Characteristics of acid mine drainage of Dexing Copper Mine

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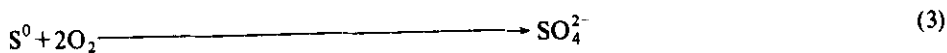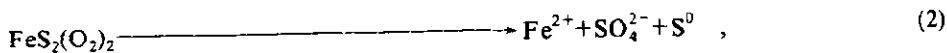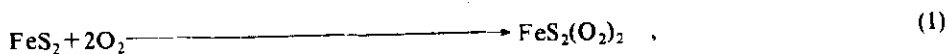Academy of Sciences, Beijing 100085, China

Abstract—This work aims at the characteristics of acid mine drainage of Dexing Copper Mine. On the basis of the results of observation and analysis of samples collected in situ, it is shown that the characteristics of the acid water are high concentrations of some elements, such as iron, sulfur, aluminium, copper and high acidity. The results show that the concentrations of iron, aluminium and sulfur are significantly correlated with the acidity of the acid water.
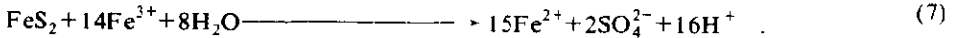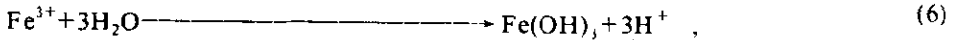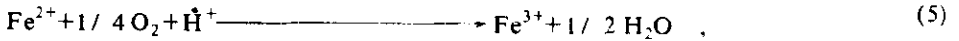
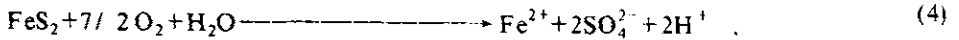**Keywords:** wastestone; wastewater; weathering.

INTRODUCTION

The pyrite is the most abundant sulfide mineral in the earth crust and it occurs in nearly all types of geological circumstances, particularly in coal, copper, zinc and lead sulfide ores. Pyrite is often abandoned as wastestone during mining. In a naturally aerobic environment, pyrite is oxidized and acid mine drainage produced. The acid water not only causes the loss of metal and sulfur resources, but pollutes the aquatic ecosystem as well. Pyrite oxidation and acid mine drainage generation were studied quite extensively in the last decades.

In natural environment, pyrite is oxidized through a sequence of chemical reactions and microbial catalysis. It is difficult to study the oxidation of pyrite quantitatively because the process of pyrite oxidation in natural environment is very complicated. McKay and Halpern (McKay, 1959) suggested that pyrite can be oxidized through the following reactions:

$$FeS_2 + 2O_2 \longrightarrow FeS_2(O_2)_2 \quad , \tag{1}$$

$$FeS_2(O_2)_2 \longrightarrow Fe^{2+} + SO_4^{2-} + S^0 \quad , \tag{2}$$

$$S^0 + 2O_2 \longrightarrow SO_4^{2-} \tag{3}$$

This process shows that the elemental sulfur can occur as an intermediate. Stumm and Morgan (Stumm, 1981) and Sullivan *et al.* (Sullivan, 1988) proposed the chemical steps as fol-

$$FeS_2 + 7/2\,O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad, \tag{4}$$

$$Fe^{2+} + 1/4\,O_2 + \overset{\bullet}{H}{}^+ \longrightarrow Fe^{3+} + 1/2\,H_2O \quad, \tag{5}$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \quad, \tag{6}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad. \tag{7}$$

Reaction (4) is considered as the necessary primary step, but is a slow step, and Reaction (7) is a fast step because the ferric iron can accelerate the oxidation rate of pyrite. However, the amount of ferric iron depends on the rate of Reaction (5), the reaction is viewed as a rate-determining step. The rate of Reaction (5) can be accelerated by microbial catalysis. Zhong Huifang *et al.* (Zhong, 1987) suggested the biological process of pyrite oxidation as follows:

