



Extraction of lithium as lithium phosphate from bauxite mine tailings via mixed acid leaching and chemical precipitation

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ABSTRACT

Phosphate can be used to facilitate the concentration and precipitation of lithium from low-concentration solutions. In this study, a novel process has been developed to extract lithium as lithium phosphate from bauxite mine tailings, which includes: 1) leaching with mixed acid (H₃PO₄ + H₂SO₄), 2) leachate neutralization, and 3) Li₃PO₄ preparation. Mixed acid was used to effectively leach lithium (Li) without roasting pretreatment, the Li leaching rate can be up to 96.67%. Subsequently, NH₃·H₂O and H₂O₂ were used to separate Al and Fe from the leachate by chemical precipitation. After investigating the effects of the temperature, NH₃·H₂O concentration, and the dilution ratios of leachate and gel solution on the Li loss rate, we propose that the optimal conditions are: zero leachate dilution ratio, 45°C temperature, 6 mol·L⁻¹ NH₃·H₂O concentration, and a gel solution dilution ratio of one, which gives a 28.22% Li loss rate. In our experiment, lithium in the mother liquor was precipitated as Li₃PO₄ with Na₂CO₃. Our results provide a simple and effective route to extract lithium from low-Li resources.

1. Introduction

Lithium (Li) is an indispensable critical element for the development of new technology and green industry, and will remain a strategic material in the foreseeable future (Wadari et al., 2020; USGS, 2020). Global demand for lithium and its compounds has been increasing, and the supply pressure is mounting (Meshram et al., 2014; Swain, 2017; Alessia et al., 2021). Lithium is mainly extracted from brines, hard-rock ores, and Li-rich clays or sedimentary deposits (Kesler et al., 2012; Liu et al., 2019; Tadesse et al., 2019). In recent years, many studies were also dedicated to Li extraction from electronic waste, seawater, and other unconventional sources (Choubey et al., 2017; Ding et al., 2019; Song et al. 2020; Liu et al. 2020; Makuza et al., 2021; Tabelin et al., 2021). Unconventional Li resources like mining waste, deep-sea ferromanganese nodules and crusts, industrial waste (e.g., geothermal/desalination brines and coal fly ash), and effluents are also attracting more research attention (Tabelin et al., 2021).

Lithium-rich bauxite ores have been reported in the French Alps and

Guizhou, southwest China (Verlaguet et al., 2011; Wang et al., 2013), and Li is enriched in clay minerals in the mine tailings (Zhang et al., 2019). Bauxite resources in SW China are abundant, especially in Guizhou, and a large number of bauxite deposits have been mined (Sun et al., 2020). Voluminous tailings are accumulated around the mines, which occupied valuable land resource, destroyed local vegetation and forests, and induced desertification. Furthermore, metals in the tailings may diffuse into and pollute the surrounding land and water bodies, endangering the environment, and imposing health risks to plants, animals and human (Asuha et al., 2018; Xiao et al., 2015; Zine et al., 2020;). Therefore, efficient Li exploitation of the tailings is crucial to both future resource management and environmental safety, and that requires innovative techniques and technology (Van der Ent et al., 2021).

Because Li in bauxite mine tailings exists mainly in clay minerals, acid leaching and roasting are the main pretreatment methods. Compare with the roasting method, the acid leaching method is better in minimizing the problems of high energy consumption, high operational cost,

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and low recovery rate (Swain, 2017; Ma et al., 2021; Yelatontsev and Mukhachev, 2021). After acid leaching, the Li concentration remains low in the leachate. A number of methods such as precipitation (Zhang et al., 2019; Alsabbagh et al., 2021), adsorption (Zhang et al., 2016; Lai et al., 2020), ion-exchange (Arroyo et al., 2019), solvent extraction (Song et al., 2020; Song et al., 2019a; Song et al., 2019b), and membrane electrolysis (Torres et al., 2020) have been developed and tested, among which precipitation has the advantages of being simple and more feasible in industrialization.

The precipitation is based on the precipitation and concentration of lithium in Li-rich solutions. Lithium carbonate (Li₂CO₃) is one of the most common lithium products, which is prepared by adding saturated sodium carbonate (Na₂CO₃) to a Li-rich solution (Mendieta-George et al., 2022). However, the solubility constant of Li₂CO₃ is 2.50 × 10⁻² at 25°C (Liu et al., 2021). The traditional Na₂CO₃ precipitation method requires the evaporation and concentration of dilute Li solutions, which is usually inefficient and energy-consuming. A potential way to solve this problem is to use phosphate, aluminum, or fluoride to precipitate and concentrate Li from dilute solution (Pinna et al., 2017; Chen et al., 2015; Song et al., 2019a; Song et al., 2019b; Zhao et al., 2019; Liu et al., 2018). Since Li₃PO₄ is almost insoluble in water (0.38 g/L at 20°C) (Song and Zhao, 2018). Compared to other reagents such as fluoride and sodium carbonate, higher recovery rate is obtained from using phosphate reagent on dilute Li solution (Xiao and Zeng, 2018). Phosphates are generally used to facilitate the concentration and precipitation of the lithium contained in diluted liquors (Mahandra and Ghahreman, 2021; Mendieta-George et al., 2022; Çelebi, 2022; Wang et al., 2022). Subsequently, Li₃PO₄ can be converted into the more widely used forms of LiOH, Li₂CO₃ or LiFePO₄ (Song et al., 2019a; Song et al., 2019b; Wei et al., 2022). This serves as a potential way to effectively extract Li from low-concentration Li resources.

