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Comparison of direct acid leaching process and blank roasting acid leaching process in extracting vanadium from stone coal

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ABSTRACT

Comparison of direct acid leaching process and blank roasting acid leaching process in recovering vanadium from a certain stone coal was carried out. The vanadium leaching efficiency in direct acid leaching process was 92.39% while in blank roasting acid leaching process was 85.43% under the comparative leaching condition of 15% (v/v) H_2SO_4, 1 mL/g, 4 h, 95 ± 1 °C and 5% (w/w) CaF_2. In essence, the mechanism of vanadium leaching was similar in direct acid leaching process and blank roasting acid leaching process. First, calcium fluoride reacted with sulfuric acid to generate hydrofluoric acid. Second, the hydrofluoric acid thoroughly broke down silicoaluminate minerals due to the generation of $[SiF_6]^{2-}$ and $[AlF_5]^{2-}$. However, the difference was that blank roasting contributed to changes in the minerals. On the one hand, blank roasting benefited the vanadium leaching because it transformed vanadium (bound to organics) into vanadium (bound to free oxides) and broke vanadium-bearing silicoaluminate minerals down. On the other hand, it also transformed pyrite into acid-consuming hematite, which increased the consumption of hydrofluoric acid. It was the generation of hematite covering the benefits from blank roasting that decreased the leaching efficiency of vanadium. It was reasonable for this stone coal where vanadium and iron mainly existed in forms of silicoaluminate and pyrite respectively to adopt direct acid leaching process with calcium fluoride.

1. Introduction

The need around the world for vanadium is increasingly growing (Zhang et al., 2011a; USGS, 2012) because of physical properties of vanadium, like high tensile strength, hardness and fatigue resistance (Archana, 2005; Moskalyk and Alfantazi, 2003). Stone coal is a particular vanadium-bearing resource in China (Liu et al., 2010) due to specifically forming factors (Anjum et al., 2012), in which there are amounts of vanadium, 118 million tons in terms of V_2O_5 (Bin, 2006). Therefore, more and more researchers are interested in extracting vanadium from stone coal.

However, it is usually difficult to extract vanadium from stone coal. The main reason is that most vanadium in stone coal exists in the crystal lattice of the aluminosilicate minerals and isomorphically replaces Al(III) in vanadium-bearing micas (Zhu et al., 2012; Zhang et al., 2011a; Bin, 2006). That is, it is necessary to break down the structure of aluminosilicate minerals to extract vanadium from stone coal. By now there are two methods: (1) transform V(III) into V(IV) and V(V) via roasting; (2) directly disintegrate aluminosilicate minerals during vanadium leaching period.

The former is to improve the state valence of vanadium to facilitate vanadium leaching. This method has well developed into the blank roasting acid leaching process. Zhu et al. (2012) roasted the stone coal from Hubei province and leached the roasted residue for 1 h using 20 (v/v) % H_2SO_4, L/S = 2:1 mL/g at 95 °C. The vanadium leaching efficiency reached 86%. The used raw stone coal contained 0.46% (wt) V, 5.45% (wt) Fe_2O_3 and 6.83% (wt) CaO, and the V(III) occupied 75%. Wang et al. (2013) roasted the stone coal from Jiangxi province and leached the roasted residue for 6 h using 15% (v/v) H_2SO_4, 5% (wt) CaF_2, L/S = 1.5:1 mL/g at 95 °C. The vanadium leaching efficiency reached at 93%. The used raw stone coal contained 0.53% (wt) V, 3.75% (wt) Fe_2O_3 and 3.29% (wt) CaO. He et al. (2008) roasted the stone coal from Hunan province and leached the roasted residue for 2 h using 6% (v/v) H_2SO_4, 1.5% (wt) CaF_2, L/S = 2:1 mL/g at 95 °C. The vanadium leaching efficiency reached at 83%. The used raw stone coal contained 0.49% (wt) V, 1.70% (wt) Fe_2O_3 and 0.65% (wt) CaO.

The latter integrates mineral decomposition and vanadium leaching. The method has developed into the direct acid leaching process. Zhang et al. (2011b) directly leached the stone coal from Hunan province for 16 h using 15% (v/v) H_2SO_4, 8% (v/v) H_2SiF_6, L/S = 1:1 mL/g at 95 °C. The vanadium leaching efficiency reached 80%. The used raw stone coal contained 0.72% (wt) V, 4.73% (wt) Fe_2O_3 and 2.52% (wt) CaO. Li et al. (2010) directly leached the stone coal from Guizhou province for 6 h using 5% (v/v) H_2SO_4, 2% (v/v) HF, 0.4% (wt) NaClO, L/S = 4:1 mL/g at 95 °C. The vanadium leaching efficiency reached at 86%. The used raw

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Table 1
The main compositions of raw ore and roasted ore.

Element	Raw ore	Roasted ore
	Content/wt.%	Content/wt.%
V	0.57	0.70
Al	3.39	4.18
TFe	2.18	2.69
K	1.41	1.74
Ca	0.31	0.39
Mg	0.90	1.11
Ba	0.043	0.053
Si	29.10	35.86
C	16.16	1.94
S	2.58	0.59

Table 2
Mineral composition of raw ore through EPMA (wt.%).