$$FeS_2 + 7/2\,O_2 + H_2O \xrightarrow{\text{bacteria}} FeSO_4 + H_2SO_4 \quad,$$
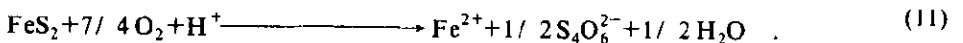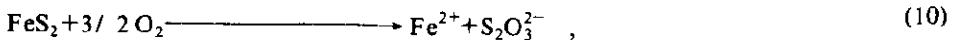
$$2FeSO_4 + 1/2\,O_2 + H_2SO_4 \xrightarrow{\text{bacteria}} Fe_2(SO_4)_3 + H_2O \quad,$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S^0 \quad, \tag{8}$$

$$S^0 + 3/2\,O_2 + H_2O \xrightarrow{\text{bacteria}} H_2SO_4 \quad. \tag{9}$$
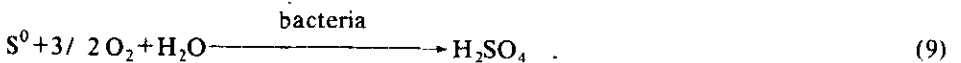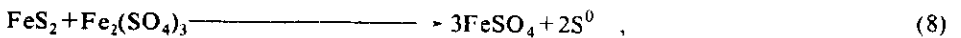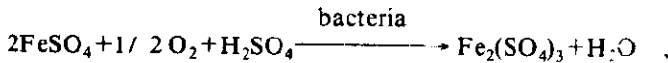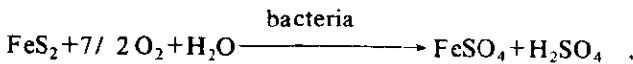
In the biological process, the first two reactions are the same as Reactions (4) and (5). Reactions (8) and (9) account for the observation of elemental sulfur as an intermediate product in the process of pyrite oxidation. The rate of pyrite oxidation by microbial catalysis can be 50–60 times (Zhong, 1987) to 5–6 orders of magnitude (Nordastrom, 1978) as high as that of chemical oxidation. It is possible that thiosulfate or polythiosulfate can occur as an intermediate in the process of pyrite oxidation from the following reactions (Lowson, 1982):

$$FeS_2 + 3/2\,O_2 \longrightarrow Fe^{2+} + S_2O_3^{2-} \quad, \tag{10}$$

$$FeS_2 + 7/4\,O_2 + H^+ \longrightarrow Fe^{2+} + 1/2\,S_4O_6^{2-} + 1/2\,H_2O \quad. \tag{11}$$

Analysis of sulfur speciation in acid mine drainage generated by pyritic wastestone weathering can help understand the process of pyrite oxidation in natural environment. Double X-ray fluorescence is one of available methods, but it is necessary that there is an analytical program of computer. Because a spectrum of sulfur speciation distribution can be only obtained

by double XRF scanning containing sulfur sample, the speciation can not be directly determined. Moreover, the shape of sulfur speciation spectrum distribution, no matter how many species of sulfur speciation in a sample there are, is hardly different. The only difference is the disposition of the spectrum distribution between sulfur speciations. The problem can be solved by nonlinearity minimal square. The program of sulfur speciation (SULS) was set up on the basis of the principle of nonlinearity minimal square by the following equation:

$$I(E) = \sum a_i \times f(B - b_i) \quad , \tag{12}$$

where $I(E)$ is the spectrum distribution of sulfur speciation determined by double XRF; a_i and b_i are the coefficients of the ith component; $(B-b_i)$ is the difference between standard and sample. a_i and b_i can be found by nonlinearity minimal square method (Gohishi, 1975).

This work aims at study on the characteristics of acid mine drainage generated by pyritic wastestone weathering of Dexing Copper Mine based on the analytical results of some elements and the results of sulfur speciation analysis in the samples collected in 1987—1988.

