Effect of processing history of pyrite on its leaching kinetics[①]

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Abstract: Different researchers often attained scattered kinetic results for the same leaching process. Usually, the difference is ascribed to the variation in mineral resource, chemical composition and, accuracy of experimental methods, while less attention is paid to the sample processing history. The present study shows that processing history of pyrite sample can cause great changes in its physico-chemical properties. Crushing, grinding and milling lead to an increase of the leachability of pyrite and the leaching becomes less temperature dependence owing to the decreasing of apparent activation energy of the reaction. The activation energy for its leaching in H_2SO_4-HNO_3 solution is depressed from 73.9 to 47.5 kJ/mol after being activated through vibrating milling for 40 min. On the contrary, aging causes the reverse change owing to the release of extra inner energy stored during mechanical treatments. Thus activity of pyrite will decrease towards its original value. Surely the processing history of concentrate sample should be taken into consideration when studying the kinetics of leaching reaction.

Key words: leaching; mechanical activation; aging

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1 INTRODUCTION

The reliable knowledge about leaching kinetic of minerals is of great importance for developing hydrometallurgical processes. But many a time, researchers obtained scattered results for the same process. For example, the apparent activation energy for the digestion of pyrite by oxygen in sulfate acid solution ranges widely from 39 to 84 kJ/mol[1-3]. Usually, the difference is ascribed to the variety in mineral resource, chemical composition and, accuracy of experimental methods. However only this is still unsatisfactory for explaining such inagreements. In fact, besides the aforementioned reasons, the ways of pretreating mineral powder such as crashing, grinding and milling which had been taken as only a physical process of reducing in size, can also introduce great changes in chemical properties and succeedingly affect the reaction kinetics[4, 5].

In addition, it is also noticed that freshly prepared pyrite is more reactive than the one aged[6]. This appears not an individual phenomenon since similar case has been found for other concentrates. One of such examples is the digestion of wolframite with sodium hydroxide solution. Both in laboratory test and commercial practice, freshly prepared wolframite concentrate is more ready to be leached than the one aged[7].

Apparently, both the sample preparation and aging have substantial effect on the reactivity of solids.

This paper presents the results of a study on such effects by leaching pyrite in sulfate acid solution with nitric acid as oxidation reagent.

2 EXPERIMENTAL

The as-received material was clumsy crystal of pyrite assayed 44.67% Fe, 51.57% S, 2.12% SiO_2. For the purpose of avoiding changes in chemical characteristics of sample by mechanical action, pyrite was crashed and sieved to only < 0.45 mm, a size range much coarse than that of < 0.074 mm for concentrate commonly used.

A farther grinding of the coarse sample was performed in a vibrating mill with the following conditions: volume of working space: 1.5 L; steel ball charge: 4.5 kg; diameter of ball: 10-15 mm; sample charge: 100 g; initial sample size: < 0.45 mm; mill revolution: 23.3 s^{-1}; amplitude: 4.5 mm; milling time: 40 min.

The leaching apparatus is a 1 000 mL flask with a glass stirrer. A water bath was used to maintain constant temperature. 800 mL of HNO_3-H_2SO_4 solution prepared from analytical grade reagents and distilled water, was filled in and heated to desired temperature. The reaction was initiated by adding 5.00 g of pyrite to the solution. 1 mL liquor sample was withdrawn with certain time interval for determination of leaching ratio through analyzing the Fe concentration. It is worthy emphasising that the stirring

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speed was controlled at 400 r/min and was practiced to be high enough for dispelling the effect of solution diffusion.

3 RESULTS AND DISCUSSION

3.1 Coarse sample

The effect of initial ferric ion concentration on pyrite dissolution is illustrated in Fig. 1. As can be seen, at the beginning of leaching there exist induction periods which make the kinetic curves into "S-shaped".

