



Selective removal of magnesium from a lithium-concentrated anolyte by magnesium ammonium phosphate precipitation

Lihua He^{a,b}, Wenhua Xu^b, Yunfeng Song^b, Xuheng Liu^b, Zhongwei Zhao^{b,*}

^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

^b School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, PR China



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ABSTRACT

Magnesium was selectively removed from a lithium-concentrated anolyte (containing Li 3.5 g L⁻¹ and Mg 14.4 g L⁻¹) by MgNH₄PO₄ precipitation method. Firstly, thermodynamic analysis of the systems Li⁺-Mg²⁺-PO₄³⁻-H₂O and Li⁺-Mg²⁺-PO₄³⁻-NH₄⁺-H₂O were studied, and the optimal operating windows in which magnesium removal is the most probable were identified. Based on the theoretical considerations, Mg₃(PO₄)₂ and MgNH₄PO₄ precipitation methods were used to remove magnesium from our lithium-concentrated anolyte, and the results showed that MgNH₄PO₄ precipitation method exhibits better performance than that of Mg₃(PO₄)₂ on the complete removal of magnesium. Under the conditions of 1.0 times of theoretical amount dosage of (NH₄)₃PO₄ and pH value 8.0, the concentration of magnesium was reduced to 11.1 mg L⁻¹, and the lithium concentration maintained 3.46 g L⁻¹, corresponding with the magnesium removal rate 99.92%, and the lithium recovery rate 98.91%. The obtained MgNH₄PO_{4(s)} precipitate was a well-crystallized bulky particle, and it is in favour of filtration. Especially, it can be used as NP compound fertilizer, which is great beneficial for reducing the costs of magnesium removal.

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1. Introduction

Since lithium battery has become more and more important as a potential new energy carrier in the world, increasing importance has been attached to the production of lithium metal and compounds [1]. In addition, the global market share of lithium used in batteries has grown significantly over the last few years. In China, for example, the price of battery-grade lithium carbonate has risen from about US\$ 6400 in 2015 to US\$ 12,000 per ton. Currently, salt-lake brines are considered as the great potential and valuable resources of the development of lithium industry in the world, and 85% of the Li produced globally is obtained from salt-lake brine [2]. Nevertheless, due to the similar chemical properties of Mg²⁺ and Li⁺, the recovery of lithium from salt lake containing high magnesium/lithium ratio is a key technical problem in the development of salt lake brine. In some areas of the world, such as the Qinghai region in China, its salt lakes exhibit characteristically high mass ratio of Mg/Li (Mg/Li reaches 40:1 and may be greater than 1800:1 in some cases) [3,4], which is difficult to extract the lithium efficiently. As another example, Uyuni

Salar brine as the largest reserves of lithium lake on earth, has still not been large-scale economically developed due to its high Mg/Li ratio (Mg/Li = 12–22:1) [5,6].

In our previous work [7–9], a new approach for lithium recovery from high Mg/Li ratio salt lake brine using LiFePO₄/FePO₄ as adsorbing materials was explored. By establishing a new electrochemical system of “LiFePO₄ (anode)|supporting electrolyte|anion-selective membrane|brine|FePO₄ (cathode)”, Li⁺ can be selectively extracted from brine in cathode chamber (Li⁺ intercalation in FePO₄ to form LiFePO₄, Li⁺ + FePO₄ = LiFePO₄), meanwhile Li⁺ is concentrated in the supporting electrolyte of anode chamber (Li⁺ deintercalation in LiFePO₄ to re-form FePO₄, LiFePO₄ = Li⁺ + FePO₄). Exchanging the negative electrode and positive electrode, and then restart the electrolytic process, lithium can be extracted continually from the brine and be concentrated in the supporting electrolyte.

Currently, the Qinghai Yiliping salt lake brine in China (chemical compositions: Li 97.5 mg L⁻¹, Mg 13.14 g L⁻¹, Mg/Li ratio 134.4) was treated by this method, and a low Mg/Li ratio lithium-concentrated anolyte (the chemical compositions: Li 3–4 g L⁻¹, Mg 9–12 g L⁻¹, Mg/Li ratio about 4, pH value 6–8) was obtained. In order to produce high quality lithium compounds, such as Li₂CO₃, LiCl and LiOH, the primary task is to remove the impurity magnesium from the lithium-concentrated anolyte.

