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Release of Metals from Iron Oxyhydroxides under Reductive Conditions: Effect of Metal/Solid Interactions

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Solubilization of heavy metals from Fe oxyhydroxides in the presence of sodium ascorbate as a reducing agent were investigated as a function of pH. Amorphous iron hydroxide (HFO) and goethite were synthesized in the presence of Pb, Cd, and Zn, using two different processes, i.e., favoring either metal adsorption (ADS) or metal substitution (coprecipitation, COP). Characterization of solids showed that there were no structural differences among the three kinds of HFO. However, in the case of goethite, it seemed that metal cations were located within the structure of COP goethite, but partially adsorbed in ADS goethite. Results evidenced that, under reductive conditions, the solubilization risk is greater for Pb than for Cd (Cd substituted in the structure) from the coprecipitation process. In the adsorption process, Cd was removed more than Pb (greater complexation constant of Pb). Moreover, irrespective of the crystalline state, solids may be partly dissolved, and release of metals could occur. © 2000 Academic Press

Key Words: reductive dissolution; adsorption; coprecipitation; iron oxyhydroxide; heavy metal.

INTRODUCTION

Periodic inundation or fluctuating groundwater levels lead to changing redox conditions in soil. Redox conditions have been recognized for a long time as a critical parameter controlling the fate of pollutants in the environment. Fe(III)-rich solids may be produced by oxygenation of Fe(II) in the oxic zone and subsequently settle into the anoxic zone, where they can be reductively dissolved to Fe(II) in the presence of a reductant. This process of reductive dissolution has been studied by many authors in order to understand the redox cycling of iron in the environment (1–3). Mechanisms and rate of solution of Fe(III) hydroxides were the purpose of many previous studies but they were restricted only to reductive dissolution. However, in the case of polluted Fe oxyhydroxides, a question remains: what kind of process occurs during the release of metals bound to the solid?

Iron hydrous oxides are often implicated in the mobility of metallic micropollutants in aqueous systems (4). Indeed, they

have an important capacity to sorb heavy metals. Thus, their dissolution and precipitation control the heavy metal solubilization in aqueous systems. Moreover, interactions between metal and iron oxyhydroxides include various processes: adsorption, surface precipitation (formation of multilayered solid species on the oxide surface), and coprecipitation or substitution (simultaneous precipitation of cation with the oxyhydroxide). Thus, depending on the type of interaction, metals exhibit different solubility behaviors.

The objective of this work was to investigate the reductive dissolution effect on the solubilization of heavy metals from spiked Fe oxyhydroxides. In this paper, we present different sets of experiments with two types of Fe oxyhydroxides (amorphous: amorphous iron hydroxide (HFO) and well crystallized: goethite α -FeOOH) and two types of metal/oxide interactions (adsorption, coprecipitation). Reductive dissolution experiments were carried out in the presence of a reducing ligand, sodium ascorbate, as an electron donor in order to promote reduction of surface Fe(III) sites and the subsequent release of both Fe(II) and cations bound to Fe oxyhydroxides. Amorphous iron hydroxide, HFO, and goethite were chosen due to their different crystallization states and capacities to adsorb or trap metals. In order to pollute both oxyhydroxides, solids were synthesized in the simultaneous presence of Pb, Cd, and Zn cations using two different methods. Thus, adsorption (ADS) goethite and HFO (in the case of adsorption) and coprecipitation (COP) goethite and HFO (in the case of coprecipitation) were obtained and compared with pure goethite and HFO (in the absence of heavy metal added). It should be noted that the ADS and COP prefixes relate simply to the synthesis scheme.

MATERIALS AND METHODS

All chemicals used in this study were of analytical grade. All solutions were prepared with doubly deionized water (Milli-Q system, Millipore). All experiments were carried out in polyethylene containers that were cleaned according to the following protocol: they were washed with detergent, soaked in 10% HNO₃ for 48 h, and rinsed with Milli-Q water for 24 h.

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Solids Syntheses

Pure synthetic goethite was prepared in the laboratory according to the Schwertmann and Cornell protocol (5). A total of 100 mL of 1 M $\text{Fe}(\text{NO}_3)_3$ and 180 mL of 5 M KOH were simultaneously mixed under a continuous pure nitrogen stream to prevent carbonate formation. The suspension was stored for 60 h in an oven at 70°C. The solid was also synthesized in the simultaneous presence of various amounts of Pb, Cd, and Zn in order to contaminate it. Two different methodologies were used, as follows:

-heavy metals were added before solid precipitation (method called coprecipitation: COP goethite);

-heavy metals were added after precipitation with a 24-h contact time (method called adsorption: ADS goethite).

The salts of heavy metal ions were all nitrates and were used as received.

These goethite precipitates were centrifuged and washed three times with Milli-Q water. The solids obtained were dried for 24 h at 60°C, sieved for homogenization, and stored in a dessicator. Total concentrations of heavy metals were evaluated after acidic digestion according to the protocol of Ritter and Sung (6–8). Pb, Cd, and Zn were analyzed by polarography (DPASV) (Table 1).

Synthetic amorphous iron hydroxide (HFO) was prepared in the laboratory according to Schwertmann and Cornell (5). A total of 1.5 mol of NaOH (pellets) was added slowly to 1 L of 0.5 M $\text{Fe}(\text{NO}_3)_3$. The solution was continuously bubbled with nitrogen. Pb, Cd, and Zn were added to the solution of $\text{Fe}(\text{NO}_3)_3$ just before (COP protocol) or after (ADS protocol) precipitation. The HFO precipitates were centrifuged and washed three times with Milli-Q water. The solids obtained were dried at 20°C, sieved for homogenization, and stored in a dessicator. Total concentrations of heavy metals were evaluated by acidic digestion according to the protocol of Ritter and Sung (6–8). Pb, Cd, and Zn were analyzed by polarography (DPASV) (Table 1).

