of the soil on the acidic sites (A and B) appears to vary between 3.5 and 5.5. In combination with the pe, which varies between 6 and

11 (Figure 3 and 4), these conditions cause Prussian blue to be only slightly soluble (Figure 1). Considering the total cyanide content of the soils this mineral may therefore very well be present.

The distribution of the total amount of cyanide over the two soil profiles is more or less similar per site but larger differences exist between site A and B. On site A the highest cyanide concentrations are found at a depth of ca. 3.0 m, which is clearly indicated by a blue coloured soil layer. Most of the time this colour became apparent when samples contained more than ca. 100 mg/kg of cyanide. The blue layer is located just on top of the water saturated zone which started at ca. 3.2 m at the moment of sampling (Figure 3). However, according to the presence of soil material with a reduced appearance the depth of this zone probably varies from ca. 2.8 m to 3.2 m due to seasonal influences.

On site B the maximum cyanide concentrations are of the same order as found on site A, but here they are found at a depth of ca. 1 - 1.5 m. The soil layer with the highest cyanide concentrations also has a blue appearance. In the first profile on site B (B1) also an increase of the cyanide concentration is observed in the upper area of the saturated zone as was found on site A. Although not as profound as on site A, again this accumulation of Prussian blue was visible in the soil samples. On site B the water saturated zone starts at a depth of ca. 3.5 m with a seasonal variation of less than 0.5 m.

The differences between site A and B with respect to the depth where the maximum amount of cyanide is found might be explained by a different history of the sites. Although on both sites the deeper soil profiles most likely are undisturbed, it is very well possible that on site A a contaminated upper soil layer was removed and that the present contamination of the soil is due to leaching of cyanide from that layer. On site B remainings of solid waste material were present at a depth of 0 - 1.2 m while such remainings were absent on site A.

In the extracts of the soil samples from both site A and B only a very small percentage of the cyanide dissolved, varying between ca. 0.1 and 5% of the total amount present. Together with the blue colour of part of the samples this indicates that Prussian blue probably is present. In case of equilibrium with this mineral only low concentrations of $\text{Fe}(\text{CN})_6(\text{t})$ will dissolve due to the low solubility of Prussian blue under acidic conditions (Figure 1). This largely agrees with the low $\text{Fe}(\text{CN})_6(\text{t})$ concentrations measured in the extracts. In most cases the calculated cyanide concentrations appear to be higher than the concentrations measured in the extracts (Figures 3 and 4). This discrepancy can be explained if it is assumed that complete equilibrium between the extracts

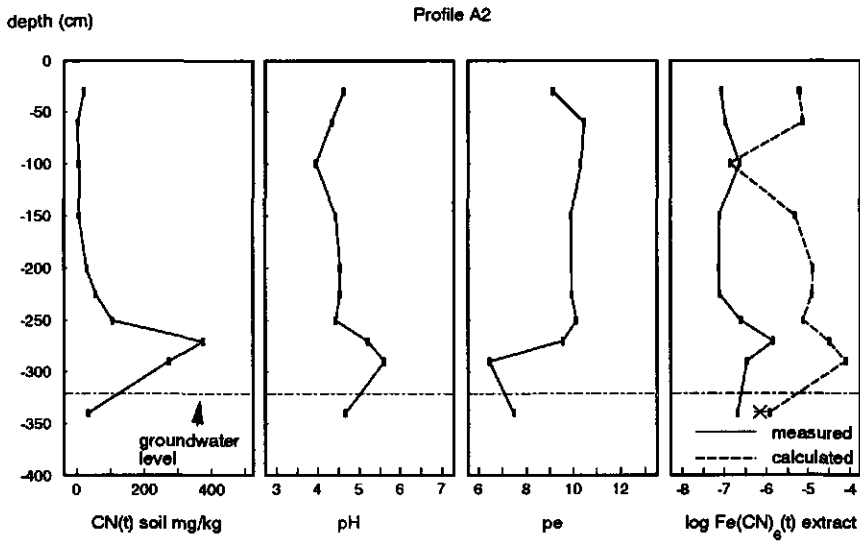
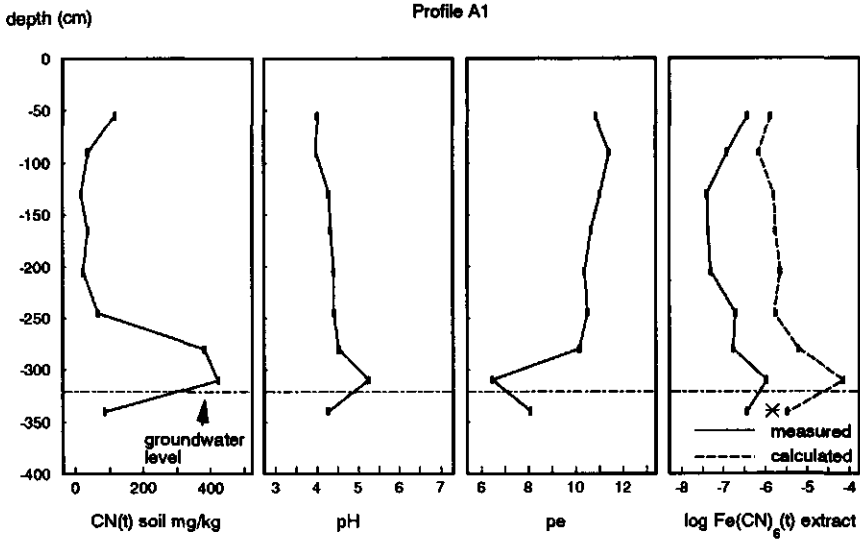


Figure 3. Profiles (A1 and A2) of total cyanide concentrations (CN(t)) in the soil, of pH, pe and total dissolved iron cyanide in the soil extracts and the iron cyanide concentration measured in the groundwater (*) of site A.

