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Martin Kubal[a]; Marek váb[a]; Jií ermák[a]; Adam Borýsek[a]
[a] Department of Environmental Chemistry, Institute of Chemical Technology, Czech Republic

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MOBILIZATION OF COPPER AND ZINC HYDROXIDES THROUGH USE OF AMMONIA

Martin Kubal,* Marek Šváb, Jiří Čermák, and Adam Borýsek

Department of Environmental Chemistry, Institute of
Chemical Technology, Technická 5, Praha 6,
166 28 Czech Republic

ABSTRACT

Copper and zinc were separated from their hydroxides and mobilized out of contaminated sandy loam and lake sediment when the metals were in the presence of ammonia concentrations ranging from 0.1 mol/L to 0.3 mol/L. In the equilibrium leaching experiments with pure hydroxides, the 2 heavy metals were mobilized by ammonia complexation in low-alkaline regions in a manner dependent on the total ammonia concentration. Within the pH range studied, the major metals present in the soils either remained practically immobile in the solid matrix (Fe) or their solubility was not directly influenced by ammonia complexation (Ca, Mg). In all cases, the maximum local increase in both zinc and copper solubility was observed at pH $\approx$ 9.5.

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*Corresponding author. Fax: 00420 2 2435 5029; E-mail: Martin.Kubal@vscht.cz

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INTRODUCTION

Heavy metals form a specific group of environmental contaminants. Metals such as copper and zinc typically exhibit the ability to accumulate in soils, sludges, or sediments and present potential risks to human health. Nowadays several remediation techniques can be applied to remove heavy metals from a contaminated porous medium. In the literature, the most frequently mentioned processes are soil washing (1–3), electrokinetic remediation (4–6), and phytoremediation (7). These heavy metal removal techniques include a step in which a particular metal is transferred from the immobile (precipitated and sorbed) state to the mobile form (dissolved in the soil aqueous phase).

When carrying out the mobilization step in soil, technicians usually cannot avoid the use of chemicals; this process is sometimes called “chemical pretreatment.” The chemicals applied to soil may either exhibit a general solubilization effect, for mineral acids or bases (8–10), or may selectively solubilize a particular metal or a group of metals, such as when complexing agents are used (11–13). A nonselectively solubilizing chemical (for example sulfuric acid) added to the polluted soil may generally dissolve contaminating heavy metals and essential metals (Ca, Mg, Fe) in a pH-dependent fashion. As a result of this general solubilization, the consumption of chemicals necessary to reach the desirable degree of heavy metal mobilization is substantially high. The resulting solution requires complicated treatment. This disadvantage can be avoided through the use of selective dissolving complexing agents, which under specific conditions are able to transfer preferably contaminating heavy metals from the immobile form into the solution. The most frequently studied complexing agents are citric acid and ethylenediaminetetraacetic acid (EDTA). In 2000, ammonia pretreatment of heavy-metal polluted soil was shown to significantly increase the effectiveness of the electroremediation process (14). However, this pretreatment step was not studied in detail. In this paper, we describe the mobilization of zinc and copper in the presence of ammonia as it was studied, first from pure metal hydroxides and then from polluted sandy loam and lake materials.

THEORETICAL

In zinc and copper polluted soil, the metals are usually present as hydroxides: $Zn(OH)_2$ and $Cu(OH)_2$. The solubilities of $Zn(OH)_2$ and $Cu(OH)_2$, which exhibit low solubility in water, are principally based on the expression for the solubility product K_s. However, the solubility of the precipitated forms is often substantially influenced by various side reactions, namely by complexation with the ligands present and by various protolytic reactions in which H^+ and/or OH^- participate. The solubility affected by side reactions can be calculated by means of a conditional solubility product K_s', which for substance M_mA_n is defined as

$$K_s' = [M']^m \cdot [A']^n = (K_s)_c \cdot \alpha^m_{M(X)} \cdot \alpha^n_{A(Y)} \tag{1}$$

where $[M']$ and $[A']$ represent conditional concentrations; $(K_s)_c$ represents the solubility product expressed in terms of equilibrium concentrations; and $\alpha^m_{M(X)}$ and $\alpha^n_{A(Y)}$ represent side reaction coefficients, which are defined by the following relationships:

$$\alpha_{M(X)} = 1 + \beta_{MX} \cdot [X] + \beta_{MX_2} \cdot [X]^2 + ... + \beta_{MX_Q} \cdot [X]^Q \tag{2}$$

$$\alpha_{A(Y)} = 1 + \beta_{AY} \cdot [Y] + \beta_{AY_2} \cdot [Y]^2 + ... + \beta_{AY_Q} \cdot [Y]^Q \tag{3}$$

where β denotes stability constants for side reaction complexes.

Useful graphical information on precipitate solubility can be provided by means of the logarithmic diagrams, which are relatively easy to construct. In graphs of hydroxides in the presence of a complexing agent, the concentrations of the various metal forms are plotted against pH for the total ligand content. For each pH value, hydroxide solubility is calculated as the sum of the concentrations of various forms of the complex.

