Original Article

Scandium extraction from silicates by hydrometallurgical process at normal pressure and temperature

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\begin{abstract}
Silicate is an important rock-forming mineral. In this work, a method called “sulfuric acid curing” was proposed, aiming to extract rare earth element scandium from silicates. Sulfuric acid curing refers to the addition of concentrated sulfuric acid to heated silicates at 60–300 °C, and subsequently water leaching of the treated silicates at 30–75 °C. The effects of sulfuric acid dosage, curing time, curing temperature, pulp density, leaching temperature and stirring speed on scandium leaching were investigated. Under the condition of sulfuric acid dosage with 0.75 times of the theoretical amount, curing time of 15 h, curing temperature of 200 °C, pulp density for L/S ratios of 30:1, leaching temperature of 75 °C, stirring speed of 100 rpm, Sc(III) concentration of 492 μg/L in the solution was achieved. XRD analysis showed that major phases of the samples hardly changed after acid curing. However, SEM-EDS examination of the samples demonstrated that morphology and particle size of minerals were changed obviously after being cured and leached. Leaching kinetics was further calculated, which can be described by the shrinking core model. The apparent activation energy for the dissolution was determined to be 55.49 kJ·mol\textsuperscript{-1}.
\end{abstract}

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1. Introduction

Silicates are a class of minerals with wide variety and high content in the earth’s crust. Currently, there are more than 800 kinds of silicates, accounting for one-third of the all known minerals. Silicates can be classified as the following six groups based on the linkage manner of tetrahedral anionic group \cite{1,2}: (1) isolated tetrahedral structure (SiO\textsubscript{4}\textsuperscript{4-}), (2) double tetrahedral structure (Si\textsubscript{2}O\textsubscript{6}\textsuperscript{2-}), (3) ring structure (Si\textsubscript{3}O\textsubscript{9}\textsuperscript{6-}, Si\textsubscript{2}O\textsubscript{12}\textsuperscript{2-} and Si\textsubscript{6}O\textsubscript{18}\textsuperscript{2-}), (4) chain structure (Si\textsubscript{3}O\textsubscript{6}\textsuperscript{2-})\textsubscript{n} and (Si\textsubscript{4}O\textsubscript{11}\textsuperscript{2-})\textsubscript{n}, (5) sheet structure (Si\textsubscript{2}O\textsubscript{2}\textsuperscript{2-})\textsubscript{n}, (6) framework group (SiO\textsubscript{2})\textsubscript{n}. Some silicates such as eudialyte, zircon, contain common economic elements such as aluminum, copper, iron, etc., also some rare earth elements such as scandium \cite{3-5}.
Scandium (Sc) is a typical rare earth element and widely distributed in the earth’s crust. The presence of Sc minerals is diverse. There are more than 100 Sc-bearing mineral species [6]. However, the lack of a considerably appreciable quantitity of Sc in minerals limited its development and application to a certain extent [7,8]. In general, minerals containing more than 20 ppm Sc can be considered as resources of Sc and deserving exploitation [8,9]. From the global distribution of Sc deposits, Sc resources have been identified in Australia, Canada, China, Kazakhstan, Madagascar, Norway, the Philippines, Russia, and Ukraine [10]. In China, Sc resources are mainly found in association with iron, tin, aluminum and tungsten ores. Compared with other metal markets, the global supply and consumption of Sc are only about 10–15 tons per year. The price of Sc metal stabilized at around $220/g between 2013 and 2018 years [11]. Sc has attracted a lot of attention in the last decades because of its unique technological applications in alloys, ceramics, lasers, fuel cells, superconductors, super-magnets and the like [12,13].

Sulfuric acid curing is a pretreatment method of minerals, in which concentrated sulfuric acid and crushed ore are mixed to react at a certain temperature. It was classified into low temperature curing (<300 °C) and high temperature curing (>300 °C) [14]. The action of sulfuric acid on silicates produces the following three results: I. The structure of the silicates is completely destroyed, resulting in the dissolution of target metals and silica to produce silica gel. II. The silicate structure is partially destroyed, resulting in the dissolution of some ions and the generation of silicate residues. III. The silicate structure does not undergo any change and does not react [15]. Therefore, sulfuric acid leaching is an effective method to extract valuable metals from silicates. Nevertheless, the formed silica gel during the silicates leaching and may result in a serious problems, such as hindering the operation of solvent extraction, ion exchange and electrolysis stages [15,16].

