



# Lithium extraction from clay-type lithium resource using ferric sulfate solutions via an ion-exchange leaching process

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## ABSTRACT

Clay-type lithium resources have been developed as an important natural lithium source secondary to hard rock sources and brine sources. In this study, a green and effective lithium extraction process employing ferric salt solutions to leach lithium-rich clay was proposed. Upon calcination treatment, 73.6% of lithium could be leached over a period of 180 min using a 15% ferric sulfate solution at 90 °C. The most suitable calcination temperature, leaching temperature, ferric sulfate concentration, and reaction time were determined to be 600 °C, 90 °C, 15% ferric sulfate, and 180 min, respectively. Ferric chloride and ferric nitrate had similar lithium leaching efficiencies under the same conditions. In addition, ferrous, sodium and calcium salts were introduced and compared in terms of their lithium extraction abilities. The results indicated that ferric ions had good selectivity for lithium leaching. The leaching process was considered to involve ion exchange between ferric ions and lithium ions.

## 1. Introduction

Lithium (Li) has been considered a critical mineral in many countries, such as the US, Japan and Australia (Cabeza et al., 2015; Australian Government, 2019; Rosales et al., 2019). In recent years, lithium and its compounds have been extensively used in rechargeable batteries, ceramics, glass, lubricating greases, and polymer production (Guo et al., 2016; Zhang et al., 2020). In addition to essential uses and increasing demands, lithium, as a strategic metal (Rosales et al., 2019), has an unbalanced global distribution and faces a risk of supply disruption in many countries (Cabeza et al., 2015; Zhang et al., 2019a). Hard rock sources (primarily in pegmatite as spodumene) and brine sources are the two main lithium resources in nature (Mohr et al., 2012; Lajoie-Leroux et al., 2018; Tadesse et al., 2019; Gu et al., 2020a; Gu et al., 2020b). Australia accounts for approximately 80% of the global lithium supply from hard rock deposits, while Chile possesses more than 50% of lithium reserves with low Mg/Li mass ratios (USGS, 2019; Zhang et al., 2019a). Due to the uneven geographic distribution of lithium resources, exploitation clay-type lithium resources and utilization of Li-bearing clays have received increasing attention (Benson et al., 2017; Wen et al., 2020).

Lithium-bearing clays have been identified as future lithium sources; in particular, after hectorite-type clay was concerned due to its large potential size (Meshram et al., 2014; Castor and Henry, 2020). Hectorite, a clay mineral found in Hector, California, that contains approximately 0.5% lithium, was found to be similar to the original saponite (Foshag and Woodford, 1936). The lithium-bearing clays around the McDermitt caldera on the Nevada-Oregon border were identified as a large lithium deposit by the USGS in the 1970s (Crocker and Lien, 1987), and lithium primarily occurs in the form of hectorite in these sediments (Glanzman et al., 1978). Since then, various methods have been developed to extract lithium from hectorite-type McDermitt clay and other Li-bearing montmorillonite clay samples (Büyükburç and Köksal, 2005; Egunlae et al., 2006; Amer, 2008; Lalasari et al., 2019).

Recently, a new clay-type lithium resource was discovered in China and was proposed to be a carbonate-hosted clay-type lithium deposit (Wen et al., 2020). The natural formation of this resource was considered to be related to the weathering sedimentation process of carbonate that exists widely in Karst areas in southwestern China. Importantly, the lithium in carbonate-hosted clay-type lithium deposits has a weak binding force and occurs mainly in the interlamination of clay minerals identified as montmorillonite (Wen et al., 2020; Gu et al., 2020a),

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suggesting a feasible extraction process for utilization. Due to lithium existing in a different form in carbonate-hosted clay-type lithium deposits, calcination and acid leaching processes were applied to extract lithium from Li-rich clay rocks (Gu et al., 2020a). However, because the acid leaching process results in acidic residues, leaching processes that do not involve acid should be developed to promote environmental friendly alternatives.

In this work, a novel process using ferric salt solutions was developed for the green and efficient extraction of lithium in Li-rich clay sample obtained from carbonate-hosted clay-type lithium resources. In comparison to acid leaching, the ferric salt solution leaching process has the advantages of lower acidity with more neutral residues. In addition, the ferric salt leaching process is sufficiently explained by the ion-exchange leaching behavior. The influences of various factors on the lithium extraction process were also investigated in this study.