SAMPLING AND ANALYSIS

According to the condition in situ, 9 sampling sites (W1—W9) were arranged along the largest acid ditch at the present in Dexing Copper Mine (Fig. 1), 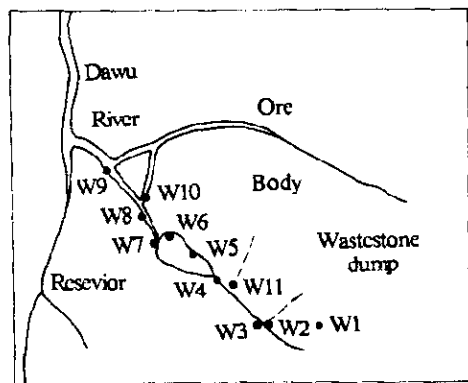and more than 80 samples of the acid mine drainage were collected in dry season (only 5 sites) and in rainy season. Furthermore, 6 samples were collected at W10 before the confluence point where the water flowing over ore body from the upstream Dawu River flows into the acid ditch. Four samples were collected from site W11 on a tributary of the acid ditch. Seven samples were collected from the surface water of the stope, in which 5 sample were collected in rainy season and others in dry season. At the same time, 14 precipitation samples of the acid mine drainage which was treated by silver-bearing salt were collected for sulfur

Fig. 1 Sketch for sampling site

speciation analysis and wastestone sample was collected for chemical composition and mineral component analyses.

The pH was measured in situ by portable pH meter (0.001 pH variation). Table 1 gives the conditions for measuring the content of sulfur, iron, calcium, aluminium, copper and magnesium by XRF with thin sample method. Analytical samples were prepared by dropping 100 μl sample solution on the center of filter which had a wax ring with 30 mm in diameter, the filter was dried under 50℃ after sample solution was diffused. Ten samples were prepared for measuring analytical reproductivity. The percent reproductivity for iron, aluminium, calcium, mag-

nesium, sulfur and copper is 2.60, 3.90, 4.01, 4.11, 3.28 and 4.57, respectively.

Table 1   Analytical conditions of XRF*

Anal. elem.	Fe	Ca	Cu	Al	Mg	S	S
Crystal	LiF	PE	LiF	PE	TAP	Ge	Ge / Ge
Counter	SC	FC	SC	FC	FC	FC	FC
Count time, S	10	20	20	20	20	20	0.005
Collimator	F	C	C	C	C	C	

* Power is 40 kV and 30 mA, analytical line is Kα.

The mineral component of the wastestone was characterized by X-ray powder diffrac-tometry.

The precipitation samples for sulfur speciation were dried under low temperature, groun-ded and made into small round flats (30 mm in diameter) under the pressure of 20T; potassium sulfate was grounded and prepared as standard. Sulfur speciation spectrum distribution was scanned by double XRF and analyzed by the program of SULS. The relative analytical error was less than 5.5% for S^{2-} and S^0, less than 15% for S^{4+} and S^{6+} respectively by comparison with samples of known speciation composition. The result of this method was compared with infrared and chemical methods, the relative analytical error was less than 15%.

RESULTS AND DISCUSSION

The chemical component of the wastestone is listed in Table 2. It shows that the sulfur con-tent is about 50 times that of the crust, copper is about 5 times.

Table 2   Contents of some elements in the wastestone

Elements	Content, %	Element	Content, ppm
Na	0.33	Pb	9.6
Ca	1.18	Zn	74.5
Mg	1.19	Mn	150.0
S	1.50	Cu	169.1
Fe	3.41		
K	3.46		
Al	11.53		

The mineral constituent of the wastestone is listed in Table 3. It shows that the major min-erals in the wastestone are quartz and aluminium silicates, and that the wastestone containing sulfides is pyritic. Copper pyrite is much less than 0.05% (average), even if all copper in the wastestone is fully constituted as copper pyrite. This indicates that the acid mine drainage of Dexing Copper Mine is mainly produced by pyrite oxidation from the wastestone dump.