The possible causalities lie in:

a. Catalytic effect of ion pair Fe^{3+}/Fe^{2+}

Fe^{3+} is considered to react directly with pyrite. The consumed ferric ions were reproduced through reaction $Fe^{2+} + NO_3^- + H^+ = Fe^{3+} + NO_2 + H_2O$. Since there is no ferric ion in the solution when the experiment had just started, the leaching rate is extremely low. However, once a few Fe^{3+} are becoming existence, pyrite dissolution will be more pronounced.

b. Increasing and enlarging of surface active sites

The slow initial leaching rate is owing to the shortage of such site. With the enlarging of old sites and creating of new ones through dissolving reaction, the leaching itself is gradually sped up.

According to mechanism a, Fe^{3+} ion was added on the purpose of erasing induction behavior but in van (see Fig. 1). So it is eligible to consider that the inductive behavior originates from mechanism b. This will be further confirmed afterwards.
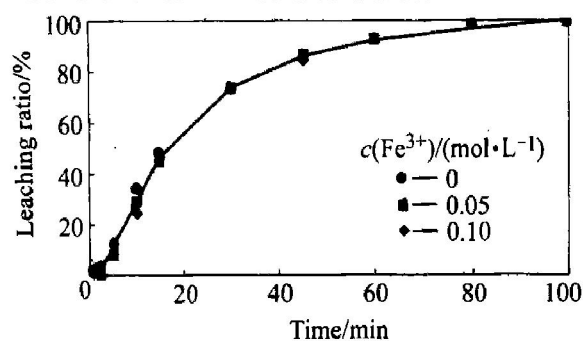

Fig. 1 Effect of initial Fe^{3+} ion concentration on leaching of pyrite
[HNO_3] = 1.5 mol/L, [H_2SO_4] = 1.5mol/L, t = 60 ℃

The effect of temperature was examined, with coarse sample (< 0.45 mm) prepared freshly and those aged for half a year, in order to determine the activation energy. The leaching curves are given in Fig. 2 and Fig. 3 and both show an increase in the pyrite conversion with the increase of temperature.

By comparing the two figures, it is easy to find that newly prepared sample is more reactive under the identical reaction conditions. For example, 55% of
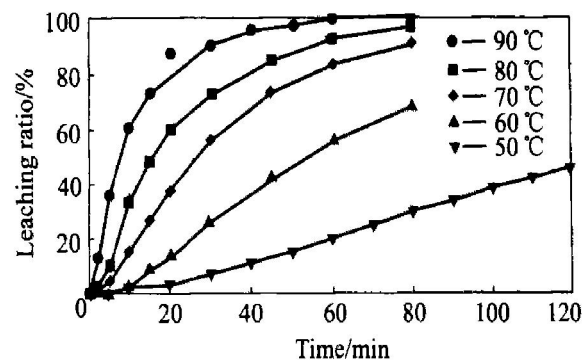

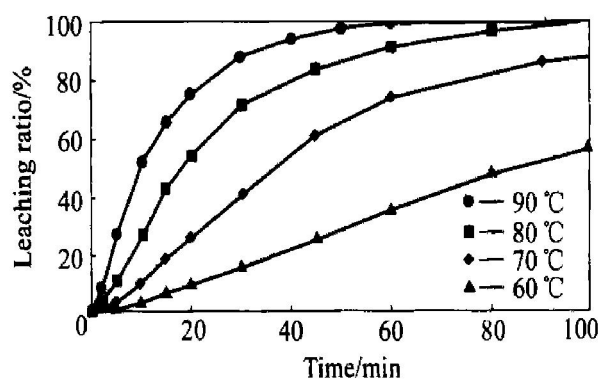**Fig. 2** Effect of temperature on leaching of pyrite (newly prepared)

Fig. 3 Effect of temperature on leaching of pyrite (aged for 6 months))

pyrite could be leached at 60 ℃ within 60 min. Correspondingly for aged sample this value is only 35%.

Since wide-sized sample was used in this research, the iso-leaching-ratio method was adapted for managing the data[8].

