

Sorption of Iron-Cyanide Complexes on Iron Oxides and in Soils

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Abbreviations

a	sorption parameter at constant pH
A	cross sectional area
α	proportion of an anion with valency z_i
ADE	advection-dispersion equation
Al_o	oxalate-extractable aluminium
ATR-FTIR	attenuated total reflectance Fourier-transform infrared
b	sorption parameter
be	batch sorption experiment
BET	Brunauer-Emmett-Teller
c	equilibrium concentration
c_0	initial concentration
ce	column experiment
C_{org}	organic carbon
D	dispersion coefficient
de	batch desorption experiment
dfi	duration of flow interruption
DOM	dissolved organic matter
E_H	redox potential
F	Faraday constant
Fe_d, Fe_o	dithionite-citrate-, oxalate-extractable iron
HPLC	high-pressure liquid chromatography
IEP	isoelectric point
J_w	volumetric water flux density
k_b	backward rate parameter
k_f	forward rate parameter
K_d	distribution constant
K_i	sorption constant of anion i
K_L	Langmuir constant
K_{sp}	solubility product constant
L	length
λ	dispersivity

MGP	manufactured gas plant
v	pore water velocity
Pe	Peclet number
pK_a	acid dissociation constant
p_v	pore volume
pzc	point of zero charge
Q	flow rate
q	Darcian flux
θ	water content
R	retardation factor
ρ_b	bulk density
S	sorbed amount
S_{max}	sorption maximum
SOM	soil organic matter
τ	tortuosity
t_{btc}	breakthrough time
V_s	ratio of solution to mass of iron oxide
UV	ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ψ_0	mean electric potential
ψ_a	electric potential experienced by sorbed anions
z_i	valency of anion i

CHAPTER 1

Introduction

INTRODUCTION

As a consequence of both man's industrial and agricultural activities, soils have experienced inputs of contaminants worldwide. Contaminants can be defined as substances which may cause potential harm to the environment including humans, animals, plants, waters, and soils. This potential often depends on the concentration of a substance. Sources and pathways of contaminants are: fertilizers; pesticides; dry, wet and gaseous deposition; disposal of hazardous waste materials; irrigation; and radioactive fallout (Sparks, 1995). Contaminated soils cover about 22×10^6 ha worldwide (Oldemann et al., 1991). Contaminants, once introduced into the soil environment, may be transported through the soil into the ground water, but they may undergo an array of chemical and biological reactions within soils. These reactions include equilibrium and kinetic processes such as dissolution, precipitation, polymerization, adsorption/desorption, redox reactions, biodegradation, and volatilization. Consequently, concentration, solubility, speciation and toxicity of contaminants in soils and aquifers are affected by these reactions (Sparks, 1995). The knowledge of these processes concerning particular contaminants is essential to estimate their fate in soils and aquifers. One of the contaminants that has been introduced into the soil environment is cyanide.

Chemistry of cyanides

Cyanides form a group of chemical compounds all of which have the cyanide group, CN, in common. Hydrogen cyanide, HCN (g, aq), and the cyanide ion, CN⁻ (aq), are referred to as free cyanides. Free cyanides are defined as the forms of molecular and ionic cyanide released into solution by the dissolution and dissociation of cyanide compounds and complexes (Smith and Mudder, 1991). Free cyanides are extremely toxic to higher animals and humans. Cyanide inactivates cytochrome oxidase, an enzyme which is essential for the utilization of oxygen. The inactivation leads to cellular asphyxiation and cellular death and therefore to suspension of all

vital functions and death.

Simple cyanides are defined as the salts of hydrocyanic acid, e.g. KCN. They dissolve completely in solution producing cyanide anions and free alkali, alkaline earth or heavy metal cations, e.g. K^+ or Hg^{2+} .

The cyanide ion acts as a monodentate ligand with C as the donor atom in many complex compounds (Sharpe, 1976). Due to their stability, these complex cyanides are subdivided into weak and strong complexes. Examples of weak complexes are tetracyanozincate, $[Zn(CN)_4]^{2-}$, or tri- and tetracyanocadmate, $[Cd(CN)_3]^-$ and $[Cd(CN)_4]^{2-}$. Among other, the strong complexes comprise iron(II/III)-cyanide complexes and hexacyanocobaltate, $[Fe(CN)_6]^{4-/3-}$ and $[Co(CN)_6]^{4-}$. The dissociation constants of weak and moderately strong metal cyanide complexes range from 10^{-28} ($[Cu(CN)_3]^{2-}$) to 10^{-17} ($[Zn(CN)_4]^{2-}$).

As indicated in the title of this thesis, exclusive attention is paid to iron-cyanide complexes. The iron(II)-cyanide complex, $[Fe(CN)_6]^{4-}$, is termed ferrocyanide, and the iron(III)-cyanide complex, $[Fe(CN)_6]^{3-}$, is termed ferricyanide. Since their stability is high and the dissociation is very slow, the octahedral iron-cyanide complexes are nearly inert. The dissociation constants in water are $10^{-36.9}$ for ferrocyanide and $10^{-43.9}$ for ferricyanide (Beck, 1987). However, the release of a cyano group from the complexes is enhanced in the presence of high levels of ultraviolet and sunlight radiation (Rader et al., 1993). In the presence of diffuse daylight, only ferrocyanide is decomposed, thus releasing a cyano group (Meeussen et al., 1992a). Ferricyanide is kinetically more labile than ferrocyanide resulting in higher toxicity of ferricyanide to two marine fish species (Pablo et al., 1996). Consequently, the toxicity of iron-cyanide complexes depends on their tendency to release toxic free cyanide. This tendency is influenced by the kinetic stability of the complexes and by the presence of light.

Ferricyanic and ferrocyanic acid are the conjugate acids of the iron-cyanide complexes. All dissociation constants pK_a of ferricyanic acid are less than 1, and so are pK_1 and pK_2 of ferrocyanic acid. For this acid, pK_4 is 4.2, and pK_3 is 2.2, respectively (Jordan and Ewing, 1962). Ferricyanide and ferrocyanide form an oxidation-reduction couple

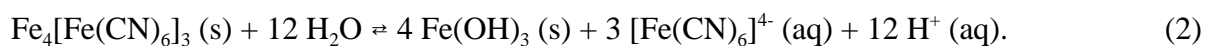


Although this reaction does not involve the hydrogen ion, it is nevertheless pH-dependent due to the difference in dissociation of the corresponding acid and in the relative proportion of the

two free ions at $\text{pH} < 7$. Consequently, ferrocyanide is more easily oxidized in neutral than in acid solutions. It is not oxidized by air in neutral or alkaline solutions in the absence of light or catalysis (Smith and Mudder, 1991).

Both ferricyanide and ferrocyanide form stable salts with other metals without undergoing exchange of the cyanide ligand. The alkali and alkaline earth iron-cyanide complexes are all soluble in water, except for $\text{Ba}_2[\text{Fe}(\text{CN})_6]$ which is moderately soluble. The heavy metal and iron salts of iron-cyanide complexes are insoluble or sparingly soluble.

The most known solid iron-cyanide-containing phase is the ferric ferrocyanide Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, which is widely used as a pigment. Berlin Blue is slightly soluble (solubility product constant $K_{\text{sp}} = 10^{-84.5}$, Meeussen et al., 1992b), and its solubility depends on pH



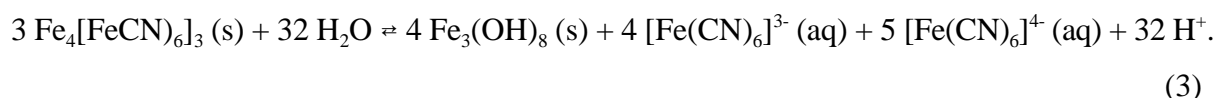
Sources and behaviour of iron-cyanide complexes in soils

Cyanide-containing organic compounds are introduced naturally into the environment by a great number of living systems (Fuller, 1985). Cyanogenic glycosides are synthesized by over 800 species of plants (Knowles, 1976). A selection of plants with cyanogenic potential is given by Fuller (1985). Glycosides yield HCN upon hydrolysis. These cyanides from natural sources do not persist in soils, because they are attacked by soil microorganisms and converted to carbonate and ammonia (Fuller, 1985).

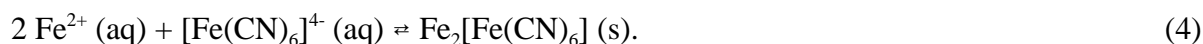
Iron-cyanide complexes are not produced by organisms, their presence in the soil environment is caused by anthropogenic inputs. Iron-cyanide-containing materials which man has introduced into the soil environment are listed in Table 1.

Purifier wastes originate from coal gasification. The cyanide-containing raw gas was scrubbed with iron oxide particles resulting in the formation of Berlin Blue. As the purifier wastes were worthless, they were commonly deposited on sites of coke ovens and gasworks causing contaminations with iron-cyanide complexes. Total cyanide concentrations in soils on sites of former coke ovens and gas plants are up to 5 g CN kg^{-1} (Kjeldsen, 1999). The dissolution of Berlin Blue is minimized at low pH (Equation (2)) and reducing conditions (Meeussen et al.,

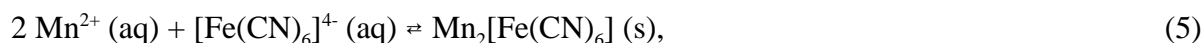
1992b). The formation of iron(II/III) oxides in the absence of electron accepting agents is possible after dissolution of Berlin Blue under reducing conditions (Meeussen et al., 1995)



Ferrous ions are released by reductive dissolution of iron oxides at low pH and cause possibly the precipitation of Berlin White



An intermediate between Berlin Blue and Berlin White is Turnbull's Blue, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, which may be present in soils on sites of former manufactured gas plants (Ghosh, 1998). In these soils, the formation of $\text{Mn}_2[\text{Fe}(\text{CN})_6]$ at neutral pH and under reducing conditions has been discussed (Keizer et al., 1995)



which is analogous to the formation of Berlin White (Equation (4)).

Soils on sites of former manufactured gas plants are very acid due to oxidation of reduced sulphur species (Environmental Resources Limited, 1987). Therefore, the mobility of iron-cyanide complexes in these soils should be low.

Table 1 Anthropogenic iron-cyanide containing materials.

Material	Iron-cyanide containing compound	Reference
Purifier wastes	Berlin Blue, ferrocyanide, ferricyanide	Shifrin et al. (1996), Mansfeldt et al. (1998)
Road salt	Berlin Blue, ferrocyanide	Ohno (1990), Paschka et al. (1999)
Paper de-inking sludge	$\text{A}_2\text{B}[\text{Fe}^{\text{II}}(\text{CN})_6]$, $\text{A} = \text{K}^+$ or Na^+ , $\text{B} = \text{Ca}^{2+}$ or $\text{B}_2[\text{Fe}^{\text{II}}(\text{CN})_6]$, $\text{B} =$ divalent transition metal	Mansfeldt (2001)
Blast furnace sludge	Potassium zinc hexacyanoferrate(II) nonahydrate, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \times 9\text{H}_2\text{O}$	Mansfeldt and Dohrmann (2001)

Berlin Blue and/or sodium ferrocyanide are added to road salt as anticaking agents. In snow-

melt runoff from a road after road salt application, the total cyanide concentration was up to 6 mg CN l⁻¹ (Paschka et al, 1999). Paper de-inking sludge is a refuse of paper recycling processes. It has been used as a soil amendment resulting in total cyanide contents up to 700 mg CN kg⁻¹ in soils (Mansfeldt, 2001). Blast furnace sludge is a waste originating from pig iron production. It has been deposited in basins and contains the crystalline iron-cyanide compound mentioned in Table 1. The total cyanide content of deposited blast furnace sludge is up to 4 g CN kg⁻¹ (Mansfeldt and Dohrmann, 2001).

As can be seen from Table 1, iron-cyanide complexes are introduced as solid phases into the soil environment except for soluble sodium ferrocyanide. Therefore, the fate of iron-cyanide complexes in soils and aquifers was investigated in terms of equilibrium dissolution/precipitation reactions (Meeussen, 1992; Ghosh, 1998) without considering kinetic aspects or subsequent sorption of dissolved iron-cyanide complexes. The dissolution of solid iron-cyanide complexes depends on pH, redox potential, and the presence of ligands promoting the dissolution of the solid phase. However, there are several aspects which complicate the fate of iron-cyanide complexes in soils.

Based on model calculations involving the partition of cyanide over free cyanide and iron-cyanide complexes as influenced by pH and redox potential and assuming equilibrium, free cyanide should be the dominant species in soil and ground water (Meeussen et al., 1992a). However, iron-cyanide complexes predominate in soil actually (Meeussen et al., 1992a; Theis et al., 1994). Colloidal transport of Berlin Blue in a contaminated soil was found by Mansfeldt et al. (1998). As judged from column experiments, the release of dissolved iron-cyanide complexes in a contaminated soil was strongly rate-limited resulting in undersaturation with respect to Berlin Blue (Weigand et al., 2001). Furthermore, Weigand et al. (2001) proposed that the presence of iron-cyanide complexes in solution is influenced by rate-limited desorption of iron-cyanide complexes adsorbed on soil phases. Meeussen (1992) proposed that sorption of iron-cyanide on mineral surfaces in subsoils is the main immobilizing process at low concentrations. The sorption of iron-cyanide complexes on some soil minerals and in soils has been investigated. These studies will be discussed in the following chapters.

The processes possibly determining the fate of iron-cyanide complexes in soil are schematically summarized in Figure 1.

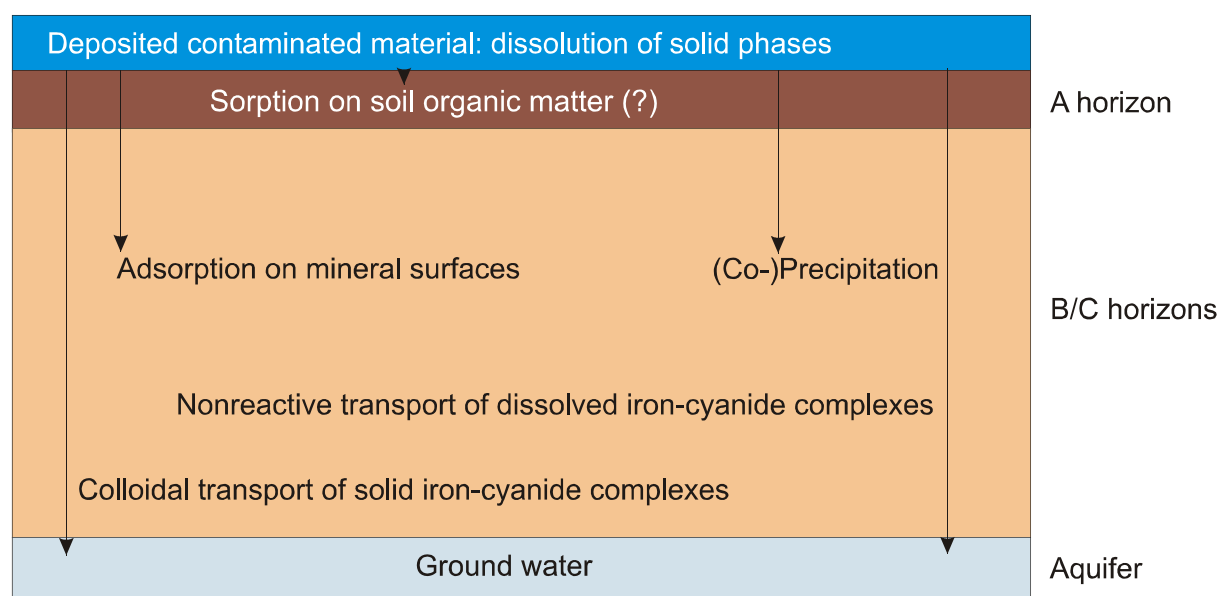


Figure 1 Fate of iron-cyanide complexes in a schematic soil profile.

Ferrocyanide can be used as a nitrogen source by *Pseudomonas fluorescens*, thus degraded to carbon dioxide and ammonia (Dursun et al., 1999). However, the presence of organic nutrients such as glucose is necessary for biodegradation, which occurs at the most at pH 5. Therefore, biodegradation should be a negligible process in acid soils on sites of former gasworks.

Sorption and desorption at the mineral/water interface

As pointed out above, sorption occurring at the mineral/water interface is assumed to be a process influencing the mobility of iron-cyanide complexes in soil and ground water. Sorption, a term including both two-dimensional adsorption and three-dimensional processes such as surface precipitation, co-precipitation and diffusion into a crystal, should be used when the retention mechanism is unknown (Scheidegger and Sparks, 1996). Adsorption is one of the most important soil chemical processes. Adsorption of ions is driven by forces ranging from weak, physical, van der Waals forces (e.g. partitioning) and outer-sphere complexation (e.g. ion exchange) to chemical interactions as shown in Figure 2 (Scheidegger and Sparks, 1996). Chemical interactions include inner-sphere surface complexation comprising ligand exchange,

covalent bonding, hydrogen bonding, and hydrogen bridges (Sparks, 1995). As shown in Figure 2, inner-sphere surface complexes can be either monodentate or bidentate.

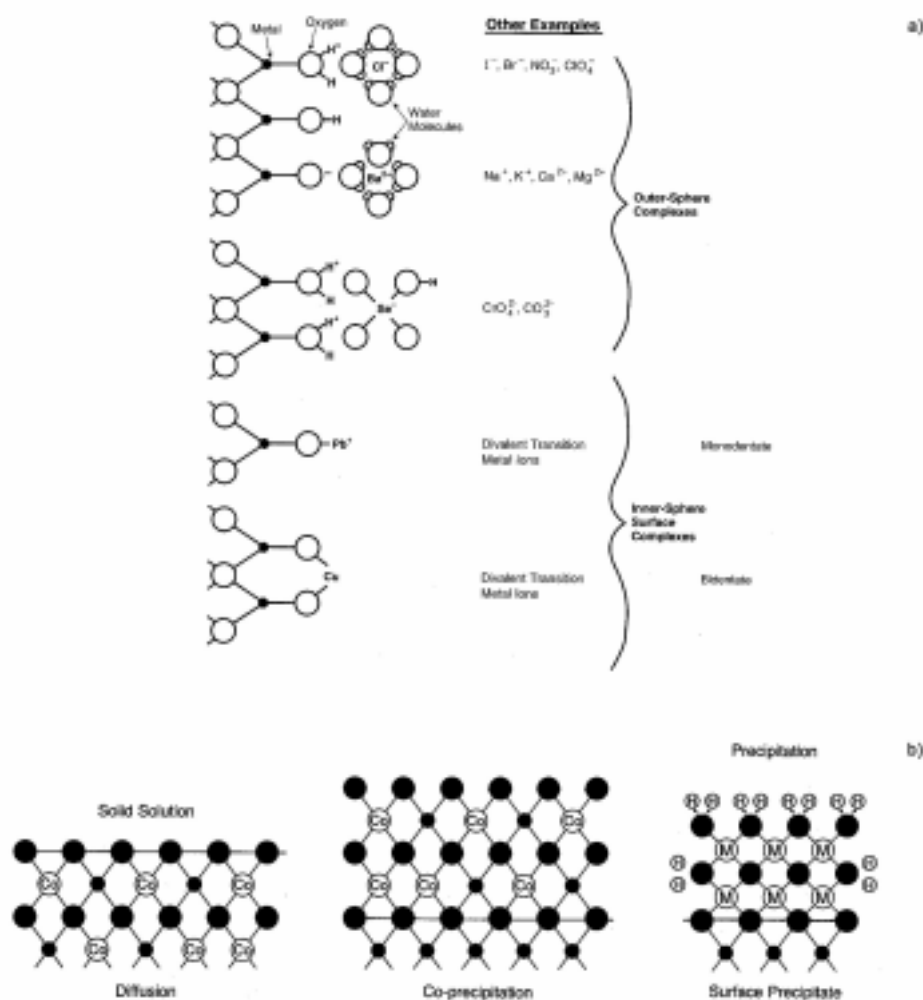


Figure 2 Possible surface complexes. (a) Surface complexes formed between inorganic ions and hydroxyl groups of an oxide surface (after Sparks (1995)); (b) diffusion and precipitation phenomena, the large shaded circles represent oxygen in the mineral and the small shaded circles represent metal ions in the mineral, M: metal; H: hydrogen; Co: cobalt (after Brown et al. (1995)).

Surface precipitation occurs at high surface coverage, whereas surface complexation tends to dominate at low surface coverage. Heterogeneous nucleation of a new solid phase involves a

new phase composed of the adsorptive, and a component from solution or from the sorbent. When the precipitate consists of chemical species derived from the aqueous solution and dissolution of the sorbent, it is referred to as a co-precipitate (Brown et al., 1995). Diffusion should be understood as mean transfer through micropores, faults or interfaces of the solid rather than through the lattice itself.

The release of adsorbed species is termed desorption. As pointed out by Barrow (1989), desorption is not a simple reversal of original adsorption. It has been often observed that not all of the adsorbate is desorbed and the reactions appear to be irreversible (e.g. phosphate desorbed from goethite (Strauss et al., 1997)). This irreversibility is also called hysteresis or non-singularity.

Outline of this thesis

The aim of this study was to investigate the sorption of the iron-cyanide complexes ferricyanide and ferrocyanide on iron oxides and in soils to enable better understanding of the fate of iron-cyanide complexes in the soil environment. As pointed out in the section above, many aspects of the mobility of iron-cyanide complexes in soils and aquifers are still unclear. However, sorption on solid phases may play an important role in the environmental behaviour of iron-cyanide complexes. Ferricyanide and ferrocyanide are stable complexes, but they differ in some chemical properties such as the oxidation state of iron, the dissociation of the conjugate acids, and the tendency to release a cyano group. Therefore, a constant aspect of iron-cyanide complex sorption to be investigated was the evaluation of differences in the sorption behaviours of ferricyanide and ferrocyanide.

Retention of the complexes by the sorbents used in this study was assumed. These sorbents included the iron (hydr)oxides goethite, α -FeOOH, and ferrihydrite, $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$, $n = 1 - 3$, uncontaminated soils, and deposited blast furnace sludge from which soils developed.

Firstly, the sorption of iron-cyanide complexes on goethite was investigated in batch experiments. Goethite is a very important sorbent for anions in soils (Cornell and Schwertmann, 1996). The mechanisms by which iron-cyanide complexes are sorbed on this iron oxide were

not completely understood previously.

Secondly, the influence of sulphate on the sorption of iron-cyanide complexes on goethite was investigated, because i) sulphate may have a competitive effect on iron-cyanide complex sorption and ii) deposited purifier wastes contain large amounts of both iron-cyanide complexes and sulphate. In this connection, the desorption of iron-cyanide complexes sorbed on goethite by chloride and phosphate solutions was examined.

Furthermore, the sorption of iron-cyanide complexes on ferrihydrite was studied using a model approach which considers changes in the surface charge of ferrihydrite due to sorption. The sorption of iron-cyanide complexes in uncontaminated soils was investigated with special attention to interactions between iron-cyanide complexes and soil organic matter. All these experiments mentioned above were performed by a batch technique.

Column experiments describe the sorption and the transport of contaminants in soils and aquifers more closely than batch experiments. Therefore, sorption and transport of iron-cyanide complexes in goethite-coated sand and in uncontaminated soil were examined under saturated flow conditions. The desorption of iron-cyanide complexes sorbed in this soil used in column experiments by phosphate and chloride was investigated additionally.

Finally, the ability of cyanide-containing deposited blast furnace sludge to sorb iron-cyanide complexes additionally was studied by a batch technique including desorption.

Organization of this thesis

The following chapters of this thesis (chapters 2 through 8) are organized as self-contained papers. They represent articles in reviewed journals which have been published or accepted or submitted, respectively. Each chapter contains a separate abstract, introduction, results, and conclusions. The final chapter (Chapter 9) presents an overall discussion, and recommendations for future research. The thesis is written in British English except for the chapters which represent articles published in American journals.

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CHAPTER 2

Sorption of iron-cyanide complexes on goethite

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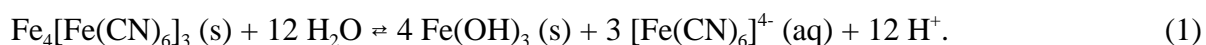
ABSTRACT

Iron-cyanide complexes are present in soils on sites of former gas plants and coke ovens. We have studied the sorption of the complexes ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, on goethite in batch experiments, including the effects of concentration, time, ionic strength, pH, and the extent of reversibility. The sorption of ferricyanide showed features of both outer-sphere and inner-sphere complexation: its extent decreased with increasing pH; it depended on ionic strength; it was quickly and completely reversible; and it induced a change in surface electric potential. In contrast, sorption of ferrocyanide depended on pH to a lesser extent and was not affected by ionic strength at different pHs. The desorption was slower and incomplete. For ferrocyanide we conclude that sorption involves inner-sphere complexation and precipitation of a Berlin-Blue-like phase on the goethite surface.

INTRODUCTION

Soils on sites of former gas plants and coke ovens are commonly contaminated with iron-cyanide compounds (Shifrin et al., 1996). This contamination is caused by the deposition of purifier wastes which originate from scrubbing of raw gas with iron oxide particles. In these soils, solid cyanides exist as the ferric ferrocyanide Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, in an impure or poorly crystallized form or both (Mansfeldt et al., 1998).

Berlin Blue is slightly soluble (solubility product constant $K_{\text{sp}} = 10^{-84.5}$, Meeussen et al., 1992) and its solubility depends on pH according to the reaction equation



The speciation of iron-cyanide complexes depends on redox potential:



Both iron-cyanide complexes are low-spin complexes. Ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, is paramagnetic, whereas ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, is diamagnetic. As can be seen from Equation (1), the solubility of Berlin Blue increases as the soils become more alkaline (Meeussen et al., 1994). Soils on sites of former coke ovens and gas plants are very acid because of oxidation of elementary sulphur which is the main component of purifier wastes (Environmental Resources Limited, 1987). This should decrease the solubility of Berlin Blue.

At low pH the surfaces of sesquioxides become protonated and can thus adsorb anions such as iron-cyanide complexes bearing large charges. If the concentrations of iron cyanides in the soil solution are too small for precipitation of Berlin Blue then adsorption of the complexes may be the main process immobilizing dissolved iron-cyanide complexes in soils (Meeussen, 1992). A possible adsorption mechanism is the relatively weak outer-sphere complexation caused by electrostatic attraction. An example for an anion that is adsorbed in this way is chloride (Hingston et al., 1972). Inner-sphere complexes are more stable. The adsorbent becomes part of the surface, and a covalent (i.e. chemical) bonding can be formed. Phosphate, for example, is an anion which is adsorbed on goethite, $\alpha\text{-FeOOH}$, by inner-sphere complexation (Tejedor-Tejedor and Anderson, 1990). However, a separation between the two mechanisms on the basis of macroscopic sorption data may be too simple, because a spectrum of intermediate behaviours is

likely (Eggleston et al., 1998).

As a result of precipitation of Berlin Blue and adsorption of iron-cyanide complexes, iron cyanides should be immobile in these acid soils. The factors influencing dissolution and precipitation of Berlin Blue were investigated in detail by Meeussen et al. (1994), but there are few studies dealing with the adsorption behaviour of iron-cyanide complexes to soils and minerals and their adsorption mechanisms. Fuller (1985) found that ferricyanide is mobile in soils as judged from column experiments. One factor influencing the retention of ferricyanide was clay content. Iron oxides had an affinity to ferricyanide, but pH was the most important chemical property. The sorption of ferrocyanide by five soils was investigated by Ohno (1990), and increasing sorption was observed with decreasing soil pH. Theis et al. (1988) postulated that the adsorption of ferricyanide on goethite is caused by electrostatic attraction because of its complete reversibility. They did not investigate the sorption behaviour of ferrocyanide. Both anions form outer-sphere complexes on $\gamma\text{-Al}_2\text{O}_3$ (Cheng and Huang, 1996; Cheng et al., 1999). Hipps et al. (1988) stated that ferricyanide is reversibly bound on $\gamma\text{-Al}_2\text{O}_3$. Both complexes can be interlayered in clay minerals such as hydrotalcite (Idemura et al., 1989; Hansen and Koch, 1994). Ferricyanide was not adsorbed by negatively charged kaolinite (Stein & Fitch, 1996). Goethite is an iron mineral that is ubiquitous in soils of temperate latitude and is often used as a model substance for the adsorption of cations and anions in soils (see Cornell and Schwertmann, 1996). For these reasons we investigated the sorption of iron-cyanide complexes on goethite. We used batch experiments and studied the effects of concentration, time, ionic strength, pH, and the extent of reversibility. The aim of this paper is to explain the mechanisms of the sorption of both iron-cyanide complexes on goethite. We use the general term sorption for any retention mechanism, which may include adsorption, precipitation, co-precipitation, and diffusion into crystals (Scheidegger and Sparks, 1996).

MATERIAL AND METHODS

Goethite: Preparation and properties

Goethite was prepared as described by Schwertmann and Cornell (1991) by precipitating ferrihydrite from alkaline solution (reaction of 1 M $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ and 5 M KOH). The product was converted to goethite at 343 K for 60 hours. It was cleaned by pressure filtration until the electrical conductivity was $< 3 \mu\text{S cm}^{-1}$. Mößbauer spectra showed a haematite content $< 0.5\%$. Goethite was also identified by XRD spectroscopy. The specific surface area (BET) was $30 \text{ m}^2 \text{ g}^{-1}$. The point of zero charge (pzc) was 8.3. It was determined using acid base titrations with various ionic strengths following Christl and Kretzschmar (1999). The intrinsic acidity constants are $\text{pK}_1 = 7.45$ and $\text{pK}_2 = 9.52$, obtained by linear extrapolation of the charge data. These values are consistent with published data (Cornell and Schwertmann, 1996).

Sorption experiments

For the sorption experiments $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (reagent grade, Riedel-de Haën) were used. From these salts, stock solutions containing $2000 \text{ mg CN}^- \text{ l}^{-1}$ were prepared. Sorption experiments were carried out by a batch technique at a temperature of 283 K and an ionic strength (I) of 0.01 M (NaNO_3) in 50-ml polyethylene bottles with 25-ml aliquots of a goethite suspension (10 g l^{-1}). Seven different pH values (3.5 to 9.0) of the goethite suspensions were obtained by adjusting with 0.025 M HNO_3 or 0.025 M NaOH. It took up to 10 days until the suspension pH was constant. Then up to nineteen different aliquots (range 0 to 1 ml) of a stock solution were added to gain initial iron-cyanide concentrations ranging from 0 to 0.49 mmol l^{-1} for each pH. The samples were shaken horizontally for 24 hours at 150 oscillations per minute.

The time-dependent sorption of the complexes on goethite was examined at suspension pH 3.5. The initial $[\text{Fe}(\text{CN})_6]$ concentration was 0.3 mmol l^{-1} , and the samples were shaken for times varying from 1 to 120 hours. The effect of ionic strength on the sorption of iron-cyanide complexes was investigated using goethite suspensions in which ionic strength was adjusted to 0.001, 0.01, 0.05, or 0.1 M (NaNO_3) at initial pH of 3.5, 5.0, 5.9, and 7.0 in triplicate. The amounts of HNO_3 added to adjust the pH were considered when calculating ionic strength. The initial $[\text{Fe}(\text{CN})_6]$ concentration

was 0.25 mmol l⁻¹. The reversibility of the sorption reaction was determined by adjusting the pH to the range of 9.2 to 9.3 with 0.1 M NaOH after goethite was equilibrated with iron-cyanide complexes for 24 hours at 283 K, an initial pH of 3.5 and an initial [Fe(CN)₆] concentration of 0.25 mmol l⁻¹. After adjusting the pH the samples were stirred for 15, 60, 120, and 240 minutes. In all experiments the phases were separated by membrane filtration (cellulose nitrate, 0.45 µm) after the reaction.

Cyanide determination

The supernatant was distilled using a micro-distillation technique (Eppendorf MicroDistiller, Hamburg). During this procedure, iron-cyanide complexes are converted to hydrogen cyanide which is absorbed by an alkaline solution. Cyanide was subsequently determined colorimetrically at 600 nm (Perkin Elmer Lambda 2, Überlingen, Germany) using a barbituric acid-pyridine solution. The total procedure is described in detail by Mansfeldt and Biernath (2000).

Interpretation

We used an equation by Barrow (1999) to describe the pH-dependent sorption of the complexes. The relationship between solution concentration c (in mmol l⁻¹) and sorbed amount S (in µmol m⁻²) is given by

$$c = a \exp(b S) S / (S_{\max} - S) \quad (3)$$

and

$$S = V_s (c_0 - c), \quad (4)$$

where V_s is the ratio of solution to mass of iron oxide, c_0 the initial concentration, and

$$a = 1 / \{ K_i \alpha \exp(-z_i F \psi_0 / RT) \} \quad (5)$$

and

$$b = -z_i F m / RT. \quad (6)$$

In this set of equations S_{\max} is the maximum sorption, K_i is a constant, α the proportion of the anion i present in solution as an ion with valency z_i , F the Faraday constant, R the gas constant, and T is the temperature (K). The electric potential in the absence of anion sorption is ψ_0 , and m is a parameter. Sorbed anions experience a mean electric potential ψ_a which decreases

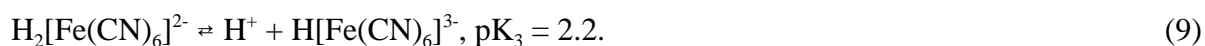
roughly linearly with increasing sorption, as shown by Posner and Barrow (1982) for the model of Bowden et al. (1980):

$$\psi_a = \psi_0 - m S. \quad (7)$$

The dissociation constants for ferrocyanic acid (Jordan and Ewing, 1962) according to the following reactions used here to calculate α are



and



All pK_a values for ferricyanic acid are less than 1, and so are pK_1 and pK_2 for ferrocyanic acid. The approach by Barrow (1999) has some advantages over the simpler equations (e.g. Freundlich): a value for maximum sorption (S_{max}) is present; the speciation of the complexes is considered (via α); and the change in electric potential as a result of sorption and due to induced change in pH is taken into account.

RESULTS

Effects of time

In the range of 1 to 120 hours the sorption of ferrocyanide did not depend on time (Figure 1). The final concentrations ranged from 0.241 to 0.239 mmol l⁻¹ without any relation with time. Hence the reaction of ferrocyanide with the goethite surface took less than 1 hour: Sorption of ferrocyanide is fast. In contrast, the final concentrations of ferricyanide decreased exponentially from 0.16 to 0.14 mmol l⁻¹ in the time range from 1 to 24 hours, after which the final concentrations remained constant to 120 hours. Hence the sorption of ferricyanide is faster than that of phosphate, which continues reacting with the goethite surface for up to 3 weeks (Strauss et al., 1997).

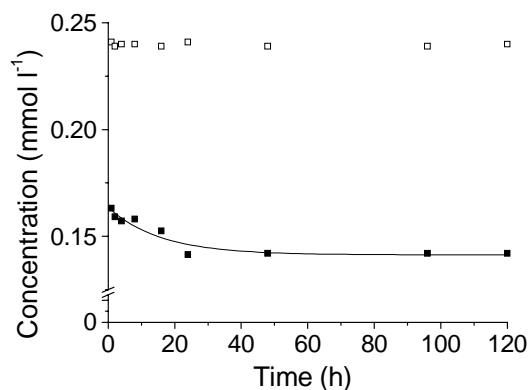


Figure 1 Time-dependent sorption of iron-cyanide complexes on goethite (■, ferricyanide; □, ferrocyanide; $c_0 = 0.3 \text{ mmol l}^{-1}$; pH 3.5).

Ferricyanide: $S = 0.14 + 0.02 \exp(-t / 15.88)$, where t is time in hours.

One of the explanations of time-dependent sorption is diffusion of sorbed ions into cracks and pores of the surface. Strauss et al. (1997) showed increasing diffusion of phosphate into micropores of the goethite surface with decreasing crystallinity. As shown by XRD spectroscopy, the goethite used here is not well crystallized and, as sorption depends on time, only ferricyanide seems able to penetrate the surface. This might be because of the large size of the ion or a weak affinity for the surface.

Because for ferricyanide there was little further change after 24 hours, all later sorption experiment were done within this time.

Effects of ionic strength

Varying the ionic strength had varied effects on the sorption of the complexes (Figure 2). Ferricyanide sorption decreased with increasing ionic strength (Figure 2a). This decrease is linear on a logarithmic scale of ionic strength. The slopes of the straight lines increase from -4 to -1.3 with increasing pH ($r^2 > 0.9$ for any regression). In other words, the effect of ionic strength on the sorption of ferricyanide depends on pH with the greatest effect at the lowest pH. If increasing ionic strength diminishes the amounts of ion sorbed, the surface must be positively charged (Barrow, 1987).

