Recovery valuable metals from lithium-containing aluminum electrolyte slag by a NaOH leaching-aging-water leaching process

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Table S1 Main element content of material

Element	F	Na	Al	Ca	K	Mg	Si
Content(wt.%)	55.5	24.76	13.65	2.91	2.70	0.30	0.04

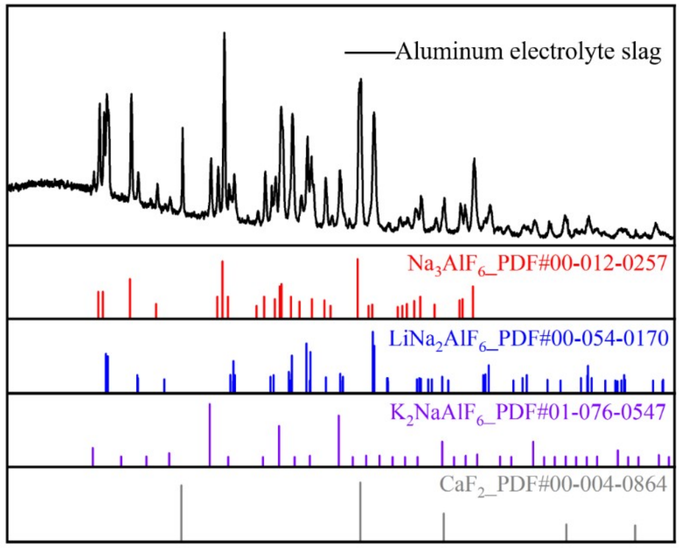

Figure S1 XRD pattern of aluminum electrolyte slag

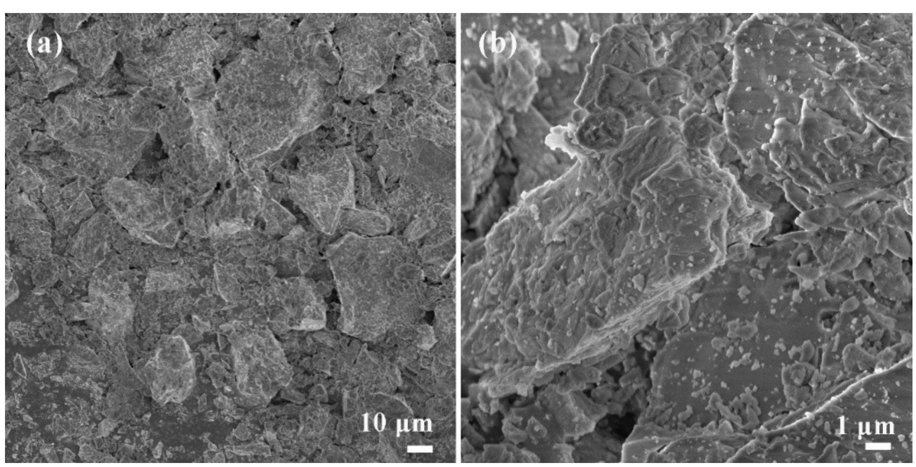

Figure S2 SEM images of aluminum electrolyte slag

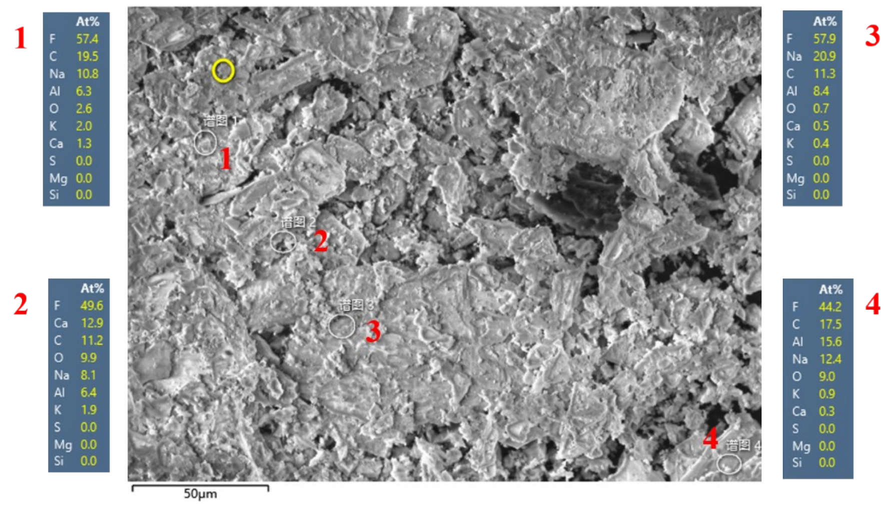

Figure S3 EDS measurements region and related data for aluminum electrolyte slag

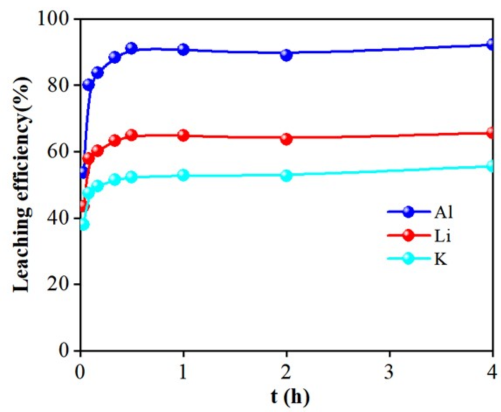

Figure S4 Leaching efficiencies of valuable metals under the conditions of 4.44 mol·L^{-1} NaOH, 90°C, L/S=9

S1. Factorial Design and Regression Equations

The primary objective of this section is to determine the factors that most significantly influence the leaching efficiency of each metal in the sodium hydroxide leaching experiments. A factorial design method from Design of Experiments (DOE) was employed to further explore the interactions between individual factors. This method is a comprehensive and efficient experimental design approach that not only analyzes differences between different levels within each factor but also examines interactions among various combinations [1, 2]. The factorial design method was also used to establish a regression model between metal ions and factors, employing nonlinear fitting to identify the interactions among the four factors. This approach can determine the key influencing factors to optimize the response variables to the greatest extent [3].

The specific procedure involves first standardizing the experimental conditions and leaching efficiency results using a z-score model to ensure comparability. Subsequently, the standardized results are inputted into Matlab 9.6.0 software for nonlinear fitting to establish a full factorial regression model of metal ion leaching