When the solubilities of zinc and copper hydroxides in the presence of ammonia are described, both hydroxyl and ammonia ligand complexation must be presented. For determining $Zn(OH)_2$ solubility, the following forms were taken into account: Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_2^{aq}$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $Zn(NH_3)^{2+}$, $Zn(NH_3)_2^{2+}$, $Zn(NH_3)_3^{2+}$, $Zn(NH_3)_4^{2+}$. $Cu(OH)_2$ solubility determination must be made based on the forms Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2^{aq}$, $Cu(OH)_3^-$, $Cu(OH)_4^-$, $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, $Cu(NH_3)_4^{2+}$, $Cu(NH_3)_5^{2+}$, $Cu(NH_3)_6^{2+}$. The formation of these zinc and copper complexes is expressed by the reaction scheme (log β value at $I = 0$ at 25°C) (15,16):

$$Zn^{2+} + OH^- = Zn(OH)^+ \qquad \log \beta = 4.2 \tag{4}$$

$$Zn^{2+} + 2OH^- = Zn(OH)_2^{aq} \qquad \log \beta = 10.2 \tag{5}$$

$$Zn^{2+} + 3OH^- = Zn(OH)_3^- \qquad \log \beta = 14.4 \tag{6}$$

$$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-} \qquad \log \beta = 15.5 \tag{7}$$

$$Zn^{2+} + NH_3 = Zn(NH_3)^{2+} \qquad \log \beta = 2.2 \tag{8}$$

$$Zn^{2+} + 2NH_3 = Zn(NH_3)_2^{2+} \qquad \log \beta = 4.4 \tag{9}$$

$$Zn^{2+} + 3NH_3 = Zn(NH_3)_3^{2+} \qquad \log \beta = 6.7 \tag{10}$$

$$Zn^{2+} + 4NH_3 = Zn(NH_3)_4^{2+} \qquad \log \beta = 8.7 \quad (11)$$

$$Cu^{2+} + OH^- = Cu(OH)^+ \qquad \log \beta = 6.0 \quad (12)$$

$$Cu^{2+} + 2OH^- = Cu(OH)_2^{aq} \qquad \log \beta = 10.6 \quad (13)$$

$$Cu^{2+} + 3OH^- = Cu(OH)_3^- \qquad \log \beta = 14.1 \quad (14)$$

$$Cu^{2+} + 4OH^- = Cu(OH)_4^{2-} \qquad \log \beta = 16.3 \quad (15)$$

$$Cu^{2+} + NH_3 = Cu(NH_3)^{2+} \qquad \log \beta = 4.0 \quad (16)$$

$$Cu^{2+} + 2NH_3 = Cu(NH_3)_2^{2+} \qquad \log \beta = 7.3 \quad (17)$$

$$Cu^{2+} + 3NH_3 = Cu(NH_3)_3^{2+} \qquad \log \beta = 10.1 \quad (18)$$

$$Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+} \qquad \log \beta = 12.3 \quad (19)$$

$$Cu^{2+} + 5NH_3 = Cu(NH_3)_5^{2+} \qquad \log \beta = 11.4 \quad (20)$$

$$Cu^{2+} + 6NH_3 = Cu(NH_3)_6^{2+} \qquad \log \beta = 8.9 \quad (21)$$

Further equations were necessary to construct the logarithmic solubility diagrams. The expressions for the hydroxide solubility products, the ionic product of water, and protolysis of ammonia, as well as the balance equations for the total soluble zinc and copper concentrations and the ammonia containing species, are as follows:

$$Zn(OH)_2(s) = Zn^{2+} + 2OH^- \qquad pK_s = 16.50 \quad (22)$$

$$Cu(OH)_2(s) = Cu^{2+} + 2OH \qquad pK_s = 19.32 \quad (23)$$

$$H_2O = H^+ + OH^- \qquad pK_w = 14.00 \quad (24)$$

$$NH_3 + H^+ = NH_4^+ \qquad pK = 9.25 \quad (25)$$

$$\begin{aligned}[Zn]_{total} = {} & [Zn^{2+}] + [Zn(OH)^+] + [Zn(OH)_2^{aq}] + [Zn(OH)_3^-] \\ & + [Zn(OH)_4^{2-}] + [Zn(NH_3)^{2+}] + [Zn(NH_3)_2^{2+}] \\ & + [Zn(NH_3)_3^{2+}] + [Zn(NH_3)_4^{2+}]\end{aligned} \quad (26)$$