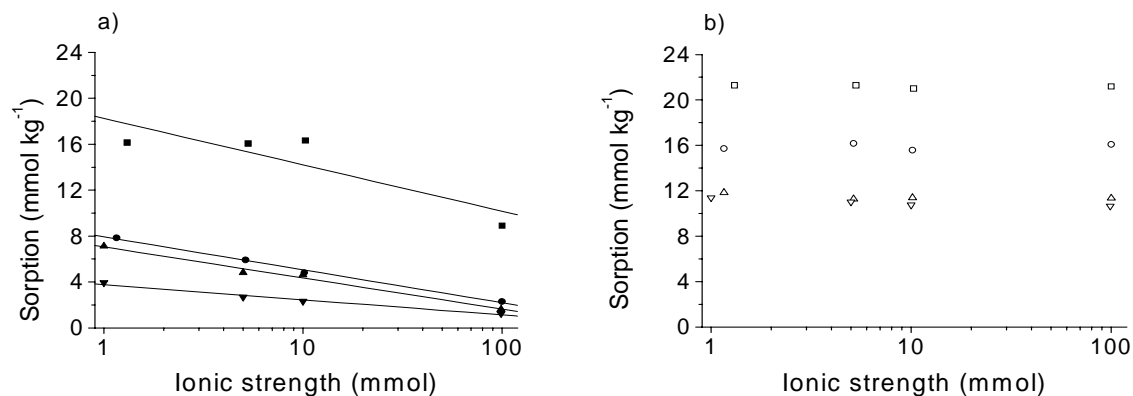


Figure 2 Sorption of iron-cyanide complexes on goethite as influenced by ionic strength at different initial pH (a, ferricyanide; b, ferrocyanide; ■/□, pH 3.5, ●/○ pH 5.0, ▲/△ pH 5.9, ▼/▽ 7.0).

At pH 7.0 the positive charge is less than at the other pHs < 7.0, so that ionic strength has the smallest effect on sorption. In contrast, ferrocyanide sorption was little influenced by ionic strength (Figure 2b). Linear regressions with pH were not significant.

The relation between pH and the amounts of ferricyanide sorbed at different ionic strengths is linear on a logarithmic scale of S (Figure 3).

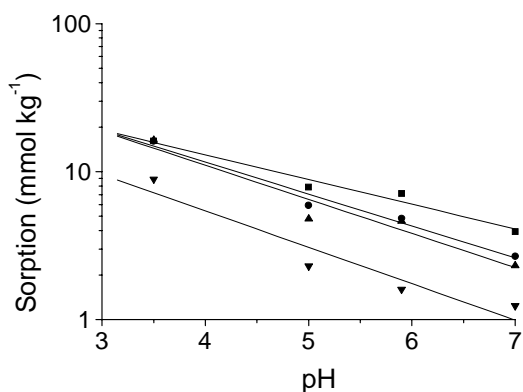


Figure 3 Sorption of ferricyanide on goethite as influenced by initial pH at different ionic strength (■, I = 0.001 M; ●, I = 0.01 M; ▲, I = 0.05 M; ▼, I = 0.1 M).

The straight lines are nearly parallel ($r^2 > 0.91$ for any linear regression), and there is no point of intersection at $\text{pH} < 8.3$. Evidently ferricyanide sorption did not diminish the pzc, because then a point of intersection at $\text{pH} < 8.3$ would exist. Ferrocyanide data are not shown, because for any pH the sorbed amounts for different ionic strengths are the same.

Effects of pH

For both ferricyanide and ferrocyanide, sorption decreased with increasing pH (Figure 4).

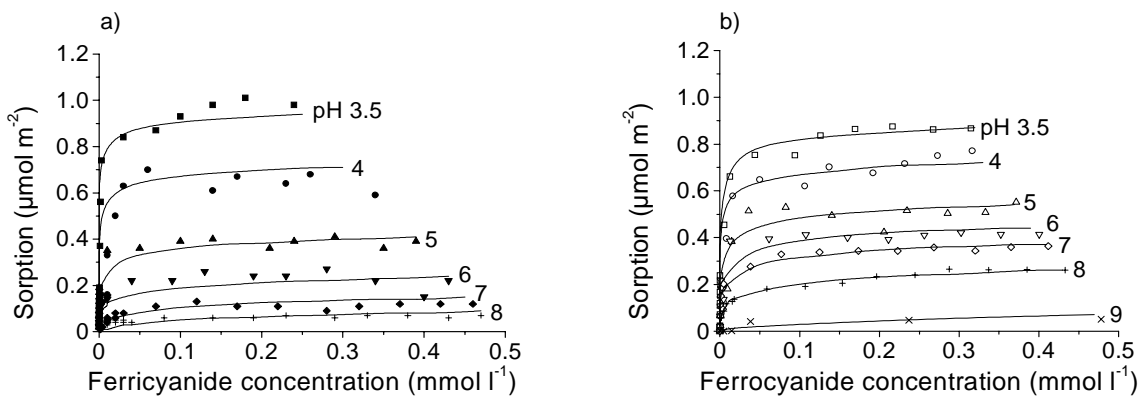


Figure 4 Sorption of iron-cyanide complexes on goethite as influenced by initial pH (a, ferricyanide; b, ferrocyanide). Isotherms are fitted to Equation (3) with individual values of a . Ferricyanide: $b = 43 \mu\text{mol}^{-1} \text{m}^2$; $S_{\text{max}} = 1.6 \mu\text{mol m}^{-2}$; $r^2 = 0.997$. Ferrocyanide: $b = 25.3 \mu\text{mol}^{-1} \text{m}^2$; $S_{\text{max}} = 1.6 \mu\text{mol m}^{-2}$; $r^2 = 0.999$.

They differ in that ferrocyanide sorption was greater in the high pH range, for example at pH 8.0, and was still detectable at pH 9.0. In both cases, the data suggest that maximum sorption would be observed only at pH lower than 3.5. Equation (3) closely describes the results for both ions. From the fitted equation, the estimated maximum S_{max} was $1.6 \mu\text{mol m}^{-2}$ for both ions. With the same goodness-of-fit, another S_{max} , $1.25 \mu\text{mol m}^{-2}$, is possible for ferrocyanide. However, these values involve extrapolation and are imprecise. Consequently, the value for ferricyanide was not significantly different from that for ferrocyanide.

The effects of pH are effectively summarized by the change in the values of the a coefficient with pH (Figure 5). As a logarithmic scale is used, the change in a is proportional to the change

in an ‘overall’ affinity term $-\log(K_i\alpha) + z_i F \psi_0 / RT$, (Equation 5). Thus, Figure 5 shows that the decline in the affinity term is steeper for ferricyanide than for ferrocyanide and that sorption of ferricyanide is affected by pH to a larger extent than that of ferrocyanide. There are two properties that vary with pH.

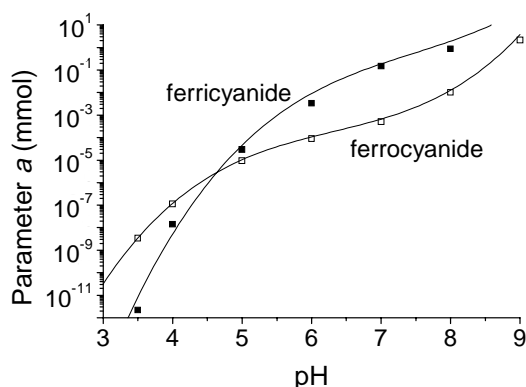


Figure 5 Relationship between initial pH and parameter a for the sorption of iron-cyanide complexes on goethite. Ferricyanide: $\ln a = -127 + 45.4\text{pH} - 5.79\text{pH}^2 + 0.259\text{pH}^3$, $r^2 = 0.99$. Ferrocyanide: $\ln a = -87.6 + 34.1\text{pH} - 5.13\text{pH}^2 + 0.271\text{pH}^3$, $r^2 = 0.99$.

One is the extent of dissociation α . As all pK_a values of ferricyanic acid are less than 1, the ferricyanide species present in the pH range used here is always $[\text{Fe}(\text{CN})_6]^{3-}$. As indicated in Equations (8) and (9), the speciation of ferrocyanide changes with pH. However, for $\text{pH} > 5.2$ more than 90% of ferrocyanide is present as $[\text{Fe}(\text{CN})_6]^{4-}$. This has to be taken into account considering the other property that varies with pH, the electric potential term ψ_0 . Its effect depends on the value for the valency z_i . The greater is the valency, other things being equal, the greater is the effect of a change in potential with pH, as shown by Barrow (1999) when comparing the sorption of trivalent citrate and divalent phosphate on goethite. Hence, the decrease in the ψ_0 term with increasing pH is appreciably greater for ferricyanide than for ferrocyanide. This, in turn, indicates that the mean centre of charge of the ferricyanide ions is closer to the surface of the goethite than that for ferrocyanide. Hence inner-sphere complexes are more likely for ferricyanide.

The b coefficient of Equation (3) reflects the change in electric potential with increasing sorption as indicated in Equations (6) and (7). The fitted values for b were $43 \mu\text{mol}^{-1} \text{m}^2$ for ferricyanide and $25.3 \mu\text{mol}^{-1} \text{m}^2$ for ferrocyanide. From Equation (6), the values of m were $14.3 \text{ mV } \mu\text{mol}^{-1} \text{m}^2$ for ferricyanide and $6.3 \text{ mV } \mu\text{mol}^{-1} \text{m}^2$ for ferrocyanide. This indicates that ferricyanide sorption induced a larger change in surface electric potential than ferrocyanide. This could have been a result of negative charge conveyed to the surface by reaction or induced by decrease in pH.

For ferrocyanide but not for ferricyanide the colour of goethite changed from orange-brown to slightly olive-green after reaction. At pH 3.5 blue particles could be seen on the goethite surface under a microscope.

The sorbed amounts of the complexes are closely correlated for $S < 15 \text{ mmol kg}^{-1}$ at pH 3.5 to 6.0 (Figure 6).

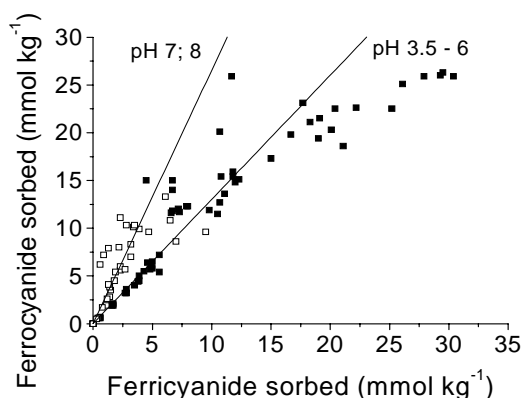


Figure 6 Relationship between the amounts of ferricyanide and ferrocyanide sorbed on goethite (filled symbols indicate pH 3.5 to 6.0, open symbols indicate pH 7.0 and 8.0).

At pH 7.0 and 8.0 a close correlation is valid for $S < 10 \text{ mmol } [\text{Fe}(\text{CN})_6]^{4-} \text{ kg}^{-1}$. For any pH value the square of the correlation coefficient r is larger than 0.98. However, for greater S values this correlation does not exist, because $S ([\text{Fe}(\text{CN})_6]^{3-})$ increases whereas $S ([\text{Fe}(\text{CN})_6]^{4-})$ remains nearly constant. For pH 3.5 to 6.0 all values for $S < 15 \text{ mmol kg}^{-1}$ are represented by a straight line with a slope of 1.31, which is nearly the charge ratio of the complexes (4/3). For pH 7.0 and

8.0 the slope increases to 2.65.

This reflects the greater sorption of ferrocyanide in this pH range. From this point of view differences exist between the sorption behaviour of the complexes depending on pH.

Reversibility

The results of the desorption experiments are shown in Table 1. As in the preceding experiments the results for the desorption of the complexes differ. Increasing the pH to 9.3 resulted in a quick and complete release of sorbed ferricyanide in the chosen time range. As sorption of ferricyanide is fairly fast, quick desorption could be expected. Further, complete desorption could be expected because ferricyanide was not sorbed at an initial pH of 9.0 and 24 hours equilibration time. Theis et al. (1988) showed similarly that ferricyanide was desorbed completely within 15 s from a crystalline goethite after changing the pH to 8.5.

Table 1 Time dependent per cental desorption of the initially sorbed amounts of iron-cyanide complexes on goethite after transferring to pH 9.2-9.3.

	% desorbed after			
	15	60	120	240 minutes
$[\text{Fe}(\text{CN})_6]^{3-}$	89	94	98	100
$[\text{Fe}(\text{CN})_6]^{4-}$	71	74	86	95

The desorption of ferrocyanide depended markedly on time. In contrast to the desorption of ferricyanide, it was slower and incomplete. A simple reason for the incompleteness is that ferrocyanide can be sorbed at pH 9.0 and perhaps at 9.3. Slow and incomplete desorption suggest the release of ions which diffused into pores. In this case, the sorption of ferrocyanide should have depended on time. Hence time-dependent sorption and desorption of ferrocyanide cannot be interpreted in terms of diffusion into the surface. As a consequence, a different retention mechanism should be proposed for ferrocyanide, as discussed below.

DISCUSSION

Differences in the sorption behaviour of the complexes were shown for time, ionic strength, pH, and reversibility. The sorption of both complexes depended on pH. However, pH-dependent sorption alone is no criterion to distinguish between outer- and inner-sphere complexation. Molybdate sorption on goethite is very sensitive to pH, but it is sorbed by a ligand exchange reaction (Hingston et al., 1972).

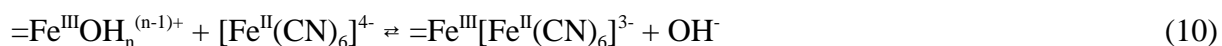
Theis et al. (1988) attributed quick and complete reversibility of ferricyanide sorption on goethite to outer-sphere complexation. We found the same desorption behaviour of ferricyanide here. Thus, we can support their conclusion from the desorption results.

At pH 9.0 (above the pzc) no ferricyanide was sorbed, and there was little sorption at pH 8.0. It is characteristic of outer-sphere complexed anions not to be sorbed at pH values above the pzc of the sorbent. Ferricyanide sorption did not lower the pzc, as shown by experiments with varying ionic strength. These results accord with outer-sphere complexation of ferricyanide. It is very likely that paramagnetic ferricyanide can be bound only electrostatically on goethite which is paramagnetic, too.

However, there were results that may be attributed to inner-sphere complexation. Based on the fitting results, ferricyanide is sorbed closer to the goethite surface than is ferrocyanide, because it induces a large change in ψ_0 with pH. As a consequence, ferricyanide should form inner-sphere complexes to a greater extent than ferrocyanide. Ferricyanide sorption is highly influenced by ionic strength. This is consistent with the position of ferricyanide close to the goethite surface derived from the fitting results. The closer the mean centre of charge of a sorbed anion is to the surface, the greater is the effect of ionic strength on the electric potential and thus on sorption.

Based on these results, ferricyanide forms both outer- and inner-sphere complexes on goethite. Perhaps its sorption is similar to that of sulphate. This anion forms outer-sphere complexes and weak inner-sphere complexes on hematite in the acidic range (Eggleson et al., 1998). A similar combination of sorption mechanisms is imaginable for ferricyanide, because the results of sorption and desorption experiments fit to this explanation.

The sorption of ferrocyanide differed in important ways from that of ferricyanide. It is sorbed at pH 9.0. This suggests inner-sphere complexation. Sorption of ferrocyanide is not influenced by varying the ionic strength. Hence electrostatic attraction alone cannot explain the sorption behaviour. Furthermore, the desorption is slow and incomplete. This suggests strong bonding on the goethite surface. Sorption of ferrocyanide at pH 9.3 cannot be excluded, but another conclusion is that further ferrocyanide exists on the goethite surface which is not adsorbed, but precipitated. If goethite is in suspension, there are always Fe^{III} ions in solution. Their concentration depends on pH. In the presence of ferrocyanide Berlin Blue will precipitate, because its solubility product is much less than any known solubility product constant of different goethite. Their K_{sp} values are in the range of 10^{-40} . The lowest pH value used in this study is 3.5, hence the Fe^{III} concentration in solution is less than $1 \mu\text{mol l}^{-1}$ if we postulate the solubility product constant mentioned above. Therefore precipitation caused by Fe^{III} in solution can explain only a very small amount of sorbed ferrocyanide, and this amount is negligible. On the other hand, blue particles on the surface were easily detected, thus precipitation of a Berlin-Blue-like phase on the surface must have taken place. In a first step, we assume inner-sphere complexation according to the following reaction:



with $n = 0 - 2$ and $=\text{Fe}^{\text{III}}\text{OH}_n^{n-1}$ being the goethite surface.

Considering the octahedral structure of ferrocyanide, the new surface complex in Equation (10) is rearranged to



This is a Berlin-Blue-like complex, because in the crystal structure of Berlin Blue each Fe is surrounded by an octahedron of CN groups, without any direct linkage between Fe^{III} and Fe^{II} (Tilley, 2000). If the new surface complex reacts with three adjacent surface groups then Berlin Blue is formed on the surface. This possible precipitation reaction requires previous inner-sphere complexation. These reactions can explain the sorption results and the olive-green colour of the goethite after equilibration with ferrocyanide. Furthermore, precipitation of Berlin Blue explains the rapid sorption, because its formation is fast. If the precipitate is Berlin Blue then its dissolution depends on time and pH, because it is soluble at pH 9.0 (Mansfeldt et al., 1998). Complete dissolution of Berlin Blue in soils is prevented by dissolution kinetics (Meeussen et

al., 1992). We propose the same behaviour for the Berlin-Blue-like complexes which we suggest are formed after previous inner-sphere complexation on the goethite surface, and of course for Berlin Blue which precipitated caused by Fe^{III} in solution. This explains the slow and incomplete desorption behaviour of sorbed ferrocyanide. However, we cannot exclude the possibility that a fraction of outer-sphere complexed ferrocyanide exists over the whole pH range. Different mechanisms depending on pH were found by Peak et al. (1999) for sulphate sorption on goethite. The reason for the ability of ferrocyanide to form inner-sphere complexes might be that complexes in which the same element is present with different oxidation states are more stable than those with the same oxidation states. In case of ferrocyanide sorption, Fe is present in two oxidation states, Fe^{III} as a constituent of goethite and Fe^{II} in ferrocyanide. Both are present in a surface complex as shown in Equation (10).

One could expect only a small amount of diamagnetic ferrocyanide to be sorbed on goethite electrostatically, yet our results show that large amounts of ferrocyanide are sorbed by goethite. This discrepancy can be resolved with the assumption of chemical bonding, inner-sphere complexation or precipitation of ferrocyanide or some combination on the goethite surface. However, from the fitting results of pH-dependent sorption the formation of inner-sphere complexes is more likely for ferricyanide than for ferrocyanide. On the other hand, it is important to note that the set of equations (Equations (3) to (7)) is a model for adsorption processes. Hence it does not include precipitation reactions as proposed for ferrocyanide sorption. If precipitation occurs, it may be questionable whether the parameters fitted solely for adsorption adequately describe the whole surface process including precipitation.

This combination of the proposed mechanisms for ferrocyanide sorption supports the opinion that distinguishing between adsorption and precipitation is difficult, because of the possible similarity of the bonding mechanisms (Corey, 1981).

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CHAPTER 3

Sorption of iron-cyanide complexes on goethite in the presence of sulfate and desorption with phosphate and chloride

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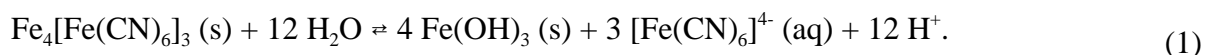
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ABSTRACT

Soils are contaminated with potentially toxic iron-cyanide complexes by some industrial activities. The influence of sulfate on the sorption of the iron-cyanide complexes ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, on goethite was investigated in batch experiments. The experiments were conducted as influenced by pH and varying sulfate/iron-cyanide complex concentration ratios. Furthermore, the desorption of iron-cyanide complexes sorbed on goethite was studied using phosphate and chloride solutions as influenced by pH and anion concentration. Over the whole pH range (pH 3.5 to 8), ferricyanide and sulfate showed similar affinities for the goethite surface. The extent of ferricyanide sorption strongly depended on sulfate concentrations and vice versa. In contrast, ferrocyanide sorption was only decreased (approximately 12%) by sulfate additions at pH 3.5. Ferricyanide was completely desorbed by 1 M chloride, ferrocyanide not at all. Unbuffered phosphate solutions (pH 8.3) desorbed both iron-cyanide complexes completely. Even in 70-fold excess, pH-adjusted phosphate solutions could not desorb ferrocyanide completely at pH 3.5. For ferricyanide we propose a sorption mechanism that is similar to the sulfate sorption mechanism, including outer-sphere and weak inner-sphere surface complexes on goethite. Ferrocyanide appears to form inner-sphere surface complexes. Additionally, we assume that ferrocyanide precipitates probably as a Berlin-Blue-like phase at pH 3.5. Hence, ferrocyanide should be less mobile in the soil environment than ferricyanide or sulfate.

INTRODUCTION

Industrial activities of mankind are the main sources of cyanides in soils, because cyanides from natural sources are consumed by soil microorganisms and do not persist (Fuller, 1985). Soils on sites of former manufactured gas plants (MGP) and coke ovens are contaminated with cyanides (Shifrin et al., 1996). This contamination is caused by the deposition of purifier wastes, which originate from stripping of raw gas onto iron oxide particles by fixation as the pigment Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. In these soils the ferric ferrocyanide Berlin Blue exists in an impure and/or less well crystallized form (Mansfeldt et al., 1998). Although it is slightly soluble (solubility product constant $K_{\text{sp}} = 10^{-84.5}$; Meeussen et al., 1992b), dissolved iron-cyanide complexes are detected in the ground water (Meeussen et al., 1994) according to a pH-dependent dissolution of Berlin Blue:



The speciation of iron-cyanide complexes depends on redox potential:



The anions in Equation (2) are ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$. The purifier wastes also contain large amounts of amorphous iron sulfide and elemental sulfur. The total sulfur content of purifier wastes can be up to 60% (Environmental Resources Limited, 1987). Sulfuric acid is produced by oxidation of reduced sulfur species. Thus, the soils acidify and sesquioxide surfaces are protonated. Anions bearing large charges such as ferri- and ferrocyanide can be adsorbed on these surfaces. Furthermore, large amounts of sulfate are released by oxidation. Hence, both sulfate and dissolved iron-cyanide complexes are present in the soil solution of these sites and compete for adsorption sites.

Additionally, iron-cyanide complexes occur in the environment due to the use of road salt (Ohno, 1990) and in soils on which blast furnace sludge has been deposited (Mansfeldt and Dohrmann, 2001).

Two major adsorption mechanisms have been recognized. They are inner-sphere and outer-sphere surface complexation. Outer-sphere surface complexation is caused by electrostatic attraction and is relatively weak. Chloride is sorbed on goethite, $\alpha\text{-FeOOH}$, by this mechanism (Hingston et al.,

1972). Inner-sphere surface complexation is more stable. The adsorbent becomes part of the surface and a covalent bonding can be formed via ligand exchange. Phosphate forms inner-sphere surface complexes on goethite (Tejedor-Tejedor and Anderson, 1990).

Different mechanisms for sulfate adsorption on goethite are presented in the literature. Inner-sphere surface complexation forming a binuclear complex was proposed by Parfitt and Russell (1977) using infrared spectroscopy. Hansmann and Anderson (1985) found that sulfate is weakly bound through electrostatic attraction on goethite using electrophoresis. Zhang and Sparks (1990) explained the mechanism by outer-sphere surface complexation and simultaneous protonation of the mineral surface using pressure-jump relaxation. Peak et al. (1999) determined both outer-sphere and inner-sphere surface complexes on goethite at $\text{pH} < 6$ and only outer-sphere surface complexes at $\text{pH} > 6$ using *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Similarly, Wijnja and Schulthess (2000) found monodentate inner-sphere sulfate surface complexes on goethite at $\text{pH} < 6$ and predominantly outer-sphere surface complexes at $\text{pH} > 6$ using Raman spectroscopy. Alewell and Matzner (1986) found that in forest soils total inorganic sulfate was extracted by phosphate while chloride desorbed only exchangeable sulfate, which was assumed to be bound as outer-sphere surface complexes. A distinction of adsorbates into inner-sphere and outer-sphere based on macroscopic adsorption data is probably not possible (Eggleston et al., 1998). A spectrum of intermediate behaviors is likely, as shown on spectroscopic information by Peak et al. (1999) and Wijnja and Schulthess (2000) for sorption of sulfate on goethite and by Eggleston et al. (1998) for sorption of sulfate on hematite.

The sorption mechanisms of iron-cyanide complexes on goethite have not been investigated as intensively as the sulfate bonding mechanism. Both iron-cyanide complexes formed outer-sphere surface complexes on $\gamma\text{-Al}_2\text{O}_3$ as inferred from surface complexation modeling using the triple-layer model (Cheng and Huang, 1996; Cheng et al., 1999). In kinetic batch experiments ferricyanide sorption on goethite was completely reversible (Theis et al., 1988). Therefore, Theis et al. (1988) concluded outer-sphere surface complexation of ferricyanide. Fuller (1985) found ferricyanide to be very mobile in soils mainly controlled by pH as judged from column experiments. Research by Ohno (1990) showed that pH was the most important parameter controlling ferrocyanide sorption by soils. Ferricyanide was not adsorbed by negatively charged kaolinite (Stein and Fitch, 1996). Rennert and Mansfeldt (2001) assumed outer-sphere and weak inner-sphere surface complexation of ferricyanide,

whereas ferrocyanide was probably sorbed as an inner-sphere surface complex and by precipitation of a Berlin-Blue-like phase on the goethite surface. The presence of sulfate even at a molar ratio (sulfate to ferricyanide) of 100 had no effect on the sorption of ferricyanide on activated carbon (Saito, 1984). The competitive effect of sulfate on iron-cyanide complex sorption on soils or minerals has not yet been investigated.

Goethite is a common iron oxide in soils, has a well-defined crystal structure and can be readily synthesized in the laboratory (Cornell and Schwertmann, 1996). Hence, it has been used as a model substance for numerous adsorption experiments (summarized by Cornell and Schwertmann, 1996). One objective of this study was to investigate the sorption of iron-cyanide complexes on goethite as influenced by the competitive presence of sulfate in batch experiments. The extent of sorption was investigated including the effects of pH and various sulfate/iron-cyanide complex concentration ratios. The second objective was to study the desorption of sorbed iron-cyanide complexes. We did this by addition of chloride or phosphate solutions, the same method Alewell and Matzner (1996) used to desorb different sulfate surface complexes. All these aspects were used to test the proposed sorption mechanisms of iron-cyanide complexes on goethite by Rennert and Mansfeldt (2001). In the following, we use the term sorption for any retention mechanism including two-dimensional adsorption and three-dimensional processes such as diffusion into crystals and precipitation.

MATERIAL AND METHODS

Goethite: Preparation and properties

Goethite was prepared following Schwertmann and Cornell (1991) by precipitating ferrihydrite from alkaline solution (reaction of 1 M $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ with 5 M KOH). The product was aged for 60 h and converted to goethite at 343 K. It was cleaned by pressure filtration until the electrical conductivity of the filtrate was $< 3 \mu\text{S cm}^{-1}$. Mößbauer spectra showed a hematite content $< 0.5\%$. The specific surface area (Brunauer-Emmett-Teller, BET) measured on freeze-dried samples was $30 \text{ m}^2 \text{ g}^{-1}$, and the point of zero charge (pzc) was 8.3 (Rennert and Mansfeldt, 2001).

Sorption and desorption experiments

For the sorption experiments $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, and Na_2SO_4 (reagent grade; Riedel-de Haën, Seelze, Germany) were used. Stock salt solutions containing 2000 mg $CN^- l^{-1}$ or 1200 mg $SO_4^{2-} l^{-1}$ were prepared. Sorption experiments were carried out by a batch technique at a temperature of 283 K in 0.01 M $NaNO_3$ in 50-ml polyethylene bottles with 25-ml subsamples of a goethite suspension ($10 g l^{-1}$). Prior to the sorption experiments, six goethite suspensions were adjusted to different pH values ranging from 3.5 to 8.0 using 0.025 M HNO_3 or 0.025 M $NaOH$. It took up to 10 days until the suspension pH was constant. Subsequently, various amounts ranging from 0 to 1 ml (iron-cyanide complexes) and 0 to 2 ml (sulfate) of the stock solutions were added to gain initial concentrations (c_i) ranging from 0 to 0.9 mmol l^{-1} for sulfate and from 0 to 0.5 mmol l^{-1} for iron-cyanide complexes. In the case of the competitive sorption experiments, aliquots of two stock solutions were added, while for the single sorption experiments, aliquots of only one stock solution were used. The samples were shaken horizontally for 24 h at 150 rpm. This time is sufficient to reach an equilibrium for the sorption of both iron-cyanide complexes on goethite (Rennert and Mansfeldt, 2001). As mentioned above, soils on sites of former coke ovens are very acid. Hence, the competitive sorption experiments with varying concentrations of sulfate or iron-cyanide complexes were conducted at pH 3.5.

For the desorption experiments goethite was equilibrated at a suspension pH of 3.5, 5.0, and 7.0 with ferrocyanide or ferricyanide ($c_i = 0.25 mmol l^{-1}$) for 24 h at 283 K. Then a $NaCl$ solution (seven concentrations ranging from 0.04 to 1 M) or a NaH_2PO_4 solution (five concentrations ranging from 0.2 to 1.5 mM) was added. As the NaH_2PO_4 solution is alkaline (pH 8.3), further experiments were conducted using pH-adjusted solutions. The solutions were adjusted to pH 3.5 or 5.0 using 0.01 M HNO_3 , added to the goethite suspensions (six concentrations ranging from 0.24 to 15 mM NaH_2PO_4), and then shaken for an additional 24 h.

After separating the phases by membrane filtration (cellulose nitrate, 0.45 μm filter), sulfate, chloride and phosphate were determined by ion chromatography with a Dionex (Idstein, Germany) DX 500 with a conductivity detector. A micro-distillation technique was used to determine cyanide (Mansfeldt and Biernath, 2000).

Data interpretation

Selectivity coefficients were calculated as described by Hingston et al. (1971). The concentrations of two competing sorbates as surface phases and in solution are expressed by:

$$\frac{S_{[\text{Fe}(\text{CN})_6]}}{S_{\text{SO}_4^{2-}}} = \frac{K_{[\text{Fe}(\text{CN})_6]} \times c([\text{Fe}(\text{CN})_6])}{K_{\text{SO}_4^{2-}} \times c(\text{SO}_4^{2-})} \quad (3)$$

where S_{ligand} is the sorbed amount of a ligand (mmol kg^{-1}), K_{ligand} is the Langmuir constant of a sorbed ligand and $c(\text{ligand})$ the equilibrium concentration of a ligand (mmol l^{-1}). Selectivity coefficients result from combining the Langmuir constants:

$$\frac{S_{[\text{Fe}(\text{CN})_6]}}{S_{\text{SO}_4^{2-}}} = K_{\text{SO}_4^{2-}}^{[\text{Fe}(\text{CN})_6]} \times \frac{c([\text{Fe}(\text{CN})_6])}{c(\text{SO}_4^{2-})}. \quad (4)$$

Hence, the selectivity coefficient concerning the competition between an iron-cyanide complex and sulfate is:

$$K_{\text{SO}_4^{2-}}^{[\text{Fe}(\text{CN})_6]} = \frac{S_{[\text{Fe}(\text{CN})_6]} \times c(\text{SO}_4^{2-})}{S_{\text{SO}_4^{2-}} \times c([\text{Fe}(\text{CN})_6])}. \quad (5)$$

The influence of phosphate on the dissolution of Berlin Blue was investigated using the speciation program ECOSAT 4.7 (Keizer and van Riemsdijk, 1999). In the system we investigated, the following compounds were initially present: NaH_2PO_4 (0.5 to 1.5 mM), goethite (10 g l^{-1}), NaNO_3 (0.01 M), Berlin Blue ($5 \times 10^{-3} \text{ mM}$), and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (0.15 to 0.21 mM). The pH was varied in the range of 3.5 to 10.

RESULTS

Sorption of iron-cyanide complexes on goethite in the presence and absence of sulfate

The sorption of iron-cyanide complexes on goethite in the presence and in the absence of equimolar sulfate concentrations is shown in Figure 1. Furthermore, the amounts of sulfate sorbed in the presence of iron-cyanide complexes are also presented. With the exception of sulfate sorption in the presence of ferrocyanide (Figure 1b), the extent of sorption of each anion decreased with increasing pH due to increasing negative charge of the goethite surface. Sulfate decreased ferrocyanide sorption only at pH 3.5 by 12% (Figure 1b). At other pH values, sorption of ferrocyanide was not influenced by equimolar additions of sulfate. The amount of sulfate sorbed in the presence of ferrocyanide was nearly constant at approximately 2 mmol kg^{-1} over the entire pH range. At all pH values, only 4% to 7% of the sulfate initially added was sorbed. Hence, in an equimolar solution of both anions, ferrocyanide was preferentially sorbed. At pH 3.5 and 4, ferricyanide sorption was reduced up to 54% by sulfate additions (Figure 1a). Over the whole pH range, the average ratio of sorbed ferricyanide to sorbed sulfate, $S ([\text{Fe}(\text{CN})_6]^{3-})$ to $S (\text{SO}_4^{2-})$, was 1.7. This is slightly more than the charge ratio, 1.5. At all pH values used here, ferricyanide is completely deprotonated, since all pK_a for ferricyanic acid values are < 1 (Jordan and Ewing, 1962). Therefore, the charge of ferricyanide was fixed at -3 when calculating the charge ratio. Thus, in equimolar solutions and in the pH range of 3.5 to 8.0 ferricyanide had a slightly greater affinity for the goethite surface than sulfate.

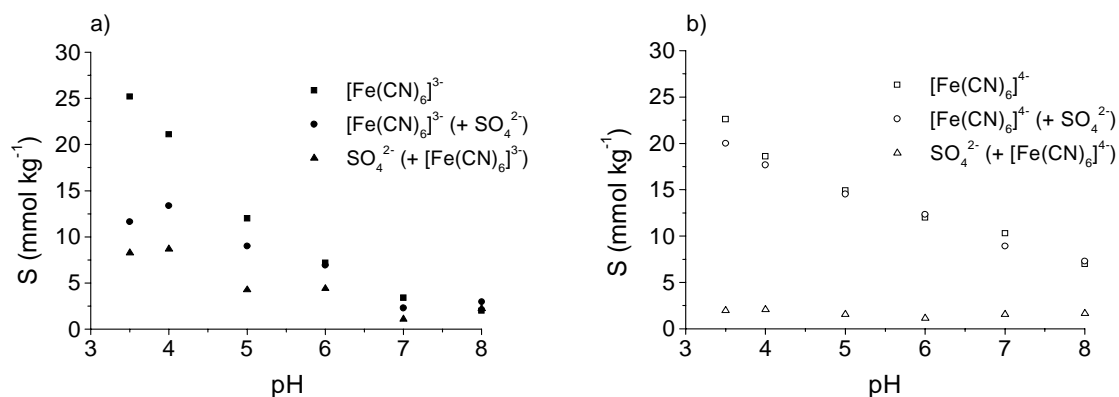


Figure 1 Sorption of iron-cyanide complexes on goethite in the presence and absence of equimolar amounts of sulfate and sorption of sulfate in the presence of iron-cyanide complexes as influenced by pH (a, ferricyanide; b, ferrocyanide). Initial concentration of each anion was 0.3 mmol l^{-1} .

Selectivity coefficients calculated according to Equation (5) are summarized in Table 1.

Table 1 Selectivity coefficients of iron-cyanide complexes and sulfate sorbed on goethite.

$K_{\text{SO}_4^{2-}}^{[\text{Fe}(\text{CN})_6]^\dagger}$		
pH	$[\text{Fe}(\text{CN})_6]^{3-}$	$[\text{Fe}(\text{CN})_6]^{4-}$
3.5	1.5	16.5
4	1.8	15.7
5	2.4	17.0
6	1.6	18.5
7	0.9	8.0
8	4.1	5.4

[†]selectivity coefficient according to Equation (5)

The selectivity coefficients for ferricyanide and sulfate reflect their similar sorption behavior as

mentioned above. In the case of ferrocyanide, the selectivity coefficients decreased with increasing pH, but at any pH ferrocyanide sorption was favored. Hingston et al. (1971) explained variations of selectivity coefficients with pK_a values of the conjugate acids of the anions used. However, for ferrocyanic acid pK_4 is 4.2 and pK_3 is 2.2 (Jordan and Ewing, 1962). Hence, the speciation of ferrocyanide cannot explain selectivity coefficient variations at $pH > 6.0$. Possibly there are other factors influencing the selectivity coefficients, for example, various sorption mechanisms depending on pH.