Solids Characterization

Crystallization states of solids were determined by X-ray diffraction analyses (XRD) on a Siemens D5000 diffractometer utilizing filtered copper $K\alpha 1$ radiations. Infrared spectra were obtained using KBr pellets with a Perkin–Elmer Fourier transform spectrometer at 2 cm^{-1} resolution. Specific surface areas were determined according to the Brunauer, Emmett, and Teller protocol on a Micromeritics ASAP 2000 apparatus.

TABLE 1
Heavy Metals Concentration into the Various Solids (ppm)

Metals	COP goethite	ADS goethite	COP HFO	ADS HFO
Pb	460	430	601	343
Cd	13	24	8.9	7.0
Zn	710	1085	1958	1033

Surface acidity constants were determined from potentiometric titrations of 10 $\text{g} \cdot \text{L}^{-1}$ of solid with NaOH (0.1 M) and HNO_3 (0.1 M) in a 0.1 M NaNO_3 medium as the supporting electrolyte (9, 10). Titrations were carried out with a Metrohm 716 DMS Titrino apparatus equipped with a Metrohm 6.0233.100 combined (3 M KCl) glass electrode.

The CEC (cation exchange capacity) was determined by the cobalthexamine method (NF X 31-130) for HFO (11). Ions linked with the solid surface are exchanged with cobalthexamine ions, thus CEC is the concentration of cobalthexamine ions eliminated from the solution. Fifty grams of solid was mixed with 50 mL of 0.017 M cobalthexamine chloride solution for 3 h, the suspension was then centrifuged, and the concentration of cobalthexamine ion remaining in the solution was measured at 470 nm with a Shimadzu 160A UV spectrophotometer. In the case of goethite it was not possible to use this method, therefore protonic exchange capacity was determined. HNO_3 (0.1 M) was added in excess to a 10 $\text{g} \cdot \text{L}^{-1}$ goethite suspension in a 0.01 M NaNO_3 medium. After a 24-h equilibration time, residual H^+ concentration was measured with a pH meter and adsorbed H^+ corresponding to the protonic exchange capacity was calculated by difference (12).

Complexation Experiments

Experiments were conducted with a solid concentration of 10 $\text{g} \cdot \text{L}^{-1}$ in 0.1 M NaNO_3 solution in the presence of a complexant, EDTA, as a function of pH. The concentration of EDTA, 0.01 M, was chosen so as to be in excess in order to desorb all cations adsorbed on the surface. Indeed, Davis and Upadhyaya (13) have shown that EDTA could be adsorbed onto a free surface site before complexing chemisorbed ions. The pH was regulated with concentrated solutions of HNO_3 or NaOH. The equilibration time was 24 h, determined by previous studies as a function of time under the same conditions for a pH fixed at 3.

Desorption/Dissolution Experiments

Experiments were conducted first with a solid concentration of 10 $\text{g} \cdot \text{L}^{-1}$ in a 0.1 M NaNO_3 medium without reducing agent. The pH was regulated with concentrated solutions of HNO_3 or NaOH. The equilibration time was 48 h, determined by previous studies as a function of time under the same conditions for a pH fixed at 4.

The same protocol was used in a second series of experiments in the presence of the reducing agent, sodium ascorbate. The sodium ascorbate concentration was determined from an estimation of the soil oxidation capacity calculated using only the total iron concentration in solids (14, 15). The equilibration time was determined by previous studies as a function of time under the same conditions for a pH fixed at 4. The different experimental conditions used are listed in Table 2. This higher equilibrium time is in accordance with the reductive dissolution mechanism (2).

Speciation calculations were carried out beforehand using the SPE computer program (16) in order to confirm that ascorbate

TABLE 2
Experimental Conditions Used in the Dissolution Experiments

	Solid concentration (g · L ⁻¹)	Ascorbate concentration (mol · L ⁻¹)	Ionic strength (mol · L ⁻¹)	Equilibrium time (h)	
				Without ascorbate	With ascorbate
HFO	10	9 × 10 ⁻²	10 ⁻¹	48	200
αFe-OOH	10	9.5 × 10 ⁻²	10 ⁻¹	48	250

did not complex Pb, Cd, and Zn cations under our experimental conditions (results not shown).

At the end of these experiments, the solid suspension was filtered through a 0.2- μ m cellulose nitrate filter (Sartorius). The filtrate was collected in a polypropylene tube to which 100 μ L of 69% HNO₃ had been added to keep all metals in solution. Samples were stored at 4°C before analysis.

Analytical Techniques

The solutions of Pb, Cd, and Zn were analyzed by voltammetry (DPASV) on a Metrohm VA 746 trace analyzer equipped with a VA 747 stand with a triple electrode system: a calomel reference electrode (3M KCl/1M KNO₃), a graphite counter-

electrode, and a mercury drop electrode. Dissolved oxygen was removed from the sample by prepurging the solution for 600 s with N₂. The deposition step was carried out at -1.2 V for 60 s followed by metal stripping.

Fe and Mn concentrations were measured by atomic absorption spectrometry, either FAAS (Varian SpectrAA 220) or Zeeman-corrected GFAAS (Varian SpectrAA 800).

