

REACTIONS OF ARSENOPYRITE IN CATALYTICAL OXIDATION ACID LEACHING SYSTEM^①

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ABSTRACT

The kinetics of the catalytical oxidation acid leaching of arsenopyrite is studied in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous system. In addition to the effect of reaction time on the extraction of arsenopyrite and distribution of products, the effects of operation factors and several additives on the reaction rate are also investigated. The experimental results show that the oxidation rate is greatly dependent on nitric acid concentration, average radius of samples and acid concentration. The elemental sulphur produced does not interfere with the progress of the reaction process. It is found that a shrinking core model with chemical reaction controlling, which is expressed as $1 - (1 - \alpha)^{1/3} = kt$, may be adopted to describe the kinetics results. The apparent activation energy is tested to be 23.6 kJ/mol.

Key words: arsenopyrite catalytical oxidation acid leaching additives

1 INTRODUCTION

Arsenopyrite and pyrite are the two common gold-carrier materials of the refractory gold ores. Papangelakis *et al*^[1] considered that the oxidation process abided by a shrinking core model with surfacial chemical reaction controlling after having investigated the kinetics of the acid leaching of arsenopyrite under the condition of 130~180 °C, 1 000 kPa oxygen partial pressure. According to the method of pretreatment of refractory gold ores with oxidation catalytical acid leach developed by the Institute of Chemical Metallurgy Academia Sinica^[2], when the reaction is conducted at 100 °C, the introduced catalytical set-up is composed of 0.11 mol/L nitric acid and sodium lignosulphonate (NaL)—a kind of surfacant with polypolar group structure. This paper shows the results of preliminary investigations on the reaction of arsenopyrite in the system.

2 EXPERIMENTAL

The experimental material used in this work is arsenopyrite provided by the Ore Sample Manufacture Laboratory of the Geological Mineral Ministry whose compositions are 26.91wt.-%Fe and 34.2wt.-%As and 13.81 wt.-%S, with a purity of 74.4 wt.-% and samples average radius of 98%—360 mesh sieve. All the reagents in this work are analytic reagent grade except that NaL is technical grade.

The experiment is carried out in a titanium autoclave with a capacity of 2 L. The data of oxygen consumption may be obtained from the interval aeration with oxygen, which may accurately express the reaction process as it is checked by chemical analysis.

The concentrations of Fe^{3+} , Fe^{2+} in the solution are determined by the volumetric analysis, those of As(Ⅲ) and As(V) by the anion chromatography, and elemental S° in

① Financially supported by the National Natural Science Foundation of China; manuscript received Dec. 9, 1992

the leach residue by the CCl_4 extraction gravimetric analysis.

3 RESULTS

3.1 Relationship between Reaction Products and Reaction Time

The relationship between the reaction products and the leaching time is shown in Fig. 1. The results indicate that Fe^{3+} rather than Fe^{2+} exists in the solution owing to the existence of nitric acid. After the conversion percentage of Fe is 25%, the percentage of the formed S^0 (percentage ratio of the produced elemental sulphur to the transformed sulphur) during the reaction is 50~55%. Most of the reacted arsenic exists in As(III) state in the solution, whose content in comparison with As(V) varies with time to some extent during the reaction. Leaching percentage of total arsenic is lower than that of total iron, which is consistent with Ref. [3].

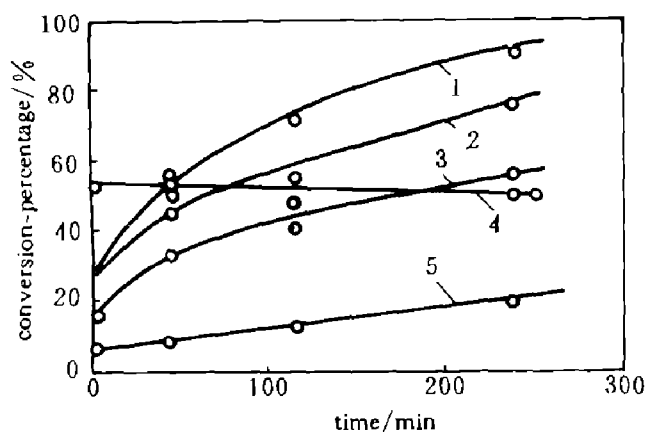


Fig. 1 The relationship between the reaction time and conversion percentage

1— Fe^{3+}/Fe ; 2— $(\text{As(III)} + \text{As(V)})/\text{As}$;
3— $\text{As(III)}/\text{As}$; 4— S^0/S ; 5— $\text{As(V)}/\text{As}$