The sorption of iron-cyanide complexes and sulfate on goethite at pH 3.5 with increasing concentrations of iron-cyanide complexes and constant sulfate concentrations is shown in Figure 2. The variable r is the initial molar concentration ratio of the anions.

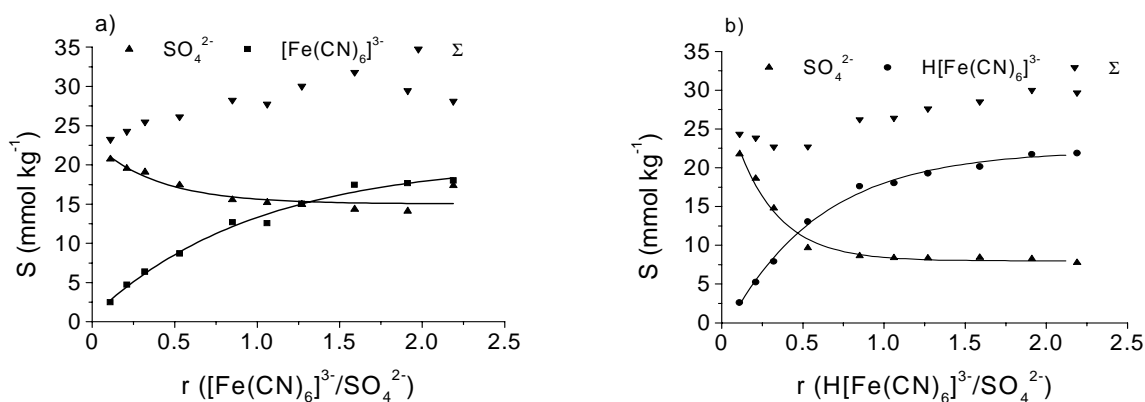


Figure 2 Sorption of iron-cyanide complexes and sulfate on goethite at variable iron-cyanide and constant sulfate concentrations at pH 3.5 (a, ferricyanide; b, ferrocyanide). Experimental conditions: c_i ($[\text{Fe}(\text{CN})_6]$) = 0.025 to 0.48 mmol l^{-1} ; c_i (SO_4^{2-}) = 0.23 mmol l^{-1} ; $I = 0.01 \text{ M}$. Regression equations for sorption data: ferricyanide, $S([\text{Fe}(\text{CN})_6]^{3-}) = 20.5 - 19.8 \exp(-r / 0.99)$; ferrocyanide, $S(\text{H}[\text{Fe}(\text{CN})_6]^{3-}) = 22.2 - 24.1 \exp(-r / 0.57)$; sulfate (presence of ferricyanide), $S(\text{SO}_4^{2-}) = 15 + 7.91 \exp(-r / 0.39)$; sulfate (presence of ferrocyanide), $S(\text{SO}_4^{2-}) = 7.99 + 21.9 \exp(-r / 0.26)$.

The lines represent exponential functions. In the case of ferricyanide (Figure 2a), the point of intersection was at 1.35. This is nearly the charge ratio of the anions and reflects the similar affinity of ferricyanide and sulfate at pH 3.5 over the range of concentration ratios. Ferrocyanide was sorbed

to a greater extent than sulfate for $r > 0.48$ (Figure 2b). These experiments show that ferrocyanide is sorbed preferentially on goethite compared with sulfate.

The sorption of iron-cyanide complexes and sulfate on goethite at pH 3.5 with increasing concentrations of sulfate and constant iron-cyanide complex concentrations is shown in Figure 3.

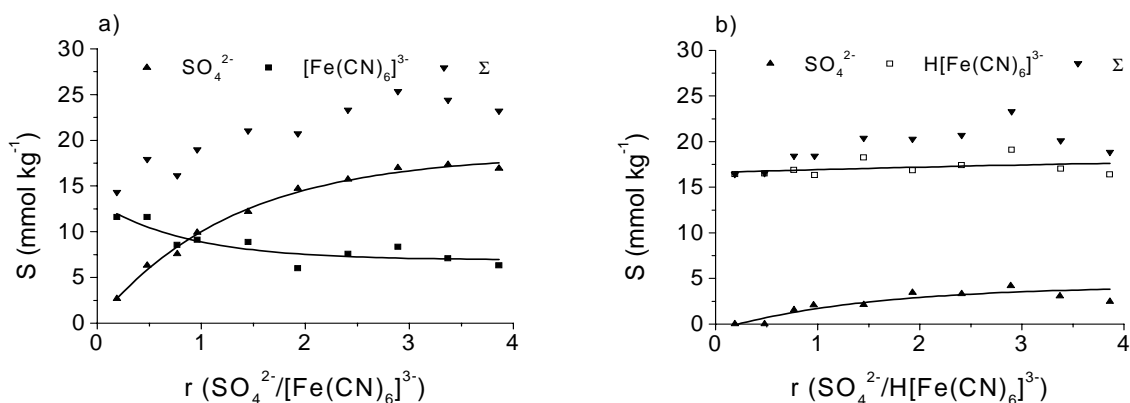


Figure 3 Sorption of iron-cyanide complexes and sulfate on goethite at variable sulfate and constant iron-cyanide concentrations at pH 3.5 (a, ferricyanide; b, ferrocyanide). Experimental conditions: c_i (SO₄²⁻) = 0.05 to 0.9 mmol l⁻¹; c_i ([Fe(CN)₆]) = 0.24 mmol l⁻¹; I = 0.01 M. Regression equations for sorption data: ferricyanide, S ([Fe(CN)₆]³⁻) = 18.5 - 18.3 exp(-r / 1.3); ferrocyanide, S (H[Fe(CN)₆]³⁻) = 17.5 - 1.5 exp(-r / 0.75); sulfate (presence of ferricyanide), S (SO₄²⁻) = 6.9 + 6.32 exp(-r / 0.87); sulfate (presence of ferrocyanide), S (SO₄²⁻) = 3.39 + 4.72 exp(-r / 0.85).

Again, ferricyanide and sulfate showed similar affinities for goethite (Figure 3a), but the point of intersection was at 0.88, which is higher than the charge ratio, 0.67. In contrast, ferrocyanide sorption was not decreased by sulfate, even when it was present in nearly fourfold excess (Figure 3b).

Desorption of iron-cyanide complexes by chloride and phosphate

The effect of chloride additions on the desorption of iron-cyanide complexes is shown in Figure 4. Only ferricyanide was desorbed by chloride. With increasing chloride concentration more ferricyanide was desorbed. Complete desorption was achieved with 0.5 M chloride. As mentioned before, the final chloride concentrations in the filtrate were measured. They were not lower than the

initial ones. Therefore, it can be concluded that chloride was not sorbed on goethite. Thus, ferricyanide desorption was caused by an increase in ionic strength and not by an ion exchange reaction. Rennert and Mansfeldt (2001) showed that ferricyanide sorption on goethite depends on ionic strength adjusted with NaNO_3 . In contrast to ferricyanide, ferrocyanide was not desorbed by chloride significantly even at concentrations up to 1 M chloride. This is consistent with the observation that ferrocyanide sorption on goethite does not depend on ionic strength (Rennert and Mansfeldt, 2001). Again, final chloride concentrations were not lower than the initial ones.

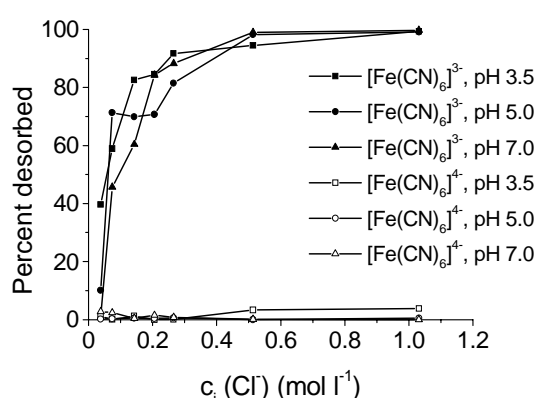


Figure 4 Desorption of iron-cyanide complexes by chloride solutions (0.04 to 1 M NaCl) at three initial pH values.

Additions of unbuffered phosphate solutions resulted in a complete desorption of both iron-cyanide complexes sorbed on goethite (Figure 5). At any initial suspension pH, ferricyanide was desorbed completely with 0.8 mM phosphate. To desorb ferrocyanide completely, 1.2 mM phosphate at pH 3.5 and pH 5.0 and 0.8 mM phosphate at pH 7.0 had to be added. As the phosphate solution is alkaline (pH 8.3), partial desorption of the complexes by unbuffered phosphate was due to raising the pH. Actually, after the desorption experiments, the pH of samples with initial pH 3.5 rose to values between 4.8 and 5.2; the group of samples with initial pH 5 rose to between 6.3 and 6.7; and the group of samples with initial pH 7 rose to between 7.5 and 7.8. Therefore, a distinction between desorption caused by the increase of pH and desorption caused by the exchange of sorbed iron-cyanide complexes with phosphate was not possible. In contrast to the chloride experiments, in any desorption experiment using phosphate, the final phosphate concentrations were smaller than the

initial ones. Hence, phosphate must have been sorbed, and the desorption of iron-cyanide complexes was the result of an exchange reaction of the surface complexes. Furthermore, additions of phosphate solutions to the goethite suspension increased ionic strength, which certainly influenced ferricyanide desorption as well.

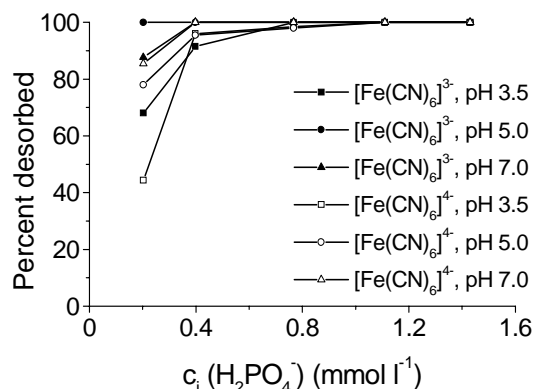


Figure 5 Desorption of iron-cyanide complexes by phosphate solutions (0.2 to 1.5 mM NaH_2PO_4) at three initial pH values.

To exclude pH-induced desorption caused by the use of unbuffered phosphate solutions, pH-adjusted phosphate solutions (pH 3.5 and 5.0) were added to goethite that was equilibrated with ferrocyanide (Figure 6). At pH 5.0, sorbed ferrocyanide was completely desorbed with 1.7 mM phosphate. However, independent of phosphate concentrations, at pH 3.5 a fraction of ferrocyanide was not desorbed (13% of initially sorbed ferrocyanide), although the phosphate concentration was 70 times greater than the initial ferrocyanide concentration. This excess phosphate should have desorbed all the adsorbed ferrocyanide.

The amounts of phosphate sorbed were evaluated with the Langmuir equation (not shown here). At both pH 3.5 and pH 5.0, the sorption maximum was in the range of 93 to 95 mmol kg⁻¹ or, with respect to the specific surface area, 3.1 $\mu\text{mol m}^{-2}$. Theoretically, it is possible that ferrocyanide, which was not desorbed, is bound in the interior of goethite crystals and cannot be desorbed in the time range we used. However, ferrocyanide diffusion into the pores of goethite crystals is unlikely due to the observed lack of time-dependent sorption within 120 h under similar reaction conditions (Rennert

and Mansfeldt, 2001). These authors proposed that ferrocyanide, which is sorbed on goethite at pH 3.5, may form a precipitated Berlin-Blue-like phase on goethite.

Modeling the pH-dependent dissolution of Berlin Blue with phosphate concentrations that were used in the desorption experiments, showed that Berlin Blue was dissolved at $\text{pH} > 7$ only. For lower pH values, the saturation index was 1. The dissolution was not increased by the presence of phosphate in the concentration range of 0.5 to 1.5 mM phosphate. Therefore, if the fraction of sorbed ferrocyanide not being desorbed at pH 3.5 is a Berlin-Blue-like phase, it should not be desorbed by phosphate solutions adjusted to pH 3.5.

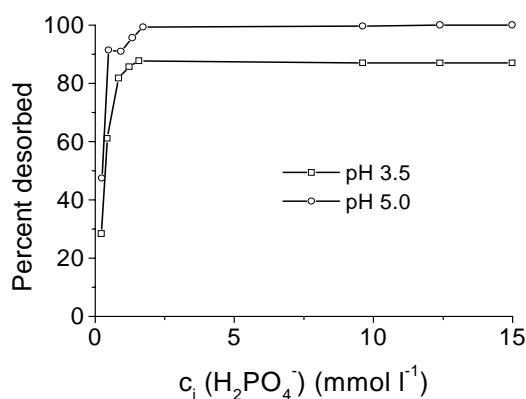


Figure 6 Desorption of ferrocyanide by pH-adjusted phosphate solutions (0.24 to 1.5 mM) at two initial pH values.

DISCUSSION

We showed that the affinities of sulfate and ferricyanide for goethite are very similar, with ferricyanide having a slightly higher affinity. The affinity of ferrocyanide for goethite is higher than that of sulfate. Soil solutions of manufactured gas plant (MGP) site soils contain more sulfate than iron-cyanide complexes (up to $125 \text{ mmol SO}_4^{2-} \text{ kg}^{-1}$ soil; Byers et al., 1994). Therefore, in MGP site soils, sulfate should be sorbed to a greater extent than ferricyanide. Consequently, ferricyanide should be mobile. However, it is not very probable that ferricyanide exists to a great extent in soil

solutions of MGP sites. Even under oxic conditions, ferrocyanide should be the dominant species in these soils due to its kinetic stability (Holleman and Wiberg, 1985). Theis et al. (1994) found ferrocyanide to be the dominant cyanide species in batch experiments with MGP site soils. Hence, high sulfate concentrations should influence cyanide mobility in these soils only to a small extent. Ferrocyanide is potentially more toxic than ferricyanide. It is converted to extremely toxic free cyanide, CN^- , when transported to surface waters and exposed to daylight (Meeussen et al., 1992a). Hence, the presence of ferrocyanide in seepage, ground, and surface water is potentially hazardous because of its photodegradation to free cyanide.

Desorption with chloride and phosphate seems to be an adequate tool to distinguish between ferrocyanide and ferricyanide sorbed on iron oxides, since chloride desorbs ferricyanide only. In subsoils of former coke oven sites a fraction of iron-cyanide complexes exists which has been transported there as Berlin Blue colloids (Mansfeldt et al., 1998). A distinction between colloidal solid phases and adsorbed iron-cyanide complexes in soils seems to be possible using phosphate solutions: alkaline phosphate solutions desorb all ferrocyanide; phosphate solutions adjusted to pH 3.5 desorb adsorbed ferrocyanide and do not dissolve Berlin Blue colloids. However, Berlin Blue colloids, which may be present in the filtrate, are digested by the distillation technique we used. Therefore, the colloids have to be separated from the bulk filtrate by ultracentrifugation.

Ferrocyanide sorption is only slightly decreased by sulfate additions at pH 3.5. Sulfate forms inner-sphere surface complexes on goethite at pH 3.5 (Peak et al., 1999) and can thus compete for surface sorption sites with ferrocyanide. At higher pH values, the outer-sphere component of sulfate sorption increases, hence its ability to lower ferrocyanide sorption decreases. Ferrocyanide cannot be desorbed by chloride. This suggests inner-sphere surface complexation of ferrocyanide. Desorption with phosphate adjusted to pH 3.5 is not complete. When using phosphate as a desorbing agent, the phosphate maximum sorption is $3.1 \mu\text{mol m}^{-2}$ as shown above. This is higher than the phosphate maximum sorption on goethite of $2.51 \mu\text{mol m}^{-2}$ calculated for bidentate linkage (Schwertmann, 1988). However, the specific surface area of goethite in suspensions is probably higher than that of dried goethite on which the BET surface area was measured. Nevertheless, we can conclude from this result that phosphate has occupied all available adsorption sites. This is also shown by the complete desorption of sorbed ferrocyanide at pH 5.0 when using pH-adjusted phosphate solutions. If ferrocyanide is not desorbed completely at pH 3.5, although all adsorption sites are occupied by

phosphate, it is not irreversibly adsorbed on goethite in terms of hysteresis. Hence, ferrocyanide sorbed at pH 3.5 does not only exist as an adsorbed fraction, but may also exist as a precipitated fraction, as a Berlin-Blue-like phase. This has been proposed by Rennert and Mansfeldt (2001). Additions of phosphate solutions adjusted to pH 3.5 do not dissolve a Berlin-Blue-like phase, this was demonstrated by the modeling results. However, this could be expected, because the solubility product constant (K_{sp}) of iron(III)phosphate is 9.9×10^{-29} (Lide, 1995), which is much greater than the K_{sp} of Berlin Blue. The dissolution of Berlin Blue strongly depends on pH with greatest dissolution occurring under alkaline conditions (Mansfeldt et al., 1998). This process is controlled by dissolution kinetics (Meeussen et al., 1992b). The proposed precipitation of a Berlin-Blue-like phase might also explain the decrease of the selectivity coefficients concerning ferrocyanide and sulfate with increasing pH. Due to the pH-dependent dissolution of Berlin Blue, it is very probable that the precipitate only exists in the acidic range. The selectivity coefficients at pH 7.0 and 8.0 may reflect the competitive adsorption of ferrocyanide and sulfate without formation of a Berlin-Blue-like phase. This, in turn, means that variations of the selectivity coefficients are, in addition to dependence on the pK_a values of the conjugate acids (as stated by Hingston et al., 1971), caused by differences in sorption mechanisms, which may be pH-dependent.

Ferricyanide and sulfate compete for the same exchange sites. The extent of sorption can be explained with the value of their charges. Rennert and Mansfeldt (2001) proposed a sorption mechanism for ferricyanide that is similar to the sulfate sorption mechanism. Ferricyanide is desorbed by chloride just as sulfate sorbed as an outer-sphere surface complex would be (Alewell and Matzner, 1996); its sorption on goethite is highly influenced by ionic strength and pH; it is quickly and completely desorbed as the pH is raised (Rennert and Mansfeldt, 2001); and it is not sorbed on goethite when $pH > pzc$, like sulfate (Geelhoed et al., 1997). Hence, we propose that the strength of ferricyanide and sulfate surface complexes on goethite is very similar.

CONCLUSIONS

According to our results, high sulfate concentrations should not diminish the immobilization of potentially hazardous ferrocyanide. Ferrocyanide and sulfate differ in their affinity for goethite. Due to its strong sorption on goethite, ferrocyanide cannot be regarded as a highly mobile anion in soils. Ferricyanide and sulfate sorb similarly on goethite.

Both iron-cyanide complexes adsorbed on goethite were desorbed by phosphate solutions adjusted to $\text{pH} \geq 5$. Since acid to neutral phosphate solutions do not dissolve Berlin-Blue-like precipitates, they could be used to separate adsorbed from precipitated fractions of ferrocyanide. This could be used as a tool to investigate the different forms of iron-cyanide complexes in contaminated soils.

The results of competitive sorption of ferrocyanide and sulfate and of desorption using chloride and phosphate solutions suggest strong sorption, which may be explained by inner-sphere surface complexation of ferrocyanide and partial precipitation as a Berlin-Blue-like phase at low pH. The results for both ferricyanide sorption and desorption indicate that its sorption is very similar to sulfate sorption. This may be attributed to similar sorption mechanisms. However, since these conclusions are inferred from macroscopic observations, spectroscopic investigations on the nature of iron-cyanide surface complexes formed on goethite are necessary.

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CHAPTER 4

Simple modelling of the sorption of iron-cyanide complexes on
ferrihydrite

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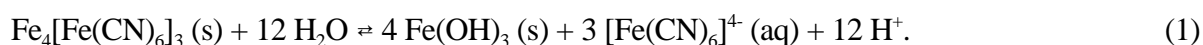
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ABSTRACT

The sorption of the iron-cyanide complexes ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, on ferrihydrite was investigated in batch experiments including the effects of pH (pH 3.5 to 8) and ionic strength (0.001 to 0.1 M). The pH-dependent sorption data were evaluated with a model approach by Barrow (1999): $c = a \exp(bS)/(S_{\text{max}} - S)$, where c is the solution concentration; S is the sorbed amount; S_{max} is maximum sorption; b is a parameter; and a is a parameter at constant pH. Ferricyanide sorption was negatively affected by increasing ionic strength, ferrocyanide sorption not at all. More ferricyanide than ferrocyanide was sorbed in the acidic range. In the neutral range the opposite was true. Fitting the pH-dependent sorption to the model resulted in a strong correlation for both iron-cyanide complexes with a common sorption maximum of $1.6 \mu\text{mol m}^{-2}$. Only little negative charge was conveyed to the ferrihydrite surface by sorption of iron-cyanide complexes. The sorption of iron-cyanide complexes on ferrihydrite is weaker than that on goethite, as a comparison of the model calculations shows. This may be caused by the lower relative amount of high-affinity sites present on the ferrihydrite surface.

INTRODUCTION

The knowledge of sorption processes occurring on surfaces of solid matrices is one of the keys towards the understanding of the migration and the fate of many chemicals in soils and aquifers. The iron-cyanide complexes ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, are not present in uncontaminated soils (Fuller, 1985). Their occurrence in the soil environment is connected with the deposition of industrial refuse such as purifier waste originating from coal gasification (Shifrin et al., 1996), blast furnace sludge originating from pig iron production (Mansfeldt and Dohrmann, 2001), or paper de-inking sludge (Mansfeldt, 2001). An additional input is given by the use of road salt, because it contains sodium ferrocyanide or Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (Ohno, 1990). The most important source of iron-cyanide complexes in soils is given by the disposal of purifier wastes on sites of former manufactured gas plants and coke ovens. These sites are present in many industrialized countries (Mansfeldt, 2000). The complexes are potentially hazardous, because they can be degraded to extremely toxic free cyanides which comprise CN^-_{aq} and $\text{HCN}_{\text{g,aq}}$. Especially ferrocyanide is decomposed to free cyanide after having been irradiated by sunlight (Meeussen et al., 1992). The behaviour of iron-cyanide complexes in soils on sites of former manufactured gas plants and coke ovens is governed by sorption and hydrolysis of Berlin Blue (Meeussen, 1992)



The speciation of iron-cyanide complexes is influenced by the redox reaction



Due to the Equations (1) and (2), ferri- and ferrocyanide can be released into the soil solution after dissolution of Berlin Blue. They sorb on phases such as goethite (Theis et al., 1988; Rennert and Mansfeldt, 2001), aluminium oxide (Cheng and Huang, 1996) and soils (Fuller, 1985; Ohno, 1990; Rennert and Mansfeldt, 2002a). The mechanism by which they are sorbed depends on both the type of the complex and of the sorbent. Ferricyanide as well as ferrocyanide were supposed to form outer-sphere surface complexes on aluminium oxide as judged from surface complexation modelling (Triple-layer model; Cheng and Huang, 1996). As ferricyanide sorption on goethite was completely and quickly reversible in kinetic batch experiments, Theis et al. (1988) proposed outer-sphere surface complexation. However, Rennert and Mansfeldt (2001, 2002b) found a sulphate-like sorption

behaviour of ferricyanide on goethite including the formation of inner-sphere surface complexes in the acidic range and of outer-sphere surface complexes in the neutral and alkaline range. They proposed a different mechanism for the sorption of ferrocyanide on goethite with inner-sphere surface complexation and precipitation of a Berlin-Blue-like phase (Rennert and Mansfeldt, 2001). Furthermore, soil organic matter may promote the sorption of both complexes in soils, as shown by Rennert and Mansfeldt (2002a). As pointed out, the sorption mechanisms of the complexes on different soil phases are still in discussion. We use the general term sorption for any retention mechanism including two-dimensional adsorption and three-dimensional processes such as precipitation or diffusion of a sorbate into a crystal.

Ferrihydrite is a poorly ordered iron oxide hydroxide for which no general formula has been generally established (Cornell and Schwertmann, 1996). It may be represented by $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$ ($n = 1$ to 3). Ferrihydrite is present in soils which are young or in which the transformation to more stable iron oxides is inhibited (Cornell and Schwertmann, 1996). Hydrous ferric oxides such as ferrihydrite have been widely used as model sorbents to examine the sorption of anions on iron oxides. A summary of these results is given by Dzombak and Morel (1990).

The objective of this study was to examine the sorption of iron-cyanide complexes on ferrihydrite as influenced by pH and ionic strength. Modelling the data using an approach by Barrow (1999) should give an insight into the surface complexes of iron-cyanide complexes formed on ferrihydrite. These results were then used for comparison to the sorption of iron-cyanide complexes on goethite.

MATERIAL AND METHODS

Preparation and properties of ferrihydrite

2-line ferrihydrite was prepared according to Schwertmann and Cornell (1991) by precipitation from alkaline solution. Briefly, about 330 ml 1 M KOH were added to 500 ml 0.1 M $\text{Fe}(\text{NO}_3)_3$ to bring the pH between 7 and 8. Ferrihydrite precipitated immediately. The product was cleaned by pressure filtration and freeze dried subsequently. The specific surface area (BET) was $215 \text{ m}^2 \text{ g}^{-1}$. 2-line ferrihydrite is not transformed to a more ordered form with time (Cornell and Schwertmann, 1996).

Sorption experiments

A batch technique was used to investigate the sorption of iron-cyanide complexes on ferrihydrite. The sorptive was ferricyanide or ferrocyanide in the form of $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ (reagent grade, Riedel-de Haën, Seelze, Germany). Stock solutions were prepared which contained 2000 mg $CN^- l^{-1}$. The experiments were carried out in 50-ml polyethylene bottles with 25-ml subsamples of a ferrihydrite suspension ($10 g l^{-1}$). Ionic strength I of the suspensions was adjusted to 0.01 M ($NaNO_3$). Prior to cyanide addition, the pH of the suspensions was adjusted to 3.5, 4.0, 5.0, 6.0, 7.0, and 8.0 using 0.025 M NaOH or 0.025 M HNO_3 . It took up to 14 days until the pH was constant. Twelve or 14 different subsamples of a stock solution ranging from 0 to 1 ml were added to the suspensions to obtain initial iron-cyanide complex concentrations ranging from 0 to 0.95 mmol l^{-1} . After the addition, the suspension pH was readjusted. The samples were shaken horizontally at 150 oscillations per minute for 24 h at 283 K in the dark as found to be sufficient to reach an equilibrium between iron-cyanide complexes and goethite (Theis et al., 1988; Rennert and Mansfeldt, 2001) and soils (Ohno, 1990). Furthermore, the effect of varying ionic strength on iron-cyanide complex sorption was investigated at pH 4.3 with an initial iron-cyanide concentration of 0.49 mmol l^{-1} and an ionic strength of 0.001, 0.01, 0.05, and 0.1 M adjusted with 1 M $NaNO_3$. Again, the samples were shaken for 24 h.

After equilibration, ferrihydrite was separated by membrane filtration (0.45 μm cellulose nitrate filter). The filtrate was digested and distilled using a micro-distillation technique (MicroDistiller, Eppendorf-Netheler-Hinz, Hamburg, Germany) in duplicate. Cyanide concentrations were subsequently determined colorimetrically at 600 nm (Lambda 2 Spectrophotometer, Perkin Elmer, Überlingen, Germany) according to the method of cyanide determination by Mansfeldt and Biernath (2000). As iron-cyanide complexes were the only cyanide species present in the filtrates, cyanide concentrations were recalculated to iron-cyanide complex concentrations.

Data analysis

According to Barrow (1999), the relationship between solution concentration c and sorbed amount S of an anion is given by

$$c = a \exp(bS) S / (S_{\max} - S), \text{ and} \quad (3)$$

$$S = V_s (c_0 - c), \text{ where} \quad (4)$$

$$a = 1 / \{K_i \alpha \exp(-z_i F \psi_0 / RT)\}, \text{ and} \quad (5)$$

$$b = -z_i F m / RT, \quad (6)$$

where S_{\max} is the maximum sorption, V_s is the ratio of volume of solution to mass of ferrihydrite, c_0 is the initial concentration, K_i is a constant, α is the proportion of the anion i present in solution with valency z_i , T is the temperature (K), F is the Faraday constant, and R is the gas constant. The electric potential in the absence of anion sorption is ψ_0 , and m is a parameter. As shown by Posner and Barrow (1982) for the model of Bowden et al. (1980), the adsorbed anions experience a mean electric potential ψ_a which decreases roughly linearly with increasing sorption

$$\psi_a = \psi_0 - mS. \quad (7)$$

The dissociation constants of ferrocyanic acid to calculate α are $pK_4 = 4.2$ and $pK_3 = 2.2$ (Jordan and Ewing, 1962). The dissociation constants of ferricyanic acid are less than 1, and so are pK_1 and pK_2 of ferrocyanic acid. Therefore, α is set to 1 for ferricyanide sorption.

The Equations (3) and (4) can be regarded as simultaneous and solved using a computer routine (Barrow, 1999). Predicted values of S and c are given for particular values of c_0 and of the parameters. A simplex routine is then used to select values of the parameters that minimised a specified sum of squares.

This model is relatively simple, but it describes the maximum sorption, and the change in electric potential as a result of sorption and due to induced change in pH. It has been used to describe the sorption of phosphate, citrate (Barrow, 1999), and iron-cyanide complexes (Rennert and Mansfeldt, 2001) on goethite.

RESULTS

Effect of ionic strength

The sorption of iron-cyanide complexes on ferrihydrite at pH 4.3 depending on ionic strength I is shown in Figure 1. At this pH, the ferrihydrite surface is positively charged. Therefore, a decrease of I should enhance anion sorption. The sorption of ferrocyanide was not affected by I , whereas the sorption of ferricyanide decreased linearly as $\log I$ increased. Within the I range tested, the amounts

of ferrocyanide sorbed were larger than that of ferricyanide. This effect of ionic strength is similar to that of the sorption of iron-cyanide complexes on goethite: ferricyanide sorption is affected by varying ionic strength; ferrocyanide sorption not at all (Rennert and Mansfeldt, 2001). However, the decrease of S with increasing I is larger with ferrihydrite (slope -4.3) than with goethite (slope -3.5).

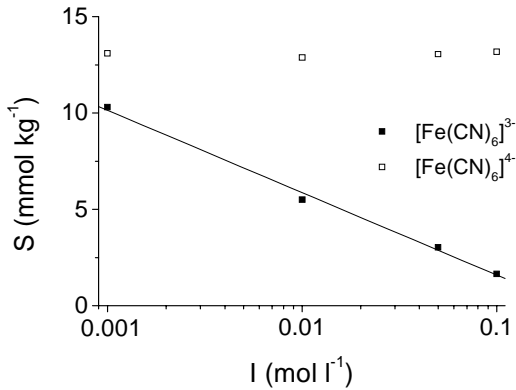


Figure 1 Influence of ionic strength (I) on the amounts (S) of iron-cyanide complexes sorbed on ferrihydrite at pH 4.3. $S([\text{Fe}(\text{CN})_6]^{3-}) = -2.68 - 4.28 \log I$, $r^2 = 0.99$.

Effect of pH

The effect of pH on the sorption of iron-cyanide complexes on ferrihydrite is shown in Figure 2.

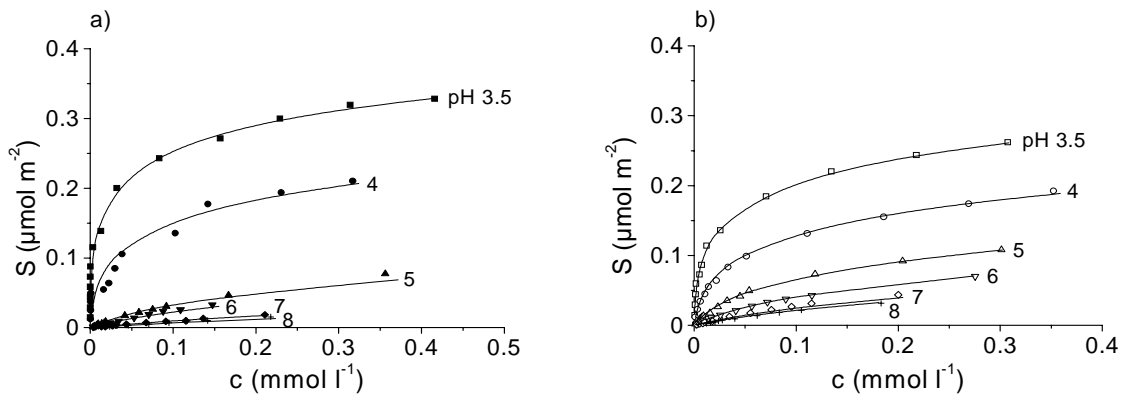


Figure 2 Sorption of iron-cyanide complexes on ferrihydrite as influenced by pH (a, ferricyanide; b, ferrocyanide). Isotherms result from fitting the data to Equation (3) with individual values of a for each pH. Ferricyanide: $b = 15.3 \mu\text{mol}^{-1} \text{m}^2$; $S_{\max} = 1.6$

$\mu\text{mol m}^{-2}$; $r^2 = 0.998$. Ferrocyanide: $b = 14.9 \mu\text{mol}^{-1} \text{m}^2$; $S_{\text{max}} = 1.6 \mu\text{mol m}^{-2}$; $r^2 = 0.999$.

Sorption isotherms were well described by Equation (3) ($r^2 = 0.998$ for ferricyanide, $r^2 = 0.999$ for ferrocyanide). The effect of pH on the sorption of both complexes was similar, because sorption decreased with increasing pH. However, it differed in that ferricyanide sorption was slightly larger at low pH than was ferrocyanide sorption. Ferrocyanide sorption was slightly larger than ferricyanide sorption in the neutral pH range. The isotherms in Figure 2 result from fitting the sorption data to Equation (3) with individual fitted values of a , common fitted values of b , and S_{max} fixed at $1.6 \mu\text{mol m}^{-2}$. The sorption of both complexes was closely described by Equation (3). In further calculations, S_{max} were used as an additional fit parameter. The results were $S_{\text{max}} = 1.55 \mu\text{mol m}^{-2}$ for ferricyanide and $S_{\text{max}} = 1.51 \mu\text{mol m}^{-2}$ for ferrocyanide. However, r^2 slightly decreased to 0.997, and the residual sum of squares slightly increased (e.g. from 1.4×10^{-3} to 1.6×10^{-3} for ferricyanide sorption) in these runs compared to those with S_{max} fixed at $1.6 \mu\text{mol m}^{-2}$. As the differences in both r^2 and the residual sum of squares are negligible, the fitted values of S_{max} and of the fixed $S_{\text{max}} = 1.6 \mu\text{mol m}^{-2}$ can be accepted as values with a reasonable goodness-of-fit. Similarly, the sorption maximum of both complexes sorbed on goethite has been found to be $1.6 \mu\text{mol m}^{-2}$ (Rennert and Mansfeldt, 2001). It is obvious that maximum sorption would be observed only at $\text{pH} < 3.5$ and at concentrations higher than those used here.

The effect of pH on the sorption of iron-cyanide complexes on ferrihydrite are reflected in the a coefficient. The change of a with pH is shown in Figure 3. The sorption of ferricyanide is affected by pH to a larger extent than that of ferrocyanide, as the decline of the a coefficient is slightly steeper.

Rearranging Equation (5) shows that the a coefficient is proportional to an overall affinity term

$$\ln a = -\ln(K_i \alpha) - z_i F \psi_0 / RT. \quad (8)$$

The values of z_i are allocated to -3 (ferricyanide) and -4 (ferrocyanide), respectively. The extent of dissociation α varies with pH. However, α is 1 in the case of ferricyanide, since all dissociation constants of ferricyanic acid are < 1 . The dissociation constants of ferrocyanic acid which are relevant for the pH range we used are $\text{p}K_4 = 4.2$ and $\text{p}K_3 = 2.2$. As α is close to unity for $\text{pH} > 5$, there will be little or no effect of α on the affinity term with increasing pH (Equation (8)). Therefore, at $\text{pH} > 5$, the lines in Figure 3 are nearly parallel. However, the effect will increase with decreasing pH. The

other property varying with pH is the electric potential ψ_0 whose effect depends on the valency of an anion, z_i . Other things being equal, the greater is z_i , the greater is the effect of a change in potential with pH. This is shown by the decrease of a with decreasing pH for ferrocyanide sorption. This effect has also been found by Barrow (1999) for the sorption of citrate and phosphate on goethite.

