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Optimization of operation conditions for extracting lithium ions from calcium chloride-type oil field brine

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Abstract: $Al(OH)_3$ was prepared to extract lithium ions from calcium chloride-type oil field brine. The influences of four factors, namely temperature, Al^{3+}/Li^+ molar ratio, OH^-/Al^{3+} molar ratio, and contact time between $Al(OH)_3$ and the brine, on the yield of lithium ions were investigated. It is found that their optimal values are 35°C, 4.5, 2.6, and 6 h, respectively. In the course of the experiment, the apparent pH value was observed. The results reveal that the apparent pH value has no remarkable influence on the yield of lithium ions. Meanwhile, the effects of the concentrations of calcium ions and magnesium ions in the brine on lithium recovery were studied. The results indicate that calcium ions have minor negative influence on the yield of lithium ions under optimal conditions, and magnesium ions slightly influence the yield of lithium ions.

Keywords: lithium; extraction; oil field brine; aluminium hydroxide

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1. Introduction

Lithium and lithium-containing compounds are widely used in many fields for their various uses. Minerals such as spodumene, lepidolite and amblygonite were used as main resources from which lithium-containing products were manufactured. During the 1980s, the technology of extracting lithium ions from salt lake brines was successfully applied to industrial process. Salt lake brines have taken the place of solid minerals as the main source for extracting lithium ions over the world [1]. Because the typical composition of brines differs and for other reasons, researchers have developed many technologies including liquid phase extraction, ion exchange, calcination, co-precipitation, salting out, *etc.* [2] to extract lithium ions from lithium-containing brines. Among these ideas, amorphous $Al(OH)_3$ was considered as a promising method. Based on the method, aluminum salts, aluminates or freshly prepared $Al(OH)_3$ were employed to extract trace amounts of lithium ions from lithium-containing brines [3-16]. In the literatures mentioned above, in regard to operating conditions, the optimal condition parameters obtained were divergent. For instance, the optimum values of temperature ranged from 25 to 90°C according to the different literatures [6-7, 13], the Al^{3+}/Li^+ molar ratio was 5/1 [13] and 125/1 [16], respectively, and with respect to the OH^-/Al^{3+} molar ratio, it has been observed that the ratio determined the amount of crystal related to the yield of lithium ions [7]. Furthermore, some researchers believed that impurities co-existing in the brines such as magnesium ions and calcium ions had negative effect on the yield of lithium ions. Since most researches were focused on extracting lithium ions from brines containing relatively

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high concentrations of magnesium ions, few literatures about extracting lithium ions from calcium-rich brine were found; thus, the effect of calcium ions on the yield of lithium ions remains uncertain. In China, huge amounts of calcium chloride-type oil field water were found, in which lithium ions were rich, with concentrations as high as about 200×10^{-6} and calcium reached 17 g/L (oil field water is groundwater associated with petroleum in a reservoir [17]). The composition of the water is given in Table 1 (it is necessary to know whether calcium ions influence extracting lithium ions using amorphous $Al(OH)_3$). In this work, crystalloid aluminum chloride and sodium hydroxide were employed to synthetic brine prepared by mixing lithium chloride and calcium chloride to determine optimum conditions for extracting lithium ions from the solution. The influence of calcium ions on the yield of lithium ions was studied. In the case of the operational conditions, the influences of four factors, namely temperature, Al^{3+}/Li^{+} molar ratio, OH^{-}/Al^{3+} molar ratio and contact time, on the yield of lithium ions, were investigated. Meanwhile, the apparent pH value of the system was observed.

Table 1. Composition of typical oil field brine

Ion	Ca^{2+}	Mg^{2+}	K^{+}	Li^{+}	Na^{+}	B_2O_3	Cl^{-}
Content / $(g\cdot L^{-1})$	16.86	1.14	11.08	0.23	92.82	2.99	187.52

Note: the amount of Na^{+} was obtained by the subtraction method.

2. Experimental

2.1. Reagents and instruments

Lithium carbonate (99.9%), anhydrous calcium chloride (96.0%), sodium hydroxide (96.0%), crystal aluminum chloride (97.0%), and hydrochloride acid (37.0%) were commercially available and used as reagents.