Analytical result of the acid mine drainage is listed in Table 4. The acidity of the acid water and concentration of iron, sulfur, aluminium, magnesium and copper in the acid water were very high. Fig. 2 gives the content variations of sulfur in different seasons. The variations may

consider to be the results from the different microbial catalysis caused by the differences

Table 3   Mineral constituents of the wastestone

Mineral	Content, %
Quartz	50
Mica	42
Feldspar	4.5
Pyrite	3.5

of temperature and rainfall among seasons. The concentration of iron, aluminium and sulfur in the acid water was significantly correlated with the acidity of the water. The reliability coefficient of the relationship between the concentration of element and acidity of the water is much less than 0.001 (Table 5 and Fig. 3). The relationship is as follows:

$$C_i = EXP (a_i + b_i \ pH) \tag{13}$$

Table 4   Analytical results of the acid water samples

unit: ppm

	pH	Fe	Ca	Al	S	Mg	Cu
Rainy season (1988)							
Range	2.22–	56.6–	50.9–	125.8–	502.6–	92.3–	2.4–
	2.86	3623.6	421.5	1174.7	7536.4	1118.3	143.2
Average	2.52	1170.3	185.7	600.5	3173.1	949.5	39.1
CV, %	7.13	81.59	44.03	52.52	59.01	55.23	69.07
Dry season (1987)							
Range	2.33–	13.8–	133.7–	139.0–	806.0–	221.2–	19.8–
	3.33	1897.9	285.6	1013.1	5206.0	784.0	56.1
Average	2.73	840.9	228.3	592.0	2856.6	471.8	34.8
CV, %	12.50	94.74	22.32	60.20	62.79	49.07	43.06

Table 5   Correlation between element and pH of the acid water

	pH	Fe	Ca	Al	S	Mg
pH	1	−0.964	−0.488	−0.901	−0.946	−0.854
Fe	+++	1	0.491	0.922	0.966	0.912
Ca	+	+	1	0.570	0.582	0.672
Al	+++	+++	+	1	0.986	0.981
S	+++	–+ +	+	+++	1	0.978
Mg	+++	+++	++	+++	+++	1

Notes: +, ++ and +++ indicate the classes of reliability

where C_i is the concentration of element i (iron, aluminium, sulfur and so on); a_i and b_i are constants. The relationships between sulfur and iron, sulfur and aluminium are given in Fig. 4. It shows that sulfur is well related to iron and aluminium.
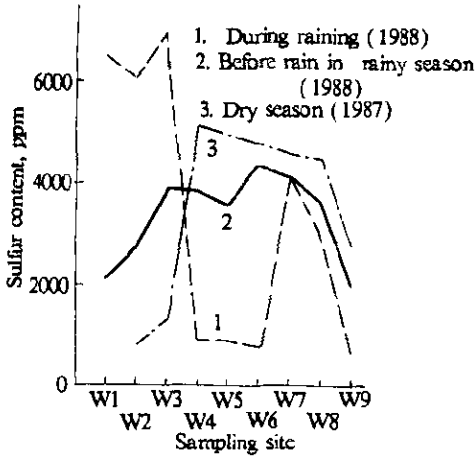
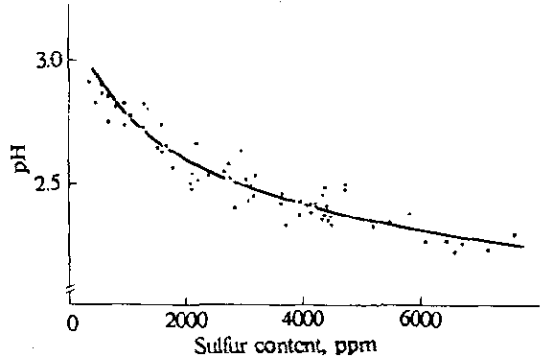Fig. 2   Concentrations of sulfur in acid water
         at different seasons

