REACTIONS OF PYRITE IN CATALYTICAL OXIDATION ACID LEACHING SYSTEM①

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ABSTRACT In H_2SO_4-HNO_3-H_2O-O_2 system, the effects of solution composition, opreration factors and several additives on the reaction rate of pure pyrite have been studied in detail under the pressure condition. The results indicated that after leaching, the product percentage of oxidation residue is about 5 wt.-% and its composition mainly is α-S^0 and $H_3OFe_3(SO_4)_2(OH)_6$. In the presence of HNO_3, the reaction rate increased by about 10 times.

Key words: catalytic oxidation acidic leaching pyrite oxidation pretreatment

1 INTRODUCTION

The gold concentrate containing FeS_2 and FeAsS generally belongs to refractory in nature. It is necessary to liberate the gold encapsulated within sulfide minerals by oxidizing before cyanidation. So far the pressure acid leach process at a temperature of 180 ℃ and an oxygen pressure of 2 200 kPa, has been practiced in Mclaughlin[1], United States, and Sao Bento[2], Brazil. Because of the high investment of this kind of process, it is necessary to reduce the operation temperature and pressure, which make big decreases not only in capital construction cost but also in equipment operation and maintenance cost.

Based on the dilute nitric acid and anionic macromolecular surfactant Na-lignosulfonate serving as a catalytic system, the authors put forward the Catalytic Oxidation Acid Leach (COAL) proccess[3-4]. As a new technological process, COAL can be conducted at 100 ℃ and 400 kPa. Sevaral refractory gold concentrates such as the concentrate containing As, As-Cu, Cu-Pb or FeS_2 have been pretreated with the COAL process, the gold extraction by cyanidation has increased signficantly and reached up to 95 wt.-%~99 wt.-%[5].

Because the pyrite and arsenopyrite are two common gold-carrier material of refractory gold ores, it is important to study its behaviour in the COAL precess. The research work about the arsenopyrite by the authors has been published[6].

The reseach work about pyrite in H_2SO_4-H_2O-O_2 system by several authors has been carried out in the literature, and it has been reviewed by Lowson[7], but it has no any report in literature for FeS_2 in H_2SO_4-HNO_3-H_2O-O_2 system. This work is about the oxidation leaching of FeS_2 pure natural mineral with COAL process.

2 EXPERIMENTAL

The experimental pyrite material used in this work was provided by the Ore Sample Manufature Laboratory of the Geological Mineral Ministry, whose compositions are 46. 2 wt.-% Fe and 52. 2 wt.-% S, with a purity of 98. 4 wt.-% and samples average radius of 90%-360 mesh sieve.

The experiment was carried out in a titanium autoclave with a capacity of 2 L. A series of data of oxygen consumption obtained during the reaction period could be converted into the conversion percentage of the pyrite α. After reaction, the concentration of Fe^{2+}, Fe^{3+},

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H^+ and the amount of S^0 in residue are dtermined by chemical analysis.

3 EXPERIMENTAL RESULTS

3. 1 *Changes During the Leaching*

During the leaching, the data of oxygen consumption, $C_{Fe^{3+}}$, C_{H^+}, residue percentage γ, S^0 and conversion percentage α of the pyrite are given in Table 1. Under the condition of 100 ℃, 400 kPa oxygen pressure and stirring speed 1 000 r/min, the leaching solution containing 0. 094 mol/L H_2SO_4, 0. 073 mol/L HNO_3 and 0. 164 mol/L FeS_2 in solid.

When 1 mol of pyrite is oxidized entirely, 3. 75 mole of oxygen is needed. But oxygen comsumption is lower than 3. 75 mol, because an amount of S^0, not all the SO_4^{2-}, is formed in the process. Nearly all of ferrum in the leaching solution exisit in Fe^{3+}, not Fe^{2+}. It shows that Fe^{2+} is easily oxidized to Fe^{3+} when HNO_3 exisited, which is different from H_2SO_4 system. The changes of acid concentration is related to the conversion of pyrite. Such as No. 60, with the initial H^+ concentration 0. 261 mol/L, when 0. 164 mol/L of pyrite conversed to $Fe_2(SO_4)_3$ and H_2SO_4, and 1. 4 g S^0 is formed in residue, the amount of H^+ should increased by 0. 079 mol/L. It is said that the concentration of H^+ in leaching solution should be 0. 34 mol/L, and roughly equal to the determined data of 0. 346 mol/L. The amount of S^0 increased with the increasing of leaching time but increasing grade tend towards slow. When NaL is added in the leaching system, the amount of S^0 produced is small in the initial stage of reaction. The elemental sulphur in residue is hardly to be oxidized in this system. The percentage of formed S^0 is about 15% of total sulphur conversed, which is lower than that in H_2SO_4 system, and shows that S^0 is easier oxidized to H_2SO_4 when nitric acid existed than that without nitric acid.