* Corresponding author at: School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, PR China.

E-mail address: zhaozw@csu.edu.cn (Z. Zhao).

Hitherto, many researches have been done in the separation of magnesium and lithium like precipitation [1,10], adsorption [11–13], solvent extraction [14–16] and nanofiltration [17–19], etc. For the precipitation method, the common operation is to use NaOH or Na₂CO₃ as the precipitant basing on the different solubility of Mg(OH)₂/LiOH and MgCO₃/Li₂CO₃. However, the precipitates of Mg(OH)₂ and MgCO₃ which always has a high surface area results in a large number of lithium entrainment loss [20]. The adsorption method can extract lithium selectively from the Mg/Li mixed solution, but it needs to find the absorbent easily prepared with high adsorption capacity, and the granulation of the absorbent for lithium recovery still faces great challenges for industrial application. Similarly, the solvent extraction methods expressed an excellent efficiency for Mg/Li separation, but the entrainment of organic into aqueous solution is another problem, which results in secondary pollution. Moreover, the mother solution entrained organic may not be recycled in the “electrochemical lithium recovery system” mentioned above owing to the membrane poisoning by the entrained organic. Nanofiltration technology for the separation of magnesium and lithium has gained momentum in recent times, and this method is an efficient technique to reduce the Mg/Li ratio from a high Mg/Li ratio brine, but not suitable for deep removal of magnesium. For example, Bi et al. [17] used the nanofiltration membrane to separate magnesium from saline lake brine, the mass ratio of Mg/Li decreased from 40 in feeds to 0.9. For another example, Li et al. [19] reported that by using a polyamide composite nanofiltration, the Mg/Li ratio decreased from initial 20:1 in the feed to 7.7:1 in the permeate.

Each method mentioned above has its own shortcomings or working restrictions, they are not suitable for removing magnesium from our lithium-concentrated anolyte. Remarkably, Mg²⁺ existing in this anolyte is defined to be an impurity, but it also used as a precipitant for phosphorus removal and NH₃-N wastewater treatment because the stable precipitate of Mg₃(PO₄)₂ or MgNH₄PO₄ [21–24]. Therefore, we postulate if taking an opposite approach, is it feasible to remove Mg²⁺ by using PO₄³⁻ as the precipitant? Actually, there is no doubt about that. The difference is, however, Li⁺ in solution also maybe precipitates as solid phase Li₃PO₄ with PO₄³⁻. In fact, Xiao et al.'s [25] have been studied the thermodynamics of Mg removal from lithium chloride solutions via a phosphate precipitation method. Nevertheless, their research focused on the removal of macro amount of Mg from a LiCl solution (14.95 g/L Li₂O and 0.45 g/L Mg²⁺, Mg/Li ratio 0.064), and great attention was paid on the residual concentration of Mg²⁺ in solution. However, the variation of lithium concentration was ignored, because a small amount of MgNH₄PO₄ slag cannot cause a large lithium loss in general. For the pending lithium-concentrated anolyte, in contrast, it is a higher Mg/Li ratio solution (Li 3–4 g L⁻¹, Mg 9–12 g L⁻¹, Mg/Li ratio about 4). Besides the residual concentration of Mg²⁺ in solution, how to avoid the entrainment loss of lithium is another crux. Therefore, the key to magnesium removal from the anolyte is to ensure that Mg₃(PO₄)_{2(s)} or MgNH₄PO_{4(s)} can precipitate preferentially. Another emphasis is to promote the phase conversion of Li₃PO_{4(s)}, which may be formed in instant of feeding, to Mg₃(PO₄)_{2(s)} or MgNH₄PO_{4(s)}, and finally achieving the selective removal of a large amount of Mg²⁺ from the low lithium concentration anolyte.

In this study, the predominance-area and distribution diagrams of Li⁺-Mg²⁺-PO₄³⁻-H₂O and Li⁺-Mg²⁺-PO₄³⁻-NH₄⁺-H₂O systems were studied in the first stage to predict the optimal operating windows for the separation of magnesium and lithium by using phosphate precipitation methods. Furthermore, the separation experiments were subsequently carried out to separate magnesium and lithium, also to verify the above assumption.