$$\begin{aligned}[\ \mathrm{Cu}]_{\mathrm{total}} = {} & [\mathrm{Cu}^{2+}] + [\mathrm{Cu(OH)}^{+}] + [\mathrm{Cu(OH)}_2^{\mathrm{aq}}] \\ & + [\mathrm{Cu(OH)}_3^{-}] + [\mathrm{Cu(OH)}_4^{2-}] + [\mathrm{Cu(NH_3)}^{2+}] \\ & + [\mathrm{Cu(NH_3)}_2^{2+}] + [\mathrm{Cu(NH_3)}_3^{2+}] + [\mathrm{Cu(NH_3)}_4^{2+}] \\ & + [\mathrm{Cu(NH_3)}_5^{2+}] + [\mathrm{Cu(NH_3)}_6^{2+}]\end{aligned} \tag{27}$$

$$\begin{aligned}[\ \mathrm{NH_3}]_{\mathrm{total}}\ (\text{for } \mathrm{Zn(OH)_2} \text{ solubility}) = {} & [\mathrm{NH_3}] + [\mathrm{NH_4^+}] + [\mathrm{Zn(NH_3)}^{2+}] \\ & + 2[\mathrm{Zn(NH_3)}_2^{2+}] + 3[\mathrm{Zn(NH_3)}_3^{2+}] + 4[\mathrm{Zn(NH_3)}_4^{2+}]\end{aligned} \tag{28}$$

$$\begin{aligned}[\ \mathrm{NH_3}]_{\mathrm{total}}\ (\text{for } \mathrm{Cu(OH)_2} \text{ solubility}) = {} & [\mathrm{NH_3}] + [\mathrm{NH_4^+}] + [\mathrm{Cu(NH_3)}^{2+}] \\ & + 2[\mathrm{Cu(NH_3)}_2^{2+}] + 3[\mathrm{Cu(NH_3)}_3^{2+}] + 4[\mathrm{Cu(NH_3)}_4^{2+}] \\ & + 5[\mathrm{Cu(NH_3)}_5^{2+}] + 6[\mathrm{Cu(NH_3)}_6^{2+}]\end{aligned} \tag{29}$$

By combining Eqs. (4–29), the relations can be derived for concentrations of particular zinc and copper species based on their dependencies on pH and free ammonia $[NH_3]$ concentration. However, the equation for the sum of all ammonia species (Eqs. 28 and 29) is transformed into the 4th-degree or the 6th-degree polynomial, which must be solved numerically for each particular pH value. For this purpose, a special program was created in the PASCAL language through which the polynomial was solved by the interval halving technique. The resulting theoretical solubility diagrams for $Zn(OH)_2$ and $Cu(OH)_2$ are shown in Figs. 1 and 2.

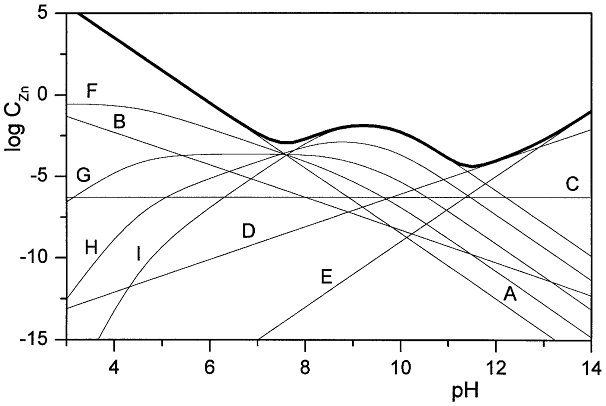

Figure 1. The logarithmic solubility diagram of $Zn(OH)_2$ as a function of pH in the presence of ammonia ($[NH_3]_{total}$ = 0.3 mol/L). The bold line represents the sum of all zinc species in solution. The thin lines represent equations (A) $\log [Zn^{2+}] = 11.5 - 2$ pH; (B) $\log [Zn(OH)^+] = 1.7 -$ pH; (C) $\log [Zn(OH)_2^{aq}] = -6.3$; (D) $\log [Zn(OH)_3^-] = -16.1 +$ pH; (E) $\log [Zn(OH)_4^{2-}] = -29.0 + 2$ pH; (F) $\log [Zn(NH_3)^{2+}] = 13.7 + \log [NH_3] - 2$ pH; (G) $\log [Zn(NH_3)_2^{2+}] = 15.9 + 2 \log [NH_3] - 2$ pH; (H) $\log [Zn(NH_3)_3^{2+}] = 18.2 + 3 \log [NH_3] - 2$ pH; and (I) $\log [Zn(NH_3)_4^{2+}] = 20.2 + 4 \log [NH_3] - 2$ pH.

