International Journal of Mineral Processing 138 (2015) 1–5

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro

Dissolution kinetics of vanadium from black shale by activated sulfuric acid leaching in atmosphere pressure

Zhong-Jun Ju, Cheng-Yan Wang *, Fei Yin

Beijing General Research Institute of Mining and Metallurgy, Beijing 100070, China

A R T I C L E I N F O

Article history:
Received 30 April 2014
Received in revised form 4 December 2014
Accepted 13 March 2015
Available online 16 March 2015

Keywords:
Vanadium
Black shale
Activated acid leaching
Kinetics

A B S T R A C T

The kinetics of vanadium dissolution from black shale by activated sulfuric acid leaching is presented. The effects of black shale particle size, sulfuric acid concentration, dosage of CaF_2, and reaction temperature on vanadium extraction rate were determined. The results obtained show that an extraction of about 80% is achieved using less than 45 μm (−45 μm) black shale particle size at a reaction temperature of 90 °C for 120 min reaction time with 100 g/L sulfuric acid concentration and in the presence of 60 kg/t ore of CaF_2. The solid/liquid ratio was maintained at 1:30 g/mL. The apparent activation energy was determined as 90.19 kJ/mol at 70–90 °C and 201.96 kJ/mol at 50–70 °C. The reaction orders with respect to sulfuric acid concentration and catalyst CaF_2 were 0.50 and 1.56, respectively.

1. Introduction

The demand for vanadium is increasing rapidly with the development of steel industry and chemical industry in recent years. China has abundant vanadium resources, but most of the vanadium resources occurred in the low-grade ore of black shale rather than in the high grade vanadium and titanium magnetite.

The process of sodium roasting–water leaching–ammonium precipitation–calcinations to extract vanadium from black shale is the most widely used nowadays. Sodium roasting process has many shortcomings such as high production costs, process complexity, poor operating conditions, labor-intensive, and a large number of hydrogen chloride gas and chlorine produced in the process can cause serious environment pollution. The recovery rate of V_2O_5 is no more than 50% throughout the process (Bie et al., 2010; Bleecker, 1912). Due to these shortcomings of sodium roasting process, researchers developed calcification roasting process which was no harmful gas emission (He et al., 2007; Moskalyk and Alfantazi, 2003) The recovery rate of V_2O_5 in the calcification roasting process is 55% to 70%, which is also not ideal. Since the roasting process has the shortcomings of low recovery rate of V_2O_5, high energy consumption and serious environment pollution, the hydrometallurgical process to extract vanadium from black shale has received considerable attention due to high recovery rate of V_2O_5 and low environment pollution. There are two kinds of acid leaching process to recover vanadium from black shale: pressure acid leaching (Li et al., 2009; Amer, 1994) and atmosphere acid leaching (Chen et al., 2010). Normal atmosphere acid leaching of black shale needs a reaction time of over 15 h. To shorten the reaction time, we developed an activated sulfuric acid leaching process to recover the vanadium from the black shale. A result of 95% vanadium recovered has been achieved in the condition of 150 g/L sulfuric acid, liquid/solid ratio 2:1 mL/g, reacting for 6 h at 90 °C with a dosage of 60 kg/t ore of CaF_2 added.

The kinetics of normal acid leaching of black shale and pressure acid leaching of black shale have been carried out by several researchers (Li et al., 2010; Liu et al., 2008; Li et al., 2008), but the kinetic characteristics of active acid leaching of black shale have been rarely reported. The main purpose of this work was to investigate the effects of reaction temperature, sulfuric acid concentration, dosage of CaF_2 and fraction size on the dissolution rate of vanadium in black shale and expecting to find the rate determining step of the leaching reaction.

2. Experimental

2.1. Material and apparatus

Black shale ore used in this study was collected from Guizhou, Zhenyuan County (China). The elemental compositions of the black shale are given in Table 1, and the vanadium compositions of different size fractions are given in Table 2. Commercial sulfuric acid was obtained from Sinopharm Chemical Reagent Co., Ltd and CaF_2 was obtained from Tianjin Chemical Reagent No. 3 Factory. The sulfuric acid had a concentration of 98% H_2SO_4 and a density of 1.84 g/mL. The CaF_2 was analytically pure. The reaction between black shale and leaching solution was performed in a 500 mL Florence flask put on a thermostatically controlled furnace.

* Corresponding author.
E-mail address: jzj03@sina.com (C.-Y. Wang).

http://dx.doi.org/10.1016/j.minpro.2015.03.005
0301-7516/

Table 1
Main chemical components of black shale (mass fraction, %).

Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Ti	V	Zn	Si	C
2.01	0.39	1.47	0.1	0.05	1.44	0.77	0.47	0.09	0.44	0.34	35.68	5.16

Table 2
V_2O_5 content of different particle sizes (mass fraction, %).

