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Calcified roasting-acid leaching process of vanadium from low-grade vanadium-containing stone coal

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Abstract The low-grade vanadium-containing stone coal used in this experiment was collected from Wuxi Country, Chongqing City, China. The experiment focused on the vanadium recovery from roasted residue through optimizing the process conditions of an effective and environmentally-friendly technology, named calcified roasting-sulfuric acid leaching technology. By single-factor experiments and orthogonal experiments, the effects of roasting temperature, roasting time, sulfuric acid concentration and leaching time on the leaching ratio of vanadium were analyzed. The results showed that the leaching ratio of vanadium reached 85.5% under the proper technological conditions of roasting temperature=950℃, roasting time=4 h, 40% concentration of sulfuric acid and leaching time=6 h.

Key words vanadium-containing stone coal; calcified roasting; acid leaching; vanadium extraction

1 Introduction

Vanadium, known as the "industrial monosodium glutamate", is an important strategic material which has found wide applications (Bert et al., 2003). In China, the amount of V_2O_5 in vanadium-containing stone coal accounts for 87% of the total reserves (Zhang et al., 2011). However, the amount of low-grade vanadium-containing stone coal accounts for over 60% of the total, and the low-grade ore zone is often mixed in the high-grade ore (Wei et al., 2010). In many mining areas high-grade ores are mined, but low-grade ores are abandoned, leading to wasting of resources. Therefore, research on the low-grade vanadium-containing stone coal is not only helpful for the full use of the resources, but also has certain reference value for the high-grade vanadium. It was reported that in some materials there was abundant vanadium-containing stone coal in Chongqing, among which the amount of V_2O_5 in the Jiushiping mining area of Wushan Country reached 3400 tons and the profits of 1.85 km^2 ore-bearing layer were 5.1 billion (Chongqing Bureau of Geology and Mineral Resources, 2007). It could bring about prominent social benefits and promote the development of local economy.

The high-salt roasting-water leaching (HSRWL) technique is a traditional method in China, which has long been used to extract vanadium from stone coals, so as to produce such caustic gases as Cl_2 and HCl (Wang and Wang, 2012). The leaching ratio of vanadium is generally about 50% (Li et al., 2009). The blank roasting technique is adopted by some enterprises to reduce the exhaust pollution, but the leaching ratio is still rather low (Wang et al., 2011). However, the calcium roasting technique not only doesn't produce chlorine gases, but also reduces the generation of SO_2 because of the sulfur fixing of calcium addictive (Hui et al., 2011). While, with the different components of local ore samples, the proportion of calcium addictive is variable, which makes it more difficult in the promotion of the calcium roasting technique. Apart from the difficulty, the calcium roasting ingredient formula, carried out by Zou et al. (2001), can be used to add the calcium addictive quantitatively in ore samples with different components. It is helpful for promoting the calcium roasting technique. In these experiments the low-grade vanadium-containing stone coal from Wuxi County, Chongqing City, was taken as research material and the calcium roasting-sulfur acid leaching technology was adopted. This paper has studied the main influential factors of extracting vanadium from the material by the single-factor experiments and orthogonal experiments, and the conclusion has been drawn that the leaching ratio of vanadium increased greatly under suitable circumstances. The results obtained from the experiments will provide a technical support for the full use of vanadium in the low-grade stone coal.

2 Experimental

2.1 Materials and apparatus

The raw low-grade stone coal used in the experiments was collected from Wuxi County, Chongqing. After X-ray fluorescence spectrum analysis (XRF) and infrared coal quality analysis, the average compositions of the ore samples are presented in Table 1. The amount of V_2O_5 is 0.28%, and the samples represent the low-grade vanadium-containing stone coal.

Main reagents: H_2SO_4 (AR), CaO (AR), $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (AR) and $KMnO_4$ (GR).

Main instruments: XQM-2L variable frequency planet-type grinding mill, infrared analyzer, muffle furnace and hot type constant temperature heating magnetic stirrer.