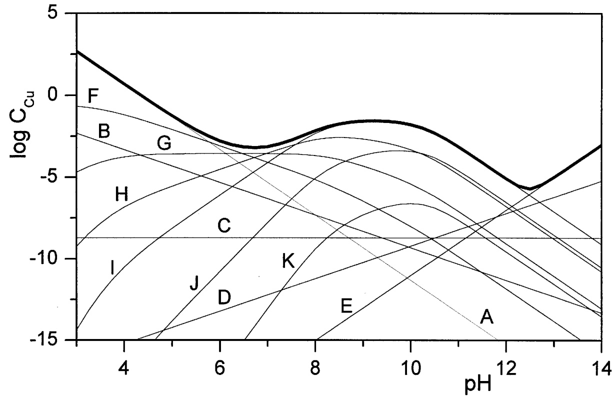

Figure 2. The logarithmic solubility diagram of $Cu(OH)_2$ as a function of pH in the presence of ammonia ($[NH_3]_{total} = 0.3$ mol/L). The bold line represents the sum of all copper species in solution. The thin lines represent equations (A) $\log [Cu^{2+}] = 8.7 - 2\ pH$; (B) $\log [Cu(OH)^+] = 0.7 - pH$; (C) $\log [Cu(OH)_2^{aq}] = -8.7$; (D) $\log [Cu(OH)_3^-] = -19.2 + pH$; (E) $\log [Cu(OH)_4^{2-}] = -31.0 + 2\ pH$; (F) $\log [Cu(NH_3)^{2+}] = 12.7 + \log [NH_3] - 2\ pH$; (G) $\log [Cu(NH_3)_2^{2+}] = 16.0 + 2 \log [NH_3] - 2\ pH$; (H) $\log [Cu(NH_3)_3{}^{2+}] = 18.8 + 3 \log [NH_3] - 2\ pH$; (I) $\log [Cu(NH_3)_4^{2+}] = 21.0 + 4 \log [NH_3] - 2\ pH$; (J) $\log [Cu(NH_3)_5^{2+}] = 20.1 + 5 \log [NH_3] - 2\ pH$; and (K) $\log [Cu(NH_3)_6^{2+}] = 17.6 + 6 \log [NH_3] - 2\ pH$.

By combining Eqs. (28 and 29), one can derive both copper and zinc solubilities from their hydroxides when they are present together in a mixture.

In the mathematical model described above only $Zn(OH)_2$ and $Cu(OH)_2$ are considered in their solid forms. When trying to make the model more realistic (for example, by introducing insoluble complexes with organic matter), we had difficulty finding reliable equilibrium data. Thus the presented model should be understood as an idealized one that provides more of estimation than an exact simulation of polluted-material leaching behaviors. This kind of simplification, in which only the pure hydroxide forms instead of real systems are considered, has already been used in the past (18) to model Zn and Pb extraction from polluted soils by oxalate.

EXPERIMENTAL

The solubility of zinc and copper in the presence of ammonia was experimentally studied using 1) well defined $Zn(OH)_2$ and $Cu(OH)_2$, 2) the sandy loam soil polluted by zinc and copper, and 3) lake sediment polluted by zinc and cop-

Table 1. Some Characteristics of the Polluted Materials Used in Solubility Experiments

Metal (mg/kg)	Sandy Loam	Lake Sediment
Zn	19 600	5300
Cu	2100	4800
Ca	16 000	17 500
Mg	2200	3800
Fe	42 800	27 500
organic carbon (%)	2.8	16.2

per. The defined hydroxides were prepared by precipitation from respective solutions of $CuSO_4$ and $ZnSO_4$ with NaOH. The freshly precipitated hydroxides were washed with distilled water until the sodium content in the water was less than approximately 0.2 ppm. The washed hydroxides were dried at 40°C. Purities of the resulting products were higher than 99.5%. The compositions of the 2 real polluted materials are shown in Table 1, while the fractionation of zinc and copper as determined by the sequential extraction technique (17) is shown in Table 2.

The polluted sandy loam originated from the industrial area of Holýšov, in the Czech Republic, where a galvanization plant had previously operated. For several decades the waste (neutralized) sludges from the galvanization process were thrown out without any treatment and accumulated in the area. In the course of time, the sludges were mixed with soil. The sandy loam sample (water content 12% wt/wt) was taken at a depth of 0.5 m. The fraction with particle sizes smaller than 1 mm was separated by a sieve, air-dried at laboratory temperature, and homogenized. The polluted lake sediment was taken from northeastern Prague (Czech Republic). The pollution came from the military airbase, where another galvanization plant was also in operation. For a long time, the neutralized sludges

Table 2. Percentages of Total Zinc and Copper Found in the Successive Leachates of Sequential Extraction Analysis

	Sandy Loam		Lake Sediment	
Fraction (%)	Zn	Cu	Zn	Cu
Exchangeable	0.3	0.3	0.3	0.2
Bound to carbonates	7.9	2.7	11.5	0.5
Bound to Fe and Mn oxides	57.4	29.4	72.2	1.5
Bound to organic matter	26.8	38.1	13.0	88.1
Residual	7.6	29.5	3.0	9.7

were released into a small river that fed the lake. In 1992, the lake was emptied because of dam reconstruction and its bottom remained open to air until 1997 when the samples used in this work were taken in the depth of 0.1–0.3 m (water content 35%). The samples were air dried at laboratory temperature and homogenized.

