Research paper

The dissolution behavior and mechanism of kaolinite in alkali-acid leaching process

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ABSTRACT

Kaolinite is a typical silicate impurity in microcrystalline graphite ore. Removal of kaolinite from graphite ores is important to achieve high purity graphite product. Alkali-acid leaching is effective to remove silicate impurity in microcrystalline graphite. For in-depth understanding of phase transformation of kaolinite in microcrystalline graphite purification process, dissolution behavior and mechanism in alkali-acid leaching process were studied in this paper. As shown in alkali-acid leaching tests and analyses (FTIR, XRD, and SEM-EDS), silicon extraction of kaolinite was mainly affected by sodium hydroxide concentration, alkali-leaching temperature, and alkali-leaching time. The dissolution mechanism of kaolinite was regarded as a three-stage process: kaolinite firstly dissolved in alkaline solution in form of soluble silicate and aluminate. Dissolved silicate and aluminate in alkaline solution then reacted with each other and aluminosilicate transient phase with Si/Al $\approx$ 1 precipitated when silicon ion concentration exceeded its equilibrium concentration. Finally, the aluminosilicate precipitate composed of nepheline and sodalite dissolved in hydrochloric acid solution. As a consequence, kaolinite dissolved completely in alkali-acid leaching process.

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1. Introduction

Microcrystalline graphite is a natural graphite with high degree of graphitization and consists of many microcrystals of different orientations (Song et al., 2010; Vilar et al., 2003; Wang et al., 2008). Ore deposits of microcrystalline graphite usually form in metamorphic rock or quartzite. Quartz, kaolinite, and sericite are typical associated minerals (Li et al., 2013). For microcrystalline graphite, silicate minerals are primary impurities. The common beneficiation processes of microcrystalline graphite ore include flotation method, alkali roasting-acid leaching method, and high-temperature method (Lu and Forssberg, 2001). Process of flotation method is as follows: Ore is sluiced to washing plant where it undergoes desliming to remove clay fractions and then subjected to a rough flotation to produce a concentrate with 70% to 80% carbon. This concentrate is transported to the refining mill for further grinding and flotation to approach 90% carbon and screened to a variety of products marketed as microcrystalline graphite containing 75% to 90% carbon (Pugh, 2000). The crystal size of microcrystalline graphite particle is superfine and dissemination relationship between associated minerals and graphite is complicated. Associated minerals may enter into froth product and reduce the concentrate grade during flotation process. So preparing flotation concentrate with fixed carbon content ≥90% is hard (Li et al., 2013; Shi et al., 2015). High-temperature

method is an effective way to prepare high-purity graphite with fixed carbon content even >99.9%. However, it is difficult to operate in actual production and the cost is high, only applied to produce high-value and necessary graphite products like nuclear graphite. Alkali roasting-acid leaching process is usually employed to prepare graphite with fixed carbon content ≥90% (Lu and Forssberg, 2002; Niu et al., 2011). In alkali roasting-acid leaching process, microcrystalline graphite mixed with alkali (NaOH) are roasted at 400–800 °C. After roasting, the slag is washed to neutral by water and then leached by acid solution (HCl or H_2SO_4). Silicate minerals in graphite ore dissolve in the form of silicate and aluminate (Niu et al., 2011). However, this process consists of two major disadvantages. One is that graphite may oxidize during alkali roasting process. It causes unnecessary waste of graphite unless the roasting is proceeded under inert atmosphere. The other is that it demands a lot of energy to dry wet flotation concentrate before roasting when flotation concentrate of graphite is raw material. Considering the characteristics of the mentioned purification methods of microcrystalline graphite, alkali-acid leaching process is ponderable to replace alkali roasting-acid leaching process to purify microcrystalline graphite concentrate. No dry process of wet raw material is required and no oxidation loss is present in alkali-acid leaching process. Compared to alkali roasting-acid leaching process, alkali-acid leaching process may be more suitable for commercialization.

Silicate minerals like kaolinite are main impurities in microcrystalline graphite ore. Understanding of dissolution behavior and phase transition of kaolinite in alkali-acid leaching process is of great significance

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for microcrystalline purification. Kaolinite is 1:1 type phyllosilicate mineral, which is composed of one silica tetrahedral sheet and one aluminum hydroxide octahedral sheet in each layer (Zhang et al., 2015; Liu et al., 2016; Bish, 1989). The material is mainly used in zeolite synthesis, paper coating, ceramics, and refractory materials (Johnson and Arshad, 2014; Lin et al., 2016; Pandey et al., 2015; Pourshahrestani et al., 2016; Wang et al., 2015; Zhu et al., 2012).