In order to overcome this problem, some methods have been applied, such as quick leaching which is based on a water-starved system and effectively rejected silica from many silicates [17]. Zhang treated low-grade zinc oxide ore with high silica utilizing sulfuric acid curing and water leaching. The ore was firstly cured for 3 h by sulfuric acid with a concentration of 55.17 % H2SO4, and then leached using water for 3 h at 50 °C with a liquid to solid ratio of 5.1 mL/g and a stirring speed of 400 rpm. A zinc recovery of 99.22 % was obtained and the dissolution of silica was as low as 0.56 % [18]. Xu developed a process for leaching zinc silicates from Guangxi Province of China using sulfuric acid as the leachate. 97.9 % zinc extraction was obtained under the conditions of 0.44 mol/L sulfuric acid concentration and a solid to liquid ratio (g/mL) of 1:6 within 120 min. leaching at 140 °C and 1.4 MPa partial pressure [19]. A method proposed by Borra makes silica remained undissolved by the consecutive combination of sulfation, roasting and leaching processes, which also allows achieving high selectivity for REEs [20,21]. Another method, dry digestion, is also an effective way to inhibit the dissolution of amorphous silica from silicates [21]. Hydrometallurgical treatment of silicates such as eudialyte has been extensively studied from Russian teams by using strong mineral acids especially sulfuric acid directly or in a two stage decomposition process for recovery of rare earths [4,22–24]. Some recent studies also shown that the silicates can effectively inhibit the formation of silica gel after this process [1]. Moreover, the products after acid curing became smaller appreciably in particles size [18].

However, there is a lack of systematical studies on the curing process. Besides, information is not available on the systematic kinetic study on Sc leaching from silicates using sulfuric acid curing. In view of these, this paper aims to research Sc leaching from silicates. Samples were first cured by sulfuric acid in a water-starved system and then leached in water without any other reagents. The effects of curing sulfuric acid dosage, curing temperature and time, also leaching temperature and time, pulp density, and stirring speed on the leaching of Sc were systematically investigated. The kinetic characteristics of silicate were also researched in curing and leaching systems.

2. Materials and methods

2.1. Minerals and reagents

Silicates were provided from repetitive magnetic beneficia-
tion studies of Yunnan Province of China. The silicates with a particle size less than 0.074 mm were gained obtained by a two-stage closed circuit grinding preparation process [25]. The silicates ground was characterized by chemical method and examined by XRD and XRF. Its chemical compositions were listed in Table 1. It can be seen that the scandium content of silicates was 60 ppm. All experimental agents were of analytical reagent, sulfuric acid reagent grades were 95–98 wt%. Deionized water was used in all tests, which was sterilized at 121 °C for 20 min by a high-pressure steam sterilizer.

2.2. Instrumental analysis

Phase analysis of the raw silicates and leached residue were carried out by X-ray diffractometer (Advance D8/Brucker). Chemical analysis of the elements in raw materials was conducted by X-ray fluorescence spectroscopy (Axios MAX). Solution filtrated with 0.22 μm filter for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Spectro Blue II) analysis for Sc. The microstructure of the solid samples was studied in a Scanning electron microscope (JSM-6490LV/JOEL) equipped with an energy dispersive spectrometer (Neptune XM 4/EDAX). Solution pH values were monitored with a pH meter (PHS-4A). Stirring leaching of the silicates was processed through magnetic stirrer (B13-3).

2.3. Experimental design

The silicates were dried in oven at 50 °C for 12 h before the experiment. For each batch sulfuric acid curing experiment, 2 g of silicates were added to different amount of acid in evaporating dish. Then these silicates were carried out under vigorous stirring in magnetic stirring plates, among them, the curing time is 3–24 h, the curing temperature is 60–300 °C, the dosage of sulfuric acid is 0.1–2 times of the theoretical acid consumption (Fig. 1). Once the procedure was completed
the treated silicates were left to cool down and subsequently leaching with deionized water at 30–75 °C and 0–700 rpm in magnetic stirring plates for 1–11 days. Certain liquid samples were taken at regular intervals every two days to measure ICP during the leaching process. After completion of the water extraction, the hot slurry was cooled to room temperature, then the samples were filtered through a 0.22 μm nylon membrane. The leaching residue was washed three times with deionized water.