In this study, we attempted to find a Li (as Li₃PO₄) extraction process from bauxite mine tailings, which includes: 1) Mixed sulfuric- and phosphoric-acid leaching (without roasting) was used to pretreat bauxite mine tailings; 2) Chemical precipitation was tested to separate lithium from the leachate and precipitate lithium as Li₃PO₄ from the Li-bearing mother liquor. We proposed an effective Li₃PO₄ precipitation (from bauxite mine tailings) process, which is simple and potential for industrialization.

2. Geological features

The tailings in this study came from the Xiuwen Yunwushan bauxite mining area in central Guizhou. The area is tectonically located in the Guiyang Tectonic Deformation Zone (in the North Guizhou Anticline) of the Yangtze plate (Bureau, 1987). The bauxite-bearing rocks are from the Lower Carboniferous Jiujiayu Formation, which lies under the Lower Carboniferous Baizuo Formation dolomite, and above the Middle-Upper Cambrian Loushanguan Formation dolomite (Gao et al., 1992). Stratigraphic column of the local bauxite-bearing rocks in the study area is shown in Fig. 1, and is usually divided into the upper (aluminous) and lower (ferric) segment: The former contains aluminous claystone, and bauxite, whilst the latter contains hematite, ferruginous claystone and chlorite claystone. The tailings used here are aluminous claystone from segment. The aluminous claystone is largely grayish white, dense, massive, and contains mainly diaspore, boehmite, kaolinite, and anatase, and minor pyrite and hematite.

3. Experimental

3.1. Materials and methods

3.1.1. Materials

After crushing, grinding, screening, mixing and bagging, samples (grain size less than 74 μm) were obtained for the following chemical/mineral composition analyses and leaching experiment.

Formation	Thickness/m	Rock type			
C _{1b}	>1	// // // //	Dolomitic shale with laystone		
		— Al — Al — Al — Al —		Aluminous claystone	
		★			Bauxite
		— Al — Al — Al — Al —			
— — — — — — — — —	Claystone				
— Fe — Fe — Fe — Fe —		Hematite and ferruginous claystone			
Є ₂₋₃ ls			>1	// // //	Dolomite

★ Sampling position

Fig. 1. Stratigraphic column of the bauxite-bearing sequence.

3.1.2. Methods

X-ray fluorescence spectrometry (XRF) was used to analyze the chemical composition of tailings. The XRD is equipped with a copper target, and 2θ angles (5° to 75°) was adopted to measure the compositions of the ore, lithium phosphate and other products obtained from the experiment. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine the Al and Li concentrations in the solution. XRF, XRD and ICP-AES were carried out in the Mining College of Guizhou University. The morphologies of Li₃PO₄ precipitation were studied by field emission scanning electron microscopy (FE-SEM). FE-SEM was carried out in the Guizhou Laboratory of Coalfield Geology Bureau.

3.2. Procedures

A combined process (incl. leaching, leachate neutralization, and Li₃PO₄ preparation) was used to extract lithium from the tailings. Schematic diagram of Li₃PO₄ preparation from the tailings is illustrated in Fig. 2, and the operation procedures are described in detail below.

3.2.1. Leaching

According to liquid–solid ratio, the mixed acid was placed into a beaker, and the sample was slowly added. The beaker was placed on a magnetic heating agitator with leaching and stirring at 300 rpm. After leaching, the mixture was filtered to obtain leaching residue and leachate. The Li and Al contents of the leachate were measured, and the Li and Al leaching rates were calculated with the following formula:

$$\epsilon_i = \frac{c_i v_0}{m_0 \omega_i} \times 100\%$$

where ϵ_i = leaching rate of Li or Al (%).

m_0 = mass of tailing (g).

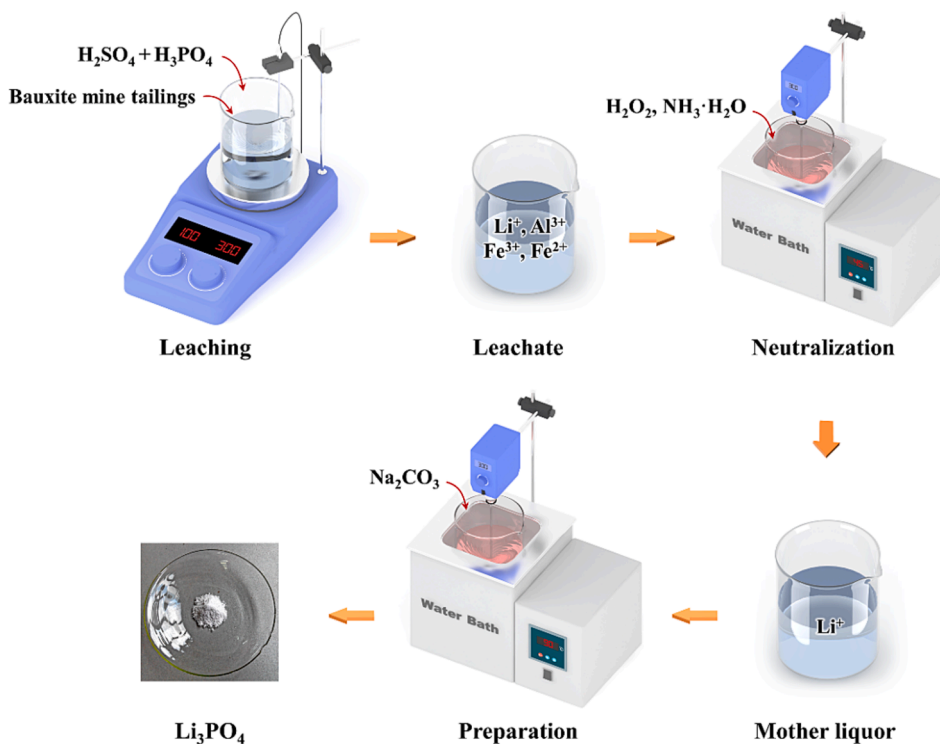


Fig. 2. Schematic scheme of Li_3PO_4 preparation from the bauxite mine tailings.