rates. Next, the model is subjected to iterative factor interaction calculations using SPSS software. Spearman correlation coefficient analysis (utilizing the Spearman function, an integrated function within the software for assessing inter-factor correlations) is employed to determine the significance (sig value) of each factor's relationship with the response variable [4]. Details of the experimental conditions considered, standardized results, and leaching efficiencies of different metal ions in the experimental factorial design are summarized in Table S2.

Table S2 Experimental design and data standardization results

No.	*Conc.* (mol·L^{-1})	*T* (°C)	*L/S* (mL/g)	*t* (h)	x_1	x_2	x_3	x_4
1	1.11	90.00	9.00	4.00	-2.94	0.03	0.06	0.45
2	2.22	90.00	9.00	4.00	-2.14	0.03	0.06	0.45
3	3.33	90.00	9.00	4.00	-1.35	0.03	0.06	0.45
4	4.44	90.00	9.00	4.00	-0.55	0.03	0.06	0.45
5	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
6	6.67	90.00	9.00	4.00	1.04	0.03	0.06	0.45
7	10.00	90.00	9.00	4.00	3.43	0.03	0.06	0.45
8	5.56	28.00	9.00	4.00	0.25	-3.52	0.06	0.45
9	5.56	60.00	9.00	4.00	0.25	-1.69	0.06	0.45
10	5.56	75.00	9.00	4.00	0.25	-0.83	0.06	0.45
11	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
12	5.56	120.00	9.00	4.00	0.25	1.75	0.06	0.45
13	5.56	150.00	9.00	4.00	0.25	3.47	0.06	0.45
14	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
15	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
16	5.56	90.00	3.00	4.00	0.25	0.03	-2.70	0.45
17	5.56	90.00	4.50	4.00	0.25	0.03	-2.01	0.45
18	5.56	90.00	6.00	4.00	0.25	0.03	-1.32	0.45
19	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
20	5.56	90.00	18.00	4.00	0.25	0.03	4.22	0.45
21	5.56	90.00	9.00	0.50	0.25	0.03	0.06	-2.28
22	5.56	90.00	9.00	1.00	0.25	0.03	0.06	-1.89
23	5.56	90.00	9.00	2.00	0.25	0.03	0.06	-1.11
24	5.56	90.00	9.00	3.00	0.25	0.03	0.06	-0.33
25	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
26	5.56	90.00	9.00	4.00	0.25	0.03	0.06	0.45
27	5.56	90.00	9.00	6.00	0.25	0.03	0.06	2.01