### Table 1 – Chemical compositions of silicates ore (wt.%).

<table>
<thead>
<tr>
<th>Si</th>
<th>Mg</th>
<th>Ca</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>O</th>
<th>Mn</th>
<th>Sc</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.49</td>
<td>6.3</td>
<td>7.5</td>
<td>4.59</td>
<td>2.88</td>
<td>13.2</td>
<td>45</td>
<td>0.247</td>
<td>0.0060</td>
<td>1.787</td>
</tr>
</tbody>
</table>

3. **Results**

3.1. **Effect of sulfuric acid dosage**

The theoretical acid consumption refers to the amount of acid required to dissolve all the oxides in minerals. Based on chemical compositions in Table 1, the theoretical consumption for sulfuric acid per gram ore in the leaching process was calculated to be 1.25 mL. In the present work, 2 g of silicates were blended with concentrated sulfuric acid 0.1–2 times of theoretical acid consumption. Afterwards, the silicates were cured for 12 h at temperature of 90 °C, and then leached with water, other leaching parameters were leaching temperature of 45 °C, liquid-solid (L/S) ratio in leaching of 50:1, stirring speed of 170 rpm and leaching time of 11 days. The experimental results are shown in Fig. 2a. The Sc(III) concentration in solution was firstly increased (0.1–0.75 times) and then decreased (0.75–2 times) with an increase in sulfuric acid dosage. Obviously, compared with the direct leaching of silicates with sulfuric acid, sulfuric acid curing was beneficial to the dissolution of Sc. In addition, when the sulfuric acid dosage was 0.75 times of the theoretical acid consumption, the concentration of Sc(II) in the solution can reach a maximum of 176 μg/L. However, when the amount of acid exceeded 0.75 times and further increased, the concentration of Sc(II) in the solution decreased from 176 to 99 μg/L. It can be seen from Fig. 2b, the pH of the solution depends on the amount of sulfuric acid used during curing, and the values of pH decreased as the amount of acid increased. When the amount of acid was within a certain range, the hydrogen ions in sulfuric acid were mainly used to decompose the silicates, so the free hydrogen ions in the solution were less. When the acid exceeded a certain range, excessive amount of free hydrogen ions was present in the solution, which promoted the formation of orthosilicic acid and inhibited the dissolution of Sc. In order to maintain a high Sc recovery, the sulfuric acid used for each batch was 1.875 mL, which was 0.75 times of the theoretical amount required for 2 g silicates.

3.2. **Effect of sulfuric acid curing time**

The effect of curing time on the extraction of Sc(III) was investigated using a sulfuric acid dosage of 0.75 times, a curing temperature of 90 °C, liquid-solid (L/S) ratio in leaching of 50:1, leaching temperature of 45 °C, stirring speed of 170 rpm and leaching time of 11 days. The results are shown in Fig. 2c. The concentration of Sc(III) in the solution increased with time, from 97 to 239 μg/L on increasing the curing time from 3 to 24 h. However, the concentration did not significantly change with further increasing in the curing time of 15–24 h. In this work, in order to make the silicates curing completely and save energy, the curing time was selected to be 15 h.

3.3. **Effect of sulfuric acid curing temperature**

The effect of curing temperature on the extraction of Sc(III) was investigated at 70, 90, 150, 200, and 300 °C, the other experimental parameters were set as follows: sulfuric acid dosage of 0.75 times, curing time of 15 h, L/S ratio of 50:1, leaching temperature of 45 °C and stirring speed of 170 rpm. The experimental results are shown in Fig. 2d. The effect of the curing temperature on Sc dissolution was similar to that of the acid dosage. Obviously, The Sc(III) concentration in solution was firstly increased (70–200 °C) and then decreased (200–300 °C) with an increase curing temperature. Correspondingly, the concentration of Sc(III) in the solution increased from 132 to 300 μg/L and then decreased to 135 μg/L. The optimum curing temperature for the curing process was therefore selected as 200 °C.

3.4. **Effect of pulp density in water leaching**

The effect of pulp density on the extraction of Sc(III) was investigated for L/S ratios of 20:1, 30:1, 40:1, 50:1, 60:1, and 70:1. The other parameters were set as follows: the sulfuric acid dosage
of 0.75 times, curing time of 15 h, curing temperature of 200 °C, leaching time of 7 d, leaching temperature of 75 °C. The results are shown in Fig. 4a. When the L/S ratio was 30:1, the concentration of Sc(III) reached 492 μg/L. When the liquid-solid ratio increased further, the concentration of Sc(III) instead of reducing; therefore, the L/S ratio of 30:1 was selected.

3.5. **Effect of leaching temperature**

The effect of leaching temperature on the extraction of Sc(III) was investigated at 30, 45, 60, and 75 °C under the following conditions: sulfuric acid dosage of 0.75 times, curing time of 15 h, L/S ratio of 30:1, leaching time of 7 days. The experimental results are shown in Fig. 4b. With an increase in leaching temperature, the concentration of Sc(III) gradually increased. When the temperature was 75 °C, the concentration of Sc(III) reached the maximum value of 492 μg/L. Therefore, the leaching temperature was set at 75 °C.

