

Adsorption characteristics of copper in rivers contaminated by acid mine drainage from copper mine

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Abstract—In this paper, the partitioning of copper between surficial sediments and overlaying water in Dawu-Le An River, which was contaminated by acid mine drainage resulted from mining activities, was studied by field investigation and acid dissolution experiment. Simulated adsorption experiments were carried out to study the adsorption of copper on amorphous iron oxyhydroxide and ore tailing particles. The results showed that it was the binding of copper onto the surface of amorphous Fe/Al oxyhydroxides and ore tailing particles that regulated the concentrations of dissolved Cu at downstream of Dawu River and its inlet into Le An River. A significant part of adsorbed copper was likely to be associated with amorphous Fe/Al oxyhydroxides coated on the surface of ore tailing particles. A simplified surface complexation model can be used to describe the adsorption behavior in the river.

Keywords: copper mine; adsorption behavior; natural waters.

1 Introduction

Adsorptive processes are thought to be important in the regulation of trace metal concentration in many natural waters. For instance, the adsorption of trace metal ions on minerals, hydrous metal oxides and suspended matter may be responsible for the distribution of metals in the aquatic environment (Benjamin, 1981; Singh, 1984).

Several researchers have investigated the binding of trace metals to oxic sediments by adsorption studies or by sequential extraction, in order to obtain an understanding of factors contributing to trace metal removal in natural water (Mouvet, 1983; Lion, 1982). However, most experiments were conducted under controlled laboratory conditions (Davis, 1978; Benjamin, 1981). The studies have indicated that in natural water, clay mineral particles play a role as a mechanical substrate for the precipitation and flocculation of hydrous Fe/Mn oxides (Singh, 1984), thus hydrous Fe/Mn oxides occur commonly as a coating on the surface of clay mineral particles. The adsorption of trace metals from water onto the oxide surfaces was thought to be an important process affecting trace metal transport in natural water, and models, especially the surface complexation models, have been widely used to describe and interpret the surface adsorption reactions (Davis, 1978; Stumm, 1981).

In this paper, the partitioning of copper between surficial sediments or suspended parti-

cles and overlaying water in Dawu-Le An River, which was contaminated by acid mine drainage resulted from mining activities, was studied by field investigation and acid dissolution experiment. Simulated adsorption experiments were carried out to study the adsorption of copper on amorphous iron oxyhydroxide and ore tailing particles. The results were compared and discussed, and a simplified surface complexation model was used to describe the adsorption. The objective of the study is to investigate the adsorption characteristics and the regulation of Cu in rivers contaminated by acid mine drainage.

2 Materials and methods

Dawu-Le An River section runs through the area of Dexing Copper Mine, which is the largest bornite mine in China. A survey on metal pollution in the river section has shown that the river section has been polluted heavily by the acid mine drainage from the copper mine (Tang, 1992). The chemical processes occurred and associated changes in the concentrations of dissolved metal pollutants in the river section have also been elaborated by Luan (Luan, 1992). Fig. 1 gives a map of the river showing the sampling sites. Water, suspended particles and surface sediment samples were collected from about 20 sites along the river. The water samples were acidified to pH 1 and were filtered through a $0.45\ \mu\text{m}$ membrane, and then were acidified again before being analyzed by ICP and IC, respectively. Chemical components in the surface sediments were analyzed by XRP.