In the solubility experiments with pure hydroxides, 1 g of $Zn(OH)_2$ and $Cu(OH)_2$, respectively, was put into a 25-mL, screw-cap, plastic bottle to which 20 mL of a 0.1–0.3 mol/L NH_4NO_3 solution was subsequently added. This source of ammonia is often used in agriculture as a fertilizer. The pH of the bottled solutions was adjusted by adding a predetermined amount of 4 mol/L NaOH in such a way that the total volume in the bottle was not substantially changed. The total amount of NaOH added into each bottle ranged from 0 to 0.2 g. Then the cap was carefully screwed shut and sealed by molten wax to prevent ammonia from escaping out of the bottle. The bottles were shaken for 24 hours, after which the pH was measured and the solution was filtered as fast as possible. The metal concentrations in the filtrate were measured by atomic absorption spectroscopy (AAS). In the solubility experiments with the polluted loam and sediment the procedure was practically the same as that for the hydroxide samples, except that 3 g of each pollution sample were put into bottles.

RESULTS AND DISCUSSION

The principal influence of ammonia on the solubility of zinc and copper from their hydroxides is shown in the theoretical diagrams in Figs. 1 and 2. As a result of ammonia complexation, the solubility of both zinc and copper is substantially increased in a low alkaline region. The formed ammonia complex $[Zn(NH_3)_4^{2+}]$ is mainly responsible for zinc solubility increases while the $[Cu(NH_3)_4^{2+}]$ complex increases the solubility of copper in a similar way. The theoretical diagrams shown in Figs. 1 and 2 can be divided into 4 regions. Up to the pH value of approximately 7.5 for zinc and approximately 6.6 for copper, the degree of ammonia complexation is so low that it has practically no influence on metal solubility. Up to these pH values, the main soluble forms of the metals are Zn^{2+} and Cu^{2+} and their total solubilities decrease with increasing pH because the increased OH^- concentration makes the solid hydroxides more stable. Within the pH range of approximately 7.5–9.3 for zinc and 6.6–9.3 for copper, the ammonia complexation increases the total solubility by forming soluble complexes while at the same time suppressing the increasing influence of OH^-. Within the pH ranges of approximately 9.3–11.5 for zinc and 9.3–12.5, the competition of the OH^- molecules is so high that the degree of ammonia complexation (and the total solubility) decreases. At pH values higher than approximately 11.5 for zinc and 12.5 for copper the influence of ammonia is negligible, but the formation of the soluble hydroxy complexes increases the total solubility at the increasing pH values.

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The solubility behavior of both zinc and copper is substantially changed if the solid hydroxide forms of these 2 metals are exposed together to the ammonia solution in a mixture. Because the ammonia complexes of copper are more stable than those of zinc, the total solubility of copper is less influenced in the mixed system. As shown in Fig. 3 the theoretical $Zn(OH)_2$ solubility is reduced more than 50% in the presence of $Cu(OH)_2$. Because of the higher copper complex stabilities, most of the NH_3 ligands are consumed in the solubilization of copper and only a small amount of the ligands remain to solubilize zinc.

The influence of the total ammonia concentration on both theoretical and experimental solubility of zinc and copper (from their hydroxides of purity higher than 99.5%) is shown in Figs. 4 and 5. Irrespective of ammonia concentration, the maximum value of the theoretical solubility in a low alkaline region was found at the pH of approximately 9.3 for both zinc and copper. In the case of zinc hydroxide, the experimentally found solubilities agreed with the theoretical calculated lines, but all the measured values were shifted on the X-axis so that the maximum value could be localized at the pH value of approximately 9.5. In the case of copper hydroxide, the measured solubilities were shifted from the theoretical lines such that the maximum solubility was at approximately pH 9.5. The experimental solubilities of copper from $Cu(OH)_2$ were lower than those predicted by the theory. This difference could be caused by the choice of the equilibrium characteristics and also by the choice to use concentrations instead of activity values in the model. The values of the stability constants and solubility products found in the literature for a particular species (at given temperature and ionic strength) might vary at certain limits because the results depend on the method and conditions of determination or on the age of the product studied.

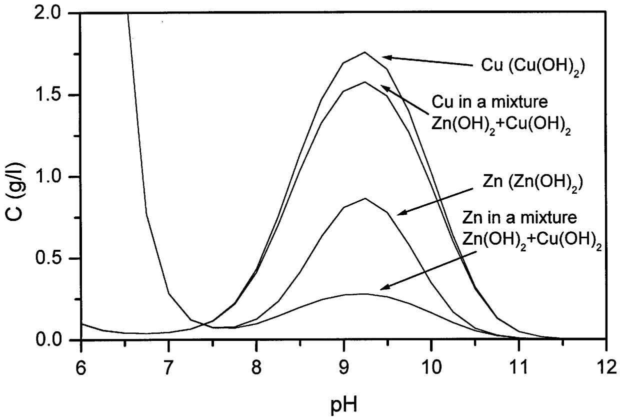

Figure 3. Theoretical solubility of $Zn(OH)_2$ and $Cu(OH)_2$ when together in the presence of ammonia ($[NH_3]_{total} = 0.3$ mol/L).

