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Research article

Научная статья



# Obtaining lithium carbonate from the black mass of lithium-ion batteries

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**Abstract:** The article explores the possibility of obtaining lithium carbonate from the black mass – an intermediate product of lithium-ion batteries recycling. X-ray phase analysis and inductively coupled plasma atomic emission spectrometry of the black mass revealed that it contains 3 % lithium. It has been established that during water leaching, 40 % to 70 % of lithium can be selectively extracted from the black mass into the aqueous phase at L/S ratios ranging from 10 to 200. During water leaching, kinetic curves were recorded at temperatures of 25 °C and 80 °C. To remove Al ions from the leaching solution, we studied the sorption of aluminate ions on weakly basic (AN-31, CRB05) and strongly basic (A500) anion exchangers under static conditions using a model Li–Al solution. It was demonstrated that in an alkaline environment, strongly basic anion exchangers with quaternary amino groups are not able to adsorb Al ions, while AN-31 and CRB05 with hydroxyl clusters in their functional groups have a capacity of 2 to 3 g/dm<sup>3</sup> in terms of aluminum ions. The sorption of aluminum from the model Li–Al solution was conducted under dynamic conditions using the CRB05 anion exchanger (N-methylglucamine) at specific flow rates of 2 and 4 column volumes per hour. Elution sorption curves were plotted, and both the dynamic exchange capacity and the total dynamic exchange capacity were determined. Additionally, we showed that aluminum ions can be removed by sorption so that their residual concentration in the raffinate drops below 0.5 mg/dm<sup>3</sup>. Sorption purification of the solution after water leaching of the black mass was performed using a weakly basic anion exchanger Diaion CRB05 and a chelate cation exchanger Purolite S950. After evaporation of the purified solution, we obtained lithium carbonate with a main substance content of 98.2 %.

**Keywords:** sorbent, lithium, ion exchange, extraction, purification, treatment.

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# Получение карбоната лития из «черной массы» литий-ионных аккумуляторов

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**Аннотация:** Исследована возможность получения карбоната лития из «черной массы» — промежуточного продукта переработки литий-ионных аккумуляторов. Проведены рентгенофазовый анализ и атомно-эмиссионная спектроскопия с индуктивно связанной плазмой «черной массы», результаты которых показали, что содержание лития в ней составляет 3 %. Установлено, что при водном выщелачивании из «черной массы» в водную фазу можно селективно извлечь от 40 до 70 % лития при соотношении Ж : Т от 10 до 200. В процессе водного выщелачивания были сняты кинетические кривые при температурах 25 и 80 °C. Для уда-

ления ионов Al из раствора выщелачивания исследовалась сорбция алюминат-иона на слабоосновных (АН-31, CRB05) и сильноосновных (A500) анионитах в статических условиях на модельном Li–Al-растворе. Показано, что в щелочной среде сильноосновные аниониты с четвертичными аминогруппами не способны поглощать ионы Al, в то время как АН-31 и CRB05, имеющие в составе функциональных групп гидроксильные группировки, обладают емкостью от 2 до 3 г/дм<sup>3</sup> по ионам Al. Проведена сорбция алюминия из модельного Li–Al-раствора в динамических условиях с использованием анионита CRB05 (N-метилглюкамин) при удельной скорости потока 2 и 4 колоночных объема в час, сняты выходные кривые сорбции, рассчитаны динамическая обменная и полная динамическая обменная емкости. Показано, что ионы Al могут быть удалены сорбцией до остаточной концентрации в рафинате менее 0,5 мг/дм<sup>3</sup>. Также была проведена сорбционная очистка раствора водного выщелачивания «черной массы» с использованием слабоосновного анионита Diaion CRB05 и хелатного катионита Purolite S950. После упаривания очищенного раствора был получен карбонат лития с содержанием основного вещества 98,2 %.

**Ключевые слова:** сорбент, литий, ионный обмен, извлечение, очистка, переработка.

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## Introduction

The production of lithium-ion batteries (LIB) holds the largest share in global lithium consumption. In 2015, LIB manufacturing accounted for 35 % of global lithium production, and by 2019, this figure surged to 65 %. The service life of LIBs is limited by various factors contributing to the degradation of electrochemical energy storage systems. Consequently, the coming years are likely to see growth in the market for recycled lithium raw materials. Without control over the disposal of spent lithium-ion batteries, this could have serious environmental consequences.

The most popular lithium product is lithium carbonate, which is used for LIB production after being upgraded by purification from the technical ( $\geq 99.0$  %  $\text{Li}_2\text{CO}_3$ ) to battery ( $\geq 99.5$  %  $\text{Li}_2\text{CO}_3$ ) grade. Lithium in the active cathode and anode masses of lithium-ion batteries exists as mixed oxides (spinel):  $\text{LiCoO}_2$  [2],  $\text{LiMnO}_4$  [3],  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [4]; phosphate  $\text{LiFePO}_4$  [5], carbide  $\text{LiC}_6$  [6], and other compounds. A mixture of cathode and anode masses of spent LIBs is an intermediate product of their processing and is referred to as “the black mass” in foreign scientific literature.

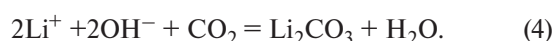
The following elements are used to transfer lithium, cobalt, and nickel from spent LIBs into solution: organic acids (oxalic, citric, ascorbic, etc.) [7; 8], including combinations with hydrogen peroxide [9–11], mixtures of organic acids (benzenesulfonic and formic) [12], inorganic acids (sulfuric, nitric, hydrochloric) [7; 13; 14], and ammonium [15; 16] and sodium [17] hydroxides.