Element	Coal	Phlogopite	Pyrite
C	82.66	–	9.88
O	7.31	26.89	–
Mg	–	1.20	–
S	–	1.10	47.66
Al	–	4.59	–
Si	–	59.41	0.30
K	–	2.70	–
V	–	2.05	–
Cl	10.03	–	–
Fe	–	2.06	42.16
Total	100	100	100

stone coal contained 0.31% (wt) V, 3.42% (wt) Fe_2O_3 and 15.05% (wt) CaO. Zhou et al. (2009) directly leached the stone coal from Hubei province for 8 h using 18% (v/v) H_2SO_4, 4.8% (wt) NH_4F, L/S = 4:1 mL/g at 95 °C. The vanadium leaching efficiency reached 92%. The used raw stone coal contained 0.99% (wt) V, 18.39% (wt) Fe_2O_3 and 0.19% (wt) CaO. Li et al. (2009) leached the stone coal from Guizhou province for 3 h using 11% (v/v) H_2SO_4, 0.8% (wt) $FeSO_4$, L/S = 1.2:1 mL/g at 180 °C. The vanadium leaching efficiency reached at 76%. The used raw stone coal contained 1.83% (wt) V, 2.70% (wt) Fe_2O_3 and 0.49% (wt) CaO, and the V(III) only accounted for 34%.

It is clear that both these two processes can achieve high vanadium leaching efficiency and fluoride is an effective aid-leaching reagent. However, the leaching conditions of these two processes for extracting vanadium from stone coal in different regions are different. Especially, the leaching conditions of each process vary for region-different stone coals. It is widely known that the process chosen is closely related to the material itself. However, the characteristics of stone coal were seldom researched, which resulted in difficulties in exploring the rules of choosing the blank roasting acid leaching process or the direct acid leaching process.

This work is to investigate the characteristics of a certain stone coal and to direct the choice of process for extracting vanadium from stone coal by comparing the mechanisms of direct acid leaching process and blank roasting acid leaching process.

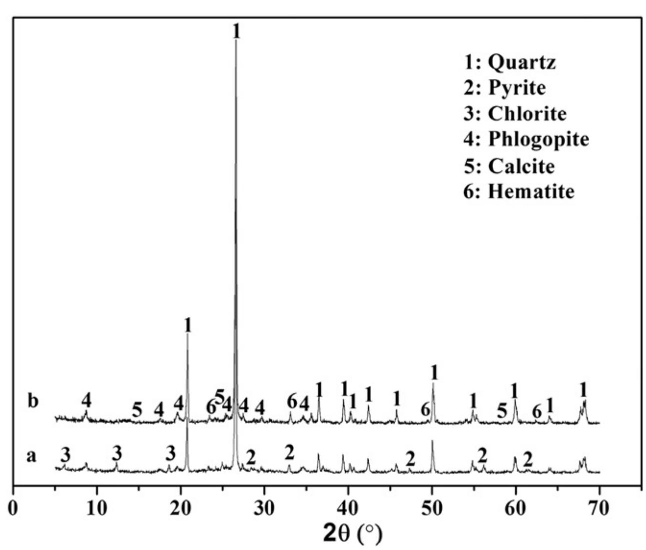

Fig. 1. XRD patterns of a) raw ore and b) roasted ore.

2. Experimental

2.1. Materials

In this work, the stone coal was obtained from Jiangxi province in China. The ore was crushed to a grain size of 0–3 mm before the leaching tests. For direct acid leaching process, the ore continued to be dry ground in vibration mill (model XZM-100) to the particle size of −74 μm accounting for 75%. The obtained ore was referred to as raw ore throughout this work. For blank roasting acid leaching process, the crushed ore was roasted in muffle furnace (model KRY-10) at 700 °C for 60 min and then dry ground via the same vibration mill to the particle size of −74 μm accounting for 75%. The roasted and gained ore was referred to as roasted ore throughout this work.

The calcium fluoride (AR) was supplied by Shanghai Shanpu Chemical Co., Ltd. All other reagents and chemicals used were of analytical reagent grade.

2.2. Methods

Firstly, the characteristics of raw ore and roasted ore can be clearly-determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-ray Diffractometry (XRD), optical microscope and electronic probe microanalysis (EPMA). Meanwhile, the main changes during blank roasting can be found. Secondly, the raw ore and roasted ore were used to leach vanadium considering the effects of sulfuric acid concentration and leaching time, respectively. As a result, the optimal comparative conditions of direct acid leaching and blank roasting acid leaching were confirmed through comparison of leaching behaviors. Thirdly, the obtained leachates and leaching residues under the optimal comparative conditions were used for a series of chemical analyses. The characters of leachates and residues can be acquired. In the end, the various chemical reactions during leaching process can be summarized by synthesizing characters of raw ore and roasted ore before leaching and the leachates and residues after leaching. Through the comparison between direct acid leaching process and blank roasting acid leaching process, the character of each process for the two processes can be understood. The optimal process of leaching vanadium from the stone coal can be determined. Furthermore, the reasonable using conditions for the processes respectively can be given.

2.2.1. Leaching tests

Leaching tests of sulfuric acid concentration's effects on leaching efficiency of vanadium were carried out in magnetic and controlling temperature stirrer (model SZCL-2A) at liquid/solid ratio (L/S) of 1 mL/g, temperature of 95 ± 1 °C, 5%(w/w) calcium fluoride for 4 h under H_2SO_4 concentration of 5%(v/v), 10%(v/v), 15%(v/v), 20%(v/v) and 25%(v/v) respectively. Similarly, leaching tests of leaching time's effects on leaching efficiency of vanadium were carried out in the same stirrer at H_2SO_4 concentration of 15%(v/v), liquid/solid ratio (L/S) of 1 mL/g,