and the Prussian blue is not reached within the extraction time of 5 days. Although the accuracy of the calculations is limited due to a high sensitivity for small deviations of pH and pe, it is remarkable that the calculated concentrations

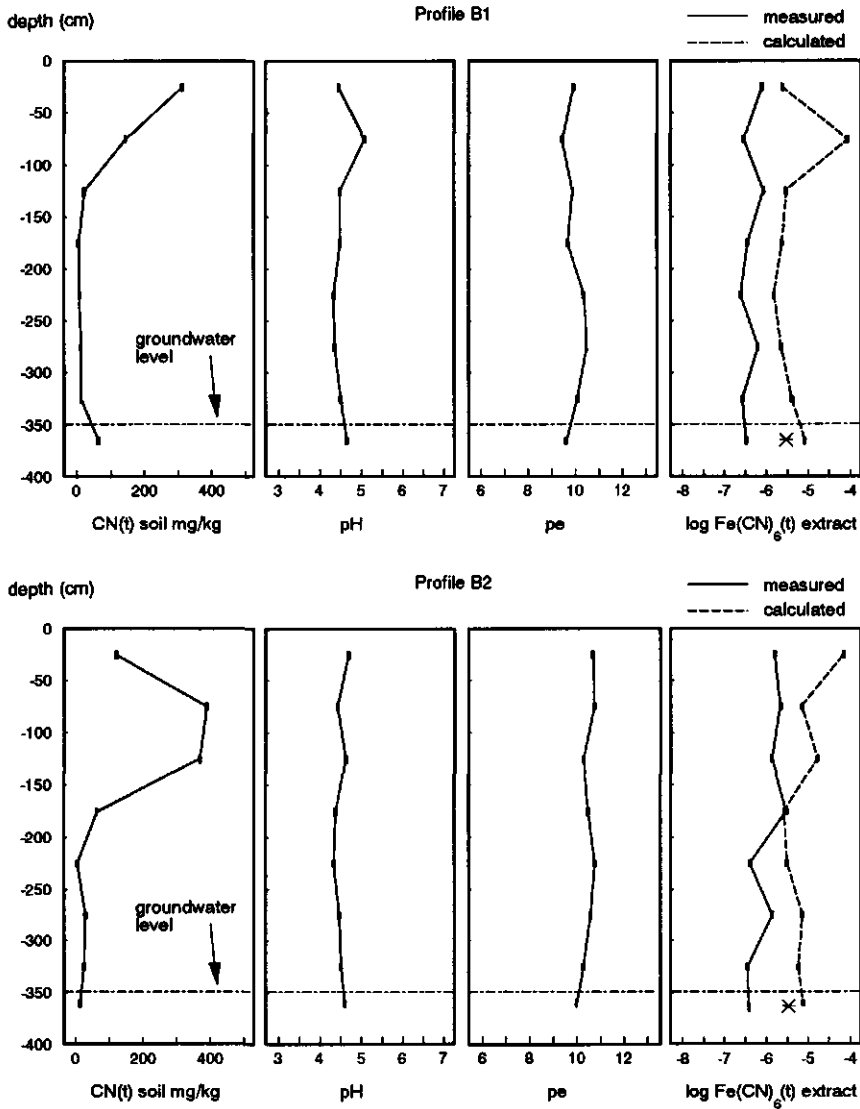


Figure 4. Profiles (B1 and B2) of total cyanide concentrations (CN(t)) in the soil, of pH, of pe and total dissolved iron cyanide in the soil extracts and the iron cyanide concentration measured in the groundwater (*) of site B.

do show a great resemblance with the concentrations observed directly in the groundwater. This indicates that the situation in the field probably closer resembles equilibrium with Prussian blue than the situation in the soil extracts does.

If the mobility of cyanide in the field is indeed largely governed by equilibrium with Prussian blue this mobility will strongly depend on pH and p_e , but also on the occurring concentration of cyanide. At concentrations low enough to prevent (re)precipitation cyanide could be quite mobile. This for example may occur after initial dissolution of cyanide from Prussian blue present in waste material. If the pH and p_e do not change after this dissolution, the dissolved cyanide has no tendency to precipitate during transport in the soil. This will only happen at a decrease of the solubility of Prussian blue due to a change in pH or p_e . This process might be an explanation for the observed accumulation of Prussian blue in the soil profiles at the start of the reduced zone. In those profiles, a lower solubility of Prussian blue is calculated in the saturated zone as compared to the soil layer above this zone. According to the observed colour of the soil samples the mean groundwater height does correspond well with the zone where cyanide has accumulated.

Alkaline site

The pH of the soil extracts from site C varies from ca. 5.5 in the upper soil layer to ca. 7.2 in deeper layers. The p_e of these extracts is lower and there also is a larger decrease in p_e with depth compared to sites A and B. Probably this is caused by the lower permeability of the clay soil compared to the sandy soils of site A and B. The total cyanide concentrations found in the soil on site C differ in several aspects from those found on sites A and B (Figure 5). In the first place the sampled profiles are not as deep as those on site A and B because of the higher groundwater level (ca. 1.3 m). Furthermore, on site C the maximum cyanide concentrations are present in a blue coloured top soil layer and are about twice as high as on site A or B. These concentrations appear to decrease strongly with depth. No accumulation of cyanide is observed in the water saturated zone, which indicates that after initial dissolution of Prussian blue in the top soil layer, precipitation doesn't occur during leaching further downwards in the profile.

Apart from the extracts of the upper soil layer, a much larger part of the cyanide dissolved in the soil extracts (27-76%) compared to both acidic soils (Table 2). The mobility of cyanide in this soil is therefore high, which is also illustrated by the high cyanide concentrations observed directly in the groundwater (indicated with asterisks in Figure 5). In contrast with the acidic soils, in this case the concentrations in the extract is strongly influenced by the total cyanide content of the soil.