ω_i = content of Li or Al in tailings (%).
 c_i = content of Li or Al in leachate (g/L).
 v_0 = volume of leachate (L).

3.2.2. Neutralization of leachate

The leachate obtained was then poured into a beaker, and then placed into a water bath with heating and stirred at 300 rpm. Meanwhile, hydrogen peroxide was added and then $\text{NH}_3\cdot\text{H}_2\text{O}$ solution was slowly added to adjust pH to 5.5 to obtain an insoluble gel, which was immediately filtered to obtain the residue and Li-bearing filtrate. The Li and Al concentrations of the filtrate were then measured.

Table 1 shows the experimental conditions for the leachate

Table 1
 Conditions for the leachate neutralization experiment.

Conditions	Leachate dilution ratio	Temperature (°C)	$\text{NH}_3\cdot\text{H}_2\text{O}$ content ($\text{mol}\cdot\text{L}^{-1}$)	Gel solution dilution ratio
Leachate dilution ratio	0	25	6	0
	1			
	2			
	3			
	4			
Temperature	0	25	6	0
		35		
		45		
		55		
		65		
$\text{NH}_3\cdot\text{H}_2\text{O}$ content	0	45	4	0
			6	
			8	
			12	
			14	
Gel solution dilution ratio	0	45	6	0
				1
				2

neutralization. The effects of leachate dilution ratio (0, 1, 2, 3, 4), temperature (25, 35, 45, 55, 65°C), $\text{NH}_3\cdot\text{H}_2\text{O}$ concentration (4, 6, 8, 12, 14 $\text{mol}\cdot\text{L}^{-1}$), and gel solution dilution ratio (0, 1, 2) on the Li loss rate were studied, and the optimum conditions were determined. The neutralization effect is expressed by the Li loss rate, of which lower rate reflects better neutralization effect:

$$\eta_i = \left(1 - \frac{\rho_i v_1}{c_i v_0}\right) \times 100\%$$

where η_i = loss rate of Li (%).
 ρ_i = content of Li in filtrate (g/L).
 v_1 = volume of filtrate (%).
 c_i = content of Li in leachate (g/L).
 v_0 = volume of leachate (L).

3.2.3. Preparation of Li_3PO_4

The Li-bearing filtrate was evaporated, cooled, crystallized, and some crystals and a Li-bearing mother liquor were obtained. The mother liquor was then heated and stirred in the water bath. Sodium carbonate was slowly added into the mother liquor to a pH of ~ 8. The reaction was continued for 30 min. After the reaction, the obtained Li_3PO_4 was immediately filtered, washed with hot water, dried, and analyzed. The flowchart of Li_3PO_4 preparation from the tailings is illustrated in Fig. 3.

4. Results

4.1. Chemical compositions

Table 2 shows that Al_2O_3 (57.70%) and SiO_2 (22.90%) (followed by TiO_2) are the major components of the tailings, and the content of Al_2O_3 is higher than its content in most secondary resources, such as fly ash and coal gangue, whose Al_2O_3 content is 30–40% (Yao et al., 2014; Yang et al., 2020; Zhang and Zhang, 2019). The Li_2O content is 0.20%, which meets the grade of industrial ore (Wang et al., 2013). In general, the grades of Al_2O_3 and Li_2O show that the tailings have high comprehensive utilization value. The Al/Si value is 2.52, which is higher than the

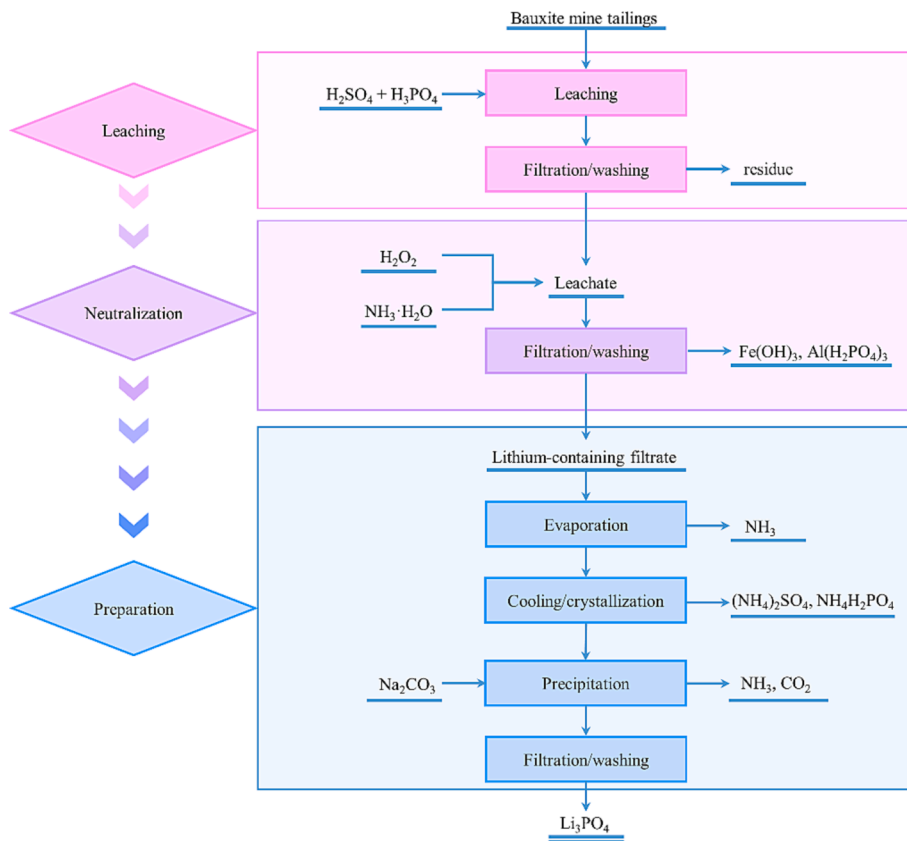


Fig. 3. Flowchart of Li_3PO_4 preparation from the bauxite mine tailings.