The times needed for attending identical leaching percentage at the same reaction temperature were read from Fig. 2 and Fig. 3 and scheduled in Table 1 and Table 2, respectively. Obviously more time is consumed for aged pyrite to attain identical reaction level as that of fresh one.

Arrhenius plots are accomplished as Fig. 4 and Fig. 5 using the data listed in Table 1 and Table 2.

Table 1 Time needed for gaining identical leaching ratio (new)   min

Leaching ratio/%	50 ℃	60 ℃	70 ℃	80 ℃	89.5 ℃
60		66.5	33.5	20.0	10.0
40	105.0	43.5	21.3	12.5	5.5
20	60.5	25.0	12.0	7.0	3.0

Table 2 Time needed for gaining identical leaching ratio (aged)   (min)

Leaching ratio/%	60 ℃	70 ℃	80 ℃	90 ℃
60	110.0	44.5	22.3	12.4
40	65.5	29.0	14.0	7.5
20	36.0	16.5	8.5	4.0

In both figures, good liner relationships are obtained for all instances. In addition, three lines in each figure are parallel to each other. This means that the mechanism keeps unchanged at different reaction extents. The apparent activation energy is derived from the Arrhenius plots as 69. 0 kJ/ mol for leaching of pyrite freshly prepared and 73. 9 kJ/ mol for that aged. Both indicate that the leaching is under the control of surface chemical reaction. But the leaching of fresh sample is less temperature dependent than the aged one since the apparent activation energy is 4. 9 kJ/ mol less.
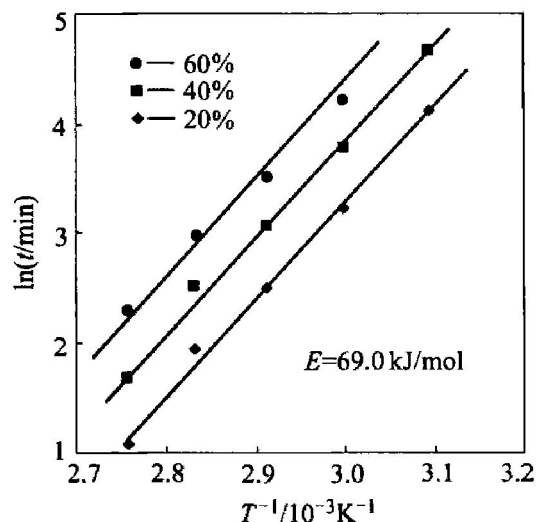

Fig. 6 Schematic reaction path of leaching

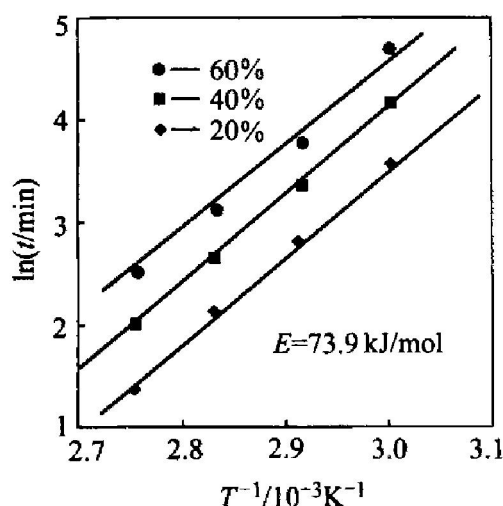**Fig. 4** Arrhenius plots for leaching of freshly prepared pyrite sample

Fig. 5 Arrhenius plots for leaching of aged pyrite sample

Fig. 6 schematically shows the leaching reaction path. Here the energy level of the active complex was taken grossly as the same. Besides, the difference in activation energy is enlarged for the purpose of emphasizing problem.

