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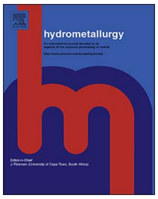

Recovery of both magnesium and lithium from high Mg/Li ratio brines using a novel process

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ABSTRACT

In this study, an integrated process was developed to separate and simultaneously recover both magnesium and lithium from brines. This technology includes production of magnesium-aluminum-carbonate-layered double hydroxide materials ($MgAlCO_3$-LDHs), removal of boron, CO_3^{2-}, and SO_4^{2-}, and precipitation of lithium carbonate. Factors such as water addition ratio, Mg^{2+}/Al^{3+} mole ratio, and lithium loss rate were investigated during $MgAlCO_3$-LDHs production. The effects of lithium concentration and $CO_3^{2-}/2Li^+$ mole ratio on lithium carbonate precipitation were also studied. It was found magnesium and lithium had been effectively separated after $MgAlCO_3$-LDHs production. The magnesium content in brine displayed a notable decrease from 117 g/L to less than 0.02 g/L with a lithium yield more than 95.0%. To concentrate lithium and precipitate lithium carbonate, 96.46% of boron, 99.2% of the CO_3^{2-}, and 99.56% of the SO_4^{2-} impurities were removed from the brine by adsorption, acidification, and precipitation, respectively. The lithium yield was more than 91% when lithium concentration in brine approximated 27 g/L and the $CO_3^{2-}/2Li^+$ mole ratio was 1.2. The purity of this product was 99.70%. Overall, this study provides an interesting vision for future integrated utilization of magnesium and lithium resources from salt lake brines with high Mg/Li ratio.

1. Introduction

Lithium, known as “the new energy metal promoting the world forward”, is widely used in lithium-ion batteries, aircraft alloys, aviation, atomic energy, medicine and other industries due to its unique electrochemical reactivity as well other properties (Feng and Zhang, 2003; Swain, 2017; Global Battery Markets, 2015; Availability of Lithium, 2016; Goonan, 2012; Diouf and Pode, 2015). In particular, the demand for lithium used in lithium ion batteries is huge and the estimated lithium ion batteries demand could increase to 66% of global lithium production by 2025 (Swain, 2017). This suggests that the demand for lithium will grow continually and rapidly over the next decade. Generally, the raw materials of lithium compounds are mainly obtained from brines and lithium-containing ores. Recovery of lithium from brine is an important means of bridging the gap between the supply and demand of lithium material because the majority, about 70%, of lithium resources are located in brines and the availability of lithium ores is limited (Song and Xiang, 2014). Furthermore, the recovery of lithium from brines is simple and inexpensive compared to hard-rock mining (Pranolo et al., 2015). Salt lakes containing lithium are mainly found in Chile, Argentina, Bolivia, USA, and China (Gruber et al., 2011). The mass ratio of Mg/Li in brines is often less than 8.0 in the first four countries listed (Song and Xiang, 2014; Vikström et al., 2013) and lithium can be extracted using a precipitation-based method. Representative salt lakes (Naumov and Naumova, 2010) used for industrial lithium production are Atacama in Chile, Hombre Muerto in Argentina and Silver Peak in the USA. However, in China, there is a characteristically high Mg/Li ratio in most lithium-rich salt lakes that often exceeds 40 with the highest being greater than 1000, making the difficulty to effectively separate magnesium and lithium from brines because the removal of Mg in large amount is costly in traditional processes by Mg precipitation. To extract lithium from high Mg-containing brine, many technologies have been developed, including solvent extraction (Xiang et al., 2016; Ji et al., 2016; Shi et al., 2017), electrodialysis (Ma et al., 2003; Ji et al., 2017; Liu et al., 2015), nanofiltration (Sun et al., 2015; Somrani et al., 2013), ion exchange and adsorption (Lawagon et al., 2016; Shi et al., 2011). However, the main issue faced by these technologies is only focused on the lithium extraction leaving the magnesium utilized ineffectively and discarded back into lakes. This represents the wasting of a valuable magnesium

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resource and is associated with high levels of environmental pollution. Thus, different studies have discussed comprehensive exploitation and recovery of lithium and magnesium resources from brine in order to realize sustainable development for future society.

Layered double hydroxides (LDHs), also called hydrotalcites or hydrotalcite-like materials, are a class of synthetic anionic clays with a general formula is $[M^{II}_{1-x}M^{III}_{x}\text{-}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$. M^{II}, M^{III} and A^{n-} represent divalent and trivalent cations in the layers and anions in the interlayer, respectively. x is the molar ratio of $M^{III}/(M^{II}+M^{III})$ and y represents the amount of water located in the interlayer galleries. The identities of the di- and trivalent cations and the interlayer anion (A^{n-}), and the value of the stoichiometric coefficient (x) widely vary, resulting in a large class of isostructural materials. The structure of the layers in LDHs resembles that of brucite-like layers in $Mg(OH)_2$ in which some of the divalent cations are replaced with trivalent ions, resulting in positively charged sheets. The typical material of this class is $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$ ($MgAlCO_3$-LDHs), which is the naturally occurring mineral hydrotalcite.

$MgAlCO_3$-LDHs are among of the most important magnesium-based function materials and are widely used as catalysts, sorbents, hosts for nanoscale reactions, and additives to plastic (Mohapatra and Parida, 2016; Nalawade et al., 2009; Kuthati et al., 2015; Duan et al., 2009). Usually, $MgAlCO_3$-LDHs products are produced with magnesium salt reagents, which can incur high production costs. Therefore, it would be both economically and environmentally beneficial to utilize magnesium from brine as a raw material for $MgAlCO_3$-LDHs production. In this paper, a novel process was developed to recover and separate both magnesium and lithium by producing $MgAlCO_3$-LDHs and precipitating lithium carbonate.