−45 μm	45–58 μm	58–74 μm	74–106 μm	106–125 μm
0.82	0.62	0.61	0.50	0.45

2.2. Procedure

15 g of black shale was added at one time to the agitated leaching solution (450 mL) of required concentration of leaching agent at the required temperature. The reaction system was agitated at a rate of 500 rev/min. At the fixed time intervals, about 1 g solid samples were taken using a vacuum filtration to separate the solid and liquid. The solid samples were washed and dried to analyze the chemical compositions, and the liquids filtered from the samples were abandoned, so that the leaching reaction system can keep the solid/liquid ratio constant at 1:30 g/mL. The percentage extraction of vanadium was calculated by formula (1).

$$\eta = 1 - \lambda\alpha_1/\alpha_2 \quad (1)$$

where η is the extraction rate of vanadium, α_1 is the content of vanadium in the residue, α_2 is the content of vanadium in the black shale before leaching and λ is the whole slag yield of the leaching reaction.

3. Results and discussions

3.1. Effect of particle size

The effect of particle size on leaching of black shale was studied using different size fractions: −45 μm, 45–58 μm, and 58–74 μm. In this series of experiments, the initial sulfuric acid concentration, the amount of CaF_2 and the leaching temperature were kept constant at 100 g/L, 60 kg/t ore and 90 °C, respectively. The solid/liquid ratio was 1:30 g/mL. The results are shown in Fig. 1.

These results show that particle size of the ore has no significant effect on the dissolution of vanadium in the black shale. In addition, about 80% of the vanadium present in the fraction −45 μm of the black shale ore was extracted after 120 min.

3.2. Effect of agitation speed

The effect of agitation speed on the vanadium extraction was studied in the range of 80–500 rev/min. The leaching reaction of −45 μm particle fraction of black shale is in 100 g/L H_2SO_4 and with 60 kg/t ore CaF_2 used at 90 °C, and the solid/liquid ratio was kept constant at 1:30 g/mL. The results presented in Table 3 show that the agitation speed only has a slight effect on vanadium extraction in the first 80 min of reaction time, and after 80 min the agitation speed has no effect on the vanadium extraction any more.

Table 3
The effect of the agitation speed on the vanadium extraction.

Reaction time, min	Vanadium extraction, %	
	80 rev/min	500 rev/min
0	0.00	0.00
10	18.93	26.91
20	29.74	35.83
40	44.16	50.09
60	56.77	60.78
80	65.77	69.70
100	74.78	75.04
120	81.99	80.39

3.3. Effect of sulfuric acid concentration

A plot of V extraction against time is presented in Fig. 2 for black shale of −45 μm particle size and sulfuric acid concentration in the range of 40–120 g/L at a constant temperature of 90 °C with 60 kg/t ore of CaF_2 involved in every experiment. The solid/liquid ratio was kept constant at 1:30 g/mL. It can be seen that the sulfuric acid concentration has some effect on the dissolution of vanadium. Extraction of 80% of vanadium is achieved by 120 g/L sulfuric leaching for 120 min, while about 60% of vanadium is extracted in 40 g/L sulfuric acid for 120 min.

3.4. Effect of reaction temperature

The effect of reaction temperature on V extraction at different reaction times is shown in Fig. 3 for black shale of −45 μm particle size at the temperature range of 50–90 °C. The sulfuric acid concentration and CaF_2 amount were 100 g/L and 60 kg/t ore, respectively. The solid/liquid ratio was kept constant at 1:30 g/mL during the series of experiments.

The obtained results indicate that the studied reaction temperatures have a significant effect on dissolution of vanadium. More than 80% of vanadium was extracted at 90 °C compared with less than 10% vanadium extracted at 50 °C after 120 min.

3.5. Effect of CaF_2 dosage

A plot of V extraction against reaction time presented in Fig. 4 shows the effect of CaF_2 on the vanadium dissolution for −45 μm particle size black shale in 100 g/L H_2SO_4 at the constant reaction temperature of 90 °C. The different amounts of CaF_2 used in this series experiment

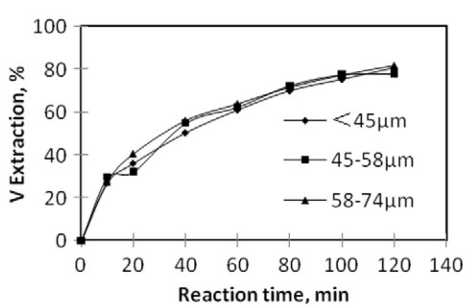

Fig. 1. Relation between V extraction and time using different black shale particle sizes (at 90 °C, 100 g/L H_2SO_4 and 60 kg/t ore CaF_2).

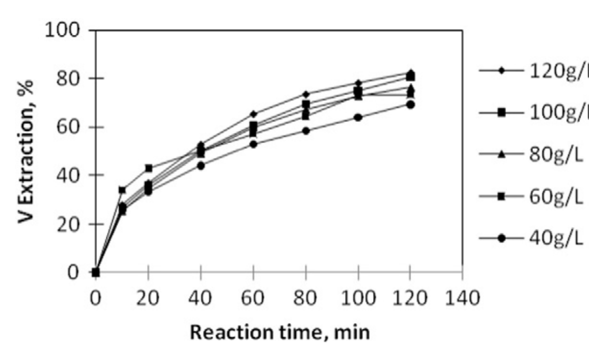

Fig. 2. Relation between V extraction and time using different sulfuric acid concentrations (−45 μm particles at 90 °C with 60 kg/t ore CaF_2).