Journal of Cleaner Production 149 (2017) 989–998

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Effects of hydration and hardening of calcium sulfate on muscovite dissolution during pressure acid leaching of black shale

Nan-nan Xue [a, b], Yi-min Zhang [a, b, c, *], Tao Liu [a, b, c], Jing Huang [a, b, c], Qiu-shi Zheng [a, c]

[a] School of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, China
[b] Hubei Provincial Engineering Technology Research Center of High Efficient Cleaning Utilization for Shale Vanadium Resource, Wuhan 430081, China
[c] Hubei Collaborative Innovation Center for High Efficient Utilization of Vanadium Resources, Wuhan 430081, China

ARTICLE INFO

Article history:
Received 18 September 2016
Received in revised form
20 February 2017
Accepted 21 February 2017
Available online 24 February 2017

Keywords:
Black shale
Muscovite dissolution
Hydration and hardening
$CaSO_4$

ABSTRACT

In the conventional process of oxygen pressure acid leaching of black shale, vanadium extraction depends on acid attack to muscovite, resulting in high acid consumption and a long leaching time. The two problems significantly reduce equipment life, increase production costs, and decrease production efficiency. To solve these problems, hydration and hardening of calcium sulfate were introduced to promote muscovite cracking, increasing the exchange reaction rate of hydrogen ion to aluminum ion. This paper investigated the effect of hydration and hardening of calcium sulfate on calcium sulfate growth and muscovite dissolution, exploring interactions between calcium sulfate and muscovite. Results indicate that in stress-damaged muscovite structure, propagation of ductile cracks in muscovite particles increases their specific surface area and weakens muscovite structural strength. These effects allow muscovite to dissolve much more easily during the pressure acid leaching process. The hydration and hardening of calcium sulfate crystals can thus facilitate muscovite dissolution.

1. Introduction

With the increasing market demand for vanadium products and the shortage of high-grade ores, it becomes increasingly necessary and urgent to exploit and utilize black-shale resources for vanadium pentoxide production (Li et al., 2014). Black shale is an important vanadium-bearing resource, which is widely distributed in many provinces of China (Anjum et al., 2012; Zhang et al., 2011). The gross reserve of vanadium from black shale in China is estimated to be about 1.18 million tons (Zhang, 2014). However, the grade of vanadium pentoxide (V_2O_5) is usually lower than 1%. Black shale is thus regarded as a complex low-grade ore. In black shale, the vanadium exists mostly as trivalent vanadium (V(III)); tetravalent and pentavalent vanadium are very scarce (Zhu et al., 2012; Wang et al., 2014; Li et al., 2013; Yuan et al., 2015; Wang et al., 2015). V(III) replaces Al(III) isomorphically in the muscovite lattice, which means that vanadium in black shale is difficult to extract.

Direct acid leaching of black shale has drawn increasing attention in recent years and has been developed into atmospheric acid leaching and pressure acid leaching. To efficiently leach vanadium, the atmospheric acid leaching process (Zhang et al., 2011a; Wang et al., 2013) usually requires addition of fluoride in forms such as hydrogen fluoride (HF), ammonium fluoride (NH_4F) or fluorite (CaF_2), or oxidant in forms such as sodium hypochlorite (NaClO) or manganese dioxide (MnO_2). But fluorides and oxidants are not environmentally friendly. To realize vanadium extraction without fluoride assistance, the oxygen pressure acid leaching process (Li et al., 2010) introduces a pressure field to raise temperature and shorten completion time. However, the two leaching processes are associated with two common, unsolved problems in achieving satisfying vanadium recovery: high acid consumption and a long leaching time. In the vanadium industry, these problems seriously reduce equipment life, increase production costs, and decrease production efficiency.

Muscovite dissolution depends on acid attack at the muscovite-solution interface (Oelkers et al., 2008; Terry, 1983). Previous research (Xue et al., 2016a) on dissolution behavior of muscovite in black shale during the oxygen pressure acid leaching process has shown that dissolution of interlayer cations produces a charge imbalance that drives hydrogen ions to form hydroxy groups with interfacial oxygen. The interfacial hydroxy groups react with

* Corresponding author. School of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, China.
E-mail address: zym126135@126.com (Y.-m. Zhang).

http://dx.doi.org/10.1016/j.jclepro.2017.02.152
0959-6526/

hydrogen ions and leave vacancies as a result of oxygen loss, producing more new surface to expose more aluminum, vanadium, and silicon. Increasing availability of new interfaces prompts continual dissolution of muscovite particles. The muscovite particle surface mainly consists of vanadium, silicon, aluminum, potassium, and oxygen in black shale and can be classified into two parts: an active region that is mainly composed of aluminum, vanadium, potassium, and oxygen, and an inert region that is mainly composed of silicon and oxygen. At acidic pH, the dissolution rate of muscovite is controlled by the breaking of tetrahedral Si—O bonds after removal of tetrahedral Al by proton-exchange reactions. Exposure of active regions introduced by acid attack has proved slow, and requires a long leaching time as well as high acid consumption.