Acid leaching presents a challenge for the further selective separation of lithium and non-ferrous metals since the resulting leaching solution contains many elements to be removed, such as Ni, Co, Mn, Al, and Fe.

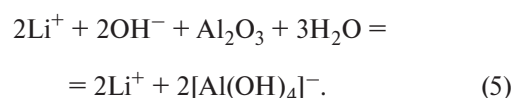
Selective lithium extraction can be achieved by water leaching of the black mass, during which most lithium ions leave the mixed oxide structure and transfer into the solution as lithium hydroxide. The proposed mechanism for lithium transfer into the solution of mixed oxides is represented by the following reaction equations [18]:



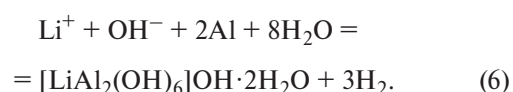
From the resulting lithium solution, lithium carbonate can be precipitated by passing carbon dioxide:



A problem arises due to aluminum contained in some cathode materials ( $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$ ) and the presence of aluminum foil particles used in lithium-ion batteries as a cathode current lead. In the alkaline environment of a lithium hydroxide solution, aluminum oxide can partially dissolve, forming a complex ion  $[\text{Al}(\text{OH})_4]^-$ :



When metallic aluminum reacts with a solution of lithium hydroxide, layered double aluminum-lithium hydroxide can form [19]:



Therefore, before lithium carbonate precipitation, Al ions should be removed from the leaching solution. This can be facilitated by sorption on anion exchangers. A literature review showed that weak base anion exchangers with tertiary amino groups (AN-31) [20] or anion exchangers with N-methylglucamine active groups (D-403) [21] can be used for the sorption removal of Al ions.

The purpose of this study was to investigate the conditions for the direct extraction of lithium from the black mass of lithium-ion batteries to obtain lithium carbonate.

Materials and methods

The object of the study was the LIB black mass obtained by grinding spent lithium-ion batteries in a shredder and sifting the resulting material through a sieve with a mesh size of 0.63 mm.

To analyze the composition of the black mass, a subsample weighing 0.5 g was dissolved in 50 cm<sup>3</sup> of a mixture of sulfuric, perchloric, and hydrochloric acids at the ratio of 2 : 2 : 1. This mixture was heated to 200 °C for 4 hours to ensure complete dissolution of the subsample, including graphite. The resulting solution was then diluted with 6 M hydrochloric acid to bring the total volume to 100 cm<sup>3</sup>. The solution was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The results (wt.%) are presented below.

Ti.....	0.08	Al.....	3.39
Mn.....	7.48	P .....	0.68
Cu.....	2.47	Li .....	3.15
Fe.....	0.87	Co.....	14.97
Ni.....	9.72		

The X-ray phase analysis of the black mass, performed on a Malvern Panalytical Empyrean powder diffractometer (PANalytical, Inc., the Netherlands), showed the presence of graphite, Co, Li<sub>2</sub>CO<sub>3</sub>, MnO, Cu, Cu<sub>2</sub>O, and Li(Fe<sub>0.16</sub>Mn<sub>1.77</sub>)O<sub>4</sub> in the sample (listed in order of decreasing content).

The experimental scheme is shown in Fig. 1. Water leaching of the black mass was performed at L/S ratios ranging from 10 to 200 to study the conditions for the most complete extraction of lithium into solution. Based on the ICP-AES analysis of the solution obtained during of the black mass leaching, a model Li-containing solution was prepared for use in experiments on static aluminum sorption. The main goal of these experiments was to select the sorbent with the highest capacity for aluminum ions. The selected sorbent was then used in experiments on the dynamic sorption of aluminum using a model Li-containing solution to select the optimal flow rate (FR) (specific loading) and calculate the sorbent dynamic exchange capacity (DEC) for Al ions. Based on the results obtained, we selected the volume of sorbent required for the sorption purification of the real black mass leaching solution from Al ions at the chosen specific loading.