No.	*Conc.* (mol·L^{-1})	*T* (℃)	*L/S* (mL/g)	*t* (h)	x_1	x_2	x_3	x_4
28	4.44	90.00	9.00	0.50	-0.55	0.03	0.06	-2.28
29	4.44	90.00	9.00	1.00	-0.55	0.03	0.06	-1.89
30	4.44	90.00	9.00	1.50	-0.55	0.03	0.06	-1.50
31	4.44	90.00	9.00	2.00	-0.55	0.03	0.06	-1.11
32	4.44	90.00	9.00	4.00	-0.55	0.03	0.06	0.45

S1.1 The analysis of Al leaching results

The variance analysis results of the model are shown in Table S3. The model has a goodness of fit of 0.86, indicating a certain degree of reliability in the regression model. Through Spearman correlation analysis, the two-tailed interaction relationships between factors and responses in the regression model were calculated. If the sig value is less than 0.05, the correlation is considered more significant. It was found that the sig values for x_2 and x_3 with respect to Al are 0.008 and 0.024, respectively, indicating that reaction temperature and L/S have a more significant correlation with aluminum leaching efficiency. The sig values for x_1 and x_4 with respect to Al are 0.501 and 0.982, respectively, suggesting that NaOH concentration and reaction time do not have a significant correlation with aluminum leaching efficiency.

Table S3 Regression model variance analysis for leaching efficiency of Al

Source	Sum of squares	Degree of freedom	Mean square
Regression	24.777	24	1.032
Residual error	0.175	8	0.022
Total before correction	24.952	32	
Revised total	1.256	31	

Dependent variable：Al

R^2 = 1 - (Residual sum of squares) / (Modified sum of squares) =0.86

S1.2 The analysis of Li leaching results

The variance analysis results of the model are shown in Table S4. The model has a goodness of fit of 0.93. According to Spearman correlation analysis, the sig values of x_1, x_2 and x_3 with respect to Li are 0.002, 0.049 and 0.003, indicating NaOH concentration, reaction temperature and L/S have more significant correlations with leaching efficiency of lithium.

Table S4 Regression model variance analysis for leaching efficiency of Li

Source	Sum of squares	Degree of freedom	Mean square
Regression	11.097	24	0.462
Residual error	0.132	8	0.016
Total before correction	11.228	32	
Revised total	1.905	31	

Dependent variable：Li

R^2 = 1 - (Residual sum of squares) / (Modified sum of squares) =0.93。

S1.3 The analysis of K leaching results

The variance analysis results of the model are shown in Table S5. The goodness of fit of the model is 0.84. The sig values of x_1, x_2, x_3, and x_4 for K are 0.447, 0.287, 0.713 and 0.823, respectively, indicating that the correlation among reaction temperature, reaction time, liquid-to-solid ratio, and the leaching efficiency of K is not significant enough.

Table S5 Regression model variance analysis for leaching efficiency of K

Source	Sum of squares	Degree of freedom	Mean square
Regression	10.684	24	0.445
Residual error	0.019	8	0.002
Total before correction	10.703	32	
Revised total	0.114	31	