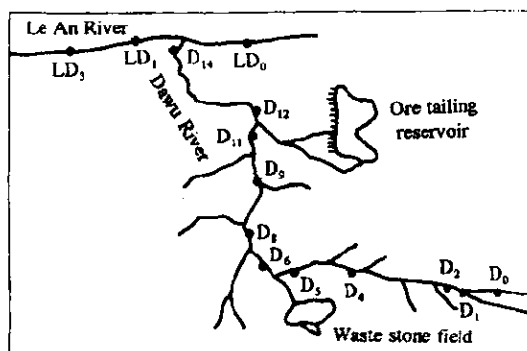


Fig. 1 Location of sampling sites on Dawu—Le An River

The experiment for acid dissolution of metals from the surface sediments was conducted by adding H_2SO_4 solution with different concentration to 5g of the surface sediments. The pH of the suspensions was about 1.6—2.0. The suspensions were shaken for 3h and equilibrated for 24h at $25\pm 1^\circ\text{C}$. The suspensions after equilibrium were filtered through $0.45\ \mu\text{m}$ filter membrane, and the supernatants were analyzed by ICP. The analysis results showed that the concentrations of Fe, Al and Cu dissolved from the three surface sediments generally increased with increasing acid strength, and the amounts of Fe, Al and Cu dissolved from the surface sediments in the $0.005\ \text{mol/L}$ H_2SO_4 solution were roughly equal to that in easily extractable (HOAC-soluble) and moderately reducible ($\text{NH}_2\text{OH HCl-HOAC}$) solutions in the

five-step sequential extraction (Mao, 1992). Thus it was assumed that this method was suitable for determining the adsorbed Cu and amorphous Fe/Al oxyhydroxides.

In order to further understand the adsorption of Cu in rivers contaminated by the acid mine drainage from copper mine, a series of simulated adsorption experiments were conducted and three types of particles were used as simulated adsorbents. Firstly, amorphous Fe oxyhydroxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) was prepared *in situ* by drop wise addition of carbonate-free NaOH solution to the ferric sulfate solution and was aged for 3h at pH 7.5 before the adsorption experiment because the freshly precipitated gel of iron has very significant sorptive capacity for metal ions (Davis, 1978) and is generally presented in suspended matters and surface sediments in the river. The gel solution of ferric sulfate contains a certain number of sulfate ions, which corresponds roughly to that in the mine water. Secondly, fine-gained ore tailing particles from ore floating plant were screened by $50\mu\text{m}$ screen. Thirdly, a mixture of amorphous Fe oxyhydroxide and ore tailing particles was prepared by drop wise addition of carbonate-free NaOH solution to the ferric sulfate solution containing the ore tailing particles. Surface characteristics of these particles were also determined by variety of methods (Luan, 1993).

The adsorption experiments were conducted in batches as follows; a measured amount of previously prepared Fe oxyhydroxide gel or ore tailing suspension was transferred from the storing bottle into several 100 ml polyethylene bottles. The ionic strength was adjusted to 0.1 mol/L by the addition of 1.0 mol/L NaNO_3 solution. The pH was adjusted by the addition of 0.1 mol/L NaOH or HNO_3 solution. 0.2—20 ppm of Cu concentrations were added to the suspensions from the stock solution which is based on the metal ion level likely to be present in Dawu-Le An River. Then CO_2 -free deionized water was added for bring the total volume of suspension to 50 ml. The suspensions were shaken for 3h and equilibrated for 20h at 25°C . The suspensions after equilibrium were filtered through $0.45\mu\text{m}$ filter membrane and the supernatants were analyzed by AAS. The experimental methods have been described in detail elsewhere (Luan, 1991). All experimental vessels and containers were precleaned by soaking in 2 mol/L HNO_3 and reagents were of analytical grade or guarantee reagent.

3 Results and discussion

3.1 Distribution of metals in water and sediments of Dawu-Le An River

Concentrations of main metal pollutants in water of Dawu-Le An River section are shown in Table 1. Other metal pollutants are not listed because their concentrations in the water are low (0.5—3 mg/L). It is seen that the water at upstream of Dawu River (Site D6 and D8) is a typical acid stream water with pH 2.6—2.8 and contains very high concentrations of dissolved metal ions, such as Fe, Al and Cu, because it received acid mine drainage from wastestone dump. A sharp change in pH and dissolved metal concentration occurred at downstream of the river as it received the alkaline wastewater from the ore floating plant. pH values rapidly increased from 2.6—2.8 to 4.8—7.2 (D12—LD1) after the mixing of the

