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

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A B S T R A C T

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-time 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 K₂O and SiO₂ 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%, 96.5%, 90%, respectively. The approach presented in this work is a promising process of comprehensive utilization of potassic silicate minerals such as K-feldspar.

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1. Introduction

Potassium (K), one of essential elements in fertilizers, can improve agricultural yields and enhance 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 production is strongly dominated by three countries: Canada, Russia, and Belarus which account for more than 90% of world potash production (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 potassium 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 CaCO₃ sintering process (Guillet, 1994), phosphogypsum sintering process (Wang et al., 2014), CaSO₄–CaCO₃ sintering process (Bakr et al., 1979), Na₂CO₃ 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., 2014a, 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 K₂SiO₃–Na₂SiO₃ solution from the
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 K2O and SiO2 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 Al2O3 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% K2O, 17.39% Al2O3, and 63.69% SiO2 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 K2SiO3 solution, and about 2/3 silica in the QS powder was leached out and transformed into the K2SiO3–Na2SiO3 solution. The solid product zeolite with higher Al/Si mole ratio was obtained as indicated in Eq. (1).

K2SiO3–Na2SiO3 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 K2SiO3–Na2SiO3 solution was obtained by carbonation of KOH–NaOH solution using CO2 gas as per Eq. (4). The final product potassium carbonate was prepared by evaporation and crystallization of K2CO3–Na2CO3 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, Na2CO3 5 g/L) to produce the NaAlO2 solution according to Eq. (6). After removing small amounts of impurity, the NaAlO2 solution reacted with CO2 gas to prepare aluminum hydroxide. The solid slag Na2CaSiO4 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).

\[
6\text{KAlSi}_3\text{O}_8 + 26\text{NaOH} \rightarrow \text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}] (\text{OH})_2 \cdot 2\text{H}_2\text{O} + 3\text{K}_2\text{SiO}_3 \quad (1) \\
+ 9\text{Na}_2\text{SiO}_3 + 10\text{H}_2\text{O}
\]

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>P2O5</th>
<th>Loss</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>QS-1</td>
<td>63.69</td>
<td>0.63</td>
<td>17.39</td>
<td>3.40</td>
<td>0.01</td>
<td>1.68</td>
<td>1.09</td>
<td>0.16</td>
<td>10.27</td>
<td>0.09</td>
<td>1.96</td>
<td>100.37</td>
</tr>
</tbody>
</table>

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

Fig. 2. Flowchart for the extraction of potassium from the potassic quartz syenite powder and its comprehensive utilization.
Table 2
Experimental conditions and results for the dissolution of QS powder.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction factors</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1 (mass ratio)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>GW-1</td>
<td>0.50</td>
<td>220</td>
</tr>
<tr>
<td>GW-2</td>
<td>0.55</td>
<td>220</td>
</tr>
<tr>
<td>GW-3</td>
<td>0.60</td>
<td>220</td>
</tr>
<tr>
<td>GW-4</td>
<td>0.65</td>
<td>220</td>
</tr>
<tr>
<td>GW-5</td>
<td>0.70</td>
<td>220</td>
</tr>
<tr>
<td>GW-6</td>
<td>0.80</td>
<td>220</td>
</tr>
<tr>
<td>GW-7</td>
<td>0.60</td>
<td>200</td>
</tr>
<tr>
<td>GW-8</td>
<td>0.60</td>
<td>250</td>
</tr>
</tbody>
</table>

R1 = NaOH/QS mass ratio.

Fig. 3. XRD pattern of the optimal solid product (GW-8: H, hydroxyacancrinite; B, biotite).

2.3. Characterization

The chemical compositions of the QS powder and the solid samples were measured by wet chemical analysis. The XRD patterns of the QS powder and the solid samples were recorded by a Rigaku D/Max-2500 diffractometer with Cu-Kα radiation. The morphologies of as-prepared samples were investigated using a Hitachi S-4800 scanning electron microscope. Thermal analysis of xonotite was carried out on a Q600 V4.4A TA instrument under air at a heating rate of 10 K/min. The whiteness value determination was carried out on YQ-Z-48B whiteness meter instrument.