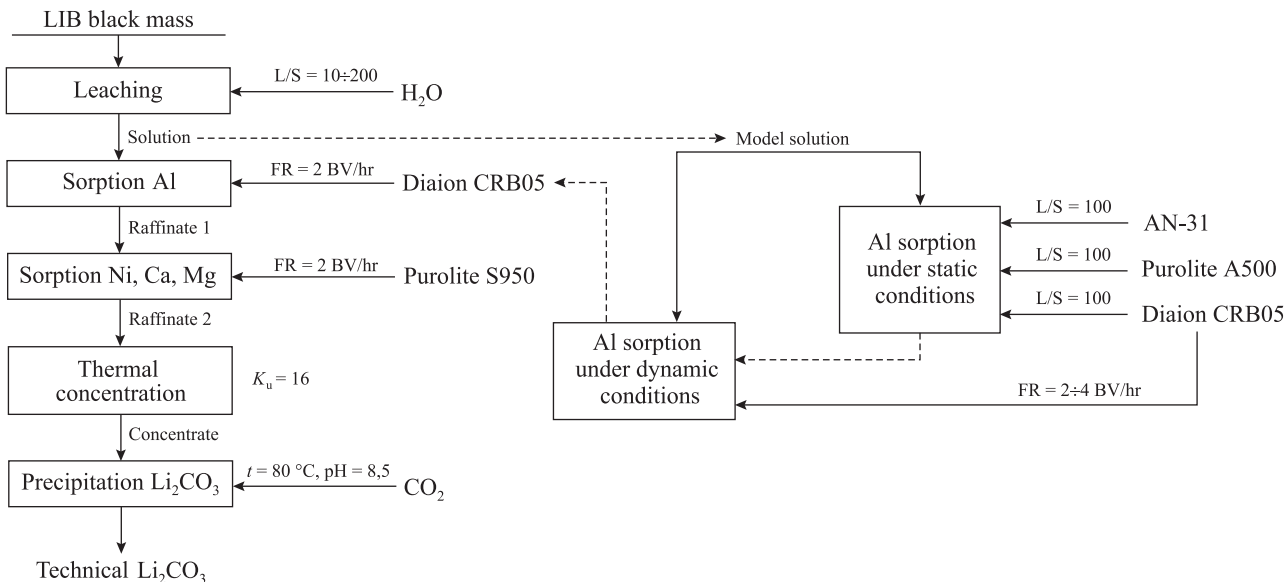


Fig. 1. Experiment scheme  
Рис. 1. Схема проведения опытов

Alongside with the aluminum sorption, we performed sorption purification of the aluminum sorption raffinate from some impurity cations (Ni, Ca, Mg) using the Purolite S950 cation exchanger. After sorption purification, the Li-containing solution was concentrated by evaporation 16 times ( $K_u = 16$ ) to achieve the Li concentration of  $25 \text{ g/dm}^3$ . After this, to precipitate lithium carbonate, carbon dioxide was passed through the concentrated Li solution heated to  $80^\circ\text{C}$  until pH reached the value of 8.5.

### Water leaching procedure

Water leaching of the black mass was performed in titanium crucibles with a volume of 100 ml at different L/S ratios (10, 50, 100, and 200) for 2 hours. The 5-position IKA RT5 stirrer (IKA-Werke GmbH & Co. KG, Germany) was used to create uniform conditions.

To record the kinetic curves of lithium leaching, water leaching of the black mass was performed in a titanium beaker with a volume of 600 ml at temperatures of  $25^\circ\text{C}$  and  $80^\circ\text{C}$  for 2 hours, with the solution being constantly stirred on an IKA C-MAG HS 7 magnetic stirrer at the ratio  $L/T = 10$ . This value was chosen as the most optimal for subsequent experiments on aluminum sorption. Samples were taken every 5 minutes, immediately filtered, and analyzed for lithium content using the ICP-AES method.

The solutions obtained during the recording of kinetic curves were combined. The data from ICP-AES analysis of the combined solution was used to prepare model systems containing Al and Li ions to study aluminum sorption under static and dynamic conditions.

### Procedure for aluminum sorption under static conditions

Aluminum sorption under static conditions was performed to select a sorbent with the highest capacity for aluminum ions. We used the anion exchangers presented in Table 1. The model solution for aluminum sorption was prepared by dissolving 9 g of lithium hydroxide monohydrate  $\text{LiOH} \cdot \text{H}_2\text{O}$  (TS 6-09-3763-85) and 1.4 g of aluminum chloride hexahydrate  $\text{AlCl}_3 \cdot \text{H}_2\text{O}$  (GOST 3759-75) in  $1 \text{ dm}^3$  of water. The resulting solution after filtration contained  $154 \text{ mg/dm}^3$  of lithium and  $1,465 \text{ mg/dm}^3$  of aluminum.

The model solution with a volume of  $50 \text{ cm}^3$  was transferred into a flask with a volume of  $100 \text{ cm}^3$  using a Research Plus automatic pipette (Eppendorf, Germany) and  $1 \text{ cm}^3$  of sorbent sample was added. The solution was stirred for 24 hours on an S-3L.A20 orbital mixer (ELMI Ltd., Latvia). After the experiment was completed,

the solutions were filtered and analyzed for the residual content of Al and Li ions.

### Procedure for aluminum sorption under dynamic conditions

Sorption of aluminum under dynamic conditions was performed on a model solution to evaluate the dynamic and total dynamic exchange capacity (DEC) of the sorbent, as well as to determine the optimal flow rate (specific loading) that ensures maximum aluminum extraction. Diaion CRB05 (N-methylglucamine) sorbent was used in the experiment. An IOK VZOR 20/16/200 ion exchange column (VZOR LLC, Russia) was filled with 30 ml of CRB05 anion exchanger and the model solution. The model solution with a specific loading of 2 and 4 bed volumes per hour (BV/hr) ( $40$  and  $120 \text{ cm}^3/\text{hr}$ , respectively) was passed through a column with a sorbent using a Masterflex L/S 7519-06 peristaltic pump (Cole-Parmer, USA) in an ascending flow. At the exit from the column, the raffinate was fractionated using a C660 fraction collector (BUCHI Labortechnik AG, Switzerland) at  $4 \text{ BV/hr}$  ( $120 \text{ cm}^3$ ).

The concentrations of Al and Li ions in the initial solution and raffinates were determined by ICP-AES. Based on the results of ICP-AES analysis of raffinate fractions, elution sorption curves were plotted, and the dynamic exchange capacity and the total dynamic exchange capacity of the sorbent were calculated.