Fig. 3   Relationship between sulfur and
         pH of the acid water

The analytical results of the acid water collected at sites W 10, W 11 and the stope are listed in Table 6. The data show that the concentration of elements in samples collected from site W 11 was higher than that samples collected from W 10 and the stope, but lower than that samples collected from site W 1 (Table 7). The results may show that microbial catalysis plays an important role in the weathering of sulfide, because the stope is being stripped, microbial catalysis is scant on it and the elemental concentration is very low; and the ratio of water to weathering area of the wastestone affects the elemental concentration.
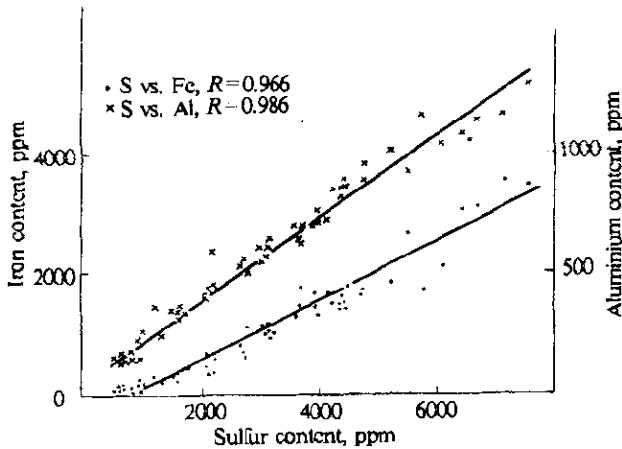

Fig. 4   Correlation to sulfur and iron or aluminium

The analytical result of the acid water at the headspring of the water (site W1) is given in Table 7. It may show that the amount of elements released from the wastestone weathering is related to rainfall. Not only does the amount of the acid water increase as rainfall, but the concentration of some elements increases as well. By comparison the data of different layers of the dump at the same time, it was found that the concentration of elements at the bottom of the dump was higher than that at the middle. The amount of elements released from the wastestone weathering were affected by the ratio of water to the surface area of the wastestone weathering.

Table 6   The pH and contents of elements at site W10, W11 and the stope

unit: ppm

Sampling site	pH	Fe	Ca	Al	S	Mg
W 10	2.65	62.9	90.1	94.2	452.9	90.3
	2.75	57.5	72.5	112.8	413.3	72.5
	3.05	33.6	22.5	42.2	151.0	34.3
	2.88	49.3	54.5	52.7	302.1	23.1
	2.83	46.9	56.1	47.8	299.6	43.7
	2.83	67.1	79.3	92.6	434.7	61.0
W 11	2.71	205.6	170.8	313.6	1325.4	258.2
	2.62	237.6	161.6	384.0	1475.1	245.1
	2.70	196.1	139.5	179.5	824.0	130.6
	2.59	232.5	149.4	272.1	1154.3	199.8
Surface water	5.00	nd	66.8	nd	21.5	33.0
in the stope	3.06	nd	51.4	nd	125.6	nd
	3.43	nd	53.1	nd	72.9	17.8
	3.29	nd	18.2	nd	22.6	14.1
	2.99	nd	35.5	nd	57.0	17.4
	8.03	nd	68.8	nd	47.1	6.67*
	8.30	nd	65.8	nd	nd	nd*

* Sampling in dry season

The analytical results of sulfur speciation are listed in Table 8. The data show that there are tetravalent and sexavalent sulfur in the acid mine drainage generated by the pyritic wastestone weathering. The highest concentration of tetravalent sulfur, 72% of total sulfur, is at site W1, but sexavalent sulfur content increases speedily as the sites are far from the wastestone dump, 71% at site W4. This shows that tetravalent sulfur in the acid water contacted with oxygen in the atmosphere can be quickly oxidized to sexavalent sulfur. The result indicates that pyritic sulfur in wastestone dump is not always directly oxidized to sexavalent sulfur in the process of pyrite oxidation, especially in the condition of scant atmospheric oxygen. On the basis of the result in this study, the process of pyrite oxidation in the wastestone of Dexing copper Mine in natural environment may be described as follows:
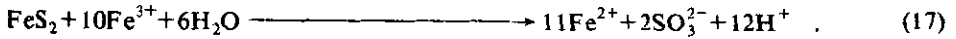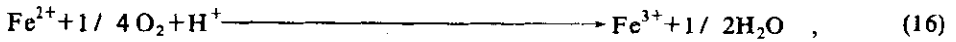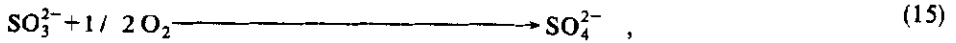
$$FeS_2 + 5/2\,O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_3^{2-} + 2H^+ \quad , \tag{14}$$

$$SO_3^{2-}+1/\ 2O_2 \longrightarrow SO_4^{2-} \quad , \tag{15}$$

$$Fe^{2+}+1/\ 4O_2+H^+ \longrightarrow Fe^{3+}+1/\ 2H_2O \quad , \tag{16}$$

$$FeS_2+10Fe^{3+}+6H_2O \longrightarrow 11Fe^{2+}+2SO_3^{2-}+12H^+ \quad . \tag{17}$$