3. 2 *Errors of Experiment and Multiple Factors Orthogonal Test*

The data of oxygen consumption obtained during the reaction period can be converted into the conversion percentage of α of pyrite. The results of six repeated test indicated that the relationship between α and leaching time can be expressed as:

$$1 - (1 - \alpha)^{1/3} = a_1 t \qquad (1)$$

The standard deviation of the rate coefficient a_1 obtained is about 3. 7%.

Because the range of operation condition of COAL had been fixed, two ways of multiple factors orthogonal and mono factor test were used in the oxidate leaching of pure pyrite natural mineral.

At the fixed operation condition of 100 ℃

Table 1 Changes of the composition during the leaching

No.	t /min	Oxygen consumption /$mol_{O_2} \cdot mol_{FeS_2}^{-1}$	Fe^{3+}/Fe_t (%)	H^+ /$mol \cdot L^{-1}$	γ (%)	S^0/S_t (%)	α
78	26	1. 19	34. 1	0. 267	66. 5	81. 4	37. 7
76	54	1. 78	48. 6	0. 313	53. 0	9. 96	53. 2
77	91	2. 50	69. 4	0. 292	34. 5	12. 8	72. 2
75	163	3. 21	87. 0	0. 333	16. 5	12. 8	90. 2
60	195	3. 38	99. 2	0. 346	7. 5	13. 4	99. 5
56*	18	1. 14	32. 0	0. 308	67. 5	2. 97	34. 0
55*	30	1. 85	47. 9	0. 268	56. 3	5. 94	47. 0
54*	63	2. 57	69. 7	0. 285	40. 0	8. 81	64. 6
53*	101	3. 27	87. 9	0. 297	24. 5	13. 4	82. 5

* 0. 025 g/L Sodium lignosulphonate (hereafter NaL) added in the leaching solution

3 h, 0.025 g/L NaL, 0.164 mol/L FeS_2, 0.3 mol/L H^+, the results of orthogonal test on four factors of the concentration of nitric acid (0.0365, 0.0730, 0.146 mol/L), oxygen partial pressure (500, 1 000, 1 500 kPa), stirring speed (600, 800, 1 000 r/min) and average particle radius of samples at three level (e. g. $L_9(3^4)$) showed that the higher the nitric acid concentration and the smaller the particle radius, the faster the reaction rate is, oxygen partial pressure and stirring rotation speed have little of effect on the reaction.

3.3 *Effects of Mono-factors*

Results of experiment on mainly factors such as concentration of nitric acid, average particle radius r_0, temperature T, amounts of NaL, Cu^{2+} and Fe^{3+} etc. are showed as follows:

3.3.1 Effects of Concentration of Nitric Acid and Sulphuric Acid

The changes of oxidate rate coefficient a_1 of pyrite was slight at the level of 0.0365 or 0.0730 mol/L HNO_3, when $C_{H_2SO_4}$ changed from 0.0285 to 0.143 mol/L.

Keeping the concentration of H^+ at the level of 0.260 mol/L when C_{HNO_3} changed from 0 to 0.256 mol/L, the reaction rate of pyrite increased rapidly (see Fig. 1). In the range of C_{H^+} from 0.15 to 0.65 mol/L, when C_{HNO_3} changed from 0.018 to 0.256 mol/L, the effects of C_{HNO_3} on the coefficient a_1 was showed in Fig. 2. Plotting $1/a_1$ *vs* $1/C_{HNO_3}$, we found the linear relationship between them. The results seem confirms that the oxidation rate is controlled by the adsorption process of nitric acid on solid surface.

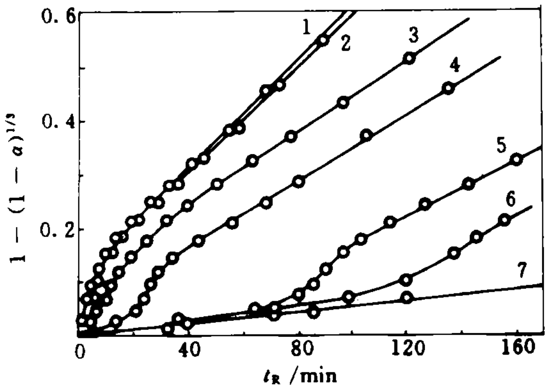

Fig. 1 The effect of C_{HNO_3} on the Leaching

C_{HNO_3} (mol/L): 1—0.256; 2—0.146; 3—0.109; 4—0.073; 5—0.0365; 6—0.0182; 7—0.000

When the concentration of nitric acid was 0.0365, 0.146, 0.183 and 0.156 mol/L respectively, and 0.167 mol/L of pyrite was oxidized, the amount of S^0 produced was 0.0453, 0.0431, 0.0438 and 0.040 mol/L and S^0/S_t was 13.8%, 13.1%, 13.3% and 12.2% respectively. The percentage of S^0 produced was reduced slightly with the increase of the concentration of nitric acid.