Table 2

Compositions of major element oxides of the bauxite mine tailing samples (%).

Al_2O_3	SiO_2	Li_2O	TiO_2	K_2O	TFe_2O_3	MgO	CaO	Al/Si
57.70	22.90	0.20	3.31	0.31	0.60	0.17	0.03	2.52

minimum value of 2 required by industry standards. TFe_2O_3 (0.60%), CaO (0.03%) and MgO (0.17%) account for less than 1% in total.

4.2. Minerals

Fig. 4 shows that the samples mainly comprise boehmite, kaolinite and anatase. The boehmite (an aluminum mineral) is the main component. And the kaolinite is clay mineral, which is a layered silicate. The Li occurrence in the tailings was measured in previous studies: Zhang and Zhang (2019) proposed that the lithium exists mainly in kaolinite and minor in boehmite. Such Li occurrence state indicates that the extraction of lithium from the bauxite mine tailings is difficult.

4.3. Leaching

Previous studies about the extraction of Li and Al from bauxite mine tailings by mixed acid treatment have achieved varying degrees of success (Zhang et al., 2021). Accordingly, the mixed acid leaching experiment was conducted under 100°C leaching temperature, 3 h leaching time, 4 mL/g liquid–solid ratio, and 300 rpm stirring rate. The results show that the leaching rates of Li and Al are as high as 96.67% and 88.35%, respectively (Table 3), indicating that the mixed acid treatment without roasting is feasible and efficient.

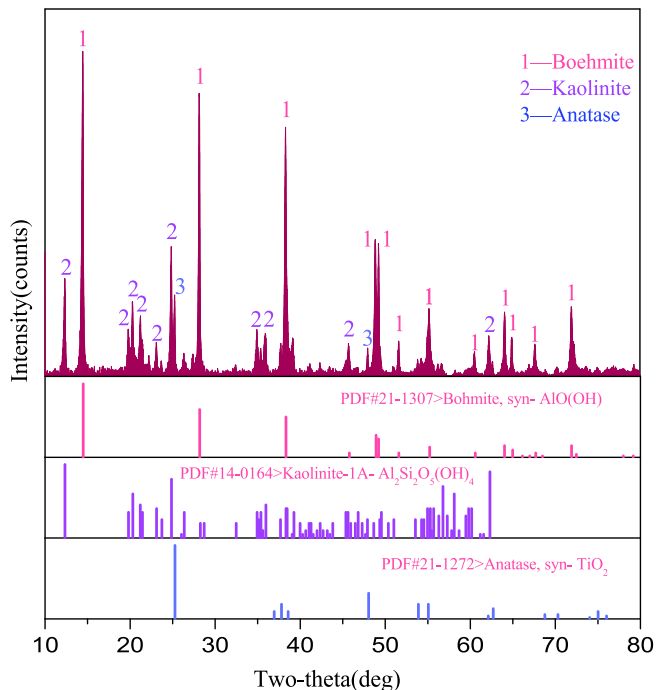


Fig. 4. XRD spectrum of the samples.

4.4. Neutralization

4.4.1. Dilution ratio of leachate

The influence of leachate dilution ratio on the Li loss rate is shown in

Table 3
Results of mixed acid leaching.

Element	Leaching rate (%)
Li	96.67
Al	88.35

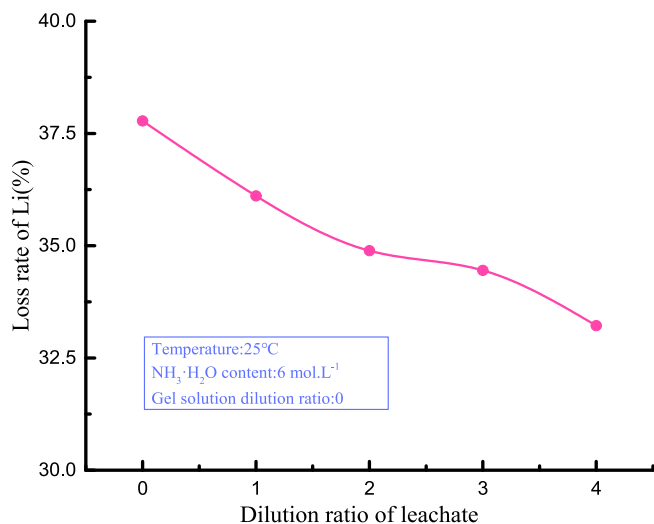


Fig. 5. Effect of leachate dilution ratio on the Li loss rate.