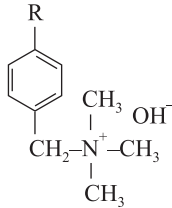
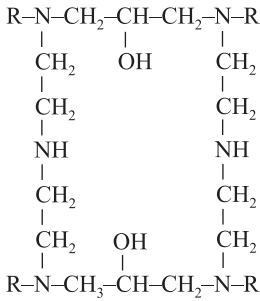
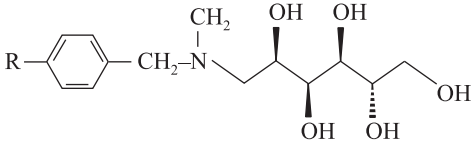
### Procedure for sorption purification of a solution after water leaching of the black mass

Fresh sorbent Diaion CRB05 was used for sorption purification of the solution ( $800 \text{ cm}^3$ ), obtained by water leaching of the black mass at the ratio  $L/S = 10$ , from Al ions. Its volume was calculated based on the obtained DEC values for aluminum ions in the model experiment, which amounted to  $2.47 \text{ g/dm}^3$  at the specific loading of  $2 \text{ BV/hr}$ . Taking into account the concentration of Al ions ( $C_0 = 112.7 \text{ mg/dm}^3$ ), the amount of CRB05 sorbent required to purify the solution obtained during water leaching of the black mass was calculated to be  $37 \text{ ml}$ .

Since the solution contains Ca, Mg, Fe and Ni ions, along with removing Al ions, the solution was additionally purified from these cations using  $37 \text{ cm}^3$  of Purolite S950 chelate resin (aminophosphonic acid), which was previously converted into the Li-form by passing through a layer of 2M sorbent of lithium hydroxide solution at a flow rate of  $111 \text{ cm}^3/\text{hr}$

Table 1. Anion exchangers used for aluminum sorption under static conditions

Таблица 1. Используемые аниониты для сорбции алюминия в статических условиях

Description	Active group	Active group structure	Working form
Purolite A500	Quaternary amine		OH <sup>-</sup>
AN-31	Tertiary amine, secondary amine		OH <sup>-</sup>
Diaion CRB05	N-methylglucamine		OH <sup>-</sup>

(3 BV/hr) for 1 hour in an ascending flow, and then washed with water at a rate of 222 cm<sup>3</sup>/hr (6 BV/hr) to displace the lithium hydroxide solution from the intergranular space.

The volume of Purolite S950 sorbent (37 cm<sup>3</sup>) was selected based on the flow rate during purification amounting to 74 cm<sup>3</sup>/hr (2 BV/hr), since the solution was simultaneously purified from anions and cations in the columns connected in sequence, with CRB05 and S950 sorbents. Before the sorption, they were dried and filled with the solution after water leaching of the black mass. The resulting purified solution (raffinate) was analyzed using the ICP-AES method.

**Lithium carbonate precipitation technique and analysis**

Since the concentration of Li (1.6 g/dm<sup>3</sup>) in the solution purified by sorption makes the lithium carbonate precipitation impossible due to its relatively high solubility in water, the raffinate was concentrated by evaporation in a titanium beaker on a magnetic stirrer to 50 cm<sup>3</sup>. During the process, the precipitate was formed, which is likely to be attributed to the interaction of lithium hydroxide with carbon dioxide contained in the air. After evaporation, carbon dioxide

was passed through the solution heated to 80 °C until pH reached the value of 8.5 for more complete precipitation of lithium carbonate. The resulting precipitate was separated from the solution by vacuum filtration, washed with alcohol and dried for 1 hour at a temperature of 150 °C.

To analyze the impurity composition, the ICP-AES method was used. The mass fraction of the main substance (lithium carbonate) was estimated by acidometric titration by dissolving its subsample, adding hydrochloric acid, heating the solution to remove carbon dioxide, and titrating the excessive hydrochloric acid with a sodium hydroxide solution.

The mass fraction of water was determined using a MX-50 moisture analyzer (AND, Japan) at a temperature of 120 °C.

**Results and discussion**

**Results of water leaching of lithium from the black mass**

The water leaching results (Table 2) showed that lithium extraction is directly proportional to the L/S ratio (Fig. 2), the maximum degree of its extraction reaching 72.5 %.



We suppose that lithium recovery is incomplete due to a number of factors. Thus, as the Li concentration in the solution increases, so does the pH value (Table 2), which creates the conditions for the aluminum oxide dissolution, to be followed by the precipitation of aluminum hydroxide, which can absorb Li ions to form double layered aluminum-lithium hydroxide [22; 23].

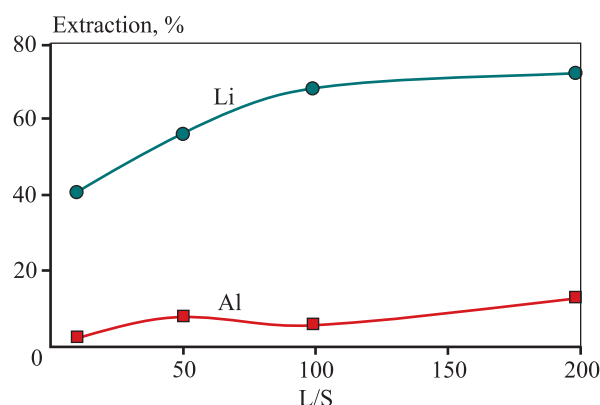
Another possible reason is related to the black mass graphite component being hydrophobic. Most anode materials for Li-ion batteries are made of lithiated graphite [24], which can reversibly intercalate and deintercalate Li ions. During leaching, a graphite film emerged and remained on the solution surface throughout the experiment. The most obvious solution to this problem is to introduce surfactants, for example sodium laureth sulfate, into the pulp, but further concentration of the solution creates difficulties with foaming and precipitate filtration, therefore surfactants were not used at this stage of the research.

The third reason why the lithium extraction is incomplete may be associated with the sorption activity of some spinels: in particular, lithium manganates [25; 26] and lithium titanates [27; 28] are Li-selective sorbents, and when they are used, lithium desorption is realized in an acidic environment.