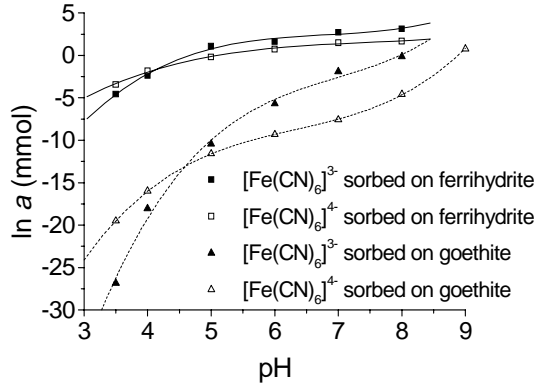


Figure 3 Relationship between pH and parameter a for the sorption of iron-cyanide complexes on ferrihydrite and on goethite. Ferrihydrite: ferricyanide, $\ln a = -50.4 + 22.5 \text{ pH} - 3.25 \text{ pH}^2 + 0.16 \text{ pH}^3$, $r^2 = 0.993$; ferrocyanide, $\ln a = -25.0 + 10.0 \text{ pH} - 1.31 \text{ pH}^2 + 0.06 \text{ pH}^3$, $r^2 = 0.997$. Goethite (adapted from Rennert and Mansfeldt, 2001): ferricyanide, $\ln a = -125 + 45.4 \text{ pH} - 5.79 \text{ pH}^2 + 0.259 \text{ pH}^3$, $r^2 = 0.99$; ferrocyanide, $\ln a = -87.6 + 34.1 \text{ pH} - 5.13 \text{ pH}^2 + 0.271 \text{ pH}^3$, $r^2 = 0.99$.

As indicated in Equation (6) and (7), the change of ψ_0 with increasing sorption is reflected by the b coefficient of Equation (3). The fitted values for b were $15.3 \mu\text{mol}^{-1} \text{ m}^2$ for ferricyanide and $14.9 \mu\text{mol}^{-1} \text{ m}^2$ for ferrocyanide. Therefore, the values of m were $5.1 \text{ mV } \mu\text{mol}^{-1} \text{ m}^2$ for ferricyanide and $3.7 \text{ mV } \mu\text{mol}^{-1} \text{ m}^2$ for ferrocyanide. These values indicate that the change in ψ_0 induced by the sorption of iron-cyanide complexes is low, and that the values for each complex do not differ greatly. Therefore, both the b values and the change in a with pH reflect a low change in electric potential caused by the sorption of iron-cyanide complexes on ferrihydrite.

DISCUSSION

The change of the a coefficient with pH for the sorption of iron-cyanide complexes on goethite and ferrihydrite under identical experimental conditions is given in Figure 3. It is very important that the concentration and the identity of the background electrolyte in experiments that should be compared are the same, as the background electrolyte influences the change of ψ_0 with pH (Barrow, 1999). As the change of a for the sorption on goethite is higher, the negative charge conveyed to the surface of ferrihydrite by sorption is lower than that conveyed on goethite. This suggests that the sorption of iron-cyanide complexes on ferrihydrite is weaker than that on goethite. It is confirmed by a comparison of the b values for the sorption on the iron oxides. The b value for ferricyanide sorption on goethite is $43 \mu\text{mol}^{-1} \text{m}^2$ and is $25.3 \mu\text{mol}^{-1} \text{m}^2$ for ferrocyanide sorption (Rennert and Mansfeldt, 2001). However, the sorption maximum of the complexes on both ferrihydrite and goethite equals $1.6 \mu\text{mol m}^{-2}$.

We showed that the decrease of the amount of ferricyanide sorbed on ferrihydrite with increasing I is larger than the decrease of the amount of ferricyanide sorbed on goethite. This additionally indicates weaker sorption of ferricyanide on ferrihydrite than on goethite.

Surface hydroxyl groups of iron oxides differ in their affinity for sorption of ions: singly-coordinated surface hydroxyl groups of goethite are involved in ligand exchange; doubly- and triply-coordinated groups form hydrogen bonds with adsorbing ligands (Parfitt, 1978; Cornell and Schwertmann, 1996). About 70% of the total hydroxyl groups (calculated over all faces) of goethite is singly-coordinated (Barron and Torrent, 1995). Sorption sites on ferrihydrite are divided in high-affinity sites (type 1) and total reactive sites (type 2) for sorption (Dzombak and Morel, 1990). These authors list a large number of results of different investigations on the site densities of the two types. From these results, the ratio of type 1 sites to type 2 sites is approximately 1:40. Therefore, the relative amount of high-affinity sites on ferrihydrite is lower than that on goethite. This could be the reason for the observed weaker sorption of iron-cyanide complexes on ferrihydrite compared to the sorption of iron-cyanide complexes on goethite. The absolute number of surface sites present on the iron oxides could not be determined, as we did not know their density per nm^2 . Values presented in the literature differ largely (Cornell and Schwertmann, 1996).

We found that slightly varying values of S_{\max} for the sorption of iron-cyanide complexes on ferrihydrite resulted in fits with large values of r^2 . This may be caused by the use of a simplex routine.

CONCLUSIONS

The sorption of the iron-cyanide complexes ferricyanide and ferrocyanide on ferrihydrite was closely described using a simple modelling approach. The sorption maximum $1.6 \mu\text{mol m}^{-2}$ may be a common value for both iron-cyanide complexes sorbed on iron oxides, since it has been found for the sorption on ferrihydrite (this study) and goethite (Rennert and Mansfeldt, 2001). As inferred from a comparison of the change in surface electric potential, sorption on ferrihydrite is weaker than on goethite, which could be explained by a lower density of high-affinity sorption sites on the ferrihydrite surface. However, since all the results presented here are inferred from macroscopic observations and simple modelling, spectroscopic investigations should be performed additionally to enlighten the nature of iron-cyanide surface complexes formed on ferrihydrite in terms of sorption mechanisms (inner-sphere versus outer-sphere surface complexes).

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CHAPTER 5

Sorption of iron-cyanide complexes in soils

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Soil Science Society of America Journal (2002) 66, 437-444

ABSTRACT

The iron-cyanide complexes ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, are of an anthropogenic source in soils. As the complexes are largely charged, sorption on the soil matrix is a possible retention mechanism for these anions. To evaluate soil properties controlling iron-cyanide complex sorption, experiments were performed with 17 uncontaminated soil horizons by a batch technique. Soil organic matter (SOM) was destroyed in six horizons. The experiments were conducted at soil pH, reaction time of 24 h, and an ionic strength of 0.01 (NaNO_3). The affinity of the iron-cyanide complexes for the soil matrix differed, because 14 samples sorbed higher amounts of ferrocyanide than of ferricyanide. Calculated sorption maxima were quantitatively explained by physical and chemical soil properties using multiple regressions. The regression equations were checked by variance analysis. The regression equations for all samples showed that the sorption of both complexes depended on organic carbon (C_{org}), clay, and oxalate-extractable iron (Fe_o). The sorption of the complexes on soils containing $< 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ was governed by pH and clay contents. Clay and oxalate-extractable aluminum (Al_o) were the most important properties influencing ferricyanide sorption on samples containing high amounts of organic carbon. On the same samples, ferrocyanide sorption was governed by oxalate-extractable aluminum. Organic matter promotes the sorption of both complexes, especially on Fluvisol samples. Destruction of soil organic matter of these samples minimized the sorption by up to 99%. Therefore organic matter in these soils may have a special affinity for iron-cyanide complexes possibly due to the reaction between iron-cyanide-N and reactive groups of soil organic matter.

INTRODUCTION

Cyanide in the form of the iron-cyanide complexes ferricyanide and ferrocyanide are not present in natural soils (Fuller, 1985). Industrial activities of mankind have led to inputs of these compounds in the soil environment. Soils on sites of former manufactured gas plants (MGP) and coke ovens are commonly contaminated with cyanide (Shifrin et al., 1996), in which cyanide is present as the ferric ferrocyanide Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (Mansfeldt et al., 1998). On these sites, dissolved iron-cyanide complexes are found in the soil solution and partially in the ground water (Meeussen et al., 1994). Berlin Blue and sodium ferrocyanide are added to road salt as anticaking agents (Paschka et al., 1999). Hence, road salt is a potential source of iron-cyanide complexes in soils. Furthermore, iron-cyanide complexes are present in soils developed from blast furnace sludge deposits (Mansfeldt and Dohrmann, 2001). Both Fe(III) and Fe(II) form very stable complexes with cyanide and both iron-cyanide complexes are nearly kinetically inert (Sharpe, 1976). However, the iron-cyanide complexes are potentially hazardous, because they are converted to extremely toxic free cyanide, CN^- and $\text{HCN}_{\text{g,aq}}$, when transported to surface water and exposed to sunlight (Meeussen et al., 1992). All dissociation constants of ferricyanic acid are < 1 and so are pK_1 and pK_2 of ferrocyanic acid. The dissociation constants pK_3 and pK_4 of ferrocyanic acid are 2.2 and 4.2 (Jordan and Ewing, 1962), respectively.

The mobility of dissolved iron-cyanide complexes in soils on sites of former MGPs and coke ovens is controlled by precipitation and dissolution of Berlin Blue and adsorption on soil minerals, if the concentrations are too small for precipitation (Meeussen, 1992). Adsorption is a possible retention mechanism for iron-cyanide complexes in uncontaminated soils as well, because the complexes have largely negative charges. Generally, anion sorption in soils depends on the contents of soil constituents bearing positive charges with the exception of anions which can form inner-sphere surface complexes on negatively charged surfaces. Apart from ionic strength, the variable charge is a function of the soil reaction. Thus, acid soils should sorb anions to a larger extent than neutral and alkaline soils. Possible sorbents in soils are aluminum and iron (hydr)oxides and clay minerals (Scheffer and Schachtschabel, 1998). Depending on pH, the overall charge of soil organic matter (SOM) is either neutral or negative. Therefore, SOM may decrease anion sorption (Yu, 1997).

Iron-cyanide complexes are sorbed by various mechanisms on inorganic soil constituents. Ferricyanide was mobile in soils, the factors influencing its sorption were pH and the contents of iron oxides and clay minerals (Fuller, 1985). Decreasing soil pH increased ferrocyanide sorption by soils (Ohno, 1990). Neither ferricyanide nor ferrocyanide were retarded by sandy aquifer material as judged from column experiments (Ghosh et al., 1999). Similar to sulfate, ferricyanide was predicted to form outer-sphere and weak inner-sphere surface complexes on goethite, α -FeOOH, whereas ferrocyanide was sorbed inner-spherically and by precipitation of a Berlin-Blue-like phase (Rennert and Mansfeldt, 2001). Outer-sphere surface complexation of ferricyanide on goethite was reported by Theis et al. (1988). Both anions formed outer-sphere surface complexes on γ -Al₂O₃ (Cheng and Huang, 1996). They were interlayered in clay minerals such as hydrotalcite (Hansen and Koch, 1994), and ferricyanide was not adsorbed on negatively charged kaolinite (Stein and Fitch, 1996). The objective of this paper was to investigate the sorption behavior of iron-cyanide complexes in uncontaminated soils by batch experiments. Physical and chemical properties of the soil samples were used to explain the extent of sorption by multiple regressions. Therefore, the statistical evaluation should yield soil properties which are important for the sorption of iron-cyanide complexes in soils. The term sorption used here includes both two-dimensional adsorption and three-dimensional processes such as diffusion into the interior of minerals and surface precipitation (Scheidegger and Sparks, 1996).

MATERIALS AND METHODS

Characterization of soil samples

Seventeen soil horizons were investigated. According to the World Reference Base for Soil Resources (Deckers et al., 1998), the soils were classified as Gleysols, Fluvisols (developed from recent fluvial and marine sediments), Podzols, Cambisols, Ferralsols, and Phaeozems. The samples were collected in excavated pits, freeze dried and sieved to 2 mm. Particle size distribution was analyzed according to Schlichting et al. (1995) by sieving and sedimentation. Contents of dithionite-citrate-extractable iron, Fe_d, and oxalate-extractable iron, Fe_o, were determined following

Mehra and Jackson (1960) and Schwertmann (1964). Contents of amorphous aluminum (hydr)oxide, Al_o , were determined by oxalate-extraction after Schlichting et al. (1995). The extracts were analyzed for Fe and Al by atomic absorption spectroscopy (PE 3100, Perkin Elmer, Überlingen, Germany). Organic carbon, C_{org} , was calculated from the difference between total and inorganic carbon. Total carbon was determined by dry combustion at 1473 K (Coulomat, Deltronik, Düsseldorf, Germany) and subsequent coulometric detection of CO_2 which was absorbed in alkaline solution. Inorganic carbon was determined with the same equipment by adding 15% (vol./vol.) $HClO_4$ to the preheated sample (333 K). Soil pH was measured potentiometrically with a WTW pH 90 (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) and a INLAB 406 electrode (Ingold, Steinbach, Germany) in 0.01 M $CaCl_2$ with a soil:solution ratio of 1:2.5. Soil organic matter was destroyed in 6 samples by treating them with 30% (vol./vol.) H_2O_2 at 333 K for at least 21 d. These samples were also used in sorption experiments. Altogether the sorption of iron-cyanide complexes by 23 samples was investigated.

Sorption experiments

For the sorption experiments $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (reagent grade, Riedel-de Haën, Seelze, Germany) were used. From these salts, stock solutions containing 2000 mg $CN^- l^{-1}$ were prepared. All sorption experiments were carried out by a batch technique in 50-ml polyethylene bottles at a temperature of 283 K in duplicate. About 1.25 g soil was suspended in 25 ml H_2O , and ionic strength was adjusted to 0.01 using 0.1 M $NaNO_3$. Then an aliquot ranging from 0 to 12.5 ml of an iron-cyanide complex solution was added to gain initial concentrations ranging from 0 to 37.4 mmol $[Fe(CN)_6] l^{-1}$. The range of concentrations differed between the samples. The highest concentrations were used with the Fluvisol samples. All experiments were conducted at soil pH. The samples were shaken horizontally for 24 h in darkness at 150 oscillations per minute. This reaction time is sufficient for both complexes to equilibrate on goethite (Theis et al., 1988; Rennert and Mansfeldt, 2001), on aluminum oxide (Cheng and Huang, 1996), and on soils (Ohno, 1990). After the experiments, the phases were separated by membrane filtration (cellulose nitrate, 0.45 μm filter). The filtrates were digested and distilled with a micro-distiller (Eppendorf-Netheler-Hinz, Hamburg, Germany) and cyanide concentrations were subsequently determined spectrophotometrically at 600 nm using a Lambda 2 spectrophotometer (Perkin Elmer, Überlingen, Germany). The whole

procedure is described in detail by Mansfeldt and Biernath (2000). As iron-cyanide complexes were the only cyanide species present in the filtrates, cyanide concentrations were recalculated to iron-cyanide complex concentrations. From each set of experiments, we took three random samples which were analyzed for free cyanide. Free cyanide was never found. All samples were stored in darkness.

Sorption isotherms

The sorption experiments were interpreted using the Langmuir-Freundlich isotherm (Sips, 1948; cited after Kümmel and Worch, 1990)

$$S = \frac{S_{\max} bc^n}{1+bc^n}, \quad (1)$$

where S is the sorbed amount ($\text{mmol} [\text{Fe}(\text{CN})_6] \text{ kg}^{-1}$); S_{\max} the maximum sorption ($\text{mmol} [\text{Fe}(\text{CN})_6] \text{ kg}^{-1}$); b and n are constants; and c is the final solution concentration ($\text{mmol} [\text{Fe}(\text{CN})_6] \text{ l}^{-1}$). We use the sorption maximum as a measure of affinity, using the parameter b as such a measure may lead to misapplications (Harter and Baker, 1977).

Statistical evaluation

All statistical calculations were performed with SPSS 9.0 (SPSS Inc., Chicago, IL). Soil properties were correlated linearly with each other and with the sorption maxima calculated following Equation (1). Multiple linear regressions were conducted with S_{\max} as dependent variable and soil properties as independent variables. In a first step, both logarithmic and original values of the variables were used. The contents of clay and C_{org} were logarithmized after being recalculated to grams per kilograms. The significance of the regression equations was checked by variance analysis (F-test). The significance and the importance as explanatory variables of the parameters were checked using T-tests. Theoretical values for F and T , which are necessary to decide whether an equation or a variable can be accepted or has to be refused at a given confidence level, were adapted from Backhaus et al. (1996). The confidence level used for variance analysis was at least 0.975. The confidence level for the T-tests varied between 0.5 and 0.999, as described below. Regression equations were recalculated without those variables which were not significant or important or both

as explanatory variables because of the results of the T-tests. Multiple regressions were performed with all soil samples ($n = 17$), with the samples containing $> 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ ($n = 8$), and with the samples containing $< 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ ($n = 9$). The six samples treated with H_2O_2 are artificial substrates and therefore not included in the statistical evaluation.

RESULTS

Chemical and physical properties of the soils are presented in Table 1. The soils were acid to neutral with pH values ranging from 3.1 to 7.0. Clay contents varied between 21 g kg^{-1} and 638 g kg^{-1} . Most of the samples contained $< 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$, the overall range was 1 g kg^{-1} to 25 g kg^{-1} . The samples contained between 1 g kg^{-1} and $49 \text{ g pedogenic iron (Fe}_d\text{) kg}^{-1}$. The contents of oxalate-extractable aluminum varied between 0.1 g kg^{-1} and 2.5 g kg^{-1} . Inorganic carbon was present in one sample only (#14), it contained $3 \text{ g inorganic C kg}^{-1}$.

Table 1 Chemical and physical properties of the soil horizons.

Sample	Soil type	Horizon	Clay	C _{org} [†]	Al _o [‡]	Fe _d [§]	Fe _o [¶]	pH
----- (g kg ⁻¹) -----								
#01	Argic Cambisol	C	156	1	0.7	7.2	1.6	5.2
#02	Haplic Podzol	E	21	9	0.1	1.0	0.2	3.1
#03	Haplic Podzol	Bsh	26	3	1.6	14.1	1.2	3.9
#04	Stagnic Gleysol	stagnic 2Bg	298	2	0.6	14.1	1.9	4.8
#05	Dystric Cambisol	Bw	211	1	0.7	41.3	0.7	3.4
#06	Haplic Gleysol	gleyic Bg	39	10	2.5	2.1	2.0	4.1
#07	Fluvic Cambisol	BC	161	8	1.1	14.9	5.5	3.6
#08	Haplic Ferralsol	ferralic B	638	4	1.0	21.6	1.2	4.1
#09	Stagnic Gleysol	stagnic Bg	160	3	1.0	6.6	4.0	3.4
#10	Dystric Gleysol	Ap	33	18	0.9	2.9	1.9	5.8
#11 ^{††}	Gleyic Fluvisol	Ah	350	11	1.1	15.9	12.6	5.8
#12 ^{††}	Eutric Fluvisol	fluvic Ah	240	25	1.5	14.8	11.6	5.3
#13	Stagnic Cambisol	Ah	90	15	0.7	5.1	3.2	3.4
#14	Calcic Gleysol	Ap	50	13	0.9	6.2	2.7	7.0
#15 ^{††}	Eutric Fluvisol	fluvic Ah	310	15	1.3	15.4	9.6	5.4
#16 ^{††}	Gleyic Fluvisol	fluvic Bg	300	13	1.1	48.9	44.8	5.9
#17	Haplic Phaeozem	mollic Ah	164	24	1.0	7.3	1.6	6.2
Samples treated with H ₂ O ₂								
#10	Dystric Gleysol	Ap	27	< 1	0.3	1.8	1.1	5.7
#11	Gleyic Fluvisol	Ah	322	1	1.1	15.1	13.7	5.8
#12	Eutric Fluvisol	fluvic Ah	375	3	1.7	14.6	12.2	5.6
#15	Eutric Fluvisol	fluvic Ah	315	1	1.2	16.2	11.1	6.1
#16	Gleyic Fluvisol	fluvic Bg	376	2	1.0	48.9	45.1	5.4
#17	Haplic Phaeozem	mollic Ah	145	3	0.9	5.5	1.3	6.3

[†] organic carbon; [‡] oxalate-extractable aluminum; [§] dithionite-citrate-extractable iron; [¶] oxalate-extractable iron;

^{††} data partially adapted from Rinklebe et al. (2000)

The sorption of iron-cyanide complexes in soil samples containing $< 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ is presented in Figure 1.

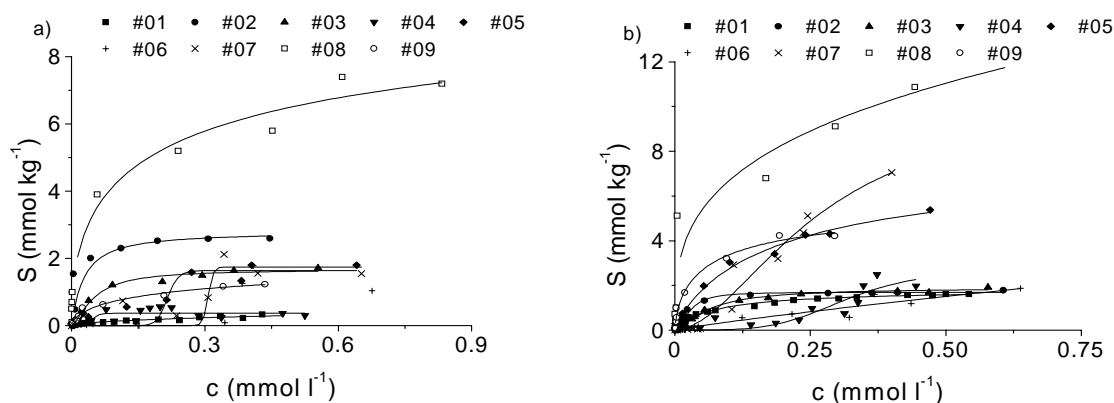


Figure 1 (a) Ferricyanide and (b) ferrocyanide sorption in soil horizons containing $< 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ (#01 C; #02 E; #03 Bsh; #04 stagnic 2Bg; #05 Bw; #06 gleyic Bg; #07 BC; #08 ferralic B; #09 stagnic Bg). Isotherms are plotted following Equation (1).

All sorption experiments were fitted to Equation (1). Mostly L-type isotherms were observed, although four S-type isotherms were found (ferricyanide: samples #05 and #07; ferrocyanide: samples #04 and #07). S-type isotherms are characterized by very small sorption at low concentrations. However, the adherence of sorption data to an isotherm provides no evidence of the actual sorption mechanism (Sposito, 1984). Isotherm parameters for these and all other experiments are given in Table 2.

Table 2 Parameter values of Langmuir-Freundlich isotherms of the sorption of iron-cyanide complexes in soils.

Sample	Horizon	[Fe(CN) ₆] ³⁻			[Fe(CN) ₆] ⁴⁻		
		S _{max}	b	n	S _{max}	b	n
		(mmol kg ⁻¹)			(mmol kg ⁻¹)		
#01	C	0.3	0.1	0.5	1.8	12.2	1.0
#02	E	2.8	50.3	1.1	3.2	1.9	0.5
#03	Bsh	1.7	83.2	1.5	5.9	0.7	0.5
#04	stagnic 2Bg	0.5	7.1	0.5	2.8	129.3	4.3
#05	Bw	5.6	0.7	0.7	7.9	3.8	0.9
#06	gleyic Bg	1.4	1.7×10^{13}	30.2	1.7	0.1	0.5
#07	BC	2.2	6.8	1.5	10.4	11.4	1.8
#08	ferralic B	11.4	1.9	0.5	18.7	2	0.5
#09	stagnic Bg	2.2	2.2	0.6	6.1	5.8	0.7
#10	Ap	54.9	0.2	1.5	53.0	0.2	2.1
#11	Ah	95.6	0.1	1.4	39.5	0.5	2.7
#12	fluvic Ah	104.6	< 0.1	3.1	122.7	0.1	1.3
#13	Ah	1.6	9.7	0.6	15.4	5.6	1.0
#14	Ap	0.1	24.5	1.0	no sorption		
#15	fluvic Ah	70.1	< 0.1	2.1	56.1	0.2	1.4
#16	fluvic Bg	44.1	0.1	1.9	36.2	0.3	0.7
#17	mollic Ah	26.7	0.1	1.9	10.5	0.8	1.7
Samples treated with H ₂ O ₂							
#10	Ap	7.3	4.6	5.1	0.9	874.3	4.1
#11	Ah	0.1	9.4	0.5	0.9	31	1.0
#12	fluvic Ah	7.0	8.0	5.0	5.8	33.4	1.6
#15	fluvic Ah	2.6	17.2	2.1	6.1	65.6	2.8
#16	fluvic Bg	0.2	1.7	0.4	1.5	11.5	1.2
#17	mollic Ah	0.8	4140	8.3	2.4	221.4	2.2

For both complexes, two groups of samples differing in their affinities for iron-cyanide complexes based on S_{max} values could be distinguished. Three samples (#01, #04, and #06) sorbed both

complexes to a very small extent. Ferricyanide was sorbed on the samples #02, #03, #05, and #09 to a small extent. Ferrocyanide sorption on the samples #05, #07, and #09 was larger. Both complexes were sorbed to the largest extent on #08. This sample was acid and contained large amounts of clay and iron oxides. In general, ferricyanide was sorbed to a smaller extent than ferrocyanide. The ratio of the sorption maxima (S_{\max} (ferrocyanide) to S_{\max} (ferricyanide) ranging from 1.2 to 6) was mostly larger than the ratio of the complex charges, the samples #02 and #06 were exceptions.

The sorption of iron-cyanide complexes in soils containing $> 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ is shown in Figure 2.

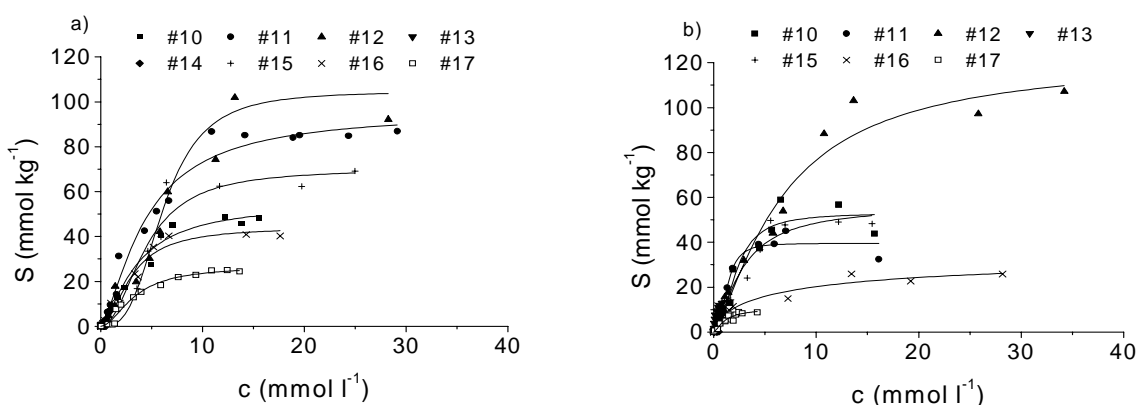


Figure 2 (a) Ferricyanide and (b) ferrocyanide sorption in soil horizons containing $> 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ (#10 Ap; #11 Ah; #12 fluvic Ah; #13 Ah; #14 Ap; #15 fluvic Ah; #16 fluvic Bg; #17 mollic Ah). Isotherms are plotted following Equation (1).

Again, the sorbed amounts between the samples varied, but these samples had a higher affinity for the complexes, because the sorbed amounts at S_{\max} were larger compared with those shown in Figure 1. The isotherms were linear over a wide range of equilibrium concentrations. For larger concentrations saturation plateaus were found. Only the samples #12 and #13 sorbed more ferrocyanide than ferricyanide at S_{\max} . The other samples had a higher affinity for ferricyanide. Especially the samples #10 to #12, #15, and #16 sorbed large amounts of iron-cyanide complexes. The samples #13, #14, and #17 sorbed iron-cyanide complexes to a distinctly smaller extent. The sorption of the complexes on soils which were treated with H_2O_2 is shown in Figure 3.

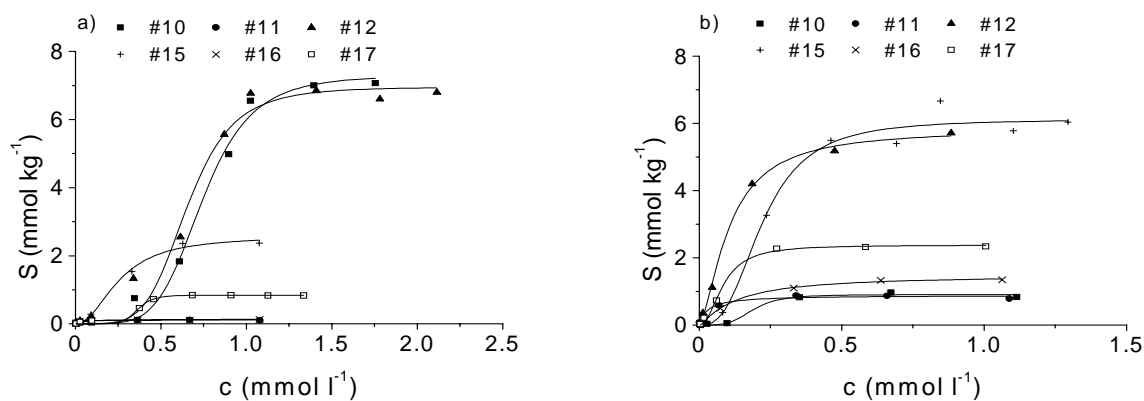


Figure 3 (a) Ferricyanide and (b) ferrocyanide sorption in soil horizons after treatment with H_2O_2 (#10 Ap; #11 Ah; #12 fluvic Ah; #16 fluvic Bg; #17 mollic Ah). Isotherms are plotted following Equation (1).

The destruction of SOM resulted in a large decrease in the sorption of both complexes. The decrease in C_{org} was in the range of 84% to 98% (calculated from data in Table 1), and it consisted roughly with the decrease in S_{max} (77% to 99%, calculated from Table 2). As a consequence, most of the samples used here sorbed small amounts of iron-cyanide complexes, because their sorption maxima were in the range of 0.2 to 2.6 mmol $[\text{Fe}(\text{CN})_6] \text{ kg}^{-1}$. This was in the range of the results of the samples shown in Figure 1. Hence, these treated samples showed a similar behavior as samples which were naturally poor in C_{org} . However, there were four samples showing sorption maxima in the range of 6 mmol $[\text{Fe}(\text{CN})_6] \text{ kg}^{-1}$. Hence, organic matter had an influence on the extent of sorption of iron-cyanide complexes on the samples used here.

Correlation coefficients of the relations between variables, including sorption maxima and soil properties, are presented in Table 3. The sorption maxima correlated with each other and with C_{org} . Furthermore, the various iron fractions correlated and so did pH and C_{org} . Therefore, the combination of the soil parameters was used to explain the sorption maxima calculated following Equation (1) using multiple regressions.

Table 3 Correlation coefficients of soil properties and sorption maxima of the sorption of iron-cyanide complexes in soils (n = 17).

	Clay	C _{org}	Al _o	Fe _d	Fe _o	Fe _d -Fe _o	pH	S _{max} ([Fe(CN) ₆] ³⁻)
Clay								
C _{org}	-0.133							
Al _o	-0.047	0.207						
Fe _d	0.535 *	-0.145	-0.066					
Fe _o	0.273	0.240	0.121	0.678 **				
Fe _d -Fe _o	0.565	-0.452	-0.219	0.613 **	-0.166			
pH	0.148	0.485 *	0.119	0.113	0.379	-0.256		
S _{max} ([Fe(CN) ₆] ³⁻)	0.311	0.623 *	0.212	0.191	0.431	-0.207	0.457	
S _{max} ([Fe(CN) ₆] ⁴⁻)	0.240	0.644 *	0.231	0.159	0.359	-0.172	0.282	0.884 **

*, ** significant at the 0.05 or 0.01 probability level, respectively.

We are aware of the fact that the following regression equations are only valid for the soils used here. It is not likely that they can be transferred to all soils quantitatively. However, they yield soil parameters qualitatively which are important for the sorption of iron-cyanide complexes in soils. As noted before, both logarithmic and original data were used. In the calculations, the results obtained from using logarithmic values were less significant compared with those with the original data. Therefore, only the results using the original data are presented. For both complexes the relation between sorption maxima and soil parameters of the 17 original soil samples was significant. For ferricyanide the corrected square of the correlation coefficient r was 0.478, and for ferrocyanide r^2 was 0.41. The regression equations for all soil samples are for ferricyanide

$$S_{\max} = -23.47 + 7.64 \times 10^{-2} \text{clay} + 2.91 C_{\text{org}} + 0.625 \text{Fe}_o, \quad (2)$$

and for ferrocyanide

$$S_{\max} = 0.18 + 6.31 \times 10^{-2} \text{clay} + 3.04 C_{\text{org}} - 5 \text{pH} + 0.485 \text{Fe}_o. \quad (3)$$

The sorption maxima of both complexes depended on the contents of clay, C_{org}, and Fe_o. They differed in the value of the constant and in that ferrocyanide sorption additionally depended on pH. As could be expected, clay and Fe_o had a positive effect, and pH had a negative effect on the sorption of iron-cyanide complexes in soils. High contents of C_{org} promoted the sorption of both anions. The correlation coefficients of the Equations (2) and (3) were relatively small, therefore multiple regressions were performed with two groups of samples differing in their C_{org} contents. The two

following regression equations were only valid for samples containing $< 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$. The regression equation for ferricyanide is

$$S_{\text{max}} = 10.82 + 1.7 \times 10^{-2} \text{clay} - 2.72 \text{pH} - 0.62 \text{Fe}_o + \text{Al}_o, r^2 = 0.873, \quad (4)$$

and is for ferrocyanide

$$S_{\text{max}} = 11.99 + 2.4 \times 10^{-2} \text{clay} - 2.45 \text{pH}, r^2 = 0.669. \quad (5)$$

Compared with the results of all soils, the correlation coefficient for both equations increased. Clay contents and pH influenced the sorption of both complexes, whereas C_{org} became irrelevant. Furthermore, the ferricyanide sorption maximum depended on Al_o . However, as indicated in Equation (4), Fe_o had a negative effect on ferricyanide sorption. Compared with Equations (2) and (3), multiple regressions with samples containing $> 10 \text{ g C}_{\text{org}} \text{ kg}^{-1}$ yielded large correlation coefficients. For these samples the regression equation for ferricyanide is

$$S_{\text{max}} = -46.07 + 0.24 \text{clay} + 100 \text{Al}_o - 10 \text{Fe}_d - \text{Fe}_o - 0.78 \text{Fe}_o, r^2 = 0.798, \quad (6)$$

and is for ferrocyanide

$$S_{\text{max}} = -61.45 + 160 \text{Al}_o - 10 \text{Fe}_d - \text{Fe}_o - 7.59 \text{pH} + 0.577 \text{C}_{\text{org}}, r^2 = 0.98. \quad (7)$$

In both equations, the sorption maximum was affected positively by Al_o and negatively by $\text{Fe}_d - \text{Fe}_o$. Only ferrocyanide sorption was promoted by C_{org} .

All regression equations (Equations (2 through 7)) were checked by variance analysis to evaluate the level at which the equation was significant. As checked by F-tests, all regression equations were significant at various confidence levels, as shown in Table 4. A regression equation is significant at a given confidence level, if the empirical F value, F_{emp} , is larger than the theoretical one, F_{theo} . The smallest level was 0.975. The statistical checks of the significance and the importance of any individual variable of the Equations (2 through 7) using T-tests are shown in Table 5.

Table 4 Variance analytical interpretation of the regression equations (2-7).

	Ferricyanide			Ferrocyanide		
	Equation [†]					
	(2)	(4)	(6)	(3)	(5)	(7)
df [‡]	16	8	7	16	8	7
r ²	0.478	0.873	0.798	0.410	0.669	0.980
Confidence level	0.990	0.995	0.975	0.975	0.990	0.995
F _{emp} [§]	5.880	14.737	7.924	3.783	9.088	86.366
F _{theo} [§]	5.290	8.810	5.520	3.730	6.360	10.050

[†] Equations: (2): $S_{\max} = -23.47 + 7.64 \times 10^{-2}\text{clay} + 2.91C_{\text{org}} + 0.625\text{Fe}_o$; (3): $S_{\max} = 0.18 + 6.31 \times 10^{-2}\text{clay} + 3.04C_{\text{org}} - 5\text{pH} + 0.485\text{Fe}_o$; (4): $S_{\max} = 10.82 + 1.7 \times 10^{-2}\text{clay} - 2.72\text{pH} - 0.62\text{Fe}_o + \text{Al}_o$; (5): $S_{\max} = 11.99 + 0.24\text{clay} - 2.45\text{pH}$; (6): $S_{\max} = -46.07 + 2.4\text{clay} + 0.1 \text{Al}_o - 0.01\text{Fe}_d\text{-Fe}_o - 7.8 \times 10^{-4}\text{Fe}_o$; (7): $S_{\max} = -61.45 + 0.16\text{Al}_o - 0.01\text{Fe}_d\text{-Fe}_o - 7.59\text{pH} + 5.77C_{\text{org}}$. [‡] degrees of freedom; [§] empirical or theoretical F value.

