

# pH variation mechanism of high sulfur-containing bauxite

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**Abstract:** In order to fundamentally solve the acidification problem of high sulfur-containing bauxite during storage, by simulating the environment of minerals storage in laboratory, the acidification mechanism and influencing factors of high sulfur-containing bauxite were studied and confirmed using the single variable method to control the atmosphere, water and other variables. The results show that the acidification is mostly caused by the oxidation of sulfur-containing bauxite, which is mainly the natural oxidation of Pyrite ( $\text{FeS}_2$ ), then the alkaline minerals dissolve in the presence of water, leading to the acidification phenomenon, which is influenced by moisture and air flow. Finally, more acid-producing substances are formed, resulting in the acidification of high sulfur-containing bauxite. The acidification of high sulfur-containing bauxite results from the combined effect of the oxygen in the air and water, which can be significantly alleviated by controlling the diffusion of the oxygen in air.

**Key words:** high sulfur-containing bauxite; pyrite; acidification mechanism

## 1 Introduction

With the rapid development of economy, aluminum consumption as well as the demand for bauxite resources has increased gradually in these years. According to the official statistics, China possesses rich bauxite resource, and the mineral resources distribution is relatively concentrated in Shanxi, Henan, Guizhou, Guangxi, Chongqing and other places, which accounts for more than 90% of the total reserves. In China, there are 5.94 billion ton bauxite deposits, 7.98 billion ton reserve base, and resource of 19.14 billion ton; the total reserves is 27.13 billion ton [1–3]. It is typical of the case of less reserve base but more inferred resource and total resource. It makes China's aluminum industry rely heavily on bauxite resources. Besides, most of bauxite is diasporic bauxite with high grade while low mass ratio of aluminum to silicon (usually more than 4%–7%), and the average content of sulfur in bauxite is between 1% and 3% (mass fraction) [4]. In order to improve the supply of high-grade bauxite resources in China and make full use of it, many scholars have studied the utilization of technology and implementation method of high sulfur-containing bauxite [5–7]. Meanwhile, in order to reduce the emission of acid mine drainage (AMD) and the heavy metal pollution and other environmental problems, scholars have carried on the related reports on a variety

of metal's AMD questions, the so-called metallic ore's acidification phenomenon in the process of storage and ore dressing. The results of the studies reveal that the auto-oxidation of metal sulfide mineral is the leading cause of AMD [8–11].

Therefore, it is quite necessary for making the best use of huge reserves of high sulfur-containing bauxite to study the acidification mechanism of high sulfur-containing bauxite. In this work, the acidification process of high sulfur-containing bauxite was investigated in simulated natural environment in laboratory, using X-ray diffraction (XRD) and chemical analysis to study the changes in composition during acidification, so as to reveal the acidification mechanism and provide the theoretical reference to the wide application of high sulfur-containing bauxite.

## 2 Materials and methods

### 2.1 Materials

High sulfur-containing bauxite used in this experiment is provided by Aluminum Corporation of China Limited. Mineral samples were taken uniformly from the ore heap, and then grinding crushed. After through 200 target screen, the average particle size is <74  $\mu\text{m}$ . The main chemical composition of bauxite is listed in Table 1.

**Foundation item:** Project(2013AA064102) supported by the National High Technology Research and Development Program of China

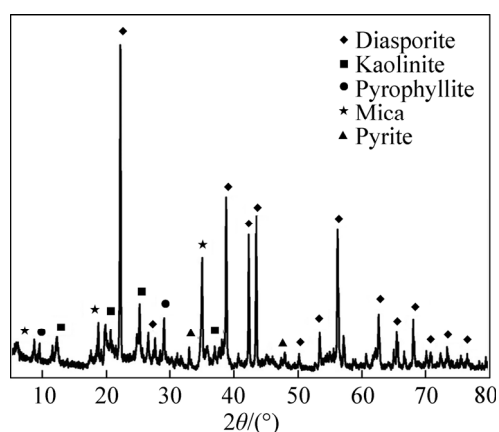
**Received date:** 2014–07–09; **Accepted date:** 2014–10–20

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**Table 1** Main chemical composition of bauxite (mass fraction, %)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe	Na <sub>2</sub> O	S
20.26	51.56	2.71	0.095	2.60

Figure 1 shows the XRD pattern of the raw sample of bauxite. The conclusion can be drawn from the analysis of chemical elements and XRD. The main compositions in bauxite samples are diasporic bauxite, kaolinite, pyrophyllite, mica, black pillar and pyrite. In high sulfur bauxite, sulfur minerals mainly exist in form of FeS<sub>2</sub>.