RESULTS

Solids at Initial Conditions

The synthetic oxides used in this study were pure. XRD patterns showed well-defined mineral phases: "2 line ferrihydrite" (Fig. 1a) and goethite (Fig. 1b). The high surface area obtained for HFO was also an indication of the amorphous structure of this solid (Table 4).

FTIR spectra were measured for the three kinds of solids in order to identify the metal/solid interaction (Fig. 2).

The low value at the low wavenumber part of the spectra corresponds to the crystalline state of the solid; if peaks are well defined, the solid is crystallized, otherwise the solid is amorphous. Thus, in Fig. 2a HFO presented an amorphous structure. Peaks at 3451 and 1633 cm⁻¹ were characteristic of 2-line

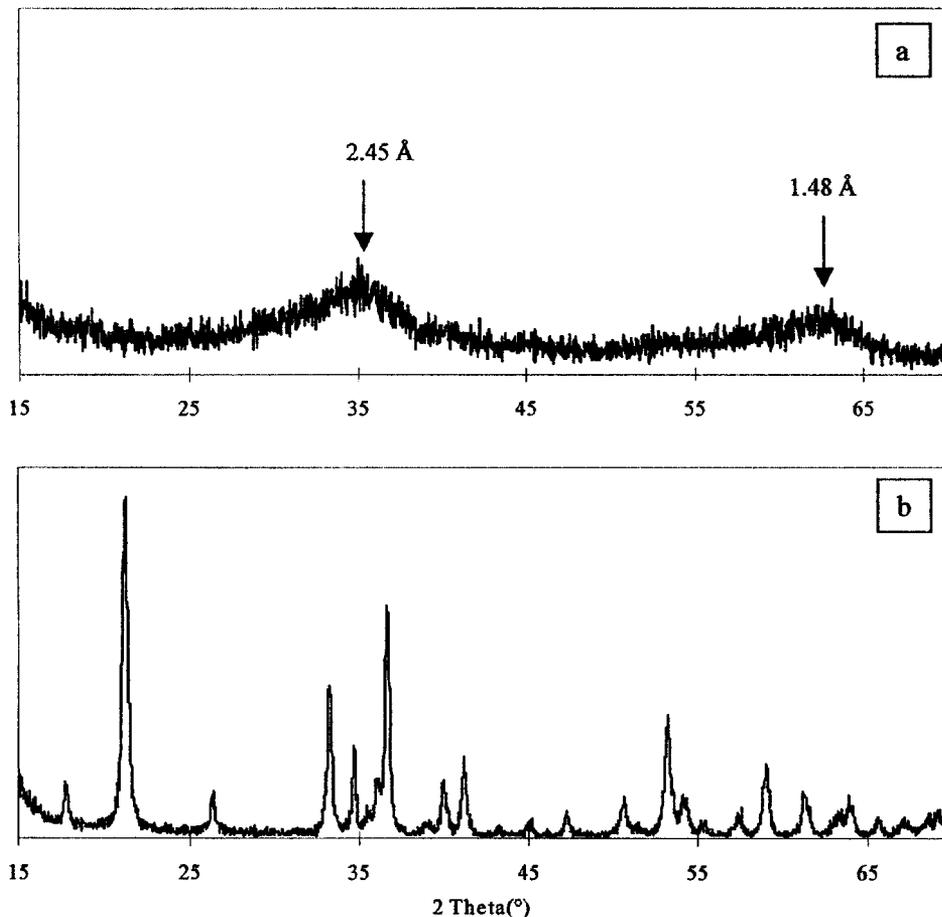


FIG. 1. X-ray diffraction patterns of pure HFO (a) and goethite (b) samples.