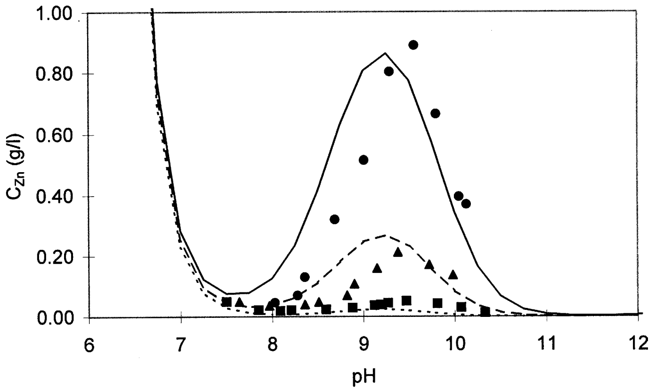

Figure 4. Theoretical and experimental solubility of $Zn(OH)_2$ in the presence of ammonia. $[NH_3]_{total}$ = 0.1 mol/L, (·········· theory, ■ experiment); $[NH_3]_{total}$ = 0.2 mol/L, (-------- theory, ▲ experiment); and $[NH_3]_{total}$ = 0.3 mol/L, (—— theory, ● experiment).

Experimentally found solubilities of zinc and copper in the sandy loam and lake sediment are shown in Figs. 6–9. For comparison, the theoretical solubilities of hydroxides (calculated for the mixture of $Zn(OH)_2$ and $Cu(OH)_2$) are included in the graphics. As in the experiments with pure, well-defined hydroxides, the local increase in zinc and copper solubility was observed in the low alkaline region for both polluted materials studied. The maximum solubilities of zinc and copper

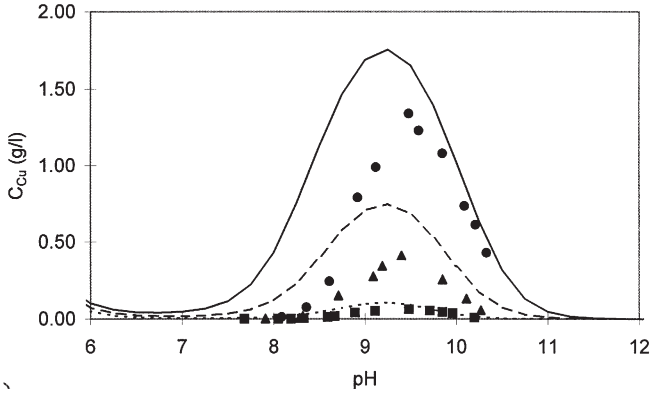

Figure 5. Theoretical and experimental solubility of $Cu(OH)_2$ in the presence of ammonia. $[NH_3]_{total}$ = 0.1 mol/L, (·········· theory, ■ experiment); $[NH_3]_{total}$ = 0.2 mol/L, (-------- theory, ▲ experiment); and $[NH_3]_{total}$ = 0.3 mol/L, (—— theory, ● experiment).

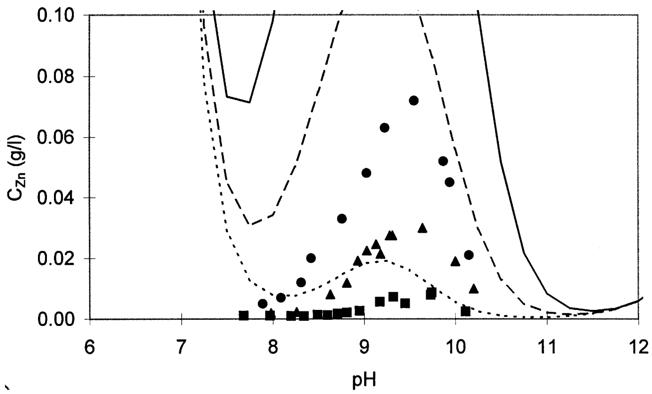

Figure 6. Solubility of zinc in polluted sandy loam in the presence of ammonia. [NH$_3$]$_{total}$ = 0.1 mol/L, (········ theory for Zn(OH)$_2$, ■ experiment); [NH$_3$]$_{total}$ = 0.2 mol/L, (-------- theory for Zn(OH)$_2$, ▲ experiment); and [NH$_3$]$_{total}$ = 0.3 mol/L, (—— theory for Zn(OH)$_2$, ● experiment).

were found at approximately pH 9.5. However, in all cases the mobilizing effect resulting from ammonia complexation in the low alkaline region was significantly lower than predicted by the theoretical calculations for a mixture of Zn(OH)$_2$ and Cu(OH)$_2$. As shown in Figs. 6–9, except for the maximum solubility found at pH 9.5, practically no similarity was found between zinc and copper solubility behavior in sandy loam and lake sediment and that observed for well-defined hy-