The transformation percentage of iron has a parabolic relationship with leaching time, but whose $1 - (1 - \alpha)^{1/3}$ is in linear relationship with kt indicating that the process of reaction is in accord with a shrinking core

model without product layers.

3.2 Influence of NaL

As known from photomicrograph and electron microscope scanning, elemental S produced from arsenopyrite has not enclosed the ore particles. Therefore, little addition of NaL has no effect on the reaction rate; then with the addition of NaL increasing continually, a negative impact on the reaction appears, for the increasing of amount of NaL absorbed in particle surface brings about more surface active sites occupied.

3.3 Effects of Stirring Rate and Oxygen Partial Pressure

The stirring rotation rate at a level of 400~1 000 r/min and the oxygen average partial pressure at a scope of 500~1 500 kPa have no effect on the reaction rate. This means that physical diffusion process is not the controlling process of arsenopyrite oxidation reaction rate.

3.4 Effect of Nitric Acid Concentration on Reaction Rate

When the initial acid concentration is kept to 0.45 mol/L and the range of nitric acid concentration is changed from 0 to 0.26 mol/L, as pointed out from Fig. 2, even in pure H_2SO_4 aqueous solution system, leaching reaction also proceeds to arsenopyrite. After adding certain amount of nitric acid, the reaction rate increases very quickly. As shown from effects of nitric acid concentration on reaction rate at different temperatures, the effects of nitric acid concentration on reaction rate decreases with the increase of temperature.

3.5 Effect of Initial Acid Concentration on Reaction

With H^+ concentration changing from 0.16 mol/L to 0.50 mol/L, and with nitric acid concentration being 0.114 mol/L, the result is plotted in Fig. 3. There, in consistency with the reaction mechanism of arsenopyrite in literature^[1], acid concentration is not a noticeable factor affecting oxygen consumption rate while the initial acid concentration higher than 0.30 mol/L; and yet oxygen consumption rate is obviously accelerated along with decreasing initial acid concentration while initial acid concentration is lower than 0.30 mol/L.

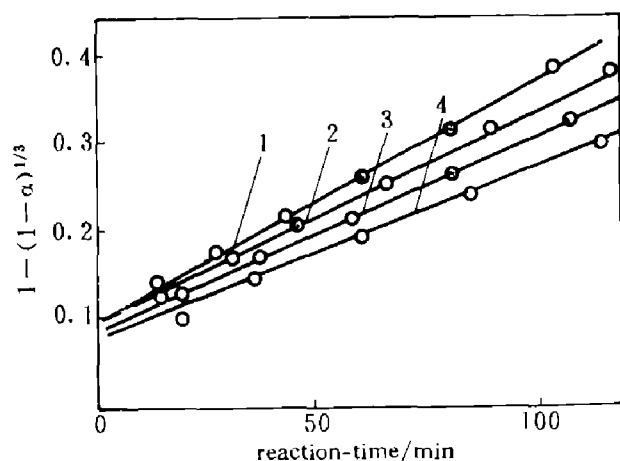


Fig. 2 The effect of nitric concentration on reaction rate at 110 °C

1—0.114 mol/L HNO_3 ; 2—0.076 mol/L HNO_3 ; 3—0.038 mol/L HNO_3 ; 4—0.019 mol/L HNO_3

3.6 Influence of Initial Average Particle Radius

The test results of Fig. 4 show that the reaction rate is of a direct ratio to the reciprocal of the particle radius, and the observation through the microscope in the beginning and at the end of reaction also show the radius of samples reducing during the reaction.