Fig. 5. The dilution ratio ranges from 0 to 4, and the experiment was conducted under 25°C, 6 mol·L⁻¹ NH₃·H₂O, and 0 gel solution dilution ratio. With increasing leachate dilution ratio, the Li loss rate decreases gradually, indicating that the leachate dilution ratio has certain effect on the Li loss rate. The dilution ratio increases with decreasing gel solution concentration, diffusion resistance, particle agglomeration, and the amount of enclosed/adsorbed lithium. Consequently, the Li loss rate decreases. After a certain point, continued leachate dilution would not further decrease the Li loss rate significantly. Although leachate dilution can help reducing Li loss in the neutralization process, it would also decrease the Li concentration in the leachate, and thereby makes its extraction more difficult. It also impacts the subsequent solid-liquid separation and evaporation. Therefore, we suggest that the leachate dilution ratio is zero.

4.4.2. Temperature

As shown in **Fig. 6**, the reaction temperature can influence the Li loss rate. The leachate dilution ratio, NH₃·H₂O content and gel solution dilution ratio are set at 0, 6 mol·L⁻¹, and 0, respectively. When the temperature increases from 25 to 45°C, the Li loss rate decreases and reaches a minimum (33.56%) at 45°C. When temperature increases from 45 to 65°C, the loss rate increases and tend to plateau. In a certain temperature range, increasing temperature can inhibit particle agglomeration, intensify thermal movement, and increase the number of effective collisions per unit time. It can also reduce the amount of Li⁺ enclosure/adsorption and thus its equilibrium concentration in the liquid-solid phase, and thereby lower the Li loss rate. However, if the temperature is too high, the adsorption rate increases, and the amount of Li⁺ adsorption per unit time increases. Meanwhile, the reaction rate to form Al(H₂PO₄)₃ is so fast that some lithium is enclosed before it can escape, and hence the Li loss rate increases. Considering that the Li loss rate reaches a minimum at 45°C, 45°C is selected as the optimal temperature for the neutralization.

4.4.3. NH₃·H₂O content

The NH₃·H₂O content has a clear influence on the Li loss rate, as shown in **Fig. 7**. Neutralization was carried out under 45°C, and zero

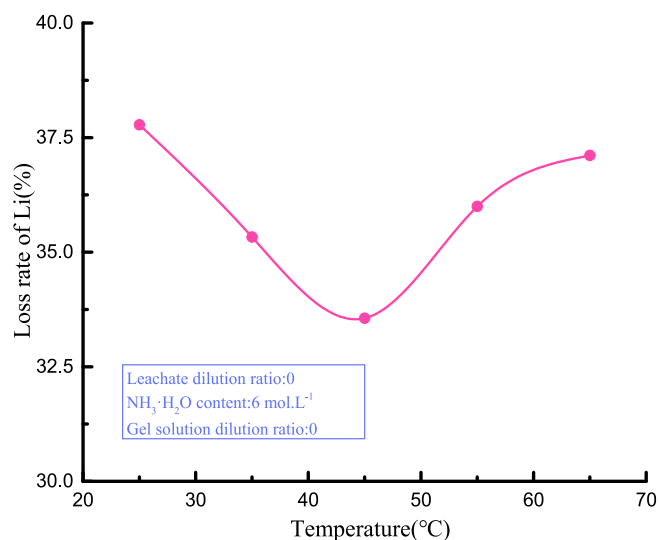


Fig. 6. Effect of temperature on the Li loss rate.

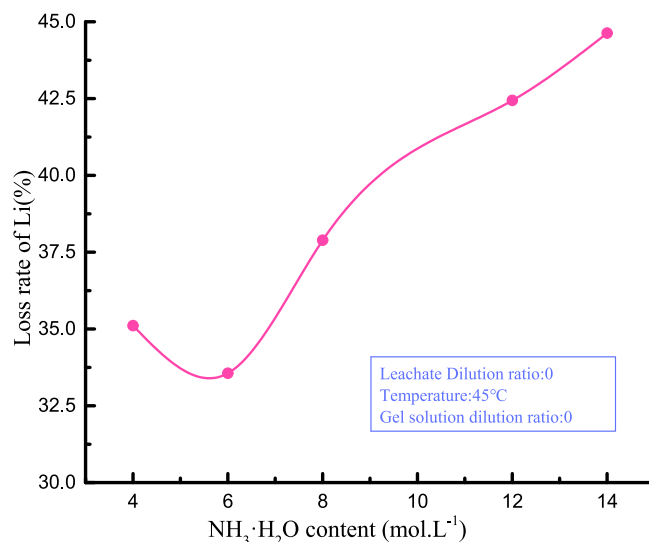


Fig. 7. Effect of NH₃·H₂O content on the Li loss rate.

dilution ratios of leachate and gel solution. With increasing NH₃·H₂O content, the Li loss rate decreases slightly. When the NH₃·H₂O content reaches 6 mol·L⁻¹, the Li loss rate reaches its minimum (33.56%). However, when the NH₃·H₂O content exceeds 6 mol·L⁻¹, the Li loss rate increases significantly. Since the NH₃·H₂O content affects directly the reaction rate, higher NH₃·H₂O content would give more alkalis, which increases the Al(H₂PO₄)₃ formation rate and larger particle agglomerates were formed. Consequently, the diffusion resistance in the solution increases, and more Li⁺ are enclosed, leading to higher Li loss rate. Conversely, lower NH₃·H₂O content would lead to slower reaction, forming finer particles with larger total surface area. This would increase the amount of Li⁺ adsorption and thus also the Li loss rate. Meanwhile, too low content of NH₃·H₂O would reduce the Li⁺ content in solution and increase the energy needed for evaporation. Hence, the optimal NH₃·H₂O content is 6 mol·L⁻¹.