Dependent variable：K

R^2 = 1 - (Residual sum of squares) / (Modified sum of squares) =0.84。

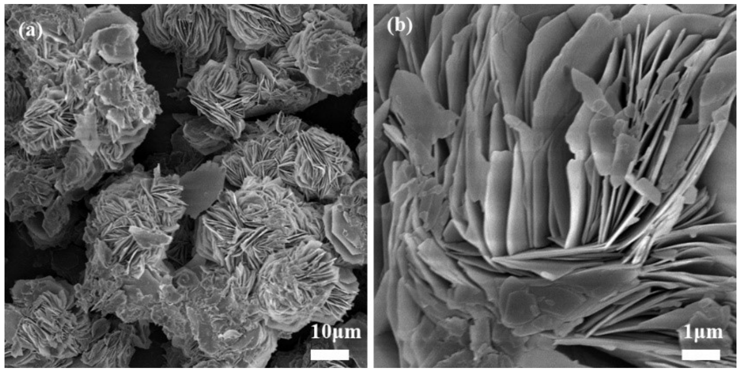

Figure S5 SEM images of precipitate after aging

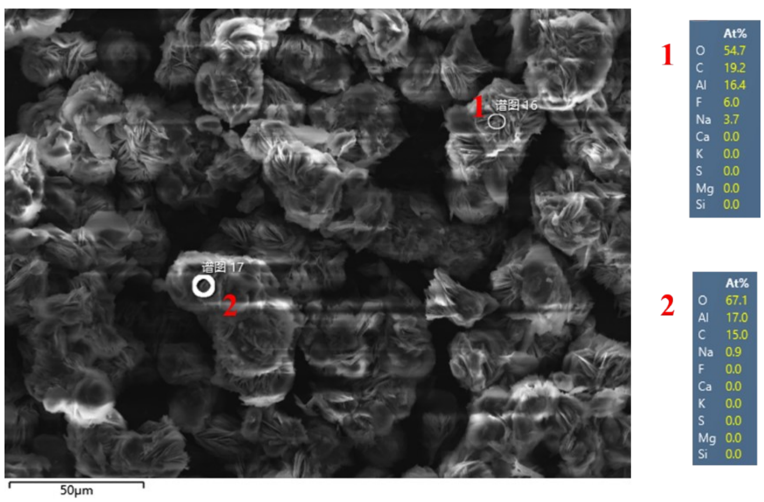

Figure S6 EDS measurements region and related data for precipitate after aging

Table S6 Mass fractions of Li and Al in Li/Al-LDHs sample

Element	Al	Li
Content (wt.%)	87.98	12.02

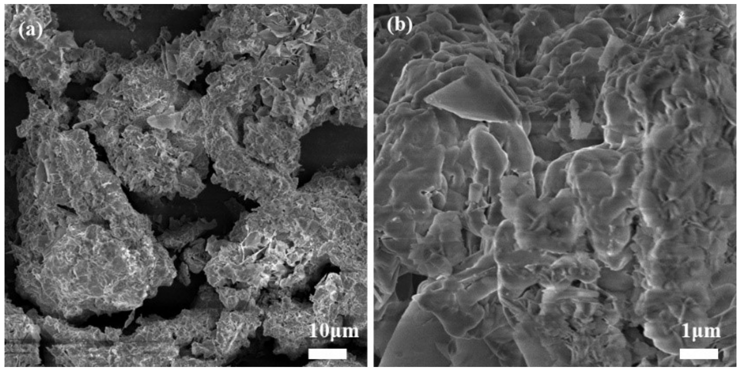

Figure S7 SEM images of Li_2CO_3

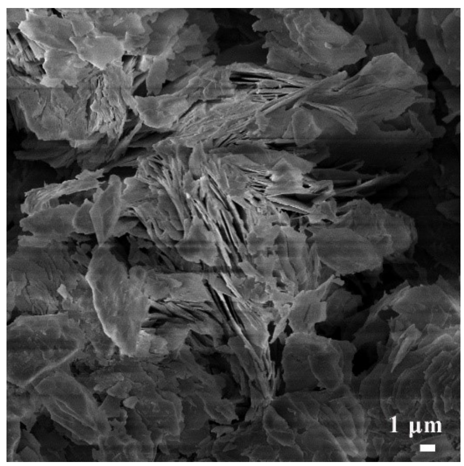

Figure S8 SEM images of AlOOH

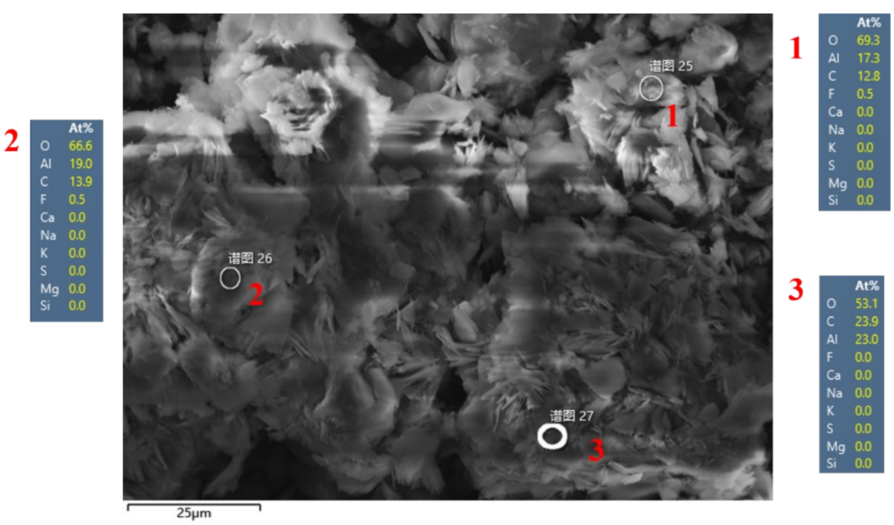

Figure S9 EDS measurements region and related data for AlOOH

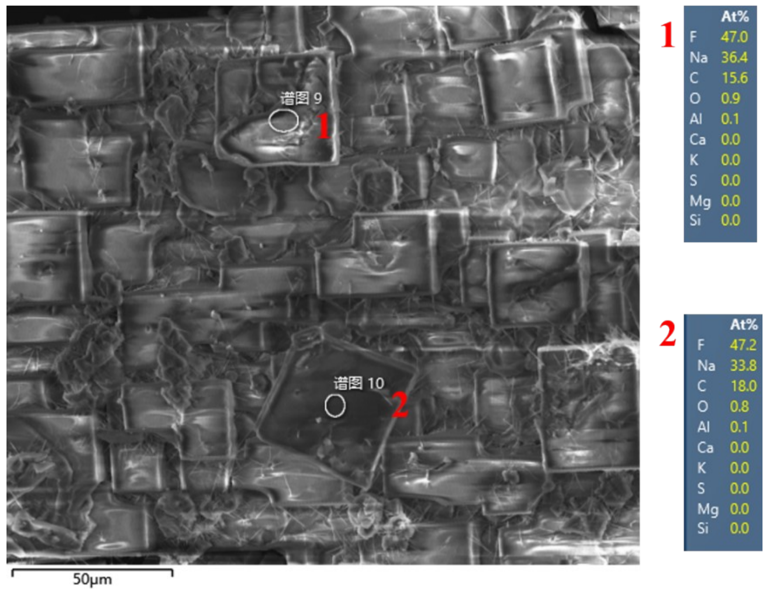

Figure S10 SEM image and EDS data for NaF product

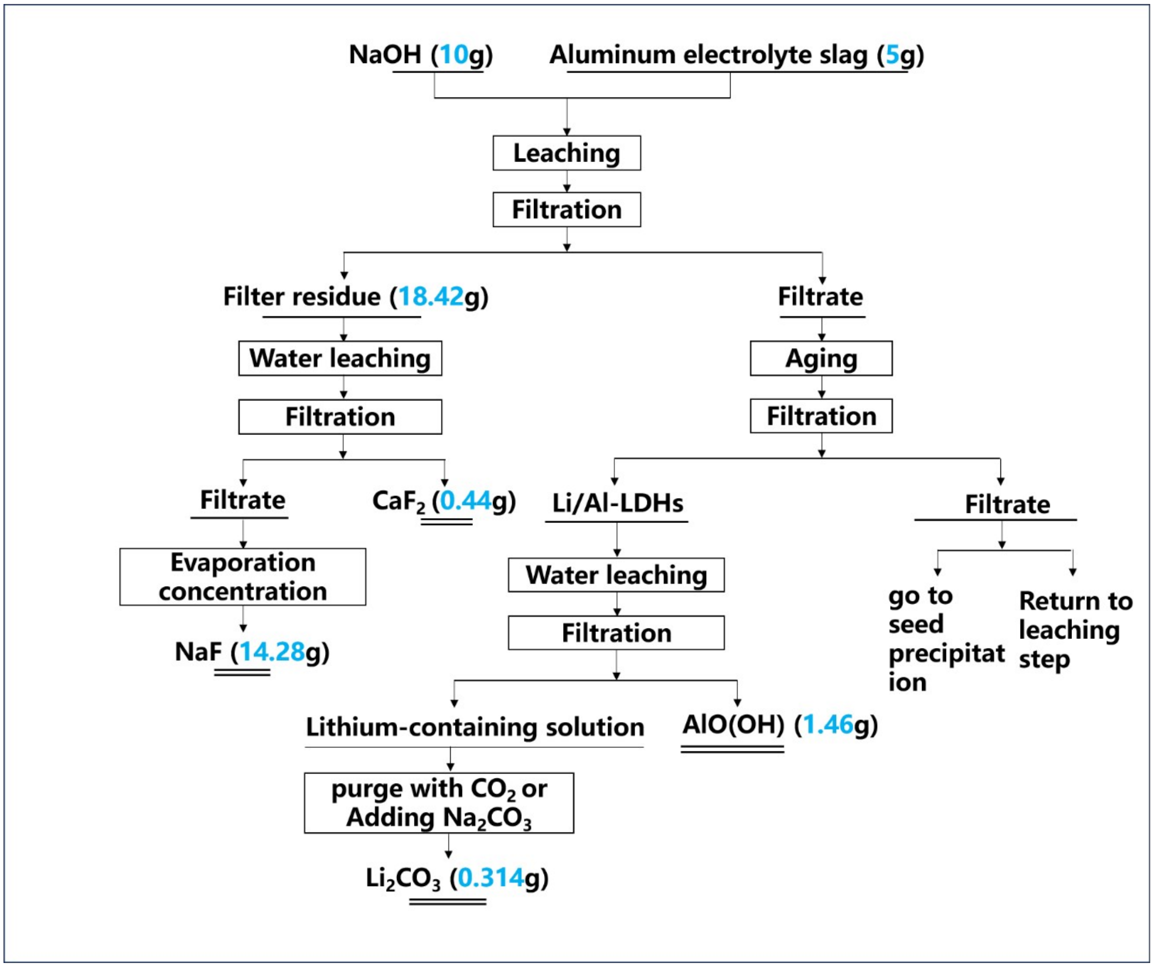

Figure S11 The mass of main product in this experiment

Accoring to Figure S11, the ideal yield for NaF is 17.48 g for the experiments using 10g NaOH, 5 g aluminum electrolyte slag and 45 mL DI water. The actual yield is 14.28 g. Considering the mass of solid is about 18.42 