## 2. Materials and methods

### 2.1. Materials and analytical methods

The Li-rich clay sample used was collected from Jinsha County, Northwest Guizhou, China. The compositions and properties of the Li-bearing clay were described in Gu et al. (2020a). The elemental composition is shown in Table S1. As reported previously, the main chemical composition of the Li-rich clay sample is as follows (wt%): 48.01% Al<sub>2</sub>O<sub>3</sub>, 33.06% SiO<sub>2</sub>, 2.25% TiO<sub>2</sub>, 1.06% Fe<sub>2</sub>O<sub>3</sub>, 3.88% K<sub>2</sub>O, 0.46% MgO, and 0.317% Li<sub>2</sub>O. The original Li-rich clay sample was homogenized, crushed and ground into fine powders. Before weighing samples for characterization, calcination and leaching experiments, powder samples were dried in a drying oven at 105 °C.

Guaranteed reagent grade ferric sulfate (Tianjin Kemiou Chemical Reagent Co., Ltd) was used for the extraction process to leach lithium in this study. The other reagents used in this study were of analytical grade, and all solutions used in the leaching process were prepared using deionized water.

The original Li-rich clay, the product calcined at 600 °C, and the leach residues were characterized by powder X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer with Cu K $\alpha$  radiation. Elemental concentrations in the leachates obtained from the leaching process were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian VISTA). The pH value of the leaching solution was measured by a portable pH meter (pHS-SC).

### 2.2. Leaching process and leaching efficiency

To investigate the effect of calcination temperature, the Li-rich clay in this study was calcined using a muffle furnace at different temperatures (400, 500, 600, 700, and 800 °C) for 1 h. The calcined products were then leached by using a 15% ferric sulfate solution at 90 °C for 180 min. The product calcined at 600 °C was selected to investigate the effect of the reaction temperature. For the leaching process, the temperature of a 15% ferric sulfate solution during a 180-min leaching process was kept at 20, 40, 60, 80, and 90 °C by means of an electric thermostatic water-bath heater. To investigate the effect of the extractant concentration, leaching reactions using different ferric sulfate concentrations (0, 1, 2.5, 5, 15, and 20%) were performed for 180 min with a solid-liquid ratio of 3.0 g/15 mL at 90 °C with constant gentle agitation. To investigate the effect of reaction time, leaching reactions using the 15% ferric sulfate solution were performed from 10 min to 240 min with a solid-liquid ratio of 3.0 g/15 mL at 90 °C with constant gentle agitation. In addition, ferric nitrate and ferric chloride were also used as extractants for lithium leaching, and all the conditions and operational processes were the same as those when using ferric sulfate. In the ferric sulfate leaching process, three parallel experiments were performed for each sample.

In contrast, 10% FeSO<sub>4</sub>, 10% Na<sub>2</sub>SO<sub>4</sub>, 10% FeCl<sub>2</sub>, 10% NaCl, 10% CaCl<sub>2</sub>, and 10% NaNO<sub>3</sub> were respectively employed for lithium leaching

from the product calcined at 600 °C to ascertain their efficiencies. To exclude the effect of hydrogen ions, the pH values of the above salt solutions were adjusted to be equal to those of their corresponding ferric salts using the corresponding dilute acid, and their lithium leaching efficiencies were also investigated. All of these solutions were used for lithium extraction from the product calcined at 600 °C under the selected leaching temperature of 90 °C for 180 min with a solid-liquid ratio of 3.0 g/15 mL and with constant gentle agitation.

At the end of 180 min, each suspension was immediately filtered using 0.45  $\mu$ m filter membranes. Each residue was washed three times using deionized water. The filtrates and washings were combined and diluted to a constant volume for analysis corresponding to each sample. From the analytical data, the percentage of extracted lithium (and that of the main impurity element, aluminum) was calculated according to the following Eq. (1):

$$\varepsilon(i, \%) = \frac{V^*c}{m^*w} \times 100 \quad (1)$$

where  $\varepsilon(i, \%)$  represents the leaching efficiency of element  $i$ ,  $V$  (L) is the total volume of the acid leaching solution combined with the washing solution,  $c$  (g/L) is the concentration of element  $i$  in the solution, and  $m$  (g) and  $w$  (%) are the mass and the content of element  $i$  in the original Li-bearing clay sample, respectively.