acid stream water with the alkaline wastewater. The concentrations of Fe, Al and Cu decreased obviously from 331.9, 119.7 and 18.7 ppm to 1.7, 2.1 and 0.3ppm, respectively, and about 70%—90% of them was in particulate phase. The change of dissolved metal contents appears to be due to the precipitation and adsorption processes that can occur at near-neutral pH conditions (pH 4.8—7.2) after the mixing. The precipitating sequence of dissolved Fe, Al and Cu metal ions from the river was consistent with the known pH-dependence of the precipitation or adsorption reactions of these cations.

Table 1 Average total (T) and dissolved (D) concentrations of main metal pollutants at Dawu—Le An River section

							Unit: ppm
	Site	pH	Fe	Al	Mn	Cu	S
Acid water before the mixing	D1—D6	2.4—2.7	(T)453.7	136.7	10.9	24.5	682.6
			(D)331.9	119.7	10.0	18.7	648.0
	D7—D11	2.8—3.0	(T)341.8	82.6	9.2	27.5	825.0
			(D)297.5	73.4	8.9	19.5	786.0
After the mixing of alkaline wastewater	D12	4.3—4.8	(T) 53.5	22.1	3.3	5.2	150.9
			(D) 12.4	13.6	2.6	2.3	127.9
Into Le An River	L01—L03	4.7—7.2	(T) 8.0	17.7	0.5	1.7	86.5
			(D) 1.7	2.1	0.3	0.08	16.1

Total and dissolvable concentrations of Fe, Al and Cu in three types of surface sediments in Dawu-Le An River section are given in Table 2. The three surface sediments are site D8 (before the mixing), site D14 (after the mixing) and site LD1 (into Le An River), respectively. Data in Table 2 may also provide a fairly good insight on distinguishing between different regions in which different chemical processes take place during the mixing. It is seen from Table 2 that the total Fe, Al and Cu in the surface sediments are rich. An orange precipitate which is X-ray amorphous Fe oxyhydroxide coats the surface sediments at upstream of the river. However, Cu concentration in the Fe-rich surface sediments is lower than that in the surface sediments at downstream of the river. This is probably due to the low pH of acid water keeping Cu in solution. In the surface sediments at upstream of the river, as shown in Table 2, above 61% of Fe/Al and 63% of Cu can be dissolved in the 0.005 mol/L H₂SO₄ solution, suggesting that part of dissolvable Fe/Al is presented in amorphous Fe/Al oxyhydroxides and the dissolvable Cu may be co-precipitated with freshly precipitated Fe/Al oxyhydroxide, because precipitation or adsorption of Cu can not occur in acid water at the low pH (pH<3.0).

Table 2 Total and the dissolvable Fe, Al and Cu in the three surface sediments at Dawu-Le An River section

Site	Unit: mg/kg		
	D8	D14	LD1
Total Fe	64200	38400	37600
Dissolved Fe	37800	8560	7640
%	58.9	22.3	20.3
Total Al	97700	75000	95500
Dissolved Al	2350	3140	2620
%	2.4	4.2	2.7
Total Cu	459.4	2598.5	1763.2
Dissolved Cu	290.3	690	435.5
%	63.1	26.6	24.7

However, only about 23%—26% of Fe/Al and Cu can be dissolved from the suspended particles or the surface sediments at downstream of the river (site, D14 and LD1). X-ray diffraction analysis has shown that besides the amorphous Fe hydroxides, crystalline silicates, iron, aluminum and clay minerals are presented in these surface sediments, and the fine-grained particles ($<10\mu\text{m}$) may make up above 80%. This is attributable to the sedimentation of large quantities of fine-grained ore tailing particles contained in the alkaline wastewater during the mixing. The dissolved fractions of Fe and Cu from the ore tailing particles in the 0.005 mol/L H_2SO_4 is as small as 6% and 3%, respectively, suggesting that most part of Fe and Cu in the ore tailing particles is in crystalline minerals which can not be dissolved in the acid strength. Thus, these results show that during the mixing, most parts of dissolved Fe, Al and Cu in the acid stream water are sedimented as solid matters to the surface sediments at downstream of the river, which could either be due to their precipitation or to their adsorption to the suspended particles. Conversely, only little of them is transported in the dissolved form into Le An River.