A variable influences the sorption maximum, if the absolute value of the empirical T, T_{emp} , is larger than the theoretical T, T_{theo} . The value of T_{theo} depends on the number of the degrees of freedom and on the confidence level at which a variable is valid. Only the confidence levels are presented in Table 5, the respective values of T_{theo} can be found in various statistical textbooks. The importance of a parameter as explanatory variable and its direction is given by the beta values in Table 5. The larger is the absolute value of beta, the larger is the explanation of this variable, and thus its importance. Therefore, we can see that sorption of both complexes on all samples (Equations (2) and (3)) was determined by the contents of C_{org} and clay. For samples containing $< 10 \text{ g } C_{\text{org}} \text{ kg}^{-1}$ (Equations (4) and (5)), the clay contents and pHs were most important for the sorption of both complexes. Unlike for the Equations (2 through 5), the results for the samples containing $> 10 \text{ g } C_{\text{org}} \text{ kg}^{-1}$ differed between the complexes. Clay contents were most important for ferricyanide sorption in these soils, for ferrocyanide sorption it were the contents of Al_o .

Table 5 Significance and importance as explanatory variables of the regression variables checked by T-tests.

		Variable					
		Clay	C _{org}	Fe _o	pH	Fe _d -Fe _o	Al _o
Equation [†]							
(2)	beta	0.343	0.623	0.188			
	T _{emp}	1.784	3.27	0.959			
	Significance	0.902	0.994	0.645			
	Confidence level	0.900	0.950	0.500			
(4)	beta	0.941		0.302	-0.538		0.206
	T _{emp}	7.045		-2.315	-4.064		1.536
	Significance	0.998		0.918	0.985		0.801
	Confidence level	0.999		0.950	0.990		0.800
(6)	beta	0.768		-0.287		-0.573	0.624
	T _{emp}	2.592		-1.318		-2.745	2.749
	Significance	0.919		0.721		0.929	0.929
	Confidence level	0.950		0.500		0.950	0.950
(3)	beta	0.320	0.736	0.165	-0.185		
	T _{emp}	1.545	3.231	0.765	-0.791		
	Significance	0.852	0.993	0.541	0.556		
	Confidence level	0.800	0.990	0.500	0.500		
(5)	beta	0.888			-0.325		
	T _{emp}	4.232			-1.549		
	Significance	0.995			0.828		
	Confidence level	0.990			0.800		
(7)	beta		0.078		-0.210	-0.476	1.048
	T _{emp}		1.302		-3.272	-6.981	15.917
	Significance		0.716		0.953	0.994	0.999
	Confidence level		0.500		0.980	0.999	0.999

[†] Equations: (2): $S_{\max} = -23.47 + 7.64 \times 10^{-2}\text{clay} + 2.91\text{C}_{\text{org}} + 0.625\text{Fe}_o$; (3): $S_{\max} = 0.18 + 6.31 \times 10^{-2}\text{clay} + 3.04\text{C}_{\text{org}} - 5\text{pH} + 0.485\text{Fe}_o$; (4): $S_{\max} = 10.82 + 1.7 \times 10^{-2}\text{clay} - 2.72\text{pH} - 0.62\text{Fe}_o + \text{Al}_o$; (5): $S_{\max} = 11.99 + 2.4 \times 10^{-2}\text{clay} - 2.45\text{pH}$; (6): $S_{\max} = -46.07 + 0.24\text{clay} + 100\text{Al}_o - 10\text{Fe}_d\text{-Fe}_o - 0.78\text{Fe}_o$; (7): $S_{\max} = -61.45 + 160\text{Al}_o - 10\text{Fe}_d\text{-Fe}_o - 7.59\text{pH} + 0.577\text{C}_{\text{org}}$.

DISCUSSION

As noted before, the mechanism, by which an iron-cyanide complex is sorbed, depends on the nature of the sorbent. The mechanisms by which iron-cyanide complexes are sorbed on inorganic soil constituents such as clay minerals and aluminum and iron oxides are largely clear, as presented in the introduction. The interactions between iron-cyanide complexes and SOM have not yet been investigated. Schenk and Wilke (1984) showed that the cyanide ion, CN^- , forms charge transfer complexes via cyanide-N with quinone groups of humic acids using infrared spectroscopy. Both iron-cyanide complexes have an octahedral structure with N located in the edges. Hence, iron-cyanide-N is potentially able to form the same complexes with quinone groups as cyanide-N. Quinone groups are oxidation products of phenols and various polycyclic aromatic hydrocarbons. They are present in soil humic acids (Stevenson, 1994). Quinone groups can react with N-containing compounds such as amino acids (Stevenson, 1994), and a reaction between quinone groups and iron-cyanide is possibly given by a nucleophilic addition reaction. This reaction type includes charge transfer complexes between cyanide-N and quinone groups, as proposed by Schenk and Wilke (1984). Hence, this reaction might explain the positive influence of SOM on iron-cyanide complex sorption. As the formation of quinones by oxidation of phenols occurs preferably in neutral and alkaline soils, it becomes clear that the qualitative composition of SOM and not the C_{org} content alone governs the extent of the reaction between iron-cyanide complexes and SOM, as proposed above. However, it is possible that there are further functional groups in SOM which may be able to sorb iron-cyanide complexes, e.g. positively charged functional groups such as R-NH_3^+ .

The promotive effect of SOM was shown by the regression equations for all samples and by the decrease of sorption of the Fluvisol samples which were treated with H_2O_2 . However, there were samples rich in C_{org} sorbing smaller amounts of iron-cyanide complexes (samples #07, #14, and #17). Hence, SOM of Fluvisols has perhaps a special affinity for iron-cyanide complexes, i.e. this SOM contains functional groups, which can react with iron-cyanide complexes, to a larger extent. In other studies dealing with the sorption of iron-cyanide complexes in soils (Fuller, 1985; Ohno, 1990; Ghosh et al., 1999), the contents of C_{org} were not mentioned. A positive influence of SOM on anion adsorption on soils cannot be expected because of the overall neutral or negative charge of SOM, if

we reduce anion sorption solely to electrostatic attraction. However, we could show that SOM promotes the sorption on some samples, hence the content of C_{org} is a soil property possibly enhancing the sorption of iron-cyanide complexes on soils.

Furthermore, the sorption of iron-cyanide complexes in soils is influenced by pH, clay, Fe_o , and Al_o . The importance of these parameters for the sorption of inorganic anions on soils has been reported in the literature. Sorption maxima of P sorption by wetland soils were predicted by the contents of Fe_o and Al_o (Reddy et al., 1998). Agbenin and Tiessen (1994) found that the phosphate sorption maxima of Brazilian soils could be explained by the contents of pedogenic iron and aluminum and fine clay. Sulfate sorption in forest soils was governed by the contents of Fe_o , Al_o , and pH (MacDonald and Hart, 1990). They used logarithmic values in multiple regressions. Based on the regression equations (3 through 5) and (7), sorption of iron-cyanide complexes is enhanced at low pH values. However, inner-sphere surface complexation of an anion on a mineral surface is possible at a pH above the point of zero charge of the mineral. As pointed out in the introduction, inner-sphere surface complexation of iron-cyanide complexes at high pH is known for ferrocyanide sorption on goethite only.

Maximum sorption of anions such as silicate or borate at high pH is caused by the fact that maximum sorption occurs near the pK_a values of the conjugate acids (Hingston, 1981). However, all pK_a values of ferricyanic and ferrocyanic acid are 4.2 or clearly lower (Jordan and Ewing, 1962). Hence, the negative effect of pH on iron-cyanide complex sorption in the regression equations is consistent with the known sorption mechanisms and the concept of the effect of pK_a values of conjugate acids. The sorption of iron-cyanide complexes on soils containing $< 10 \text{ g } C_{org} \text{ kg}^{-1}$ could be explained by the soil properties mentioned above. Sorption of anions such as iron-cyanide complexes on clay minerals and sesquioxides is given by the ability of the anions to form inner- or outer-sphere surface complexes or both. Therefore, anion sorption in soils generally depends on the contents of the mineral constituents mentioned above and pH. The extent of ferrocyanide sorption on neutral samples is not larger than that of ferricyanide. The opposite could be inferred from the pH-dependency of iron-cyanide complex sorption on goethite (Rennert and Mansfeldt, 2001). Therefore, only the combination of soil properties may explain the extent of sorption suitably, because the mechanisms of iron-cyanide complex sorption on mineral constituents differ.

The lower affinity of samples containing small amounts of C_{org} for iron-cyanide complexes cannot be explained by sorption kinetics, because it was shown that the sorption on iron and aluminum (hydr)oxides is finished after a reaction time of 24 h (Cheng and Huang, 1996; Rennert and Mansfeldt, 2001).

CONCLUSIONS

Sorption of ferricyanide and ferrocyanide in soils seems to be more complex than the sorption of other inorganic anions because of the promoting influence of SOM. The sorption capacities of the soil samples differed over a wide range. This is important for the mobility of iron-cyanide complexes which have been introduced into the natural soil environment. Soils containing high amounts of organic carbon and aluminum oxides and acid soils containing high amounts of aluminum oxides should sorb iron-cyanide complexes to a large extent, and should thus minimize the translocation of these anions into the ground water. Most Fluvisols investigated here have a high sorption capacity for iron-cyanide complexes. This capacity is caused by the presence of organic matter having a high affinity for iron-cyanide complexes. Further research is necessary to enlighten the nature of the interactions between iron-cyanide complexes and soil organic matter as well as to identify the functional groups which are responsible for these interactions.

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CHAPTER 6

Sorption and transport of iron-cyanide complexes in
goethite-coated sand

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ABSTRACT

Iron-cyanide complexes are present in soil and ground water due to anthropogenic inputs. We studied the sorption and the transport of the complexes ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, and ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, in goethite-coated sand in column experiments under saturated conditions as influenced by flow velocities and flow interruptions. Isotherm parameters obtained from batch experiments of iron-cyanide complex sorption on goethite were used to simulate breakthrough curves in goethite-coated sand. The breakthrough curves of ferrocyanide were inversely modeled. The transport of both complexes was retarded and rate-limited. Only ferricyanide breakthrough curves revealed concentration drops after flow interruptions. Simulations with batch parameters roughly reflected breakthrough curves of ferricyanide, but not of ferrocyanide. Ferricyanide sorption and desorption could not be described with the same isotherm indicating hysteresis. Since the sorption fronts of ferrocyanide breakthrough curves revealed the formation of a shoulder, it was concluded that ferrocyanide sorption in column experiments could not be described by a single isotherm which is based on a singular sorption process. Therefore, sorption of ferrocyanide on goethite was assumed to be influenced by more than one sorption mechanism. Inverse modeling of ferrocyanide breakthrough data using the Langmuir isotherm resulted in erroneous sorption maxima.

INTRODUCTION

The iron-cyanide complexes ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, and ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, are from anthropogenic sources in soils (Fuller, 1985). Their presence in soils and aquifers is caused by the deposition of industrial refuse such as purifier wastes originating from coal gasification (Shifrin et al., 1996), blast furnace sludge originating from pig iron production (Mansfeldt and Dohrmann, 2001), or paper de-inking sludge originating from paper recycling (Mansfeldt, 2001). An additional input to the soil environment is given by the use of road salt which contains Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, or sodium ferrocyanide, $\text{Na}_4[\text{Fe}(\text{CN})_6]$ as anticaking agents (Paschka et al., 1999).

The mobility of iron-cyanide complexes in soils on sites of former manufactured gas plants, on which purifier wastes have been deposited, is governed by pH and redox potential, both influencing the dissolution and precipitation of Berlin Blue (Meeussen, 1992). It is the most important cyanide phase in these soils (Meeussen et al., 1994; Mansfeldt et al., 1998). If, however, iron-cyanide complex concentrations are too small for precipitation, sorption of these anions on the solid soil matrix may be the main immobilizing process (Meeussen, 1992).

The sorption of both iron-cyanide complexes on goethite, $\alpha\text{-FeOOH}$, as a model substance of a sorbent in soil was investigated by Rennert and Mansfeldt (2001, 2002b) in batch experiments. They proposed various sorption mechanisms for the iron-cyanide complexes, for ferrocyanide a combination of inner-sphere surface complexation and surface precipitation of Berlin Blue and for ferricyanide outer-sphere and weak inner-sphere surface complexation. The sorption of ferricyanide on goethite was also investigated by Theis et al. (1988) using batch experiments as well as experiments with small columns. They deduced outer-sphere surface complexation of ferricyanide from their results. Fuller (1985) used soil material in column experiments to examine the sorption of ferricyanide. The most important property governing sorption was soil pH followed by the contents of clay minerals and iron oxides. Due to early breakthrough in column experiments, Ghosh et al. (1999) suggested nonreactive transport of ferrocyanide in neutral sandy aquifer material. In batch experiments with uncontaminated soils, the sorption of both iron-cyanide complexes was promoted in acid soils containing large amounts of aluminium and iron oxides, clay minerals, and, in some cases, soil organic matter (Rennert and Mansfeldt, 2002a). The release of iron-cyanide complexes

from a contaminated former manufactured gas plant site soil in column experiments under dispersive flow conditions was strongly rate-limited (Weigand et al., 2001). Their results indicated that both the dissolution of Berlin Blue and the desorption of iron-cyanide complexes was rate-limited. In none of these studies, the sorption and transport of iron-cyanide complexes was modeled numerically.

The main aim of this study was to investigate the sorption and the transport of ferricyanide and ferrocyanide in goethite-coated sand in column experiments under saturated conditions as influenced by flow velocities and flow interruptions. Goethite-coated sand was used, because it can be regarded as a model of a subsurface soil horizon lacking of soil organic matter. Furthermore, sorption parameters obtained from batch experiments with iron-cyanide complexes and goethite were used in numerical simulations of the breakthrough of the complexes in goethite-coated sand.

MATERIAL AND METHODS

Preparation and properties of goethite and goethite-coated sand

Goethite-coated sand was used as model porous medium. Goethite was prepared according to Schwertmann and Cornell (1991) by precipitating ferrihydrite from alkaline solution. Ferrihydrite was converted to goethite by aging for 60 h at 343 K. The product was cleaned by pressure filtration. The point of zero charge of goethite was 8.3, and its specific surface area measured by N₂ adsorption was 30 m² g⁻¹ (Rennert and Mansfeldt, 2001). We used acid washed seasand (Riedel-de Haën, Seelze, Germany) which contained 70% medium sand (0.2 - 0.63 mm) and 30% fine sand (0.063 - 0.2 mm). The sand was heated to 1100 K to destroy organic matter. After cooling, the sand was suspended (1.8 g ml⁻¹) and a goethite suspension (0.3 g ml⁻¹; pH 2.5) was added to the sand suspension. Highly coated sand was obtained by this procedure (Scheidegger et al., 1993). In contrast to Scheidegger et al. (1993), the goethite-sand suspension was left standing for 60 h at room temperature and occasionally stirred. Then excess goethite was removed by wet sieving (0.63 mm sieve). Subsequently, the goethite-coated sand was freeze dried after washing with de-ionized water. It contained 369 µg goethite g⁻¹ sand. Similarly, Filius et al. (1999) obtained 440 µg goethite g⁻¹ sand using the method by Scheidegger et al. (1993). As shown by XPS spectroscopy and specific surface

area analysis, pure goethite and goethite coating the sand do not differ (Scheidegger et al., 1993). Iron concentrations were determined by atomic absorption spectroscopy (PE 3100, Perkin Elmer, Überlingen, Germany) after microwave digestion (MWS-1, Berghof, Eningen, Germany) of the goethite-coated sand with 65% HNO₃. The specific surface area (BET) of the goethite-coated sand was $< 1 \text{ m}^2 \text{ g}^{-1}$. The pH of the goethite-coated sand measured in 0.01 M CaCl₂ with a substrate to solution ratio of 1:2.5 was 4.9.

Column experiments

We used columns made of PVC (emc, Erfurt, Germany) with a length L of 10 cm, an inner diameter of 4 cm, and a cross sectional area A of 12.57 cm^2 . The columns were packed to uniform bulk density (approximately 1.6 g cm^{-3} in all experiments) with goethite-coated sand. At the bottom and at the top, the columns were capped with ceramic porous plates. The background electrolyte 0.01 M NaNO₃ was fed to the column using a peristaltic pump (Ismatec MCP with a CA 4 pump head, Ismatec Laboratoriumstechnik, Wertheim, Germany) to obtain saturated conditions. Prior to the experiments, the background solution and all other feeding solutions were degassed. The columns were saturated at a flow rate $Q = 0.3 \text{ ml h}^{-1}$ from bottom to top to prevent air entrapment.

The flow regime was characterized by applying the tracer chloride at three flow rates ($Q = 0.5$; 1.0 ; or 1.5 ml min^{-1}) as pulse inputs of 0.01 M NaCl added to the background electrolyte. In one tracer experiment, chloride was applied by continuous feed. Aliquots of 2 ml of the effluent were collected in a fraction collector (Linear II, Reichelt Chemietechnik, Heidelberg, Germany). Chloride concentrations were determined by ion chromatography with electrical conductivity detection (DX 500, Dionex, Idstein, Germany) after appropriate dilution. A tracer breakthrough was carried out prior to all experiments with iron-cyanide complexes. After the tracer experiments, 12 to 25 pore volumes of the background electrolyte were used to leach chloride from the column.

For the sorption and transport experiments of iron-cyanide complexes, solutions of K₃[Fe(CN)₆] or K₄[Fe(CN)₆] (reagent grade, Riedel-de Haën, Seelze, Germany) containing 0.05 mM [Fe(CN)₆]¹⁻ in the background solution were used. Pulse inputs of an iron-cyanide complex solution were fed to the column at three flow rates ($Q = 0.5$; 1.0 ; or 1.5 ml h^{-1}). The number of pore volumes, pvs, of an iron-cyanide complex solution added varied between the experiments: ferricyanide, 2.5 pvs ($Q = 0.5 \text{ ml h}^{-1}$); 3.0 pvs ($Q = 1.0 \text{ ml h}^{-1}$); 6.9 pvs ($Q = 1.5 \text{ ml h}^{-1}$); ferrocyanide, 2.7 pvs ($Q = 0.5 \text{ ml h}^{-1}$); 3.1 pvs

($Q = 1.0 \text{ ml h}^{-1}$); 5.5 pvs ($Q = 1.5 \text{ ml h}^{-1}$). After replacing the iron-cyanide complex solution with the cyanide-free background electrolyte solution and further flow for 1.3 pore volumes, the flow was interrupted for 16 to 20 h. When investigating the sorption of ferricyanide at $Q = 0.5 \text{ ml min}^{-1}$, the flow was interrupted for four times ranging from 1 to 96 h after 1.6, 1.8, 2.0, and 3.3 pvs. Again, fractions of the effluent solutions were collected. The pH was measured potentiometrically with a WTW pH 90 (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) and an INLAB 406 electrode (Ingold, Steinbach, Germany). Cyanide was determined according to Mansfeldt and Biernath (2000) using a micro-distillation technique (MicroDistiller, Eppendorf-Netheler-Hinz, Hamburg, Germany). All experiments with ferrocyanide were performed in darkness.

Data analysis

Bulk density, ρ_b , and volumetric water content, θ , were measured directly. The latter was determined gravimetrically after the experiments. Mean pore water velocity, v , was calculated from the flow rate Q ($v = Q / (A \times \theta)$). The breakthrough data are given as reduced variables. Reduced concentrations (c/c_0) were given by the ratio of effluent and influent concentrations. The number of pore volumes eluted (pv), i.e. reduced time, was calculated by

$$pv = (q \times t_{bt}) / (\theta \times L) \quad (1)$$

where $q = Q/A$, Darcian flow, and t_{bt} = breakthrough time of the respective concentration. The hydraulic regime was characterized by inverse modeling of the tracer breakthrough data. In the following, [L], [M], and [T] indicate units of length, mass, and time, respectively. The computer code CXTFIT 2.1 (Toride et al., 1995) was used to determine the dispersion coefficient D ($\text{L}^2 \text{T}^{-1}$) and the retardation factor R by fitting the breakthrough data of chloride to the advection-dispersion equation, ADE

$$\frac{\partial}{\partial t}(\theta c + \rho_b s) = \frac{\partial}{\partial x}(\theta D \frac{\partial c}{\partial x} - J_w c) \quad , \quad (2)$$

where c is the flux averaged concentration of the liquid phase [M L^{-3}], s is the concentration of the sorbed phase [M M^{-1}], D is the dispersion coefficient [$\text{L}^2 \text{T}^{-1}$], θ is the volumetric water content [$\text{L}^3 \text{L}^{-3}$], J_w is the volumetric water flux density [L T^{-1}], and ρ_b is the bulk density [M L^{-3}].

Chloride adsorption by the solid phase is described by a linear isotherm as

$$s = K_d \times c, \quad (3)$$

where K_d [$M^{-1} L^3$] is a distribution constant. Assuming steady-state flow, Equation (2) is rearranged to Equation (4) using Equation (3)

$$R = 1 + \frac{\rho_b K_d}{\theta}, \quad (4)$$

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}, \quad (5)$$

where $v = J_w/\theta$ is the mean pore water velocity.

Tracer breakthrough derived D values of a given column were used for the simulation of iron-cyanide complex breakthrough curves in this column.

Simulations of the sorption and the transport of iron-cyanide complexes were performed with the numerical computer code CARRY 6.0 (Totsche et al., 1996). CARRY operates with a bulk solid phase composed of different sorption sites, which can be discriminated in terms of bulk density fractions. In all simulations, goethite was regarded as the sorbent. Therefore, the bulk density fractions of goethite (given by $\rho_{Gt} = \text{mass}_{Gt} / (L \times A)$, where Gt indicates goethite) were used in the simulations as the reactive bulk density fractions. CARRY input files require values of dispersivity λ [L] ($\lambda = D/v$) and tortuosity τ ($\tau \approx \theta/\theta_{sat}^{2/3}$, where θ_{sat} is the saturated water content (Millington and Quirk, 1961)). In order to describe the retention of iron-cyanide complexes during the transport in goethite-coated sand, data of the sorption of iron-cyanide complexes on goethite were used (Rennert and Mansfeldt, 2001). Their batch sorption experiments were carried out as influenced by pH in the presence of the background electrolyte 0.01 M NaNO_3 . For the present study, their data were interpreted with the Langmuir isotherm

$$s = \frac{s_{max} \times K_L \times c}{1 + K_L \times c}, \quad (6)$$

where s_{max} is the sorption maximum [$M M^{-1}$], and K_L is the Langmuir constant [$M^{-1} L^3$]. As both isotherm parameters for both iron-cyanide complexes decreased exponentially with increasing pH, values of the parameters at each equilibrium pH in column experiments were calculated. These values were $s_{max} = 1.67 \times 10^{-3} \text{ g g}^{-1}$ and $K_L = 176862 \text{ g}^{-1} \text{ cm}^3$ for ferricyanide (pH 6.3) and $s_{max} = 2.79$

$\times 10^{-3} \text{ g g}^{-1}$ and $K_L = 384326 \text{ g}^{-1} \text{ cm}^3$ for ferrocyanide (pH 6.2) in the column experiments. These parameters were used to simulate iron-cyanide complex breakthrough curves with CARRY. Sorption of the complexes was described by Equation (6) instead of Equation (3). Sorption on all surfaces sites was assumed to be rate-limited (first-order kinetics), and the forward (sorption) rate parameter k_f varied between 10^{-4} and $10^{-2} \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$. Consequently, the backward (desorption) rate parameter k_b (given by $k_b = k_f / K_L$) varied between $5.7 \times 10^{-10} \text{ min}^{-1}$ and $5.7 \times 10^{-8} \text{ min}^{-1}$ for ferricyanide and between $2.6 \times 10^{-10} \text{ min}^{-1}$ and $2.6 \times 10^{-8} \text{ min}^{-1}$ for ferrocyanide.

Inverse modeling of the ferrocyanide breakthrough data was performed using the computer code MCMFIT (Bajracharya and Barry, 1995). It estimates parameter values by nonlinear least-squares fitting for nonlinear adsorption of a single solute species with one-dimensional transport. In MCMFIT, a general adsorption isotherm by Barry (1992) is used (Equation (7))

$$s = \alpha_1 \{1 - [1 + (\alpha_2 c)^{\alpha_3}]^{\alpha_4}\}, \quad (7)$$

which represents the Langmuir isotherm (Equation (6)) with $\alpha_1 = s_{\max}$ and $\alpha_2 = K_L$, when $\alpha_4 = -1$ and $\alpha_3 = 1$. In the modeling procedures, the parameters K_L , s_{\max} , and k_f were fitted, whereas physical parameters such as v and D were kept constant.

RESULTS

Breakthrough of chloride

Measured data and modeled breakthrough curves of the tracer chloride in goethite-coated sand are presented in Figure 1. Tracer breakthrough curves were symmetrical, indicating linear equilibrium sorption and physical equilibrium, i.e. the absence of preferential flow. The position of the desorption fronts differed, because the number of pore volumes added ranged from 0.49 to 2.44. Parameters resulting from fitting chloride breakthrough data to the ADE (Equation (2)) are shown in Table 1.

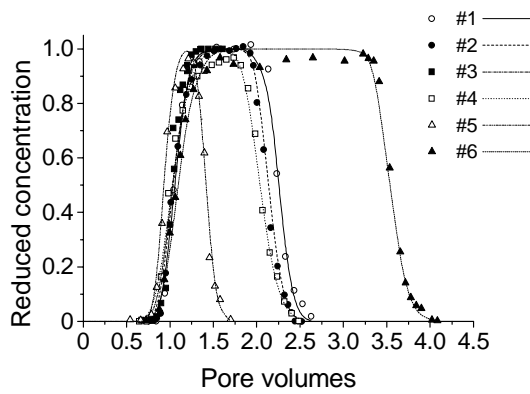


Figure 1 Breakthrough curves of chloride in goethite-coated sand at three pore water velocities. Breakthrough curves are numbered according to Table 1. Symbols indicate measured data, the lines result from fitting the data to Equation (2).

Table 1 Experimental parameters of chloride breakthrough curves in goethite-coated sand and results of fitting the breakthrough data to the advection-dispersion equation (Equation (2)).

No	Q^a ($\text{cm}^3 \text{ min}^{-1}$)	θ^b ($\text{cm}^3 \text{ cm}^{-3}$)	v^c (cm min^{-1})	R^d	D^e ($\text{cm}^2 \text{ min}^{-1}$)	Pe^f	r^{2g}	pvs^h
#1	0.5	0.40	0.104	1.06	0.0061	178	0.993	1.20
#2	0.5	0.40	0.104	1.04	0.0074	134	0.994	1.01
#3	1.0	0.39	0.204	1.04	0.0256	82	0.990	-
#4	1.0	0.38	0.209	1.04	0.0202	102	0.993	1.1
#5	1.5	0.39	0.305	0.93	0.0180	166	0.996	0.49
#6	1.5	0.39	0.305	1.11	0.0311	98	0.992	2.44

^a flow rate; ^b volumetric water content; ^c pore water velocity ($v = q/\theta$); ^d retardation coefficient; ^e dispersion coefficient; ^f column Peclet number ($Pe = vL/D$); ^g square of the correlation coefficient, ^h number of pore volumes added (#3 continuous feed).

All curve fittings resulted in large correlation coefficients r (given as their squares in Table 1). As can be seen from the retardation factors R ranging from 0.93 to 1.11, chloride was nearly an inert tracer. Column Peclet numbers (Pe) ranged from 82 to 178. In spite of these variations, a strongly advective flow regime was indicated in all experiments. The D values were used in simulations of iron-cyanide complex breakthrough presented below.

Breakthrough of ferricyanide

Measured data and simulated ferricyanide breakthrough curves in goethite-coated sand at three pore water velocities are shown in Figure 2. The experimental parameters of all iron-cyanide complex breakthrough curves are summarized in Table 2.

At all pore water velocities, ferricyanide revealed early breakthrough (at $pv < 1$). The sorption fronts were steep, and the maximum concentration $c/c_0 = 1$ was reached quickly (after about 1.5 pv). In the absence of preferential flow, early breakthrough can be attributed to nonlinear sorption. The steep rise was enhanced by the strongly advective flow regime as well. The positions of the sorption fronts did not depend on the pore water velocity. At the desorption fronts, the relative ferricyanide concentrations increased after the flow interruptions. This indicates rate-limited desorption of sorbed ferricyanide. Then the concentrations quickly dropped. Ferricyanide was not completely leached from goethite at the smallest pore water velocity (Table 2).

Rate-limited sorption should induce a dependence of the positions of the breakthrough curves upon flow velocities. However, the flow velocities were large, which might explain the lack of dependence observed. The large flow velocities also caused the quick initial breakthrough, because there was not enough time to attain an equilibrium, hence illustrating kinetic nonequilibrium of ferricyanide sorption. Figure 2a shows the effect of flow interruptions on ferricyanide concentrations when ferricyanide was continuously fed to the column (the first three flow interruptions). The relative concentrations decreased after the flow interruptions, but returned quickly to the initial values before the flow interruption began. The decrease was caused by rate-limited sorption (Brusseau et al., 1989b). Therefore, sorption as well as desorption of ferricyanide on goethite-coated sand were rate-limited.

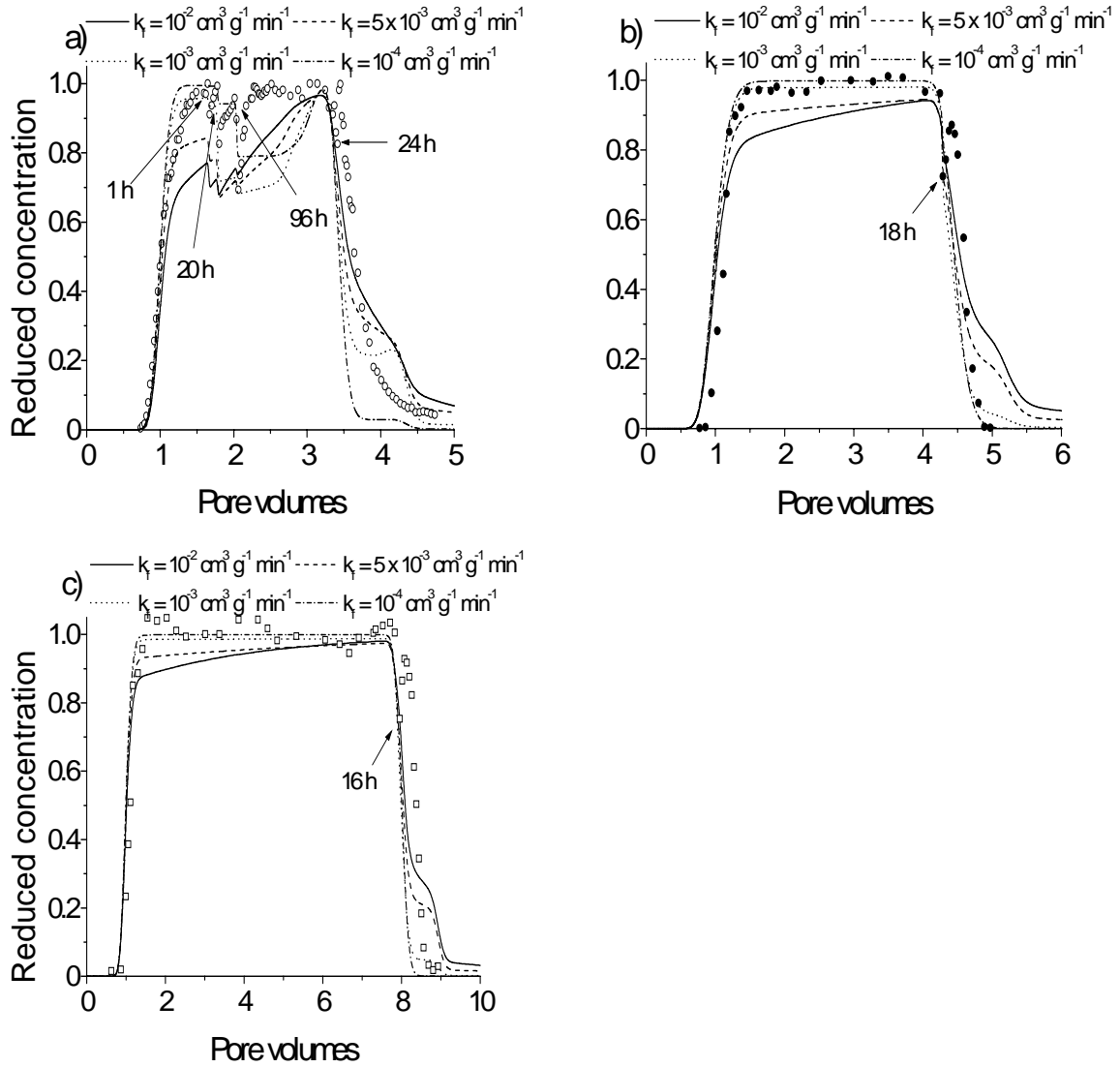


Figure 2 Breakthrough curves of ferricyanide in goethite-coated sand at three pore water velocities (a, $v = 0.104 \text{ cm min}^{-1}$; b, $v = 0.215 \text{ cm min}^{-1}$; c, $v = 0.305 \text{ cm min}^{-1}$). Lines result from simulations using batch-derived Langmuir isotherm parameters (Equation (6), $s_{\text{max}} = 1.67 \times 10^{-3} \text{ g g}^{-1}$, $K_L = 176862 \text{ ml g}^{-1}$) with four different rate parameters k_f . Arrows indicate the beginning of a flow interruption.

Table 2 Experimental parameters of iron-cyanide complex breakthrough curves in goethite-coated sand.

Parameter ^a	Ferricyanide			Ferrocyanide		
v (cm min ⁻¹)	0.104	0.215	0.305	0.104	0.209	0.305
L (cm)	10	10	10	10	10	10
A (cm ²)	12.57	12.57	12.57	12.57	12.57	12.57
ρ _b (g cm ⁻³)	1.67	1.63	1.64	1.60	1.67	1.60
ρ _{Gr} (g cm ⁻³)	6.2 × 10 ⁻⁴	6.0 × 10 ⁻⁴	6.0 × 10 ⁻⁴	5.9 × 10 ⁻⁴	6.2 × 10 ⁻⁴	5.9 × 10 ⁻⁴
θ (cm ³ cm ⁻³)	0.38	0.37	0.39	0.38	0.38	0.39
pv (cm ³)	48.1	46.6	49.1	48.2	47.5	49.5
d f i (h)	1 - 96	18	16	18	18	20
λ (cm)	0.054	0.123	0.060	0.071	0.098	0.102
c (mmol l ⁻¹)	0.05	0.05	0.05	0.05	0.05	0.05
pvs added	2.5	3.0	6.9	2.7	3.1	5.5
recovery (%)	83	100	100	68	91	92

^av, pore water velocity; L, length of the column; A, cross sectional area; ρ_b, bulk density; ρ_{Gr}, bulk density of goethite; θ, volumetric water content; pv, pore volume; d f i, duration of flow interruption; λ, dispersivity; c, concentration of influent solution; pvs added, number of pore volumes added; recovery, percent of iron-cyanide complexes detected during desorption.

In batch experiments, the sorption of ferricyanide on goethite was finished after 24 h (Rennert and Mansfeldt, 2001). In contrast, the kinetics of ferricyanide sorption in the column experiments presented here differed from these in batch experiments, as the drop in the relative concentrations was larger after the flow interruption which lasted 96 h than that after the flow interruption which lasted 20 h.

For all parts of Figure 2, measured data were reflected by the simulated breakthrough curves using Langmuir isotherm parameters except for the data after the flow interruptions. Simulations of the breakthrough curves were carried out at constant pH (6.3). This was an adequate simplification, because the effluent pHs were in the narrow range of 6.0 to 6.4. In this pH range, neither did the speciation of ferricyanide change (all dissociation constants of ferricyanic acid are < 1 (Jordan and Ewing, 1962)), nor did the surface properties of goethite differ greatly.

Especially the quick rise of concentrations after the flow interruptions was not reflected by the simulations. However, the simulation with the rate parameter k_f set to $10^{-3} \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$ (Figure 2a) described the measured sorption front sufficiently and was in good agreement with the measured smallest concentrations after the second and third flow interruption. The effects of flow interruptions on the concentrations were poorly simulated at higher flow velocities as shown in Figure 2b and 2c again indicating that the flow velocities were large compared to the rate of sorption.

When we did not interrupt the flow during the experiments, the simulations with Langmuir parameters derived from batch experiments with $k_f = 10^{-3} \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$ were approximate descriptions of the actual breakthrough curves for all pore water velocities. All sorption fronts were reflected by simulations with the parameters mentioned above. The effects of flow interruptions at the desorption fronts on the concentrations did not become clear by the simulations. The larger was the forward rate parameter k_f used in the simulations, the larger was the increase of the concentrations after the flow interruption at the desorption fronts. However, the larger was k_f , the poorer were the simulations of the sorption fronts. This in turn indicates that the backward rate parameters k_b to simulate the desorption fronts must be larger than those calculated from the forward rate parameter k_f and the Langmuir constant K_L . In this case, K_L is not constant due to differences in sorption and desorption indicating kinetic nonequilibrium of ferricyanide sorption.