4.4.4. Dilution ratio of gel solution

Fig. 8 shows that with increasing gel solution dilution ratio, the Li loss rate decreases greatly. The experiment was performed under 45°C, zero leachate dilution, and 6 mol·L⁻¹ NH₃·H₂O. Compared with leachate dilution, diluting the gel solution has a better effect. Hot water

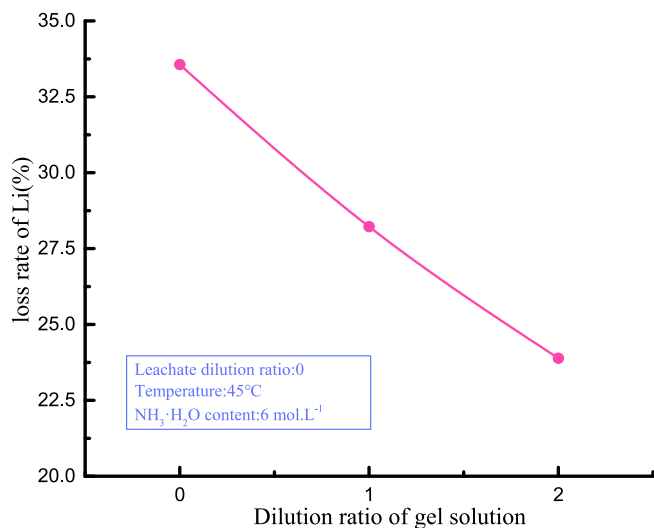
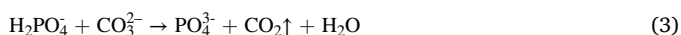
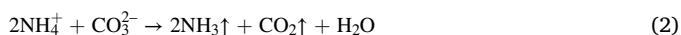


Fig. 8. Effect of gel solution dilution ratio on the Li loss rate.

(45°C) was added immediately after the reaction to dilute the gel solution. It is found that the higher the dilution ratio, the lower the Li loss rate. Because the reactions of formulas (11) were carried out in a hot acidic solution with high Al^{3+} concentration, substantial $\text{Al}(\text{H}_2\text{PO}_4)_3$ was generated, which significantly increased the diffusion resistance of the gel solution. The addition of hot water and stirring can reduce the gel viscosity, increase the chance of particle collision, and liberate some of the enclosed/adsorbed Li ions. Although continuous rise of the gel dilution ratio can further reduce the Li loss rate, the water to be evaporated and the associated energy consumption would increase immensely if the dilution ratio becomes too large. Therefore, the optimal gel dilution ratio is selected to be one, at which the Li loss rate is 28.22%.

4.5. Preparation

In this experiment, Na_2CO_3 was utilized to produce Li_3PO_4 . After adding Na_2CO_3 , CO_3^{2-} first reacted with H^+ to produce CO_2 , and then it underwent a double hydrolysis reaction with NH_4^+ , releasing large amount of NH_3 and CO_2 . Afterward, H_2PO_4^- reacted with CO_3^{2-} to form PO_4^{3-} and CO_2 . Due to the large amount of NH_4^+ and H_2PO_4^- in the concentrated solution, much of the Na_2CO_3 would be consumed. To avoid introducing too much water, solid Na_2CO_3 was added. Li^+ can react with PO_4^{3-} and CO_3^{2-} to form white Li_3PO_4 and Li_2CO_3 precipitates. But the solubility product of Li_3PO_4 (2.37×10^{-11}) is much lower than that of Li_2CO_3 (2.50×10^{-2}) (Liu et al., 2021), and precipitation generally proceeds toward the one with lower solubility product. Therefore, Li^+ would combine with PO_4^{3-} to form Li_3PO_4 instead of Li_2CO_3 . For the Li_3PO_4 preparation, the optimal pH is around 6 to 9 (Xiao and Zeng, 2018) and the optimal temperature is generally 90°C (Liu et al., 2021). Due to the large amount of Na^+ introduced by the addition of Na_2CO_3 , some Na_2SO_4 and Na_3PO_4 would be crystallized from the cooling saturated solution, which needs to be washed with hot water during the filtration to avoid affecting the Li_3PO_4 purity. Major chemical reactions that occur during the Li_3PO_4 preparation include:



4.6. Characterization of Li_3PO_4

4.6.1. XRD analysis

Fig. 9 represents XRD spectrum of the white precipitate using Na_2CO_3 and the JCPDS standard spectrum of Li_3PO_4 , respectively. The diffraction peaks of the white precipitate are in good agreement with their respective reference peaks of Li_3PO_4 standard spectrum, which confirms the white precipitate is Li_3PO_4 .

4.6.2. SEM analysis

As shown in SEM image (Fig. 10), the Li_3PO_4 particles (size: $\sim 1 \mu\text{m}$) are small and prismatic, and these small particles agglomerate to form larger clusters. The crystalline morphology of Li_3PO_4 particles is good and uniform.

5. Discussion

5.1. Mechanism of leaching

Both kaolinite and boehmite are insoluble, and it is ineffective to leach lithium from the bauxite mine tailings by sulfuric acid treatment without roasting. To strengthen the direct leaching process and improve the Li leaching rate, phosphoric acid was used to form a mixed leaching agent with sulfuric acid. Since phosphoric acid has strong coordination ability after hydrolysis and form complex ions with metals (Li and Zhao, 2016), phosphoric acid has good solubility for many insoluble minerals.