The analysis of kinetic curves (Fig. 3) shows that in the first 20 minutes of the leaching process, Li ions actively transfer into the solution and then the process slows down.

The ICP-AES analysis of the combined solution after the black mass leaching (Table 3) showed that the Al content in the solution exceeds  $100 \text{ mg/dm}^3$ . In addition, the solution contains other impurity elements (Ca, Mg, Fe, Ni) that can negatively affect the quality of the resulting lithium carbonate.

Numerous studies [29–31] are devoted to the sorption removal of Ca and Mg cations, as well as a number of other metals and choosing a sorbent is not an issue,



**Fig. 2.** Dependence of lithium and aluminum extraction on the L/S ratio during water leaching of the black mass

**Рис. 2.** Зависимость извлечения лития и алюминия от соотношения Ж : Т при водном выщелачивании «черной массы»

since many chelate cation exchangers form more stable complexes with cations of bivalent metals than with Li ions. As noted above, the Al ions present in the solution in the form of  $[\text{Al}(\text{OH})_4]^-$ — pose a problem, so further investigation was aimed at finding a suitable anion exchanger.

### Results of aluminum sorption under static conditions

The results of sorption under static conditions show that strong base anion exchangers cannot remove hydroxoaluminate ions, while weak base anion exchangers AN-31 and CRB05 in an alkaline environment have a capacity from 2 to  $3 \text{ g/dm}^3$  (Table 4). The mechanism of aluminum sorption on these sorbents is apparently based on the formation of a complex due to them having hydroxyl groups, and not due to ion exchange, since the amino groups are not protonated in an alkaline environment. This is evidenced by the results of aluminum sorption on the strong base anion exchanger Purolite A500, which cannot absorb aluminate ions due to the absence of hydroxyl groups.

**Table 2. Results of water leaching of lithium from the LIB black mass**

Таблица 2. Результаты водного выщелачивания лития из «черной массы» литий-ионных аккумуляторов

pH <sub>equil</sub>	L/S	Content, mg/dm <sup>3</sup>		Li/Al	Extraction, %		Li/Al
		Li	Al		Li	Al	
10.72	198	115.2	22.4	5.14	72.5	13.1	5.54
10.81	98	218.4	20.9	10.45	68.2	6.1	11.26
10.93	50	354.5	57.1	6.21	56.2	8.4	6.69
11.09	10	1301.0	96.6	13.47	41.2	2.8	14.51

**Table 3. The result of ICP-AES analysis of the solution for water leaching of the black mass before and after the sorption purification**

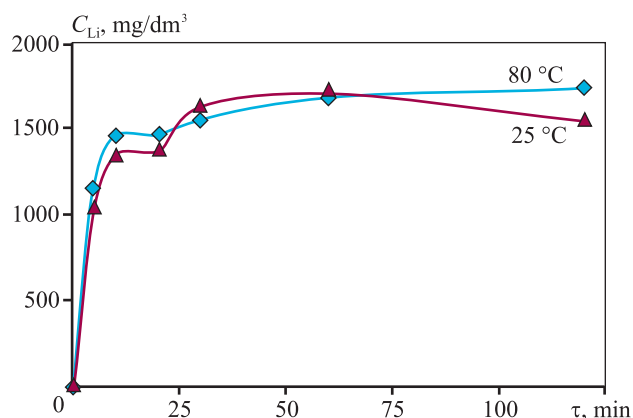
Таблица 3. Результаты ИСП-АЭС анализа раствора водного выщелачивания «черной массы» до и после сорбционной очистки

Element	Content, mg/dm <sup>3</sup>	
	Before purification	After purification
Ti	<0.1	<0.1
Ca	13.8	0.5
Mn	<0.1	<0.1
Cu	<0.1	<0.1
Fe	2.6	0.75
Ni	4.0	1.95
Al	112.7	<0.5
Mg	3.0	0.6
Na	148.2	67.05
P	7.7	5.4
K	141.1	127.5
Li	1648.9	1661.4
Co	<0.1	<0.1

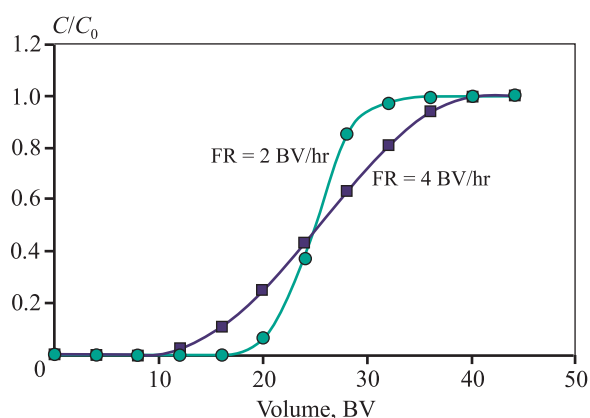
Since CRB05 has a higher capacity for aluminum ions (2.86 g/dm<sup>3</sup>) than AN-31 (2.15 g/dm<sup>3</sup>), it was chosen for further sorption experiments under dynamic conditions.

### Results of aluminum sorption under dynamic conditions

In the model experiment on the aluminum dynamic sorption, our main task was to determine the dynamic and total dynamic exchange capacities, as well as to select the optimal flow rate for purifying the real solution after water leaching of the black mass from aluminum ions. Fig. 4 features the elution curves of aluminum sorption at the flow rates (FR) of 2 and 4 BV/hr. It can

**Fig. 3.** Kinetic curves representing leaching of lithium ions from the black mass

**Рис. 3.** Кинетические кривые выщелачивания ионов лития из «черной массы»

**Fig. 4.** Elution curves of aluminum sorption on CRB05 sorbent

**Рис. 4.** Выходные кривые сорбции алюминия на сорбенте CRB05

be observed that at the specific loading of 2 BV/hr, aluminum ion breakthrough occurs later, which enables to obtain a larger volume of raffinate purified from aluminum ions than at FR = 4 BV/hr with the same amount of sorbent.

