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Phase Transformation and Dissolution Behavior of Pyrite in the Roasting-Sulfuric Acid Leaching Process of Vanadium-Bearing Stone Coal

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Abstract: The selective leaching of vanadium and iron has been one of the main concerns in the field of vanadium recovery from stone coal, but the source of iron ions and their release characteristics were still unclear. In this work, the dissolution of pyrite and its roasted product, under conditions in accordance with the vanadium leaching process from stone coal by blank roasting-acid leaching, were studied. The results indicated that the leaching performances of V and Fe in stone coal were significantly correlated, with both depending on the leaching parameters of the H₂SO₄ concentration, the leaching temperature, the leaching time and the solid to liquid ratio. Under air conditions, with a roasting temperature of 700 °C, the roasted product of pyrite was hematite. Approximately 45% of the roasted product dissolved at its optimal leaching condition—35% higher than that of the raw pyrite. However, any further improvement was difficult, due to the difference in texture between its outer sphere and inner core. The results demonstrated that the roasting treatment led to a significant increase in the release of iron ions during the vanadium leaching process. The pre-removal of pyrite from the raw ore was necessary to reduce the concentration of iron ions in the leachate.

Keywords: vanadium; stone coal; impurity ions; acid leaching; pyrite

1. Introduction

Stone coal is a unique vanadium resource with a massive reserve in China, and the extraction of vanadium from stone coal has attracted attention for a long time. Muscovite is the primary vanadium-bearing mineral in stone coal because the V³⁺ substitutes the Al³⁺ from the dioctahedral structure as an isomorphism in muscovite [1,2]. Therefore, it is challenging to extract vanadium from stone coal.

Currently, blank roasting-acid leaching is an effective technique to recover vanadium from stone coal. Sulfuric acid is widely used as a leaching reagent, coupling with fluorides (CaF₂, HF, and NH₄F) to enhance the vanadium leaching efficiency [3,4]. However, the selectivity of vanadium is not as good as expected. Many impurity ions, especially iron ions, are inevitably leached along with the vanadium, which is detrimental to its subsequent purification and enrichment, and ultimately increases the cost of vanadium recovery [5]. Generally, the concentration of iron ions is 2.0–4.0 times higher than that of the vanadium ions in the leachate [6–8]. The separation of vanadium and iron ions has been one

of the main concerns in the field of vanadium recovery from stone coal [9]. Many extraction reagents have been introduced to separate the vanadium and iron ions in the leachate [10,11]. In addition, novel leaching reagents and leaching technology, such as oxalic acid, have been used to reduce the iron leaching at its source, achieving a highly selective leaching of vanadium over iron [12]. However, their industrial application is unsatisfactory due to environmental and economic problems.

It is commonly believed that the iron ions in leachate come from pyrite or its roasted product. However, the process of pyrite combustion is complicated, and depends on combustion parameters such as temperature, particle size, flow condition and the atmosphere [13–15]. The phase transition behaviors of pyrite in coal combustion systems have been widely reported [16,17]. Hematite and magnetite are commonly believed to be the main roasting products, alongside some pyrrhotites and sulfates [18,19], which present significant differences in dissolution behaviors [20,21]. However, it is unclear what the roasted products of pyrite are, in the blank roasting treatment of vanadium-bearing stone coal, which is significantly different from the coal combustion system in combustion parameters. Furthermore, the dissolution behavior of pyrite and its roasted product under the vanadium leaching conditions are not particularly well analyzed. The aforementioned two combustion parameters are essential for evaluating and developing vanadium-iron separation technology in the extraction of vanadium from stone coal.

This work studied the correlation between the leaching behaviors of V and Fe, from the mica-type vanadium-bearing stone coal in the acid leaching process. Both X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were conducted to further analyze the phasal and structural transformations of pyrite after roasting and acid leaching treatment. This work further aimed to reveal the dissolution characteristics of pyrite in the extraction process of vanadium from stone coal. The results can provide useful guidance for the exploration of new technologies to be used in the source separation of vanadium over iron.

2. Materials and Methods

2.1. Materials

The raw ore of a mica-type stone coal was obtained from Hubei, China. The grades of V and Fe were 0.41% and 3.36%, respectively. The main mineral phases were quartz, mica, calcite, feldspar and pyrite. The mica minerals contained approximately 90.0% of vanadium, and the pyrite contained approximately 90.0% of iron. The detailed results of chemical and phase analyses of the raw ore and its roasted products at 700 °C can be found in previous works [22]. The stone coal was ground to -0.074 mm by a vibration mill.