It is shown in this figure that the total energy level is relatively lower for reaction system which has a lower reaction activation energy. This can only be attributed to the variation of inner energy level of pyrite samples considering the fact that other substan-
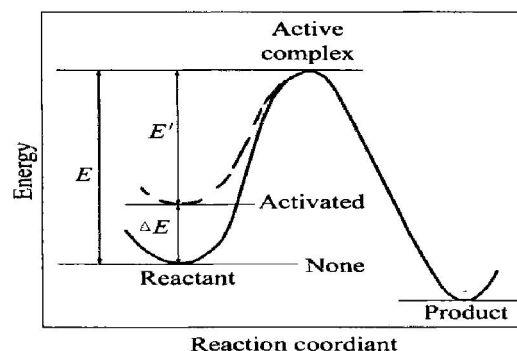
ces in the leaching system such as H_2O, HNO_3 and H_2SO_4 are the same. Hence, it is reasonable to say that the inner energy of aged pyrite is lower than that of the newly-prepared one.

According to the theory of mechano-chemistry, when violate mechanical force is acting on a crystal, part of mechanical energy can be transferred into chemical one and stored inside the crystal as microstrain and crystal imperfections. Sometimes, the crystal is even turned into amorphous phase. Thus the solid is being set at an unstable state of high energy and succeedingly ready for chemical reaction. This effect is called mechanical activation[9, 10].

Although the pyrite crystal used in this study was only crushed coarsely to a size of < 0. 45 mm, mechanical energy intense enough had acted on it and unavoidably, activation effect, whatever weak, had occurred. If such pyrite sample is aged for a long time, the extra energy accumulated inside will be gradually released and the solid will slowly verge the most stable state as the original clumpy crystal that had undergone millions years of geological period. As a result, the reactivity will decrease, too.

Here even though grossly treated sample was used, the above experiments still showed that processing history had changed the reactivity of solid. Therefore to avoid misleading, attention should be paid to it when studying leaching kinetics.

As mentioned formally, in Ref. [1], it was also reported that aging of pyrite sample caused losing of reactivity. The author assigning this phenomenon to the inhibition of oxidation layer formed on the surface of particles when aged. But at least it is not the major case for current study. Otherwise, though induction period still should increase after aging (more time is needed for destroying the inhibiting layer), once the layer had dissolved thoroughly, reacting surface of the fresh and aged pyrite samples should be the same.

Then the reaction kinetics, especially the apparent activation energy should have been identical.

3. 2 Intensively milled sample

The aforementioned experiments were carried out with only coarse sample (< 0. 45 mm). A more violent change could be expected when pyrite was processed intensively. In fact, the size of commonly used samples (for example, < 0. 074 mm) are much less than < 0. 45 mm. So, experiments had been done with sample milled by vibrating mill for 40 min. (The size of milled pyrite decrease sharply to < 0. 03 mm). The results are illustrated in Fig. 7.
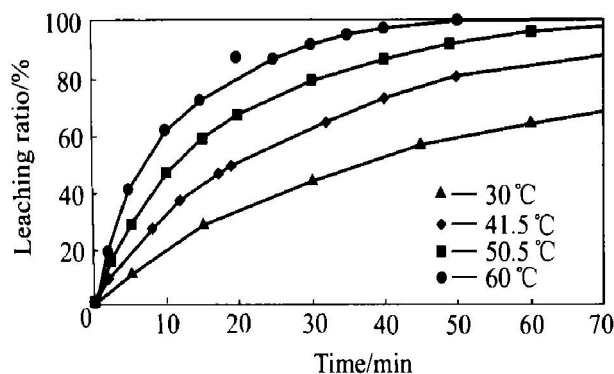

Fig. 7   Effect of temperature on leaching of pyrite activated for 40 min

Comparing Fig. 2 with and Fig. 3, there appears no induction period on the curves through the whole temperature range studied. Obviously, the disappearance is owing to the rise in concentration of surface active sites as a result of intensive milling. Again, this verified the mechanism b for induction period.

Moreover, the leaching had been enhanced to a great extent. At 60 ℃ when the HNO_3 concentration is only one-third of that for Fig. 2 and Fig. 3, pyrite dissolved thoroughly within 60 min. But the leaching ratio itself is not sound for clarifying problem since after milling the surface area had also increased. Resorting to apparent activation energy is convenient.