The ratios of concentration of Cu dissolved from the surface sediments to its concentration in the water of Dawu-Le An River section are plotted against pH and showed in Fig. 2. The concentration of Cu, whether in the suspended particulate phase or in the surface sediments, exhibits an increasing tendency with the increase of pH. It is obvious that such a pH-dependence is relative to its precipitation or to its adsorption onto suspended particles.

Because the pH of the water at downstream of the river is usually in the range of 4.6—6.5, the role of the precipitation as a control on the concentrations of dissolved Cu may be negligible according to the chemical equilibrium calculation. However, the results of the simulated adsorption have shown that abrupt adsorption of Cu on the simulated particles just take place at pH in the range of 4.5—6.5. It may be assumed that the concentration of dissolved Cu at downstream of the river is mainly controlled by the adsorption to the particles sedimented in the surface sediments. Among the particles, the Fe/Al oxyhydroxides are relatively abundant with high specific surface and are known to have a strong surface affinity to

trace metal ions (Davis, 1978; Benjamin, 1981).

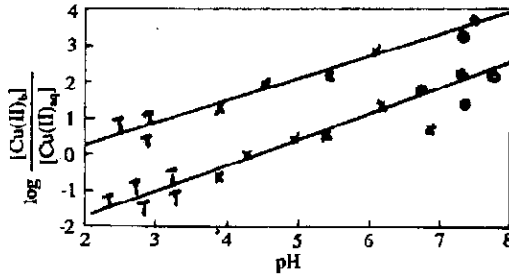


Fig. 2 The ratios of the concentration of Cu dissolved from the suspended phase and the surface sediments to its concentration in water as a function of pH (T) before the mixing, (x) after the mixing, (o) in Le An River

3.2 Adsorption of Cu ion on simulated particles

The adsorption of Cu ion on the amorphous Fe oxyhydroxide and on the ore tailing particles in 0.1 mol/L ionic strength (NaNO₃) solution are shown in Fig. 3 and Fig. 4, respectively. The results show that the adsorption of Cu ion onto the amorphous Fe oxyhydroxide and the ore tailing particles is strongly pH-dependent and is characterized by a sharp "adsorption edge" (Benjamin, 1981). The adsorption edge is at pH 4.2–4.5 for the amorphous Fe oxyhydroxide and at pH 4.5–4.9 for the ore tailing particles. Above 90% of the adsorbed Cu and about 60% Fe can be dissolved when the equilibrated adsorption solution is acidified in the 0.005 mol/L H₂SO₄ solution, suggesting that complete adsorption of Cu may not take place from the aged iron precipitates.

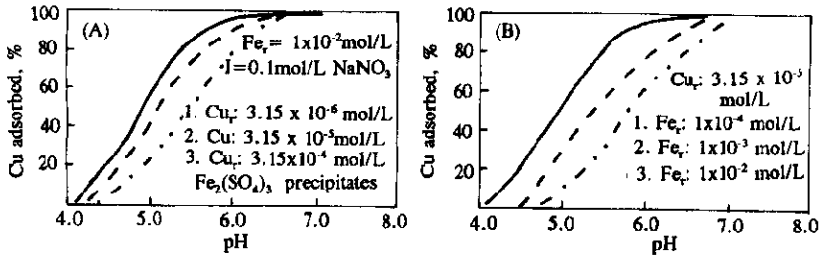


Fig. 3 Fractional adsorption of Cu on amorphous Fe oxyhydroxide as a function of pH and concentrations of Cu (A) and Fe_T(B)