2.2 Experimental methods

The vanadium in stone coal exists as V(Ⅲ) and V(Ⅳ). Only after being transformed into V(Ⅳ) and V(Ⅴ) at a high oxidizing roasting temperature, the vanadium could be leached out by sulfuric acid (Zhu et al., 2010). In the experiments calcium oxide was taken as a calcium roasting addictive. The samples were crushed and ball-milled to -0.074 mm in size. The powders were then dried in an oven at 100℃ for 2 hours. According to the calcium roasting ingredient formula, the quality of calcium oxide has been calculated. The calcium oxide was added in the powders and well mixed. The mixed sample was put into the muffle furnace and roasted at a certain temperature, and then the roast was leached in a certain concentration of sulfuric acid, heated and stirred at 95℃. The solution was filtered, followed by the determination of the vanadium content by the potassium permanganate oxidation-ammonium ferrous sulfate titrimetric method, then by the calculation of the leaching ratio of vanadium.

3 Results and discussion

3.1 Single-factor experiment results

The effects of roasting temperature, roasting time, sulfuric acid concentration and leaching time on leaching ratio were investigated by single -factor experiments. The fixed conditions of the experiments are presented as follows: stone coal was 20 g, solid-to-liquid ratio was 3:1 and water bath heating temperature was 95℃.

3.1.1 Effect of the roasting temperature

By roasting for 4 hours and leaching in 20% H_2SO_4 for 4 hours, the relationship has been established between roasting temperature and vanadium leaching ratio, as is shown in Fig. 1. It could be easily found that the leaching ratio of vanadium increased with increasing roasting temperature, the ratio at 950℃ reached the highest, i.e., 72.7%. At the temperature of 700 to 750℃, vanadium existed as VO^{2+} and the leaching liquid was blue. At the temperature of 800℃, vanadium mainly existed as VO_2^+ and the liquid was yellow. This showed that low-valence vanadium could not be totally oxidized at a lower temperature. While it was mainly because of the production of agglomerate and glass compounds that hindered the oxygen diffusion, that led to a decrease in leaching ratio at 1000℃ (He et al., 2009; Xu and Zhang, 1993).The glass compound was hard to be dissolved in acid. Once the vanadium was enwrapped, it could not be leached out (He and Feng, 2007).

3.1.2 Effect of the roasting time

By roasting at 950℃ and leaching in 20% H_2SO_4 for 4 hours, the relationship has been established between roasting time and leaching ratio, as is shown in Fig. 2. It could be concluded that vanadium was gradually oxidized and the leaching ratio increased with increasing roasting time. When the roasting time reached 4 hours, the leaching ratio would be the largest. The leaching liquid was blue when roasting time was 1 hour, and the liquid was yellow after 2 hours. This demonstrates that the vanadium, with a shorter roasting time, could not be totally oxidized as mineral structure could not be fully destroyed. When the roasting time was prolonged to 5 hours, the leaching ratio, on the contrary, would tend to decrease. A long time of sample mineral roasting would lead to the second roast of the sample, producing silicon oxide. The silicon oxide wrapped vanadium, resulting in the decrease of vanadium leaching ratio (Li et al., 2007).

Table 1 The main chemical components of low-grade vanadium-containing stone coal/(wt.%)

Component	V_2O_5	Si	C	Ca	Fe_2O_3	Al_2O_3	S	Mn	Others
Content	0.28	34.69	25.83	2.45	2.89	1.15	0.44	0.37	31.9

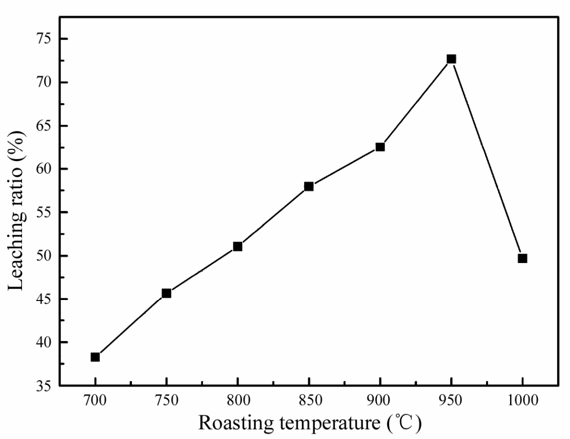

Fig. 1. Relationship between leaching ratio and roasting temperature.