3.7 Effect of Temperature

The apparent activation energy was tested to be 23.6 kJ/mol from Fig. 5, which is lower than the general activation energy controlled by chemical reaction. However, by

means of physical determination, the diffusion layers of the elemental sulfur have not found. Within the range of experimental conditions it is suggested with the respective effect of oxygen partial pressure, stirring rate, amount of NaL and original particle radius on the oxidation acid leaching rate of arsenopyrite that the oxidation reaction of arsenopyrite is not dominated by diffusion.

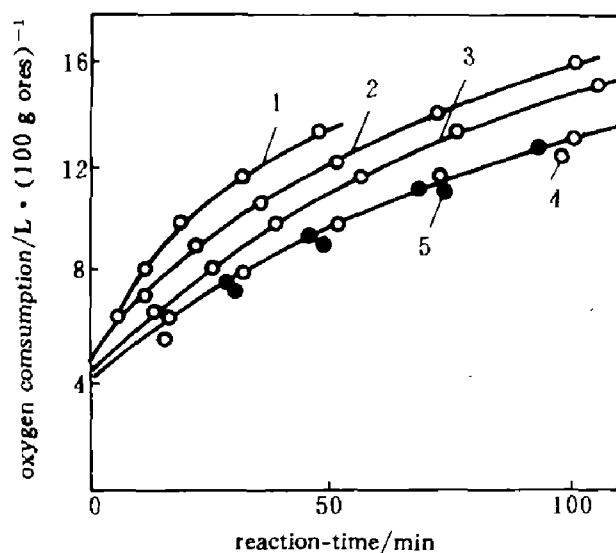


Fig. 3 The influence of initial acid concentration on oxygen consumption

1—0.16 mol/L H^+ ; 2—0.21 mol/L H^+ ; 3—0.26 mol/L H^+ ; 4—0.31 mol/L H^+ ; 5—0.51 mol/L H^+

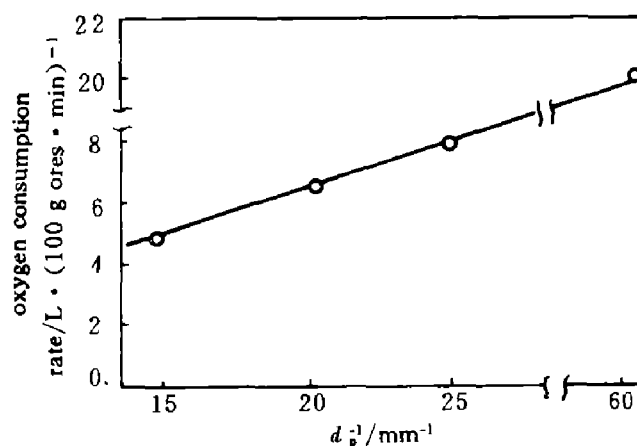


Fig. 4 The relationship between reaction rate and the initial particle radius

The reason that the apparent activation energy of this reaction set-up was lower,

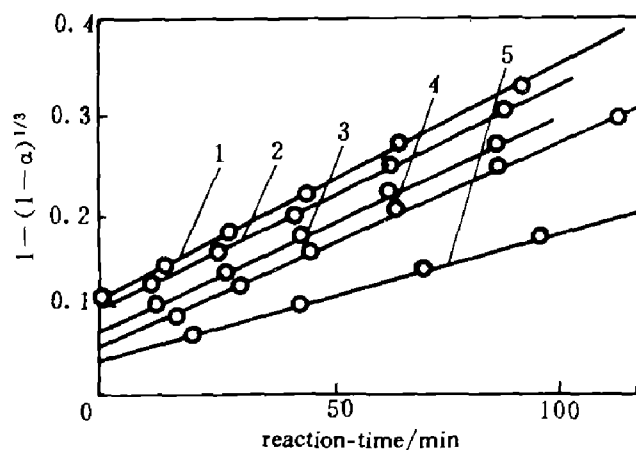


Fig. 5 The effect of temperature on the oxidation reaction of FeAsS

1—110 °C ; 2—100 °C ;
3—95 °C ; 4—90 °C

may be the result of the intricate conduct of the nitric acid in the solution, so further research about this respect remains to be done.