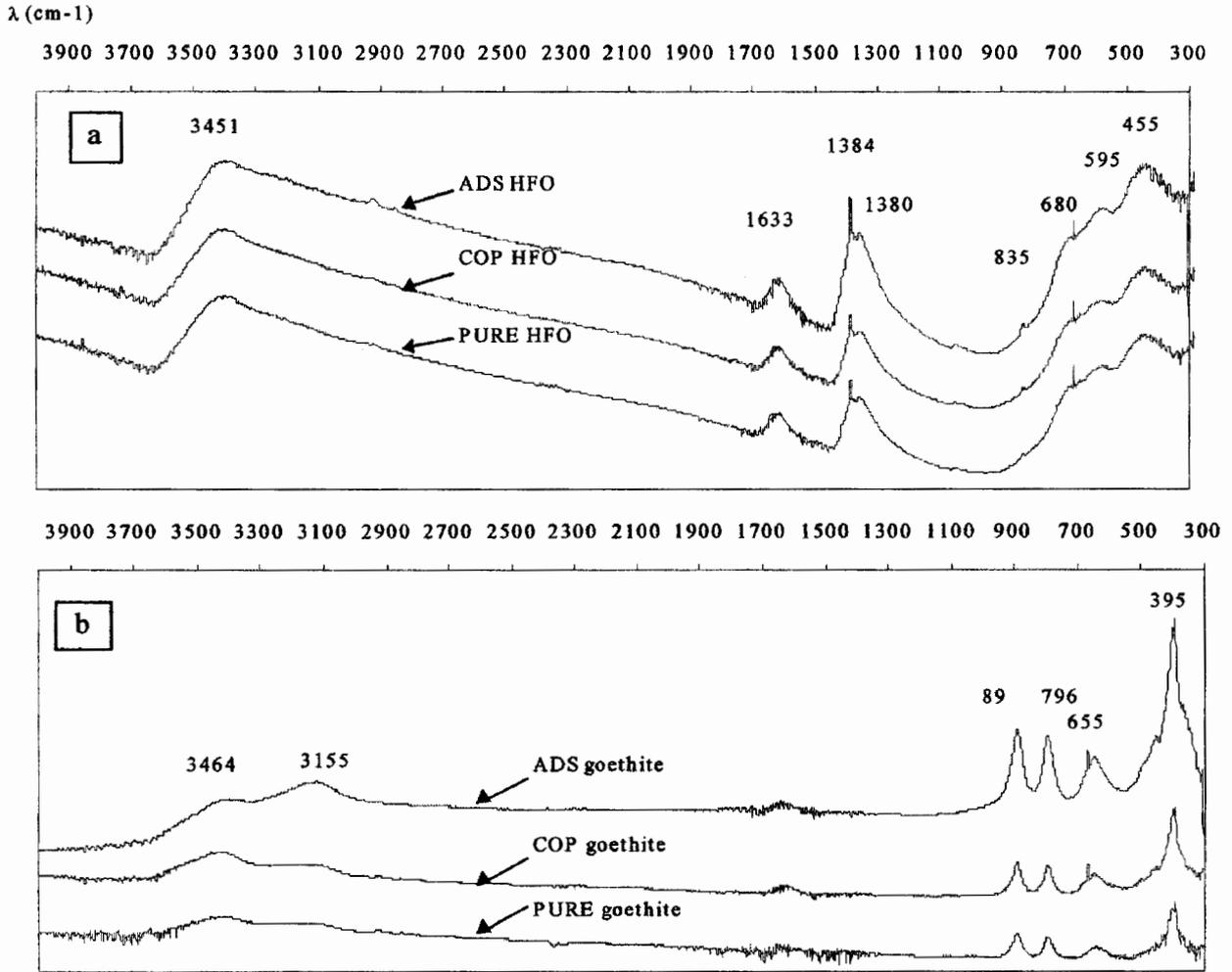


FIG. 2. Infrared spectra of HFO (a) and goethite (b).

ferrihydrite (17); those at 1380 and 1384 cm^{-1} correspond to nitrate residue relevant to the synthesis. Moreover, Fox (18) showed the existence of a nitrate-substituted ferric hydroxide $\text{Fe}(\text{OH})_{2.35}(\text{NO}_3)_{0.65}$. Spectra obtained for the three types of HFO were totally similar. FTIR analyses did not lead to any conclusions about the interactions between metal and different oxides.

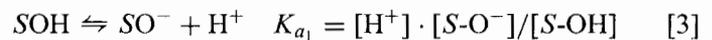
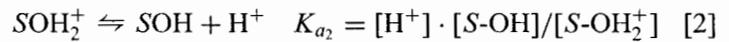
In Fig. 2b peaks were well defined in the low wavenumber part of the spectra. This configuration corresponds to a well-crystallized structure. Peaks at 898, 796, and 655 cm^{-1} are characteristic of goethite. The peak at 3155 cm^{-1} corresponds to the OH-stretching, and those at 3430 and 1680 cm^{-1} to water contained into KBr. These results showed no difference between the three solids (notably for the peak corresponding to the OH-stretching) and did not allow to deduce the nature of metal/solid bond.

To show a difference of metal/solid interaction into the various solids, surface titrations were realized on the different types of HFO and goethite. Acidity constants and the pH of zero point charge, pH_{zpc} , of the oxides were calculated with the following

equations and simplifications (9, 10, 19):

$$[S]_{\text{tot}} = [S\text{-OH}_2^+] + [S\text{-OH}] + [S\text{-O}^-], \quad [1]$$

where $[S]_{\text{tot}}$ is the total concentration of surface sites assimilated to the CEC.



with

$$\text{pH}_{\text{zpc}} = \frac{1}{2} (\text{p}K_{a_1} + \text{p}K_{a_2}). \quad [4]$$

For each point of the titration,

$$Q = (\text{Ca} - \text{Cb} + [\text{OH}^-] - [\text{H}^+]) / m, \quad [5]$$

where Q is the surface charge ($\text{mol} \cdot \text{g}^{-1}$), Ca is the acid added

TABLE 3
Acidity Constants and pH_{zpc} Values

	pK_{a1}	pK_{a2}	pH_{zpc}
Pure goethite	7.35 ± 0.05	4.95 ± 0.05	6.15 ± 0.05
COP goethite	7.26 ± 0.08	4.61 ± 0.01	5.94 ± 0.04
ADS goethite	8.15 ± 0.06	5.21 ± 0.06	6.68 ± 0.06
Pure HFO	8.1 ± 0.3	4.5 ± 0.1	6.3 ± 0.2
COP HFO	8.5 ± 0.2	4.2 ± 0.1	6.3 ± 0.2
ADS HFO	8.4 ± 0.3	4.5 ± 0.1	6.4 ± 0.2

($\text{mol} \cdot \text{L}^{-1}$), Cb is the base added ($\text{mol} \cdot \text{L}^{-1}$), and m is the solid concentration ($\text{g} \cdot \text{L}^{-1}$).

$$\text{If } \text{pH} < \text{pH}_{zpc}, \text{ then } K_{a2} = ([S]_{\text{tot}} - Q) \cdot [H^+] / Q. \quad [6]$$

$$\text{If } \text{pH} > \text{pH}_{zpc}, \text{ then } K_{a1} = Q \cdot [H^+] / ([S]_{\text{tot}} - Q). \quad [7]$$

If surface adsorption occurred, solid pH_{zpc} should be more basic. For each oxyhydroxide synthesized in this study, pH_{zpc} values obtained are listed in Table 3.

pH_{zpc} were very similar for each HFO, whatever the metal loading process. It seemed that no adsorption process occurred. On the contrary, ADS goethite presented a larger pH_{zpc} than COP or pure goethite. We can conclude that effectively heavy metals were partly adsorbed on the ADS goethite surface.