## 3. Results and discussion

### 3.1. Influencing factors of Li extraction

The main mineral phases in the clay resource were identified as diaspore ( $\alpha$ -AlO(OH)), illite ((K,H<sub>3</sub>O)(Al,Mg,Fe)<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>[(OH)<sub>2</sub>(H<sub>2</sub>O)]), montmorillonite ((OH)<sub>4</sub>Si<sub>8</sub>Al<sub>4</sub>O<sub>20</sub>·nH<sub>2</sub>O) and anatase (TiO<sub>2</sub>) as reported by Gu et al. (2020a). Since sulfuric acid has been reported to be effectively selective for the extraction of exchangeable lithium after calcination treatment, a ferric iron salt was used in the leaching process, as the ionic radius of ferric ion (Fe<sup>3+</sup>) is similar to that of lithium ion. Using ferric ion solutions as green leaching solutions was also based on the fact that ferric ion solution was low-acidic and low-cost (Dai et al., 2020). Because aluminum is the main impurity with high concentrations in the leachate solutions, the aluminum leaching efficiency during the ferric salt leaching process was compared and discussed.

#### 3.1.1. Effect of the calcination temperature

Calcination treatment of Li-bearing clay is a necessary step in the ion exchange leaching process, and the calcination temperature has been investigated by using sulfuric acid for leaching (Gu et al., 2020a). The Li-bearing clay calcined at various temperatures (400, 500, 600, 700, and 800 °C) was leached using a 15% ferric sulfate solution at 90 °C for 180 min. The lithium and aluminum leaching efficiencies are presented in Fig. 1. Similar to the sulfuric acid leaching process (Gu et al., 2020a), the ferric sulfate solution could also obtain a remarkable increase for lithium extraction when the calcination temperature increased from 400 to 500 °C. However, in the sulfuric acid case, the lithium leaching efficiency decreased moderately as the calcination temperature increased from 600 to 800 °C, whereas in this study, ferric sulfate presented a small change of lithium leaching efficiencies from 73.6 to 64.2% when the Li-bearing clay was calcined at the temperature range from 600 to 800 °C. This result indicated that ferric ions had a better selectivity than hydrogen ions when the layered structures underwent calcination at 800 °C. A possible explanation for this finding is that calcined montmorillonite can be pillared by ferric ions to maintain lithium exchangeability in the layers. Montmorillonite, a layered clay mineral belonging to the smectite group, is able to exchange cations between the layers and on the external surface (González-Rodríguez et al., 2015), and Fe-pillared montmorillonite has been reported in the literatures with applications of adsorption or catalysis (Borgnino et al., 2009; Chen et al.,

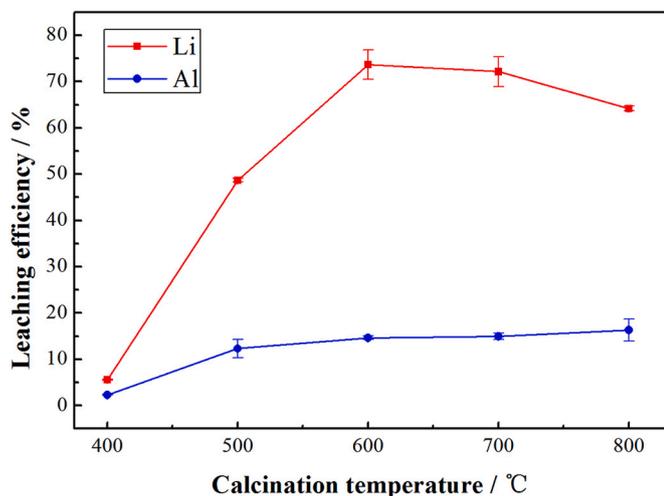


Fig. 1. Effect of the calcination temperature on the lithium and aluminum leaching efficiencies (15% ferric sulfate, 1 g, 5 mL, 90 °C, 180 min).

2009; Fang et al., 2016). From these results, it can be concluded that ferric ions in the solution first pillared the calcined montmorillonite and then exchanged with the lithium in its layers. This behavior may explain why the iron ion leaching process maintained a persistent lithium release (or gradually declined) based on clay calcined at 800 °C, while the sulfuric acid process reached a lithium efficiency of approximately 50% according to Gu et al. (2020a). The present work showed that 600 °C is suitable as the optimal calcination temperature.

On the other hand, the aluminum leaching efficiency was in the range of 12.3–16.3% when the clay was subjected to calcination from 500 to 800 °C. Even though the leaching efficiencies of aluminum were much lower than those of lithium from the solid samples, the concentrations of aluminum were much higher than those of lithium in the solutions. Aluminum separation would be challenging in a subsequent operation. In this study, the aluminum leaching efficiencies were a little lower than those in the process using sulfuric acid, indicating that the ion-exchange leaching process using ferric ions is selective for lithium. Also, the leaching solutions were beneficial for subsequent separation and purification.

