

Investigation of the Process of Lithium Chloride Extraction from Brine of the Salt Lakes of the Aral Sea Region

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Abstract: *The purpose of the research is to create a technology for processing hydromineral raw material into products of lithium salts and rare earth elements, as well as to develop a highly efficient technology for production of lithium, lithium compounds and rare earth elements of the Aral region.*

The chemical and mineralogical composition of the hydromineral raw material of the Aral region lakes has been studied by the method of precipitation. The conditions for obtainment of lithium concentrates have been studied. The conditions for lithium minerals concentration and production of concentrates for lithium chloride extraction have been investigated. Purification of lithium concentrates off ions of calcium and magnesium, as well as effective methods of lithium precipitation in the form of lithium carbonate have been studied. The extraction methods for processing lithium-containing sediments and sorption methods of lithium extraction from brines have been investigated. Water-salt systems for the directed search of effective methods for obtainment of lithium salts from brine and sediments of salt lakes have been studied.

Index Terms: *hydromineral raw material, salt solution, sludge, lithium chloride, rare earth elements.*

I. INTRODUCTION

Lithium is the lightest alkali metal, declared to be the “future and strategic metal”, is widely used in the fields of porcelain and glass production, refrigeration engineering, metallurgy, medicine, aerospace industry, arms industry, nuclear energy, electronics, alloys and batteries, etc. Lithium resources exist in nature either in solid ores or liquid brine. However, the limited reserves of solid lithium ores and high expenses incidental to its extraction, indicate that lithium extraction from salts will be the future trend.

At present lithium and its compounds are widely used in the world and the annual demand for lithium is 65-70 thousand tons. Rich amounts of lithium, up to 80% are concentrated in natural waters. Therefore, foreign countries: the USA, Chile, Italy, Japan and others constantly conduct research on lithium extraction from specific natural waters,

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since the source of raw materials is ground water which is cheap full-value raw material [1].

The largest deposits of lithium are met in granitic pegmatites of the sodium-lithium type as lithium in nature is closely associated with sodium (due to the similarity of the energy characteristics of lithium ions and sodium ions), especially in deposits of residual crystallization. However, in recent years, deposits of sedimentary type and underground saline waters, and waters of salt lakes have become increasingly important [2], [3].

FMC Lithium Division from the United States, as well as SQM from Chile, are now the world market leaders, each of them controls 30% of the world lithium market. In South America, this metal is mined at the bottom of dried salt lakes. Numerous studies [4], [6] are devoted to extracting REE (rare earth elements) from brine and solid deposits.

II. PROPOSED METHODOLOGY

A. Methods for Obtaining Rare Earth Metals

Currently sorption methods are widely used in applied radiochemistry: in the processing of their radiated nuclear fuel, isolation and separation of REE and transuranic elements (TUE), as well as in the processing of liquid radioactive waste (LRW). Synthesized ion-exchange materials of the AXION series (Am, Pu) are gel phosphorus-nitrogen-containing ion-exchange polymers, which have a high selectivity related to REE and TUE ions in strongly acidic media. High prospectivity of the AXION ion-exchange materials for extraction of uranium, REE and TUE from nitrates, as well as for indium extraction from the waste of zinc production, is presented. Well-known scientists extract tantalum and niobium from concentrates by the extraction method. Depending on the chosen scheme at the concentrating processing plant, it is possible to obtain concentrates with a content of 20-45% of Nb₂O₅ and 2-4.5% of Ta₂O₅. The method of extraction from fluoride-sulphate solutions was used for extraction and separation of niobium and tantalum. The effect of HF, H₂SO₄ consumption and other concentrate decomposition conditions have been investigated. The transition of Ta, Nb and related elements into the solution, the effect of the volume ratio of the organic and aqueous phases of Vo:Vb were studied. In accordance with the research results, a principal scheme was proposed [5].



Octanol-1 was used as an extractant. According to this scheme, the planned extraction of Ta and Nb in the solution during the concentrate decomposition is not less than 95% and 98% respectively, to the finished product – 92% and 94%, respectively.