**Table 4. Results of aluminum sorption under static conditions**

Таблица 4. Результаты сорбции алюминия в статических условиях

Sorbent	Solution volume, cm <sup>3</sup>	Sorbent volume, cm <sup>3</sup>	Sorbent mass, g	Concentration, mg/dm <sup>3</sup>		SEC, g/dm <sup>3</sup>	
				Al	Li	Al	Li
A500	50	1	0.3372	153.6	1469.6	0.04	0
AN-31	50	1	0.2713	111.4	1429.2	2.15	1.80
CRB05	50	1	0.3588	97.2	1475.6	2.86	0

The ICP-AES analysis of raffinates showed that the CRB05 dynamic exchange capacity at the specific loading of 2 BV/hr amounted to 2.47 g/dm<sup>3</sup>, which is two times higher than at FR = 4 BV/hr (1.23 g/dm<sup>3</sup>). Meanwhile, the total DEC for Al ions in both cases was about 3.5 g/dm<sup>3</sup>. Their concentration in the raffinate before their breakthrough did not exceed 0.5 mg/dm<sup>3</sup> (below the ICP-AES detection limit).

### Results of sorption purification of a solution after water leaching of the black mass

The sorption purification of the Li-containing solution after water leaching of the black mass at the specific loading of 2 BV/hr on Diaion CRB05 and Purolite S950 ion exchangers enabled to completely remove Al ions and partially remove Ca, Mg, Fe and Ni ions (Table 3).

The resulting purified solution was used to obtain lithium carbonate.

### Results of lithium carbonate precipitation

The X-ray phase analysis of the white precipitate formed during thermal concentration (evaporation) of the water leaching solution purified from impurities showed that its main component is lithium carbonate and a phase with a cubic crystal system (space group  $R\bar{3}m$ ) is present as an impurity (~2 %), its structure being similar to that of lithium cobaltite [32], however, its reliable identification proved impossible.

The proportion of the main substance amounted to 98.2 %. The resulting lithium carbonate in terms of the content of alkali and alkaline earth metals is comparable to technical lithium carbonate obtained from natural sources (Albemarle, USA, Rockwood Lithium, USA), but currently many manufacturers do not regulate the content of some elements, such as Ti, Co, Cu, Al and Ni, which are not typical for lithium carbonate obtained from natural hydro- and solid mineral sources.

Aluminum accounts for the largest share of impurities in lithium carbonate, although it was not detected in the solution after sorption removal due to the ICP-AES detection limit for Al ions — 0.5 mg/dm<sup>3</sup>. Apparently, the solution contained a certain amount of aluminum ions, which contaminated lithium carbonate in the course of the solution concentration during evaporation. In this regard, further research will be aimed at determining optimal sorption conditions and solving another problem — relatively low lithium extraction during water leaching (40–70 %).

**Table 5. Results of chemical analysis of the precipitate based on lithium carbonate**

Таблица 5. Результаты химического анализа осадка на основе карбоната лития

Element, compound	Content, wt. %	Method of analysis
Li <sub>2</sub> CO <sub>3</sub>	98.2	Acidometry
Ti	0.0170	ICP-AES
Ca	0.0204	ICP-AES
Mn	0.0006	ICP-AES
Cu	N/D	ICP-AES
Fe	0.0053	ICP-AES
Ni	N/D	ICP-AES
Al	0.0888	ICP-AES
Mg	0.0146	ICP-AES
Na	0.0111	ICP-AES
P	0.0304	ICP-AES
K	0.0105	ICP-AES
Co	N/D	ICP-AES
B	0.0052	ICP-AES
S	0.0006	ICP-AES
H <sub>2</sub> O	0.2	Gravimetry

## Conclusion

In the course of investigations aimed at obtaining lithium carbonate from the black mass of lithium-ion batteries, we explored the process of water leaching of lithium at various L/S ratios. During the study, we:

- derived the dependencies of lithium extraction on the L/S ratio and plotted kinetic leaching curves;
- explored the process of sorption removal of aluminum from the model alkaline Li—Al solution using some weak base anion exchangers (CRB05 and AN-31);
- determined the capacity of anion exchangers under static and dynamic conditions;
- plotted elution aluminum sorption curves for specific flow rates of 2 and 4 bed volume per hour;
- performed sorption purification of the solution after aqueous leaching of the black mass using a weak base anion exchanger Diaion CRB05 and a chelate cation exchanger Purolite S950.

After evaporation of the purified solution, we obtained lithium carbonate with a content of the main substance of 98.2 %.