### 3.1.2. Effect of leaching temperature

To investigate the effect of the reaction temperature, Li-bearing clay calcined at 600 °C was leached using a 15% ferric sulfate solution at different temperatures for 180 min with a solid-liquid ratio of 1 g: 5 mL. The lithium and aluminum extraction efficiencies are shown in Fig. 2, and the XRD patterns of the product calcined at 600 °C and the residues at different temperatures are illustrated in Fig. 3. As seen from Fig. 2, the lithium leaching efficiency increased substantially from room temperature (20 °C) to 80 °C, whereas from 80 to 90 °C, the change was relatively small, with an increase in lithium leaching efficiency from 69.9 to 73.6%. As reported in previous studies in the literature on the modification of montmorillonite with a ferric solution, the reaction temperature is important (Borgnino et al., 2009; Fang et al., 2016). Thus, increasing the reaction temperature facilitated formation of Fe-pillared montmorillonite and then favored the exchange process between ferric and lithium ions.

At different reaction temperatures, less than 15% of the aluminum was liberated, which can be attributed to the dissolution of Al-containing minerals, such as the aluminum oxide transformed from diaspora. It is worth noting that the aluminum leaching efficiencies were distinctly low in comparison to those observed in the process using sulfuric acid. This could be assigned to the fact that 15% ferric sulfate solution has a lower acidity level than that of 15% sulfuric acid solution, which affects the dissolution of aluminum oxide. This finding confirms

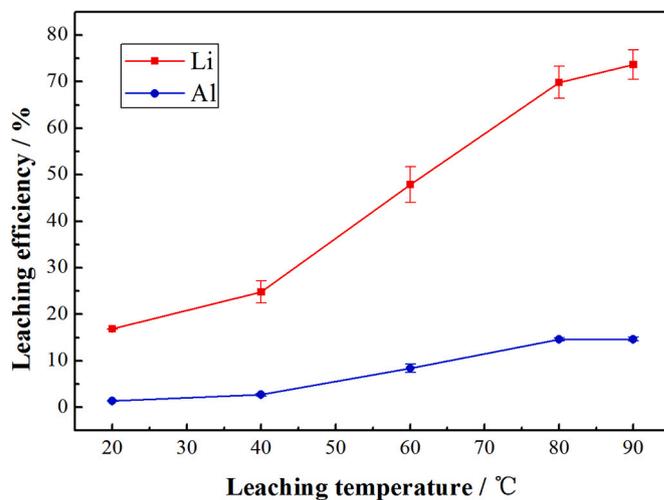


Fig. 2. Effect of the reaction temperature on the lithium and aluminum leaching efficiencies (15% ferric sulfate, 1 g: 5 mL, 180 min).

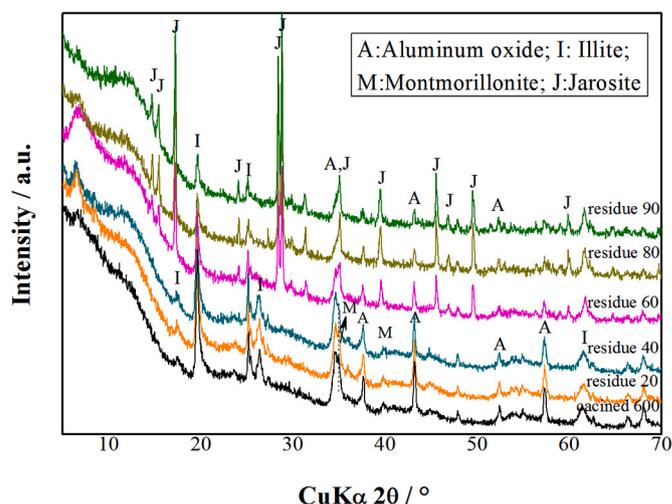


Fig. 3. XRD patterns of the calcined Li-bearing clay (at 600 °C) and the leach residues after using  $\text{Fe}_2(\text{SO}_4)_3$  at reaction temperatures of 20 °C (residue 20), 40 °C (residue 40), 60 °C (residue 60), 80 °C (residue 80), 90 °C (residue 90).

the better selectivity of the ferric sulfate solution for lithium extraction.