Extraction of lithium from hydromineral raw material is a necessary and topical task because of the limited ore reserves (the main reserves of lithium have been identified as associated with deposits of tantalum, niobium, wolfram and tin). The extraction, reagent or adsorption methods are used for lithium extraction from solutions. The electrocoagulation method with soluble iron-aluminum anodes was tested [6] to obtain lithium from the thermal waters of oil fields; the degree of lithium extraction was 70.5%. The results obtained showed high performance and low energy intensity of the process. However, it requires further development. In particular, the issues of thickening, filtration and utilization of the isolated lithium-containing sediment have not been solved. Work continues on the extraction of lithium out of multicomponent solutions using chemisorption on aluminum hydroxide [7]. Lithium is precipitated using various aluminum-containing reagents: sodium hydroalumocarbonate, active forms of aluminum hydroxide, soluble salts of aluminum, and various composite mixtures [6].

Methods for lithium extraction from solutions of magnesium chloride by extraction, using an extractant with iron-containing butyl phosphate, with the addition of water-insoluble carboxylic acid and re-extraction of lithium with a solution of hydrochloric acid with obtainment of the target product with a low content of lithium are known [8].

A large deposit with proven reserves of lithium is located in the east of Kazakhstan in the Kalbinsky Range. However, theoretically, a larger lithium deposit is located in the Aral Sea region at the bottom of the dried-up sea. Information about lithium reserves in the salt marshes of the Aral Sea region was mentioned in the old Soviet reference books [9].

A considerable amount of lithium is found in lakes and lake slimes, groundwaters, in sea water (1.5-10.5 wt.%). In the process of obtaining lithium salts from hydromineral raw material, the inorganic and organic sorbents were used, depending on lithium content in various forms of compounds. Extraction of lithium from complex mineral compounds was not always resolved successfully because of the low degree of lithium extraction into a marketable product.

The volume of brine of the Southern and Northern Basins of the Zhaksykylysh lake contains 40-60mg/l of lithium(not more than 0.2% of Mg²⁺, not more than 0.4% ofCa²⁺, not more than1.2% of SO₄²⁻). In slimes, the content far exceeds and amounts 60-120mg/kg. To obtain the lithium concentrate of the required quality the brine is first enriched. The available reserves of hydromineral raw material (in lakes and lake muds, brine and saline deposits) in the Aral region provide the annual need in lithium.

Technological principles for the use of mineral raw material available in the Aral region will be developed taking into account the particular qualities of this hydromineral raw

material.Modernization of chemical equipment is planned to ensure the integrated use of raw material according to non-waste technology.

Thus, a detailed study of all the above-listed processes of the proposed technology enables to get new results and determine the optimal conditions: of the extractant flow rates, temperature and time of the process of extraction of lithium and REE.

III. RESULTS

The brine of salt lakes of the Aral Sea region was used for the experiment. The composition of the brine is presented in Table I.

Table I.Composition of the Zhaksykylysh field brine*

Number of sample	30-1.	30-2.	30-3.	30-4.
Li7 mg/kg	263.5	311,94	128,38	142,01
B11 mg/kg	102,93	750,75	95,18	225,84
Na23 mg/kg	70639,89	89061,56	75962,03	83489,99
Mg24 mg/kg	23513,35	43707,03	17750,59	19025,78
Al27 mg/kg	24,84	237,44	16,68	9,9
La139 mg/kg	0,005	0,021	0,005	0,002
Ce140 mg/kg	0,008	0,021	0,005	0,009
Pr141 mg/kg	0,003	0,005	0	0

Note: *brine selected from different trajectories of the field From the data in Table I, it follows that lithium content in the samples fluctuates within the limits of 128,38-263,50 mg/kg and rare-earth elements are almost insignificant.

For the experiment, the brine sample is previously averaged out, an aliquot is taken (Table II), placed in a 100ml flask mounted on a magnetic stirrer with an rpm governor (set to 600 rpm), then butyl alcohol (30 ml) is added. The sample,consisting of a layer of alcohol and water, is stirred for the predetermined time. A white precipitate, consisting of sodium chloride, deposits at the alcohol-water interface in the process of mixing with the use of anhydrous butanol. After predetermined time (Table II), the sample is put into a separatory funnel, where after the separation of butanol and water, the lower aqueous layer is discharged. The alcohol layer is stripped to dryness in a vacuum (water-jet air pump). The watery residual matter is “dried”off in a drying oven at the temperature of 130°C.