**Fig. 1** XRD pattern of sample of bauxite

## 2.2 Acidification simulation experiments of bauxite

Adding different amounts of deionized water to a specific amount of bauxite samples, for example, dispersing 2 g minerals into 0, 1 and 5 mL of deionized water, the samples were stored in the states of dry, wet and water immersion, respectively. The two groups were under different ventilation conditions: one was preserved in open system in simulated natural environment system (stacked outdoor); the other group is preserved in the simulated semi-closed system (centrifugal tube sealing). The experimental design is described in Table 2.

**Table 2** Design of experiments

Number	Processing 1	Processing 2
1	Dry	Open system
2	Wet (about 50% of moisture content)	Open system
3	Immersion	Open system
4	Dry	Semi-closed system
5	Wet (about 50% of moisture content)	Semi-closed system
6	Immersion	Semi-closed system

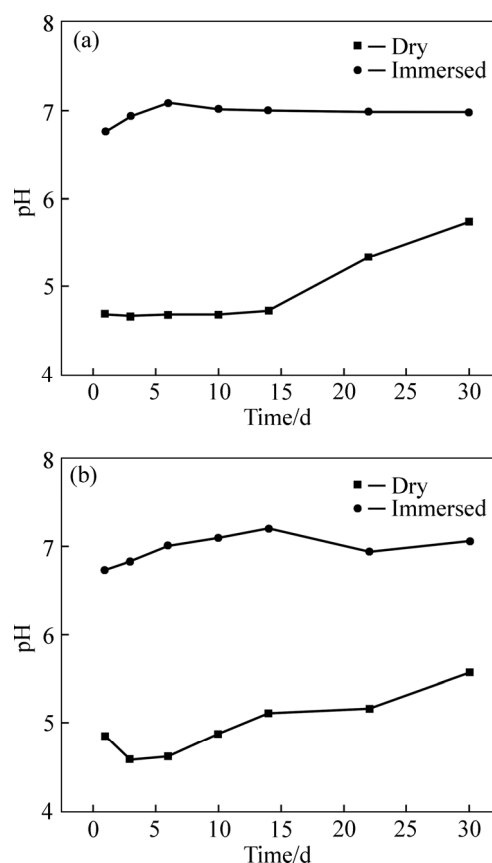
Samples were preserved for a certain time at the same temperature; then the solution was prepared with a given solid to liquid ratio (minerals to suspension mass

ratio of 1:10). The supernatant fluid was taken after the solution was stable for a period of time (2 h) and pH value of the solution was measured by Mettler-Toledo Comprehensive Tester at room temperature (about 30 °C), and the contents of different elements in the solution and the valence state were tested. The main task of this work is to investigate the impact of the oxygen, H<sub>2</sub>O, reaction time and other parameters on the bauxite acidification.

## 3 Results and discussion

### 3.1 Influence of air on high-sulfur containing bauxite acidification

From Figs. 2(a) and (b), by comparing the open group and semi-closed ones, the pH value of the immersed sample is significantly higher than the pH value of the dry sample. The results of these two groups have something in common: the pH value of bauxite under drying condition keeps stable at first, and then begins to rise; while the pH value of the immersed ones increases originally followed by a tardy decrease. The pH value differences are from two aspects: one is the dissolution of alkaline minerals; the other is that oxygen in the air diffuses more than oxygen in the water by 2 to 3 orders of magnitude due to the essential distinction of oxygen's diffusion in the air, and the mass transfer speed is high, which brings about the oxidation of pyrite and

**Fig. 2** pH values varying with time under different conditions: (a) Open group; (b) Semi-closed group

eventually makes the pH value of solution grow relatively slow [12–13].