According to the dissociation constants of phosphoric and sulfuric acid at 25°C and atmospheric pressure (Table 4) (Xiao and Zeng, 2018), sulfuric acid hydrolyzes more readily than phosphoric acid in the mixed acid solution. Sulfuric acid dissociates H^+ to inhibit the dissociation process of phosphoric acid in formulas [6] and [7], and phosphoric acid exists mostly in the form of phosphoric acid and dihydrogen phosphate. Kaolinite and boehmite have layered structures connected by hydrogen bonds between each unit layer. In the strong acid solution provided by sulfuric acid, the hydrogen bonds on the aluminium-oxygen octahedron surface are readily broken, Li and Al are exposed to react with phosphoric acid to generate heteropoly acids or heteropoly acid salts, which promotes the dissolution of kaolinite and boehmite. The leaching reaction of Li and Al in tailings with mixed acid is shown in formulas [10] and [11] (Zhang et al., 2021). As the reactions proceed, the hydrolysis of phosphoric acid increases. Mixed acid is gradually consumed by the reaction, and Li and Al are efficiently leached from the tailings.

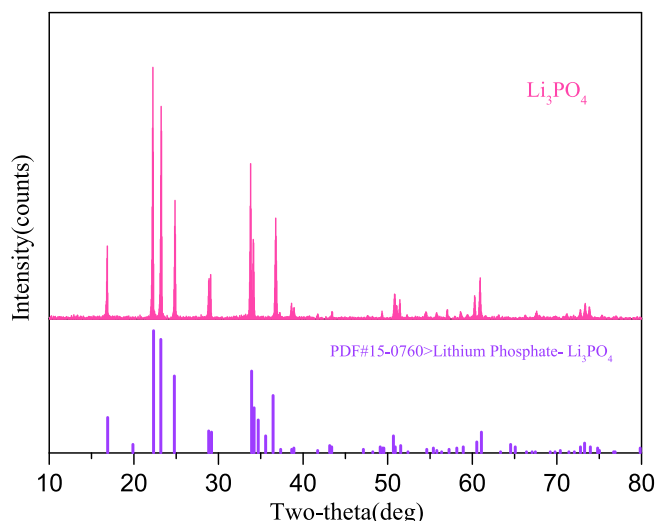


Fig. 9. XRD spectrum of Li_3PO_4 .

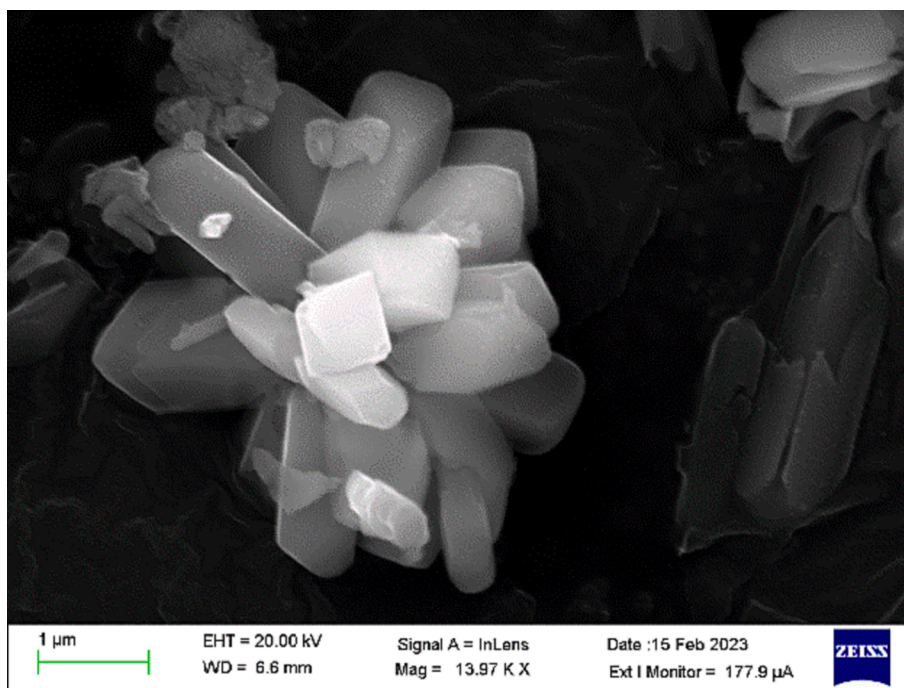


Fig. 10. SEM image of Li_3PO_4 particles.

Table 4

Dissociation constants of sulfuric and phosphoric acids.

No.	Acid	Formulas	K_a	$\text{p}K_a$
[5]	H_3PO_4	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	$7.52 \times 10^{-3} (K_1)$	$2.04 (\text{p}K_1) 7.20$
[6]		$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$	$6.31 \times 10^{-8} (K_2)$	$(\text{p}K_2) 12.36$
[7]		$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$	$4.4 \times 10^{-13} (K_3)$	$(\text{p}K_3)$
[8]	H_2SO_4	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	$1.0 \times 10^3 (K_1)$	$-3.0 (\text{p}K_1) 1.99$
[9]		$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$1.02 \times 10^{-2} (K_2)$	$(\text{p}K_2)$

$3\text{Li}_2\text{O}_{(s)} + 2\text{H}_2\text{SO}_{4(q)} + 2\text{H}_3\text{PO}_{4(q)} = 2\text{H}_2\text{LiPO}_{4(q)} + 2\text{Li}_2\text{SO}_{4(q)} + 3\text{H}_2\text{O}_{(q)}$ [10].
 $3\text{Al}_2\text{O}_{3(s)} + 6\text{H}_2\text{SO}_{4(q)} + 4\text{H}_3\text{PO}_{4(q)} = 2\text{H}_3\text{Al}(\text{PO}_4)_2(q) + 2\text{Al}_2(\text{SO}_4)_3(q) + 9\text{H}_2\text{O}_{(q)}$ [11].

