



Mechanism of vanadium extraction from stone coal via hydrating and hardening of anhydrous calcium sulfate



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ABSTRACT

In order to increase the muscovite/solution active regions in black shale during pressure acid leaching process, a novel reinforcing method is proposed: the hydrating and hardening of anhydrous calcium sulfate (CSA). By adopting this method, the vanadium extraction reached 95.45% after 5 h at a temperature of 150 °C with a sulfuric acid concentration of 20 vol% and potassium sulfate addition of 7 %wt. The addition of potassium sulfate accelerated the hydration of CSA to converts into calcium sulfate dihydrate (CSD). Under hydrothermal conditions, the CSD dissolved and crystallized to transform back into CSA. The transformation of CSD → CSA hardened CSA crystals and caused local stress and generated expansion and cracking to muscovite particles. This produced more muscovite/solution active regions to make aluminum and vanadium ions exposed to the attack of hydrogen ions, prompting vanadium release from muscovite lattice.

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1. Introduction

The stone coal is a type of vanadium-bearing siliceous shale found in China, which was mainly formed before the middle Devonian Epoch (Anjum et al., 2012; Zhang et al., 2011). The vanadium mostly exists in the crystal lattice of muscovite or illite where V(III) replaces Al(III) as isomorphism (Zhu et al., 2012). As a result, the vanadium release comes from the structural dissolution of muscovite or illite in stone coal.

Muscovite dissolution depends on the acid attack at muscovite/solution interface (Oelkers et al., 2008; Crundwell, 2014). Hydrofluoric acid can easily dissolve silicate minerals (Terry, 1983). Wang et al. (2014), compared the direct acid leaching process of stone coal with and without CaF₂ and concluded that calcium fluoride broke down silico-aluminate minerals by reacting with sulfuric acid to generate hydrofluoric acid. High temperature assists muscovite dissolution. Li et al. (2010) studied the effect of pressure acid leaching of stone coal on the vanadium extraction and showed that increasing the temperature improved the muscovite dissolution in stone coal and accelerated the vanadium release. Nickel (1973) reported the dissolution rates of muscovite at 25 °C and pH = 0.2, 3.6, 5.6 and 10 measured in stirred tank reactors. Knauss and Wolery (1989) measured muscovite dissolution rates at 70 °C as a function of pH in flow-through reactors. These data indicated that the dissolution rate decreased with increasing pH at acid conditions, minimized at near to neutral pH and increased with further pH increase at basic pH.

The muscovite particle surface in stone coal mainly consists of V, Si, Al, K, and O and can be classified into two parts: active region that is mainly composed of Al, V, K, and O and inert region that is mainly composed of Si. Oelkers et al. (2008) and Crundwell (2014) found that at acidic pH the dissolution rate appeared to be controlled by the breaking of tetrahedral Si—O bonds after adjoining tetrahedral Al had been removed by proton exchange reaction. The larger specific surface area will increase muscovite/solution active regions. This is beneficial for raising the rate of the exchange reaction between hydronium ions and muscovite. The acid attack of muscovite particles makes the specific surface area increase slowly so that the muscovite/solution active regions increase less, which results in poor leaching kinetics and recoveries. Therefore, promoting the particle cracking to expose more muscovite/solution active regions could improve the vanadium extraction from stone coal.

Calcium sulfate (gypsum (CaSO₄·2H₂O), hemihydrate (CaSO₄·0.5H₂O) and anhydrite (CaSO₄)) are relatively insoluble. During pressure acid leaching process of stone coal, anhydrite is formed as a new and stable solid phase following calcite acid dissolution. In the published papers about anhydrite hydration, the sulfate can effectively stimulate the hydration of anhydrite to improve crystal intensity and orientation growth (Zhai et al., 2011; Bai et al., 2008; Peng et al., 2008; Sievert et al., 2005). Zhou (2015) found that gypsum quickly became hemihydrate at 160 °C and autoclave time of 10 min, but when the autoclave time was 4 h, the hemihydrate completely became columnar anhydrite crystal. The anhydrite crystals obviously grew in size and overlapped each other. Feng et al. (2015), studying microstructural origins of cement paste degradation by external sulfate attack, built a model to predict localized

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Table 1

Main chemical compositions of the stone coal by ICP-AES (wt.%).

V	Si	Al	Fe	Ca	K	Mg	Na	Ba	Ti	S	C
0.43	33.62	4.88	3.36	4.16	2.03	1.20	0.81	0.67	0.25	3.60	10.30

deformation and the onset of damage by coupling the growth of new solids with linear thermoelastic finite element calculations of stress and strain fields. Accordingly, we proposed that it may be feasible to control the orientation growth of calcium sulfate hydrates through adding sulfate to produce local deformation to muscovite particles for more muscovite/solution active regions.

Therefore, this work investigated the effect of sulfate on the vanadium extraction, the lattice bonding structure, and particle morphology in order to explain the mechanism of muscovite structure collapse in stone coal by hydrating and hardening of anhydrous calcium sulfate.