The lithium leaching efficiency increased with increasing reaction temperature; however, when the temperature was higher than 60 °C, a new phase of jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) was observed in the obtained residues (Fig. 3). Jarosite compounds occur widely in nature and are widely used to precipitate impurities in the metallurgical industry (Dutrizac and Chen, 2009); for example, precipitation of potassium jarosite causes passivation of chalcopyrite during leaching (Córdoba et al., 2009; Kartal et al., 2020). In the metallurgical industry, jarosite precipitation is widely used for iron removal as an impurity (Dutrizac, 2008). Here, the jarosite generated in the current study was considered to benefit from the removal of potassium impurities in the leaching solutions and also could precipitate superfluous ferric sulfate in solutions. As the reaction temperature increased, the concentrations of potassium (sodium) and superfluous iron in the leachate decreased gradually (Table S2), indicating the formation of jarosite and verifying a beneficial process. Thus, in terms of the ion-exchange leaching process of the present work, a reaction temperature of 90 °C was suggested to be optimal to achieve effective lithium extraction.

### 3.1.3. Effect of ferric sulfate concentration

The amount of ferric sulfate in the leaching process is important because various concentrations of ferric sulfate have different solution pH values. In this section, Li-bearing clay calcined at 600 °C was selected to investigate the variations in lithium extraction with different ferric sulfate concentrations. The concentration of ferric sulfate in the initial leaching solution was set at 0, 1, 2.5, 5, 10, 15, and 20%. In this process, the reaction temperature, solid-liquid ratio, and reaction duration, were maintained at 90 °C, 5:1 mL/g, and 180 min, respectively. As shown in Fig. 4, water leaching liberated only 4.65% of lithium from the calcined clay. However, this value increased significantly to 39.7% when 1% ferric sulfate was introduced, implying a significant effect of ferric ions. The extraction of lithium reached 73.6% when the ferric sulfate concentration was 15%. When the ferric sulfate concentration was set as 20%, 79.4% of the lithium could be leached, accompanied by an additional 4.44% aluminum (up to 19.1%) in the solution, which is an important impurity that will present difficulties for subsequent separation. Therefore, a concentration of 15% ferric sulfate was selected as the optimum concentration of the leaching reagent for lithium extraction.

### 3.1.4. Effect of the leaching time

The reaction time is an important factor affecting the lithium extraction efficiency. In this section, the influence of reaction time on Li extraction was investigated for durations from 10 to 240 min using Li-bearing clay calcined at 600 °C under the constant conditions of a 15% ferric sulfate solution, 90 °C, and a solid-liquid ratio of 1 g: 5 mL. The results are shown in Fig. 5. It can be observed that the lithium extraction efficiency reached close values of 73.6 and 73.9% at 120 and 180 min, respectively. A gradual increase in leaching efficiency in the early stage and a slight decrease at a reaction time of 240 min could be observed. The leaching time of 2–3 h was not long in comparison to the time required for lithium recovery from spodumene (Kuang et al., 2018; Xing et al., 2019). In addition, at 120 and 180 min, the aluminum leaching efficiencies were approximately 14.5%. The findings of this study suggest that 180 min is the optimal condition for lithium recovery from the clay sample.

## 3.2. Comparison of different reagents used for leaching

Since lithium in the montmorillonite interlayers can be exchanged by the ferric sulfate solution as discussed above, ferric chloride and nitrate were also investigated under the same conditions, and their lithium leaching extraction efficiencies (Figs. S1 and S2) were similar to that of the ferric sulfate solution. The highest lithium leaching efficiency

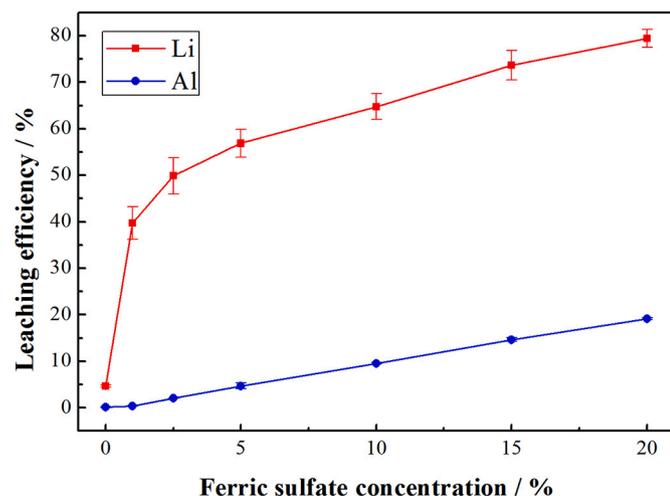


Fig. 4. Effect of the ferric sulfate concentration on the lithium and aluminum leaching efficiencies (1 g:5 mL, 90 °C, 180 min).

