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Simulation experiment of pyritic wastestone weathering

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Abstract—The relationships for the rate of the pyritic wastestone weathering and leaching amount, surface area of the wastestone weathering, oxidant in the weathering system and the acidity of weathering solution were simulated. It was found that, on the basis of the logarithmic relationship between releasing amount of sulfur and leaching amount, the weathering rate of sulfide in the pyritic wastestone was changed exponentially with leaching amount. The relationships between the rate and weathering surface area of the wastestone and the rate and oxidant were exponential. It was indicated that there was scarcely relationship between the rate and acidity of the weathering solution.

Keywords: wastestone; pyrite; weathering.

INTRODUCTION

It is an important environmental problem that acid mine drainage generated by pyritic wastestone weathering accommodates acid water pollution. As the process of pyrite oxidation is very complicated in natural environment, it is very difficult to study the process quantitatively. Sullivan *et al.* (Sullivan, 1986a; 1986b) have studied the oxidation of crystalline pyrite and pyrite in pyritic coal wastestone. Oxidant, such as oxygen, hydrogen peroxide and ferric iron were used in some experiments (Wiersma, 1984; McKibben, 1986). Weathering surface area, acidity of weathering solution, microbial catalysis were simulated by many scientists (Warren, 1956; Steger, 1978; Cornelius, 1958).

In this research, leaching simulation experiment was carried out for studying pyrite oxidation in pyritic wastestone of Dexing Copper Mine. The relationship between amount of pyrite oxidized by leaching and leaching amount during pyritic wastestone weathering was established. The difference between methods by leaching in open system and by blowing oxygen in close system was examined. Different sized pyritic wastestone was used in simulation experiment to examine the relationship between rate of oxidation and the weathering surface area. The effects of ferric iron and hydrogen peroxide, and the acidity of leaching solution on pyrite oxidation were studied.

As many minerals contain iron in pyritic wastestone of Dexing Copper Mine and the mass ratio of iron to sulfur in pyritic wastestone (about 2) is higher than that in pyrite (0.9), therefore, sulfur product was selected for determination of the rate of oxidation in pyritic wastestone.

MATERIALS AND EXPERIMENTATION

Wastestone was sampled from the dump of Yangtaowu in Dexing Copper Mine. It was smashed and mixed in lab. The chemical content and mineral constituent of the wastestone were analyzed by XRF and XRD (Dai, 1990). The sample was divided into five fractions and grounded into 0.84–0.33, 0.33–0.25, 0.25–0.15, 0.15–0.105 and 0.105–0.074 mm fractions respectively.

The effects of the wastestone weathering surface area and leaching amount on the releasing amount of sulfur were simulated as follows: five different sized samples were leached by distilled water. The leachate was collected for analyzing the concentration of SO_4^{2-} by IC and bromine water was added to the leachate.

The effect of ferric iron on the oxidation rate of pyrite was studied. $Fe(NO_3)_3$ powder was mixed with the sample of same size fraction. The mixing ratio of $Fe(NO_3)_3$ to sample is 0.5%, 1.0%, 1.5%, 2.0% and 2.5% (wt%) respectively. The mixed samples were leached by distilled water.

The effect of the concentration of oxygen on the weathering of sulfide was studied with same sized sample and with different concentration of hydrogen peroxide (0.3%, 0.9%, 1.5%, 2.1% and 2.7% v/ v, H_2O_2/ H_2O).

The effects of pH of leaching solution and nitrate in the leaching solution on pyrite oxidation were studied. NH_4NO_3 was added in distilled water to have amount of nitrate be the same as that of $Fe(NO_3)_3$ in the sample used for oxidation experiment and pH of the leaching solution was adjusted by NH_4OH and HNO_3. The pH of the solution without nitrate was adjusted by HCl.

RESULTS AND DISCUSSION

The relationship between the amount of sulfur released from the wastestone sample and leaching amount are shown in Fig. 1. It is shown that the sulfur released from the pyritic wastestone is exponentially varied with leaching amount. The releasing amount of sulfur from weathering can be related with leaching amount as follows.

$$\ln C_i = a_i + b \ln P \quad (R > 0.98, \ n = 6), \tag{1}$$

where C_i is the releasing amount of sulfur (mg / kg) from surface area i; a_i is a constant which is related to surface area i; b is a constant, 0.456 ± 0.035 (1SD), not related to surface area; P is the leaching amount (in rainfall units, mm). The reliability of correlation is $P < 0.001$. The result is similar to that given by McKibben and Bames (McKibben, 1986) witn blowing oxygen in a closed system. Their exponent, b, is 0.49 ± 0.05 (1SD).

