Separation of aluminum and silica from coal gangue by elevated temperature acid leaching for the preparation of alumina and SiC

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ABSTRACT

Coal gangue is regarded as a potential source of aluminum and silica. In this work, acid leaching behaviors of aluminum, iron, and silica in coal gangue were investigated using hydrochloric acid as leaching agent. Chemical and mineralogical compositions of coal gangue and the leached residue were determined by X-ray diffraction (XRD), X-ray fluorescence, and Fourier transform infrared spectroscopy. XRD results indicated that kaolinite and boehmite were the predominant minerals in coal gangue. During elevated temperature acid leaching, mineral phases gradually decomposed, and aluminum and iron ions were dissolved in the acid leaching solution. However, the carbonaceous material and the product of silica were not dissolved in acid and were abundant in leached residue. The extraction efficiency of Al and Fe from coal gangue depended on coal gangue size, liquid–solid ratio, temperature and leaching time. Extraction efficiency of Al and Fe increased with increased liquid–solid ratio, temperature, and leaching time. Under the same conditions, SiO_2 content in the ash of leached residue also increased. The optimum technological conditions for aluminum and iron extraction were obtained with a coal gangue size of 74 μm at a liquid–solid ratio of 3:1 to react at 180 °C for 4 h. After evaporation and crystallization, selective precipitation by adding sodium hydroxide solution, carbon decomposition, and calcination, alumina with a purity of 98.70% was prepared from acid leaching solution. Finally, a suitable amount of low ash anthracite was introduced to the leached residue, and the product of SiC was produced by carbon thermal reduction method. The product had a yield and purity of 72.72% and 76.01%, respectively.

1. Introduction

Coal gangue accompanied by coal seam is a mixture of organic and inorganic compounds with low carbon content and calorific value, and it is produced by coal mining and washing. Coal gangue output accounts for around 10%–15% of coal production (Liu and Liu, 2010). According to statistics (Ye et al., 2010), the accumulative total of its stockpile may exceed 4.5×10^9 tons in China, and the amount increases by $(1.5–2.0) \times 10^8$ t annually. Coal gangue is a type of industrial solid byproduct that does not only waste a large number of resources but also occupy a large amount of land. Moreover, coal gangue contaminates the air, soil, and water when stacked for a long time. The chemical composition of coal gangue is complex: it has organic carbon and a large number of valuable mineral resources, such as silica, aluminum oxide, ferric oxide, calcium oxide, magnesium oxide, potassium oxide, and several trace elements. In recent years, increasing attention has been given to expand the application range of coal gangue worldwide. Coal gangue is mainly used for making cement (Zhang et al., 2011), brick (Zhou et al., 2014), pottery (Lü et al., 2014), as well as generating electricity and gas (Xiao et al., 2010), and other materials (Quan and

Wang, 2014; Ren et al., 2014). However, the development and utilization of coal gangue are far from sufficient for their low- and medium-value applications as mentioned above. For high-value applications, coal gangue is considered as a potential resource for extracting aluminum, silicon, and carbonaceous materials. Therefore, exploring a new way of preparing high-performance materials from coal gangue and improving its usage efficiency are necessary.

Alumina is widely used as a catalyst and adsorbent. It is also used in the production of metallic aluminum. China, as the largest producer of aluminum, requires a large amount of metallurgical-grade alumina. Numerous studies have been conducted for the extraction of alumina from bauxite, fly ash, and other minerals containing aluminum (Bao and Nguyen, 2010; Klauber et al., 2011; Li et al., 2009; Nayak and Panda, 2010; Reddy et al., 1999; Shemi et al., 2012; Wu et al., 2012; Zhao et al., 2013). The methods for extracting alumina can generally be summarized into alkaline and acid methods. Currently, the alkaline method is used in the industry to produce alumina from high-grade bauxite. Alkali enables the alumina in ores to transform into a sodium aluminate solution, while iron, titanium, and most of the silicon become insoluble residue. However, for low-grade bauxite and clay minerals, silica is converted into solid waste because of the reaction of alkali with silica. Therefore, the alkaline method is not suitable for the simultaneous extraction and separation of aluminum and silicon. For the

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production of alumina by acid method, aluminum bearing minerals are treated with an inorganic acid such as sulfuric acid and hydrochloric acid, and the corresponding aluminum salt solution is then obtained. Subsequently, the aluminum salt solution can either undergo evaporation and crystallization to produce aluminum salt, or it can undergo alkali neutralization to precipitate aluminum hydroxide. Finally, the aluminum salt or aluminum hydroxide is calcined to obtain the alumina. Compared with the alkaline method, the acid method has the advantage of short process, low energy consumption, less residue, and easy and complete separation of silicon and aluminum. Hence, the use of the acid leaching method is more attractive. Zhao et al. (2013) conducted some research for the acid leaching of low-grade gibbsite. Their results showed that the aluminum and iron leaching rates were over 95% and the filter residue was mainly silica. Furthermore, the effect of fluoride additions on the aluminum extraction with hydrochloric acid from coal spoils was studied by Bailey (Bailey and Chapman, 1983). This study indicated that high aluminum recoveries were obtained in a very short leaching time, and the carbonaceous material in the coal spoils was not damaged in the leaching period and can thus be used as fuel. However, the main barrier in acid leaching is the co-leaching of impurities, such as Fe, Ka, Ca, Mg, Ti, and so on, which should be removed in subsequent operations. Consequently, the kinds of acid and purification technology of filter liquor are also important factors that should be taken into consideration. In addition, expensive acid-resistant equipment is required in the acid method, and the recovery of acid is more complex. Therefore, at present, researchers are studying the acid method as a technical reserve by using low-grade bauxite and clay minerals.