## References

1. Sarkarov R.A., Belan S.I., Guseinov N.M. Assessment of the current state and prospects for the production of lithium and its compounds in Russia. *Industrial'naya ekonomika*. 2022;1(2):57–68. (In Russ.).  
[https://doi.org/10.47576/2712-7559\\_2022\\_2\\_1\\_57](https://doi.org/10.47576/2712-7559_2022_2_1_57)  
Саркаров Р.А., Белан С.И., Гусейнов Н.М. Оценка современного состояния и перспективы добычи лития и его соединений в России. *Индустриальная экономика*. 2022;1(2):57–68.  
[https://doi.org/10.47576/2712-7559\\_2022\\_2\\_1\\_57](https://doi.org/10.47576/2712-7559_2022_2_1_57)
2. Mizushima K., Jones P.J., Wiseman J.B., Goodenough J.B.  $\text{Li}_x\text{CoO}_2$  ( $0 < x < -1$ ): A new cathode material for batteries of high energy density. *Materials Research Bulletin*. 1980;15:783–789.  
[https://doi.org/10.1016/0025-5408\(80\)90012-4](https://doi.org/10.1016/0025-5408(80)90012-4)
3. Thackeray M.M., Johnson P.J., De Picciotto L.A., Bruce P.G., Goodenough J.B. Electrochemical extraction of lithium from  $\text{LiMn}_2\text{O}_4$ . *Materials Research Bulletin*. 1984;19(2):179–187.  
[https://doi.org/10.1016/0025-5408\(84\)90088-6](https://doi.org/10.1016/0025-5408(84)90088-6)
4. Zaghbi K., Simoneau M., Armand M., Gauthier M. Electrochemical study of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as negative electrode for Li-ion polymer rechargeable batteries. *Journal of Power Sources*. 1999;81:300–305.  
[https://doi.org/10.1016/S0378-7753\(99\)00209-8](https://doi.org/10.1016/S0378-7753(99)00209-8)
5. Padhi A.K., Nanjundaswamy K.S., Goodenough J.B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *Journal of the electrochemical society*. 1997;144(4):1188.  
<https://doi.org/10.1149/1.1837571>
6. Shi P., Li T., Zhang R., Shen X., Cheng X. B., Xu R., Huang X. C. Liu H., Zhang Q. Lithiophilic  $\text{LiC}_6$  layers on carbon hosts enabling stable Li metal anode in working batteries. *Advanced Materials*. 2019;31(8):1807131.  
<https://doi.org/10.1002/adma.201807131>
7. Aaltonen M., Peng C., Wilson B.P., Lundström M. Leaching of metals from spent lithium-ion batteries. *Recycling*. 2017;2(4):20. <https://doi.org/10.3390/recycling2040020>
8. Lie J., Liu J.C. Closed-vessel microwave leaching of valuable metals from spent lithium-ion batteries (LIBs) using dual-function leaching agent: Ascorbic acid. *Separation and Purification Technology*. 2021;266:118458.  
<https://doi.org/10.1016/j.seppur.2021.118458>
9. Golmohammadzadeh R., Faraji F., Rashchi F. Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review. *Resources, Conservation and Recycling*. 2018;136:418–435.  
<https://doi.org/10.1016/j.resconrec.2018.04.024>
10. De Oliveira Demarco J., Cadore J. S., da Silveira de Oliveira F., Tanabe E. H., Bertuol D. A. Recovery of metals from spent lithium-ion batteries using organic acids. *Hydrometallurgy*. 2019;190:105169.  
<https://doi.org/10.1016/j.hydromet.2019.105169>
11. Esmaeili M., Rastegar S.O., Beigzadeh R., Gu T. Ultrasound-assisted leaching of spent lithium ion batteries by natural organic acids and  $\text{H}_2\text{O}_2$ . *Chemosphere*. 2020;254:126670.  
<https://doi.org/10.1016/j.chemosphere.2020.126670>
12. Fu Y., He Y., Chen H., Ye C., Lu Q., Li R., Xie W., Wang J. Effective leaching and extraction of valuable metals from electrode material of spent lithium-ion batteries using mixed organic acids leachant. *Journal of Industrial and Engineering Chemistry*. 2019;79:154–162.  
<https://doi.org/10.1016/j.jiec.2019.06.023>
13. Gao W., Liu C., Cao H., Zheng X., Lin X., Wang H., Zhang Y., Sun Z. Comprehensive evaluation on effective leaching of critical metals from spent lithium-ion batteries. *Waste Management*. 2018;75:477–485.  
<https://doi.org/10.1016/j.wasman.2018.02.023>
14. Urbańska W. Recovery of Co, Li, and Ni from spent Li-ion batteries by the inorganic and/or organic reducer assisted leaching method. *Minerals*. 2020;10(6):555.  
<https://doi.org/10.3390/min10060555>
15. Nayl A.A., Elkhatab R.A., Badawy S.M., El-Khatteb M.A. Acid leaching of mixed spent Li-ion batteries. *Arabian Journal of Chemistry*. 2017;10:S3632–S3639.  
<https://doi.org/10.1016/j.arabjc.2014.04.001>
16. Ku H., Jung Y., Jo M., Park S., Kim S., Yang D., Rhee K., An E.M. Sohn J., Kwon K. Recycling of spent lithium-ion battery cathode materials by ammoniacal leaching. *Journal of hazardous materials*. 2016;313:138–146.  
<https://doi.org/10.1016/j.jhazmat.2016.03.062>
17. Gaye N., Gueye R.S., Ledauphin J., Balde M., Seck M., Wele A., Diaw M. Alkaline leaching of metals from cathodic materials of spent lithium-ion batteries. *Asian Journal of Applied Chemistry Research*. 2019;3(2):1–7.  
<https://doi.org/10.9734/AJACR/2019/v3i230088>
18. Kim D., Quang N. D., Hien T. T., Chinh N. D., Kim C., Kim D. 3D inverse-opal structured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Anode for fast Li-ion storage capabilities. *Electronic Materials Letters*. 2017;13(6):505–511.  
<https://doi.org/10.1007/s13391-017-7101-x>
19. Wang S.L., Lin C.H., Yan, Y.Y., Wang M.K. Synthesis of Li/Al LDH using aluminum and LiOH. *Applied Clay Science*. 2013;72:191–195.  
<https://doi.org/10.1016/j.clay.2013.02.001>
20. Chistyakov A.A., Chirkst D.E., Cheremisina O.V. Sorption of aluminate from alkaline solutions on D-403 anion exchanger. *Russian Journal of Physical Chemistry A*. 2011;85(11):1995–1999.  
<https://doi.org/10.1134/s0036024411110069>

