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Influence of mechanical activation on leaching kinetics of arsenopyrite①

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[Abstract] The influence of mechanical activation on the leaching kinetics of arsenopyrite was studied using a planetary centrifugal mill. It shows that mechanical activation can enhance the leaching process of arsenopyrite in a nitric-sulfate acidic solution. The leaching ratio within 20 min leaching time can increase from 2% to 80% ~ 100%; 10 and 20 minutes' activation can depress the apparent activation energy of leaching reaction from 54.5 kJ/mol to 39.0 kJ/mol and 34.0 kJ/mol, respectively. This means that the leaching reaction becomes little dependent on temperature, and arsenopyrite can change from refractory to flexible one; mechanical activation also increases the interplanar distance between crystal faces. The displacement of atoms from its equilibrium position indicates the increase in inner energy.

[Key words] mechanical activation; mechanochemistry; arsenopyrite; leaching; kinetics
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1 INTRODUCTION

As pyrite, arsenopyrite are known as one kind of refractory auriferous mineral, gold may be almost atomically disseminated throughout mineral grains, resulting in that even fine grinding still leaves most of them physically bound within relatively large particles[1]. So a standard cyanidation used by industry became ineffective towards such ores and, therefore, pretreatment is required before cyanidation[2]. Unfortunately, arsenopyrite is very stable in chemical characteristics. In common research, people had to resort to extrem chemical conditions such as high temperature, high pressure, high acidity or high basicity to destruct it[3,4]. In practice, the effects of those methods are limited while large amount of energy resouce as well as chemical materials being consumed. Besides, problems of environment also created. One can see, in all those works people made use of only exterior factors maybe owing to the fact that the characteristics of minerals is regarded as unchangeable.

With the rapid development of cross subject, mechanochemistry, it is recognized that the chemical characteristics of a solid will change when suffering intense mechanical action. Such action may destroy mineral lattice, induce dislocations or even change crystal into amorphous phase. During such treating process, part of mechanical energy changes into chemical one and being stored inside solid. Successful solid gains an increased inner energy and shows relatively higher reactivity[5~12].

We tried a new way for pre-treating of gold-containing arsenious sulfide ore. With an eye to the interior fact, we expect to enhance the digestion process by increasing the chemical reactivity of arsenopyrite and change such gold containing material from refractory to flexible one. In the present paper, part of research on the effect of mechanical activation on leaching kinetics of arsenopyrite is reported.

2 EXPERIMENTAL

The as-received material was clumpy crystal of arsenopyrite. For the purpose of avoiding changes in chemical characteristics of sample by mechanical action, arsenopyrite was only crushed and sieved to < 0.45 mm, a size range much coarse than that of < 0.074 mm for concentrate commonly used.

X-ray diffraction shows that the sample is monoclinic arsenopyrite. Its chemical composition is shown in Table 1.

Table 1 Chemical composition of arsenopyrite used (%)

Element	Content	Element	Content
Fe	33.53	As	44.92
S	19.17	SiO_2	2.38

Mechanical activation was conducted in a planetary centrifugal mill with the following condition: size of working space: d 7.0 mm × 6.0 mm; steel ball charge: 500 g; diameter of ball: 10 mm; sample charged: 20 g; centrifugal acceleration: 98 m/s^2. The leaching apparatus was a 1000 mL flask with a

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glass stirrer. 800 mL of HNO_3—H_2SO_4 solution prepared from analytical grade reagents and distilled water, was filled in the flask and heated to desired temperature. A condenser was installed to keep the volume of the solution being constant. The reaction was initiated by adding 5.00 g of arsenopyrite to the solution. 1 mL liquor sample was withdrawn each time with certain time interval for determination of leaching ratio through analyzing the Fe concentration. It is worthy emphasizing that the stirring speed was controlled at 400 r/min and was proved to be high enough for dispelling the effect of solution diffusion.