The sorption and desorption behavior of ferricyanide was qualitatively consistent in batch as well as in column experiments, because sorption and desorption kinetics differed in both approaches. The desorption of ferricyanide in batch experiments induced by raising the pH was complete after 4 h, whereas it took 24 h until ferricyanide was equilibrated on goethite (Rennert and Mansfeldt, 2001). Due to the effect of flow interruptions, early breakthrough, and different sorption and desorption kinetics, the transport of ferricyanide in goethite-coated sand was affected by rate-limited and nonlinear sorption.

Breakthrough of ferrocyanide

Measured data and simulated ferrocyanide breakthrough curves in goethite-coated sand at three pore water velocities are shown in Figure 3. Similar to ferricyanide, ferrocyanide exhibited early breakthrough. For all pore water velocities, the measured breakthrough curves were not symmetrical. Except for the breakthrough curve shown in Figure 3c, the breakthrough of ferrocyanide was not

complete, because the maximum concentration $c/c_0 = 1$ was not reached. This indicates rate-limited sorption. Again, different pore water velocities had no effect on the breakthrough curves, as the positions of the steep rise of the sorption fronts were identical.

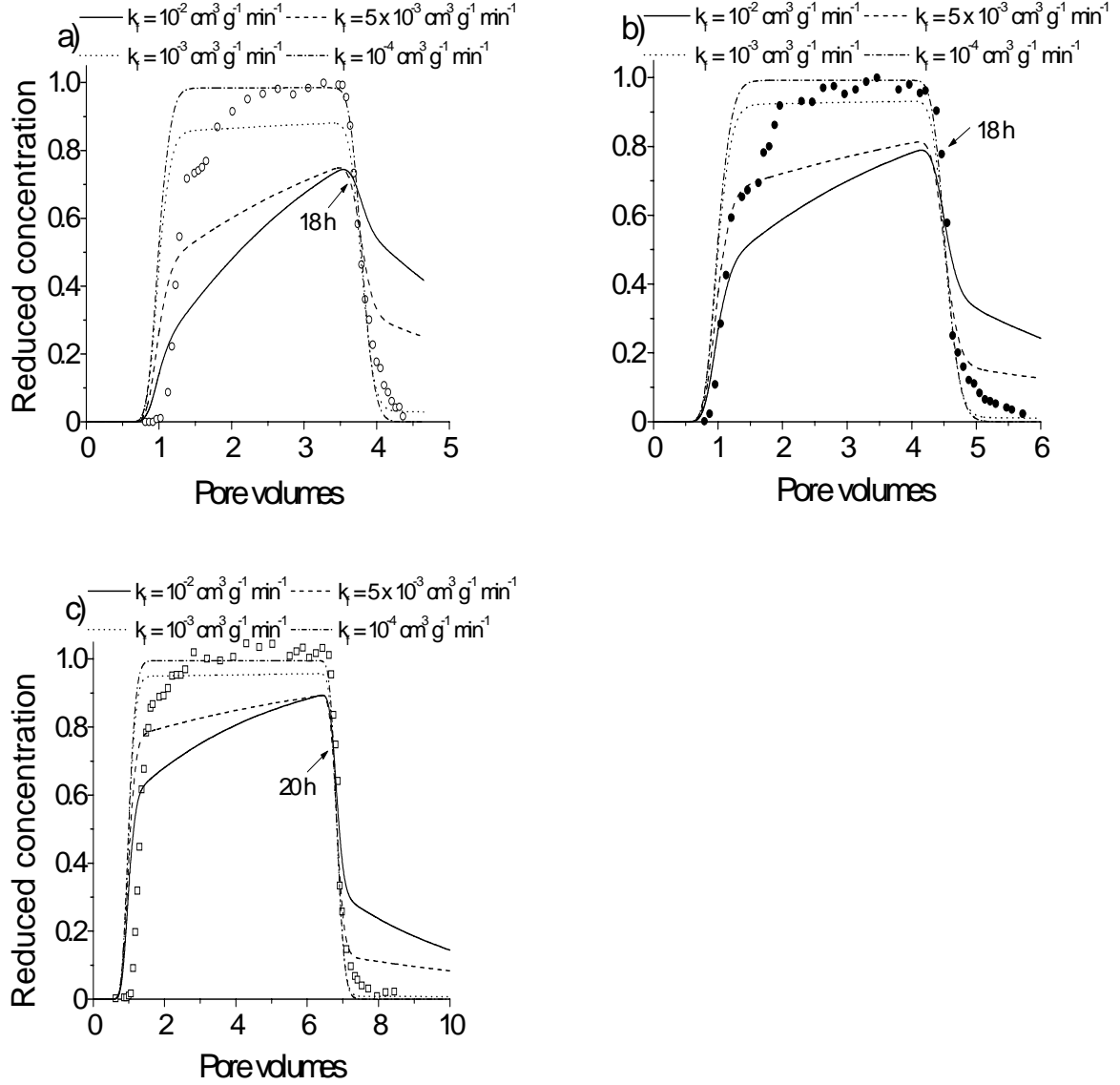


Figure 3 Breakthrough curves of ferrocyanide in goethite-coated sand at three pore water velocities (a, $v = 0.104 \text{ cm min}^{-1}$; b, $v = 0.209 \text{ cm min}^{-1}$; c, $v = 0.305 \text{ cm min}^{-1}$). Lines result from simulations using batch-derived Langmuir isotherm parameters (Equation (6), $s_{\max} = 2.79 \times 10^{-3} \text{ g g}^{-1}$, $K_L = 384326 \text{ ml g}^{-1}$) with four different rate parameters k_f . Arrows indicate the beginning of a flow interruption.

The sorption fronts could be separated into three parts: a steep rise (0 to ≈ 1.5 pv); a plateau (1.5 to ≈ 2 pv); and subsequent converging on the maximum concentration (> 2 pv). The combination of these three parts may be designated as a shoulder. Shoulder formation suggests complex and nonsingular sorption phenomena. The desorption fronts dropped quickly to low concentrations and exhibited slight tailing. The flow interruptions had no effect on the shape of all breakthrough curves. The sorption as well as the desorption fronts exhibited slight tailing. Tailing of a sorption front can be attributed to physical or chemical nonequilibrium or both (Brusseau et al., 1989a). Physical nonequilibrium affects the transport of both reactive and nonreactive solutes due to diffusive mass transfer between nonadvective and advective flow regions. Peclet numbers of chloride breakthrough curves always indicated advective flow (Table 1). Furthermore, breakthrough of only slightly retarded chloride did not show any tailing (Figure 1). Therefore, physical nonequilibrium can be excluded and the tailing of the ferrocyanide breakthrough curves is caused by rate-limited and/or nonlinear sorption. Rate-limited sorption was indicated by the dependence of ferrocyanide recovery on the pore water velocity (Table 2).

In contrast to the results of the column experiments, induced by raising the pH the sorption of ferrocyanide on goethite in batch experiments did not depend on time, but desorption was rate-limited (Rennert and Mansfeldt, 2001). The measured concentrations after the flow interruptions did not indicate rate-limited desorption of sorbed ferrocyanide. However, we should not rate these data as a proof of the absence of rate-limited desorption, because the duration of the flow interruptions might not have been adequate to observe an effect of a flow interruption on measured concentrations. All breakthrough curves simulated with parameters derived from batch experiments did not reflect the measured data properly. Due to the same reasons as pointed out for the simulations of ferricyanide breakthrough curves, the simulations of ferrocyanide breakthrough curves were carried out at constant pH. In all simulations, it was assumed that sorption of ferrocyanide occurs on homogeneous sorption sites, and that sorption is rate-limited. The simulated breakthroughs were earlier than the measured ones indicating that the amount of ferrocyanide sorbed was larger in column experiments or that sorption was rate-limited in column experiments. The shoulder was not reproduced by any simulation. This indicates that ferrocyanide sorption in column experiments could not be predicted by parameters obtained in batch experiments, although the sorbent was the same.

Apart from the occurrence of a shoulder, inverse modeling of ferrocyanide sorption demonstrated the inapplicability of the Langmuir isotherm. Fitted parameters are given in Table 3, and modeled breakthrough curves in Fig. 4. These breakthrough curves reflected the measured data except for the shoulder. As described for the simulated breakthrough curves, again it was impossible to fit the shoulder, and therefore it was not possible to fit the whole breakthrough curves using Langmuir isotherms. Although the fittings resulted in large values of r^2 , the fitted sorption maxima s_{\max} indicated that the measured breakthrough curves were not adequately described. Considering the specific surface area of goethite, the fitted sorption maxima (Table 3) were in the range of 236 to 617 $\mu\text{mol m}^{-2}$. These values are erroneous, as can be seen from a comparison with literature data obtained in batch experiments: the sorption maxima of iron-cyanide complexes on goethite are 1.6 $\mu\text{mol m}^{-2}$ (Rennert and Mansfeldt, 2001); the sorption maximum of strongly sorbed phosphate on goethite is 2.51 $\mu\text{mol m}^{-2}$ (Schwertmann, 1988). As a consequence, the fittings presented show that significant correlation does not imply causal connection.

In further calculations, the general isotherm (Eq. [7]) with all parameters was used to fit ferrocyanide breakthrough data. All these calculations (not shown here) did not fit the shoulder. This additionally indicates the failure of a single isotherm approach in describing the measured ferrocyanide breakthrough curves.

Table 3 Langmuir isotherm parameters resulting from fitting ferrocyanide breakthrough data to Equation (6). Pore water velocity was not fitted.

v^a (cm min^{-1})	s_{\max}^b (g g^{-1})	K_L^c (ml g^{-1})	k_f^d ($\text{cm}^3 \text{g}^{-1} \text{min}^{-1}$)	r^{2e}
0.104	0.05	900	3.1×10^{-2}	0.991
0.209	0.10	1207	2.5×10^{-2}	0.986
0.305	0.13	808	9.9×10^{-2}	0.976

^a pore water velocity; ^b sorption maximum; ^c Langmuir constant; ^d forward rate parameter; ^e square of the correlation coefficient

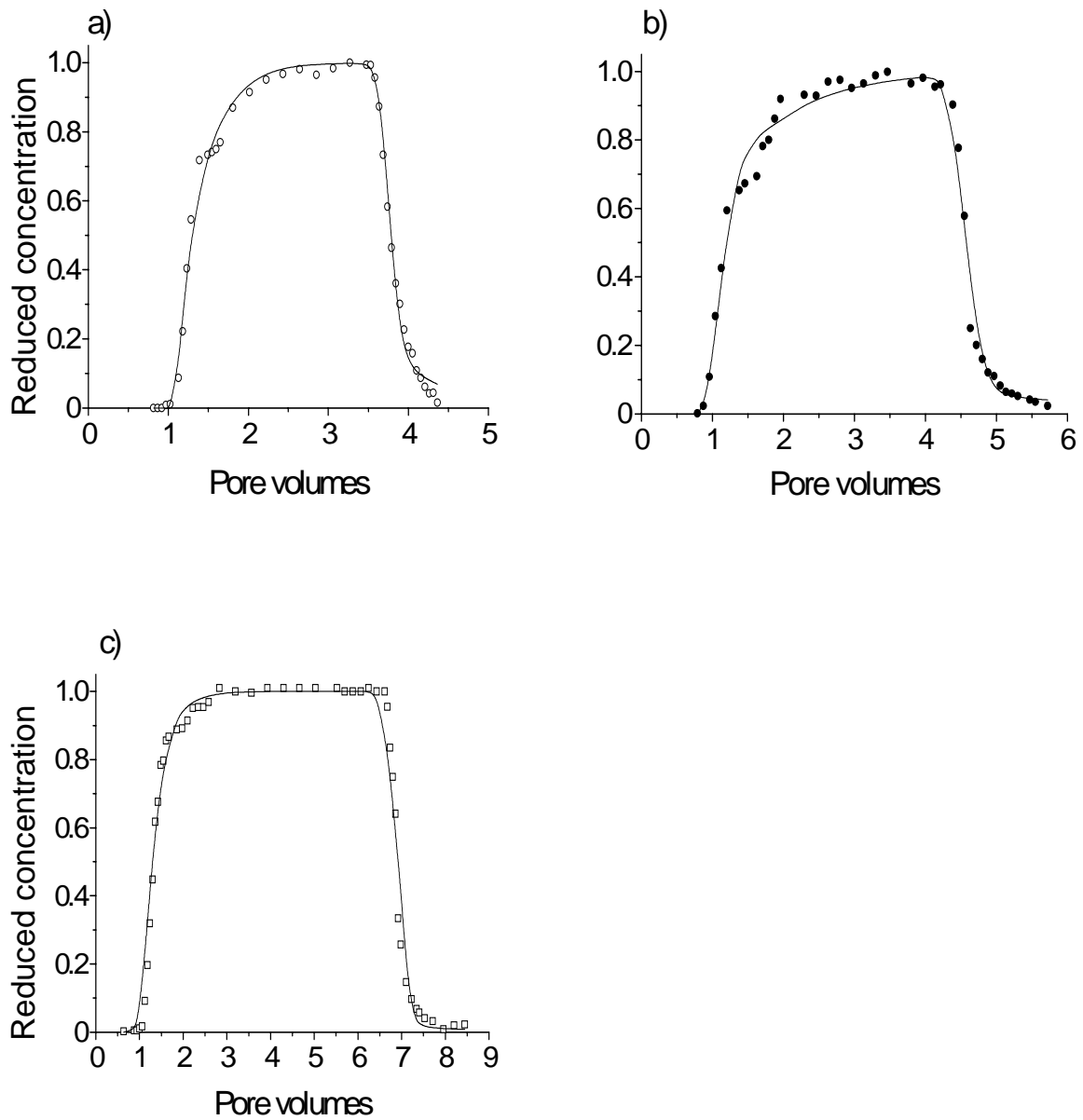


Figure 4 Breakthrough curves of ferrocyanide in goethite-coated sand at three pore water velocities (a, $v = 0.104 \text{ cm min}^{-1}$; b, $v = 0.209 \text{ cm min}^{-1}$; c, $v = 0.305 \text{ cm min}^{-1}$). Lines result from fitting the data to the Langmuir isotherm (Equation (6)). Fitted parameters are given in Table 3.

DISCUSSION

The sorption and transport behavior of the iron-cyanide complexes differed as summarized in Table 4.

Sorption of ferricyanide on goethite-coated sand in column experiments is slower than that of ferricyanide on goethite in batch experiments. As pointed out before, the batch-derived parameters yielded approximate descriptions of the breakthrough curves except for the data after the flow interruptions. This indicated that the surface chemistry in both batch and column experiments is sufficiently described by Langmuir isotherms. Consequently, the process of ferricyanide sorption on goethite should be the same in both experimental approaches.

Table 4 Comparison of ferricyanide and ferrocyanide sorption and transport behavior in goethite-coated sand.

Aspect	Ferricyanide	Ferrocyanide
Effect of flow velocity ^a	no	no
Effect of flow interruption	yes	no
Transport affected by	nonlinear and rate-limited sorption; hysteresis	nonlinear and rate-limited sorption; hysteresis (?)
Desorption	rate-limited	rate-limited
Simulation with batch parameters	reflected measured breakthrough curves except for data after flow interruptions	did not reflect measured breakthrough curves at all
Inverse modeling	not performed	erroneous results

^a on the position of initial breakthrough

The failure of simulations with batch-derived parameters to describe the effects of flow interruptions on measured breakthrough data may be caused by the necessity to use larger backward rate parameters for desorption which differ from those calculated from the forward rate parameters and

the Langmuir constants. These different rate parameters result in sorption and desorption fronts which are not congruent. This might be caused by hysteresis. Differences in the transport of ferricyanide to the goethite surface in the case of sorption and from the goethite surface in the case of desorption would result in hysteresis, thus in different sorption and desorption fronts, respectively. Another possibility of the occurrence of hysteresis is structural change of the goethite surface due to sorption.

Our results agree with the findings of Theis et al. (1988) mostly. In their study ferricyanide exhibited early breakthrough in small columns filled with goethite. They also found a single reaction which was rate-limited due to surface mass transfer. Desorption was quick and complete, and hysteresis was not observed. However, their breakthrough experiments were not complete, as the desorption fronts were not investigated. Therefore, differences between the sorption and desorption fronts, which indicate hysteresis, could not be observed in their investigations.

As for ferricyanide, the ferrocyanide sorption fronts differed from the desorption fronts. This indicates hysteresis for ferrocyanide sorption, too. As mentioned before, Langmuir isotherm parameters obtained from batch experiments and from inverse modeling of breakthrough data did not reflect measured ferrocyanide breakthrough curves in goethite-coated sand. The problem in both approaches was to describe the shoulder after 1.5 pv which indicated chemical nonequilibrium. As far as we know, this is the first study to present the formation of a shoulder during transport of an inorganic anion. Possible reasons of shoulder formation are i) sorption of more than one sorbate on the surface or ii) sorption of one sorbate by more than one sorption mechanism. Shoulder formation due to heterogeneous sorbate solutions has been shown and discussed by Weigand and Totsche (1998) for the transport of dissolved organic matter, DOM, in goethite-coated sand. As DOM comprises a continuum of different organic substances, a fractionation of DOM during the transport into subcomponents differing in their reactivities occurs. However, ferrocyanide in the sorbate solution is not fractionated in our experiments, because i) at experimental pH ferrocyanide was completely dissociated (the dissociation constants for ferrocyanic acid are $pK_4 = 4.2$; $pK_3 = 2.2$; $pK_2 = pK_1 < 1$ (Jordan and Ewing, 1962)), and ii) ferrocyanide was not partially decomposed to free cyanide, because the experiments were performed in the absence of light. It has been established that decomposition of aqueous ferrocyanide occurs during irradiation by UV light or in the presence of a catalyst only (Rader et al., 1993). Therefore, fractionation of ferrocyanide cannot explain the shoulder

formation. The other aspect of shoulder formation is the presence of different sorption mechanisms. Rennert and Mansfeldt (2001, 2002b) proposed a combination of inner-sphere surface complexation and precipitation of a Berlin-Blue-like phase to explain the ferrocyanide sorption mechanism on goethite in the acidic range. However, the experimental pH was > 6 . At this pH, dissolution of goethite resulting in ferric ions in solution is negligible. This cation is required for the precipitation of Berlin Blue. Therefore, the formation of Berlin Blue during the experiments is excluded.

However, the presence of different sorption mechanisms is a possible reason for the failure of batch-derived parameters in predicting breakthrough curves. At least one of these sorption mechanisms should be rate-limited. If one of these sorption mechanisms is co-precipitation or precipitation, the goethite surface is changed due to sorption, which might explain hysteresis. The batch-derived parameters imply a homogeneous sorption process which does not occur in column experiments. The main questions arising from this conclusion are: what are these different sorption mechanisms; what are the relative proportions of these mechanisms in explaining the extent of sorption; and how can they be quantified in terms of sorption parameters in order to simulate breakthrough curves numerically.

Many studies reported on the transfer of batch-derived parameters to column experiments. A comparison of batch- and column-derived cadmium and methylene blue sorption data is given by Bürgisser et al. (1993). The sorption of neither substances was influenced by kinetics. The results of both experimental techniques were in good agreement using Freundlich isotherms. Similar naphthalene sorption coefficients measured by batch and column methods were found by MacIntyre et al. (1991). The agreement among coefficients was attributed to fast kinetics and linear sorption. Sorption nonequilibrium during transport can result in lower R values compared with those estimated from a batch isotherm (Brusseau et al., 1991). Batch data of benzene and dimethylphthalate sorption on sandy soils overestimated retardation coefficients compared with column data (Maraqa et al., 1998). On the other hand, retardation of uranium(VI) in subsurface media was underestimated by batch-derived adsorption isotherms (Barnett et al., 2000). Simulating the transport of uranium(VI) with a fractional order kinetic model yielded a good approximation of observed breakthrough data. These examples show that the transfer of batch-derived parameters to column experiments results in good agreement if the experimental conditions uniform flow field and laminar flow are fulfilled, and if sorption processes are known, i.e. they can be described in terms of isotherms, and are identical in

both experimental approaches. Conversely, if unknown sorption kinetics and hysteresis occur in column experiments, the prediction of breakthrough curves by batch-derived data should fail.

The “nonreactivity” of ferrocyanide in neutral sandy aquifer material assumed by Ghosh et al. (1999) may be caused by a strongly advective flow regime. As they did not give any information on the dispersivity of the system nor on sorption parameters, nonreactive behavior of ferrocyanide could not be inferred from their data. Rate-limited sorption of ferrocyanide combined with a strongly advective flow regime would yield a ferrocyanide breakthrough curve as they presented. Generally, goethite-coated sand at $\text{pH} > 6$ as used in this study can be regarded as a kind of neutral sandy aquifer material which significantly retarded both iron-cyanide complexes.

CONCLUSIONS

The transport of both iron-cyanide complexes in goethite-coated sand is characterized by rate-limited and nonlinear sorption.

In the case of ferricyanide, the sorption on goethite-coated sand in column experiments is roughly reflected by batch-derived Langmuir isotherm parameters, because the effects of flow interruptions on breakthrough curves are poorly simulated. This might be caused by different sorption and desorption kinetics resulting in hysteresis. However, the reaction of ferricyanide on the goethite surface should be the same in batch as well as in column experiments. A model including hysteresis should be used to simulate ferricyanide breakthrough curves in goethite-coated sand rather than a single isotherm approach.

The transfer of batch-derived sorption parameters on breakthrough curves derived from column experiments fails in the case of ferrocyanide. This might be caused by a heterogeneous sorption process of ferrocyanide on the goethite surface during transport. A single sorption isotherm as in batch experiments cannot be used to describe the sorption of ferrocyanide on goethite-coated sand in column experiments. Further research is necessary to enlighten the sorption processes of ferrocyanide during transport.

Column experiments are environmentally more realistic compared with batch experiments to predict the fate of chemical compounds in soil. This should be kept in mind when trying to transfer batch-derived ferrocyanide sorption data to sorption and transport processes occurring in soils on sites contaminated with ferrocyanide.

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CHAPTER 7

Sorption and transport of iron-cyanide complexes in
uncontaminated soil investigated in column experiments

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ABSTRACT

The occurrence of the iron-cyanide complexes ferrocyanide, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and ferricyanide, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ in soil and ground water is caused by disposal of industrial wastes and by the use of road salt containing ferrocyanide. We investigated the sorption and transport of iron-cyanide complexes in sandy uncontaminated soil (Ap horizon, Dystric Gleysol; 857 g sand kg^{-1} , organic C 18 g kg^{-1} , pH 5.8) in column experiments at saturated conditions and two concentrations, 0.03 and 10 mM $[\text{Fe}(\text{CN})_6]$. When using 10 mM, flow was interrupted for 36 h. Batch desorption experiments using phosphate and chloride were conducted to evaluate fractions of sorbed iron-cyanide complexes differing in their affinity for the soil matrix. Tracer breakthrough experiments using chloride indicated strongly advective flow in all experiments. The transport of both iron-cyanide complexes was characterized by rate-limited and nonlinear sorption affected by hysteresis. Rate-limited sorption was shown by the decrease of effluent concentrations after flow interruptions and by tailing. Nonlinear sorption became evident by the retardation of the breakthrough curves depending on influent concentrations. Breakthrough of ferrocyanide took longer than of ferricyanide indicating stronger sorption of ferrocyanide. The extent of iron-cyanide complex desorption depended on i) the amount of iron-cyanide complexes sorbed previously, ii) the type of complex sorbed, and iii) on the solution used to desorb. For an experiment, higher amounts of iron-cyanide complexes sorbed resulted in lower desorption; more ferricyanide than ferrocyanide was desorbed and phosphate desorbed more iron-cyanide complexes than chloride. Precipitation of iron-cyanide complexes following desorption experiments was indicated by the presence of blue precipitates in the soil matrix. Consequently, the sorption behavior of iron-cyanide complexes in uncontaminated soil was complex due to rate-limited and nonlinear sorption and precipitation. The experiments revealed that soils may act as a sink for iron-cyanide complexes at low concentrations, e.g. originating from the use of road salt or occurring in contaminated seepage and ground water. However, the long-term behavior of iron-cyanide complexes in this soil is characterized by continuous desorption.

INTRODUCTION

Iron-cyanide complexes ferrocyanide, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and ferricyanide, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, occur in soils and aquifers due to anthropogenic inputs from industrial wastes of cyanide-containing materials. Purifier wastes from coal gasification contain the ferric ferrocyanide Berlin Blue, $\text{Fe}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ (Shifrin et al., 1996). Blast furnace sludge, a waste of pig iron production, contains potassium zinc ferrocyanide nonahydrate, $\text{K}_2\text{Zn}_3[\text{Fe}^{\text{II}}(\text{CN})_6] \times 9\text{H}_2\text{O}$ (Mansfeldt and Dohrmann, 2001). De-inking sludge originating from paper recycling is used as a soil amendment and contains ferrocyanide in the form of $\text{A}_2\text{B}[\text{Fe}^{\text{II}}(\text{CN})_6]$, where $\text{A} = \text{K}^+$ or Na^+ , and $\text{B} = \text{Ca}^{2+}$ or a divalent transition metal, or $\text{B}_2[\text{Fe}^{\text{II}}(\text{CN})_6]$ (Mansfeldt, 2001). Unintentional input of ferrocyanide to the soil environment is given by the use of road salt containing Berlin Blue and/or sodium ferrocyanide, $\text{Na}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$, which are commonly added to road salt as anticaking agents (Ohno, 1990; Paschka et al., 1999). Model calculations by Paschka et al. (1999) showed that total cyanide concentrations in snow-melt runoff from a road after road salt application were up to 6 mg CN L^{-1} . In surface waters adjacent to sand-salt piles, total cyanide concentrations were up to 0.2 mg CN L^{-1} (Ohno, 1990).

Although the acute toxicity of metal-cyanide complexes is low, iron-cyanide complexes are potentially hazardous, because extremely toxic free cyanide, $\text{HCN}_{\text{g, aq}}$ and CN^-_{aq} , can be released in the presence of ultraviolet and sunlight radiation (Rader et al., 1993). Therefore, the transport of iron-cyanide complexes from soil into ground water and surface water is an environmental concern. On the other hand, both complexes are very stable due to their dissociation constants ($10^{-43.9}$ for ferricyanide, $10^{-36.9}$ for ferrocyanide; Beck, 1987). Consequently, exchange of the CN group or exchange of Fe with other cations in the iron-cyanide complexes is negligible.

Iron-cyanide complexes are known to be sorbed on soils (Ohno, 1990; Rennert and Mansfeldt, 2002a) and various soil constituents such as goethite (Theis et al., 1988; Rennert and Mansfeldt, 2001b, 2002b), amorphous aluminum oxide (Cheng and Huang, 1996), and ferrihydrite (Rennert and Mansfeldt, 2001a). The complexes are intercalated in hydrotalcite-like layered double hydroxides (Shaw et al., 1990; Hansen and Koch, 1994).

The nature of the interaction between iron-cyanide complexes and the sorbents mentioned above depends on both the type of the complex and the sorbent. Both ferricyanide and ferrocyanide were

sorbed by outer-sphere complexation on amorphous aluminum oxide (Cheng and Huang, 1996) as judged from surface complexation modeling, and precipitation of the complexes on the oxide surface did not occur as inferred from cyclic voltammetry (Shaw et al., 1990). The sorption behavior of ferricyanide and ferrocyanide on goethite was more complex as concluded from batch sorption/desorption experiments which included the effects of time, ionic strength, pH, and presence of sulfate (Rennert and Mansfeldt, 2001b, 2002b). Outer-sphere complexation and weak inner-sphere surface complexation was proposed for ferricyanide, whereas ferrocyanide was assumed to be sorbed by inner-sphere surface complexation and by precipitation of a Berlin-Blue-like phase in the acidic pH range (Rennert and Mansfeldt, 2001b, 2002b). The sorption of iron-cyanide complexes on ferrihydrite was similar to that on goethite, but weaker as judged from model calculations (Rennert and Mansfeldt, 2001a). Sorption of iron-cyanide complexes in soils was promoted by low pH, high contents of clay minerals, oxalate-extractable iron, and, in some cases, soil organic matter as inferred from multiple regression analysis and sorption experiments with soils in which soil organic matter was destroyed (Rennert and Mansfeldt, 2002a).

The aim of this study was to investigate the sorption and the transport of iron-cyanide complexes in uncontaminated soil by column experiments under saturated flow conditions as influenced by iron-cyanide complex concentration and flow interruptions. A relatively high concentration of iron-cyanide complexes was used to obtain a general insight into the sorption behavior of iron-cyanide complexes in uncontaminated soil. Low concentration of iron-cyanide complexes was used to enlighten the fate of iron-cyanide complexes under environmentally relevant conditions, e.g. occurring in snow-melt runoff from a road after road salt application or in contaminated seepage and ground water on sites of former manufactured gas plants. Batch desorption experiments were conducted to investigate different fractions of iron-cyanide complexes sorbed in soil.

The term sorption was used for all retention processes including two-dimensional adsorption and three-dimensional phenomena such as precipitation, co-precipitation, and diffusion as proposed by Scheidegger and Sparks (1996).

MATERIAL AND METHODS

Soil characterization

Soil was an Ap horizon of a Dystric Gleysol (Typic Halaquept) from Wageningen, The Netherlands. The soil was under agricultural production for 100 years. Soil chemical and physical properties were previously reported by Schmidt (1998) and Rennert and Mansfeldt (2002a): sand (0.063 - 2 mm) 857 g kg⁻¹; silt (0.002 - 0.063 mm) 109 g kg⁻¹; clay (< 0.002 mm) 33 g kg⁻¹; soil pH 5.8 (measured in 0.01 M CaCl₂); dithionite-citrate-extractable Fe 2.9 g kg⁻¹; oxalate-extractable Fe 1.9 g kg⁻¹; oxalate-extractable Al 0.9 g kg⁻¹; organic C 18 g kg⁻¹; total N 1.2 g kg⁻¹.

Column experiments

Dry soil was packed into cylindrical columns made of PVC (emc, Erfurt, Germany) with a length, L, of 7.4 cm and an inner diameter of 4 cm to a uniform bulk density. Porous ceramic plates were secured at the top and bottom of the columns. All displacing solutions were degassed before they were fed into the columns using a HPLC pump (Beckman System Gold, Beckman Instruments, München, Germany). Columns were saturated from bottom with 0.01 M NaNO₃ as a background electrolyte. All experiments were conducted under saturated conditions with a Darcian flux, q, of 0.02 cm min⁻¹.

The hydraulic regime was characterized by applying pulse inputs (0.75 to 1.75 pore volumes, pv) of 0.01 M NaCl as a tracer dissolved in the background electrolyte. A tracer experiment was carried out prior to all experiments with iron-cyanide complexes. For sorption experiments, solutions of K₃[Fe(CN)₆] or K₄[Fe(CN)₆] (reagent grade, Riedel-de Haën, Seelze, Germany) containing either 0.03 or 10 mM [Fe(CN)₆] in a background solution of 0.01 M NaNO₃ were used. In batch experiments, it was found that this soil sorbed both iron-cyanide complexes to large amounts at an initial concentration of 10 mM [Fe(CN)₆] (Rennert and Mansfeldt, 2002a). The low concentration 0.03 mM was used, because it was within the concentration range given by Paschka et al. (1999) for snow-melt runoff and within the concentration range found in seepage and ground water on sites of former manufactured gas plants as summarized by Kjeldsen (1999). The column as well as all tubes were wrapped with aluminum foil to minimize light interference when investigating the transport of

ferrocyanide. When using the 10 mM iron-cyanide complex concentration, about 2.4 pore volumes of an iron-cyanide complex solution were fed into the column, and then flow was interrupted for 36 h. After resuming flow an additional 1.6 pore volumes of 10 mM iron-cyanide complex solution was introduced to the column before being replaced by the background electrolyte. Experiments were terminated after about 10 pore volumes.

When using the 0.03 mM iron-cyanide complex concentration, pulse inputs (ferricyanide, 35 pore volumes; ferrocyanide, 36 pore volumes) were applied to the columns. Flow was not interrupted and the experiments were terminated after 53 pore volumes.

In all experiments, aliquots of the effluent solutions were collected in a fraction collector (Linear II, Reichelt Chemietechnik, Heidelberg, Germany). The solutions were then analyzed for chloride (tracer experiments), cyanide and pH (sorption experiments). All samples containing iron-cyanide complexes were stored in darkness.

Desorption experiments

After the column experiments, the soil was oven-dried at 333 K for 48 h. The desorption of residual bound iron-cyanide complexes was investigated using a batch technique with about 2.5 g soil and 25 ml of a solution containing either 1 M NaCl, 0.2 M NaH₂PO₄ (pH adjusted to 3.5), or 1 M NaOH in 50 ml polyethylene bottles in triplicate. Cyanide in the 1 M NaOH extracts represented total CN (Mansfeldt and Biernath, 2001). The samples were shaken horizontally for 24 h at 100 oscillations per minute in the dark. The phases were then separated by membrane filtration (0.45 µm cellulose nitrate filter). The filtrates were analyzed for cyanide in duplicate.

Analyses

Chloride concentrations in the effluent solutions were analyzed by ion chromatography with electrical conductivity detection (Dionex DX 500, Idstein, Germany). Cyanide concentrations in the effluent fractions as well as in the filtrates from the desorption experiments were determined using a micro-distillation technique according to Mansfeldt and Biernath (2000). All solutions were digested and distilled using a micro-distiller (Eppendorf-Netheler-Hinz, Hamburg, Germany). Subsequently, cyanide was determined colorimetrically with chloramine-T and barbituric acid-pyridine solution at 600 nm using a Lambda 2 spectrophotometer (Perkin Elmer, Überlingen,

Germany). The presence of free cyanide in the solutions was checked, and it was never found. Therefore, all cyanide analyzed colorimetrically was attributed to iron-cyanide complexes.

Data analysis

Bulk density, ρ , and volumetric water content, θ , were measured directly. The latter was determined gravimetrically after the experiments. Mean pore water velocity, v , was calculated from the flow rate Q ($v = Q / (A \times \theta)$), where A is the cross sectional area of the column. Relative concentrations, c/c_0 , are given by the ratio of effluent and influent concentrations. Breakthrough times are given as the number of pore volumes, pv , eluted,

$$pv = (q \times t_{btc}) / (\theta \times L),$$

where $q = Q/A$, Darcian flow, and t_{btc} = breakthrough time of the respective concentration. The computer code CXTFIT 2.1 (Toride et al., 1995) was used to determine the dispersion coefficient, D , and the retardation factor, R , by fitting the chloride breakthrough data to the advection-dispersion equation. Dispersivity, λ , is then given by D / v .

RESULTS

Column experiments

Experimental conditions of chloride breakthrough experiments and fitted parameters in uncontaminated soil are given in Table 1. Chloride breakthrough curves are shown in Figure 1. The columns in all experiments were nearly uniformly packed, because the parameters ρ , θ , and pv differed slightly only. Fitting the chloride breakthrough data to the advection-dispersion equation was highly significant, as the squares of the correlation coefficient r ranged from 0.974 to 0.999. The dispersion coefficients D ranged from $2.5 \times 10^{-3} \text{ cm}^2 \text{ min}^{-1}$ to $4.42 \times 10^{-3} \text{ cm}^2 \text{ min}^{-1}$, resulting in dispersivities λ from 0.067 to 0.123 cm. Therefore, the flow regime was strongly advective in all experiments, as column Peclet numbers Pe ranged from 60 to 111 ($Pe = L / \lambda$). As a further result of these fittings, the chloride retardation factors R were obtained, which ranged from 1.22 to 1.33. This indicated that chloride was not a conservative tracer, but slightly retarded by the soil.

Table 1 Experimental and fitted parameters of chloride breakthrough curves in uncontaminated soil.

Parameter [†]	Column experiment			
	#1	#2	#3	#4
c (mmol l ⁻¹)	0.01	0.01	0.01	0.01
v (cm min ⁻¹)	0.035	0.036	0.036	0.034
L (cm)	7.4	7.4	7.4	7.4
ρ (g cm ⁻³)	1.51	1.52	1.5	1.49
θ (cm ³ cm ⁻³)	0.45	0.44	0.44	0.47
pv (cm ³)	41.7	41.5	42.5	43.8
D (cm ² min ⁻¹)	2.36 × 10 ⁻³	4.42 × 10 ⁻³	3.30 × 10 ⁻³	3.10 × 10 ⁻³
λ (cm)	0.067	0.123	0.069	0.092
Pe	111	60	81	81
R	1.33	1.29	1.28	1.22
r ²	0.999	0.974	0.995	0.993

[†] c, concentration of influent solution; v, pore water velocity; L, length of the column; ρ, bulk density; θ, volumetric water content; pv, pore volume; D, dispersion coefficient; λ, dispersivity; Pe, column Peclet number; R, retardation factor; r², square of the correlation coefficient.