g after NaOH leaching, the loss of yield may be due to the overflow and residual in the breaker during evaporation and washing. Besies, the ideal yield of Li2CO3 is 0.85g. The acutual value is 0.314 g, and the loss of yield is due to ~40% of Li stay in the solid, ~24% of Li was in the water leaching solution or loss during the treatment.

Table S7 Consumption in different methods for recovery lithium into Li_2CO_3 (1kg) from the lithium-containing slags

	RMC/kg	Heating	TAC/kg	TBC/kg	TSC/kg	Ref.
① Na_2CO_3 leaching; ② Li_2CO_3 precipitation.	4.1	One-stage leaching: 180°C; Multi-stage leaching: 80°C.	/	Na_2CO_3:3.07	/	5
① Roasting; ② HNO_3 acid leaching; ③ Impurity removal by neutralization and filtration; ④ Li_2CO_3 precipitation.	25.64	Roasting: 650°C; Nitric acid leaching: 60°C; Evaporation and concentration of Li_2CO_3: 90°C.	HNO_3(68wt.%):174.21	CaO:3.12; Na_2CO_3:10.04	/	6
①HNO_3-$Al(NO_3)_3$ leaching； ②Neutralization of the leaching solution； ③Li_2CO_3 precipitation.	19.23	① Leaching temperature: 80°C； ② Leaching solution neutralization: 80°C； ③ Li_2CO_3 precipitation temperature: 95°C	HNO_3(68wt.%):71.27	NaOH:28.51; Na_2CO_3:15.27	$Al(NO_3)_3$: unstated	7
① H_2SO_4 Leaching； ② Impurity removal； ③ Li_2CO_3 precipitation	12.56	① Leaching temperature: 80°C； ② Li_2CO_3 precipitation temperature: 95°C	H_2SO_4(98%):2.82	NaOH:1.83; Na_2CO_3:0.77	EDTA: unstate	8
① Na_2CO_3 leaching; ② LiAlLDH precipitation. ③ water leaching; ④ Li_2CO_3 precipitation.	15.92	leaching: 90°C water leaching: 120-200°C	/	NaOH 31.85 Na_2CO_3:2.55	This work	

Note: RMC: Raw material consumption; TAC: Total Acid Consumption; TBC: Total Base Consumption; TSC: Total Salt Consumption.

Table S8 The estimated input cost and output value in this method

Input cost	NaOH	ore	Na_2CO_3	water	electric	Summary
kg	31.85	15.9	2.55			
RMB/t	1030	2500	1050			
RMB	32.80	39.75	2.68	1.6	6	**82.83**
Output value	NaF	Li_2CO_3				
kg	45.48	1				
RMB/t	6000	87000				
RMB	272.87	87.00				**359.87**

Note: the value of chemicals is according to the report value in https://www.chemicalbook.com/

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