5.2. Mechanism for neutralization

Precipitation method is the earliest utilized in industrial plants, which has several advantages, such as simple process, low cost, and feasibility. It has been intensively studied for lithium extraction from an economical perspective in the past decades (Swain, 2017). Therefore, pretreatment of the leachate via precipitation method is generally used to separate Li from other metal ions. After precipitation, the filter liquors are then obtained for lithium extraction.

The highest concentration of ion in the leachate is Al^{3+} , followed by small amount of Fe^{3+} and Fe^{2+} . The content of CaO and MgO is 0.03% and 0.17% each (Table 2), Mg^{2+} and Ca^{2+} in the leachate is not considered here. Al^{3+} is quite abundant in the leachate, whereas Li concentration is relatively low. Thus, most of Al need to be removed, and then the general flowsheet of evaporation and crystallization is applied to facilitate the concentration of Li contained in filter liquors. The precipitation of metal ions is mainly controlled by pH value. Al^{3+} , Fe^{3+} and Fe^{2+} are separated by precipitating at different pH values. The pH values for complete precipitation of Fe^{3+} , Al^{3+} and Fe^{2+} are 4.1, 5.2 and 9.7, respectively (Zhang et al., 2019; Xiao and Zeng, 2018). Among them, it is noteworthy that Fe^{2+} is not precipitated separately, and is likely oxidized by H_2O_2 to Fe^{3+} . The leaching agent is sulfuric and phosphoric acids, so it is strongly acidic. $\text{NH}_3 \cdot \text{H}_2\text{O}$ are commonly used to neutralize acidic solutions. In this study, $\text{NH}_3 \cdot \text{H}_2\text{O}$ is added to neutralize the leachate to precipitate Fe^{3+} and Al^{3+} completely, the pH of the

neutralization is 5.5.

Important chemical reactions during the leachate neutralization are summarized in Table 5. Hydrogen peroxide firstly oxidized Fe^{2+} to Fe^{3+} , during which the solution changed from light green to light yellow, the reaction is shown in formulas [12]. When the pH was less than 2, formulas [13] is the main reaction. The K_a of sulphuric acid is greater than that of phosphoric acid as shown in formulas [5], [8] and [9], which indicates that $\text{NH}_3 \cdot \text{H}_2\text{O}$ reacted with H^+ dissociated by sulfuric acid at first. Fe^{3+} and Al^{3+} mostly existed in form of soluble salts, such as $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$. When the pH was greater than 2, sulfuric acid was completely consumed by $\text{NH}_3 \cdot \text{H}_2\text{O}$, small amount of reddish-brown precipitate appeared, Fe^{3+} began to precipitate as $\text{Fe}(\text{OH})_3$, which ended until the pH reached 4.1. The reaction can be seen in formulas [14]. When the pH was ~ 3 , small amount of white $\text{Al}(\text{H}_2\text{PO}_4)_3$ appeared, gradually forming an insoluble gel. Because $\text{NH}_3 \cdot \text{H}_2\text{O}$ started to react with H^+ dissociated by phosphoric acid, at the same time, H_2PO_4^- combined with Al^{3+} to generate $\text{Al}(\text{H}_2\text{PO}_4)_3$, as shown in formulas [15]. After the reaction, the pH value of the solution is ~ 5.5 , sulfuric and phosphoric acid existed mainly as SO_4^{2-} and H_2PO_4^- (Table 4), Li^+ occurs in the form of soluble Li_2SO_4 and LiH_2PO_4 . However, due to the high Al content in the leaching solution, lithium would be enclosed and adsorbed on the generated $\text{Al}(\text{H}_2\text{PO}_4)_3$ in the reaction, resulting in Li loss.

6. Conclusions

From our experimental results, we propose a simple yet effective procedure to extract lithium as lithium phosphate from bauxite mine tailings. The Li_2O content in tailings is 0.20%. Li was leached by mixed acid ($\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4$) without roasting pretreatment, and the Li leaching rate can reach 96.67%. Using chemical precipitation, Li can be

Table 5

Major types of chemical reactions during the leachate neutralization.

No.	Ion	Reaction	pH
[12]	Fe^{2+}	$2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$	1 ~ 2
[13]	H^+	$\text{H}^+ + \text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$	1 ~ 5.5
[14]	Fe^{3+}	$\text{Fe}^{3+} + 3\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 \downarrow + 3\text{NH}_4^+$	3 ~ 4.1
[15]	Al^{3+}	$\text{Al}^{3+} + 3\text{H}_2\text{PO}_4^- \rightarrow \text{Al}(\text{H}_2\text{PO}_4)_3 \downarrow$	3 ~ 5.5

separated from Al and Fe in the leachate by using H_2O_2 and $\text{NH}_3\cdot\text{H}_2\text{O}$ during the neutralization. Nevertheless, Li would be enclosed and adsorbed on the precipitated $\text{Al}(\text{H}_2\text{PO}_4)_3$ and $\text{Fe}(\text{OH})_3$, resulting in Li loss. Thus, the effects of temperature, $\text{NH}_3\cdot\text{H}_2\text{O}$ content, and the dilution ratio of leachate and gel solution on the Li loss rate were explored. We have determined the optimal conditions to be: 45°C , zero leachate dilution, $6\text{ mol}\cdot\text{L}^{-1}$ $\text{NH}_3\cdot\text{H}_2\text{O}$, and the dilution ratio of gel solution is one. This gives a Li loss rate of 28.22%. In the process of preparation, Li was effectively precipitated as Li_3PO_4 by adding Na_2CO_3 from the mother liquor. The proposed procedure has the potential advantage of extracting lithium from low-Li resources.

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.

Data availability

No data was used for the research described in the article.

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