Kinetics of kaolinite dissolution is critical to the interpretation and modeling of geochemical processed at Earth's surface (Yang and Steefel, 2008). A number of studies of kaolinite dissolution under acidic or alkaline conditions have been carried out previously (Aldabsheh et al., 2015; Khawmee et al., 2013; Silva et al., 2014). Ganor (Cama et al., 2002) evaluated the combined effect of pH and temperature on far-from-equilibrium kaolinite dissolution rates (temperatures of 25, 50, and 80 °C and in the pH range 2–4.2). The resulting apparent activation energy was 7.0 ± 1.1 kcal/mol and the reaction order was 0.40 ± 0.14. Most of those studies, however, focused on the determination of the pH and temperature dependence of the dissolution rates in far-from-equilibrium, highly undersaturated dilute solutions. These studies aim at determining the stability of kaolinite and predicting its reaction kinetics in natural system. For understanding various geochemical processes ranging from soil formation to hydrothermal ore deposition, researches on dissolution and precipitation of kaolinite in high-temperature environment have been reported (Bauer et al., 1998). Jean Luc Devidal (Devidal et al., 1997) studied the dissolution of kaolinite at 150 °C, 40 bar and pH 2, 6.8, and 7.8. The studies showed variation of dissolution/crystallization rates with chemical affinity and aqueous A1 and Si concentrations are described with a coupled transition state theory (TST)/Langmuir adsorption model by adopting the concept that reaction rate is controlled by the decomposition of a silica rich/aluminum deficient precursor complex. Andreas Bauer (Bauer and Berger, 1998) studied kaolinite dissolution using batch experiments in high molar (0.1–4 M) KOH solutions at 25 °C and 80 °C. The kaolinite dissolution was characterized by a linear release of silica and Al as a function of the log of time. This relationship can be explained by a reaction affinity effect, which is controlled by the octahedral layer dissolution. The activation energy of kaolinite dissolution increase from 33 ± 8 kJ/mol in 0.1 M KOH solutions to 51 ± 8 kJ/mol in 3 M KOH solutions. These studies focused on the determination of the ionic concentration, pH, and temperature dependence of the dissolution rates and precipitation rate. In addition, solubility of precursor complex formed in precipitating process has rarely been researched.

As seen from the studies mentioned above only few studies on the dissolution of natural kaolinite under high-alkaline and high-temperature conditions can be found in the literature. This study aims to advance the understanding of how alkaline concentration, alkali-leaching temperature and alkali-leaching time affect kaolinite dissolution and hydrolysis under high-alkaline and high-temperature solution. Characteristic of the precipitate in alkali-leaching process and its dissolving property in acid solution is also studied.

2. Experimental

2.1. Materials and reagents

The kaolinite used in the experiments was obtained from Kingaroy deposit and supplied by Unimin Australia in Queensland, Australia. The chemical compositions of raw kaolinite are shown in Table 1. The

degree of crystallinity of raw kaolinite was high and a little quartz and mica were existed in sample (XRD pattern of raw kaolinite was shown in supplementary material).

Unless otherwise stated, all chemicals used in the experiments and analysis were of analytical reagent grade (used as receive without further purification) and de-ionized water was used in preparation of all solution in the experiment.

2.2. Characterization

The mineral compositions of kaolinite samples were determined by X-ray diffraction (XRD) using a Philips X' Pert Pro Alpha diffract meter, with Cu Kα radiation ($\lambda = 1.5406$ Å) at a tube current of 40 mA and a voltage of 35 kV. Data of those samples was collected over 2θ value from 3° to 70° at a scan speed of 1°/min. A NOVA NANOSEM 230 scanning electron microscope (SEM) equipped with energy disperse spectroscopy (EDS) was used for morphological analysis. The samples were gold-coated before SEM-EDS analysis. The PANalytical Axios mAX X-ray fluorescence analysis (XRF) instrument was applied to determine the chemical composition of kaolinite. Voltage and current of X-ray tube used were 25 kV and 144 mA respectively. The 740 Fourier transform infrared spectrometer (FTIR) made by Nicolet was applied to determine the functional groups of kaolinite. FTIR studies in the range 400–4000 cm^{-1} were conducted using KBr disc pellets. Si content in solution was analyzed on the basis of silicon-molybdenum blue spectrophotometer (Lenchuk et al., 2015; Yu et al., 2013).

2.3. Procedure

All dissolution experiments were performed in a laboratory autoclave with a volume of 200 mL (Made by Xi' an Taikang Biotechnology Co., LTD, China). The entire dissolution process includes alkali leaching, water washing, acid leaching, water washing, and drying, as described in Fig. 1. The inlet solutions were comprised of demineralized H$_2$O, NaOH, and kaolinite. Firstly, mixtures of sodium hydroxide solution and raw kaolinite powder were in autoclave. After that, the leached residue was washed to neutral by water to remove the water soluble component through the filter. Then the washed redisue was leached with hydrochloric acid in a conical flask. Finally, the acid-leached residue was washed to neutral and dried in an oven.

In earlier studies involving an exhaustive analysis of the solubility of several aluminosilicate minerals in alkaline media, Si and Al dissolution was synchronized all times (Cama and Ganor, 2015). Kaolinite is a typical layered silicate. Dissolution rate of Si in kaolinite was used to describe the solubility of kaolinite in leaching process. The dissolution rate of Si in alkali solution (A_{Si}) and dissolution rate of Si in both alkali solution and acid solution (T_{Si}) were calculated according to Eqs. (1) and (2):

$$A_{Si}(\%) = \frac{S_1}{S_0} \tag{1}$$

$$T_{Si}(\%) = \frac{S_1 + S_2}{S_0} \tag{2}$$

Where, S_0 is the quantity of Si in raw kaolinite, S_1 is the quantity of Si in NaOH leaching liquid, and S_2 is the quantity of Si in HCl leaching liquid, as indicated in Fig. 2.

Table 1
Chemical composition of kaolinite (%).

Component	Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	TiO$_2$	CaO	MgO	K$_2$O	P$_2$O$_5$	Loss on ignition
Content	36.708	45.618	0.661	0.906	0.133	0.042	0.24	0.037	16.23