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Chemical processes of acid mine drainage in the aquatic system of copper mine area

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Abstract—The chemical reactions that occurred in Dawn River were studied by simulated experiments in laboratory. According to the analyses of samples and simulated experiments, the chemical transformation and the distribution of metal pollutants in the river were then discussed.

Keywords: chemical processes; metal pollutants; acid mine drainage; copper mine.

INTRODUCTION

Dawu River run through the area of Dexing Copper Mine. General survey carried out in the river indicated that the aquatic system has been heavily polluted by the acid mine drainage from waste stone dump and the alkaline wastewater from ore floatation plant. Consequently, the chemical reactions of metal pollutants should occur in the river when the different sorts of wastewater mixed with the natural water. For understanding chemical reactions and species of metal pollutants in the river, the chemical processes and the effects of metal pollutants in the river system were studied and discussed.

EXPERIMENTAL METHODS

A large number of water and sediment samples were collected at about 20 sites along the river in different seasons in 1987—1988. The distribution of sampling sites are shown in Fig. 1 of foregoing paper. The chemical components in water and sediments, such as Fe, Al, Mn, Cu, Cd, Pb, Zn, Ca, Mg, Na, K and S were determined by ICP and XRF, respectively.

The main chemical reactions that might occur in the river were simulated in laboratory. Oxygenation of ferrous iron in synthetic concentrated ferric solution at low pH and in acid mine drainage as well as the catalytic effects of copper and clay particles were studied in an air bubbling apparatus. The hydrolysis-precipitation processes of iron and aluminum in the acid drainage were studied by basic titration using an autotitrator. The precipitation rate of main pollutants in acid drainage at different pH values were evaluated. Flocculation of ore tailing particles by iron and aluminum from acid mine water was observed in field and laboratory experiments and will be further studied. The adsorption of Cu, Pb and Cd on ore tailing particles and amorphous Fe oxyhydroxide were carried out in controlled laboratory conditions.

RESULTS AND DISCUSSION

Concentration and seasonal variation of main pollutants in Dawu-Le An River

A summary of the level of average concentrations for the main pollutants at different sites in Dawu-Le An River during 1987–1988 is given in Table 1. It is seen that at the upper stream of the river (site D6), due to the discharged acid mine water, the pH has become very low with the average of about 2.7–2.8 and the contents of main pollutants were very high. For example, the averages of total iron, aluminum, sulfur, copper and manganese presented to be 453.7, 136.7, 687.2, 24.5 and 10.9 ppm, respectively, and more than 90% of them were dissolved species. The concentration of ferrous iron was 55.0 ppm. Owing to the discharges of domestic sewage and surface runoff along the river, the precipitation and sedimentation occurred continuously. After receiving the alkaline wastewater, the pH increased and the precipitation became even stronger. Discharged ore tailings were also transported along the river. The concentrations of main pollutants at lower reach of Dawu River decreased evidently, and the majority of them has settled to the bed sediments. In addition, the distribution of species also changed in the transport process. Before the mouth to Le An River, the metal contents were not high, especially for dissolved species. For example, the averages of total Fe, Al, Cu and Mn in the site of D14 were about 22, 30, 7.0 and 3.7 ppm, respectively, and about 50–60% of them were in the particulate phase.

However, care should also be taken to the effects of seasonal variation of conditions on the concentration and speciation of main pollutants in Dawu-Le An River. The differences can be clearly seen between dry and rainy seasons.

During the dry season, the impact of acid mine water from Dawu to Le An River may be less effective, though the metal contents at upper stream of the river were still high and the pH was low. The total flows of acid mine water into Dawu River were approximately equal to the flow of alkaline wastewater. Thus, after mixing of them, the pH rapidly increased from 2.8–3.0 to 4.2–5.4, and the contents of main pollutants at the lower reach decreased evidently as the results of neutralization precipitation, adsorption and sedimentation processes. More than 80% of Fe, Al, Cu, Zn and S were transported in the form of particulate. After flowing into Le An River, the metal concentrations at that season were lower than that the permissible limit level.

The picture has been changed during the rainy season. The acid mine water flow velocity increased so much, that it could not be mixed fully with the alkaline water flow. Then the two currents were running somewhat separately, and a polluted zone of acid mine water with high flow rate was observed in Le An River during the rainy season. In this zone, the pH decreased from 5.4 to 3.6, and a remarkable increase of concentration of pollutants were observed, such as, the concentrations of total Fe, Al, Cu, Mn and Zn were as high as 228.4, 81.9, 11.8, 4.2 and 3.6 ppm respectively. The concentration of ferrous iron has also risen from 2.8 to 23.5 ppm. This acid mine water current would directly flow into Le An River for a much longer distance and increased the pollution there notably. For example, the pH in the river decreased from 7.5 to 4.0 and the concentration of the dissolved metal ions as Cu^{2+} and Al^{3+} increased from about 1–2 to 3–10 ppm.