3. Results and discussion

3.1. $K_2O$ leaching from the QS powder

In the previous work, it was concluded that reaction factors (NaOH/ QS mass ratio, reaction temperature) had an influence on the hydrothermal dissolution of the QS powder in NaOH solution (Ma et al. 2015). In order to achieve higher extractions of $K_2O$ and $SiO_2$, the experiments were performed with in ranges of NaOH/QS mass ratio and reaction temperature. The results for the extractions of $K_2O$ and $SiO_2$ are listed in Table 2. The extraction of $K_2O$ and $SiO_2$ were calculated by the following formulas:

$$\eta_{K_2O} = \left(1 - \frac{K_{product}}{K_{reactant}} \times \frac{A_{reactant}}{A_{product}}\right) 	imes 100\%$$

(8)

$$\eta_{SiO_2} = \left(1 - \frac{S_{product}}{S_{reactant}} \times \frac{A_{reactant}}{A_{product}}\right) 	imes 100\%$$

(9)

where $K_{reactant}, K_{product}$ are the contents of $K_2O$ in the QS powder and the solid products, $S_{reactant}, S_{product}$ are the contents of $SiO_2$ in the QS powder and the solid products, $A_{reactant}, A_{product}$ are the contents of $Al_2O_3$ in the QS powder and the solid products, respectively.

Dissolution of the QS powder with NaOH/QS mass ratio of 0.50 to 0.80 at 220 °C for 2 h was conducted. It is seen that the extractions of $K_2O$ and $SiO_2$ were increased rapidly with NaOH/QS mass ratio ranging from 0.50 to 0.60. However, when the NaOH/QS mass ratio was more than 0.60, the extractions of $K_2O$ 92% and $SiO_2$ 63% were almost identical due to partial potassium occurring in biotite. Biotite, $(K(Mg,Fe))_{3}AlSi_{3}O_{10}(OH)_2$, a kind of layered aluminosilicate mineral with some valuable elements of magnesium and potassium, was easily dissolved by inorganic acid (HCl and $H_2SO_4$) reported in the literatures (Varadachari 1997; Luo et al. 2015). The XRD results (Fig. 3) indicated that biotite could not be dissolved in NaOH solution. Therefore, the NaOH/QS mass ratio of 0.60 was used for the subsequent experiments. In considering reaction temperature, the extractions of $K_2O$ were 79.0%, 89.0%, and 93.2%, and the extractions of $SiO_2$ were 59.0%, 61.3%, and 62.5% when dissolving the QS powder at 200 °C for 2 h, at 220 °C for 2 h, and at 260 °C for 2 h, respectively. It is evident that reaction temperature has a greatly effect on the dissolution of QS powder under conditions of 200–260 °C. The optimal extractions of $K_2O$ and $SiO_2$ were 93.2%, 62.5% after reaction with NaOH/QS mass ratio of 0.60 at 260 °C for 2 h.

Under the optimized conditions for the dissolution of QS powder, the contents of chemical composition of the filtrate $K_2SO_4–Na_2SO_4$ solution are $K_2O$ 67.5, $Na_2O$ 111.2, $SiO_2$ 136.0 (in mass concentration, g/L), respectively. The solid product is composed of hydroxyacancrinite, seen from XRD pattern in Fig. 3. The solid product with Al/Si mole ratio of 0.72 (seen in Table 3) could be used as the starting material for production of aluminum hydroxide.

Table 3
Chemical composition of the optimal solid product (wt%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>P2O5</th>
<th>Loss</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW-8</td>
<td>41.31</td>
<td>0.74</td>
<td>25.36</td>
<td>4.75</td>
<td>0.01</td>
<td>1.15</td>
<td>0.63</td>
<td>17.51</td>
<td>1.93</td>
<td>0.28</td>
<td>6.47</td>
<td>100.14</td>
</tr>
</tbody>
</table>
3.2. Preparation of acicular wollastonite and potassium carbonate