3.6. **Effect of stirring speed in leaching**

The effect of stirring speed in leaching was investigated for stirring speed of 0, 170, 230, 300, and 500 rpm under the following conditions: sulfuric acid dosage of 0.75 times, curing time of 15 h, L/S ratio of 30:1, leaching temperature of 75 °C, leaching time of 7 days. The results are shown in Fig. 4c. The leaching efficiency of the Sc increased with stirring speed increased, from 235 to 306 μg/L on increasing the curing time from 0 rpm to 100 rpm. The leaching efficiency did not significantly change with further increasing in stirring speed, so an appropriate stirring speed was selected as 100 rpm.

3.7. **Kinetic analysis**

The leaching reaction is the liquid-solid reaction. It can be concluded that a variety of models have been applied in literatures. During the liquid-solid reaction, the most commonly used reaction types are the overall reaction model and shrinking core model. Since mineral contains CaO, insoluble CaSO₄ may be formed and attached to the surface of the unreacted minerals during the reaction. Therefore, it was more appropriate to select the shrinking core model to describe this reaction process. The model has three control step equations: surface chemical reaction control, product layer diffusion control and mixed control of them [26–28]. Assuming that surface chemical reaction was the rate limitation step, the chemical reaction may be expressed in the following Eq. (1) [29]:

$$1-(1-X)^{1/3} = K_at$$  \( (1) \)

Similarly, when the diffusion of minerals through product layer diffusion control, the following expression of the shrinking core model can be used [30]:

$$1-2/3X-(1-X)^{2/3} = K_dt$$  \( (2) \)

Eqs. (1) and (2) are conventional topochemical models and can be used to describe the silicates dissolution process, when surface chemical reactions or products control the entire pro-
cess. However, if the insoluble CaSO₄ and silica gel produced during the silicates dissolution plays an important role in the final stages of water leaching, then a model that considers both chemical reaction at the surface and diffusion through the product layer together control the overall rate would be more realistic, kinetics was represented by mixed control model equation [31]:

\[
[1-(1-X)^{1/3}] + B [1-2/3X-(1-X)^{2/3}] = K_i t
\]  

(3)

where X is the reacted fraction of Sc, Kᵣ is the rate constants which is calculated from Eq. (1), (2) and (3), respectively, where B = Kᵣ/Kₐ and t is the reaction time.

The data given in Figs. 2(d) and 4b were analyzed with the above shrinking core models Eqs. (1)–(3). The results of the kinetic analysis of the leaching experiments including the apparent rate constants (Kₑ, Kᵣ and Kᵢ) and correlation coefficients (R²) were given in Table 2. Among these three models, it was found that all of the results more fit with the product layer diffusion control model compared with the surface chemical reaction control or the mixed control model. Therefore, the dissolution reaction was controlled by the product layer diffusion control.

The reaction rate constant K was a function of temperature, and the effect of temperature on it can be expressed by the Arrhenius formula Eq. (4). The above equation can be changed to Eq. (5) [32].

\[
K = Ae^{-E_a/RT} 
\]

(4)

\[
\ln K = \ln A - \frac{E_a}{RT} 
\]

(5)

where K is the reaction rate constant, A is the frequency factor, Ea is the reaction activation energy, T is the leaching temperature and R is the gas constant.

The result of the amount of sulfuric acid of 0.75 times, the curing time of 15 h, the curing temperature of 200 °C, the solid-liquid ratio of 1:30, the stirring speed of 100 rpm, and leaching temperature at 30, 45, 60, 75 °C were selected to calculate the activation energy. From the Eq. (5), activation energy was calculated to be 55.49 kJ/mol.

4. Discussion

Silicon dioxide existing in the silicates was converted to Si₂(SO₄)₃ after the stage of leaching of sulfuric acid curing as follows from Eq. (6)

\[
H_2SO_4+1/3SiO_2 → 1/3Si_2(SO_4)_3 + H_2O
\]

(6)

The mineral contains a high content of silicon, so the formation of silica gel cannot be avoided during the leaching process (Fig. 3). The formation of silica gel depends on the pH and ionic strength of the solution [33]. When concentrated sulfuric acid was used in the right amount, these acids were mainly used to destroy the structure of minerals during curing processes. However, when the amount of acid exceeded the optimal dosage, the amount of free hydrogen ions in the leaching solution increased with the increase of sulfuric, which was easy to form silica gel with silica dioxide. This gelatinous
precipitate may blind ore particles from further dissolution and reduce the leaching kinetics significantly [4,21]. What’s more, the amount of sulfuric acid increased made the viscosity of the solution raised. Elements Si, Fe, Ca, S and O could be detected in particles (Fig. 6), shown that CaSO₄ was enriched in these particles. This increased the leaching resistance, thereby restricted the progress of leaching reaction.