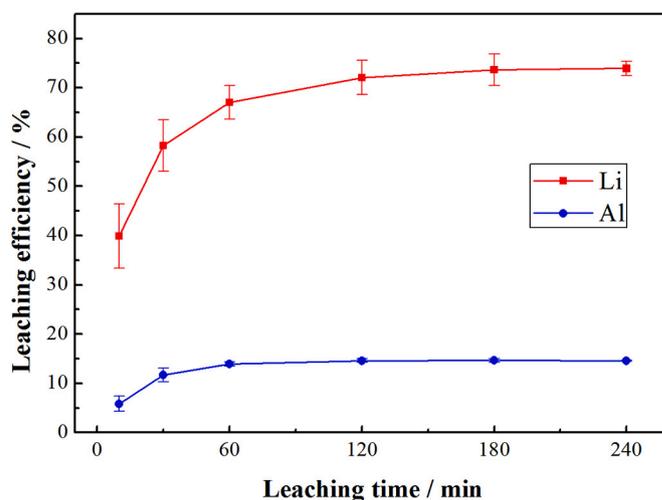
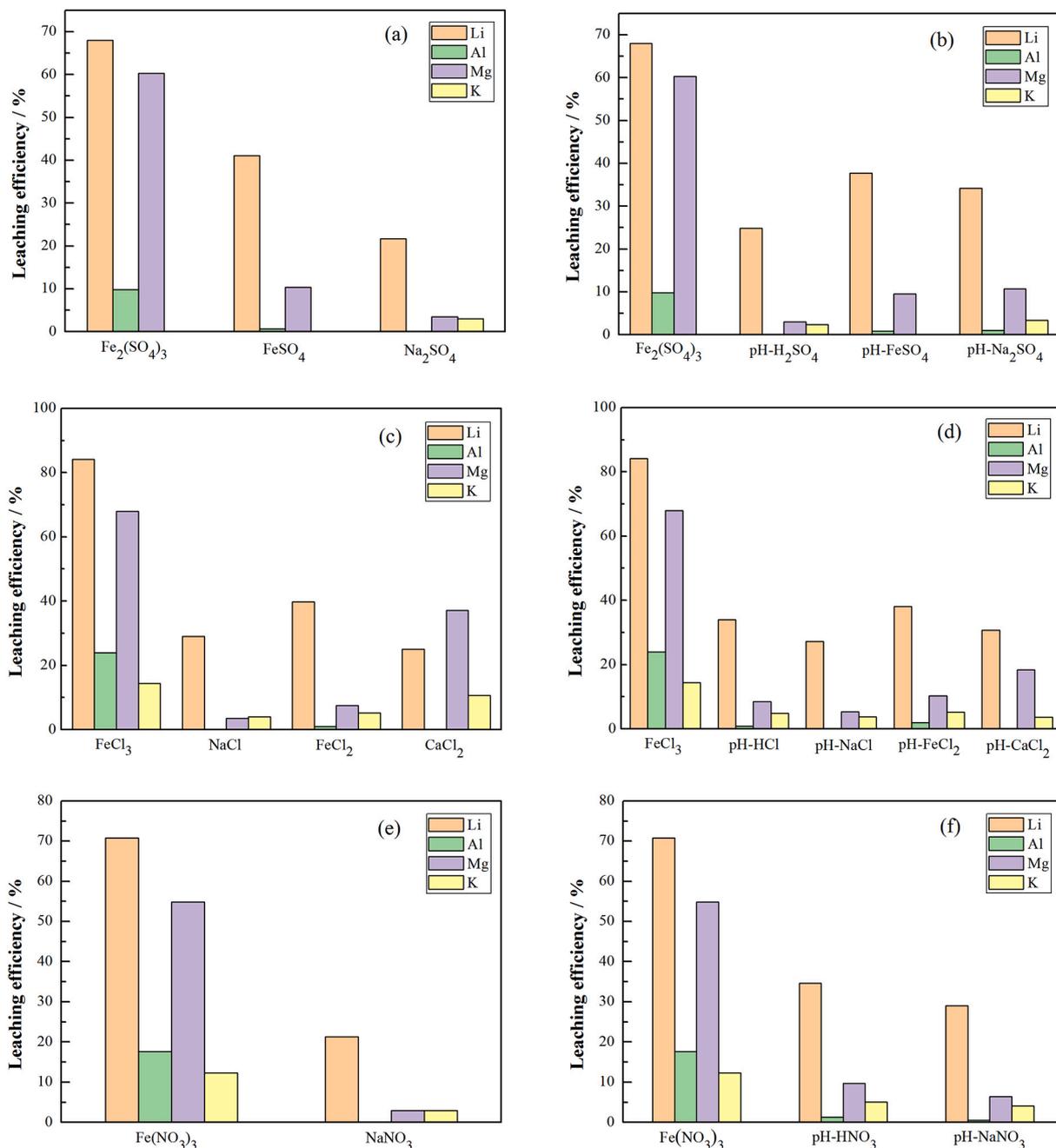