Table 1 The average of main pollutants in Dawu river (1987–1988)

Site		pH	TFe	Fe(II)	Al	Mn	Cu	Zn	S	SO_4^{2-}
1. Before receiving of acid drainage										
D4	T	2.82	149.35		76.50	7.82	19.88	0.96	377.15	
	D		78.43	31.04	57.82	6.18	17.30	0.66	333.84	815.20
2. After receiving of acid drainage										
D6	T	2.73	453.65		136.72	10.94	24.47	1.79	682.65	
	D		331.90	55.06	119.72	10.00	18.69	0.85	648.45	1545.90
3. Before receiving of alkaline wastewater										
D11	T	2.98	190.16		68.45	5.14	11.39	1.58	331.48	
	D		117.09	26.86	59.06	4.80	10.46	0.93	277.60	436.64
4. After receiving of alkaline wastewater										
D12	T	4.40	53.48		22.10	3.34	5.20	0.52	150.95	
	D		12.38	22.23	13.63	2.57	4.08	0.25	127.90	381.84
5. Lower reach of Dawu River										
D13*	T	4.79	33.90		20.66	4.08	5.38	0.00	182.80	
	D		5.90	4.80	4.68	3.30	4.73	0.00	121.90	385.27
D13**	T	3.16	95.00		21.72	1.88	5.32	0.74	127.82	
	D		59.96	39.95	21.72	1.66	3.87	0.42	113.50	
6. Before running into Le An River										
D14	T	4.80	22.48		30.86	3.71	7.03	0.89	157.10	
	D		6.02	2.79	16.89	3.58	4.63	0.33	125.5	240.30
7. Unmixed acid flow in Dawu River during rainy season										
D14	T	3.64	218.89		80.96	4.14	11.75	3.34	298.50	
	D		57.69	25.51	31.28	3.94	7.54	0.75	257.10	467.52
8. Le An River before receiving of Dawu River										
LD0	T	7.68	2.51		1.14	0.12	0.08	0.03	1.86	
	D		1.12	0.00	0.40	0.05	0.04	0.00	1.10	2.10
9. Le An River after receiving of Dawu River										
LD1*	T	7.36	3.98		3.87	0.14	0.50	1.74	48.30	
	D		0.02	0.05	0.01	0.00	0.00	0.00	8.71	11.70
LD1**	T	3.97	32.03		31.54	0.90	2.27	0.64	125.50	
	D		14.21	4.12	9.39	0.79	2.27	0.07	48.46	147.80
LD3*	T	7.44	1.08		0.16	0.12	0.08	0.04	8.69	
	D		0.35	0.00	0.09	0.02	0.03	0.00	7.63	12.60
LD3**	T	4.67	21.29		7.46	0.42	1.02	0.06	23.50	
	D		1.73	1.67	2.23	0.30	0.79	0.06	17.70	76.37

T-total; D-dissolved; * in dry season; ** in rainy season

The contents of total iron, copper and sulfur in sediments at different sites of Dawu and Le An River show that the sediments at upper stream of the river (D6–D8) were rich in Fe (10–15%), mainly freshly precipitated iron hydroxide. Ore tailing particles make up a large portion of sediments at the lower reach. The contents of Fe and S decreased remarkably, but the contents of Cu were much higher than that at the upper reach.

Simulating experiments in laboratory

In order to understand the transformation processes of metal pollutants in Dawu-Le An River, it is important to clarify a series of chemical reactions in various conditions, such as the oxidation of ferrous iron in acid mine water, the hydrolysis-precipitation of Fe, Al in different pH values, the adsorption of Cu, Pb and Cd on fine ore tailing particles and Fe, Al hydrous oxides, and their aggregation and sedimentation processes.

1. Oxygenation of Fe(II) in acid drainage water

At first, it was simulated in synthetic water. The composition of simulated solution was 100 ppm of Fe(II) in 0.05 mol/ L of $Fe_2(SO_4^{2-})_3$ with pH of 2.1. The results showed that the oxidation rate of Fe(II) in this solution was very slow. Only less than 10% of Fe(II) was transformed into Fe(III) in 118 days. In the presence of Cu, the oxidation rate of Fe(II) can be increased just a little, about 10% of the Fe(II) was oxidized in 90 days. However, the oxidation of Fe(II) in the acid mine water sample collected in field, as plotted in Fig. 1, was much faster than that in the simulated solution, about 60% of the ion was oxidized in 15 days. In the presence of clay particles, the reaction was going even more rapidly, the oxidized products increased from 60% to 80%. In fact, the oxidation rate in field by investigated result was much more rapid than that in the laboratory. According to the analytical results of the field water samples, more than 80–90% of Fe(II) could be oxidized within 7–10 days.