The natural pyrite sample was collected from Hubei, China. The chemical analysis indicated that the major elements were Fe (45.65 wt.%) and S (53.02 wt.%), with a small amount of talc. The powder of pyrite was prepared by the dry hand-grinding of the pure crystals in an agate mortar with a diameter of less than 0.038 mm. The data presented in this work were recorded with the same sample to avoid sample-dependent variation. All other reagents used in the experiments were of analytical grade.

2.2. Roasting Treatment

The roasting treatment was conducted in a muffle furnace (KRY-10, Yiheng, Shanghai, China) under air condition. The temperature of the muffle furnace was preset to 700 °C before the mineral sample was settled. Following this, the mineral samples were roasted for 60 min at the preset temperature.

2.3. Acid Leaching Experiments

The sulfuric acid leaching experiments were carried out in a 250 mL flask for the stone coal sample, and in a 100 mL flask for the pure pyrite sample, with a temperature-controlled rotary platform at a rotating speed of 300 rpm. The influences of the sulfuric acid concentration, the leaching temperature,

the leaching time and the solid to liquid ratio were all taken into consideration. The leaching solution and residue were also collected for the leaching efficiency calculation, phase and morphology analyses.

2.4. X-ray Diffraction (XRD) Analysis

The XRD analysis was conducted with a PANalytical Empyrean X-ray diffraction (PANalytical B.V., Almelo, The Netherlands) using Cu K α radiation.

2.5. Microscopic Morphology Analysis

The microscopic morphology observation was conducted by a JEOL JSM-IT300 scanning electron microscope (SEM, JEOL, Tokyo, Japan), equipped with a Bruker QUANTAX200-30 energy dispersive spectrometer (Bruker, Berlin, Germany).

3. Results

3.1. The Correlation Between the Dissolution of V and Fe in the Blank Roasting-Sulfuric Acid Leaching Process

The leaching efficiency of V and Fe, from the raw stone coal and its roasted product at 700 °C, were investigated under different H₂SO₄ concentrations, leaching temperature, leaching time and solid to liquid ratios. The experimental parameters are listed in Table 1, and the results are shown in Figures 1 and 2.

Table 1. The experimental parameters in the leaching of the raw ore and the roasted ore.

Groups	H ₂ SO ₄ Concentration (wt.%)	Leaching Temperature (°C)	Leaching Time (h)	Solid to Liquid Ratio (g:mL)
a	variable	90	4	1:2
b	40	variable	4	1:2
c	40	90	variable	1:2
d	40	90	4	variable

Figure 1. The leaching efficiency of V and Fe from the raw ore at different leaching conditions. Variables: (a) the H₂SO₄ concentration; (b) the leaching temperature; (c) the leaching time; (d) the solid to liquid ratio.

Figure 2. The leaching efficiency of V and Fe from the roasted ore at different leaching conditions. Variables: (a) the H_2SO_4 concentration; (b) the leaching temperature; (c) the leaching time; (d) the solid to liquid ratio.

The leaching efficiency of Fe in raw ore was approximately 20%, under all of the experimental conditions (Figure 1). The variations of H_2SO_4 concentration, leaching temperature, leaching time and solid to liquid ratio did not have much of an affect. The highest leaching efficiency of Fe in raw ore was approximately 22%. On the other hand, the leaching efficiency of V highly depended on the leaching parameters—especially the sulfuric concentration, leaching time and leaching temperature. The optimal leaching parameters for V extraction were: H_2SO_4 concentration at 50%, leaching temperature at 95 °C, a leaching time of 5 h and a solid to liquid ratio of 1:4. However, the highest leaching efficiency of V was only 18% at its optimal condition. It has been demonstrated that the muscovite, which is the main vanadium-bearing mineral in stone coal, was resistant to attack by the hydrogen ions in the absence of fluoride [23]. In summary, the dissolution of Fe and V from the minerals in raw ore proved difficult, in line with previous reports [24]. Moreover, the releasing of Fe was faster than that of V.

For the roasted ore, the leaching efficiency of Fe and V both presented a positive correlation to the concentration of H_2SO_4 (Figure 2a), with a final leaching efficiency of 70% and 72%, respectively. The leaching efficiency of Fe gradually increased from 20% to 70% (Figure 2b), with a rise in the leaching temperature from 60 °C to 95 °C. In regards to the leaching efficiency of V, it was lower than 25% when the leaching temperature was lower than 80 °C, and saw a sharp increase from 25% to 60% when the leaching temperature increased from 80 °C to 90 °C. The dissolution of V and Fe was also time-dependent (Figure 2c)—the leaching efficiency of Fe reached 50% in 1 h, and reached an equilibrium within 3 h, with a final leaching efficiency of 62%. In comparison, the leaching efficiency of V was at 37% in 1 h, further increasing to 65% in the following 4 h. As shown in Figure 2d, the leaching efficiency of Fe and V both decreased with an increase in the solid to liquid ratio. The optimal solid to liquid ratio for the leaching of vanadium from the roasted ore was 1:3.