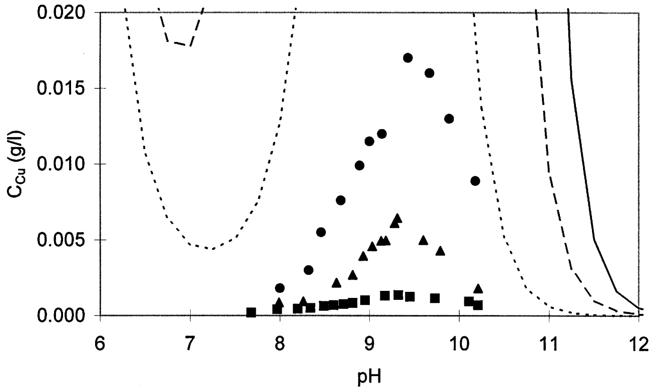

Figure 7. Solubility of copper in polluted sandy loam in the presence of ammonia. [NH$_3$]$_{total}$ = 0.1 mol/L, (········ theory for Cu(OH)$_2$, ■ experiment); [NH$_3$]$_{total}$ = 0.2 mol/L, (-------- theory for Cu(OH)$_2$, ▲ experiment); and [NH$_3$]$_{total}$ = 0.3 mol/L, (—— theory for Cu(OH)$_2$, ● experiment).

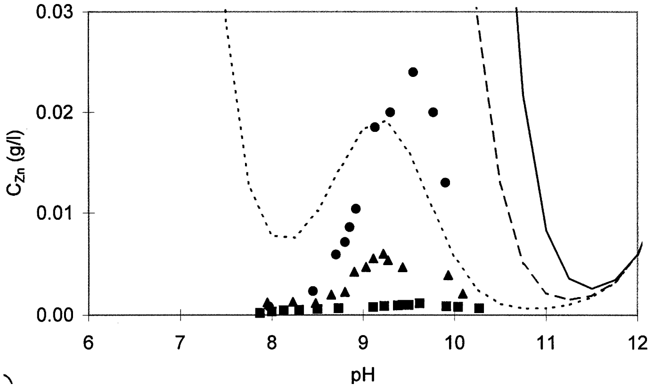

Figure 8. Solubility of zinc in polluted lake sediment in the presence of ammonia. $[NH_3]_{total}$ = 0.1 mol/L, (·········· theory for $Zn(OH)_2$, ■ experiment); $[NH_3]_{total}$ = 0.2 mol/L, (-------- theory for $Zn(OH)_2$, ▲ experiment); and $[NH_3]_{total}$ = 0.3 mol/L, (—— theory for $Zn(OH)_2$, ● experiment).

droxides. The experimentally found solubility values in sandy loam and lake sediment were substantially lower than those predicted for zinc and copper hydroxide, which suggested that in both the polluted materials, the heavy metals were present in the less soluble forms than the $Zn(OH)_2$ or $Cu(OH)_2$ used in the experiments. The data in Table 2 allows one to see that in both the polluted materials, zinc and copper were mostly present in the fractions bound to Fe and Mn oxides

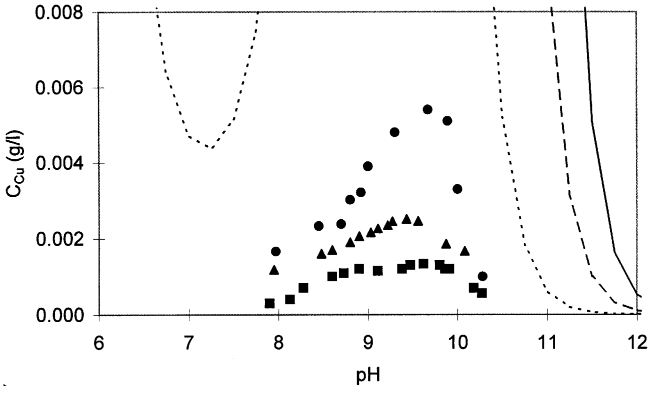

Figure 9. Solubility of copper in polluted lake sediment in the presence of ammonia. $[NH_3]_{total}$ = 0.1 mol/L, (·········· theory for $Cu(OH)_2$, ■ experiment); $[NH_3(]_{total}$ = 0.2 mol/L, (-------- theory for $Cu(OH)_2$, ▲ experiment); and $[NH_3]_{total}$ = 0.3 mol/L, (—— theory for $Cu(OH)_2$, ● experiment).

and to organic matter. Obviously the 2 heavy metals, which originally had been released in the hydroxide forms, were subjected to the stabilizing processes during long exposure in the soil or sediment matrix. However, the extent to which this stabilization proceeded (and the detailed knowledge of the resulting species) was difficult to determine from the sequential extraction analysis. An attempt to make the theoretical model more complex, by introducing sorption on inorganic oxides or complexation with organic matter, was consequently not successful because it was practically impossible to find reliable acceptable thermodynamic data for such a model.