2. Materials

The stone coal used in the study was obtained from Hubei province, South China. The ICP-AES (IRIS Advantage Radial, USA) results and the XRD (Bruke D8 Advance, Germany) pattern of the stone coal are given in Table 1 and Fig. 1 respectively. V, Si, Al, and Ca respectively accounted for 0.43%, 33.62%, 4.88%, and 4.16% of total mass. The major minerals in the stone coal were quartz, muscovite, illite, pyrite, and calcite from Fig. 1. Potentiometric titration was used to determine the chemical phase of the vanadium (Zhang, 1992). The results of this analysis, shown in Table 2, indicate that the vanadium is present mainly in the muscovite and illite phases. The distribution characteristics of quartz,

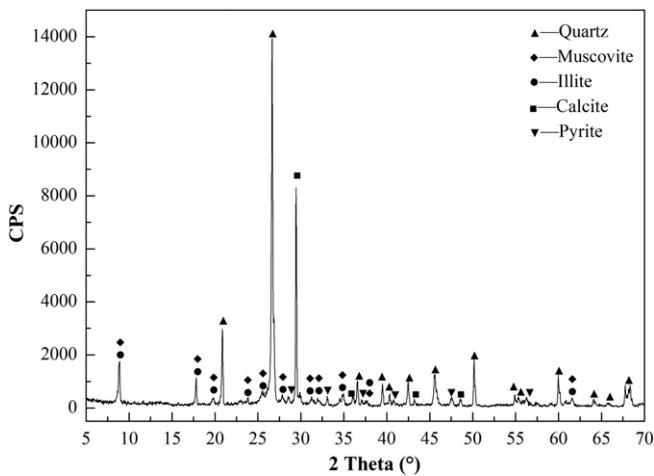


Fig. 1. The XRD pattern of the stone coal.

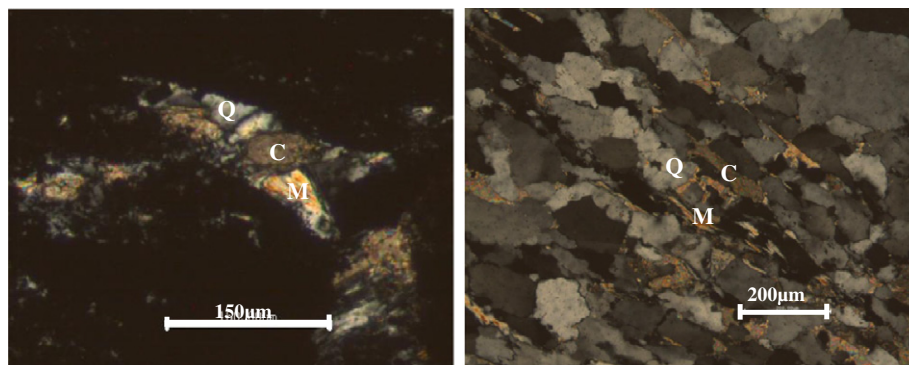


Fig. 2. Microscopic distribution characteristics of quartz, muscovite, and calcite in the stone coal.

muscovite and illite, and calcite in the stone coal were observed using an optical microscope (AxioCan ERC 5s, Carl Zeiss, Germany). Micrographs of the ore are shown in Fig. 2. Calcite is usually as intergrowth with quartz and muscovite.

3. Experimental setup and procedure

The effect of sulfate, acid concentration, leaching time and temperature on vanadium extraction was examined by means of batch stirred experiments. Each test was carried out in a pure zirconium autoclave with a volume of 2 L (Model GSH-2, Zhaoyang Chemical Machinery Co., Ltd., China) and conducted at a preset temperature that was controlled by a programmable temperature controller with a deviation of ± 3 °C. Oxygen was provided from an oxygen cylinder, and the purity of oxygen was 98%. Before all experiments, the stone coal was crushed to 3 mm and then ground by using a ball mill (Model XMQL-600, Hengle Mineral engineering equipment Co., Ltd., China) to 0–0.074 mm. The ground stone coal is hereafter called “the sample.” The sample, the sulfate additive, and the prepared H₂SO₄ solution were loaded into the autoclave at the liquid–solid ratio of 1.5 mL/g and mixed adequately through mechanical stirring at 350 rpm. The autoclave was first heated without the introduction of oxygen. The heating-up time was 1 h. When the temperature reached the preset value, oxygen was introduced into the autoclave and maintained at 1.5 MPa. When the reaction period was over, cooling water was fed through the cooling pipe to cool the slurries. The leachate and the residues were finally obtained after solid–liquid separation.

The vanadium concentration of the leachate was analyzed by titration with ferrous ammonium sulfate. The vanadium extractions was taken as index and calculated using the following equation:

$$\eta = \frac{C \cdot L}{\alpha \cdot M} \times 100\%$$

where: η is the vanadium extraction (%), α is the vanadium grade in stone coal (%), C is the vanadium concentration in leachate (g/L), L is the leachate volume, and M is the feeding mass of ground stone coal (g).

4. Results and discussion

4.1. Comparative leaching experiments

The leaching experiments of raw ore at different additives in Fig. 3 were carried out under temperature of 150 °C, leaching time of 5 h, and acid concentration of 20 vol%. Interestingly, the leaching with the addition of K₂SO₄, Na₂SO₄, and FeSO₄ at the same molar mass of sulfate ions (4×10^{-4} M per gram of the sample) all increased the vanadium extraction above that achieved without sulfate. The vanadium extraction remained unchanged when adding KCl. It can be deduced that sulfate ions were responsible.

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