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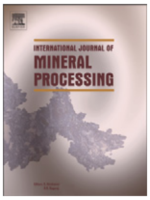

Hydrothermal extraction of potassium from potassic quartz syenite and preparation of aluminum hydroxide

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ABSTRACT

Potassic quartz syenite, composed of microcline and quartz, is a promising source for the recovery of potassium, alumina, and silica values. Hydrothermal extraction of potassium by dissolution of the potassic quartz syenite powder in NaOH solution and utilization of alumina and silica in the potassic quartz syenite powder for preparation of acicular wollastonite and aluminum hydroxide were explored in this research. It mainly contains alkali-hydrothermal process, causticization process, and low-lime sintering process. The samples were characterized by using wet chemical analysis, X-ray diffraction, and scanning electron microscopy. The results indicated that the optimal extractions of K_2O and SiO_2 from the potassic quartz syenite powder were 93.2% and 62.5%, respectively. The purities of as-prepared acicular wollastonite, potassium carbonate, and aluminum hydroxide were 93.8%, 96%, 99%, respectively. The approach presented in this work is a promising process of comprehensive utilization of potassic silicate minerals such as K-feldspar.

1. Introduction

Potassium (K), one of essential elements in fertilizers, can improve agricultural yields and enhence food security. Based on estimates of the United States Geological Survey, potash ores are expected to last about 400 years at the current rate of extraction (Jasinski, 2014). Potash production is strongly dominated by three countries: Canada, Russia, and Belarus which account for more than 90% of world potash (Manning, 2010). In contrast, K deficits have been reported especially for the African continent (Sheldrick and Lingard, 2004) as well as for China and India (Römheld and Kirkby, 2010). Therefore, in order to ensure potash self-sufficiency in developing countries, exploration for conventional new deposits and development of new potash mines will continue throughout the 21st century (Ciceri et al., 2015). The potassic silicate minerals such as K-feldspar are considered promising to produce potassium salts in the near future (Ciceri et al., 2015; Ma et al., 2014a).

The principle mineral in the potassic rocks is microcline. Dissolution of microcline for the subsequent preparation of potassium compounds and utilization of alumina and silica as byproducts represent challenges for using this type resource (Ciceri et al., 2015). Producing potash alone is insufficient to cover the cost of either wet or high temperature processing. Several methods have been reported for the dissolution of microcline over the past 100 years (Rao et al., 1998), including $CaCO_3$ sintering process (Guillet, 1994), phosphogypsum sintering process (Wang et al., 2014), $CaSO_4$–$CaCO_3$ sintering process (Bakr et al., 1979), Na_2CO_3 sintering process (Ma et al., 2005), chloride roasting method (Jena et al., 2014; Zhang et al., 2012), and hydrothermal method (Nie et al., 2006; Su et al., 2014; Ma et al., 2014b, 2015). Compared with other methods, the hydrothermal method has been considered to be a approach with lower consumptions of disposable mineral resources and energy, higher utilization of the potassium ore resources, and clean productions (Ma et al., 2014a).

Most commercial production of alumina from bauxite is performed by a process patented by Bayer in 1888 (Bayer 1888). With the diminishing of bauxite resources as well as the increase in alumina demand, utilization of high-alumina coal fly ash (Shemi et al., 2012; Yao et al. 2014; Li et al. 2014; Guo et al. 2014a), coal gangue (Guo et al. 2014a,b), bauxite red mud (Guo et al. 2014b; Samal et al. 2013), which has the characteristics of relatively low content of alumina and high content of silica, has attracted extensive attentions. In addition, the solid product obtained from the dissolution of potassic quartz syenite with higher Al/Si mole ratio could be also used to product alumina (Yang et al. 2010).

Wollastonite, a new non-metallic industrial mineral, has been used in ceramics, plastic, rubber, paint, metallurgy, and paper making industries (Magallanes-Perdomo et al. 2011; Demidenko et al. 2001; Yu et al. 2014). Normally, ultrafine wollastonite is made from natural wollastonite ore by superfine grinding. However, the natural high-quality acicular wollastonite is very limited and cannot satisfy industrial demand (Virta 2014; Wu et al. 2013). Using the K_2SiO_3–Na_2SiO_3 solution from the

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Table 1
Chemical composition of the QS powder (wt.%).

Samples	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Loss	Total
QS-1	63.69	0.63	17.39	3.40	0.01	1.68	1.09	0.16	10.27	0.09	1.96	100.37

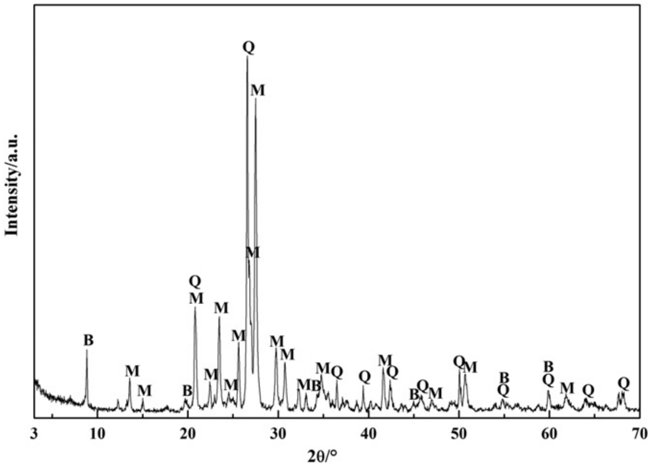

Fig. 1. XRD pattern of the QS powder (QS-1: M, microcline; Q, quartz; B, biotite).

dissolution of potassic quartz syenite and lime milk to prepare the acicular wollastonite has potential industrial application.