If the pH at which 50% of Cu is adsorbed may be defined as pH₅₀, it is seen that, as shown in Fig. 3 and Fig. 4, the pH₅₀ value would vary with the concentration of Cu ion or of the particles. The pH₅₀ is at pH 5.4–5.9 for the amorphous Fe oxyhydroxide and is at pH 5.7–6.2 for the ore tailing particles. The pH₅₀ of Cu on the amorphous Fe oxyhydroxide is about 0.3–0.5 pH units lower than that on the ore tailing particles, suggesting that although Cu could be adsorbed onto the ore tailing particles, it is adsorbed more readily onto the amorphous Fe oxyhydroxide at low pH.

The chemical equilibrium calculation for Cu in the 0.1 mol/L NaNO₃ solution, as shown in Fig. 5, has shown (Luan, 1993) that dissolved Cu²⁺ is the dominant chemical species in

the solution with $\text{pH} < 6.3$. As pH continues to increase, CuOH^+ will be the dominant chemical species, and chemical precipitation will become a dominant mechanism for Cu removal when pH is greater than 7.0. Thus, it is obvious that the removal of Cu from the solutions with $\text{pH} 4.2-7.0$ is relative to the adsorption of M^{2+} , CuOH^+ ions.

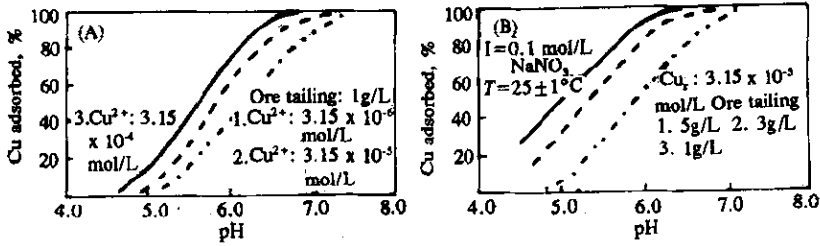


Fig. 4 Fractional adsorption of Cu on the ore tailing particles as a function of pH and concentrations of Cu(A) and the ore tailing particles (B)

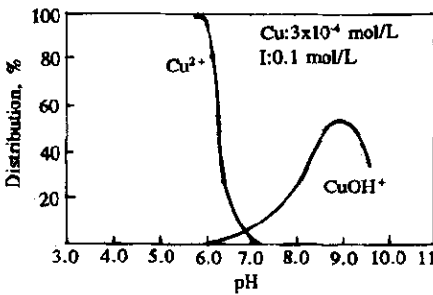


Fig. 5 Copper species distribution in 0.1 mol/L NaNO_3 solution as a function of pH

The adsorption of Cu on the mixture of amorphous Fe oxyhydroxide and ore tailing particles which is prepared by dropwise adding carbonate-free NaOH solution to the ferric sulfate solution containing ore tailing particles is given in Fig. 6. The adsorption-pH edge of Cu on the mixture particles is equal to that of Cu on the $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and the fraction of Cu on the mixture increase obviously, as shown in Fig. 6, as concentration of Fe(III) in the mixture increases. The results suggest that the adsorption of Cu on the mixture of freshly precipitated Fe oxyhydroxide and ore tailing particles is likely to be associated with surface coatings of the hydrous Fe oxide on the surface of ore tailing particles.

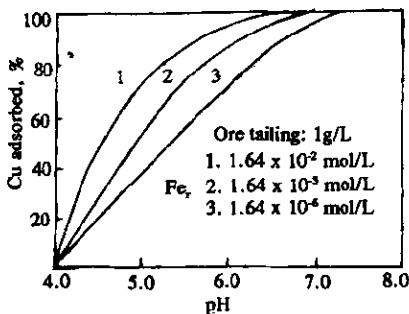


Fig. 6 Fractional adsorption of Cu on the mixture of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and ore tailing particles as a function of pH (A) and of concentration of Fe (B)