The lime milk and K$_2$SiO$_3$–Na$_2$SiO$_3$ solution was reacted with Ca/Si of 1.0 at varies temperature (180 °C, 200 °C, 220 °C, 260 °C). The experimental conditions and results are listed in Table 4, and the morphologies of products are shown in Fig. 4. The causticization of SiO$_2$ is up to 98% at all reaction temperatures and reaction times. It is beneficial to prepare high purity potassium carbonate from the KOH–NaOH solution. The solid product was calcium hydroxide and C–S–H gel with spherical particle when causticization of the K$_2$SiO$_3$–Na$_2$SiO$_3$ solution at 180 °C for 4 h. The rod-like tobermorite was generated at 200 °C for 4 h. The tobermorite was transformed into the foshagite at 240 °C for 4 h, which has a uniform acicular morphology. The acicular xonotlite was prepared at 260 °C for 6 h. Thus, it was inferred that the transformation of C–S–H → tobermorite → foshagite → xonotlite was occurred with increase in reaction temperature (Wu et al. 2013; Hong and Glasser 2004). The final product was the majority of xonotlite and the minority of foshagite at 260 °C for 6 h, which was illustrated in Fig. 5.

In order to prepare acicular wollastonite, the product xonotlite and foshagite was calcined in open-air system. The TG-DTA plot of sample (GW-13) obtained at 260 °C for 6 h is given in Fig. 6. The endothermic peaks at 149.61 °C and 687.11 °C correspond to the loss of the adsorbed water and the chemical structure water of xonotlite and foshagite. The exothermal peak at 844.39 °C represents the phase transformation of xonotlite into wollastonite. Based on the thermal analysis result, the acicular wollastonite was prepared by calcining xonotlite at 850 °C for 2 h. The chemical composition of as-prepared wollastonite is given in Table 5. XRD pattern and SEM image of as-prepared wollastonite are

<table>
<thead>
<tr>
<th>Samples</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Causticization rate (%)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW-9</td>
<td>180</td>
<td>4</td>
<td>97.6</td>
<td>C, C–S–H</td>
</tr>
<tr>
<td>GW-10</td>
<td>200</td>
<td>4</td>
<td>98.4</td>
<td>T</td>
</tr>
<tr>
<td>GW-11</td>
<td>220</td>
<td>4</td>
<td>98.5</td>
<td>F, T</td>
</tr>
<tr>
<td>GW-12</td>
<td>260</td>
<td>4</td>
<td>99.2</td>
<td>F</td>
</tr>
<tr>
<td>GW-13</td>
<td>260</td>
<td>6</td>
<td>99.5</td>
<td>X, F</td>
</tr>
</tbody>
</table>

C, calcium hydroxide; C–S–H, gel; T, tobermorite; F, foshagite; X, xonotlite.

Fig. 4. SEM images of the products obtained in causticization of the K$_2$SiO$_3$–Na$_2$SiO$_3$ solution (a, 180 °C; b, 200 °C; c, 220 °C; d, 260 °C for 4 h; e, 260 °C for 6 h).
shown in Figs. 7 and 8. It is clear from the figure that the wollastonite with acicular morphology has a small amount of impurity calcium silicate. According to its chemical composition analysis and whiteness value determination, the purity of wollastonite is 93.8%, and the whiteness is 92%. More importantly, it was shown that only 0.36% K2O was in the wollastonite and most of the K2O was in the solution after causticization.

The K2CO3 – Na2CO3 solution was obtained by carbonization of the KOH – NaOH solution using CO2 gas. Potassium carbonate was prepared after the K2CO3 – Na2CO3 solution was evaporated at variable temperature under the condition of vacuum (Liu et al. 2011; Valyashko and Urusova 2003; Valyashko 2005). The chemical composition of as-prepared potassium carbonate is listed in Table 6. The purity of potassium carbonate is more than 96%.

3.3. Preparation of aluminum hydroxide

The solid product hydroxyxancrinite with Al/Si mole ratio of 0.72 was used as the starting material for production of aluminum hydroxide using low-lime sintering process. The reaction was occurred at lower temperature using low-lime sintering process than traditional lime sintering process and lime-soda sintering process (Yao et al. 2014; Yang et al. 2014). Experiments were carried out by varying the sintering temperature and sintering time. The experimental conditions and results are given in Table 7. The extraction of Al2O3 was calculated as the following formula:

\[
\eta_{\text{Al}_2\text{O}_3} (\%) = \left[1 - \left(\frac{A_{\text{slag}}}{A_{\text{clinker}}} \times \frac{C_{\text{clinker}}}{C_{\text{slag}}} \times \frac{C_{\text{clinker}}}{C_{\text{slag}}} \times \frac{C_{\text{slag}}}{C_{\text{clinker}}} \right)\right] \times 100\%\]

where \(A_{\text{clinker}}, A_{\text{slag}}\) are the contents of Al2O3 in the sintered clinker and the solid slag, \(C_{\text{clinker}}, C_{\text{slag}}\) are the contents of CaO in the sintered clinker and the solid slag, respectively.