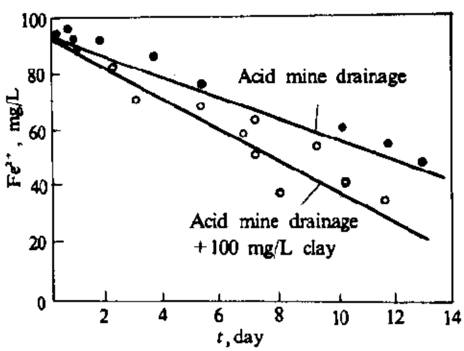

Fig. 1 The oxidation rate of Fe(II) in acid mine water

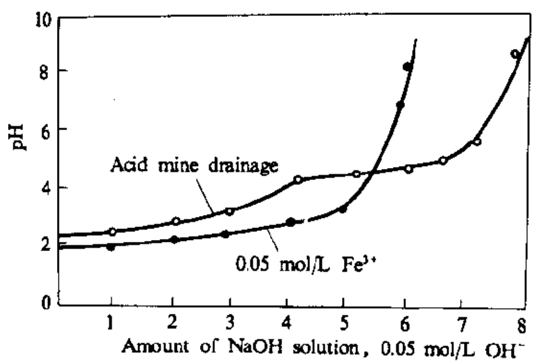

Fig. 2 Titration curves for acid mine drainage and $Fe_2(SO_4)_3$) solution with 0.05 mol/ L NaOH solution

2. Hydrolysis-precipitation of iron and aluminum

In Fig. 2, the titration curves for acid water with 0.05 mol/ L NaOH basic solution were plotted. Curve *A* is the result for the acid drainage water sample and curve *B* is the result for the simulating solution of 0.025 mol/ L $Fe_2(SO_4^{2-})_3$, corresponding to the concentration of 0.05 mol/ L Fe(III) in acid mine drainage.

It is seen from curve *B* that the pH value of $Fe_2(SO_4^{2-})_3$ solution exhibited a slow change before pH 3.0 in titration. However, local visible precipitates started to occur at pH 2.4–2.6 and a large quantity of flocs were formed at about pH> 3.0. It means that in concentrated solution, the hydrolysis-precipitation reaction of Fe(III) at pH< 3.0 produced a series of hydroxyl complex ions and then the precipitates of $Fe(OH)_3$. In this process, the reactions released corresponding H^+ ions to solution and resulted in a gentle change of pH.

However, the titration curve *A* of acid drainage water presented two inflection points. The first point occurred at about pH 3.0 and the second point occurred at about pH 4.5. These would be related to the hydrolysis-precipitation reactions of both Fe(III) and Al(III). The reactions of Fe occurred mainly in the range of pH 2.5—3.5 and the reactions of Al(III) occurred mainly at pH 4.0—5.5. It was the similar situation in the Dawu River and has been demonstrated by the analysis of sediment samples.

3. The removal of trace metals

The experimental results for precipitaiton of Fe, Al and Mn hydroxides and the removal of heavy metal ions of Cu, Zn and Cd from the solution as a function of pH value are given in Fig. 3 and Fig. 4, respectively.

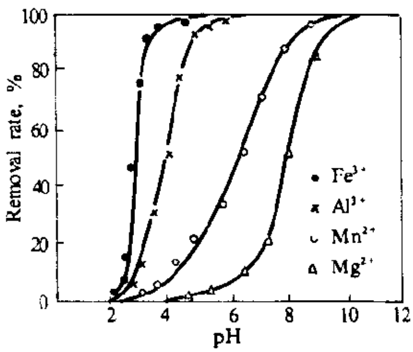

Fig. 3 Precipitations of Fe^{3+}, Al^{3+}, Mn^{2+} and Mg^{2+} in acid drainage water as a function of pH

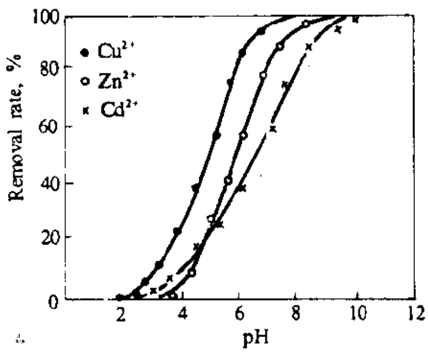

Fig. 4 Removal of Cu, Zn and Cd with Fe, Al, Mn hydroxides in acid drainage water as a function of pH

The results showed that Fe(III) precipitated first and more than 95% were removed from acid water at pH > 3.0. The precipitation of Al(III) was completed at pH> 5.0. Mn was removed at pH 6.0—7.0. Heavy metal ions as Cu, Pb and Zn were removed in the range of pH 5.0—8.0 by adsorption and coprecipitation.