3 RESULTS AND DISCUSSION

Fig. 1 shows the kinetic curves for virgin and treated samples. It appears that the leaching can be enhanced a great deal after being mechanical activated in centrifugal mill. About 20 min induction time is necessary for virgin arsenopyrite to react with solution. Only 2% has been leached after 20 min, this datum increases a little to 12% when leaching time extended to 50 min; But after being activated mechanically, more than 80% of arsenopyrite will react within 20 min for all cases shown in the figure. The induction time also becomes very shorter but has not disappeared as that for pyrite reported in our former papers[11].

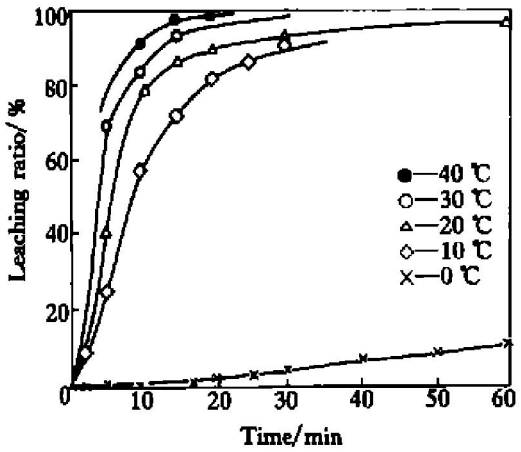

Fig. 1 Kinetic curves for leaching virgin and treated samples
([HNO_3] = 0.50 mol/L, [H_2SO_4] = 1.5 mol/L)

Increase of specific surface area, one result of mechanical activation process during milling for the present case, is also beneficial for leaching. So it will be unilateral to discuss the activation effect according to only the phenomenon of speeding up in leaching. It is reliable to using the kinetic parameter, apparent activation energy, to discuss the effect of mechanical activation since it reflects the kinetic character of leaching reaction and is independent of the surface area of solid reactant.

Fig. 2 is the kinetics curves for leaching of virgin sample at temperature of 55~ 70 ℃. There exists a relatively long induction period for each temperature level which ranges from 20 min to 50 min depending on temperature. Then the leaching reaction begins to speed up until again being bottled when approaching a leaching ratio of 40%. Corresponding to such phenomenon, it is found that the suspending mineral particles began to agglomerate to form several blocks of floccule and revolved in flask. Meanwhile, the color of particles turned from black to olivine. About 70% of sulfur contained is being converted into elementay sulfur when arsenopyrite is oxidized in a nitric acid media[13]. It is plausible that the newly-produced sulfur covering on unreacted core serves as agglomerant. Reaction with particles incorporated inside should be controlled by diffusion and lead to a sudden depressing of leachability. So the apparent activation energy will be calculated using curves lower than 40% ratio.

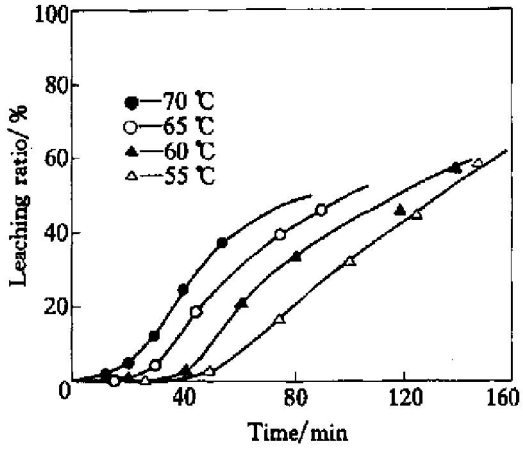

Fig. 2 Effect of temperature on leaching kinetics of virgin sample
([HNO_3] = 1.50 mol/L; [H_2SO_4] = 1.5 mol/L)

According to what proposed in Ref. [12], Arrhenius plot is drown as Fig. 3 using reverse temperature and logarithmic time for leaching 8% and 20% in Fig. 2. Activation energy of 54.4 kJ/mol, which indicates the process under surface chemical reaction control, is obtained.