Results obtained for HFO had an accuracy less than that of goethites. This difference was directly linked to the mineralogical structure of the oxides. Titrations of better crystallized and stable goethite were more easily repeatable.

The chemical characteristics of HFO and goethite synthesized in this study were compared to characteristics of other similar iron hydroxides (Table 4). Values for each parameter agreed

TABLE 4
Chemical Characteristics of Pure Hydroxides

Oxides	Surface		pK_{a1}	pK_{a2}	pH_{zpc}	References
	N_2 -BET ($\text{m}^2 \cdot \text{g}^{-1}$)	Surface sites ($\mu\text{mol} \cdot \text{m}^{-2}$)				
Pure goethite	36	5.00	7.35	4.95	6.15	This work
Goethite	21	3.79	8.97	5.67	7.32	(21)
Goethite	14.7	9.18	9	6.7	7.85	(20)
Pure HFO	273	1.46	8.1	4.5	6.3	This work
HFO	267	3.75	8.09	5.08	6.59	(21)
HFO	600	3.75	8.93	7.29	8.11	(36)

with data obtained by other authors. The small difference could be explained by the various ionic strength titration conditions or by the differences in origin of solid preparation and storage protocols. Indeed, Muller and Sigg (20) used a commercial solid and Nowack (21) stored his precipitates in "Nanopure" water.

Desorption/Dissolution Experiments

Goethite. COP goethite in presence of sodium ascorbate was solubilized at around 4% (equal to the quantity of Fe in the solution) (Fig. 3). This dissolution induced a release of 55% of Cd, 85% of Pb, and 10% of Zn. Dissolution of iron and consequently other metals was highly dependent on the pH. Lakind and Stone (22) and Mulvaney *et al.* (23) tried to explain this phenomena by the Fe^{2+} readsorption on the surface sites of the solid. Thus, this readsorption limited matrix dissolution. However, Deng (3) showed that readsorption was not the cause of the phenomenon, but it was due to the pH dependence of reducing agent adsorption capacity on the solid surface.

The concentration of the reducing agent was calculated as a function of the total quantity of iron in the solid. Thus, Fe

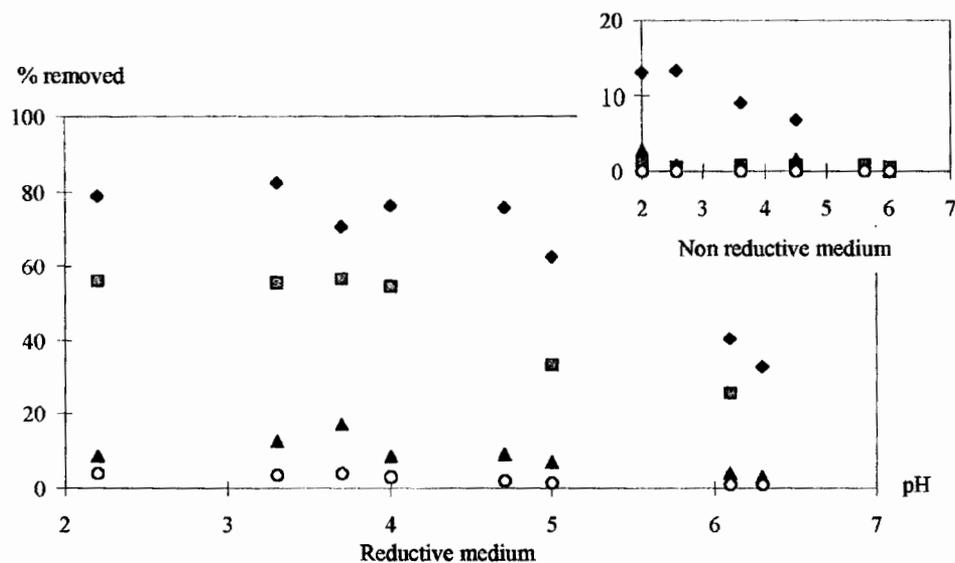


FIG. 3. Heavy metals release from COP goethite: (■) Cd, (◆) Pb, (▲) Zn, and (○) Fe.

dissolution should have been significant, but this was not the case. Goethite was the best crystallized iron oxyhydroxide and the least soluble (24).

Pb is the most easily released into the solution. However, in the environment, it is commonly admitted that Cd is the element most easily released into soils and sediments. Cd presents the lowest surface affinity constants. In COP goethite, metals were added to the solution before solid precipitation. Previous analyses have shown that no adsorption process was identified in this solid. It seemed that, in this study, Cd(II) may have been located within the oxide structure. Indeed, after studies of metal solubility in the presence of iron oxyhydroxide, Ainsworth *et al.* (25) have shown that Cd could be substituted for Fe(III) in the goethite structure. Moreover, Spadini *et al.* (26), using EXAFS, proposed the formation of a mixed phase $\alpha(\text{Cd}_{0.005}\text{Fe}_{0.995})\text{OOH}$ when Cd^{2+} was coprecipitated with goethite.

These results evidenced that, under reductive conditions, a crystallized solid could release metals bound to it in the solution, even in the case of a very low matrix dissolution.

ADS goethite was more solubilized than COP goethite (Fig. 4). Trolard and Tardy (27) have shown that substituted goethite is more stable and dissolved more slowly in acidic and reductive solution than nonsubstituted goethite.