According to the equilibrium calculations no Prussian blue can be present at the pH and pe levels measured in the soil extracts, even at the lower pH in the soil samples from the upper layer (Figure 5). Therefore, all present iron cyanide should be dissolved in an equilibrium situation. However, this does not agree with the apparent presence of Prussian blue in the upper soil layer. This can be explained by the assumption that equilibrium between the soil samples from the upper layer and the extract is not reached within five days. The relatively low pH of the extracts of these samples is probably caused by

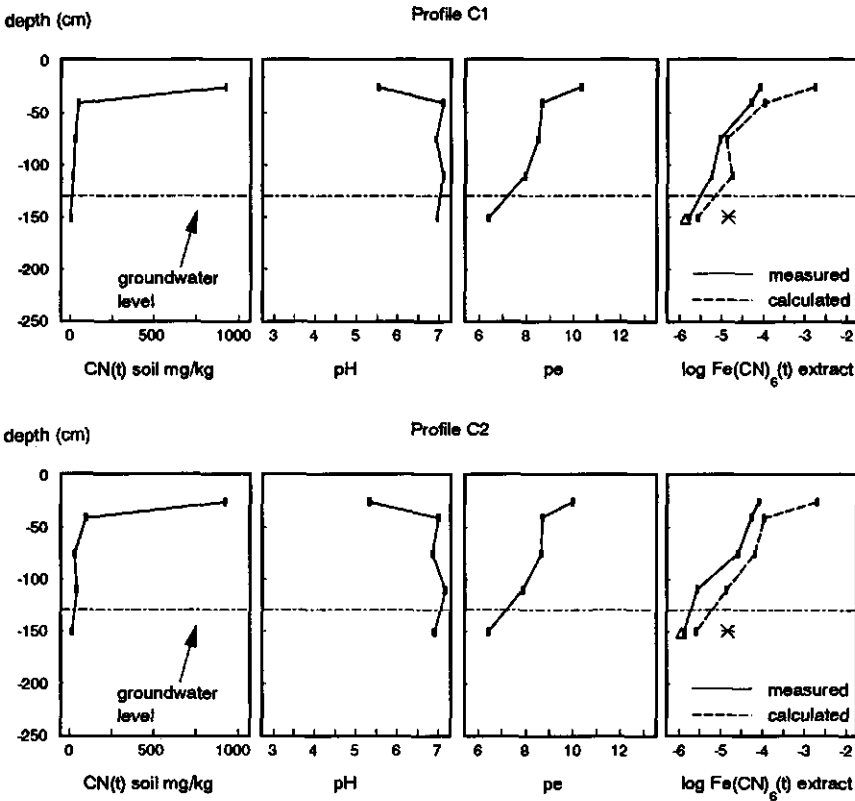


Figure 5. Profiles (C1 and C2) of total cyanide concentrations (CN(t)) in the soil, of pH, pe and total dissolved iron cyanide in soil extracts and the iron cyanide concentration as measured in the groundwater of site C (*), and after correction for the dilution as applied in the extraction(Δ).

dissolution of Prussian blue and simultaneous precipitation of iron (hydr)oxide (equation 1). At equilibrium this pH will be even lower. Due to this effect a very local acidic environment develops in which Prussian blue is much less soluble than in the more alkaline surrounding soil solution. This effect may cause mineral Prussian blue to persist in soils although at the average pH of the soil it would dissolve completely. In such a situation the dissolution rate of Prussian blue depends on the transport rate of protons away from the dissolving mineral. This transport rate is governed by both the hydrological situation and the pH and buffer capacity of the surrounding solution, which for example may be influenced by the concentration of HCO_3^- . During the extraction this transport rate may have been high due to the effect of mixing. This may have caused a relatively high dissolution rate compared to the field situation, although this increased rate apparently is not high enough to reach an equilibrium situation within five days (Table 2). Another possible cause for the disequilibrium situation is slow chemical dissolution kinetics of Prussian blue.

Table 2. Total cyanide concentrations in soil samples from site C and percentage extracted with 0.01 M CaCl_2

Depth (cm)	Profile C1		Profile C2	
	CN(t) (mg.kg^{-1})	Extracted (%)	CN(t) (mg.kg^{-1})	Extracted (%)
-25	922	5.8	938	5.4
-40	58.6	58	52.4	66
-75	21.1	75	31.2	51
-110	29.6	36	16.4	27
-150	5.96	76	5.98	64

The iron cyanide leaching from the dissolving Prussian blue in the upper soil layer will not precipitate at the pH and pe levels observed in the deeper soil layers. The calculations predict that all the cyanide in these layers will be present in dissolved form. However according to the measurements part of the iron cyanide remains in the soil solid phase after extraction (Table 1). According to the low cyanide content of these layers it is not likely that the deeper soil layers are contaminated with Prussian blue containing waste material. Slow dissolution kinetics of this mineral therefore cannot cause the incomplete

dissolution during the extraction. This can only be explained assuming other mechanisms like adsorption or possibly precipitation of other iron cyanide minerals to bind iron cyanide to the soil solid phase. The observed differences in effectivity of the extraction between the soil layers might then be due to variation in binding capacity per layer. Nevertheless, this process is far less effective as precipitation of Prussian blue and iron cyanide therefore remains very mobile in the alkaline soil. The concentrations reaching the groundwater in this soil are not determined by equilibrium with Prussian blue but by the dissolution rate of this mineral in the contaminated top soil layer. The limited dissolution kinetics of Prussian blue enable this mineral to persist in alkaline soils decades after its disposal in cyanide containing waste material.