3.3.2 Effects of Initial Average Particle Radius

The COAL of pyrite is a heterogeneous reaction system. Only a few amount of S^0 was produced in the leaching process without encasement produced. So we can suppose that particles of pyrite are homogeneous sphere in size, and the relationship between the conversion percentage α and leaching time can be expressed as

$$1-(1-\alpha)^{1/3}=\left(\frac{K}{\rho\cdot r_0}\right)\cdot t = a_1 t \qquad (2)$$

where r_0 is the intitial particle radius, and ρ is the density of pyrite

It can be seen from Eq. (2) that the coeff-

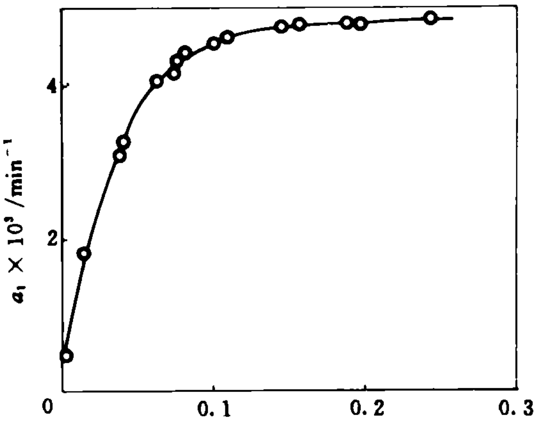

Fig. 2 The relationship between C_{HNO_3} and a_1

icient a_1 is inversely proportional to the initial radius of particles.

Results of experiment on the samples of different particle size showed that the coefficient a_1 is linear relationship with $1/\bar{d}_0$ (see Fig. 3), where $\bar{d}_0$ is defined as the arithmetic mean value of the maximum and minimum diameters between two neighboring sieves. When sieving residue was leached, we found that the particle radius gently decrease following the leaching process.

3. 3. 3 Effects of temperature

The effects of temperature are showed in Fig. 4. Plotting $1/t$ *vs* $\ln a_1$, the apparent activation energy of COAL process of pyrite was shown to be 50. 6 kJ/mol. It shows that the rate-determining step of the leaching process is not physical diffusion. The apparent activation energy of leaching process without NaL is 38. 5 kJ/mol.

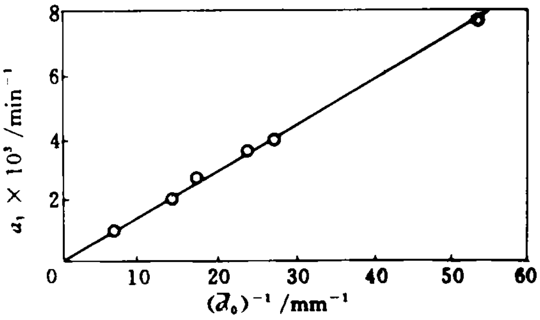

Fig. 3 The relationship between $\bar{d}_0$ and a_1

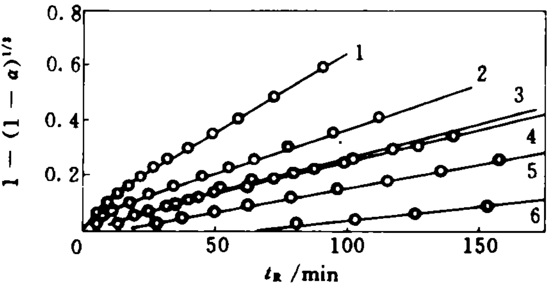

Fig. 4 The effect of temperature on leaching

0. 094 mol/L H_2SO_4, 0. 073 mol/L HNO_3;
1 000 r/min, 400 kPa;
Temperture: 1—110 ℃; 2—100 ℃;
3—90 ℃; 4—88 ℃; 5—80 ℃; 6—79 ℃