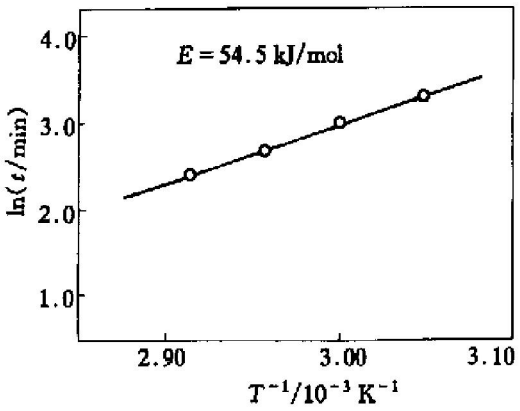

Fig. 3 Arrhenius plot for leaching to virgin sample

Fig. 4 and Fig. 5 give the kinetic curves for leaching of samples with 10 and 20 min activation. The corresponding Arrhenius plots, Fig. 6 and Fig. 7, reveal that the activation energy is of 39.0 and 34.0 kJ/mol, respectively.

The trend of change in apparent activation energy with mechanical treating time can be seen in Fig. 8. The apparent activation energy for leaching arsenopyrite can be depressed from 54.5 to 39.0

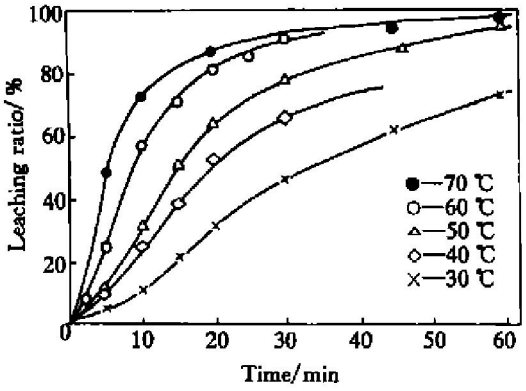

Fig. 4 Effect of temperature on leaching kinetics of sample activated for 10 min
([HNO_3] = 0.50 mol/L; [H_2SO_4] = 1.5 mol/L)

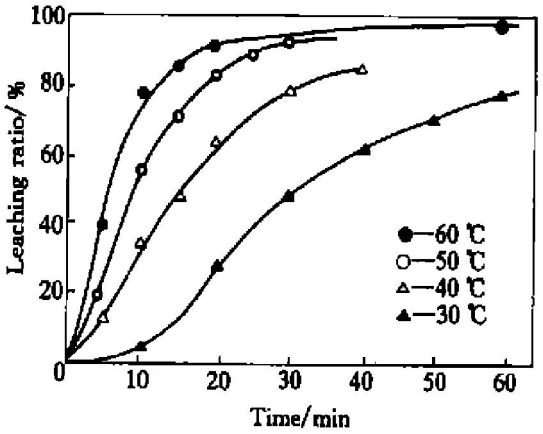

Fig. 5 Effect of temperature on leaching kinetics of sample activated for 20 min
([HNO_3] = 0.50 mol/L; [H_2SO_4] = 1.5 mol/L)