The relationship between the rate of oxidation and oxidation surface area of pyrite was simulated by many scientists, but the conclusions were not the same. In this paper, the surface area of the wastestone weathering was estimated using following equation:

$$S = \frac{W}{Wa} \cdot Sa \tag{2}$$

where W is the weight of sample, Wa and Sa are the weight and surface area of a particle with the available diameter D. Assuming the particles were spherical, the surface area of the sample, S, should be

$$S = \frac{6W}{\rho D} \quad , \tag{3}$$

where ρ is the density of the wastestone. Equation (3) shows that the surface area of sample is proportional to sampling weight and inversely to particle size. The weathering surface area of experiment sample could be calculated. The relationship between releasing amount of sulfur, C_i and the weathering surface area is shown in Fig. 2. It shows that the relationship is exponential as follows:

$$\ln C_i = a_i + bi \ln S \quad , \qquad (R > 0.97, n = 5) \ , \tag{4}$$

where a_i and b_i are constants related to the leaching amount.

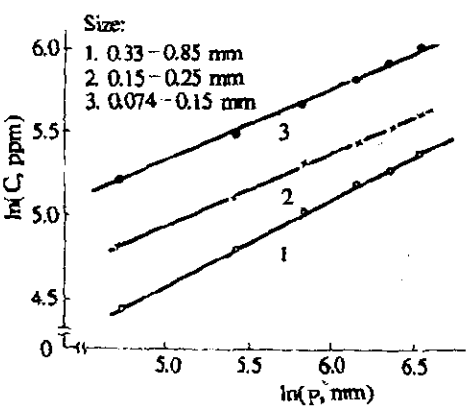

Fig. 1 Correlation between amount of sulfur released from pyritic wastestone weathering and leaching amount
Size : 1. 0.33–0.84mm 2. 0.15–0.25mm
3. 0.074–0.105mm

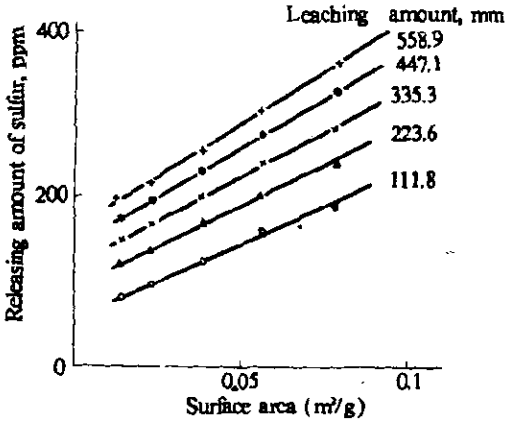

Fig. 2 Relationship between amount of sulfur released from pyritic wastestone weathering and the surface area of sample

This result agrees with Bailey (1976) and Stenhouse (1952) which are

$$R \propto S^n \tag{5}$$

and

$$R \propto 1/d^2 \ . \tag{6}$$

The effect of acidity of leaching solution on the rate of pyrite oxidation was simulated. As pH in the simulation was between the pH of the acid mine drainage generated by the wastestone and that of rain in this district. The amount of sulfur released from the experimental wastestone weathering at different pH and same surface area of sample is listed in Table 1. It shows that releasing amount of sulfur was not related well to the pH of leaching solution and to the amount of nitrate used in experiments.