Furthermore, the symmetry of the chloride breakthrough curves and the highly significant fittings indicated the absence of physical nonequilibrium.

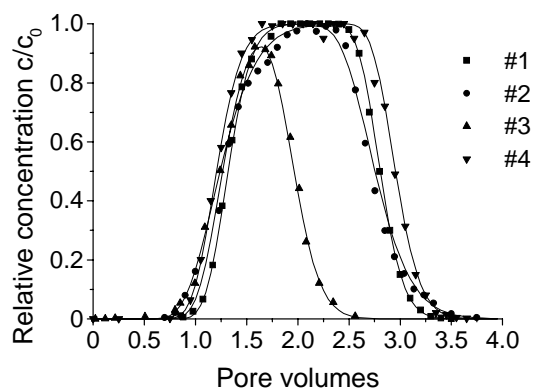


Figure 1 Breakthrough curves of chloride in uncontaminated soil. Lines result from fitting the sorption data to the advection-dispersion equation.

Experimental conditions of iron-cyanide complex breakthrough experiments are given in Table 2.

Table 2 Experimental parameters of iron-cyanide breakthrough curves in uncontaminated soil.

Parameter [†]	Ferricyanide		Ferrocyanide	
	-	Flow interruption	-	2360 min
		2384 min		
c (mmol l ⁻¹)	0.031	10.1	0.032	10.7
v (cm min ⁻¹)	0.034	0.035	0.035	0.036
L (cm)	7.4	7.4	7.4	7.4
ρ (g cm ⁻³)	1.49	1.51	1.5	1.51
θ (cm ³ cm ⁻³)	0.47	0.45	0.46	0.44
pv (cm ³)	43.8	41.7	42.5	41.5
λ (cm)	0.092	0.067	0.069	0.123

[†] c, concentration of influent solution; v, pore water velocity; L, length of the column; ρ, bulk density; θ, volumetric water content; pv, pore volume; λ, dispersivity.

Breakthrough curves of iron-cyanide complexes at the high initial concentration (10 mM) are presented in Fig. 2. Ferricyanide revealed early (at < 1 pore volume) and steep breakthrough. The concentration was constant after about 1.4 pore volumes. After the flow interruption, the concentration decreased to $c/c_0 = 0.6$, which indicated rate-limited sorption. Then the concentration rose quickly to the maximum value, $c/c_0 = 1$. After replacing the feeding solution with cyanide-free background electrolyte solution, the concentrations quickly dropped and were then constant on a low level, $c/c_0 = 0.006$ ($\approx 12 \text{ mg } [\text{Fe}(\text{CN})_6]^{3-} \text{ l}^{-1}$).

Similarly, ferrocyanide showed early breakthrough, but not as steep as that of ferricyanide. After about 1.7 pore volumes, the slope decreased. Ferrocyanide sorption was also rate-limited, as c/c_0 dropped from 0.75 to 0.54 after the flow interruption. The maximum concentration $c/c_0 = 1$ was not reached after resuming the flow. Like in the case of ferricyanide, the desorption front of ferrocyanide exhibited tailing at about $c/c_0 = 0.04$ ($\approx 80 \text{ mg } [\text{Fe}(\text{CN})_6]^{4-} \text{ l}^{-1}$), but tailing was on a higher level than that of ferricyanide breakthrough. The breakthrough curves showed that sorption of both complexes was rate-limited. The ferrocyanide breakthrough was less steep than that of ferricyanide, which might indicate that ferrocyanide was sorbed more strongly.

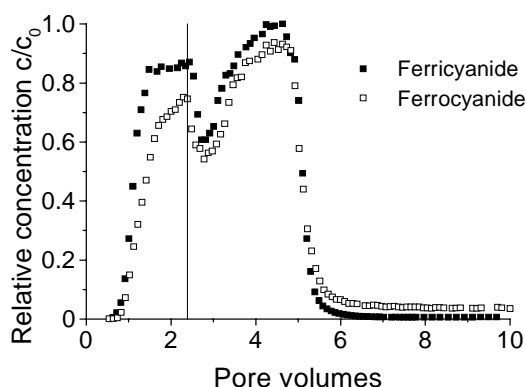


Figure 2 Breakthrough curves of ferricyanide and ferrocyanide in uncontaminated soil (influent concentration was 10 mM $[\text{Fe}(\text{CN})_6]$). The vertical line indicates the beginning of a flow interruption.

Breakthrough curves of iron-cyanide complexes at the low initial concentration (0.03 mM) are presented in Figure 2.

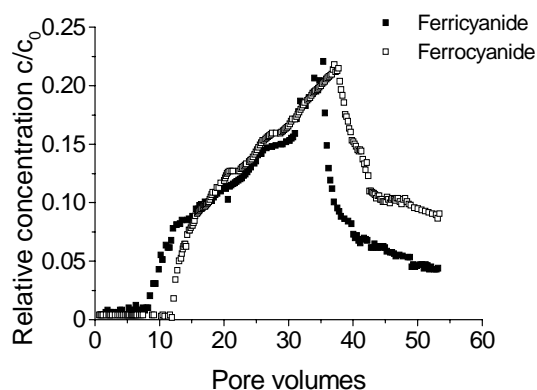


Figure 3 Breakthrough curves of ferricyanide and ferrocyanide in uncontaminated soil (influent concentration was 0.03 mM $[\text{Fe}(\text{CN})_6]$).

Note the different y-axis scale compared to Fig. 2. Both breakthrough curves were extremely asymmetrical, and the breakthrough of both complexes was retarded compared to the curves in Fig. 2, as the rise of relative concentrations began after 8 pore volumes (ferricyanide) and 10 pore volumes (ferrocyanide). Even after about 35 pore volumes eluted, only 22% of the influent concentration were detected in the effluent for both iron-cyanide complexes indicating slow increase of the relative concentrations with time. The desorption fronts of both complexes were largely affected by tailing, as ferrocyanide concentrations remained nearly constant at $c/c_0 = 0.1$, and ferricyanide concentrations at $c/c_0 = 0.05$. Based on relative concentrations, the tailing levels for both complexes were higher when using the low concentrations.

Desorption experiments

The results of the desorption experiments with two different solutions are shown in Table 3. The total amounts of iron-cyanide complexes sorbed after conducting the column experiments differed, as two different influent concentrations were used. A great difference between the amounts of the two iron-cyanide complexes sorbed was found when using the high influent concentration. The percental extraction of iron-cyanide complexes was higher for the soils used in the low concentration experiments. Generally, less iron-cyanide complexes were extracted by chloride than by phosphate and less iron-cyanide complexes were extracted from soil when the influent solution contained

ferrocyanide compared to soil that sorbed ferricyanide indicating stronger sorption of ferrocyanide. Stronger sorption of ferrocyanide is caused by the different sorption mechanisms of the two iron-cyanide complexes as pointed out in the introduction. Iron-cyanide complexes desorbed by chloride can be attributed to a weakly bound fraction, comparably to outer-sphere complexed sulfate extracted from forest soils by 1 M Cl⁻ (Alewell and Matzner, 1996). According to Rennert and Mansfeldt (2002b), all ferricyanide sorbed on goethite, and presumably on other iron (hydr)oxides, was desorbed by chloride. Iron-cyanide complexes, which formed inner- and outer-sphere surface complexes on goethite, are extracted by pH-adjusted 0.2 M H₂PO₄⁻ solution (Rennert and Mansfeldt, 2002b). Therefore, the difference between the amounts extracted by 1 M Cl⁻ and 0.2 M H₂PO₄⁻ ($\Delta_{\text{extracted}}$ in Table 3) may be attributed to inner-sphere complexed iron-cyanide complexes. Consequently, ferrocyanide formed more inner-sphere surface complexes on the soil surface than ferricyanide.

Table 3 Cyanide concentration in soil after the column experiments and percental extraction of cyanide.

Sample	[Fe(CN) ₆] [†] (mg kg ⁻¹)	----- % extracted by [‡] -----		$\Delta_{\text{extracted}}$ (%) [§]
		PO ₄	Cl	
+ 10 mM [Fe(CN) ₆] ³⁻	229	23.7	18.4	5.3
+ 10 mM [Fe(CN) ₆] ⁴⁻	435	18.2	9.2	9.0
+ 0.03 mM [Fe(CN) ₆] ³⁻	48.8	99.0	91.4	7.6
+ 0.03 mM [Fe(CN) ₆] ⁴⁻	49.0	67.8	53.4	14.4

[†] total cyanide extracted by 1 M NaOH and recalculated to [Fe(CN)₆]

[‡] extracted by 0.2 M NaH₂PO₄ (pH adjusted to 3.5) or by 1 M NaCl

[§] % extracted by PO₄ - % extracted by Cl

Only in soil used in the experiments with the high concentrations of iron-cyanide complexes, blue particles were clearly visible. These blue particles were not present in soil before the experiments were conducted indicating precipitation of cyanide-containing phases during the experiments.

Precipitates are not dissolved by pH-adjusted 0.2 M H_2PO_4^- solution (Rennert and Mansfeldt, 2002b). However, 23.7% was the maximum extracted with the phosphate solution from soil used in the high concentration experiments. Consequently, the results of the desorption experiments indicated the presence of more sites in soil for sorption, and therefore the presence of more fractions of iron-cyanide complexes sorbed in soils than previously known.

DISCUSSION

The asymmetrical breakthrough curves presented for both iron-cyanide complexes indicated that transport may be influenced by nonlinear sorption, rate-limited sorption, physical nonequilibrium (i.e. heterogeneous porous media) or by a combination of these processes (Brusseau, 1998). Physical nonequilibrium can be excluded due to the shapes of chloride breakthrough curves in the sandy substrate (Fig. 1) and the modeling results (Table 1). Rate-limited sorption of iron-cyanide complexes was shown by the effect of flow interruption (Fig. 2). As can be seen from a comparison of the Fig. 2 and 3, the position of the breakthrough curves depended on the influent concentration. Consequently, retardation depended on concentration, which was caused by nonlinear sorption (Crittenden et al., 1986). Furthermore, the slopes of the breakthrough curves decreased with decreasing concentrations. Therefore, the transport of both iron-cyanide complexes in uncontaminated soil was characterized by rate-limited and nonlinear sorption. In batch experiments investigating the sorption of iron-cyanide complexes in soils, Rennert and Mansfeldt (2002a) found nonlinear sorption for both complexes in this soil with Langmuir sorption maxima of $58.5 \text{ mmol kg}^{-1}$ for ferricyanide and $70.2 \text{ mmol kg}^{-1}$ for ferrocyanide. They showed that sorption of iron-cyanide complexes was largely governed by soil organic matter, SOM. Ferricyanide sorption was diminished by 87% and ferrocyanide sorption by 98% after destruction of soil organic matter. Therefore, SOM should also govern sorption in this soil investigated in column experiments as it should be the most important sorbent. Unfortunately, the reactions of iron-cyanide complexes with SOM have not been investigated in detail yet. Schenk and Wilke (1984) showed the reaction between CN-N and quinone

groups of soil humic acids using IR spectroscopy. This is a possible reaction explaining the interaction of iron-cyanide complexes and SOM (Rennert and Mansfeldt, 2002a).

However, according to the transport experiments as well as to the desorption experiments, sorption in this soil is more complicated. Precipitation reactions are indicated by the presence of blue particles in soil after the column experiments. Precipitation of Berlin Blue from solution should be excluded, as the pH of the effluent solution ranged from 6.0 to 6.9. The blue phases may originate from co-precipitation on the soil surface or from precipitation of iron-cyanide complexes with alkali and alkaline earth cations. These precipitates are also bluish (Mansfeldt, 2001).

Further observations indicate precipitation, specifically, ferricyanide concentrations revealed a plateau before flow interruption, but shifted quickly to the maximum concentration after resuming the flow. This behavior indicates precipitation, because after resuming flow, assuming sorption processes did not change, concentrations should raise to the same level as before flow was interrupted. It is imaginable that precipitates inactivate the soil surface partially, and adsorption occurs continuously on the now limited soil surface resulting in the relatively quick shift of concentrations to a high level after resuming the flow. Precipitation processes explain the asymmetrical breakthrough curves which indicate the occurrence of hysteresis. Hysteresis can be caused by changes of the sorbent surface due to precipitation as described above. Consequently, the sorption and desorption fronts are not congruent.

The extent of iron-cyanide complexes extraction depended on the amounts of residually bound iron-cyanide complexes (Table 3), and therefore on the influent concentration. Generally, precipitation and/or co-precipitation is more likely at high surface coverage than at low surface coverage (Scheidegger and Sparks, 1996). Therefore, adsorption should dominate retardation of iron-cyanide complexes at an initial concentration of 0.03 mM, and both adsorption and precipitation should dominate retardation at an initial concentration of 10 mM. This, additionally to the batch desorption experiments shown in Table 3, becomes clear from the tailing of the desorption fronts of the breakthrough curves at different concentrations, because in the case of the low concentration, tailing is on higher levels compared to the experiments with the high concentration. Unlike precipitates, adsorbed iron-cyanide complexes are desorbed by the flow of the background electrolyte to some extent.

As the strength of interactions between iron-cyanide complexes and SOM is still unknown, an appropriate agent to desorb the complexes is unknown, too. However, it is very unlikely that the solutions used are such an appropriate agent. Therefore, it is not possible to attribute iron-cyanide complexes not being desorbed to precipitates or to iron-cyanide-SOM complexes quantitatively.

Precipitates were found in soil in which ferricyanide was sorbed, although iron-cyanide present in solid phases contain ferrocyanide. Therefore, it is likely that reduction of ferricyanide to ferrocyanide occurred. An example is the formation of a Berlin-Blue-like film on the surface of layered double hydroxide by ferricyanide after reduction to ferrocyanide (Shaw et al., 1990). The presence of Zn was necessary for the formation of this film, and Al was involved when available. As shown by Leal et al. (1998), ferricyanide was reduced to ferrocyanide by a large number of organic compounds, e.g. phenols, alcohols, ketones, sugars, and aromatic hydrocarbons. These compounds are present in functional groups of SOM, which is therefore a possible soil constituent catalyzing the reduction of ferricyanide, whereas Fe and Al oxides do not act as a redox catalyst.

Simulations with batch derived Langmuir parameters taken from Rennert and Mansfeldt (2002a) as well as inverse modeling using linear, Freundlich and Langmuir isotherms failed, because the calculated data did not describe the actual breakthrough curves at all (simulations not shown here). However, this could have been expected due to the complexity of sorption behaviors revealed in the experiments. It is not useful to use a single isotherm to describe sorption which is characterized by inner-sphere-, outer-sphere complexation, precipitation, and, additionally, sorption kinetics. In order to simulate iron-cyanide complex breakthroughs sufficiently, mathematical and chemical descriptions of all the processes involved is necessary, but this is not possible with the data and information from the literature.

Ghosh et al. (1999) assumed nonreactive transport of iron-cyanide complexes in neutral sandy aquifer material as judged from column experiments. Although their data did not prove nonreactivity, low retardation of the complexes in their experiments can be attributed to neutral pH, low amounts of sesquioxides, and lack of reactive organic matter. After Fuller (1985), ferricyanide sorption in column experiments was dominated by soil clay contents and soil pH. He also used a leachate from a gas works site soil in displacement experiments and inferred precipitation of Berlin Blue from breakthrough curves. This might be caused by the presence of ferrocyanide, which is the dominant iron-cyanide species in leachate from gas works site soils (Theis et al., 1994).

The investigations by Fuller (1985), Ghosh et al. (1999), and Rennert and Mansfeldt (2002a) showed that the extent as well as the strength of iron-cyanide complex sorption in soils depended on soil composition. This is implicated by the various types of interactions of iron-cyanide complexes on mineral and organic surfaces and by largely heterogeneous soil composition. Therefore, the results presented here cannot be transferred to all soils. However, due to the large influence of SOM on sorption, iron-cyanide complexes should be less mobile in humic A horizons than in neutral subsurface horizons. Predictions of the sorption of iron-cyanide complexes in contaminated gas works site soils derived from the results presented here are difficult, because i) iron-cyanide complexes are deposited as solid phases, and ii) the contents of SOM may be low. The release of iron-cyanide complexes from contaminated soil has been found to be rate-limited as judged from column experiments under dispersive flow conditions (Weigand et al., 2001).

Based on Na concentrations, total cyanide concentrations in surface water samples adjacent to road salt storage facilities were predicted by Ohno (1990). The observed cyanide concentrations were always lower than the predicted ones. Sorption of iron-cyanide complexes in soils may be the reason for this discrepancy. However, as shown by rate-limited desorption of iron-cyanide complexes in the column experiments presented in this study, soils do not act as an instantaneous sink necessarily, because continuous desorption may occur due to hysteresis. Therefore, the release of sorbed ferrocyanide originating from road salt in soils may be low, but lasting. Ferricyanide sorption is presumably diminished by the large chloride concentration in snow-melt runoff, but ferricyanide is not added to road salt.

CONCLUSIONS

Both ferricyanide and ferrocyanide revealed a complex sorption behavior in uncontaminated soil due to rate-limited and nonlinear sorption and transport affected by hysteresis and precipitation of iron-cyanide containing phases. The knowledge of the type of iron-cyanide complexes present in soil, i.e. ferricyanide or ferrocyanide, is necessary for the prediction of their fate in soil and ground water, because of different sorption and transport behaviors of both complexes. A short-term consequence

of ferrocyanide inputs is sorption in soil. However, the extent of sorption depends on soil properties (contents of soil organic matter and Fe oxides, pH), and sorption is rate-limited. Thus, soils are not instantaneous sinks for ferrocyanide. The long-term behavior of sorbed ferrocyanide is characterized by rate-limited desorption, and therefore by continuous release of sorbed ferrocyanide into soil solution.

It is necessary to enlighten the sorption mechanisms of iron-cyanide complexes and soil organic matter in future investigations. These investigations should include spectroscopic techniques to identify functional groups of soil organic matter, which sorb iron-cyanide complexes. Furthermore, precipitates formed during iron-cyanide complex transport in soil should be identified. Then a model for predictions of iron-cyanide complex sorption and transport may be possible to formulate.

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CHAPTER 8

Sorption and desorption of iron-cyanide complexes in
deposited blast furnace sludge

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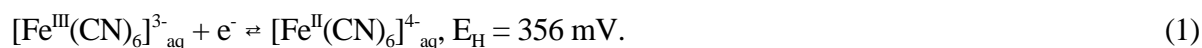
Water Research (2002), accepted

ABSTRACT

Blast furnace sludge is a waste originating from pig iron production and contains small amounts of iron-cyanide complexes. Leaching of iron-cyanide complexes from deposited blast furnace sludge into the ground water seems to be possible in principle. We investigated the sorption of the iron-cyanide complexes ferrocyanide, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and ferricyanide, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, in 22 samples of deposited blast furnace sludge in batch experiments. Subsequently, desorption of iron-cyanide complexes was investigated using 1 M NaCl. Sorption in 5 samples was evaluated with Langmuir isotherms. The blast furnace sludge samples were neutral to slightly alkaline (pH 7.6 to 9) and consisted of X-ray amorphous compounds and crystalline iron oxides primarily. X-ray amorphous compounds are assumed to comprise coke-bound carbon and amorphous iron, zinc, and aluminum oxides. The experiments that were evaluated with Langmuir isotherms indicated that the extent of ferricyanide sorption was higher than that of ferrocyanide sorption. Saturation of blast furnace sludge with iron-cyanide complexes was achieved. Sorption of iron-cyanide complexes in 22 blast furnace sludge samples at one initial concentration showed that 12 samples sorbed more ferrocyanide than ferricyanide. The extent of sorption largely differed between 0.07 and 2.76 $\mu\text{mol} [\text{Fe}(\text{CN})_6] \text{ m}^{-2}$ and was governed by coke-bound carbon. Ferricyanide sorption was negatively influenced by crystalline iron oxides additionally. Only small amounts of iron-cyanide complexes sorbed in blast furnace sludge were desorbed by 1 M NaCl (ferrocyanide, 3.2%; ferricyanide, 1.1%, given as median). This indicated strong interactions of iron-cyanide complexes in blast furnace sludge. The mobility of iron-cyanide complexes in deposited blast furnace sludge and consequently contamination of the seepage and ground water was designated as low, because i) deposited blast furnace sludge is able to sorb iron-cyanide complexes strongly, ii) the solubility of the iron-cyanide-containing phase, $\text{K}_2\text{Zn}_3[\text{Fe}^{\text{II}}(\text{CN})_6] \times 9\text{H}_2\text{O}$, is known to be low, and iii) a worst case scenario of the transport of iron-cyanide complexes within the blast furnace sludge deposit indicated strong retardation of the complexes within the next 100 years.

INTRODUCTION

Blast furnace sludge originates from pig iron production. Before reuse in the operation process, the top gas of a blast furnace is cleaned up by wet purification resulting in a muddy blast furnace sludge. As the sludge is worthless, it is pumped and stored in surface deposits where the sludge is de-watered. Blast furnace sludge mainly consists of coke and iron oxides (Lopez et al., 1991). Recently, the crystalline cyanide-containing compound $K_2Zn_3[Fe^{II}(CN)_6] \times 9H_2O$ has been identified in blast furnace sludge by X-ray diffraction analysis (Mansfeldt and Dohrmann, 2001). Its solubility product constant, $K_{sp} = 5.5 \times 10^{-39}$, indicates low solubility (Bellomo, 1970). The total cyanide content in blast furnace sludge can be up to 4 g CN kg⁻¹ (Mansfeldt and Dohrmann, 2001). This compound contains the iron-cyanide complex ferrocyanide, $[Fe^{II}(CN)_6]^{4-}$, which can be oxidized to ferricyanide, $[Fe^{III}(CN)_6]^{3-}$, in aqueous solution



Soils can develop on sites of abandoned blast furnace sludge deposits (Mansfeldt and Dohrmann, 2001). Generally, iron-cyanide complexes are of anthropogenic origin in soils. Industrial activities have led to contaminations with iron-cyanide complexes in soil and ground water. Further sources of iron-cyanide complexes in soil and ground water are:

- deposition of purifier wastes containing Berlin Blue, $Fe_4[Fe(CN)_6]_3$, on sites of former manufactured gas plants and coke ovens (Shifrin et al., 1996);
- use of road salt containing Berlin Blue and/or $Na_4[Fe(CN)_6]$ (Ohno, 1990; Paschka et al., 1999);
- and use of paper de-inking sludge containing $A_2B[Fe^{II}(CN)_6]$ ($A = K^+$ or Na^+ , $B = Ca^{2+}$) or $B_2[Fe^{II}(CN)_6]$ ($B =$ divalent transition metal) as a soil amendment (Mansfeldt, 2001).

Iron-cyanide complexes are potentially hazardous, because they can be converted to extremely toxic free cyanide, CN^-_{aq} and $HCN_{g,aq}$, in the presence of UV light (Rader et al., 1993). This might occur when iron-cyanide complexes are transported into surface water via the ground water, or when ground water contaminated with iron-cyanide complexes is used for irrigation.

Various solid phases are known to sorb iron-cyanide complexes e.g. goethite, $\alpha\text{-FeOOH}$ (Theis et al., 1988; Rennert and Mansfeldt, 2001b, 2002b), ferrihydrite, $Fe_2O_3 \times nH_2O$, $n = 1$ to 3 (Rennert and

Mansfeldt, 2001a), amorphous aluminum oxide, $\gamma\text{-Al}_2\text{O}_3$ (Cheng and Huang, 1996), soils (Ohno, 1990; Rennert and Mansfeldt, 2002a), and activated carbon (Saito, 1984).

The objective of this study was to investigate the ability of deposited blast furnace sludge to sorb iron-cyanide complexes and the desorption of sorbed iron-cyanide complexes by 1 M NaCl. We used this solution, because it desorbs weakly adsorbed, i.e. outer-sphere complexed, iron-cyanide complexes only (Rennert and Mansfeldt, 2002b). Chemical and mineralogical properties of the blast furnace sludge samples were used to explain the extent of sorption by multiple regression analysis. These experiments were carried out to improve the understanding of the fate of iron-cyanide complexes in blast furnace sludge deposits.

MATERIAL AND METHODS

Blast furnace sludge samples

Twenty-two samples from an abandoned blast furnace sludge deposit in the Ruhr-area, North-Rhine Westphalia, Germany, were collected in nine excavated pits. The deposit had been in operation between 1930 and 1983. Today the site is covered by vegetation. Humus accumulation in the surface layer indicates the beginning of soil development.

The samples were taken from depths ranging from the top of the pits to 100 cm. They were dried at 333 K and sieved to 2 mm. Total cyanide contents and pH of the samples were adapted from Mansfeldt and Dohrmann (2001). The BET surface areas were determined by N_2 adsorption. Blast furnace sludge was characterized by X-ray diffraction, XRD, as described by Mansfeldt and Dohrmann (2001). The contents of X-ray amorphous compounds and iron oxides were quantified from the XRD spectra by Rietveld analysis using the program AutoQuan which is part of the Rietveld software BGMN (Bergmann, Dresden, Germany).

Sorption experiments

All sorption experiments were carried out in darkness by a batch technique using 50-ml polyethylene bottles at 283 K, 150 horizontal oscillations per minute, and a reaction time of 24 h. This reaction

time has been found to be sufficient to reach an equilibrium in all studies investigating the sorption of iron-cyanide complexes mentioned in the introduction. Three sets of experiments were carried out. The sorption of iron-cyanide complexes was investigated with varying concentrations with five blast furnace sludge samples. This was done to estimate the extent of sorption using sorption isotherms. In the second set of experiments, the sorption of iron-cyanide complexes in 22 blast furnace sludge samples was investigated at one initial concentration. In the third step, the desorption of iron-cyanide complexes from the samples of the second set was examined. All experiments were carried out in duplicate.

For the first set of sorption experiments, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (reagent grade, Riedel-de Haën, Seelze, Germany) were used. From these salts stock solutions containing $2000\text{ mg CN}^- \text{ l}^{-1}$ were prepared. About 1.25 g blast furnace sludge was suspended in 25 ml demineralized H_2O and up to 12 subsamples of a stock solution were added to gain initial concentrations ranging from 0 to 4.8 mmol $[Fe(CN)_6] \text{ l}^{-1}$. The initial concentrations varied depending on the sample and the iron-cyanide complex. Ionic strength was adjusted to 0.01 M ($NaNO_3$).

Again, about 1.25 g blast furnace sludge and 25 ml demineralized H_2O were used for the second set of experiments (22 blast furnace sludge samples). The initial iron-cyanide complex concentration was 3.8 mmol $[Fe(CN)_6] \text{ l}^{-1}$. The same stock solutions were used as mentioned above. Ionic strength was 0.01 M.

After all sorption experiments, the phases were separated by membrane filtration (0.45 μm cellulose nitrate filter). For the desorption experiments, the filters of the second set of experiments were air-dried. Then, about 0.5 g of the dried samples was suspended in 10 ml 1 M NaCl and shaken for further 24 h. Again, the phases were separated by membrane filtration.

All filtrates were distilled using a micro-distillation technique (MicroDistiller, Eppendorf-Netheler-Hinz, Hamburg, Germany). By this procedure, iron-cyanide complexes are converted to HCN which is absorbed by an alkaline solution. Subsequently, cyanide was determined colorimetrically at 600 nm (Lambda 2, Perkin Elmer, Überlingen, Germany) using a barbituric acid-pyridine solution. All colorimetric analyses were carried out in duplicate. The total procedure is described in detail by Mansfeldt and Biernath (2000). Additionally, the presence of free cyanide in the filtrates was checked. Free cyanide was never found. Therefore, all cyanide in the distillates originated from iron-cyanide complexes.

Data analysis

The first set of sorption experiments was evaluated with the Langmuir isotherm

$$S = \frac{S_{\max} \times K \times c}{1 + K \times c}, \quad (2)$$

where S is the sorbed amount ($\mu\text{mol m}^{-2}$), S_{\max} is the sorption maximum ($\mu\text{mol m}^{-2}$), c is the equilibrium concentration (mmol l^{-1}), and K (l mmol^{-1}) is the Langmuir isotherm constant.

Statistical analysis

All statistical calculations were performed with SPSS 10.0 (SPSS Inc., Chicago). Multiple linear regressions were conducted with the amounts of iron-cyanide complexes sorbed ($\mu\text{mol m}^{-2}$) from the second set of experiments as dependent variables and chemical blast furnace sludge properties as independent variables. The significance of the regression equations were checked by variance analysis (F-test) on a confidence level of 0.99. The significance and the importance as explanatory variables of the parameters were checked using T-tests. Regression equations were recalculated without those variables which were not significant or important or both as explanatory variables due to the results of the T-tests.

Calculation of iron-cyanide complex transport

In order to obtain an approximation of the fate of iron-cyanide complexes in the blast furnace sludge deposit from which the samples were taken, we calculated the transport of iron-cyanide complexes within the first 1 m of the deposit. These calculations were conducted with the numerical computer code CARRY (Totsche et al., 1996) in which the one-dimensional water movement was described with the advection-dispersion equation, and sorption of iron-cyanide complexes was described with Langmuir parameters obtained from the first set of sorption experiments. We used the following parameters: saturated water content $\theta = 0.82 \text{ cm}^3 \text{ cm}^{-3}$; dry bulk density $\rho = 0.49 \text{ g cm}^{-3}$ (Mansfeldt, 2002); water input into the deposit by precipitation was 200 mm a^{-1} according to the climatic water balance of this region (de Haar et al., 1979); and iron-cyanide complex concentration in the pore water was $1.12 \times 10^{-2} \text{ mmol l}^{-1}$ (Mansfeldt, 2002). In the calculations, we assumed equilibrium

sorption (i.e. no kinetic effects), absence of lateral and preferential flow, and a dispersive flow regime for a duration of 100 a.

RESULTS

Chemical properties of the blast furnace sludge samples are presented in Table 1. The data were partially adapted from Mansfeldt and Dohrmann (2001). All samples were neutral or slightly alkaline with pH values ranging from 7.6 to 9.0. All blast furnace sludge samples consisted of X-ray amorphous compounds primarily. These compounds should comprise coke-bound carbon and amorphous iron, zinc, and aluminum oxides. In contrast to inorganic carbon, coke-bound carbon varied in a range from 46 to 405 g C kg⁻¹. Crystalline iron oxides were present in considerable amounts, ranging in their sum from 23 to 154 g kg⁻¹. Therefore, similar to the results of Lopez et al. (1991), coke-bound carbon and iron oxides are important constituents of blast furnace sludge samples investigated here.

Table 1 Chemical and mineralogical properties of 22 blast furnace sludge samples. Data for pH and cyanide are adapted from Mansfeldt and Dohrmann (2001).

Parameter	Mean	Minimum	Maximum
pH [†]	8.2	7.6	9.0
BET surface area (m ² g ⁻¹)	62 ± 19 [‡]	15	90
	----- (g kg ⁻¹) -----		
coke-bound carbon	187 ± 108	46	405
inorganic carbon	19 ± 6	8	28
X-ray amorphous	628 ± 87	474	813
Σ HMW [§]	83 ± 41	23	154
total cyanide	1.4 ± 0.9	0.4	3.9

[†] determined in 0.01 M CaCl₂; [‡] standard deviation; [§] sum of haematite, magnetite and wüstite

The BET surface areas ranging from 15 to 90 m² g⁻¹ are higher than those found by Lopez-Delgado et al. (1996) for two blast furnace sludge samples differing in their coke content (27 and 17 m² g⁻¹). They observed a decrease of the BET surface area with increasing coke content, as they also analyzed a coke sample (8 m² g⁻¹). This relationship is not given for the samples used here. In our blast furnace sludge samples, cyanide is present as K₂Zn₃[Fe^{II}(CN)₆] × 9H₂O (Mansfeldt and Dohrmann, 2001) with contents ranging from 0.4 to 3.9 g CN kg⁻¹. Quartz, kaolinite and elementary iron were detected in almost all samples additionally. The sorption of iron-cyanide complexes in blast furnace sludge at different concentrations is shown in Figure 1.

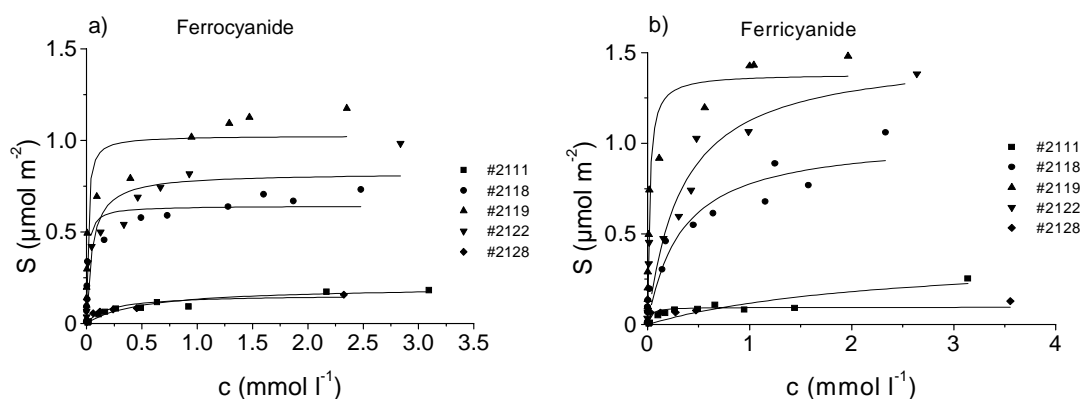


Figure 1 Sorption of iron-cyanide complexes in blast furnace sludge (a, ferrocyanide; b, ferricyanide). Langmuir parameters for ferrocyanide sorption: #2111, $S_{\text{max}} = 0.2 \mu\text{mol m}^{-2}$; $K = 1.9 \text{ l mmol}^{-1}$; #2118, $S_{\text{max}} = 0.64 \mu\text{mol m}^{-2}$; $K = 71.7 \text{ l mmol}^{-1}$; #2119, $S_{\text{max}} = 1.0 \mu\text{mol m}^{-2}$; $K = 83.4 \text{ l mmol}^{-1}$; #2122, $S_{\text{max}} = 0.82 \mu\text{mol m}^{-2}$; $K = 18.8 \text{ l mmol}^{-1}$; #2128, $S_{\text{max}} = 0.16 \mu\text{mol m}^{-2}$; $K = 4.7 \text{ l mmol}^{-1}$. Langmuir parameters for ferricyanide sorption: #2111, $S_{\text{max}} = 0.39 \mu\text{mol m}^{-2}$; $K = 0.4 \text{ l mmol}^{-1}$; #2118, $S_{\text{max}} = 1.0 \mu\text{mol m}^{-2}$; $K = 3.0 \text{ l mmol}^{-1}$; #2119, $S_{\text{max}} = 0.38 \mu\text{mol m}^{-2}$; $K = 53.7 \text{ l mmol}^{-1}$; #2122, $S_{\text{max}} = 1.51 \mu\text{mol m}^{-2}$; $K = 2.9 \text{ l mmol}^{-1}$; #2128, $S_{\text{max}} = 0.1 \mu\text{mol m}^{-2}$; $K = 38.3 \text{ l mmol}^{-1}$.

The sorption of both iron-cyanide complexes was approximately described by Langmuir isotherms. Sorption of both complexes was similar, as the affinity of the blast furnace sludge samples for iron-cyanide complexes decreased in the sequence #2119 > #2122 > #2118 > #2111 \approx #2128. Generally, the extent of ferrocyanide sorption was smaller than that of ferricyanide sorption. At large

concentrations, the samples were saturated with iron-cyanide complexes. Therefore, an initial concentration of 3.8 mmol $[\text{Fe}(\text{CN})_6]^-$ was used in the second set of experiments, because all blast furnace sludge samples were saturated at this initial concentration.

The sorption of iron-cyanide complexes in blast furnace sludge at an initial concentration of 3.8 mmol $[\text{Fe}(\text{CN})_6]^-$ and subsequent desorption by 1 M NaCl is summarized in Table 2. Except for two samples (ferrocyanide, #2102 and #2114), which released cyanide during the sorption experiments, all blast furnace sludge samples sorbed considerable amounts of both complexes. The sorbed amounts differed largely for ferrocyanide (0.16 to 2.13 $\mu\text{mol m}^{-2}$) as well as for ferricyanide sorption (0.07 to 2.76 $\mu\text{mol m}^{-2}$).