3.8 Influence of Fe^{3+} , Cu^{2+} on Reaction rate

The test indicates that Fe^{3+} , added in the form of $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, at the concentration range of 0 to 0.098 mol/L, and Cu^{2+} , in the form of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, with concentration range of 0 to 0.0084 mol/L do not affect the leach rates.

4 DISCUSSION

4.1 Comparison of Action of Arsenopyrite in $\text{H}_2\text{SO}_4\text{-O}_2$ Aqueous Solution and $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ Aqueous Solution

Even in the H_2SO_4 aqueous solution, owing to the lower potential of oxidation of arsenopyrite, certain reaction rate can be measured. Following the addition of nitric acid, due to its catalytic oxidation action, the rate of reaction increases. For example, at 100 °C, and in the nitric acid solution of 0.08 mol/L, it only takes half time to reach the same reaction conversion percentage, and at 90 °C, it takes only one-third time.

Owing to the nitric acid, the behavior of arsenopyrite is different from that in the H_2SO_4 aqueous solution. The rate in the latter has a direct ratio to the first power of oxygen partial pressure. At the existence of nitric acid in the H_2SO_4 aqueous solution, the reaction rate is independent of the oxygen partial pressure. Therefore, in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous solution, the oxidation reaction of arsenopyrite may take place in lower operating pressures and the higher pressure here is unnecessary.

In the H_2SO_4 aqueous solution, the increasing acid concentration may improve the reaction rate. However in the presence of nitric acid, the decreasing of acid concentration is on contrary conducive to increase the reaction rate instead. For this reason, the leaching reaction of the arsenopyrite in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous solution may take place in lower acid concentration.

Therefore, oxidation of arsenopyrite in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous solution is faster than that of in the $\text{H}_2\text{SO}_4\text{-O}_2$ aqueous solution, mainly displaying in higher reaction rate and lower oxygen partial pressure.

4.2 Comparing Reaction of Arsenopyrite with That of Pyrite in $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ Aqueous Solution

The activation energy of pyrite is 35.8 kJ/mol in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous solution, and yet that of arsenopyrite in the above solution is only 23.6 kJ/mol, which illustrates that oxidation of pyrite is more difficult than that of arsenopyrite. Meanwhile, the reaction rate of pyrite is slightly influenced by acid concentration, but that of arsenopyrite is more seriously.

At 100 °C and in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous solution, the relation between the reaction rate of pyrite and nitric acid concentra-

tion is similar to that between the reaction rate of arsenopyrite and nitric acid concentration, but the leaching rate of pyrite is more highly affected by the alteration of nitric acid concentration than that of arsenopyrite.

Obviously, while pretreating refractory gold concentrates made up of pyrite and arsenopyrite with the catalytic oxidation acid leaching, it may be induced that the operation conditions are chiefly restricted by pyrite.

5 CONCLUSIONS

(1) The kinetics of the oxidation reaction of arsenopyrite in the $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-O}_2$ aqueous solution may be expressed as $1 - (1 - \alpha)^{1/3} = kt$;

(2) The reaction apparent activation energy in the above system is proved to be 23.6 kJ/mol. The reaction rate has no direct relationship with stirring speed, oxygen partial pressure, the addition of Cu(II) and Fe(III) , respectively, but is inversely proportional to the initial radius of particles;

(3) Following the increase of nitric acid concentration, the oxidation rate of arsenopyrite increases. While at the high initial acid concentration ($> 0.30 \text{ mol/L}$), the increase of acid concentration does not affect obviously the oxidation reaction rate, however, while at the low initial acid concentration ($< 0.30 \text{ mol/L}$), and with the acid concentration in this system decreasing, the oxidation reaction rate is contrarily improved;

(4) The experimental results show that the oxidation rate is principally dependent on nitric acid concentration, average radius of samples and acid concentration. While the pretreatment of refractory gold concentrates containing arsenopyrite and pyrite is carried out, its operation conditions are greatly restrained by pyrite.

REFERENCES

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