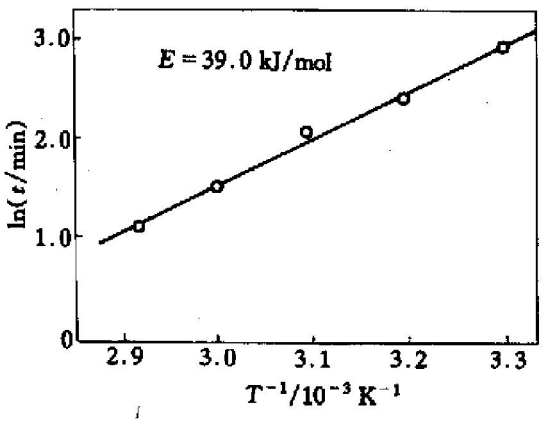

Fig. 6 Arrhenius plot for leaching of sample activated 10 min

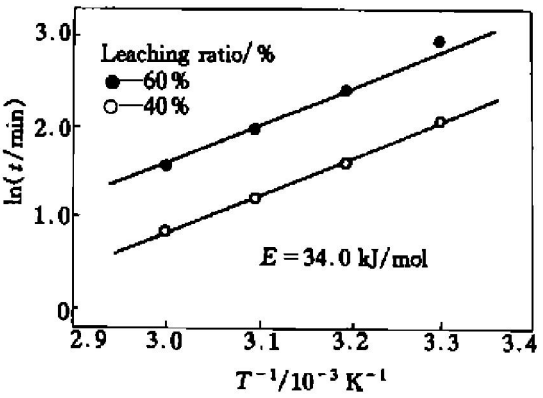

Fig. 7 Arrhenius plot for leaching of sample activated 20 min

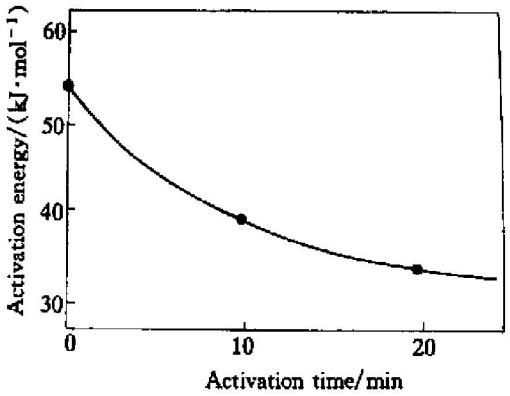

Fig. 8 Influence of activation time on apparent activation energy

kJ/mol while under same conditions that for pyrite changes from 73.9 to 57.7 kJ/mol. The differences for both minerals are 15.5 and 16.3 kJ/mol, respectively. Maybe we can say the activation effects are approximate to the meaning of activation energy. Arsenopyrite, as other mineral cryststals, has experienced million years of geological evolvement and is in a thermodynamic stable condition of low energy. In the process of mechanical activation, part of mechanical energy is changed into chemical one and stored inside mineral in form of various imperfections. The reactivity of mineral crystal should be increased since it gains extra inner energy and becomes relatively unstable in thermodynamics. Then less energy is need for mineral to change into state of middle active complex. In other words, the apparent activation energy becomes smaller.

Such increase in inner energy can be verified by results of X-ray diffraction analysis. The interplanar distance between crystal faces from X-ray diffraction analysis is listed in Table 2. Obviously, all of them have increased after mechanical treatment. This means the distance between atoms composing crystal becomes larger. If chemical bond between atoms is taken as a spring with elastic coefficient of k, when inter atom distance increased Δ, energy stored in the

Table 2 Interplanar distance of arsenopyrite by X-ray diffraction

hkl	Virgin sample	Activated for 20 min
111	3.6488	3.663
200	2.653	2.666
121	2.441	2.446
012	2.403	2.412
222 113	1.822	1.825
202	1.604	1.604
313	1.535	1.539

spring should be $(1/2)\,k\,\Delta^2$.

With prolonged activating time more energy will be absorbed and cause further more change in activation energy. But imperfections in crystal will gradually become saturated; the efficiency for mechanical energy changing into chemical one will be deteriorated. The decrease in apparent activation energy tested also become relaxing.

Activation energy, an important parameter, shows the dependence of chemical reaction on temperature. Decrease in it means the leaching of arsenopyrite become less dependent on temperature. Then maybe it is unnecessary for leaching reaction to carry on it at high temperature as we had used to do. In other words, arsenopyrite has changed from "refractory" to "flexible". Such change provides possibility for developing green metallurgical process with moderate, soft chemical conditions.

3 CONCLUSIONS

1) Mechanical activation can greatly enhance the leaching of arsenopyrite in HNO_3—H_2SO_4 acidic solution. 80% ~ 100% of arsenopyrite can be leached within 20 min depending on activation temperature while for virgin sample only 2% can be done.

2) The apparent activation energy of leaching can be depressed from 54.5 kJ/mol for virgin sample to 39.0 and 34.0 kJ/mol after 10 and 20 min mechanical treatment, respectively. Leaching becomes less dependant on temperature.

3) Arsenopyrite can change from "refractory" to "flexible" by mechanical activation. Such change provides possibility for developing green metallurgical process with moderate, soft chemical conditions.

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