3. 3. 4 Effects of the Amount of NaL Added

The range of NaL added is from 0 to 0. 1 g/L, responding to 0～0. 5 wt. -% of pyrite. The effects of the amount of NaL added was showed in Fig. 5. Fig. 5 shows that the coefficient a_1 raise a little at the amount of NaL added from 0. 005 to 0. 025, because NaL as a surfacant is favourable to moisten the particles of pyrite and improves the hydrophobic characteristics of the elemental sulphur formed in the leaching process. However, when more the amount of NaL adsorbed by the pyrite

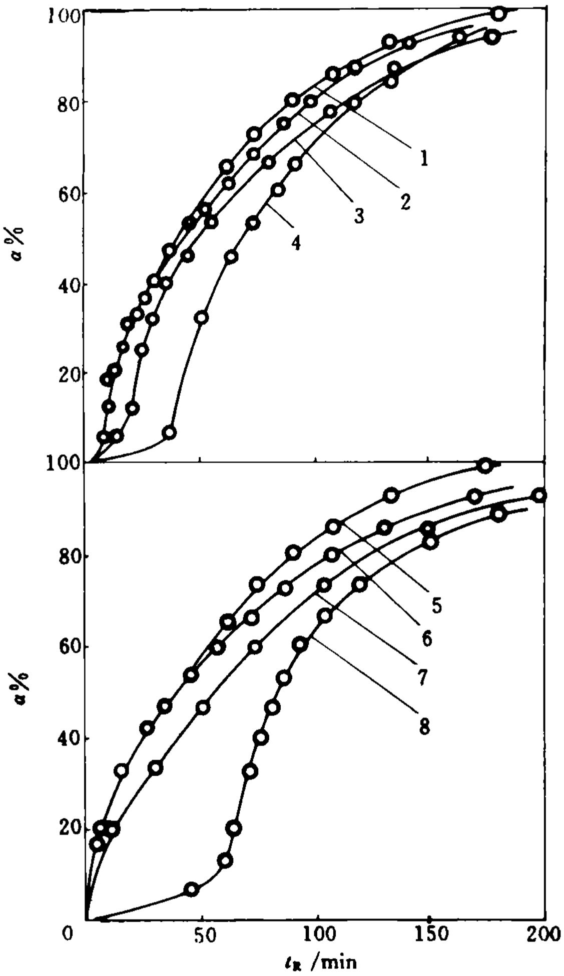

Fig. 5 The effect of NaL amount added on leaching

NaL(g/L): 1—0. 010; 2—0. 005;
3—0. 025; 4—0. 050; 5—0. 001 0;
6—0. 002 5; 7—0. 000; 8—0. 100

increased, and more efficient reactionable surface of pyrite was covered by NaL, which prevents nitric acid from being adsorbed and resulted in the formation of reaction induction period and the decrease of oxidation rate.

3. 3. 5 Effects of Oxygen Partial Pressure and Stirring Speed

Keeping the levels of 1 000 r/min, 0. 0939 mol/L H_2SO_4, 0. 073 mol/L HNO_3, 0. 167 mol/L FeS_2 and 100 ℃, when the oxygen partial pressure is 300, 500, 1 000 and 1 500 kPa respectively, the relationship between the conversion percentage α and leaching time can be expressed as:

$$1-(1-\alpha)^{1/3}=0.0040t$$

It means that a_1 doesn't change with P_{O_2}.

At the same condition, when the stirring speed was 500, 600, 700, 800 and 1 000 r/min respectively (whose linear speed was 1. 47, 1. 76, 2. 06, 2. 35 and 2. 94 m/s respectively), a_1 didn't change with the stirring speed.

Because the coefficient a_1 independed on oxygen partial pressure and stirring speed, the physical diffusion is not the rate-determining step of the oxidation reaction.

3. 3. 6 Effects of Cu^{2+} or Fe^{3+}

A few amount of Cu^{2+} or Fe^{3+} added didn't affect the oxidation rate of pyrite and the ratio of S^0 produced. However, when the amount of Cu^{2+} was more than 0. 015 mol/L, the oxidation rate of pyrite could decrease, because more efficient reactionable surface of pyrite was covered by Cu^{2+}, which prevents nitric acid from being adsorbed and resulted in the decrease of oxidation rate.

4 DISCUSSION

4. 1 *Expression of the Reaction Rate*

According to the results of multivariate experiment, the reaction process rate can be expressed by Eq. 1.