Conclusions

- The large differences in mobility of cyanide between soil sites with different pH and p_e can quantitatively be explained by the dissolution equilibrium of Prussian blue.
- The concentrations of cyanide as measured in the groundwater at contaminated acidic sites correspond very well with the concentrations that are calculated based on equilibrium with Prussian blue.
- Although precipitation of cyanide is possible in acidic soils, it still can reach the groundwater in concentrations exceeding present Dutch soil quality standards.
- According to theory Prussian blue is very soluble in alkaline soils. The fact that this mineral is still present decades after its discharge is due to slow dissolution kinetics.
- The concentrations leaching from contaminated alkaline soils are determined by the dissolution rate of Prussian blue.

Acknowledgments

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Chapter 8

Epilogue

Epilogue

This chapter describes the main results of the research reported in this thesis and the implications of these results in the field of environmental policy.

Chemical determination of cyanide

Although not one of the initial aims of this research, it proved necessary to develop an automated method to differentiate free cyanide from hexacyanoferrate and thiocyanate (chapter 2). Thiocyanate is not a form of cyanide, but interference by this substance in the cyanide determination had to be minimised. It was expected to be present on former gasworks sites due to biodegradation of cyanide in the presence of sulphur.

The analytical method differentiates between the two forms of cyanide and thiocyanate by comparing the results of separate measurements. The concentration of cyanide is determined by measuring the amount of cyanide plus thiocyanate and subsequently subtracting the amount of thiocyanate as determined in a separate measurement. A disadvantage of this method is that the determination of cyanide also requires determination of thiocyanate. Apart from extra effort, this means the accuracy of cyanide determinations depends on the ratio between the concentrations of cyanide and of thiocyanate. In other words, when the concentration of thiocyanate is much higher than the concentration of cyanide, the determination of cyanide becomes less accurate.

For that reason we developed direct methods for the determination of free and total cyanide. These are described in chapter 4, using the understanding of the decomposition kinetics of hexacyanoferrate described in chapter 3. Both methods are insensitive to thiocyanate, but the total cyanide determination as developed still requires 24 hours of illumination and is slower than the method described in chapter 2.

Chemical speciation of dissolved cyanide

The first aim of this research was to assess the main forms in which cyanide is present in contaminated soils and groundwater. It was known that contamination of gasworks sites had taken place with cyanide mainly in the form of Prussian blue, a hexacyanoferrate mineral. As described in chapter 3, this hexacyanoferrate is not thermodynamically stable in groundwater and will tend to decompose to free cyanide. Nevertheless, on the former gasworks sites that were investigated no free cyanide was found although hexacyanoferrate

was abundant. Experiments confirmed that this was probably caused by the slow decomposition kinetics of dissolved hexacyanoferrate. This implies that concentrations of free cyanide in groundwater are not determined by equilibrium with hexacyanoferrate, but by the difference between the rate of formation of free cyanide from hexacyanoferrate and the rate of elimination of free cyanide by biodegradation and evaporation. Judging from the absence of free cyanide in groundwater the latter rate is apparently much higher. Therefore, hexacyanoferrate remains the predominant cyanide species in the soil.

The results, however, do not imply that hexacyanoferrate is a completely safe form of cyanide, because under the influence of daylight complete decomposition to free cyanide occurs within hours or days.

Where soil contamination is due to with cyanide in the free form, this cyanide will only react with iron (hydr)oxide to form hexacyanoferrate at very high concentrations of free cyanide. At lower cyanide concentrations, free cyanide will not form hexacyanoferrate at all. Even at high concentrations part of the cyanide will remain in the free form. It is therefore likely that where contamination of soils with free cyanide occurs a significant part of it will remain in this free form.

Interaction of dissolved cyanide with the soil solid phase

The mobility of substances in soils is largely dominated by interaction of dissolved substances with the soil solid phase. For hexacyanoferrate it was found that this interaction was largely governed by precipitation of a mineral, most probably Prussian blue (chapter 5). For equilibrium with this mineral, the concentration of hexacyanoferrate in groundwater and its dependence on parameters like pH and redox potential are governed by the composition and solubility product of Prussian blue. Both composition and solubility product were determined in chapter 6. The results were used to calculate hexacyanoferrate concentrations as a function of pH and p_e in equilibrium with Prussian blue and iron (hydr)oxide. According to these calculations the solubility of Prussian blue strongly depends on pH and redox potential, and varies between slightly soluble at pH 4 to very soluble at pH levels higher than ca. 6. In oxidized soils the solubility is also influenced by the redox potential, but not as strongly as by the pH. This implies that when precipitation of Prussian blue is the main process by which hexacyanoferrate constitutes part of the soil solid phase it is expected to be very mobile in alkaline soils and rather immobile in acidic soils.

The field observations showed much higher cyanide concentrations in the groundwater of neutral or alkaline soils when compared with those for acid soils. At first sight it may seem puzzling that after so many years Prussian blue can still exist in soils with an alkaline pH, because the solubility of the Prussian blue is predicted to be extremely high under these conditions. That this mineral can persist for such a long time under these conditions is probably due to kinetic reasons. Either the low dissolution kinetics of the Prussian blue per se, or the transport of base in the form of e.g. HCO_3^- from the surrounding soil to the mineral may act as the rate limiting process. The concentration of cyanide in the groundwater under neutral or alkaline soils is thus determined by kinetic factors and not completely by equilibrium.

Evaluation of risks of cyanide contaminated soils

The main purpose of this research was to obtain more insight into the chemical behaviour of cyanide in soils in order to enable a better estimation of the possible risks to human health and the environment posed by the presence of cyanide in the soil, especially on former gasworks sites. This research revealed that on former gasworks sites virtually all cyanide is present in the form of hexacyanoferrate, which is of low toxicity compared with the free form of cyanide. Current risk evaluations are based on the assumption that a large part of the cyanide is present in the free form and will therefore greatly overestimate the risks of adverse effects.