- Чистяков А.А., Чиркст Д.Э., Черемисина О.В. Сорбция алюмината из щелочных растворов на анионите D-403. *Журнал физической химии*. 2011;85(11): 2137–2141.
21. Cheremisina O.V., Ponomareva M.A., Sagdiev V.N. Sorption extraction of gallium and aluminum from alkaline solutions on the AN-31 anion-exchange resin. *Izvestiya. Non-Ferrous Metallurgy*. 2017;(3):56–64. (In Russ.). <https://doi.org/10.17073/0021-3438-2017-3-56-64>
  - Черемисина О.В., Пономарева М.А., Сагдиев В.Н. Сорбционное извлечение галлия и алюминия из щелочных растворов на анионите АН-31. *Известия вузов. Цветная металлургия*. 2017;(3):56–64. <https://doi.org/10.17073/0021-3438-2017-3-56-64>
  22. Ramazanov A.Sh., Sveshnikova D.A., Ataev D.R. Kinetics of lithium cation sorption with freshly precipitated aluminum hydroxide from natural brine. *Sorbtionnye i khromatograficheskie protsessy*. 2021;21(2):225–234. (In Russ.). <https://doi.org/10.17308/sorpchrom.2021.21/3356>
  - Рамазанов А.Ш., Свешникова Д.А., Атаев Д.Р. Кинетика сорбции катиона лития свежесозажденным гидроксидом алюминия из природного рассола. *Сорбционные и хроматографические процессы*. 2021;21(2):225–234. <https://doi.org/10.17308/sorpchrom.2021.21/3356>
  23. Jiang H., Yang Y., Sun S., Yu J. Adsorption of lithium ions on lithium-aluminum hydroxides: Equilibrium and kinetics. *The Canadian Journal of Chemical Engineering*. 2020;98(2):544–555. <https://doi.org/10.1002/cjce.23640>
  24. Zhang H., Yang Y., Ren D., Wang L., He X. Graphite as anode materials: Fundamental mechanism, recent progress and advances. *Energy Storage Materials*. 2021;36:147–170. <https://doi.org/10.1016/j.ensm.2020.12.027>
  25. Wajima T., Munakata K., Uda T. Adsorption behavior of lithium from seawater using manganese oxide adsorbent. *Plasma and Fusion Research*. 2012;7:2405021. <https://doi.org/10.1585/pfr.7.2405021>
  26. Chitrakar R., Kanoh H., Miyai Y., Ooi K. Recovery of lithium from seawater using manganese oxide adsorbent ( $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ) derived from  $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ . *Industrial & Engineering Chemistry Research*. 2001;40(9):2054–2058. <https://doi.org/10.1021/ie000911h>
  27. Hossain S.M., Ibrahim I., Choo Y., Razmjou A., Naidu G., Tijing L., Kim J., Shon H.K. Preparation of effective lithium-ion sieve from sludge-generated  $\text{TiO}_2$ . *Desalination*. 2022;525:115491. <https://doi.org/10.1016/j.desal.2021.115491>
  28. Li X., Chen L., Chao Y., Chen W., Luo J., Xiong J., Zhu F., Chu X., Li H., Zhu W. Amorphous  $\text{TiO}_2$  — derived large — capacity lithium ion sieve for lithium recovery. *Chemical Engineering & Technology*. 2020;43(9): 1784–1791. <https://doi.org/10.1002/ceat.201900374>
  29. Volkova T.S., Rudskikh V.V. Study of the possibility of purifying lithium chloride solution to remove impurities by sorption method. *Russian Journal of Applied Chemistry*. 2019;92(8):1113–1121. <https://doi.org/10.1134/S1070427219080093>
  - Волкова Т.С., Рудских В.В. Исследование возможности очистки раствора хлорида лития от примесей сорбционным методом. *Журнал прикладной химии*. 2019;92(8):1021–1029. <https://doi.org/10.1134/S0044461819080097>
  30. Kiefer R., Höll W.H. Sorption of heavy metals onto selective ion-exchange resins with aminophosphonate functional groups. *Industrial & Engineering Chemistry Research*. 2001;40(21):4570–4576. <https://doi.org/10.1021/ie010182i>
  31. Milyutin V.V., Nekrasova N.A., Rudskikh V.V., Volkova T.S. Preparation of high-purity lithium carbonate using complexing ion-exchange resins. *Russian Journal of Applied Chemistry*. 2020;93:549–553. <https://doi.org/10.1134/S1070427220040096>
  - Милютин В.В., Некрасова Н.А., Рудских В.В., Волкова Т.С. Получение высокочистого карбоната лития с использованием комплексообразующих ионитов. *Журнал прикладной химии*. 2020;93(4): 540–544. <https://doi.org/10.31857/S0044461820040088>
  32. Hertz J.T., Huang Q., McQueen T., Klimczuk T., Bos J.W.G., Viciu L., Cava R.J. Magnetism and structure of  $\text{Li}_x\text{CoO}_2$  and comparison to  $\text{Na}_x\text{CoO}_2$ . *Physical Review B*. 2008;77(7):075119. <https://doi.org/10.1103/PhysRevB.77.075119>

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