The aforementioned leaching results indicated that the leaching efficiency of V and Fe from the roasted ore was much higher than that from the raw ore, and the release of Fe was faster than that of V. The maximum leaching efficiency of V from stone coal was approximately 75% under its optimal leaching conditions, and the leaching efficiency of Fe was 73% under the same conditions.

Correlations among the leaching parameters of H_2SO_4 concentration, leaching temperature, leaching time, and solid to liquid ratio, alongside the leaching efficiency of V and Fe, were analyzed by redundancy analysis (RDA) with Canoco software. These results are shown in Figure 3.

Figure 3. Redundancy analysis (RDA) of the leaching parameters and the leaching efficiency of V and Fe. (a) the raw ore; (b) the roasted ore.

For the raw ore (Figure 3a), the leaching efficiency of V presented a positive correlation to the leaching parameters of H_2SO_4 concentration, leaching temperature and leaching time, while presenting a negative correlation to the solid to liquid ratio. However, the leaching efficiency of Fe only showed a positive correlation to the leaching temperature, and its efficiency was, therefore, independent of the H_2SO_4 concentration, the leaching time and the solid to liquid ratio. The correlation between the leaching efficiency of V and Fe was insignificant. For the roasted ore (Figure 3b), the leaching efficiency of V and Fe presented a highly consistent trend. The leaching efficiency of V positively related to the H_2SO_4 concentration and the leaching temperature. Similarly, the leaching efficiency of Fe was positively related to the H_2SO_4 concentration, the leaching temperature and the leaching time. However, they both negatively related to the solid to liquid ratio. Interestingly, the correlation between the leaching efficiency of V and the leaching time, was insignificant compared with other parameters.

The acid leaching results indicated that the V in raw ore largely failed to be leached by direct acid leaching, but approximately 20% of Fe bearing mineral was dissolved. The leaching efficiency of V increased to 70% when the stone coal was roasted. Therefore, it can be concluded that the roasting treatment is a prerequisite for the efficient leaching of V from mica-type stone coal, as expected [25]. The V(III) in the stone coal is oxidized to V(IV) and V(V) in the blank roasting treatment, which was easily leached by the sulfuric acid [1]. However, the roasting treatment also significantly promoted the dissolution of the Fe bearing mineral, which will increase both the level of difficulty and the cost in subsequent purification and enrichment processes. The promotion of the release of iron ions can be attributed to the phase change of pyrite caused by the roasting treatment.

3.2. The Dissolution Behavior of Pyrite and Its Roasted Product

The influence of H_2SO_4 concentration, leaching temperature, leaching time and solid to liquid ratio on the dissolution of pyrite and its roasted product at 700 °C, were investigated. The detailed experimental parameters are listed in Table 2, and the results are shown in Figure 4.

Table 2. The experimental parameters in the leaching of the pyrite and its roasted product.

Groups	H_2SO_4 Concentration (wt.%)	Leaching Temperature (°C)	Leaching Time (h)	Solid to Liquid Ratio (g:mL)
a	variable	90	4	1:40
b	40	variable	4	1:40
c	40	90	variable	1:40
d	40	90	4	variable

Figure 4. The dissolution of pyrite and its roasted product at different conditions. Variables: (a) the H_2SO_4 concentration; (b) the leaching temperature; (c) the leaching time; (d) the solid content.

As shown in Figure 4a, the highest dissolution percentage of the raw pyrite was only around 11%, even when the H_2SO_4 concentration reached 40%. By contrast, there was a clear linear dependence between the concentration of H_2SO_4 and the dissolution percentage of the roasted product of pyrite—approximately 20% with an H_2SO_4 concentration of 10%, further increasing to 45% when the H_2SO_4 concentration increased to 40%.

The dissolution percentage of the raw pyrite was less than 11%, even at its highest leaching temperature of 90 °C (Figure 4b). The leaching temperature significantly influenced the dissolution of the roasted product. The dissolution percentage increased from 11% to 45%, with the leaching temperature elevated from 50 °C to 90 °C after 4 h of leaching, in accordance with the leaching behavior of Fe in roasted stone coal. So, increasing the leaching temperature is proven to be beneficial to the dissolution of the roasted product of pyrite.

For the raw pyrite sample, the dissolution percentage increased from 9% to 11%, with the leaching time increased from 1 to 5 h—much lower than that of its roasted product (Figure 4c). The dissolution of the roasted product rapidly increased to 40% in the first 3 h, and slowly increased to 46% in the last 2 h. This means that the residual section in the roasted product was difficult to dissolve any further.