When sintering temperature is 950 °C, the extraction of Al2O3 is only 77.9%. Increasing temperature up to 1000 °C, it is more than 90.4%. However, the standard leaching rate of Al2O3 drops to 88.0% with reaction temperature of 1150 °C. Therefore, the optimal sintering temperature ranges from 1000 to 1100 °C. The sintering time has a strong influence on the standard leaching rate of Al2O3. It increases from 68.9% to 90.4% with sintering time ranging from 0.5 h to 2.0 h. The opposite trend is observed with sintering time of 2.5 h. It is evident that higher temperature and longer time have a disadvantage of the extraction of Al2O3 due to over-burning phenomenon. The maximum
alumina extraction of 90.5% was achieved under the sintering conditions of 1050 °C for 2.0 h.

The NaAlO2 solution with mass concentration of Na2O 87.97, K2O 2.42, Al2O3 100.34, and SiO2 3.48 (g/L) was obtained after leaching of the sintered clinker. The small amount of impurity was removed by lime milk. The final product aluminum hydroxide was prepared by carbonation of the NaAlO2 solution using CO2 gas. The main chemical composition of as-prepared aluminum hydroxide is listed in Table 8. XRD pattern and SEM image of as-prepared aluminum hydroxide are shown in Figs. 9 and 10.

It can be seen from Fig. 9 that the as-prepared aluminum hydroxide possesses a structure of gibbsite. The as-prepared aluminum hydroxide is spherical in shape with the average particle size of about 10 μm as shown in Fig. 10. The purity of as-prepared aluminum hydroxide is up to 99%, and its quality has reached to the required standard (GB/T 4294-1997) of premium grades.

The solid slag Na2CaSiO4 as shown in Fig. 11 was used to recycle NaOH solution. Calcium silicate was precipitated at the same time and can be used as the raw material for the preparation of materials used in wall construction (Yurkov and Aksel’rod 2005). The recovery of NaOH is up to 94% with liquid to solid ratio of 4 at 160 °C for 2 h (Zhang et al. 2011).

3.4. Evaluation of the systemic process

For the purpose of leaching potassium and utilizing the alumina and silica from potassic quartz syenite, the new technique presented in this work is an efficient way with an optimal potassium extraction of 93.2% and three byproducts (aciccular wollastonite, aluminum hydroxide, calcium silicate).

In addition, this systemic process is lower energy consumption for hydrothermal dissolution of potassic quartz syenite at lower temperature in the alkali-hydrothermal process, lower consumptions of disposable mineral resources for utilization of only lime in the causticization process, lower CO2 emissions for its recycle utilization in the carbonization process, and higher utilization of the potassium ore resources for production of four products. Therefore, this systemic process is efficient, energy-saving, and clean for comprehensive utilization of potassium, alumina, and silica in potassic quartz syenite.

4. Conclusion

Hydrothermal extraction of potassium, preparation of acicular wollastonite and aluminum hydroxide were explored using potassic quartz syenite as the raw material. The optimal extractions of K2O and SiO2 from potassic quartz syenite were 93.2%, 62.5% with NaOH/syenite mass ratio of 0.60 at 260 °C for 2 h. Acicular wollastonite was synthesized after causticization of the K2SiO3–Na2SiO3 solution using lime milk at 260 °C for 6 h followed calcination of xonotlite at 850 °C for 2 h. The final product acicular wollastonite is in purity of 93.8% and in whiteness of 92%. Potassium carbonate
hydroxide was prepared by carbonation of the NaAlO$_2$ solution. The as-prepared aluminum hydroxide is spherical in shape with the average particle size of about 10 μm and in purity of 99%.

It can be concluded from the experimental results that this system process is efficient, energy-saving, and clean. Furthermore, it appears to be suitable for the comprehensive utilization of potassium, alumina, and silica in potassic silicate minerals such as K-feldspar.

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