SEM-EDS image of the silicates after H₂SO₄ curing can be seen in Fig. 6. Grains with high Si content were found in the treated concentrate indicated that the siliceous precipitate formed during the curing process. It was also consistent with the experimental phenomenon (Fig. 3). This confirmed the result already reported in the literature [4]. What’s more, compared with the original mineral SEM image, the microstructure of the mineral changed significantly. The surface of the raw mineral was relatively flat. However, many corrosion pits were found on the surface of the treated minerals, indicating that the curing treatment destroyed the structure of the minerals to some extent. In addition, compared with the raw mineral by direct acid leaching, the grain size of the cured mineral was significantly smaller after water leaching (Fig. 6b). This may be due to the fact that the sulfuric acid curing treatment imparted a certain amount of energy to the minerals, which caused the hydrolysis of Si-O-Si linkages of silicates, resulting in the dissolution of the minerals. Nevertheless, the main phase of minerals did not change significantly before and after curing (Fig. 5).

The corrosion effect of sulfuric acid on minerals gradually increased with the extension of the curing time and the increase of the curing temperature at the appropriate sulfuric acid dosage. An increase in temperature would accelerate the chemical reaction kinetics [34]. This process prompted to decompose of the silicates and to generate the micro-fracturing of particles, which resulted in an increase in porosity of the particles [18]. Therefore, the leaching of Sc was more favorable. However, as the temperature continued to rise, the dissolution of silicon in silicates also increased, which was not conducive to the leaching of scandium. On the other hand, since the specific surface area of samples held a great significance in the process of minerals leaching, it could
Fig. 5 – XRD pattern of silicates (A), direct acid leaching residue (B) and acid curing leaching residue (C). 1. Magnesiohornblende ferrous, 2. Magnesiohornblende, 3. Ferrotschermakite, 4. Actinolite, heated, 5. Actinolite.

be deduced that the particles bunched up with the excessive curing as increasing the temperature to 300 °C [35]. Therefore, 200 °C was verified as an appropriate curing temperature.

Under a certain amount of sulfuric acid, the concentration of sulfuric acid in solution was changed by the change of liquid-solid mass ratio. When the ratio decreased, the concentration of sulfuric acid in the solution increased, and the diffusion driving force also increased. Thus, the dissolution of the Sc increased. Furthermore, the difference in pulp concentration indicated that the free water content in the solution was different. The more free-water there was in the silicone-containing solution, the easier it was to form silica gel. Therefore, high pulp concentration could inhibit the extraction of scandium. After the minerals were cured, the soluble scandium might mainly adhere to the mineral surface with a relatively weak force. Therefore, when the stirring speed reached 100 rpm in the leaching stage, the soluble scandium may be completely extracted. Therefore, the dissolution of scandium was not changed apparently with the continuous increase of stirring speed.

Compared to direct sulfuric leaching, advantages of curing with acid were significantly improved the dissolution of Sc. Moreover, sulfuric acid curing had the following advantages over other methods of extracting rare earth elements from silicates. (1) No need for pre-treatment of minerals such as roasting, mechanical activation and the like. (2) No need to add impregnating agent such as fluoride ion, hydrogen peroxide during the leaching process. (3) It was not necessary to add additional sulfuric acid to keep the leaching system acidic. The following conceptual flowsheet on silicates hydrometallurgical processing is developed (Fig. 7).

5. Conclusions

Scandium can be extracted from silicates by hydrometallurgical process at normal pressure and temperature with pretreatment by sulfuric acid curing. Sulfuric acid dosage with 0.75 times of the theoretical amount, curing time of 15 h, curing temperature of 200 °C, pulp density for L/S ratios of 30:1,
leaching temperature of 75 °C and stirring speed of 100 rpm are the optimal conditions in the whole process. Morphology and particle size of minerals were changed obviously after being cured and leached, and insoluble silica precipitates were also generated in the water leaching. In addition, the obtained solution can be then treated for scandium purification and separation by conventional methods. The scandium dissolution reaction from silicates was controlled by the product layer diffusion control and the apparent activation energy was determined to be 55.49 kJ mol⁻¹. This work will would provide a reference for the extraction of rare earth elements from silicates at normal pressure and temperature.

Conflicts of interest

The authors declare no conflict of interest.

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