2. Experimental

2.1. Materials and apparatus

The brine (brine A) was collected from the Taijinaier salt lake on the Qinghai-Tibet plateau in China and then saturated with bischofite ($MgCl_2\cdot 6H_2O$) after evaporation. The composition of the brine is listed in Table 1. The Mg/Li mass ratio was 19.22. Aluminum chloride hexahydrate (AR, 97%, Sinopharm Chemical Reagent Co., Ltd., China), sodium carbonate (AR, 99.8%, Sinopharm Chemical Reagent Co., Ltd., China), sodium hydroxide (AR, 96%, Tianjin Damao Chemical Reagent Factory, China), barium chloride dehydrate (AR, 99.5%, Tianjin Guangfu Technology Development Co., Ltd., China), and boron adsorbent resin (LSC-800, Sunresin New Materials Co., Ltd., Xi'an, China) were used as received. Deionized water (resistivity, 18.25 MΩ·cm) was obtained by an ultrapure water machine (UPT-II-20T, Chengdu Ultrapure Technology Co., Ltd., China).

A water-bath (SHJ-E, Jintan MEITE instrument manufacturing co., Ltd., china) was used to control reaction temperature. Flame atomic absorption spectroscopy (AAS, Analyst 800, PE of USA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICAP 6500 DUO, Thermo Electron Corporation) were used to determine the concentration of elements. X-ray diffraction (XRD, PRO PANalytical X'Pert, Cu Kα1) was applied to identify the solid phase. MS-2000 and Malvern Nano ZS laser particle analyzer (Malvern Instruments Ltd.) were employed to determine the particle size of lithium carbonate and $MgAlCO_3$-LDHs production, respectively. The morphology of the $MgAlCO_3$-LDHs was assessed with a field emission scanning electron microscopy (SU8010/Aztec (X-MaxN), Hitachi, Japan).

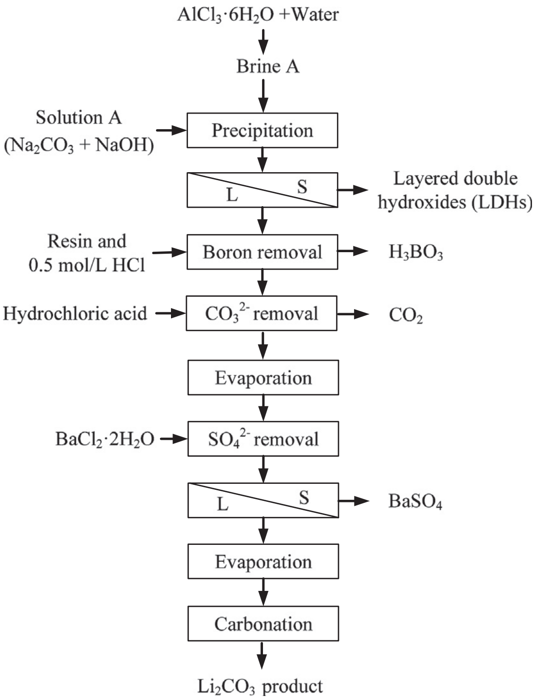

Fig. 1. Flowsheet for the co-preparation of LDHs and lithium carbonate.

2.2. Analytical methods

The compositions of the brine samples were determined using the methods previously described in the reference "*the analysis method of the brine and salt*" (Zhai et al., 1988). Mg^{2+} ion was determined by EDTA complexometric titration with eriochrome black T as an indicator at pH 9. K^{+} and SO_4^{2-} ion concentrations were measured by gravimetric method with sodium tetraphenylborate and barium chloride, respectively. Cl^{-} ion and boron were analyzed by mercurimetry element and mannitol conversion acid base titration, respectively. Li^{+} ion was determined by flame atomic absorption spectroscopy. While Na^{+} ion in brine was calculated under ion charge balance principle. Concentrations of each ion were measured twice and then averaged. The accuracy of the analysis was less than 0.5%. For $MgAlCO_3$-LDHs, the Mg^{2+} and Al^{3+} ion concentrations were analyzed by ICP-AES.

2.3. Separation and precipitation experiments

The schematic diagram of the integrated process is depicted in Fig. 1. The main steps in the process are production of $MgAlCO_3$-LDHs (Mg recovery), boron extraction (boron removal), acidification (residual CO_3^{2-} removal), evaporation and precipitation. The precipitation step includes removal of SO_4^{2-} and production of lithium carbonate.

2.3.1. Production of $MgAlCO_3$-LDHs

$MgAlCO_3$-LDHs were produced from the brine by double-drop method. Briefly, deionized water and $AlCl_3\cdot 6H_2O$ salt were added to brine A, and then both of the resultant mixture and solution A were simultaneously added dropwise into a round-bottom flask at a rate that allowed reaction mixture pH to be maintained at 10. Because brine A is saturated with bischofite (413.12 g·L^{-1} $MgCl_2$), water was added to

Table 1
Ionic composition of Taijinaier salt lake brine (g/L).

Brine	Density (g/mL)	Mg^{2+}	Na^{+}	K^{+}	Li^{+}	B_2O_3	SO_4^{2-}	Cl^{-}	Mg/Li ratio
Taijinaier	1.3666	117.06	27.70	0.16	6.09	33.29	22.88	343.29	19.22