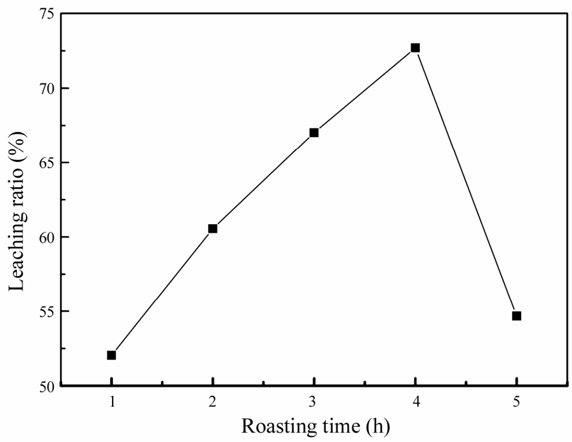

Fig. 2. Relationship between leaching ratio and roasting time.

3.1.3 Effect of the sulfuric acid concentration

By roasting at 950℃ for 4 hours and leaching for 4 hours, the relationship has been established between sulfuric acid concentration and leaching ratio, as is shown in Fig. 3. As seen from Fig. 3, the leaching ratio of vanadium from calcifying roasted residue was very low in the low concentration of 10% sulfuric acid, and the leaching solution was blue-green. Meanwhile, the leaching ratio increased quickly and then remained quite stable with increasing concentration of sulfuric acid. However, the leaching ratio became slightly lower when the concentration of sulfuric acid was 50%, as the ore was caked with a large amount of heat released after adding roasted residue, which could affect the contact between solid and liquid. As there existed quite a lot of substances consuming acid in the ore, sulfuric acid of higher concentration was needed in the leaching process (Cao et al., 2010). When the concentration of sulfuric acid was 40%, the leaching ratio would reach 82.1%.

3.1.4 Effect of the leaching time

By roasting at 950℃ for 4 hours and considering that the change of the influence of leaching time was small when the concentration of sulfuric was relatively high, 20% H_2SO_4 was used in this single-factor experiment. The relationship between leaching time and leaching ratio is shown in Fig. 4. The leaching ratio increased with increasing leaching time. The leaching ratio gradually became stable when leaching lasted for 5 hours and reached 80.1% after 6 hours. The moisture volatilization over time led to the reduction of liquid-solid ratio. The leaching ratio decreased slightly when leaching time was 7 hours.

3.2 Orthogonal experiment results

The orthogonal experiments were made to study the effects on vanadium leaching ratio in varying-degree four factors: roasting temperature, roasting time, sulfuric acid concentration and leaching time. In the experiments there was used 4-factor and 3-level orthogonal array L_9 (3^4). Factor A was roasting temperature (in ℃) (850, 900, and 950). Factor B was roasting time (in hour) (2, 3, and 4). Factor C was sulfuric acid concentration (in %) (20, 30 and 40). Factor D was leaching time (in hour) (4, 5 and 6). The orthogonal experiment results are listed in Table 2. Based on the range analysis, it is indicated that $R_A>R_B>R_C>R_D$. It can be seen that the roasting temperature may affect the leaching ratio significantly, but roasting time and sulfuric acid concentration slightly. The effect of roasting temperature is small.