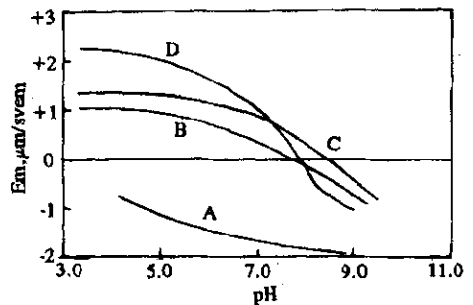
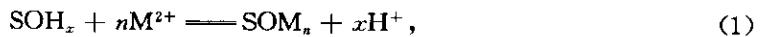


Fig. 7 Electrokinetic values (EM) of ore tailing particles (A), amorphous Fe oxyhydroxide (B), the mixture of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and ore tailing particles (C), and flocs of ore tailing particles coagulated with acid mine water (D)

The coating of hydrous Fe oxide on the surface of ore tailing particles can be demonstrated by measurement for electrophoretic mobility (*EM*) of the mixture particles in Fig. 7. The *EM* value of the ore tailing particles is negative in measured pH ranges (4.0—9.5) and its isoelectric point (pH_{iep}) may occur below 3.0, but the *EM* of the amorphous Fe oxyhydroxides is positive below pH 7.8 and its pH_{iep} is about pH 7.8. However, the *EM* values of the mixture and flocs of ore tailing particles coagulated by acid mine drainage are also positive near natural pH range and their pH_{iep} occur at pH 7.5—8.5. It has been indicated that the adsorption of soluble hydrolysis products leads to the formation of a layer of amorphous hydroxide precipitate on the particle surface and the charge reversal of the coagulated particles (James, 1972; Matijevic, 1976). The results show that the adsorption/coagulation of ore tailing particles by soluble hydrolysis products of Fe(III) can rapidly occur when $\text{Fe}_2(\text{SO}_4)_3$ solution is added to the ore tailing suspension or during the mixing of acid mine water and alkaline wastewater, and the ore tailing particles offer a nucleus for the coating.

3.2 Application of simplified surface complexation model

According to surface complexation models (Davis, 1978; Stumm, 1976), the binding of trace metals on surface of hydrous metal oxides and mineral particles may be considered as a complex formation reactions between the solid surface sites and the cations in solution. The surface complex reactions are strongly dependent not only on pH, but also on the surface characteristics of particles, as well as on the type and concentrations of metal ions in solution. A simplified model may be used to describe the adsorption (Johnson, 1986):



where

$$K_{\text{ad}} = \frac{[\text{SOM}_n][\text{H}^+]}{[\text{SOH}_x][\text{M}^{2+}]^n} \quad (2)$$

The terms $[\text{SOH}_x]$ and $[\text{SOM}]$ represent the surface density of free sites and concentration of surface metal complex, respectively. K_{ad} is only the conditional equilibrium constant for the surface complex formation or the integrated adsorption because the surface charges have been omitted for simplicity. x represents the average number of protons (H^+) released into solution per metal ion adsorbed. $[\text{M}^{2+}]$ represents the sorbate concentration in the equilibrium solution. In the river section contaminated by acid mine drainage, amorphous Fe/Al oxyhydroxides provide a large excess of surface sites, thus we may assume that the density of the surface sites is equal to the concentration of the amorphous Fe/Al oxyhydroxides in solution $[\text{SOH}_T]$, i. e., $[\text{SOH}_x] = [\text{SOH}_T]$, and $[\text{SOM}_n]$ is assumed to be equal to the concentration of adsorbed M^{2+} , $\{\text{SOM}_n\} = [\text{SOM}]$, thus

$$K_{\text{ad}} = \frac{[\text{SOM}][\text{H}^+]^x}{[\text{SOH}_T][\text{M}^{2+}]^n}, \quad (3)$$

which yields

$$\log \frac{[\text{SOM}]}{[\text{SOH}_T][\text{M}^{2+}]^n} = \log K_{\text{ad}} + xp\text{H} \quad (4)$$

This implies that if the simplified surface complex model in Eq. (4) is valid, the ratios

versus pH should theoretically get a straight line with intercept $\log K_{ad}$ and slope x . These ratios versus pH for Dawu-Le An River section and for the simulated experiment are plotted in Fig. 8 according to the simplified model given by Eq. (4).