2. Experimental section

The chemical compositions of the lithium-concentrated anolyte are Li⁺ 3.5 g L⁻¹, Mg²⁺ 14.4 g L⁻¹. The separation process was carried out in a 200 mL three-necked flask equipping with a magnetic stirrer, a thermometer and a pH electrode. Firstly, 100 mL anolyte was added to the three-necked flask, and then a certain amount of Na₃PO₄ or (NH₄)₃PO₄ was added to the prepared anolyte. The pH values of the solutions were adjusted by 1.0 mol L⁻¹ NaOH and/or 5.0 mol L⁻¹ HCl. After stirring at room temperature for 2 h, the slurry was aged at temperature 80 °C for 3 h. Subsequently, the precipitates were collected by filtration and washed several times with deionized water. Then the obtained precipitates were dried at 80 °C for 8 h in an electricity heat drum wind drying oven. All reagents used were of analytical grade.

The concentrations of Li⁺ and Mg²⁺ in the filtrate (mother solution) were measured by AAS (Atomic Absorption Spectrometry, Persee of Beijing, China) and ICP-AES (IRIS intrepid XSP, Thermo Electron Corporation), respectively. X-ray diffraction (XRD) profiles of the precipitates were measured with TTR-III (Cu Kα radiation, Rigaku Corporation) at a speed of 6°/min. The particle morphology was observed by SEM (JXA-8800R, JEOL Ltd.).

3. Thermodynamic approach for Mg²⁺ removal

To find the optimal conditions for magnesium removal by phosphate precipitation method from the lithium-concentrated anolyte, detailed researches of the thermodynamic properties of the Li⁺-Mg²⁺-PO₄³⁻-H₂O and Li⁺-Mg²⁺-PO₄³⁻-NH₄⁺-H₂O systems were done. To this end, the first step was inventorying the various species, which exist in the system. According to the reports in the literatures, 22 species (H⁺, OH⁻, NH₃, NH₄⁺, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, H₃PO₄, Li⁺, LiOH, LiHPO₄, LiNH₃, Li(NH₃)₂, Li(NH₃)₃, Mg²⁺, MgOH⁺, MgPO₄⁻, MgHPO₄, MgH₂PO₄⁺, MgNH₃²⁺, Mg(NH₃)₂⁺ and Mg(NH₃)₃⁺) were assumed to exist in the solution. Additionally, 5 insoluble compounds (Li₃PO_{4(s)}, MgHPO_{4(s)}, MgNH₄PO_{4(s)}, Mg₃(PO₄)_{2(s)}, and Mg(OH)_{2(s)}) were assumed to exist. This inventory leads to 22 equilibriums and 15 mass balance equations listed in Table 1, and each of them giving rise to an equation from the mass action law, in which the equilibrium constant values were taken from the handbook of chemistry edited by Kotrlý [26] and Spaight [27] respectively. In the second stage, various combinations of these equations were considered depending on the nature of the solid phases that may be in equilibrium with the solution, and 13 systems were considered (Table 2). For each system of equations, the room temperature aqueous system was also completely defined for each pH value. Among all the calculated possibilities (i.e., the 13 systems of equations), the most thermodynamically stable one, at a given value of pH, corresponded to the lowest total magnesium, lithium, ammonia and phosphate concentrations, and the solutions of these 13 systems were carried out via the Microsoft Excel 2013.

3.1. Li⁺-Mg²⁺-PO₄³⁻-H₂O system

To verify the feasibility of magnesium removal by PO₄³⁻ as Mg₃(PO₄)_{2(s)} formation in theory, the predominance-area and distribution diagrams of Li⁺-Mg²⁺-PO₄³⁻-H₂O system under the conditions of [Li]_Tⁱ = 0.5 mol L⁻¹, [Mg]_Tⁱ = 0.6 mol L⁻¹, [P]_Tⁱ = 0.4 mol L⁻¹ were calculated firstly, and the results were shown in Fig. 1.

As seen from Fig. 1(center), seven predominance-areas existed at the given pH values in the calculation system, and the stable solid phases varied from MgHPO_{4(s)} to Mg₃(PO₄)_{2(s)}, Li₃PO_{4(s)} and then Mg(OH)_{2(s)}, including two or three phases coexistence regions, with the increasing pH value in turn. More specifically,

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