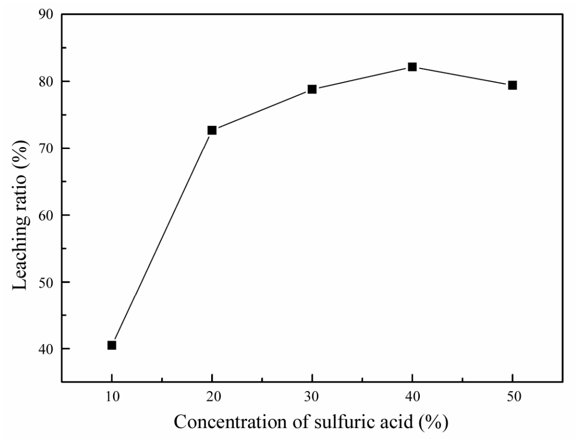

Fig. 3. Relationship between leaching ratio and sulfuric acid concentration.

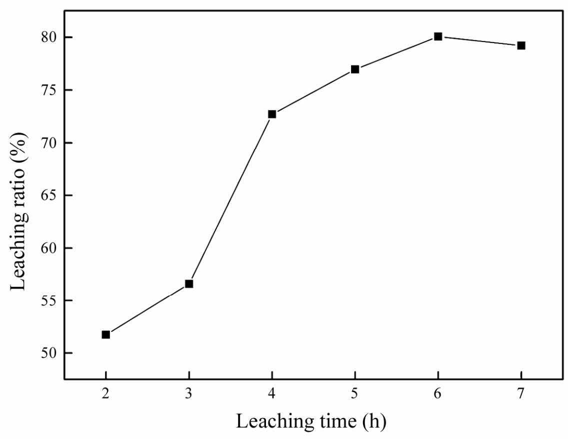

Fig. 4. Relationship between leaching ratio and leaching time.

Table 2 Orthogonal experiment results

Experiment	A (℃)	B (h)	C (%)	D (h)	Leaching ratio (%)
1	850	2	20	4	55.96
2	850	3	30	5	59.90
3	850	4	40	6	65.37
4	900	2	30	6	67.81
5	900	3	40	4	69.31
6	900	4	20	5	73.66
7	950	2	40	5	70.68
8	950	3	20	6	72.64
9	950	4	30	4	78.80
K_{j1}	181.31	195.95	202.26	204.07	
K_{j2}	210.78	201.93	206.59	204.32	
K_{j3}	222.12	217.83	207.32	205.82	
k_1	60.44	65.32	67.42	68.02	
k_2	70.26	67.31	68.86	68.11	
k_3	74.04	72.61	69.11	68.61	
R	13.60	7.29	1.69	0.58	

3.3 Experiments on proper technologic conditions

The proper conditions of calcified roasting-aid leaching technology were obtained by a series of single-factor experiments and orthogonal experiments. The proper conditions are presented as follows: roasting temperature=950℃, roasting time=4 hours, sulfuric acid concentration=40% and leaching time=6 hours. Under those conditions, the leaching ratio of vanadium would reach 85.5%. Han Ruxu showed the vanadium leaching ratio of stone coal varied between 55% and 63%, in which vanadium content was 1.08% (Han et al., 2011). Therefore, the vanadium leaching ratio was more effective under the proper conditions of this paper.

4 Conclusions

This experiment focuses on the study of the calcified roasting-aid leaching technology of vanadium in the low-grade vanadium-containing stone coal by taking calcium oxide as calcium additive. The following conclusions can be drawn:

(1) The calcified roasting-aid leaching technology of vanadium is an effective and environmentally-friendly technology.

(2) The effects of the factors (roasting temperature, roasting time, sulfuric acid concentration and leaching time) on the vanadium leaching ratio in stone coal are described as follows: roasting temperature affects the leaching ratio significantly, followed by

roasting time and sulfuric acid concentration, with the effect of leaching time being smallest.

(3) The proper conditions of calcified roasting-aid leaching technology for the material used in the experiments are: low-grade vanadium-containing stone coal, roasting temperature=950℃, roasting time=4 hours, the concentration of sulfuric concentration=40%, and leaching time=6 hours. Under those conditions, vanadium leaching ratio will reach 85.5%.

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