Here the release order of metals was modified. Cd was more solubilized than Pb and Zn in the solution. This result was confirmed by the value of the surface complex constants, $\log K_{\text{FeOPb}}^{\text{S}} = 2.30$ and $\log K_{\text{FeOCd}}^{\text{S}} = -1.05$ (28).

These experiments consisted of desorption and dissolution. The aim was to solubilize the solid matrix in order to remove metals bound to it. The dissolution at around 15% of Fe evidenced a solubilization of the ADS goethite surface. As this dissolution appeared at the solid surface, all adsorbed metals should be released in the aqueous solution. But this is not the case. It

seemed that Pb and, to a lesser extent, Zn were readsorbed onto the solid as soon as they were desorbed. This process is confirmed by the adsorption strength between metals and goethite: $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$ (24).

Both series of experiments evidenced the role of the metal/solid link on the dissolution rate of the matrix under reductive conditions. If ions are substituted in the structure, Fe solubilization is weak and metals release in the solution depending on the nature of the metal.

HFO. Under nonreductive conditions, heavy metal remobilization from COP HFO was low. Fe release was around 10%, so the solid matrix was affected. However, this dissolution depended on pH (Fig. 5).

Ascorbate addition induced a large increase in all metals in the pH range studied. Pb was the metal least removed in the aqueous solution. However, if metals had been trapped in the solid structure as in COP goethite, Pb should have been released most. Ford *et al.* (29) studied the influence of the Pb, Ni/adsorbent interaction on the crystallization kinetics of amorphous iron oxide. They showed that Ni inhibited oxide crystallization by forming a second phase in the matrix and Pb created an inner-sphere complex with surface sites from the start and did not play a part in the crystallization. We conclude that Pb could be adsorbed on the COP HFO surface. However, surface titration seemed to show that no adsorption process occurred onto this type of solid. Moreover, if Pb or Zn were adsorbed on the surface at acidic pH under reductive conditions, they should be released at around 100% for acidic pH, and this is not the case. Two hypothesis could explain this phenomena:

-Pb and Zn were effectively adsorbed onto the surface, and as soon as they were released in the solution they were readsorbed onto the intact surface;

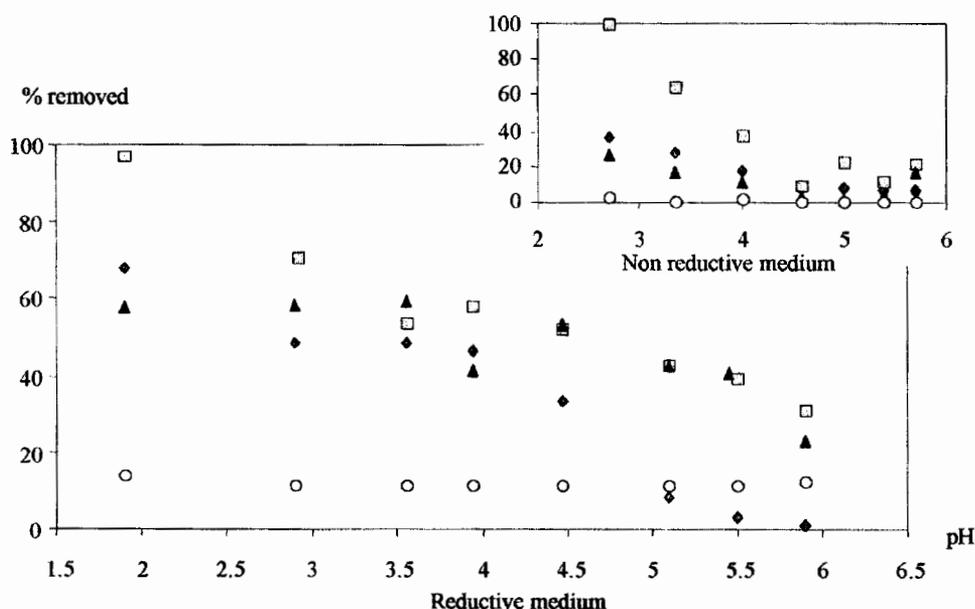


FIG. 4. Heavy metals release from ADS goethite: (■) Cd, (◆) Pb, (▲) Zn, and (○) Fe.

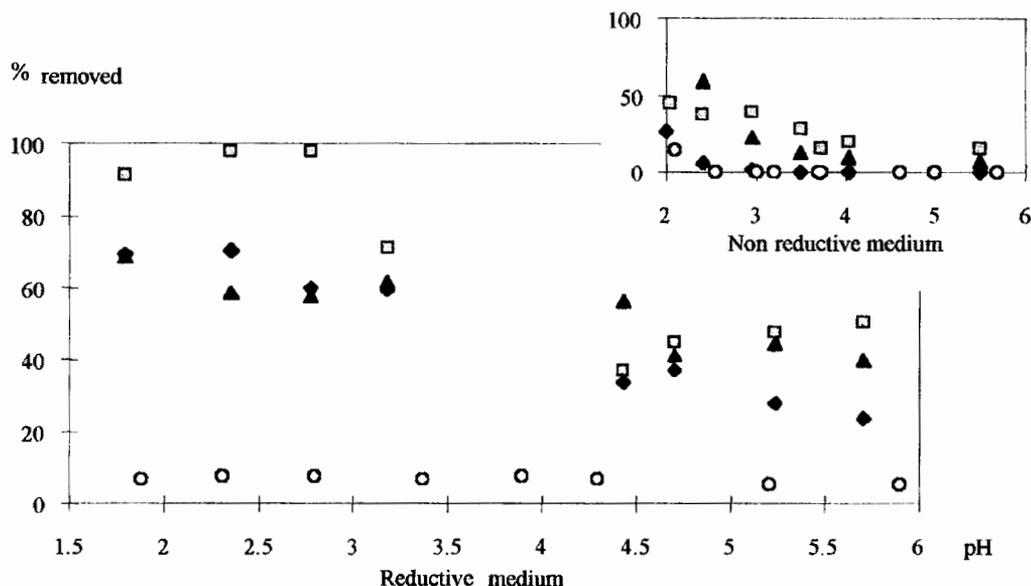


FIG. 5. Heavy metals release from COP HFO: (■) Cd, (◆) Pb, (▲) Zn, and (○) Fe.