However, the results of the investigation of former gasworks sites cannot be generalized to other cases. As already mentioned cyanide is not always spilled or disposed of in the form of hexacyanoferrate. When cyanide is released in the free form or in the form of less stable metal cyanide complexes, as has probably happened in the case of electroplating processes, it will NOT react with the iron present in the soils to form hexacyanoferrate. This will only happen at very high free cyanide concentrations, which may sometimes have occurred very near to a waste discharge point. But even under such conditions this reaction will not proceed completely and part of the cyanide will remain in the free form. Although low concentrations of free cyanide are biodegradable under aerobic conditions, little is known about biodegradability and stability under anaerobic conditions. If free cyanide is more stable under such conditions, it might well remain present on contaminated sites.

Of course one should be very careful in making risk evaluations, but the huge difference in toxicity between hexacyanoferrate and free cyanide, combined with the extremely slow transformation of hexacyanoferrate to free cyanide in the dark and the biodegradability of free cyanide, demands that

these species be distinguished in cases of soil contamination. The chemical determination methods developed during this research are an appropriate tool to perform this differentiation. In case of soil contamination with hexacyanoferrate, risk evaluations should take into account the large effect of the pH on its solubility and mobility.

Further research

Although a number of questions on the subject of the speciation of cyanide in soils have been answered in this thesis, numerous problems still remain to be solved.

In the field of chemical determination of cyanide, the method proposed in chapter 4 is certainly a step in the right direction towards a simple, reliable method for the determination of free cyanide and hexacyanoferrate, but the illumination time needed in the current procedure is quite long. However, with more insight into the wave-length needed to decompose hexacyanoferrate it might be possible to reduce this time significantly by increasing the intensity of the light source in the appropriate range.

Although the speciation of cyanide in the groundwater under former gasworks sites has been clarified, and is primarily determined by decomposition kinetics, it is theoretically possible that certain catalysts present in soils increase the decomposition rate of hexacyanoferrate and thereby cause the development of significant concentrations of free cyanide. A first step towards evaluating this possibility might be to study the effect of substances which are known to catalyse the decomposition of hexacyanoferrate, such as Sn and Hg. Cu is also reported to have catalytic properties in this respect, but the opposite effect was observed in this research (chapter 4).

Probably of more importance for understanding the speciation of dissolved cyanide is information on the decomposition rates of free cyanide. Although a lot of work has been reported on biodegradation under aerobic conditions and optimal conditions in, for example, wastewater treatment plants (where biodegradation proceeds well), little is known on biodegradation under anaerobic soil conditions. If degradation of free cyanide under such conditions is also feasible, this would imply that cyanide is only persistent in soils in forms with relatively low toxicity, which would have a large impact on the evaluation of possible risks posed by cyanide-contaminated soil sites.

Although the interaction of dissolved hexacyanoferrate with the soil solid phase can, to a large degree, be described by assuming precipitation of Prussian blue as the dominating process, it is possible that precipitation of other hexacyanoferrate minerals occurs under conditions where Prussian blue is

highly soluble. Options are precipitation with Zn, Ca or Mn possibly in combination with K. Precipitation of such minerals could decrease the hexacyanoferrate concentrations at alkaline pH levels.

The apparent existence of Prussian blue in such alkaline soils decades after contamination took place might also be explained by extremely slow dissolution of this mineral. This is possibly caused by limited transport rates to the dissolving mineral of the solution accepting the protons released. More insight into this process would be helpful in estimating dissolution rates and concentrations of dissolved cyanide in the groundwater on alkaline sites. Furthermore, these insights could be used more generally where dissolution kinetics play an important role: e.g. cleaning of contaminated soils by extraction, or estimation of leaching rates of mineral contaminants from waste material.

In the acidic pH range, at hexacyanoferrate concentrations low enough to prevent precipitation of Prussian blue, adsorption becomes the main process by which hexacyanoferrate is retained by the soil. These concentrations can still easily exceed the Dutch soil quality standards for cyanide. More information about adsorption of hexacyanoferrate at the soil solid phase would provide better insight into the mobility of cyanide in soils under conditions where precipitation no longer occurs.

Summary

Chemical Speciation and Behaviour of Cyanide in Contaminated Soils

Cyanide is known as a highly toxic substance. It is present as a serious contaminant of the soil on several hundred industrial sites in the Netherlands, a large number of which are former gasworks sites. These gasworks produced gas from coal for domestic use from the middle of the last century until the 1960s. Due to their history these sites are mainly located in urban areas. The risk of adverse effects on human health and the environment posed by these sites depends largely on the form in which cyanide is present in the soils and on its behaviour.

The main aim of this research was to increase the insight into the chemical speciation and the behaviour of cyanide in soils, in order to enable a better evaluation of the risks involved.

After a general introduction in the first chapter, a new automated method of chemical determination of cyanide is described in chapter two, which enables differentiation between free cyanide, hexacyanoferrate and thiocyanate. The differentiation between free cyanide and hexacyanoferrate is important because of the huge difference in toxicity and behaviour of these species. Thiocyanate is a substance known to interfere in cyanide determinations and which might be present on contaminated sites as a product of biodegradation of cyanide. Three different determinations are necessary to establish the chemical speciation. The total amount of cyanide plus thiocyanate is determined after u.v. destruction and distillation. The amount of free cyanide plus thiocyanate is determined without destruction or distillation, and the amount of thiocyanate as such is determined by the same method but after masking free cyanide with formaldehyde. Because this method is able to detect low concentrations of free cyanide in the presence of hexacyanoferrate, the high sensitivity of hexacyanoferrate for decomposition by visible light became apparent. It was already known that these complexes released free cyanide under the influence of direct sunlight, but we observed complete decomposition of hexacyanoferrate to free cyanide when solutions were exposed to diffuse daylight for several days. These findings make it necessary to carefully shield samples from light when the partitioning of cyanide over the free and the complexed form is to be determined.