Table 7   Analytical result of the acid water in site W1

unit: ppm

pH	Fe	Ca	Al	S·	Mg	Cu	Sampling condition
2.38	1361.9	247.5	787.9	4080.1	668.7	45.6	a f
2.36	1420.5	233.9	862.3	4297.7	681.9	50.4	b f
2.54	389.0	221.6	437.7	2108.4	449.7	35.6	a·p
2.50	438.0	202.8	413.2	2061.4	430.7	39.9	b·p
2.29	3461.9	275.7	1302.9	7536.4	1084.6	79.6	c f
2.22	3623.6	246.3	1061.4	6566.4	964.2	93.7	d f
2.26	3116.0	279.3	1148.1	6677.0	989.9	92.3	e f

a, a· : without rain in rainy season   b, b· : the day after a storm

c, d : during raining   e : the day after rainy days

f : the sample collected from the bottom of the dump   p : the sample collected from the middle dump

Table 8   Sulfur speciation in the acid water*

Sampl. sites	W1	W3	W4	W5	W7
Tetravalent, %	72	70	29	29	28
Sexavalent, %	28	30	71	71	72

* Percentage of total sulfur

Formation of secondary materials from weathering products of geological material containing sulfides was studied by Filipek et al. (Filipek, 1987), Sullivan et al. (Sullivan, 1986) and Boulegue (Boulegue, 1977). It is proved that the quality of acid mine drainage generated by sulfides weathering is affected by secondary materials formed during the acid mine drainage formation. The ratio of S/ Fe in the acid water of Dexing Copper Mine is listed in Table 9. It was shown that secondary material of iron could be formed in the dump on the basis of the ratio at site W1 during dry and less rainy days, but the ratio would be decreased during raining. The ratio at sites W5—W9 indicates that the secondary mineral formation of iron is increased by rain water. In addition, pyrite (FeS_2) is the main species of sulfide in the wastestone of Dexing Copper Mine, copper pyrite and other sulfides are much less, and the molar ratio of S/ Fe of pyrite weathering product is about 2, but the ratio in the acid water is more than 2. It was shown that ionic iron released from the wastestone weathering could form secondary materials during the acid water generation and transport.

Table 9   The molar ratio of S / Fe in the acid water

Site	a	b	c	d1	d2	e
W 1	9.436	8.193	7.319	3.703	3.155	3.731
W 2	6.851	6.508	7.079	4.325	4.852	5.724
W 3	5.145	4.325	5.705	3.526	3.515	3.600
W 4	4.008	3.578	/	6.083	10.059	/
W 5	4.812	5.018	10.676	7.276	8.500	6.471
W 6	6.300	5.969	7.129	29.569	12.029	10.632
W 7	4.739	4.850	4.643	5.127	4.213	4.730
W 8	4.452	4.901	5.033	4.496	4.638	4.594
W 9	5.415	6.642	12.718	10.105	7.551	6.994

a, b, c, d, e are the same as in Table 7

CONCLUSION

The characteristics of the acid water generated are as follows:

1. Concentrations of some elements in the acid water and the acidity of the water are very high and different from rainy season to dry season.

2. From the relationships among elements, and between elements and acidity of the acid water, it may be considered that the acidity of the acid water is not only controlled by sulfur released from the wastestone weathering, but iron and aluminium as well.

3. The result of sulfur speciation indicates that the initial oxidation product of pyritic sulfur in the wastestone dump of Dexing Copper Mine may be tetravalent sulfur as an intermediate product which can be quickly oxidized.

4. The amount of some elements released from the wastestone weathering may be related to the surface area of the wastestone weathering and rainfall.

5. The ratio of S / Fe shows that the secondary materials may be formed during the acid water generation and transportation.

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