-The final pH of solid precipitation was 12. Under this alkaline condition, metals could precipitate as a hydroxide complex, and the concentrations of Pb and Zn in the solution correspond to the dissolution of these surface precipitates (30).

Results obtained for the ADS HFO were similar to results obtained for COP HFO (Fig. 6). Cd is removed almost 100%, so is probably adsorbed at the surface, and Pb and Zn have the same behavior under reductive conditions. It seemed that there were no structural differences between both HFOs.

A solubility computer simulation was carried out in order to determine whether Pb and Zn solubilization was due to dissolution of hydroxide complexes. Formation constants of hydroxide

and carbonate complexes were used. To simulate our experimental conditions, literature thermodynamic constants (31, 32) were recalculated for an ionic strength of 10^{-1} M according to the Davies equation. Carbonate concentrations were calculated from atmospheric CO_2 .

Experimental data plotted in Fig. 7 correspond to the concentrations of ions released in the solution. These experimental points were never in concordance with calculated solubility lines. Thus, Zn and Pb, under our experimental conditions and pH ranges, did not exhibit a solubilization comparable to the precipitates $Zn(OH)_2s$ and $Pb(OH)_2s$. It seemed that no metal had precipitated at the HFO surface. They were either adsorbed or substituted to the surface.

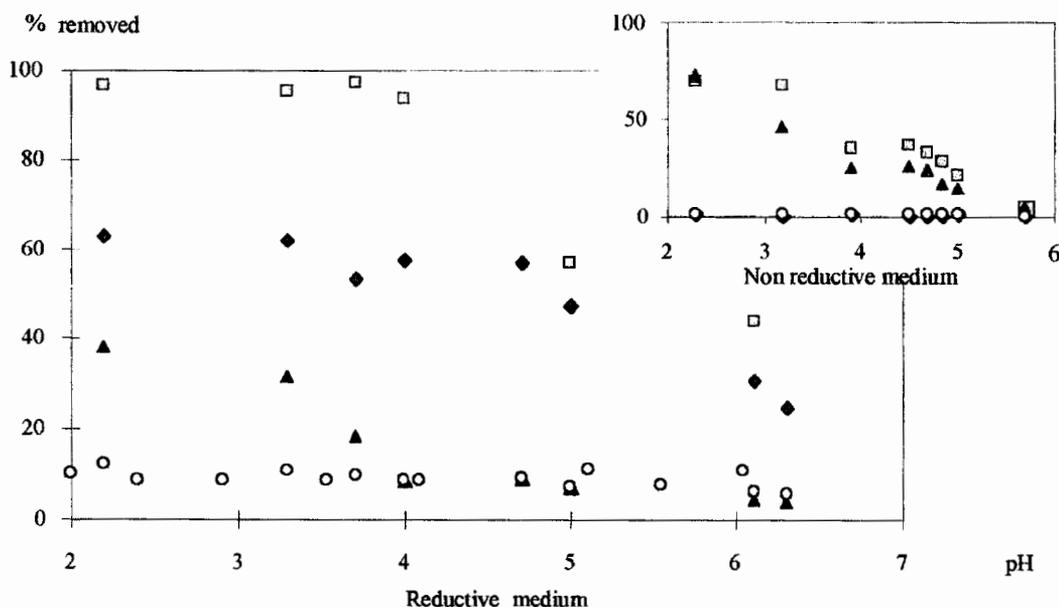


FIG. 6. Heavy metals release from ADS HFO: (■) Cd, (◆) Pb, (▲) Zn, and (○) Fe.

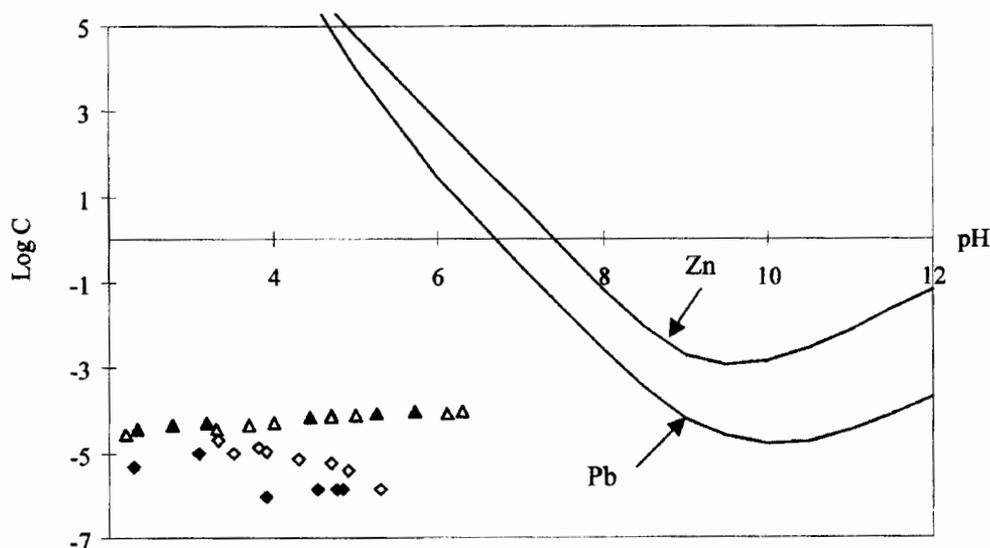


FIG. 7. Cation release from ADS HFO (open symbols) or COP HFO (filled symbols). (\blacktriangle) and (\blacklozenge) correspond, respectively, to Zn and Pb. The lines represent the calculated solubility limit of Zn and Pb.

