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Recovery of lithium from alkaline brine by solvent extraction with β-diketone

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ABSTRACT

Lithium recovery from alkaline brines by counter-current method using β-diketone was investigated. By comparing effect of different co-extractants and diluents on lithium extraction, HBTA-TOPO-kerosene system was determined as the extraction system.

In extraction process, 0.4 mol/L HBTA and 0.3 mol/L TOPO in kerosene performed as extractant and three theoretical stages were required to reach 95% extraction according to McCabe Thiele diagram. 1 mol/L HCl and 3 mol/L HCl solution were used as scrubbing agent and stripping agent respectively. In regeneration stage, 2 mol/L NaOH was used as regeneration agent to remove free acid entrained in organic phase and exchange H^+ of hydroxyl. Bench experiments indicated that the respective number of extraction, scrubbing, stripping and regeneration were 3, 1, 2 and 1 stage.

A 7-stage extraction process was conducted in a mixer-settler for 30 h to reach stable state, average extraction rate of lithium was 96% and lithium concentration in stripping solution was 15 g/L. Concentration of impurity ions in stripping liquor was < 1 g/L. No third phase or emulsification was observed during the operation. In summary, HBTA-TOPO-kerosene extraction system was verified an effective method to recovery lithium from alkaline brine.

1. Introduction

Lithium is one of the most important elements in the earth, it has important application in nuclear, medicines, ceramics and especially in batteries (Batyrbekov, Gordienko, Ponkratov, et al., 2016; Lüders, Zinth, Erhard, et al., 2017; Pereira, Franco, Ribeiro, et al., 2016; Sang, Hui, Kim, et al., 2016; Sun, Liu, Gong, et al., 2017). The explosive development of electrical vehicles and portable electrical devices has led to a significant increase in lithium consumption in recent years (Hannan, Lipu, Hussain, et al., 2017). Lithium exists in three forms in nature: brines, pegmatites, and sedimentary rocks. With depletion of ore resources and increasing demand of environment protection, lithium development is shifting to liquid state resources (Choubey, Kim, Srivastava, et al., 2016; Sverdrup, 2016). The research on recovery of lithium from brine has focus on solvent extraction, nanofiltration, precipitation and adsorption. Among these methods solvent extraction which has the advantage of low cost, easy operation and environmentally amiability is attracting increasing attention (Shi, Jing, Xiao, et al., 2017; Xiang, Liang, Zhou, et al., 2017).

β-diketone and neutral organophosphorus extractant in kerosene was verified an effective extraction system in separation of lithium over other alkali metal ions (Seeley & Baldwin, 1976; Ishimori, Imura, & Ohashi, 2002; Pranolo, Zhu, & Cheng, 2015; Healy, 1968). However, extraction, scrubbing, stripping and regeneration performance of the β-diketone and organophosphorus extraction system in real brine system was rarely reported. In addition, experiment of extraction was mostly on bench scale previously, the process was not tested with extraction equipment. Mixer-settlers units which have satisfactory separation effect and simple operation were used widely in hydrometallurgical flowsheets. They were ideal equipment to test the process before industrial amplification (Ali, Daoud, Zeid, et al., 2002; Gharehbagh & Mousavian, 2009; Sun & Lee, 2015; Tang, Petranikova, Ekberg, et al., 2017).

In current study, HBTA (benzoyl-1,1,1-trifluotoacetone) and TOPO (trioctylphosphine oxide) in kerosene was used as extractant to recover lithium from brine with high Na/Li molar ratio, the operating

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Table 1
Main organic reagents used in the work.

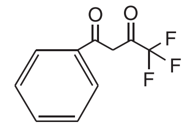
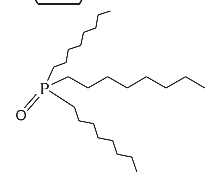
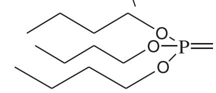
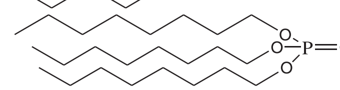
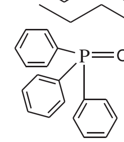
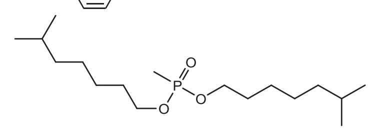
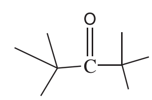
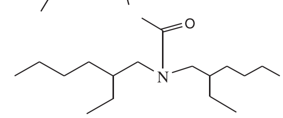
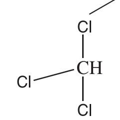
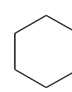
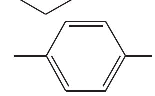
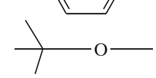
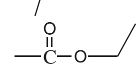
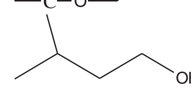
Abbreviate	Purity	Full name	Chemical structure
HBTA	> 98%	Benzoyl-1,1,1-trifluotoacetone	
TOPO	> 98%	Trioctylphosphine oxide	
TBP	> 98%	Tri-butyl-phosphate	
TOP	> 98%	Tri-octyl-phosphate	
TPPO	> 98%	Tri-phenyl-phosphine oxide	
DIMP	> 98%	Di-iso-octyl methylphosphonat	
MIBK	> 98%	Methyl-iso-butyl ketone	
N523	> 95%	*N*,*N*-bis(2-ethylhexyl)actamide	
Chloroform	> 98%	Trichloromethane	
Cyclohexane	> 98%	Cyclohexane	
p-xylene	> 98%	*p*-xylene	
MTBE	> 98%	Methyl-tertbutyl ether	
Acetic ether	> 98%	Acetic ether	
Isoamylol	> 98%	Isoamylol	

Table 2
Main ions in the brine.

	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	$B(OH)_3$	pH
Concentration, mol/L	0.288	2.17	0.026	$1.25 * 10^{-5}$	$2.08 * 10^{-4}$	0.1	10.80

conditions for extraction, scrubbing, stripping and regeneration were determined by bench-scale experiment. The process was operated on a 7-stage mixer-settler for > 30 h, lithium extraction efficiency, separation of lithium and sodium through the process was investigated.

2. Experimental

2.1. Reagents and apparatus

The HCl and NaOH used in the experiment were of analytical purity and supplied by Sinopharm Chemical Reagents Co., Ltd. Main organic