Table 1 Amount of sulfur released at different pH, ppm

Leaching amount, mm	pH 2.0	3.0	4.0	5.0	6.0
111.8	114.9	113.1	121.0	108.3	116.8
111.8	(116.4)*	(114.2)*	(113.7)*	(115.3)*	(112.6)*
223.6	150.9	150.3	164.4	148.9	154.0
335.6	175.0	179.7	196.7	176.2	183.4
447.1	192.9	197.8	222.4	197.4	203.4
558.9	219.1	214.2	247.5	218.2	223.4
670.7	234.7	229.4	268.2	236.9	244.2
NO_3^- conc. mol/L	0.05	0.04	0.03	0.02	0.01

* Result of leaching solution without nitrate

The relationship of the amount of sulfur with leaching amount, sulfur content and weathering surface area of the wastestone is given in Fig. 3. It shows that the amount of sulfur released was related to the sum of logarithmic leaching amount (P), sulfur content (X), and weathering surface area of the pyritic wastestone (S) are as follows:

$$\ln C = a + b \ln P + c \ln X + d \ln S \quad , \tag{7}$$

where C is the amount of sulfur released from the pyritic wastestone weathering; a, b, c and d are constants. The reliability of the relationship was tested by F test, $P << 0.001$.

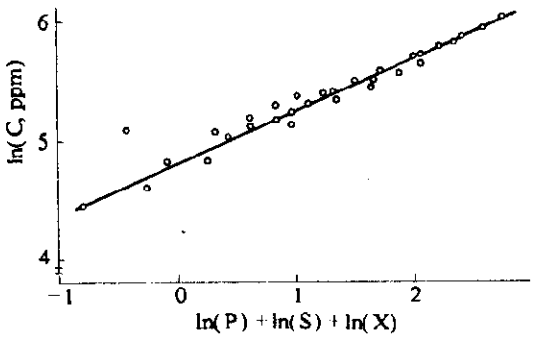

Fig. 3 Relationship among amount of sulfur released from the wastestone weathering with leaching amount, sulfur content and weathering surface area of pyritic wastestone

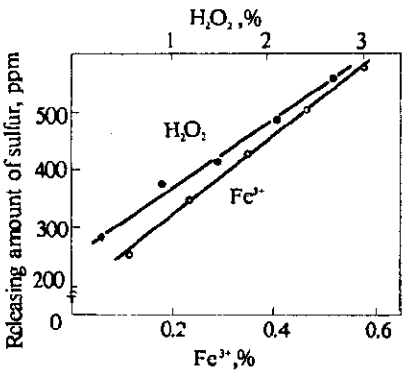

Fig. 4 Relationship between releasing amount of sulfur and amount of oxidants (Fe^{3+} and H_2O_2)

From Fig. 4, the relationship between the releasing amount of sulfur and ferric iron with same surface area of sample and same leaching amount showed that the amount of sulfur released from the wastestone wea- thering was increased with amount of ferric iron mixed. The comparison of sulfur released from mixed ferric iron with unmixed (Fig. 5) showed that ferric iron on the pyritic wastestone weathering was very signi- ficant and that the releasing amount of sulfur was increased linearly with the amount of ferric iron mixed.

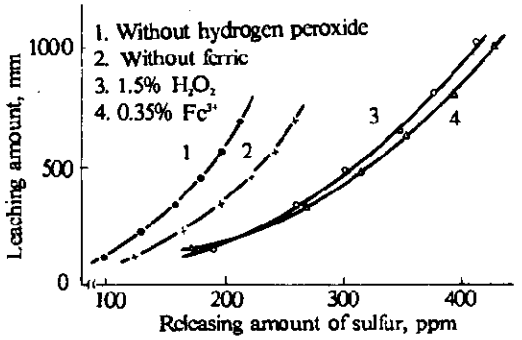

Fig. 5 Comparison of the amount of sulfur released from pyritic wastestone weathering with and without oxidant
1. without hydrogen peroxide 2. with ferric 3. 1.5% H_2O_2 4. 0.35% Fe^{3+}

Hydrogen peroxide was used in the simulation experiments of pyritic wastestone weathering (Fig.4 and Fig.5). The result shows that the amount of sulfur released from the wastestone weathering increased linearly with the amount of hydrogen peroxide in leaching solution. The function of hydrogen peroxide is the same as that of ferric iron.

CONCLUSION

The effect of leaching in an open system on pyrite oxidation was in accordance with that of blowing oxygen in a closed system. Sulfur released from the pyritic wastestone weathering was increased with leaching amount. Oxidation rate of pyrite in pyritic wastestone increased with weathering surface area.

It may be considered that the function of hydrogen peroxide is similar to ferric iron and the rate of pyrite oxidation increased with the amount of the oxidants.

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