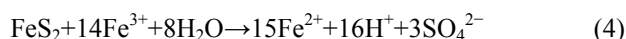
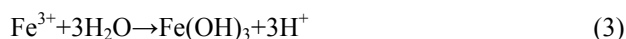
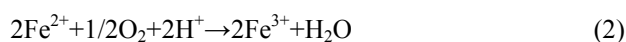
### 3.2 Influence of moisture on high sulfur-containing bauxite acidification.

Seen from Fig. 3, the pH values of the two groups exist obvious difference with the contents of H<sub>2</sub>O. In general, the pH value of the sample increases with the increase of content of H<sub>2</sub>O. By comparing the results of two groups, the change of the pH value under dry condition, which is consistent with the immersed sample, presents a trend of rising slowly after the first stability (Figs. 3(a) and (b)). Overall, the pH value of the dried sample is much lower than that of the other sample. The reason is that the presence of water prevents the diffusion of oxygen in the air, thus resulting in the halfway oxidation of pyrite and less acid forms, which is a disadvantage when competing with the solution of alkaline minerals and ultimately leads to the elevation of pH value. The pH value of the immersed sample increases dramatically and then reduces slowly because of the rapid dissolution of alkaline minerals at the beginning and the relatively slow oxidation of pyrite. When mineral is immersed by water, it is sluggish for

oxygen diffusion, thereby the oxidation and acid-producing of pyrite are restrained [14]; the competition between the dissolution of alkaline minerals and the oxidation accompanied by acid-producing of pyrite creates the phenomenon described above.

### 3.3 Acidification mechanism of high sulfur-containing bauxite

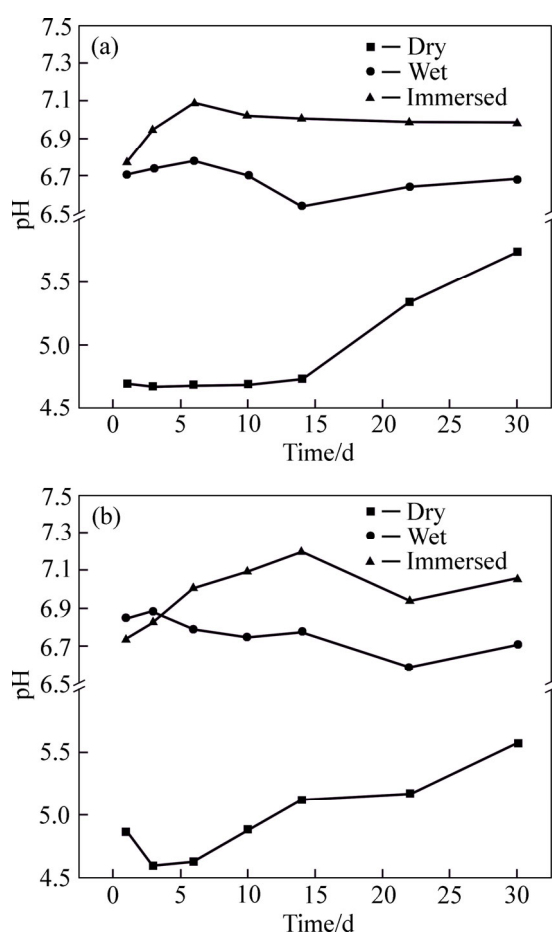
The acid mineral in high sulfur-containing bauxite is mainly pyrite. Many researchers have studied the oxidation processes of pyrite [15–18]. The mechanism of pyrite oxidation is expressed by the following series of reactions in the presence of water:



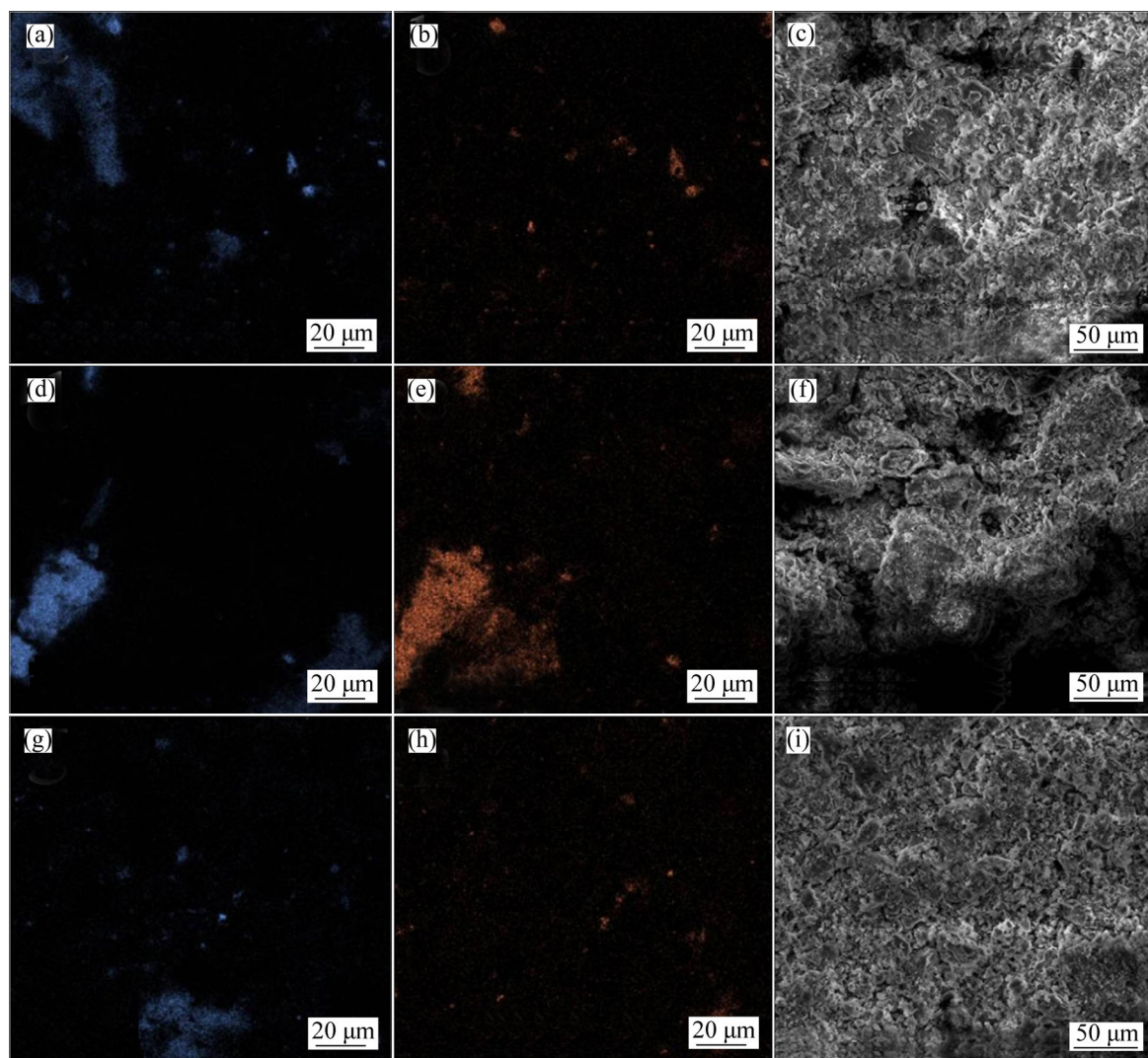
From reactions (3) and (4), acid is produced, making the pH value of solution reduced. The dissolution of the alkaline mineral makes the pH value elevate, meanwhile the oxidation of pyrite reduces the pH value. These two processes react simultaneously, which leads to the subsequent phenomenon of the drop after the first downward, and the growth speed becomes slow. The reaction equilibrium constant of reaction (1) is  $7.74 \times 10^{-29}$ , which is the limiting step of the response, thus making the pH value of the sample after processing totally close to 7. Figure 4 shows the element distribution of the sample in open group treated before and after 30 d.