The content of lithium ions was determined with a GBC-908AA flame atomic absorption spectrometer. Calcium ions, magnesium ions, chloride anions, potassium ions, and boron trioxide were analyzed according to Ref. [18]. Temperature was maintained using a constant temperature bath.

2.2. Experimental design

Four groups of experiments were designed. The purpose of the experiments was to investigate the effects of four factors, namely temperature, Al^{3+}/Li^{+} molar ratio, OH^{-}/Al^{3+} molar ratio and contact time between $Al(OH)_3$ and the brine, on the yield of lithium ions. In each group of experiments, the corresponding optimal value was determined according to the maximum yield of lithium ions.

2.3. General procedure

Aluminum chloride and sodium hydroxide were added in sequence to a previously prepared mixture of calcium chloride (0.9242 mol/L, 10.00 mL) and lithium chloride (0.9979 mol/L, 2.80 mL). The resulting mixture was maintained at a certain temperature and stirred vigorously. Starting time was counted immediately after sodium hydroxide was added. Solid phase and liquid phase were separated by filtration, and the solid phase was washed by distilled water (70-80 mL). The contents of lithium ions and calcium ions in filtrates were analyzed. The yield of lithium ions and the content of calcium ions that remained in the solution were calculated. Just before the experiment was completed, the apparent pH value of the system was determined and noted.

2.4. Results and discussion

(1) Influence of temperature on the yield of lithium ions.

The yields of lithium ions at different temperatures are shown in Fig. 1. It is clear that with the increase of temperature, the yield increases first then decreases smoothly. The yield reaches maximum at 35-40°C. This trend is consistent with the results reported in Refs. [6], [13] and [15], but not in agreement with that in Ref. [3]. In each experiment, more than 90% of calcium ions are still left in the solution. It seems that the change in temperature has little influence on the amount of calcium ions. Thus 35°C was chosen as the optimal value for temperature.

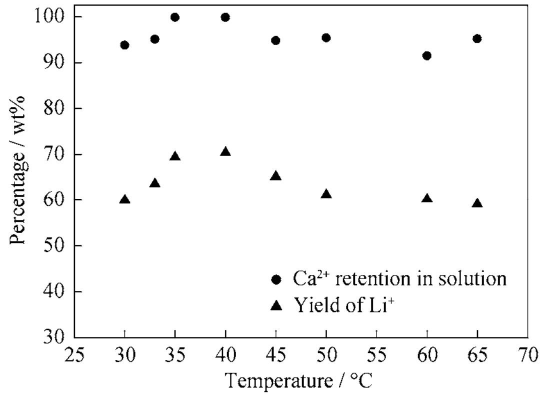

Fig. 1. Changes in the yield of Li^{+} and Ca^{2+} retention in the solution with temperature.

(2) Effect of Al^{3+}/Li^{+} molar ratio on the yield of lithium ions at 35°C.

According to the yield of lithium ions in Fig. 2, it can be seen that the yield increases and then decreases as the Al^{3+}/Li^{+} molar ratio increases. When this ratio is 4.5, the yield reaches the highest point. This value was chosen as the optimal Al^{3+}/Li^{+} molar ratio. Meanwhile, more than 90% of calcium ions remained in the solution. It appears that as more Al^{3+} ions are introduced, more amorphous $Al(OH)_3$ forms, more lithium ions can be adsorbed and the yield of lithium ions increases, but the yield of lithium ions does not increase linearly with the increase in the amount of $Al(OH)_3$. Most of calcium ions are still left in the solution.

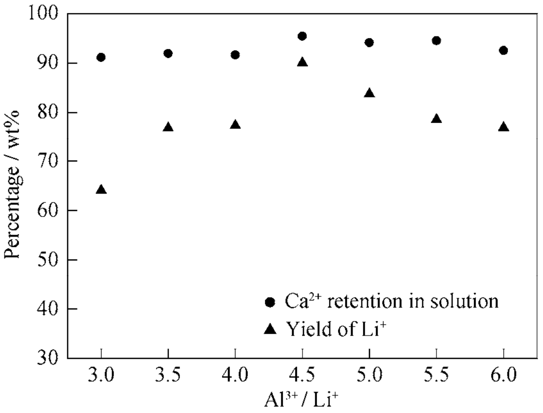

Fig. 2. Yield of Li^{+} and Ca^{2+} retention in solution *vs.* Al^{3+}/Li^{+}.