Fig. 5. Effect of the reaction time on the lithium and aluminum leaching efficiencies (15% ferric sulfate, 1 g: 5 mL, 90 °C).

achieved 90.3% when 15% ferric chloride was used at 90 °C, for 180 min, from clay calcined at 700 °C. In addition to the high leaching efficiencies, more important benefits of using ferric salt are that the leaching process is green and that weakly-acidic residues are discharged. For example, the pH of the leach residue obtained when using 15% ferric sulfate in this study was greater than 3.0, while 15% sulfuric acid generated residues with a pH of less than 1.0 (Gu et al., 2020a), even though these solutions have similar lithium leaching efficiencies. Although all the three ferric salts have proven to have selectivity for lithium extraction, sulfate that can be removed and separated by formation of jarosite, has been suggested as an appropriate agent for lithium leaching applications from clay-type lithium resources.

The cations commonly used for montmorillonite modification (Kozaki et al., 2005; Li et al., 2012; Zhang et al., 2019b) were selected for comparison to investigate the leaching efficiency in this study. Contrast experiments were performed at 90 °C for 180 min and using 10% cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Fe}^{2+}$ ), in sulfate, chloride or nitrate solutions. Moreover, to eliminate the influence of low pH caused by the hydrolysis of ferric ions, the pH of solutions of different cations were adjusted using the corresponding acids, and they were also compared under the same leaching conditions. All the obtained results are illustrated in Fig. 6. For the unadjusted solutions, as shown in Fig. 6 a, c, and e, the lithium leaching efficiencies of the three ferric solutions were: 10%  $\text{FeCl}_3$  > 10%  $\text{Fe}(\text{NO}_3)_3$  > 10%  $\text{Fe}_2(\text{SO}_4)_3$ . This trend could be generally ascribed to the available mole concentration of ferric ions. Ferric sulfate with a concentration of 10% has a higher amount of available ferric ions than ferric nitrate, but it presents a lower leaching efficiency than that of ferric nitrate, which may be due to ferric consumption in the jarosite precipitation process. Sodium and calcium ions can also substitute montmorillonite interlayer ions (Li et al., 2012); however, their lithium leaching efficiencies in this study were between 20% and 30%, which were significantly lower than those using ferric ions. Both ferric and ferrous ions could be adsorbed into the montmorillonite layers (Qin et al., 2015); nevertheless, as seen in Fig. 6 a and c, ferrous sulfate and ferrous chloride could exchange 37.7 and 39.8% of lithium, respectively, even with relatively low leaching efficiencies of impurities, such as aluminum and magnesium (Fig. 6 a, c). In conclusion, given the present leaching results, ferrous ions did not have an ideal lithium recovery.

Considering that 10% ferric sulfate, 10% ferric chloride and 10% ferric nitrate have a pH value of approximately 1.0 or less, dilute acids and 10% of sodium, calcium, and ferrous sulfate, chloride and nitrate were respectively adjusted using their corresponding acids and were used as lithium leaching agents. As shown in Fig. 6 b, c, and f, there was

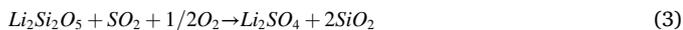
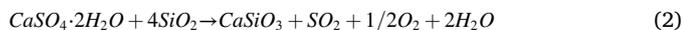


**Fig. 6.** Leaching efficiencies of metals using (a) 10% sulfates, (b) 10% sulfates adjusted to the same pH as that of ferric sulfate using sulfuric acid, (c) 10% chlorides, (d) 10% chlorides adjusted to the same pH as that of ferric chloride using hydrochloric acid, (e) 10% nitrates, and (f) 10% nitrates adjusted to the same pH as that of ferric nitrate using nitric acid.