In order to evidence any possible adsorption process, a series of extraction experiments in presence of a complexant was performed (Fig. 8). The use of EDTA allowed an appreciation of chemically adsorbed metals at the surface (33). Since EDTA extraction led to a quantification of chemisorbed metals, such a test also allowed comparison of the strength of metals for adsorption and coprecipitation (34). As our intention was to desorb metals without matrix dissolution, EDTA was chosen for its slow dissolution kinetics for iron oxide (35). Moreover, with an excess of EDTA, the formation of soluble ion-EDTA complexes was favored (13). However, a partial dissolution of iron oxide appeared. For this reason, results are given as a function of the percentage of dissolved iron.

EDTA extracted ca. 10 to 30% Cd from the ADS HFO and 10 to 20% from the COP HFO, suggesting that Cd was effectively partly adsorbed on the surface. Moreover, since dissolution of oxide was less than 0.4%, Cd extracted had probably been surface bound to these oxides irrespective of the synthesis method. ADS HFO seemed to bind Pb more strongly than COP HFO. However, Pb was extracted by EDTA whichever the solid, thus

it was only partly surface bound. In the case of Zn, EDTA did not extract this metal from either solid. Zn was probably incorporated into both HFO matrices. From these and preceding results, it appeared that the behavior of ADS and COP HFO was approximately similar due to the amorphous structure.

DISCUSSION

Under reductive conditions, solubilization of metals present in iron oxyhydroxides (HFO and goethite) was increased. However, this remobilization was dependent on the crystalline state of the solid and on the metal/solid link (adsorption or coprecipitation). Contrary to a complexant, the reducing agent has the possibility of dissolving a solid matrix. Thus, cations adsorbed and substituted on the solids could be released into the solution.

If metals were partly adsorbed on the oxide surface, a low dissolution of the solid surface induced a high remobilization of this ion. However, Pb with a strong affinity for the solid surface may be readsorbed on the undestroyed surface as soon as it is released. On the contrary, Cd with a weak surface affinity stay

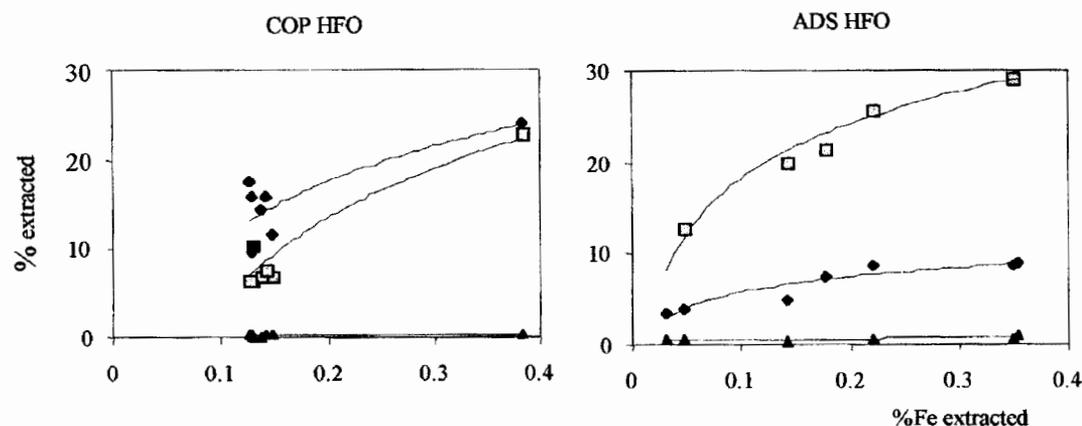


FIG. 8. (\blacksquare) Cd, (\blacklozenge) Pb, and (\blacktriangle) Zn extracted by EDTA from COP HFO and ADS HFO as a function of dissolved Fe.

TABLE 5
Influence of Various Parameters on Metal Release under
Reductive Conditions

	Amorphous structure	Crystalline structure	Adsorption	Substitution
Amorphous structure	/	/	++	+
Crystalline structure	/	/	+	-
Adsorption	++	+	/	/
Substitution	+	-	/	/

Note. ++, high release; +, medium release; -, low release.

in the solution. Thus, for metals fixed through an adsorption process, the risk of contamination was greater for Cd than for Pb and even weak reductive conditions could induce high metal release into the environment.

If metals were substituted into the solid matrix, solubilization of the solid was not favored. The release order of metals was modified. Pb was the most released into the solution. Thus, for metals fixed in the coprecipitation process, the risk of contamination was greater for Pb than for Cd.

Finally, under reductive conditions, irrespective of the crystalline state, solids could be partly solubilized. Even if this solubilization was low, a release of metals bound to it could occur.

Thus, in the case of a coprecipitated crystallized solid, reductive conditions induce metals remobilization whereas a complexant has no effect.

SUMMARY

The influences of the different parameters on the remobilization of heavy metals from polluted solids are summarized on Table 5.

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