4. Flocculation of ore tailing particles

The aggregation of ore tailing particles with the Fe and Al hydroxides during the mixing of acid drainage water and alkaline wastewater has been observed in field obviously. These processes in acid drainage water was studied in laboratory and the main results observed are shown in Fig. 5, in which the concnetration of ore tailings is 1.0 g / L.

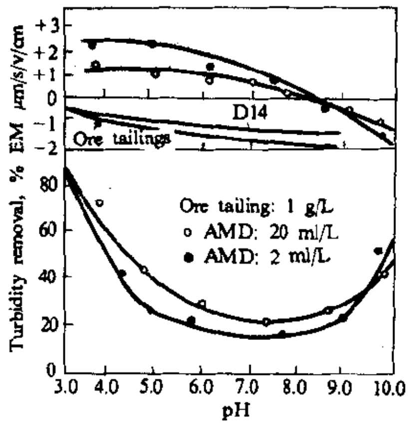

Fig. 5 Aggregation of ore tailing particles in acid mine drainage as a function of pH

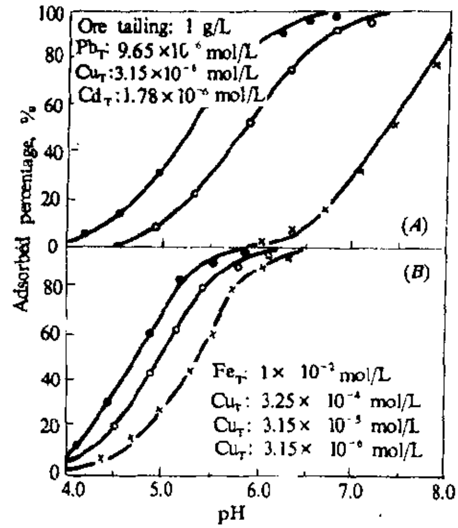

Fig. 6 Adsorption of Cu, Pb and Cd on ore tailing particles (*A*) and Fe oxyhydroxide (*B*)

In the experiments, turbidity removal and particle size growth were observed evidently. The fine ore tailing particles settled most rapidly in the range of pH 5.0–9.0. At low pH range, the particles aggregated slowly due to the coagulation with Fe^{3+} and Al^{3+} in acid water. Rapid aggregation in the middle pH range was due to the coagulation with polymeric species of Fe and Al and the enmeshment by the floccus of $Fe(OH)_3$ or $Al(OH)_3$ precipitates. Electrophoretic mobility (EM) curve in Fig. 6 indicated that ore tailing particles were negatively charged above pH 3.5. Coagulated particles in acid drainage water exhibited positively charged below pH 8.5. It was assumed that the transformation from negative charge of ore tailings into the positive charge of aggregates was the result of adsorption of the highly charged hydrolyzed species of Fe(III) and Al(III) at lower pH and that the charge decrease of aggregates at higher pH was the result of surface coating of low charged precipitates of Fe and Al hydroxides.

5. The adsorption on ore tailings and Fe oxyhydroxides

The representative adsorption pH edges of Cu, Pb and Cd on the ore tailing particles and amorphous Fe oxyhydroxide are shown in Fig. 6 *A* and *B*, respectively.

The results showed that the adsorption processes of heavy metal ions on both solids are strong and pH dependent. In acid drainage water, the surface of ore tailing particles were often coated of Fe and Al hydrous oxides and their adsorption in fact was a composite reaction. The strongly binding of heavy metals to the surface of composite aggregates would be a regulating factor of the dissolved concentrations of them in water at the lower reach of Dawu-Le An River.

CONCLUSIONS

There might be at least six sorts of physico-chemical processes which occurred in field and controlled compositively the speciation and concentration of metals in river. Such as the dilution and diffusion of acid drainage or alkaline wastewater in river, the neutralization and pH variation during mixing of acid and alkaline waters, the oxidation and its rate for transformation for Fe(II) to Fe(III), the hydrolysis, polymerization and precipitation of Fe and Al species, the adsorption of heavy metals on the hydroxides and ore tailing particles, the coagulation, flocculation and settlement of the particulates in river. In this paper, only some results of laboratory experiment were described above generally. Other results in detail shall be published in successive papers.

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