In the experiments with the polluted materials, the solubilities of the 3 major metals present, Ca, Mg, Fe, were measured as well were those of Zn and Cu. The solubilities of iron were less than the AAS detection limit (<0.1 mg/L) in the pH region studied. The solubilities of calcium and magnesium are shown in Figs. 10 and 11. For both metals, the solubilities are slightly dependent on pH, but they are not practically influenced by the presence of ammonia. The relatively high solubilities of calcium and magnesium compared with those of zinc and copper observed in both sandy loam and lake sediment could result from the reaction with OH^- to form $Ca(OH)_2$ and $Mg(OH)_2$ respectively. To a few hundred ppm for calcium and about 10 times less for magnesium, calcium and magnesium is frequently solubilized in many soils. With increasing pH values, the solubilities of calcium and magnesium hydroxides are slightly lowered and the solubility product is kept constant. Unlike the 2 heavy metals, the solubilities of calcium and magnesium did not exhibit local increases within the low alkaline region. Of the

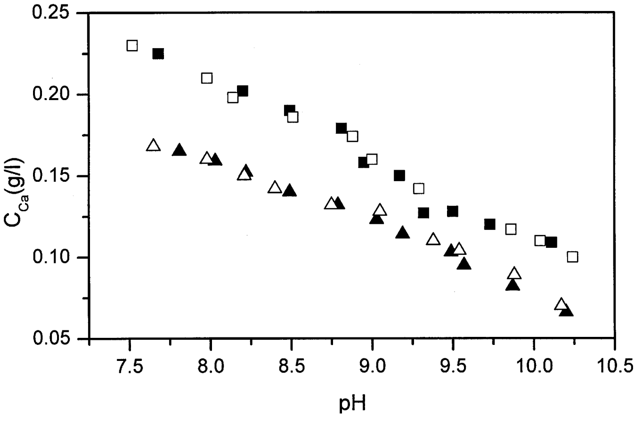

Figure 10. Solubility of calcium from sandy loam (■ $[NH_3]_{total} = 0.3$ mol/L, □ without ammonia) and from lake sediment (▲ $[NH_3]_{total} = 0.3$ mol/L, △ without ammonia).

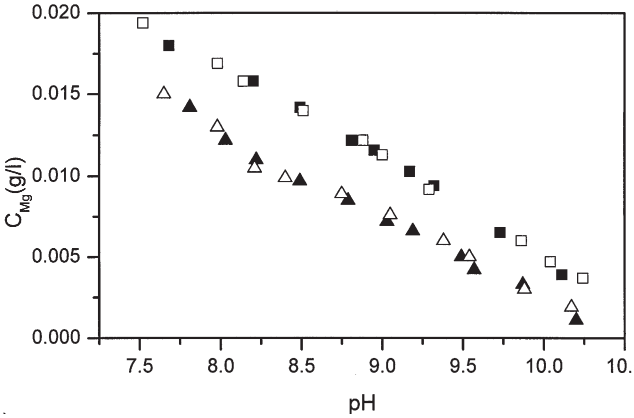

Figure 11. Solubility of magnesium from sandy loam (■ $[NH_3]_{total} = 0.3$ mol/L, □ without ammonia) and from lake sediment (▲ $[NH_3]_{total} = 0.3$ mol/L, △ without ammonia).

5 metals measured, the only 2 in which the solubility was directly influenced by ammonia complexation were zinc and copper. As a result, the effect of ammonia in the 2 polluted materials can be considered selective.

CONCLUSIONS

The solubilities of zinc and copper from their hydroxides and 2 real polluted materials were increased in the presence of ammonia within the low alkaline region. The solubility increase reached a maximum value at pH ≈ 9.5 for both zinc and copper and was caused by the ammonia complexation, which was selective with respect to major essential metals present in the polluted materials studied. Theoretical calculations made for the system $Zn(OH)_2—NH_3—H_2O$ and $Cu(OH)_2—NH_3—H_2O$, respectively, showed that in the case of zinc, the $[Zn(NH_3)_4^{2+}]$ complex is mainly responsible for the solubility increase in slightly alkaline pH while in the copper-containing system, the $[Cu(NH_3)_4^{2+}]$ complex mainly participates in the effect observed. The experimentally found solubilities of Zn and Cu from their pure, well-defined hydroxides in the ammonia solutions of 0.1–0.3 mol/L were in relatively good agreement with the theoretical calculated solubilities. However, the solubilities of zinc and copper in polluted sandy loam and lake sediment were substantially lower than predicted for the pure hydroxides, which suggested that the stability of the 2 metals in these materials was much higher than predicted and were found for $Zn(OH)_2$ and $Cu(OH)_2$.

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