As seen in Table 2, in the process of the experiments, the apparent pH value is basically constant, but the yield of lithium ions fluctuates notably. It seems that the pH value has no notable effect on the yield of lithium ions.

Table 2. Apparent pH value of the system

Al^{3+}/Li^{+} molar ratio	Apparent pH value
3.0	3.863
3.5	3.828
4.0	3.898
4.5	3.900
5.0	3.892
5.5	4.002
6.0	3.951

(3) Influence of OH^{-}/Al^{3+} molar ratio on the yield of lithium ions.

As shown in Fig. 3, the yield of lithium ions increases sharply and then descends smoothly with the increase of OH^{-}/Al^{3+} molar ratio. When the ratio is 2.6, the yield reaches the highest point. This ratio was selected as the optimal value for OH^{-}/Al^{3+} molar ratio. In addition, more than 90% of calcium ions remained in the solution. The possible reason for this tendency is that with the increase of OH^{-}, more $Al(OH)_3$ forms, and more lithium ions are adsorbed. As the adsorption of $Al(OH)_3$ to lithium ions reaches equilibrium, the yield of lithium ions no longer increased. Meanwhile, the amount of Ca^{2+} decreased largely only when the abundant OH^{-} (e.g. $OH^{-}/Al^{3+} = 3.1$) was added.

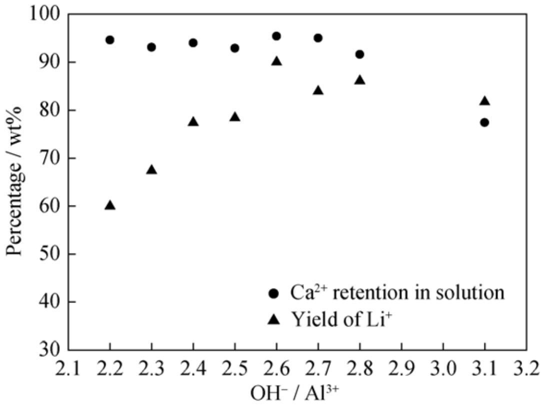

Fig. 3. Yield of Li^{+} and Ca^{2+} retention in solution *vs.* OH^{-}/Al^{3+}.

According to Table 3, the apparent pH value increases with the increase of the ratio. The apparent pH value does not fluctuate sharply when the ratio is changed from 2.2 to 2.8; the apparent pH value fluctuates to 7.712 only when the ratio reaches 3.1. At this point the yield of lithium ions is still basically unanimous with 4.422. It also seems that the apparent pH value has no significant influence on the yield of lithium ions.

Table 3. Apparent pH value of the system

OH^{-}/Al^{3+} molar ratio	Apparent pH value
2.2	3.648
2.3	3.686
2.4	3.775
2.5	3.853
2.6	3.900
2.7	3.952
2.8	4.422
3.1	7.712

(4) Contact time between Li^{+} and $Al(OH)_3$.

It can be seen from Fig. 4 that the yield of lithium ions increases sharply and then decreases slightly when the contact time is extended. When time passes 6 h, about 90% of lithium ions are adsorbed. The contact time has no remarkable effect on calcium ions, and about 90% of calcium ions are retained in the solution. Thus 6 h was chosen as the optimal value for the reaction time.