a small promotion of lithium leaching in the pH-adjusted  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ , and  $\text{CaCl}_2$  system. On the other hand, a slight decrease in lithium leaching was observed for  $\text{FeSO}_4$ ,  $\text{FeCl}_2$  and  $\text{NaCl}$  after pH adjustment. The reason was not very clear, but it was certain that pH does not control the ion exchange process. Likewise, the dilute acids with the same pH value of their respective ferric salts did not present ideal lithium leaching efficiencies. Sulfuric acid was reported to be effective for lithium extraction, and the amount is one of the key factors (Gu et al., 2020a); however, the amount of acid used to adjust the pH in this study was too small to achieve a high extraction efficiency. In summary, these findings showed that ferric salts had good effectiveness for lithium extraction from the Li-bearing clay, and the ferric ion itself was crucial during the ion-exchange process instead of hydrogen ions in the system.

### 3.3. Mechanism of calcination and leaching

The process of lithium extraction from clay resources has been successively studied after the discovery of hectorite and Li-montmorillonite (Lalafari et al., 2019). Mild conditions such as water leaching, hydrothermal treatment and acid direct leaching can only release less than 1% of lithium from the clay (Crocker and Lien, 1987). High temperature treatment (approximately 1000 °C) of clay blending with additives converts silicates to sulfates, in which the structure of lithium-bearing mineral (hectorite) in clay is destroyed. The new-generated lithium sulfate can be separated in water solutions (Lien, 1985; Büyükburç and Köksal, 2005; Peerawattuk and Bobicki, 2018). The main reactions that occur at high temperatures are described in the following equations (Büyükburç and Köksal, 2005).



Analogously, lithium in the crystal structure of spodumene can be replaced by hydrogen or sodium ions when the monoclinic structure is subjected to high temperatures ( $> 1000\text{ }^\circ\text{C}$ ) (Kuang et al., 2018; Song et al., 2019; Karrech et al., 2020). It seems that high temperature treatment can cause the release of lithium in the structure of silicates. The above findings of lithium extraction from hectorite clay and those from other Li-bearing clay confirm that lithium in the clays exists in the structure of silicates and that high temperature treatment is required for lithium extraction.

In the current study, lithium ions in the clay obtained from Guizhou and Yunnan, China (Wen et al., 2020; Gu et al., 2020a) are thought to exist in the layers of montmorillonite as one of the exchangeable cations connected by van der Waals forces. Compaction occurred during the clay sedimentation process and directly caused strong bonding between the mineral layers (Dellisanti et al., 2006; Chow et al., 2017). The Li-bearing clay samples in this study were dense rocks (Fig. S3), indicating a strong compaction process. For this reason, lithium cannot be exchanged from the clay directly, which is different from the cation exchange capacity of montmorillonite (Kozaki et al., 2010; Li et al., 2012; Chen et al., 2017). Even though the samples were treated by grinding, clay minerals still occurred as aggregates. Treatment with calcination caused the samples to disaggregate and generate gaps or cracks accompanied by the process of dehydroxylation of clay minerals and diaspore. Moreover, calcination probably causes a gradual collapse of the layer structure of the Li-bearing clay minerals (Gu et al., 2020a), leading to ease of ion exchange. The function of calcination of this system differs to the high temperature for treatment of other Li-bearing resources, e.g., hectorite and spodumene.

#### 4. Conclusions

Lithium-rich clay is a potential lithium resource. In this work, a novel, green, and efficient leaching process using a ferric salt solution was demonstrated for lithium extraction from calcined lithium-rich clay samples. Calcination treatment of Li-bearing clay was necessary for subsequent lithium extraction. When ferric sulfate was used as the leaching reagent, up to 64.2–73.6% of lithium could be leached from samples calcined at 600–800  $^\circ\text{C}$ . High leaching temperatures can promote leaching efficiencies and result in the generation of jarosite to precipitate superfluous iron, sulfate and impurities. The most suitable ferric sulfate concentration and reaction time were suggested to be 15% ferric sulfate and 180 min, respectively, and under these conditions, 73.6% lithium was leached. Ferric chloride and ferric nitrate exhibited lithium leaching efficiencies similar to that of ferric sulfate under these conditions, while the ferrous, sodium and calcium salts leached no more than 39.8% of the lithium. It was concluded that ferric ions have good selectivity for lithium leaching. The leaching process was considered to involve ion exchange between ferric ions and lithium ions in the calcined clay sample.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.hydromet.2021.105759>.

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