As shown in Figure 4d, the dissolution percentage of pyrite and its roasted product both slightly decreased with the increase of solid content. For the roasted product, when the solid content was 0.5 g/40 mL, the dissolution percentage of the sample was 44%—approximately 7% higher than that of the group with a solid content of 2.5 g/40 mL. In regard to the iron ions, the concentration of iron ions in the leachate increased significantly with the increase in solid content. It could be deduced from the above results that the roasted product of pyrite was inadequately dissolved.

The leaching performance of pyrite and its roasted product showed that the dissolution of both pyrite and its roasted product had a positive correlation with the H_2SO_4 concentration, the leaching temperature and the leaching time, but had a negative correlation with the solid content. The raw pyrite was difficult to dissolve compared with its roasted product. In addition, the dissolution percentage of the roasted product was less than 45% in experimental conditions, and it proved difficult to improve further. This indicates that the dissolution of the roasted product of pyrite did not compare favorably with that of the pyrite cinder [20]. The phase and morphology analyses of the leaching

residue of the roasted product were carried out by XRD and SEM to work out why the roasted product of pyrite could not be further dissolved.

3.3. The Phase and Structure Transformations of Pyrite after Roasting and Acid Leaching Treatment

The XRD patterns of the roasted pyrite and its leaching residue under different leaching times are shown in Figure 5.

Figure 5. XRD patterns of the leaching residue of the roasted pyrite at different leaching times. (a) the roasted sample; (b) the leaching residue of the roasted sample with a leaching time of 1 h; (c) leaching residue of the roasted sample with a leaching time of 4 h.

The hematite was the sole Fe-containing phase in the roasted product of pyrite at 700 °C, in accordance with the theoretical results [19]. The phase of magnetite did not appear due to adequate oxygen in the roasting process. The main phase of its leaching residue was still hematite. While the hematite dissolved, the diffraction peak of the talc intensified with the increased leaching time. The XRD analysis indicates that there are no apparent changes in the components of the roasted product of pyrite before and after acid leaching. The microscopic morphology of the roasted product and its leaching residue under different leaching time was observed by SEM.

The SEM images indicated that the roasted product of pyrite was porous and stacked (Figure 6a). The increased porosity resulting from the decomposition of pyrite has been well documented [26]. The particles leached in sulfuric acid solution for 1 h (Figure 6b) presented higher roughness with many pits, and the roughness further increased with the leaching time (Figure 6c). However, local details showed that the particles leached for 4 h were dense and had a smooth surface. It can be concluded from the morphology variation and the leaching behavior that the outer sphere of the roasted product is porous and easily dissolved. However, the inner core of the roasted product is dense and difficult to be dissolved. A graphical representation (Figure 7) reveals the dissolution process of the roasted product, based on both the acid leaching results and the microscopic morphology analysis.

Figure 6. Microscopic morphology of the roasted product of pyrite and its leaching residue at different leaching times. (a) the roasted sample; (b) the leaching residue with a leaching time of 1 h; (c) the leaching residue with a leaching time of 4 h.

Figure 7. Graphical diagram for the dissolution process of the roasted product.

The pyrite particles after complete oxidation turn into hematite. The roasted product includes two different textures due to the complex reaction in the roasting process. The outer rim is porous, and the inner core is dense. The texture determines the dissolution behavior of the roasted product. The porous outer sphere dissolves much faster than the dense inner core. So, the dissolution percentage of the roasted product increases rapidly at the beginning of the leaching treatment, and then increases slowly with the extension of the leaching time.

3.4. Implications for the Extraction of Vanadium from Stone Coal

The roasting treatment is a prerequisite for the efficient leaching of V from the mica-type stone coal, as the V in raw ore was resistant to leaching by sulfuric acid. However, the roasting treatment also led to the pyrite's transformation into hematite, whose leaching behavior was similar to that of the vanadium-bearing minerals at their optimal leaching parameters. That is to say, the selective leaching of vanadium over iron, is impossible in the vanadium extraction process from stone coal by the blank roasting-sulfuric acid leaching method. Therefore, it is necessary to remove the pyrite from the raw ore prior to the roasting treatment, in order to reduce the concentration of iron ions in the leachate.

4. Conclusions

The leaching behaviors of V and Fe from stone coal both depended on the following leaching parameters: the concentration of sulfuric acid, the leaching temperature, the leaching time and the solid to liquid ratio. The leaching of V and Fe were significantly correlated. The roasted product of pyrite was hematite under the conditions in the blank roasting treatment of stone coal. The dissolution of the roasted product was much higher than that of the pyrite under the same leaching parameters. In conclusion, the roasting treatment led to a significant increase in the dissolution of iron in the blank roasting-acid leaching process of vanadium-bearing stone coal. Consequently, the pre-removal of pyrite from the raw ore before the roasting treatment is necessary to reduce the difficulty of the separation of V and Fe in the leachate.

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