According to Table 4, when the contact time is prolonged, the apparent pH value decreases smoothly; and after 6 h, the value basically remains about 3.900. It appears that there is no

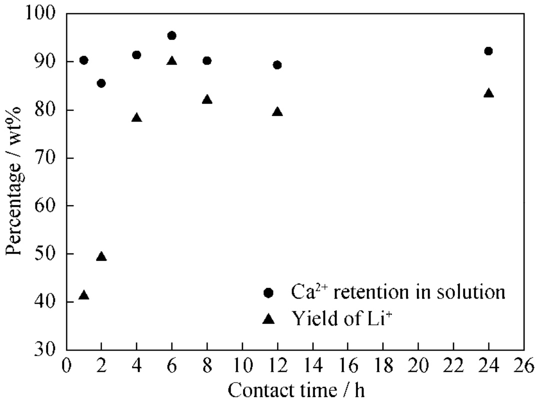

Fig. 4. Yield of Li^+ and Ca^{2+} retention in solution vs. contact time.

Table 4. Apparent pH value of the system

Time / h	Apparent pH value
1	4.527
2	4.217
4	3.961
6	3.900
8	3.869
12	3.894
24	3.843

evidence to prove the interaction between the apparent pH value and the yield of lithium ions in the course of the experiment.

According to the previous work, we can deduce the optimum parameters for the maximum lithium recovery as below: temperature 35°C, Al^{3+}/Li^+ molar ratio 4.5, OH^-/Al^{3+} molar ratio 2.6, and contact time 6 h.

(5) Effect of the concentration of calcium ions.

To verify the parameters obtained above, a series of solutions containing different amounts of calcium ions and the same concentration of lithium ions were prepared. In each experiment, the prepared calcium chloride (10.00 mL) was mixed with the prepared lithium chloride solution (2.80 mL). The results are shown in Fig. 5.

As shown in Fig. 5, the yields of lithium ions in different solutions are almost constant, which is consistent with the results obtained previously. About 90% of calcium ions are left in the solution. It can be deduced that calcium ions have no remarkable influence on the yield of lithium ions.

(6) Application of optimized operation conditions for extracting lithium ion in concentrated oil field brine.

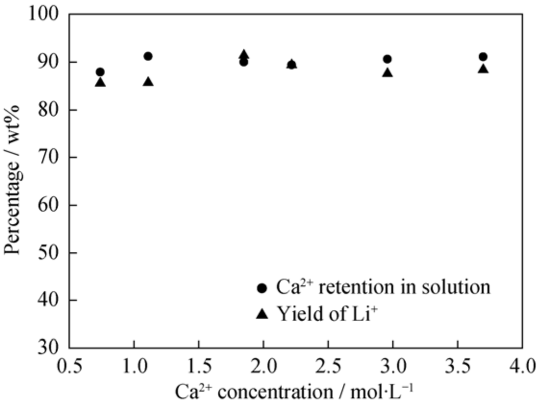

Fig. 5. Yield of Li^+ and Ca^{2+} retention in solution vs. contact time.

The optimized parameters obtained previously were applied to extract lithium ions from the concentrated oil field brine. 10.00 mL brine was used. The brief composition of the brine is listed in Table 5, and the test results are listed in Table 6.

Table 5. Composition of the concentrated oil field brine

Ion	Ca^{2+}	Mg^{2+}	K^+	Li^+	Na^+	B_2O_3	Cl^-
Content / $(g \cdot L^{-1})$	100.10	5.75	46.38	1.29	22.63	15.63	277.27

Note: the amount of Na^+ was obtained by the subtraction method.

Table 6. Composition of the solution yielded after the extraction

Ion	Ca^{2+}	Mg^{2+}	Li^+
Percentage / wt%	93.5	64.4	24.4

It was found that 75.6% of lithium was extracted, and 93.5% of calcium ions were preserved in the solution (Table 6), but 35.6% of magnesium ions were removed from the solution.

3. Conclusion

In this work, experiments on extracting lithium ions from the prepared solution and the oil field water containing high concentration of calcium ions were carried out using crystalloid aluminum chloride and sodium hydroxide as reagents. The optimal values for temperature, Al^{3+}/Li^+ molar ratio, OH^-/Al^{3+} molar ratio and contact time were obtained. The parameters obtained were confirmed by a series of solutions containing different amounts of calcium ions and concentrated oil field water, respectively. Experimental results show that the concentration of calcium ions has no remarkable influence on lithium ion extraction under the optimized experimental conditions. It seems that the apparent pH value has no significant influence on the yield of lithium ions as well.

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