From Fig. 2~4, we can obtain following:

$$a_1=1.39\times10^{-1}\left(\frac{C_{HNO_3}}{1+18.9C_{HNO_3}}\right)\quad(3)$$

$$a_1=1.50\times10^{-4}\left(\frac{1}{\bar{d}_0}\right)\quad(4)$$

$$a_1=5.04\times10^{-4}\exp\left(-\frac{6089}{T}\right)\quad(5)$$

According to the kinetics concept of chemical reaction and the shrinking core model without product on surface, the effects of concentration of nitric acid, particle size and temperature on the coefficient a_1 can be expressed by

$$a_1=K\cdot\left(\frac{C_{HNO_3}}{1+18.9C_{HNO_3}}\right)\times\left(\frac{1}{\bar{d}_0}\right)\exp\left(-\frac{\Delta E}{RT}\right)\quad(6)$$

If the rate of oxidation process is controlled by chemical reaction, incidence Eq. 3~5 with Eq. 6, we can obtain the expression of the coefficient a_1 as

$$a_1=3.96\times10^{4}\left(\frac{C_{HNO_3}}{1+18.9C_{HNO_3}}\right)\times\left(\frac{1}{\bar{d}_0}\right)\exp\left(-\frac{6089}{T}\right)\quad(7)$$

According to the results of experiments carried out in the range of 70~100 ℃, 300 ~1 500 kPa, $\bar{d}_0$ =0. 0185~0. 163 mm, 500 ~ 1000 r / min of the stirring speed , 0. 02 ~ 0. 235 mol/L H_2SO_4, 0~0. 253 mol/L HNO_3 and 0~0. 025 g/L NaL, the coefficient a_1 is about(0. 94~7. 50)$\times10^{-3}$ min^{-1}. Comparing them with that calculated by Eq. 7, the standard deviation of a_1 from 30 tests of various factor is $2.9\times10^{-5}min^{-1}$, it shows that they are very close.

The practical value of Eq. 7 was confirmed by Tuanjiegou gold mine, which contains about 43% FeS_2 and the balance is mainly gangue. When the particle size is 99% other -320 mesh, at 100 ℃, 400 kPa, L/S=5, 0. 15 mol/L H_2SO_4 and 0. 119 mol/L HNO_3, about 80% of FeS_2 is oxidized in 60 min. Based on the operation condition, the coefficient a_1 calculated by Eq. 7 is 7.08×10^{-3} min^{-1}, and the leaching time calculated by Eq. 1 is 58 min which is quite like as the real oparation time.

4. 2 *Exploration on Reaction Mechanism*

The rate-determining step of reaction was discussed basing on the facts followed:

(1) Physical inspection showed that com-

position of residue after leaching was mainly α-S^0 and a few $H_3OFe_3(SO_4)_2(OH)_6$, and no encapsulation.

(2) The higher activation energy marked that the rate-controlling step might be the chemical reaction.

(3) The reaction rate was independent of the oxygen partial pressure and the stirring speed. So the physical diffusion is not the rate-controlling step of the oxidation reaction.

(4) The relationship between the oxidation rate and the concentration of nitric acid can be expressed by the adsorption rate equation of nitric acid.

(5) More Cu^{2+}, Fe^{3+} or NaL added could prevent nitric acid from being adsorbed on efficient reactionable surface of pyrite and resulted in the decrease of oxidation rate.

In summary, we can infer that the rate-determining step of the leaching process may be the chemical adsorption of nitric acid on efficient reactionable surface of pyrite, which is similar to the conclusion in Ref. 7 that the rate-determining step of the leaching process may be the chemical adsorption of oxygen on pyrite surface in the H_2SO_4-O_2-H_2O system.

5 CONCLUSIONS

(1) Comparing with in H_2SO_4-O_2-H_2O solution, the oxidation leaching rate of pyrite in H_2SO_4-HNO_3-O_2-H_2O solution increased by about 10 times attributing to the catalysis of HNO_3.

(2) Effects of a few amount of NaL lie in improving the hydrophobic characteristics of the elemental sulphur formed during the leacing process and make it easy to be oxidized.

(3) Adding NaL or not, the reaction activation energy is 50. 6 and 38. 5 kJ/mol respectively. The oxidation rate is independent of the oxygen partial pressure and the stirring speed respectively, but is inversely proportional to the radius of particles. The rate-determining step of the leaching process is the chemical diffusion of nitric acid on efficient reactionable surface of pyrite.

(4) The oxidation process rate of pyrite can be described by the shrinking core model without product on surface, by which the opertion time needed in the COAL process of the gold concentrate containing FeS_2 can be evaluated.

(5) Because the reaction rate of pyrite is independent of the oxygen partial pressure, it can be expected that the COAL process be carried out at a lower pressure than 400 kPa.

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