The speciation of cyanide in the groundwater on several former gasworks sites was studied with this method of determination. On the investigated sites no free cyanide was found, all the dissolved cyanide appeared to be present in the form of hexacyanoferrate. However, according to thermodynamic equilibrium calculations these complexes are not stable under the conditions with respect to pH, redox potential and total dissolved cyanide concentrations found in soils. In an equilibrium situation at least part of the cyanide has to be present in the free form. Apparently a disequilibrium situation exists in soils which is probably due to extremely slow decomposition kinetics of hexacyanoferrate. The decomposition kinetics of hexacyanoferrate in the dark were studied under different pH and redox conditions. It appeared that the decomposition rate is influenced by both parameters in such a way that it is first-order-dependent on hexacyanoferrate in the reduced protonated forms ($\text{HFe}(\text{CN})_6^{3-}$ and $\text{H}_2\text{Fe}(\text{CN})_6^{3-}$). The decomposition rates of both species were determined, and used to calculate the half-life of hexacyanoferrate as a function of pH and redox potential. Under soil conditions this half-life may vary from years under acid and reduced conditions, to hundreds of years under oxidised alkaline conditions. Therefore the formation of free cyanide from hexacyanoferrate in soils probably proceeds much more slowly than its evaporation or biodegradation, which explains its absence in groundwater.

With this understanding of the decomposition kinetics of hexacyanoferrate, a new method to decompose hexacyanoferrate and to separate it from free cyanide was developed. This was used as a pretreatment for chemical determination. Decomposition of hexacyanoferrate prior to total cyanide determination was performed with visible light. This treatment has the advantage that it does not release cyanide from thiocyanate as u.v. light does, so total cyanide concentrations can be obtained with one measurement. For free cyanide determinations, decomposition of hexacyanoferrate is suppressed by addition of Cu^{2+} , a mild oxidizing agent able to convert hexacyanoferrate to the more stable oxidized form.

Because hexacyanoferrate appeared to be the predominant form of cyanide, the behaviour of this cyanide species governs the overall behaviour of cyanide in soils. In general, the behaviour of substances in soils is determined by interaction between dissolved species and the soil solid phase. This interaction determines concentrations occurring in the groundwater and also the mobility and bioavailability of a substance. In chapter 5 it was established that in the case of hexacyanoferrate this interaction is dominated by precipitation of Prussian blue, a mineral containing iron and hexacyanoferrate. In the case of equilibrium between groundwater and Prussian blue, concentrations of hexa-

cyanoferrate are determined by the solubility product and composition of this mineral. Both parameters were not known exactly and therefore they were experimentally obtained in chapter 6.

The solubility product and the composition of Prussian blue were determined from experiments in which it was precipitated from solutions containing hexacyanoferrate and iron chelated with citrate, EGTA, EDTA and NTA. The composition was determined from the ratio between precipitating iron and hexacyanoferrate, the solubility product was estimated from the pH at which precipitation started. Using these data the concentration of hexacyanoferrate in equilibrium with Prussian blue was calculated as a function of pH and p_e . Although Prussian blue is known as a slightly soluble mineral, the results revealed that this solubility ranges from hardly soluble at acidic pH values to completely soluble at alkaline pH levels. The concentrations calculated in the acidic range agreed to a large extent with the concentrations measured in extracts of acidic contaminated soil samples.

If the behaviour of hexacyanoferrate is largely dominated by precipitation of Prussian blue, this implies that there will be a large difference between cyanide in acid and in alkaline soils. In alkaline soils where Prussian blue will not precipitate, hexacyanoferrate will be very mobile. In acid soils, the concentrations of hexacyanoferrate in groundwater and the mobility of hexacyanoferrate will be decreased by precipitation of this mineral.

Existing data of cyanide concentrations occurring on contaminated sites were evaluated and several contaminated sites were sampled to study the mobility of cyanide in the field. Much higher cyanide concentrations appear to occur in the groundwater of alkaline sites compared to the acid soil sites, which is in agreement with the differences in solubility of Prussian blue. Despite its high solubility Prussian blue is still found on alkaline soil sites which might be explained by transport-limited dissolution kinetics. Although cyanide is much less mobile on the acidic sites, the concentrations of cyanide in the groundwater still exceed the present Dutch quality standard.

In the last chapter it is concluded that differentiation between free cyanide and iron cyanide complexes is necessary for appropriate evaluation of the possible risks of cyanide-contaminated soils. The determination methods developed provide a useful tool to perform this. Furthermore, risk evaluations based on the presence of iron cyanide complexes should take into account the strong influence of the pH on their solubility and mobility.

Samenvatting

Chemische Speciatie en Gedrag van Cyanide in Verontreinigde Bodems

Cyanide staat vooral bekend als een zeer giftige stof, die snel werkt en naar bittere amandelen ruikt. In de vorm van cyaankali of blauwzuur is het een belangrijk ingrediënt van vele misdaad- en spionageverhalen, en heeft waarschijnlijk, wat deze toepassing betreft, slechts concurrentie te duchten van arsenicum. Naast deze vorm van gebruik speelt cyanide ook een belangrijke rol in een aantal industriële chemische processen. Als gevolg van de toepassing bij dergelijke processen is cyanide op enkele honderden plaatsen in Nederland in de bodem terecht gekomen. Een belangrijk deel van deze plaatsen bestaat uit voormalige gasfabrieksterreinen en terreinen van galvaniseerbedrijven.