Therefore, an eco-friendly method to enhance vanadium extraction during oxygen pressure acid leaching of black shale was proposed: muscovite dissolution via the stress-strengthening of anhydrite ($CaSO_4$) growth. Calcite usually occurs as intergrowth with quartz and muscovite in black shale. During the acid leaching process of black shale, anhydrite is formed by calcite dissolution directly and without any phase transition. Gypsum ($CaSO_4 \cdot 2H_2O$), one of the calcium sulfate hydrates, is the stable solid phase at low temperatures; however, above 100 °C, anhydrite becomes the stable phase (Azimi and Papangelakis, 2010; Atoji, 1959). Previous research (Xue et al., 2016b) has shown that vanadium recovery can reach 95.45% after leaching for 5 h at 150 °C with 20% sulfuric acid solution, 7% potassium sulfate (K_2SO_4), and 1.5 MPa O_2—10% higher than vanadium recovery after leaching at the same condition without K_2SO_4. Increasing temperature from room temperature to 150 °C can generate rapid conversions of $CaSO_4 \rightarrow CaSO_4 \cdot 2H_2O \rightarrow CaSO_4$ with K_2SO_4 stimulation. K_2SO_4 accelerated $CaSO_4$ hydration, and high temperature generated hardening of $CaSO_4$ on muscovite surfaces, producing complex stress and strain to crack muscovite particles and enhance muscovite dissolution.

Therefore, hydration and hardening of $CaSO_4$ (HHC) performed an important role in the process of muscovite dissolution. The interaction of $CaSO_4$ and muscovite has not been examined in published papers. This paper investigated the main influences (temperature, $CaSO_4$ concentration, and K_2SO_4 dosage) of controlling the hydration and hardening of $CaSO_4$ on vanadium recovery, the combination morphology between $CaSO_4$ and muscovite, and changes in mineral phase and structure, aiming at evaluating interactive behaviors of $CaSO_4$ and muscovite in the process of HHC.

2. Materials and sample pretreatment

Black shale contains inorganic and organic components, with much higher content of inorganic compared with organic materials, similar to coal. The black shale used in the study was obtained from Hubei province, South China. The ICP-AES (IRIS Advantage Radial, USA) results are given in Table 1 and the XRD pattern of the black shale is shown in Fig. 1. The V_2O_5 grade is 0.76% of total mass from Table 1 and the major minerals in black shale are quartz, muscovite/illite, calcite, and pyrite from Fig. 1. The vanadium mainly replaces Al in the lattices of muscovite/illite.

For ease of adjusting $CaSO_4$ concentration in the experiments, the first step is to eliminate calcite in raw black shale. Soaking in a hydrochloric acid solution can eliminate organics and clay colloidal particles on the muscovite surface, which is good for the nucleation and growth of metal salts on its surface (Li et al., 2010a). Black shale samples were thus treated in hydrochloric acid solution at room temperature (25 °C) for 1 h. Calcium content, vanadium loss, and average particle size of the pretreated samples are shown in Fig. 2. Vanadium loss was less than 1% and the average particle size (D50) changed slightly. Based on Lin and Clemency's study (Lin and Clemency, 1981), the octahedral sheet and tetrahedral sheet have not been damaged in the general pretreating process of muscovite, indicating that the treatment had no influence on muscovite structure. As hydrochloric acid concentration increased (see Fig. 3), vanadium recovery declined to the level of vanadium recovery achieved after raw black shale was leached without K_2SO_4 stimulation, which showed that residual calcium had no effect on vanadium leaching. Therefore, the sample pretreated with 4%vol hydrochloric acid solution was chosen as research object.

The morphology of black shale was observed by scanning electron microscope (JSM-5610, Jeol, Japan) and shown in Fig. 4. Muscovite particles had compact surface with no holes or cracks (Fig. 4-2). $CaSO_4$ concentration in the experiments was controlled

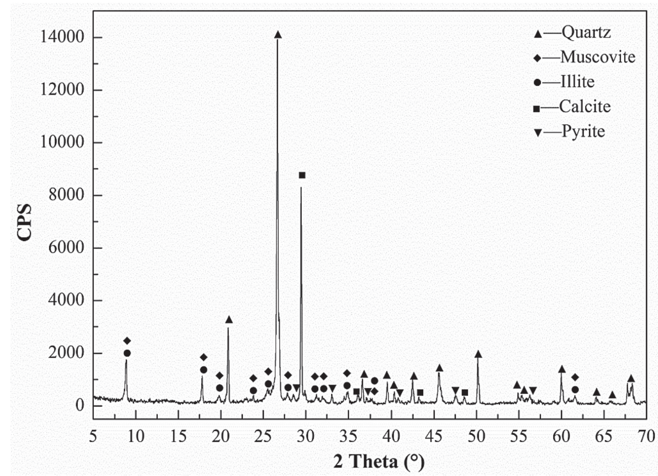

Fig. 1. The XRD pattern of the black shale.

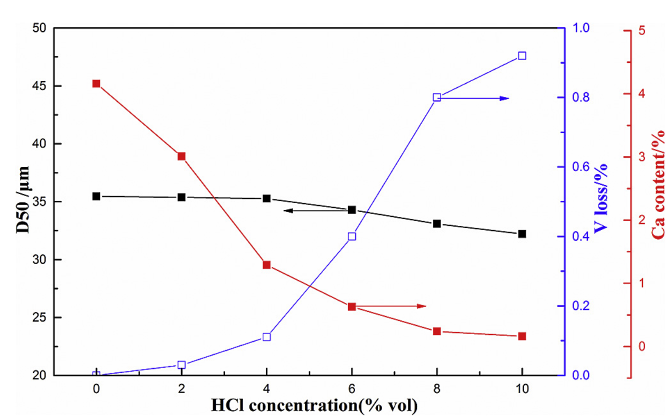

Fig. 2. Variation of vanadium loss, calcium content and D50 of the black shale at different HCl concentrations.

Table 1
Elemental compositions of the black shale (wt.%).

V_2O_5	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	BaO	TiO_2	S	C	Else
0.76	53.53	9.21	6.35	5.82	2.44	2.00	1.09	0.75	0.42	3.60	10.30	3.73