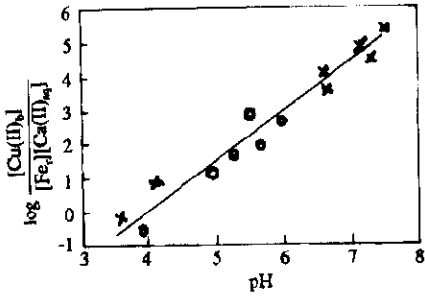


Fig. 8 The ratios of the moles of adsorbed Cu to its concentration in water of Dawu-Le An River (x) and in the equilibrated solution (o) as a function of pH

A comparison for the data obtained by Eq. (4) shows that the data from downstream of Dawu-Le An River and from the simulated adsorption experiments are comparatively coincident. The conditional surface complexation constant ($\log K_{ad}$), the average number of protons released per Cu ion adsorbed (x), and the average adsorption density of Cu on the oxyhydroxides are -5.94 , 1.42 and $2.9-3.7 \times 10^{-2}$ mole Cu per mole Fe/Al for downstream of Dawu-Le An River section, and are -4.89 , 1.36 and $2.8-3.0 \times 10^{-2}$ mole Cu per mole Fe for the simulated adsorption experiment using the amorphous Fe oxyhydroxide, respectively. The data agree roughly with the results obtained by many authors in laboratory experiments using amorphous Fe oxyhydroxide and relatively high Cu concentration. The intrinsic surface complexation constant ($\log K^{int}$) for the adsorption of Cu^{2+} on amorphous Fe oxyhydroxide ($SOH + Cu^{2+} = [SO \leftarrow Cu^{2+}] + H^+$) is -4.1 (Davis, 1978), it suggests that the adsorbed Cu at downstream of Dawu-Le An River section is mainly in the form of Cu^{2+} . However, the K_{ad} obtained from downstream of Dawu-Le An River section is smaller than that obtained from the simulated adsorption experiments. This is probably due to the higher surface adsorption densities at downstream of Dawu-Le An River section. It has been observed by this simulated experiments, as shown in Fig. 3, and other author (Benjamin, 1981) that the K_{ad} decreases at high surface adsorption densities. The phenomenon that more than one proton released per Cu ion adsorbed has been explained as bidentate binding or simultaneous adsorption and hydrolysis (Benjamin, 1981).

4 Conclusions

The distribution of Cu between the water and the surface sediments at Dawu-Le An River section has been investigated using the field data and by dissolution and simulated adsorption experiments. The results show that the concentration of dissolved Cu at Dawu-Le An River section which is contaminated by acid mine drainage from a copper mine is closely related with the amorphous Fe/Al oxyhydroxides, because the Fe/Al oxyhydroxides are relatively abundant in the surface sediments. At upstream of the river, the concentration of dissolved Cu is mainly controlled by its co-precipitation with freshly precipitated Fe/Al oxyhydroxides which can occur at low pH ($pH < 4.0$). However, at downstream of the river, the concentration of dissolved Cu appears to be mainly controlled by the adsorption on the amorphous Fe/Al oxyhydroxides and its coating on surface of the fine-grained ore tailing particle

which are sedimented in the surface sediments after the mixing of acid mine water and alkaline wastewater containing ore tailing particles.

The adsorption of Cu on amorphous Fe oxyhydroxides is strongly pH-dependent and is characterized by a sharp "adsorption edge". The data obtained by the simplified surface complexation model agree roughly with the results obtained by many authors in laboratory experiments using amorphous Fe oxyhydroxide. Thus the adsorption may be described by the simplified surface complexation model as a result of specific adsorption.

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