In gasfabrieken werd vanaf halverwege de vorige eeuw tot aan de opkomst van het gebruik van aardgas, in de zestiger jaren van deze eeuw, op uitgebreide schaal gas, het zogenaamde stadsgas, gemaakt uit steenkool. Bij dit proces ontstond ook cyanide, in de vorm van blauwzuurgas. Dit werd uit het stadsgas verwijderd door het door ijzerhoudend bodemmateriaal (ijzeroer) te leiden. Hierbij bond het cyanide zich aan het ijzer en bleef in het bodemmateriaal achter. Doordat dit materiaal na gebruik vaak ter plekke werd gebruikt om het erf te verharderen, bevatten voormalige gasfabrieksterreinen vaak hoge gehalten aan cyanide.

Oorspronkelijk hebben dergelijke gasfabrieken vaak aan de rand van het dorp of de stad gestaan. Door de groei van steden en dorpen liggen de verontreinigde terreinen tegenwoordig echter meestal midden in de bebouwde kom. In een groot aantal gevallen zijn de terreinen opnieuw bebouwd of grenzen direct aan bebouwde percelen. De risico's voor de volksgezondheid en het milieu, die de aanwezigheid van cyanide in de bodem van deze terreinen met zich mee kan brengen, zijn sterk afhankelijk van de vorm waarin cyanide aanwezig is en van het gedrag van dit cyanide in de bodem.

In dit onderzoek is daarom getracht te achterhalen in welke vormen cyanide in verontreinigde bodems voorkomt. En daarnaast om meer inzicht te krijgen in het gedrag van deze vormen wat betreft voorkomende concentraties, omzettingen en mobiliteit. Met deze inzichten kunnen de risico's van bodemverontreiniging met cyanide beter worden beoordeeld.

Na een algemene inleiding in het eerste hoofdstuk wordt in hoofdstuk 2 een nieuwe methode beschreven om cyaniden te meten. Hiermee kan onderscheid gemaakt worden tussen cyanide in de vrije vorm, ijzercyanide-complexen (of hexacyanoferraten) en thiocynaat. Een dergelijke meetmethode is belangrijk vanwege de grote verschillen in giftigheid en fysisch-chemisch gedrag tussen deze verbindingen. Om in een watermonster de afzonderlijke concentraties van deze stoffen vast te stellen zijn drie metingen nodig. De som van de concentraties van de drie stoffen wordt bepaald na belichting met ultraviolet licht en distillatie van het monster. De concentratie vrij cyanide plus thiocynaat wordt gemeten zonder belichting of distillatie, en de concentratie thiocynaat wordt op dezelfde manier bepaald na maskering van vrij cyanide met formaldehyde. Uit de verschillen tussen de drie metingen kunnen vervolgens de concentraties van de afzonderlijke stoffen worden afgeleid.

Tijdens het ontwikkelen van deze meetmethode is gebleken dat opgeloste ijzercyanide-complexen onder invloed van daglicht snel en volledig uit elkaar vallen tot vrij cyanide. Ultraviolet licht of volle zon zijn hiervoor niet nodig. Dit maakt het noodzakelijk om watermonsters zorgvuldig in het donker bewaren indien daarin de verdeling van cyanide over de vrije en de met ijzer gecomplexeerde vorm bepaald moet worden.

Met de nieuwe meetmethode is in het grondwater van een aantal voormalige gasfabrieksterreinen de verdeling van cyanide over de verschillende vormen bestudeerd. Zo goed als al het cyanide blijkt hier in de vorm van ijzercyanide-complexen aanwezig te zijn. Vrij cyanide is niet aangetroffen. Volgens berekening zijn ijzercyanide-complexen echter in grondwater niet thermodynamisch stabiel. Bij chemisch evenwicht moet vrijwel al het cyanide zich in de vrije vorm moeten bevinden. Blijkbaar is in het grondwater geen sprake van chemisch evenwicht, wat waarschijnlijk wordt veroorzaakt door het extreem langzame uiteenvallen van ijzercyanide-complexen in het donker.

Doordat de ontwikkelde meetmethode in staat is om lage concentraties vrij cyanide aan te tonen in relatief hoge concentraties ijzercyanide-complexen, is het mogelijk om de snelheid te bepalen waarmee in het donker vrij cyanide uit gecomplexeerd cyanide ontstaat. Het blijkt dat deze snelheid wordt beïnvloed door de pH en de redoxpotentiaal, en eerste-orde afhankelijk is van het gedeelte van de ijzercyanide-complexen in gereduceerde en geprotoneerde vorm ($\text{HFe}(\text{CN})_6^{3-}$ en $\text{H}_2\text{Fe}(\text{CN})_6^{3+}$). Van deze beide vormen is de decompositie-snelheid bepaald en gebruikt om de halveringstijd van ijzercyanide-complexen als functie van pH en redoxpotentiaal te berekenen. Deze halveringstijd varieert in de bodem van minimaal enkele jaren, onder zure, gereduceerde omstandigheden tot honderden jaren onder alkalische, geoxideerde

omstandigheden. Hierdoor zal de vorming van vrij cyanide uit ijzercyanide-complexen, ten opzichte van de snelheid waarmee vrij cyanide door biologische afbraak en vervluchtiging kan verdwijnen, uiterst langzaam verlopen. Ophoping van vrij cyanide in de bodem is daardoor niet waarschijnlijk.

In hoofdstuk 4 wordt beschreven hoe het verkregen inzicht in de factoren die het uiteenvallen van ijzercyanide-complexen beïnvloeden is gebruikt bij het ontwikkelen van een methode om deze complexen beter te scheiden van vrij cyanide, en bij het ontwikkelen van een methode om deze complexen juist om te zetten in vrij cyanide. De scheidingsmethode wordt toegepast als voorbehandeling voor de meting van vrij cyanide. Hierbij wordt het uiteenvallen van ijzercyanide-complexen tijdens de distillatie onderdrukt door toevoeging van Cu^{2+} , een oxiderende stof die ijzercyanide-complexen omzet in de stabielere geoxideerde vorm. Het omzetten van ijzercyanide-complexen in vrij cyanide gebeurt door belichting van monsters met een TL-lamp, en wordt toegepast als voorbehandeling voor de meting van totaal-cyanide. Het voordeel van deze methode, ten opzichte van belichting met ultraviolet licht, is dat deze belichting geen omzetting van thiocynaat naar cyanide veroorzaakt, waardoor de concentratie totaal-cyanide met één meting bepaald kan worden.