Unlike in the first set of experiments, 12 blast furnace sludge samples sorbed more ferrocyanide than ferricyanide. The sample #2123 revealed the greatest affinity for both complexes. For comparison, the modelled maximum sorption of both iron-cyanide complexes on goethite and ferrihydrite is 1.6 $\mu\text{mol m}^{-2}$ (Rennert and Mansfeldt, 2001a, b). Considering sample pH, blast furnace sludge sorbed both iron-cyanide complexes to a higher extent than the iron oxides used by Rennert and Mansfeldt (2001a, b).

The two samples which desorbed ferrocyanide during the sorption experiments (#2102 and #2114) did not differ in their chemical and mineralogical properties compared with the other samples. Therefore, the reason for desorption remained unclear.

Table 2 Sorption of iron-cyanide complexes at an initial concentration of 3.8 mmol [Fe(CN)₆]
l⁻¹ in blast furnace sludge and percental desorption by 1 M NaCl.

Sample	Ferrocyanide			Ferricyanide		
	sorbed		desorbed	sorbed		desorbed
	(mmol kg ⁻¹)	(μmol m ⁻²)	(%)	(mmol kg ⁻¹)	(μmol m ⁻²)	(%)
#2100	23.6	0.39	4.4	19.3	0.32	1.3
#2101	107.4	0.51	4.3	28.8	0.32	0.9
#2102	-71.9			19.1	0.34	15.3
#2103	31.9	0.44	3.1	18.9	0.26	1.4
#2105	21.3	0.24	9.4	15.2	0.17	6.6
#2107	29.4	0.38	12.4	27.0	0.35	9.3
#2108	38.1	0.59	3.3	18.8	0.29	0.9
#2111	10.6	0.18	3.2	14.7	0.25	9.1
#2112	27.9	0.40	14.0	21	0.30	8.1
#2114	-54.2			23.4	0.36	1.9
#2116	62.1	1.34	0.1	78.6	1.69	0.1
#2117	71.1	0.94	0.2	93.7	1.24	0.1
#2118	53.5	0.71	0.1	67.0	0.89	0.2
#2119	58.4	1.13	0.7	73.9	1.43	0.5
#2121	47.9	1.36	0.2	74.5	2.12	0.2
#2122	14.3	0.98	0.4	20.1	1.38	0.4
#2123	81.5	2.13	0.1	105.6	2.76	0.1
#2125	34.4	0.98	3.9	28.6	0.81	0.7
#2127	19.0	0.25	16.0	5.3	0.07	12.8
#2128	11.2	0.16	6.4	9.1	0.13	4.2
#2129	49.3	0.71	1.8	40.5	0.58	0.3
#2130	24.5	0.45	6.8	20.5	0.38	2.6

The sorption data were evaluated by multiple linear regressions. In the case of ferrocyanide sorption, coke-bound C was the only significant explanatory variable,

$$S = 0.05 + 0.73 \times \text{coke-bound C}, r^2 = 0.61. \quad (3)$$

The contents of X-ray amorphous compounds have not been used for regression analysis, because of autocorrelation with coke-bound C. Ferricyanide sorption was significantly explained by coke-bound C and the sum of crystalline Fe oxides,

$$S = 0.19 + 0.68 \times \text{coke-bound C} - 0.2 \times \text{sum Fe oxides}, r^2 = 0.74. \quad (4)$$

Coke-bound carbon was more significant and more important as explanatory variable, as indicated by T-tests. The iron oxides influenced ferricyanide sorption negatively which might be caused by repulsion of ferricyanide at the negatively charged oxide surface. Sorption of ferricyanide on iron oxides such as goethite and ferrihydrite is low at neutral pH and does not occur on negatively charged surfaces (Rennert and Mansfeldt, 2001a, b).

The relationship between the contents of coke-bound C and the amounts of iron-cyanide complexes sorbed is shown in Figure 2.

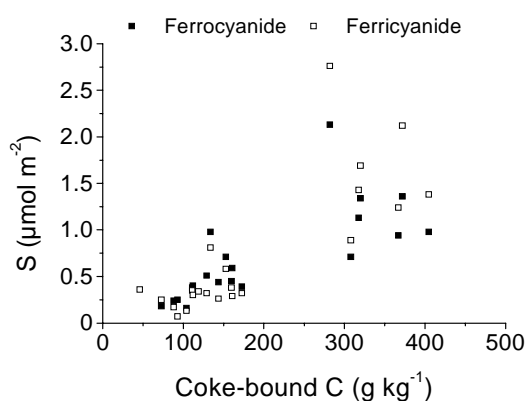


Figure 2 Relationship between coke-bound C and the amounts of ferrocyanide and ferricyanide sorbed in blast furnace sludge.

The extent of desorption differed between the blast furnace sludge samples, but generally, very small amounts of iron-cyanide sorbed in blast furnace sludge were desorbed by 1 M NaCl only. Maximum desorption was 16% (ferrocyanide, #2127). The median of ferrocyanide desorption was 3.2%, and that of ferricyanide desorption was 1.1%. These values indicated that 1 M NaCl was not an appropriate desorbing agent for iron-cyanide complexes sorbed in blast furnace sludge.

In the transport calculations, sorption of iron-cyanide complexes was described by Langmuir parameters averaged from the results of the first set of sorption experiments. The parameters were

$K = 36.1 \text{ l mmol}^{-1}$ and $S = 30.5 \text{ mmol kg}^{-1}$ for ferrocyanide sorption, and $K = 19.7 \text{ l mmol}^{-1}$ and $S = 36.6 \text{ mmol kg}^{-1}$ for ferricyanide sorption, respectively. Assuming that all cyanide is present as ferricyanide, the concentration in the seepage water at 1 m depth would be $3.7 \times 10^{-5} \text{ mmol l}^{-1}$ (i.e. $7.8 \mu\text{g l}^{-1}$) after 100 a. In the case of ferrocyanide, the concentration would be $1.8 \times 10^{-5} \text{ mmol l}^{-1}$ (i.e. $3.8 \mu\text{g l}^{-1}$) after 100 a.

DISCUSSION

As indicated by Lopez-Delgado et al. (1996), the isoelectric point (IEP) of blast furnace sludge is determined by the coke content: the higher is the coke content, the lower is the IEP ranging from 1.4 to 3.3. The neutral pH values of blast furnace sludge samples used here are far beyond the range of IEP values mentioned above. Although we do not know the IEP values of the blast furnace sludge samples, it is reasonable to assume the IEP values to be lower than the pH values due to the large amounts of coke-bound carbon present in the blast furnace sludge samples. Adsorption of anions caused by weak forces, i.e. outer-sphere surface complexation, will not occur on negatively charged surfaces, i.e. when $\text{IEP} < \text{pH}$. However, most of the samples sorbed considerable amounts of both iron-cyanide complexes. Additionally, the proportion of iron-cyanide complexes sorbed that was desorbed by 1 M NaCl was low for almost all samples. Both aspects indicate strong sorption of iron-cyanide complexes on blast furnace sludge surfaces, and (co-)precipitation cannot be excluded.

According to the regressions, coke-bound carbon is the most important sorbent for iron-cyanide complexes in blast furnace sludge. Ferricyanide interacts strongly with activated carbon, as a 100-fold excess of sulfate does not influence ferricyanide sorption (Saito, 1984). Similar to our results, ferricyanide is more sorbable on activated carbon than ferrocyanide (Saito, 1984). Strong sorption of iron-cyanide complexes in blast furnace sludge can be attributed to the interaction between iron-cyanide-N and coke-bound carbon possibly by a nucleophilic addition reaction, as similarly proposed by Guo et al. (1993) for the sorption of free cyanide on activated carbon and Schenk and Wilke (1984) for the sorption of free cyanide on humic substances.

Sorption on other constituents of blast furnace sludge such as iron and aluminum oxides cannot be excluded. However, in the slightly alkaline pH range and at $\text{pH} > \text{IEP}$, sorption of iron-cyanide complexes on these oxides should be low (Cheng and Huang, 1996; Rennert and Mansfeldt, 2001a, b). Maybe iron-cyanide complexes desorbed by 1 M NaCl originate from iron-cyanide complexes sorbed on these oxides.

The mobility of iron-cyanide complexes in deposited blast furnace sludge should be designated as low because of the following aspects. Firstly, iron-cyanide complexes in blast furnace sludge are present as $\text{K}_2\text{Zn}_3[\text{Fe}^{\text{II}}(\text{CN})_6] \times 9\text{H}_2\text{O}$. This compound is very slightly soluble under the predominant pH values of blast furnace sludge (about pH 8). Its solubility increases under extremely alkaline conditions (Mansfeldt and Dohrmann, 2001). However, an increase of pH in deposited blast furnace sludge due to progressive soil development can be excluded. Secondly, the longer blast furnace sludge is deposited, the more stable and insoluble become iron-cyanide complexes in blast furnace sludge (Mansfeldt and Dohrmann, 2001). Thirdly, if iron-cyanide complexes are released from the compound $\text{K}_2\text{Zn}_3[\text{Fe}^{\text{II}}(\text{CN})_6] \times 9\text{H}_2\text{O}$ due to dissolution and are transported with seepage water, blast furnace sludge itself can sorb the complexes strongly. Consequently, the transport of iron-cyanide complexes within the first 1 m of the blast furnace sludge deposit was strongly retarded as shown by the transport calculations. These calculations can be regarded as a worst case scenario, because we did not consider lateral water flow or physical non-equilibrium which would retard the transport additionally. However, it must be kept in mind that the calculations were carried out under some simplifying but reasonable assumptions and are valid only for the first 1 m of the deposit whose depth is 15 m altogether.

As a consequence from these aspects, iron-cyanide complexes in blast furnace sludge do not cause acute harm for the environment with regard to cyanide.

CONCLUSIONS

Deposited blast furnace sludge containing a crystalline iron-cyanide complex compound sorbs the iron-cyanide complexes ferrocyanide and ferricyanide strongly. Sorption is governed by coke-bound

carbon present in blast furnace sludge. According to the desorption experiments, the iron-cyanide complexes do not differ in their bonding strength. Spectroscopic investigations on the nature of the interactions between iron-cyanide complexes and coke-bound carbon are recommended. Due to strong sorption, strongly retarded transport and the stability of the cyanide-compound present in blast furnace sludge ($K_2Zn_3[Fe^{II}(CN)_6] \times 9H_2O$), contamination of seepage and ground water on sites of blast furnace sludge deposits with dissolved iron-cyanide complexes is very unlikely. Acidification due to progressive soil development would enhance the extent of iron-cyanide complex sorption, because the surfaces of potential mineral sorbents become protonated and thus positively charged. However, blast furnace sludge contains high amounts of lead and zinc (Lopez et al., 1991; Mansfeldt and Dohrmann, 2001). Therefore, potential ecological danger caused by deposited blast furnace sludge is given by heavy metals rather than by stable cyanide compounds.

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CHAPTER 9

Epilogue

General discussion

In the preceding chapters, the sorption and the transport of iron-cyanide complexes on iron oxides and in soils was investigated by batch and flow techniques. Sorption of the complexes on all sorbents became evident by both techniques. Therefore, sorption can be an important process immobilizing iron-cyanide complexes in the soil environment.

The complexity of sorption phenomena was obvious, because in all experimental approaches, the two complexes differed in their sorption behaviours with regard to the extent of sorption and to the nature of interactions. Therefore, sorption mechanisms of iron-cyanide complexes on the sorbents goethite, ferrihydrite, and indirectly soil organic matter were proposed qualitatively. The results and conclusions yielded a general insight into the sorption phenomena, but it was not possible to prove mechanisms or to give the stoichiometry of the bonding of an iron-cyanide complex on a sorbent surface. The results concerning sorption mechanisms and processes obtained from the preceding chapters and from the literature are summarized in Table 1. In none of these studies, sorption was investigated by spectroscopic techniques (except for Hansen and Koch, 1994). Therefore, the terms strong, intermediate, and weak interaction are used to describe the affinity for the respective sorbent. Strong interaction may be understood as inner-sphere surface complexation or chemical surface complexation, and weak interaction as outer-sphere surface complexation or weak bonding due to electrostatic forces.

Table 1 Affinities of iron-cyanide complexes for different sorbents.

	Ferricyanide	Ferrocyanide		
Sorbent	Type of interaction		Reference	Technique ^a
Goethite	intermediate	strong	Chapters 2 and 3	be, de
Goethite	weak	ni ^b	Theis et al. (1988)	be, de, ce
Ferrihydrite	intermediate	intermediate	Chapter 4	be
Amorphous aluminium oxide	weak	weak	Cheng and Huang (1996)	be
Hydrotalcite	ni	strong	Hansen and Koch (1994)	be
Soils	depending on soil composition; strong for SOM ^c	depending on soil composition; strong for SOM	Chapter 5	be
Soil	strong	strong	Chapter 7	ce, de
Soils	depending on soil composition	ni	Fuller (1985)	ce
Aquifer material	ni	no interaction (?) ^d	Ghosh et al. (1999)	ce
Contaminated soil	ni	presumably strong	Weigand et al. (2001)	ce
Blast furnace sludge	strong	strong	Chapter 8	be, de
Activated carbon	strong	strong	Saito (1984)	be

^a be, batch sorption experiments; ce, column experiments; de; batch desorption experiments; ^b not investigated; ^c soil organic matter; ^d see discussion in Chapters 6 and 7

The results presented in Table 1 show that the affinity of iron-cyanide complexes for a sorbent depends on the type of the sorbent as well as on the type of the complex. Similarly, different sorption mechanisms were found for the oxoanions of selenium and arsenic differing in their oxidation states (Wijnja and Schulthess, 2000; Arai et al., 2001). Therefore, differences between the sorption behaviours of ferricyanide and ferrocyanide are not surprising, as the complexes differ in their chemical properties (Chapter 1). Furthermore, differences in the affinities of the

complexes for the goethite surface are explained by chemical properties of the sorbent as discussed in Chapter 2.

The affinities of ferrocyanide for the surfaces of goethite and amorphous aluminium oxide, respectively, differ. Similar results have been found for sulphate and selenate sorption on these oxides (Wijnja and Schulthess, 2000). Furthermore, the strength of anion sorption can change with varying experimental (and thus environmental) conditions such as pH, as shown for ferrocyanide sorption on goethite in Chapter 2, for sulphate sorption on goethite (Peak et al., 1999), for arsenite sorption on aluminium oxide (Arai et al., 2001), and for selenate sorption on goethite (Wijnja and Schulthess, 2000).

Due to overall negative or neutral charge, soil organic matter may decrease anion sorption in soils (Yu, 1997; except for borate sorption, which is increased by SOM (Yermiyahu et al., 1995)). However, a promotive effect of SOM on iron-cyanide complex sorption was shown in Chapter 5.

The results of competitive sorption experiments investigating the effect of sulphate on iron-cyanide complex sorption (Chapter 3) demonstrated that ferricyanide and sulphate sorb very similar on goethite, whereas ferrocyanide was sorbed more strongly than sulphate. The same conclusions as for sulphate should be valid for selenate. This, in turn, indicates that nitrate and chloride are weaker sorptives compared with iron-cyanide complexes.

Strong interactions between organic surfaces and iron-cyanide complexes were shown in Chapters 5, 7, and 8. As these interactions depended on the reaction of iron-cyanide-complex-N and functional groups of organic substances, weak sorption of other inorganic anions on organic surfaces should be expected.

As a consequence from all these results, a comparison of the strength of iron-cyanide complex sorption and that of sorption of other inorganic anions can be drawn in consideration of the sorbent only. An example is ferrocyanide and sulphate, ferrocyanide is sorbed more strongly than sulphate on goethite, but the strength of the interactions of both anions on amorphous aluminium oxide should be the same.

Combining the results of this study and those available from the literature, it is obvious that the behaviour of iron-cyanide species in soil and ground water is very complex. Dissolution of iron-cyanide containing solid phases plays a key role for the mobilization of dissolved iron-cyanide

complexes. The dissolution of iron-cyanide containing phases was investigated as influenced by pH and redox potential under the assumption of a local equilibrium (Meeussen et al., 1992b; Ghosh, 1998). However, there are further aspects influencing the dissolution of these phases: Berlin Blue was found in alkaline soils even after decades after being dumped indicating slow dissolution kinetics (Meeussen, 1992); cyanide mobility in non-acidic soils may be governed by the activity of manganese ions (Keizer et al., 1995); soil hydrology may be an important aspect, because solubility may be physically determined by preferential soil water flow (Köster, 2001); and both dissolution and desorption of iron-cyanide complexes is rate-limited (Weigand et al., 2001).

Apart from these uncertainties with regard to the dissolution of solid phases, in none of the studies investigating the fate of iron-cyanide complexes in the soil environment, adsorption of dissolved species was taken into account sufficiently. As discussed in Chapters 6 and 7, the investigation of the transport of ferrocyanide in neutral sandy aquifer material by Ghosh et al. (1999) is an oversimplification in the opinion of the author of this thesis, because they characterized the transport as nonreactive based on incomplete breakthrough curves.

Further difficulties arise when trying to transfer the results of sorption experiments shown in Table 1 to processes occurring in soil under natural conditions actually. Firstly, the transport of iron-cyanide complexes in various substrates was influenced by rate-limited sorption or desorption or both (Chapters 6 and 7; Theis et al., 1988; Weigand et al., 2001). These results were obtained from column experiments which are more realistic than batch experiments because of e.g. narrower soil/solution ratios or more realistic flow velocities. However, in most of the studies listed in Table 1 batch techniques were used, and rate parameters obtained from batch experiments cannot be transferred to the kinetics of processes naturally occurring in soil. Secondly, the evaluation of sorption mechanisms of iron-cyanide complexes on soil mineral surfaces is important indeed, but quantitative conclusions for processes in soil cannot be drawn without large restrictions. An important aspect is that soil minerals, e.g. iron oxides to be investigated, are synthesized by laboratory techniques. These synthetic phases are not present in soil in these forms, because e.g. soil goethite is aluminium-substituted to distinct degrees (Cornell and Schwertmann, 1996) and comprises of phases differing in their specific surface areas, points of zero charge etc. Furthermore, minerals in soil are commonly coated by organic

matter. The importance of soil organic matter for the sorption of iron-cyanide complexes was shown in the Chapters 5 and 7. Consequently, the extent as well as the mechanism of iron-cyanide complex sorption on a mineral may vary with the degree of organic coatings.

Soil development on iron-cyanide contaminated sites including the formation of SOM after the end of waste disposal may be an important factor for the sorption of iron-cyanide in soil due to sorption on SOM, but also due to the presence of dissolved organic matter, DOM, in soil solution. DOM comprises a heterogeneous continuum of organic substances and it may have different impacts on the mobility of iron-cyanide complexes. Due to the nature of DOM sorbed on soil minerals (organic coating), sorption of iron-cyanide complexes on soil minerals may be enhanced or decreased depending on the nature of DOM sorbed on the mineral surface. The mobility of iron-cyanide complexes may be affected when sorbed on DOM (co-transport). Additionally, DOM sorbed on soil minerals may affect the desorption of iron-cyanide complexes sorbed on soil minerals due to stabilization effects.

Adsorption as well as precipitation should be taken into account when evaluating the environmental fate of iron-cyanide complexes in contaminated soils. However, many iron-cyanide containing solid phases; their dissolution behaviours; adsorption mechanisms of dissolved iron-cyanide complexes on various solid phases; and processes possibly overseen are still unknown. However, all these processes should be known to obtain a deeper insight into the fate of iron-cyanide complexes in the soil environment. Consequently, many investigations should be performed.

Recommendations for further research

Several questions and problems arose from this work which could (or maybe should) be objects of further research to understand the environmental fate of iron-cyanide complexes definitely. These objects can be divided into two groups: research concerning the release of iron-cyanide complexes in contaminated soils, and research concerning sorption processes of iron-cyanide complexes on various solid phases.

However, before proceeding to this research, it is important to clarify which iron-cyanide complex is actually present in soil and ground water. In the preceding chapters, differences in the sorption behaviours of ferricyanide and ferrocyanide concerning the strength as well as the extent of sorption were demonstrated. Because of these differences, the knowledge of the cyanide species distribution in soil solutions is important in order to predict the efficacy of sorption processes.

It is commonly accepted that cyanide in the ground water and in soil solutions on sites of former MGPs and coke ovens are mainly present as iron-cyanide complexes (Meeussen et al., 1994; Ghosh, 1998), although model calculations by Meeussen et al. (1992a) indicated that free cyanide should predominate. Their results demonstrate that modelling the species distribution may not be performed under the assumption of a local equilibrium, because of the large differences between the modelled and the measured species distribution. Analytical speciation of cyanide species is complicated by the use of distillation techniques in most studies. Different cyanide species are converted to free cyanide during distillation. Therefore, cyanide measured colorimetrically in distillates comprises the sum of different cyanide species previously present. However, there is only one study investigating the speciation of iron-cyanide complexes in soil extracts derived from contaminated MGP site soils using ion chromatography (Theis et al., 1994). They found ferrocyanide to be the dominant species. Furthermore, they detected thiocyanate, SCN^- , tricyanocuprate, $[\text{Cu}(\text{CN})_3]^{2-}$, tetracyanonickelate, $[\text{Ni}(\text{CN})_4]^{2-}$, and two unknown iron- and copper-cyanide complexes. Speciation of cyanide complexes in solution is possible by isotachophoresis and capillary electrophoresis as well. Theis et al. (1994) examined soil extracts, but an investigation on cyanide species distribution in soil solution and ground water (i.e. *in situ* solutions) has not yet been performed, and is therefore strongly recommended. These future investigations should include the effects of pH and redox potential on species distribution as these *in situ* solutions are dynamic systems depending on changes of the geochemical milieu. The importance of the redox potential for iron-cyanide complex species distribution is given by the different sorption behaviours of the complexes and by the fact that ferrocyanide is not oxidized by air. Therefore, oxidation of ferrocyanide in soil solutions should be investigated at different redox potentials and in the presence of different redox catalysts.

Furthermore, the presence of colloidal iron-cyanide phases in soil solution and ground water should be studied. These phases were found in soil extracts by Mansfeldt et al. (1998).

The presence of Berlin Blue in a coke oven site soil was shown by Mansfeldt et al. (1998) using Mößbauer spectroscopy. Based on model calculations of the results of iron-cyanide dissolution in contaminated non-acidic soils, Keizer et al. (1995) suggested manganese ferrocyanide, $\text{Mn}_2[\text{Fe}^{\text{II}}(\text{CN})_6]$, as a possible cyanide containing phase in MGP site soils. However, they did not prove its presence spectroscopically. In paper de-inking sludge used as a soil amendment, Mansfeldt (2001) suggested solid iron-cyanide phases such as $\text{A}_2\text{B}[\text{Fe}^{\text{II}}(\text{CN})_6]$, with $\text{A} = \text{K}^+$ or Na^+ , and $\text{B} = \text{Ca}^{2+}$ or divalent transition metal, or $\text{B}_2[\text{Fe}^{\text{II}}(\text{CN})_6]$. The formation of these phases is theoretically possible in subsoils and aquifers of coke oven and MGP sites, too. Apart from pH, the redox potential may be an important factor for the formation and the stability of iron-cyanide containing solid phases actually present in soils on contaminated sites. Therefore, further investigation on the identification of iron-cyanide phases present in soils including the conditions of their formation by wet chemical and spectroscopic techniques is recommended. The identification of these phases including their dissolution behaviours is essential for the prediction of the release of dissolved cyanide species.

The solid iron-cyanide phases mentioned above are stable compounds, and their dissolution strongly depends on narrow pH and redox conditions (Meeussen et al., 1992b; Mansfeldt, 2001) as shown in Chapter 1. However, these conditions might be modified by the presence of DOM in the soil solution of soils on iron-cyanide contaminated sites which were subject to soil development. DOM contains low molecular organic acids which can enhance the solubility of iron-cyanide containing phases (e.g. oxalic, citric, and acetic acid; own unpublished data). This effect and the effects of DOM on iron-cyanide complex sorption as shown in the general discussion above have not been investigated yet, thus further research is recommended.

Further important sorbents in soil are manganese oxides. Iron-cyanide complexes are possibly sorbed on these oxides. Manganese(IV) oxides can oxidize adsorbed species such as arsenite (Huang, 1991). Therefore, oxidation of ferrocyanide to ferricyanide sorbed on manganese(IV) oxides is imaginable resulting in Mn^{2+} ions in solution. These ions may form the precipitate $\text{Mn}_2[\text{Fe}^{\text{II}}(\text{CN})_6]$ with ferrocyanide. Therefore, studies on the sorption of iron-cyanide complexes on manganese including the effect of redox potential are recommended.

As Wijnja and Schulthess (1999) pointed out, structural information at the molecular level about the types of complexes and the coordination state of adsorbed species combined with macroscopic observations of adsorption are essential for defining realistic model representations of ion adsorption at the mineral/water interface. The sorption mechanisms of iron-cyanide complexes on many potential sorbents in soils have not yet been investigated spectroscopically. These sorbents, of course, include the iron oxides used in this thesis. The promotive effect of soil organic matter on sorption of iron-cyanide complexes in soils and the importance of organic carbon present in blast furnace sludge has been shown. Consequently, the nature of iron-cyanide complex interactions on mineral as well as on organic surfaces should be investigated spectroscopically.

All these investigations should result in a model which incorporates dissolution of iron-cyanide containing phases, precipitation of solid phases, adsorption on various surfaces, colloidal transport including the effects of pH, redox potential, soil hydrology, and progressive soil development to predict the fate of iron-cyanide complexes in soil and ground water.

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SUMMARY

The presence of the iron-cyanide complexes ferrocyanide, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and ferricyanide, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, in soil and ground water is caused by anthropogenic inputs of iron-cyanide-containing wastes. Iron-cyanide complexes have to be regarded as contaminants, because they are potentially convertible to toxic free cyanide, CN^-_{aq} and $\text{HCN}_{\text{g, aq}}$. As known from other studies, the mobility of iron-cyanide complexes in the soil environment is influenced by dissolution and precipitation of iron-cyanide-containing solid phases. Sorption on solid phases is assumed to influence the mobility of iron-cyanide complexes additionally. The aim of this study was to investigate the sorption of ferrocyanide and ferricyanide on iron oxides and in soils by batch and column experiments to enable better understanding of the fate of these complexes in soil and ground water.

Different sorption mechanisms of the complexes were found in batch experiments using goethite, $\alpha\text{-FeOOH}$, as the sorbent. As the sorption of the complexes was variously affected by reaction time, ionic strength, pH-dependency and pH-dependent desorption, it was proposed that ferricyanide was sorbed by outer-sphere and weak inner-sphere surface complexation. Ferrocyanide was proposed to be sorbed by inner-sphere surface complexation and precipitation of a Berlin-Blue-like phase (Berlin Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$). These sorption mechanisms could be confirmed by the competitive effect of sulphate on the sorption of iron-cyanide complexes on goethite and by the desorption using chloride and phosphate.

Modelling the sorption of iron-cyanide complexes on ferrihydrite, $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$ ($n = 1 - 3$), showed that the sorption on ferrihydrite was quantitatively comparable to the sorption on goethite, as the modelled sorption maximum was $1.6 \mu\text{mol } [\text{Fe}(\text{CN})_6] \text{ m}^{-2}$ for both oxides. However, sorption on ferrihydrite seemed to be weaker than that on goethite, as the calculated negative charge conveyed to the ferrihydrite surface due to sorption was lower than that conveyed to the goethite surface.

The sorption of iron-cyanide complexes in 17 uncontaminated soil horizons differing in soil chemical and soil physical properties was investigated in batch experiments. Sorption of both complexes depended on the contents of organic carbon, clay, and oxalate-extractable iron.

Especially soil organic matter of Fluvisols had a large affinity for the complexes, because destruction of organic matter minimized sorption up to 99%. Sorption was attributed to interactions of iron-cyanide-N and reactive functional groups of soil organic matter.

The sorption and the transport of the iron-cyanide complexes in goethite-coated sand was investigated in column experiments at saturated flow conditions as influenced by flow velocities and flow interruptions. The transport of both complexes was characterized by rate-limited and nonlinear sorption. Ferricyanide breakthrough curves were roughly reflected by simulations with batch-derived sorption parameters. Ferricyanide sorption was influenced by hysteresis. The sorption fronts of ferrocyanide revealed a shoulder that was explained by different sorption mechanisms, similar to sorption on goethite in batch experiments.

The sorption and the transport of iron-cyanide complexes in a humic soil horizon was also investigated in column experiments under saturated flow conditions as influenced by concentrations and flow interruptions. Sorption was nonlinear, because the positions of the breakthrough curves of both iron-cyanide complexes depended on concentrations. Rate-limited sorption was indicated by retarded desorption and the effects of the flow interruptions on the breakthrough curves. Amongst other things, precipitation of iron-cyanide containing solid phases was indicated by blue particles in soil after the column experiments for both iron-cyanide complexes. Batch desorption experiments indicated strong interactions of both complexes and the soil matrix, presumably caused by bonding on soil organic matter by the same mechanism as proposed above.

Blast furnace sludge, a waste originating from pig iron production, contains iron-cyanide complexes in the form of the solid phase $K_2Zn_3[Fe(CN)_6]_2 \times 9H_2O$. The sorption of iron-cyanide complexes in 22 surface samples of deposited blast furnace sludge was investigated in batch experiments. Nowadays, this blast furnace sludge is a substrate for soil development. The neutral to alkaline blast furnace sludges sorbed iron-cyanide complexes partly to a large extent. The most important sorbent was coke-bound carbon. Desorption experiments revealed strong interactions between iron-cyanide complexes and deposited blast furnace sludge.

The results presented in this thesis show that sorption processes of iron-cyanide complexes on iron oxides and in soils are complex. The extent as well as the strength of ferricyanide and ferrocyanide sorption depends on both the type of the complex and of the sorbent. The mobility

of iron-cyanide complexes in the soil environment is governed by chemical substrate properties, because sorption is enhanced at low pH and high contents of reactive soil organic matter, iron and aluminium oxides. Furthermore, the slow kinetics of the different sorption processes is very important for their efficacy as to the retention of iron-cyanide complexes in soil and ground water. Therefore, the mobility of the dissolved complexes cannot be designated as high as it has been done in some previous studies.

ZUSAMMENFASSUNG

Die Eisencyankomplexe Hexacyanoferrat(II), $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, und Hexacyanoferrat(III), $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, kommen in Böden und Grundwässern auf Grund anthropogener Einträge eisen-cyanhaltiger Abfälle vor. Eisencyankomplexe müssen als Schadstoffe angesehen werden, da sie potenziell zu toxischem freiem Cyanid, CN^-_{aq} und $\text{HCN}_{\text{g, aq}}$, zerfallen können. Wie aus anderen Untersuchungen bekannt ist, wird die Mobilität von Eisencyankomplexen in Böden von Lösung und Ausfällung eisen-cyanhaltiger Festphasen beeinflusst. Es wird angenommen, dass die Mobilität von Eisencyankomplexen zusätzlich von der Sorption an Festphasen beeinflusst wird. Das Ziel dieser Arbeit war, die Sorption der Eisencyankomplexe an Eisenoxide und in Böden in Schüttel- und Säulenversuchen zu untersuchen, um ein besseres Verständnis des Verbleibs dieser Komplexe in Böden und Grundwässern zu ermöglichen.

Unterschiedliche Sorptionsmechanismen der Komplexe wurden in Schüttelversuchen mit Goethit, $\alpha\text{-FeOOH}$, als Sorbent gefunden. Wegen der für die Komplexe differierenden Ergebnisse unter den Randbedingungen Reaktionszeit, Ionenstärke, pH-Abhängigkeit und pH-bedingte Desorption wurden für Hexacyanoferrat(III) die Bindung durch Anlagerungs- sowie schwache Durchdringungskomplexe und für Hexacyanoferrat(II) die Bindung durch Durchdringungskomplexe sowie Ausfällung einer Berliner-Blau-artigen Phase (Berliner Blau: $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) als Sorptionsmechanismen vorgeschlagen. Diese Mechanismen wurden durch das Konkurrenzverhalten von Sulfat bei der Sorption von Eisencyankomplexen an Goethit und durch die Desorption mittels Phosphat und Chlorid bestätigt.

Die Modellierung der Sorption von Eisencyankomplexen an Ferrihydrit, $\text{Fe}_2\text{O}_3 \times n\text{H}_2\text{O}$ ($n = 1 - 3$), ergab, dass die Sorption an Ferrihydrit quantitativ mit der an Goethit wegen des für beide Oxide identischen Sorptionsmaximums von $1,6 \mu\text{mol } [\text{Fe}(\text{CN})_6] \text{ m}^{-2}$ vergleichbar war. Die Sorption an Ferrihydrit war schwächer als an Goethit, da, anhand der Modellrechnungen, durch die Sorption weniger negative Ladung auf die Ferrihydritoberfläche als auf die Goethitoberfläche übertragen wurde.

Die Sorption der Eisencyankomplexe in 17 unbelasteten Bodenhorizonten unterschiedlicher bodenchemischer und bodenphysikalischer Eigenschaften wurde in Schüttelexperimenten

untersucht, wobei die Sorption beider Komplexe von den Gehalten an organischem Kohlenstoff, Ton und oxalatlöslichem Eisen abhing. Die organische Bodensubstanz von Auenböden hatte eine starke Affinität für Eisencyankomplexe, da die Zerstörung der organischen Substanz eine Verringerung der Sorption von bis zu 99% zur Folge hatte. Sorption findet auf Grund von Bindungen zwischen Eisencyankomplex-N und reaktiven funktionellen Gruppen der organischen Bodensubstanz statt.

Die Sorption und der Transport der Eisencyankomplexe in goethitbelegtem Sand wurden in Säulenexperimenten bei gesättigtem Fluss und variablen Fließgeschwindigkeiten untersucht, wobei Flussunterbrechungen durchgeführt wurden. Der Transport beider Komplexe war durch ratenlimitierte und nichtlineare Sorption gekennzeichnet. Durchbruchkurven des Hexacyanoferrat(III) wurden grob durch Simulationen mit aus Schüttelversuchen abgeleiteten Sorptionsparametern angenähert. Die Sorption dieses Komplexes unterlag einer Hysterese. Die Sorptionsfronten des Hexacyanoferrat(II) wiesen eine Schulter auf, die mit unterschiedlichen Sorptionsmechanismen, ähnlich wie bei der Sorption an Goethit in Schüttelversuchen, begründet wurde. Ebenfalls in Säulenversuchen wurden die Sorption und der Transport der Eisencyankomplexe in einem humosen Oberboden bei gesättigtem Fluss in Abhängigkeit der Konzentration untersucht, wobei Flussunterbrechungen durchgeführt wurden. Da die Positionen der Durchbruchkurven beider Eisencyankomplexe konzentrationsabhängig waren, war die Sorption nichtlinear. Ratenlimitierte Sorption wurde anhand verzögerter Desorption und der Effekte der Flussunterbrechungen deutlich. Ausfällungen eisencyanhaltiger Festphasen zeigte sich u.a. an blauen Partikeln im Boden nach den Säulenversuchen mit beiden Eisencyankomplexen. Desorptionsexperimente in Schüttelversuchen wiesen auf starke Bindungen beider Komplexe im Boden hin, vermutlich bedingt durch Bindung an die organische Bodensubstanz nach dem oben genannten Mechanismus.

Gichtgasschlämme, ein Abfallprodukt der Roheisenerzeugung, enthalten Eisencyankomplexe in Form der Festphase $K_2Zn_3[Fe(CN)_6]_2 \times 9H_2O$. In Schüttelversuchen wurde die Sorption von Eisencyankomplexen in 22 Oberflächenproben deponierter Gichtgasschlämme untersucht, die heute bodenbildendes Substrat sind. Die neutralen bis schwach alkalischen Gichtgasschlämme sorbierten z.T. große Mengen Eisencyankomplexe. Der wichtigste Sorbent war koksbürtiger

Kohlenstoff. Desorptionsexperimente zeigten starke Bindungen zwischen Eisencyankomplexen und deponierten Gichtgasschlämmen.

Die in dieser Arbeit gezeigten Ergebnisse verdeutlichen, dass Sorptionsprozesse von Eisencyankomplexen, die an Eisenoxiden und in Böden auftreten, komplex sind. Sowohl das Ausmaß als auch die Stärke der Sorption von Hexacyanoferrat(II) und Hexacyanoferrat(III) hängen von der Art des Komplexes und des Sorbenten ab. Die Mobilität von Eisencyankomplexen in Böden wird von chemischen Substrateigenschaften gesteuert, da Sorption verstärkt bei niedrigem pH-Wert und hohen Gehalten an reaktiver organischer Bodensubstanz und Eisen- und Aluminiumoxiden statt findet. Weiterhin ist die langsame Kinetik der unterschiedlichen Sorptionsprozesse von großer Bedeutung für ihre Wirksamkeit in Bezug auf die Retention von Eisencyankomplexen in Böden und Grundwässern. Daher kann die Mobilität der gelösten Komplexe nicht als hoch bezeichnet werden, wie es in einigen vorherigen Studien geschah.

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