With the same management as former, the Arrhenius plot was drawn as Fig. 8. Again good linear relationship is gained. From the slop of parallel lines, the apparent activation energy was calculated to be 47. 5, which is 21. 5 and 26. 4 kJ/mol less than those for freshly prepared and aged pyrite. The leaching became even less dependent on temperature owing to mechanical activation.

In fact, metallurgists had made efforts to make use of the mechanical activation effect. Balaz and E-bert[11] reported their work about enhancing the H_2O_2 digestion of sphalerite by milling the concentrate. Our research group had successfully applied mechanical activation to tungsten hydrometallurgy and develo-
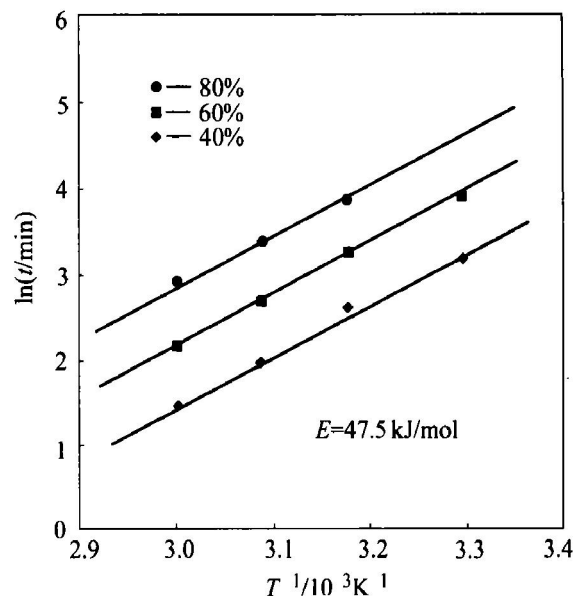

Fig. 8   Arrhenius plot for leaching of pyrite intensively milled for 40 min

ped a commercial process for caustic soda digesting scheelite. The mechanical activation is so effective that scheelite is easily leached with less than 1. 5 stoichiometric amount NaOH at temperature of about 150 ℃, though it is considered that NaOH can not be used to leach $CaWO_4$ in industry[12].

Aging effect of the milled sample is also investigated. The result is plotted as Fig. 9. A speedier losing of reactivity can be seen. It seems that the higher the energy level increases, the more staring the aging effects.
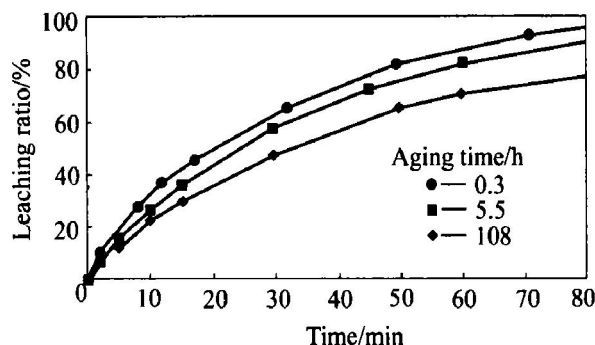

Fig. 9   Effect of aging on leachability of intensively milled pyrite sample

Big error will be introduced if the mechanical activation effect is neglected. This should be a main reason for the scatted kinetic results mentioned at the beginning of this paper. Moreover, neglecting of aging effect will make things more complicated especially when solid is intensively activated.

4 CONCLUSION

The processing history of pyrite sample can cause

changes of its physico-chemical properties. Crushing, grinding and milling lead to an increase of the leachablity of pyrite and the leaching become less temperature dependence owing to the decreasing of apparent activation energy of the leaching reaction. Meanwhile, aging cause the release of extra inner energy stored during mechanical treatment. Succeedingly activity of pyrite will decrease towards its original value. Surely the processing history of concentrate samples should be taken in consideration when studying the kinetics of leaching reaction.

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