As shown in Fig. 4, in the raw sample, Fe element gets a dispersive distribution, and the distribution is more concentrated after processing, which is similar to that of S element. The results indicate that the main phase of sulfur minerals (FeS<sub>2</sub>) reduces after being treated and other sulfur-containing ores are dissolved.

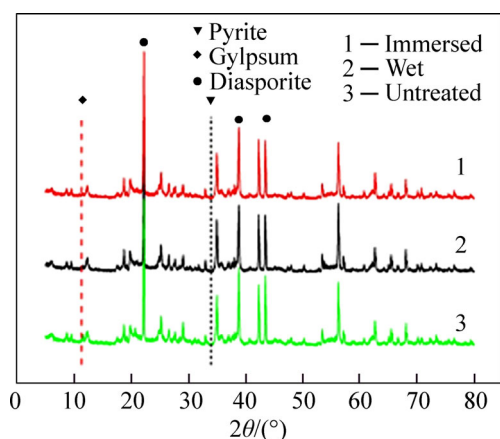
Figure 5 shows the XRD pattern of samples before and after processing. It is shown that the diffraction peak of the plaster stone after processing turns weaker, and the characteristic peak intensity of pyrite keeps relatively stable. Combined with Fig. 4, it can be seen that the breaking degree of pyrite is closely related to the degree of oxidation. The smaller the particle size of pyrite is, the more thoroughly the reaction goes on. Therefore, the distribution of Fe in the treated samples is more concentrated than the untreated samples. The content of elements in the sample is shown in Fig. 6. As can be seen from the picture, samples after treatment fail to detect the signal of Mg, which shows that the minerals containing Mg (oblique chlorite and lizardite) in the samples have been dissolved while the content of S element keeps almost the same and the content of Ca element declines in the meantime. That is to say, with the content of pyrite



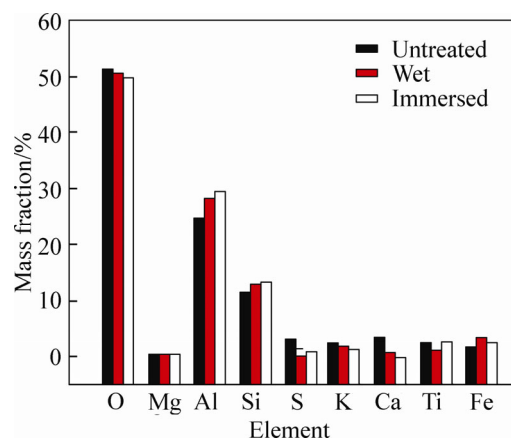
**Fig. 3** pH values varying with time with different contents of H<sub>2</sub>O: (a) Open group; (b) Semi-closed group



**Fig. 4** SEM images (a, d, g) and distribution diagrams of S (b, e, h) and Fe (c, f, i): (a, b, c) Untreated minerals; (d, e, f) Wet samples of open group; (g, h, i) Immersed samples of open group



**Fig. 5** XRD patterns of samples



**Fig. 6** Mass fraction of different elements from EDS data

keeping almost the same,  $\text{CaSO}_4$  with the capacity to produce acid has been dissolved partly in water. Therefore, it can be determined that Ca-containing alkaline minerals which are able to dissolve in water play a key role in the acidification of bauxite.

## 4 Conclusions

The acidification process of bauxite is mainly related to oxidation of pyrite, in which water plays a key role because it dissolves alkaline minerals and also

accelerates the pyrite's oxidation in the open system. The acidification process of bauxite is accelerated in the presence of water if sufficient oxygen is supplied. The acidification process of bauxite is more completed under the condition of being immersed in the water. It is indicated that the nature of minerals' acidification is the result of the competition between acid and alkali. In other words, this eventually leads to the acidification of ore when the rate of alkaline minerals dissolving and generating alkali is higher than the rate of pyrite oxidizing to produce acid.

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(Edited by FANG Jing-hua)