Omdat cyanide in de bodem vooral in de vorm van ijzercyanide-complexen aanwezig blijkt te zijn, bepalen deze complexen hier het gedrag van cyanide. Voor dit gedrag is vooral de interactie tussen opgeloste complexen en de vaste fase van de bodem van belang. Deze interactie bepaalt de verdeling over de vaste en de opgeloste fase van de bodem, en beïnvloedt op deze manier de mobiliteit en de biologische beschikbaarheid van de ijzercyanide-complexen. In hoofdstuk 5 wordt vastgesteld dat deze interactie wordt gedomineerd door precipitatie van Berlijns blauw, een mineraal dat ijzer en ijzercyanide bevat en in verschillende vormen kan voorkomen. In geval van evenwicht tussen een dergelijk mineraal en opgelost ijzercyanide wordt de concentratie in het grondwater bepaald door de samenstelling en het oplosbaarheidsproduct van het mineraal.

Dit oplosbaarheidsproduct en deze samenstelling zijn in hoofdstuk 6 experimenteel bepaald door precipitatie van Berlijns blauw uit een oplossing met daarin ijzercyanide-complexen en ijzer (gecomplexeerd met citraat, EGTA, NTA of EDTA). De samenstelling van Berlijns blauw is hierbij afgeleid uit de verhouding waarin ijzer en ijzercyanide uit de oplossing verdwijnt. Het oplosbaarheidsproduct is berekend uit de redoxpotentiaal en de activiteiten van ijzer en ijzercyanide in oplossingen in evenwicht met dit mineraal. Met behulp van deze gegevens is, als functie van pH en redoxpotentiaal, de concentratie opgelost ijzercyanide in evenwicht met Berlijns blauw en

ijzerhydroxide berekend. Deze berekeningen laten zien dat deze oplosbaarheid sterk afhankelijk is van de pH, en varieert van zeer slecht onder zure omstandigheden tot zeer goed boven pH 7.

Op grond van het oplosgedrag van Berlijns blauw is te verwachten dat er, wat betreft mobiliteit van ijzercyanide, grote verschillen zullen bestaan tussen bodems met een lage, en bodems met een hogere pH. In zure bodems zal de mobiliteit laag zijn door precipitatie van Berlijns blauw. In bodems met een hogere pH zal geen precipitatie optreden waardoor ijzercyanide hier veel mobieler kan zijn.

Om deze mobiliteit in het veld te bestuderen zijn bestaande gegevens over concentraties ijzercyanide die voorkomen in het grondwater van verontreinigde locaties verzameld en zijn enkele terreinen bemonsterd (hoofdstuk 7). Uit de resultaten hiervan blijkt inderdaad dat in het grondwater op terreinen met een hogere pH veel hogere concentraties ijzercyanide voorkomen dan in het grondwater op terreinen met een lagere pH. In gronden met een hogere pH wordt echter tientallen jaren na storting vaak nog steeds cyanide in de vorm van Berlijns blauw aangetroffen, ondanks het feit dat het daar in principe goed oplosbaar is. Dit kan verklaard worden door een erg lage, mogelijk transport-gelimiteerde, oplosbaarheid van Berlijns blauw. Alhoewel in zure bodems de maximale concentratie ijzercyanide in het grondwater beperkt wordt door precipitatie van Berlijns blauw, is de oplosbaarheid van dit mineraal niet laag genoeg om te verhinderen dat ijzercyanide-concentraties in het grondwater de huidige norm hiervoor overschrijden.

In het laatste hoofdstuk (hoofdstuk 8) wordt vastgesteld dat het voor beoordeling van de risico's van bodemverontreiniging met cyanide allereerst noodzakelijk is om onderscheid te maken tussen vrij cyanide en ijzercyanide-complexen. Hierbij kunnen de ontwikkelde meetmethoden een nuttig gereedschap zijn. In geval van verontreiniging met ijzercyanide-complexen dient verder bij het maken van een risico-evaluatie rekening gehouden te worden met de enorme invloed van de pH op de oplosbaarheid en mobiliteit van deze complexen.

Levensloop

Hans Meeussen werd geboren op 16 april 1960 te Rotterdam (Overschie) en groeide op in een huis waarin van 1866 tot 1879 de voormalige Overschiese gasfabriek was gevestigd. Hij doorliep het H.A.V.O. en het Atheneum aan het Emmauscollege te Rotterdam en begon in 1982 met een studie Milieuhygiëne aan de Landbouwniversiteit te Wageningen. In 1988 rondde hij deze studie af met een afstudeervak Informatica en een afstudeervak Bodemhygiëne en Bodemverontreiniging. Van mei 1988 tot december 1991 werkte hij als toegevoegd onderzoeker bij de vakgroep Bodemkunde en plantevoeding van de Landbouwniversiteit aan het onderzoek dat in dit proefschrift beschreven wordt. Sinds januari 1992 werkt hij bij deze vakgroep aan een onderzoek naar het chemische gedrag en transport van stoffen die kunnen uitspoelen uit zogenaamde reststoffen (b.v. hoogovenslakken en vliegias). De resultaten van dit onderzoek zijn nodig om te kunnen beoordelen of dergelijke reststoffen geschikt zijn voor gebruik als bouwmetaal.