Studies (Paul et al., 2006; Seferinoglu et al., 2003) have shown that low-temperature acid leaching is not suitable in extracting aluminum, which exists in the form of stable minerals. To improve the reactivity of minerals and the aluminum extraction efficiency, thermal activation is usually performed as a pretreatment for minerals, followed by acid leaching (Hussain and Jamal, 2000; Livingston et al., 1983a). Thermal activation could lead to a significant increase in the extraction rate of aluminum, because various chemical reactions and phase changes occurred caused by the clay and non-clay minerals (Livingston et al., 1983b). Nonetheless, thermal activation is more complex and the extraction efficiency of aluminum remains low. However, study has shown that the leaching rate of aluminum by direct acid leaching can be boosted by improving the reaction temperature (Wu et al., 2012). This process did not require thermal pretreatment, and the extraction time was significantly reduced.

SiC is receiving considerable attention for its superior characteristics, such as high hardness, low density, high oxidation resistance, and high temperature strength. Therefore, it has broad prospects in terms of industrial applications (Ding et al., 2014; Kim et al., 2014). Industrial SiC is made from high-quality petroleum coke mixed with quartz in a resistance furnace at a high temperature. Progress has been made in the production of SiC in recent years, and the results showed that particular alternative siliceous materials are ideal raw materials for synthesizing SiC (Cheng and Hsu, 2006; He et al., 2001).

In the current paper, the leaching behaviors of aluminum, iron, and silica in coal gangue by high-temperature direct acid leaching were systematically studied. Furthermore, alumina and SiC were produced from the leach liquor and leached residue, respectively. This process not only improves the comprehensive utilization of coal gangue but also expands the choice of raw materials for the production of alumina and SiC.

2. Experiment

2.1. Materials and methods

In this experiment, coal gangue was obtained from the Ordos coal mine, Inner Mongolia, China. The hydrochloric acid with a concentration of 37% was of analytical grade chemicals and was produced by Tianjin Chemical Company. The hydrochloric acid was diluted with deionized

water to a concentration of 25% for acid leaching. Depending on the liquid–solid ratio, the corresponding volume of hydrochloric acid was added.

The inner container of the high-pressure reaction kettle is made of Teflon (PTFE). Ball milling was conducted in a planetary ball mill by using stainless steel tanks and ball for 4 h. The ball–powder weight ratio was 6:1. Ball milling can decrease the coal gangue particle size and increase the contact area with the hydrochloric acid. As thus, the acid leaching process can be accelerated. In addition, in the preparation of SiC, ball milling is advantageous in blending the leached residue and added carbon of the anthracite well.

Mineralogical analysis of coal gangue was conducted by X-ray diffraction (XRD) using Cu Kα radiation in a Rigaku D/Max 2500 diffractometer, with a scan speed of $4°·min^{-1}$. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet company spectrometer in the range of $400–4000 cm^{-1}$, and the resolution was better than $0.5 cm^{-1}$. The coal gangue and the leached residue were incinerated at 815 °C in a muffle furnace, then X-ray fluorescence (XRF) was used to determine the chemical compositions in the high temperature ash of the coal gangue and the product of alumina on a PANalytical Axios mAX equipment. The extraction efficiencies of aluminum and iron were calculated using the following formulas:

$$\eta_{Al} = \frac{m_R(Al) - m_E(Al)}{m_R(Al)} \times 100\% \tag{1}$$

$$\eta_{Fe} = \frac{m_R(Fe) - m_E(Fe)}{m_R(Fe)} \times 100\% \tag{2}$$

$$\omega(SiO_2) = \frac{m(SiO_2)}{m(sum)} \times 100\% \tag{3}$$

where η is the extraction rate of aluminum and iron, and m_R and m_E represent the Al and Fe contents in the coal gangue ash before and after acid leaching, respectively. Moreover, $m(SiO_2)$ indicates SiO_2 content in the leached residue, and $m(sum)$ means the total ash content in the leached residue. Therefore, $\omega(SiO_2)$ denotes SiO_2 content in the ash of the leached residue in %.

2.2. Experimental procedure

A flow diagram for these experiments, including HCl leaching and the preparation of Al_2O_3 and SiC, is shown in Fig. 1.

Acid leaching experiments for coal gangue were performed by treating 30 g of coal gangue with 25% HCl in the high pressure reaction kettle. The experiments were systematically studied by varying coal gangue size, liquid solid ratio, leaching temperature, and leaching time. After the acid leaching experiments, the residue containing silica and the carbon material was separated from the leach liquor through a Buchner funnel by using a suction pump.

Alumina was extracted from the acid leaching liquor. Initially, the leach liquor containing dissolved aluminum, iron, and other species was concentrated by evaporation, and precipitation of aluminum chloride, ferric chloride and other solid chlorides. Subsequently, to extract the desired aluminum, other metals such as iron, titanium, calcium, and magnesium should be removed. Thus, enough sodium hydroxide solution was added to the chloride to get a pH value of 13.0. Then, a brown metal hydroxide precipitate was obtained, which was removed from the solution by filtration. Afterwards, CO_2 was bubbled into the purified solution containing aluminum ions, until the amount of the white gelatinous precipitate no longer increased. Thereafter, the white gelatinous precipitate was removed by filtration and fully washed with hot deionized water. Finally, the product of high-purity alumina was obtained from the white gelatinous precipitate by calcination at 1100 °C for 1 h, and can be used as metallurgical grade alumina and chemical alumina.