Considering the above-mentioned demand and supply, a systematic study has been undertaken on the recovery of potassium, alumina, and silica values from potassic quartz syenite in this work. The experiments explored the effects of NaOH/syenite mass ratio and reaction temperature on the extractions of K_2O and SiO_2 from dissolution of potassic quartz syenite in NaOH solution. The effects of reaction temperature and reaction time on preparation of acicular wollastonite in the causticization process, and the effects of sintering temperature and sintering time on the extraction of Al_2O_3 in the low-lime sintering process were also studied. Moreover, this approach for comprehensive utilization of potassic quartz syenite was evaluated.

2. Experimental

2.1. Materials

Potassic quartz syenite (QS), derived from Nanling county, Anhui province, China, was used as the raw material. After crushing and grinding, 50% of the particles are less than 12.9 μm and 90% of the particles are less than 62.5 μm. The chemical composition of the QS powder measured by wet chemical analysis is listed in Table 1. It contains 10.27% K_2O, 17.39% Al_2O_3, and 63.69% SiO_2 as the major valuable components. The X-ray diffraction pattern of the QS powder is shown in Fig. 1. Based on the principle of mass balance, the contents of main minerals in the QS powder are microcline 65.4%, quartz 23.3%, biotite 4.0%, kaolinite 4.1%, and magnetite 3.2%.

2.2. Experimental principles

The QS powder can be dissolved in NaOH solution through alkali-hydrothermal treatment (Ma et al. 2015; Zhao et al. 2004; Locati et al. 2010). Potassium in the QS powder was leached out and transformed into the K_2SiO_3 solution, and about 2/3 silica in the QS powder was leached out and transformed into the K_2SiO_3–Na_2SiO_3 solution. The solid product zeolite with higher Al/Si mole ratio was obtained as indicated in Eq. (1).

The K_2SiO_3–Na_2SiO_3 solution was reacted with lime milk to produce xonotlite and KOH–NaOH solution according to Eq. (2). The final product acicular wollastonite was prepared by calcination at 850 °C for 2 h, shown in Eq. (3). The K_2CO_3–Na_2CO_3 solution was obtained by carbonation of KOH–NaOH solution using CO_2 gas as per Eq. (4). The final product potassium carbonate was prepared by evaporation and crystallization of K_2CO_3–Na_2CO_3 with variable temperature.

The solid product zeolite, mixing with sodium carbonate and calcium carbonate was sintered at 1050 °C for 2 h. The sintered clinker was dissolved in standard mixture solution (NaOH 15 g/L, Na_2CO_3 5 g/L) to produce the $NaAlO_2$ solution according to Eq. (6). After removing small amounts of impurity, the $NaAlO_2$ solution reacted with CO_2 gas to prepare aluminum hydroxide. The solid slag Na_2CaSiO_4 was used to recover NaOH solution and to produce calcium silicate which is a starting material for the preparation of materials used to construct walls, this reaction is represented by Eq. (7).

The main chemical reactions that occurred in this research are as equations from (1) to (7).

$$\begin{aligned}6KAlSi_3O_8 + 26NaOH \rightarrow Na_8[Al_6Si_6O_{24}](OH)_2 \cdot 2H_2O\downarrow + 3K_2SiO_3 \\ + 9Na_2SiO_3 + 10H_2O\end{aligned} \tag{1}$$

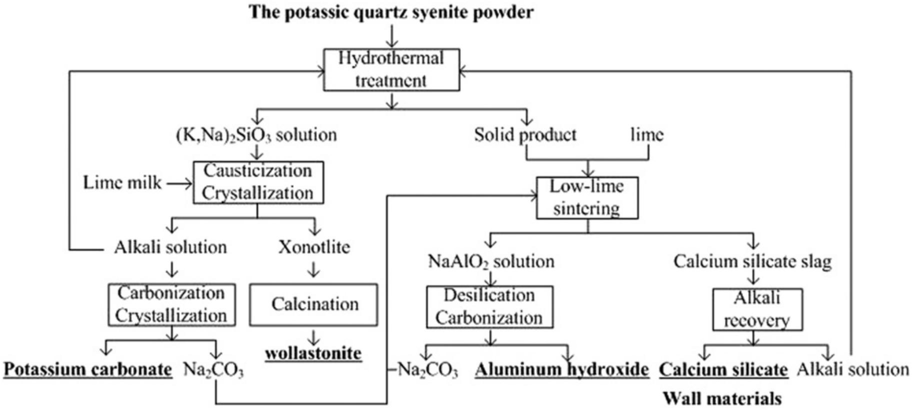

Fig. 2. Flowchart for the extraction of potassium from the potassic quartz syenite powder and its comprehensive utilization.