IV. DISCUSSION

The obtained precipitate was studied in an ICP device to determine lithium content. According to the results obtained the degree of lithium extraction was calculated. The precipitate was studied using SEM. The results of the experiment are presented in Tables II and III and shown in Figs. 1, 2 and 3.

Table II .Change in precipitation yield, depending on the brine volume

V tests, ml	m, gr	Time of extraction, min	Degree of extraction of LiCl, %
10	0,3498	15	86,9
20	0,3032	15	84,4
30	0,3097	15	84,2
50	0,3031	15	83,9

From the data of Table II it can be seen that with an increase in the brine volume at a fixed rate of flow of butyl alcohol extractant and time, the degree of lithium extraction gradually decreases. The degree of lithium extraction is 96.9% at the brine flow rate equal to 10 ml, the degree of lithium extraction decreases to 83.9% with the increase of the brine flow rate up to 50 ml. Fig. 1 shows the mass yield depending on the volume of the extractable brine.

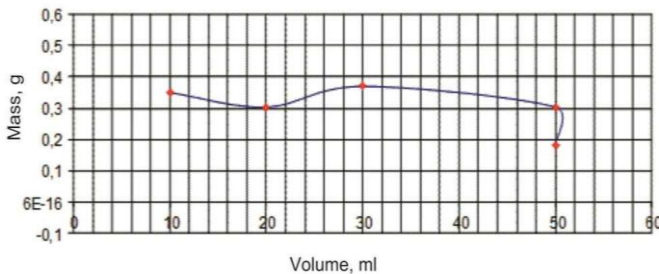


Fig. 1. Mass yield depending on the extractable brine volume

From Fig. 1 it can be seen that the precipitate mass changes under the same conditions with the change of the volume of extractable brine. The greater the flow rate of brine is, the smaller is the mass. In the course of extraction of 10 ml of brine, the precipitate yield is 0.3498 g, and during the extraction of 50 ml of brine the precipitate yield is 0.3031 g.

Later, brine extraction was carried out in the time interval of 10-30 min. The results of the experiment are presented in Table III.

Table III . Dependence of the degree of lithium chloride extraction on the process time

No.	V tests, ml	V of extractive agent, ml	Time of extraction, min	m, gr.	Degree of extraction LiCl, %
23-1	10	30	10	0,3218	86,9
23-2	10	30	15	0,4784	96,7
23-3	10	30	20	0,4708	95,9
23-4	10	30	25	0,4226	92,6
23-5	10	30	30	0,3639	88,7

From the data of Table III, it follows that at fixed rate flow of 10 ml of brine and volume of extractant equal to 30 ml and with an increase in the extraction duration, the degree of lithium extraction gradually increases. At the duration of 10min, the degree of lithium extraction is 86.95%, at 15 min it is 96.7%, and further it is 30 min, the degree of lithium extraction decreases and is 88.7%. It means that the highest degree of lithium extraction is reached in the course of 15 min. At the same time at first the mass yield of the brine precipitate increases, then with the increase of extraction time, the mass yield of the precipitate decreases. Fig. 2 shows the precipitate yield depending on time.

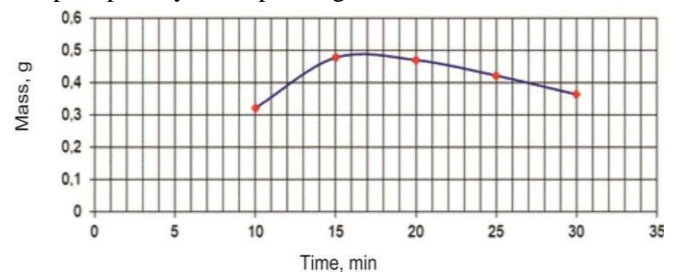


Fig. 2. Mass yield depending on the volume of the extractable brine

From Fig. 2 it can be seen that the precipitate weight is 0.32183 gr. at the time of 10 min and at 15 min the precipitate weight is 0.47845gr. Then from 20 min up to 30 min the precipitate mass yield decreases and is 0.36393 gr. I.e. the mass yield and the degree of lithium extraction decrease at the same time. The precipitate probably consists of salts of lithium chloride and sodium. To determine the composition of the precipitate after the separation of lithium chloride, the divided mass was studied on SEM. Fig. 3 presents the elemental analysis of the precipitate.

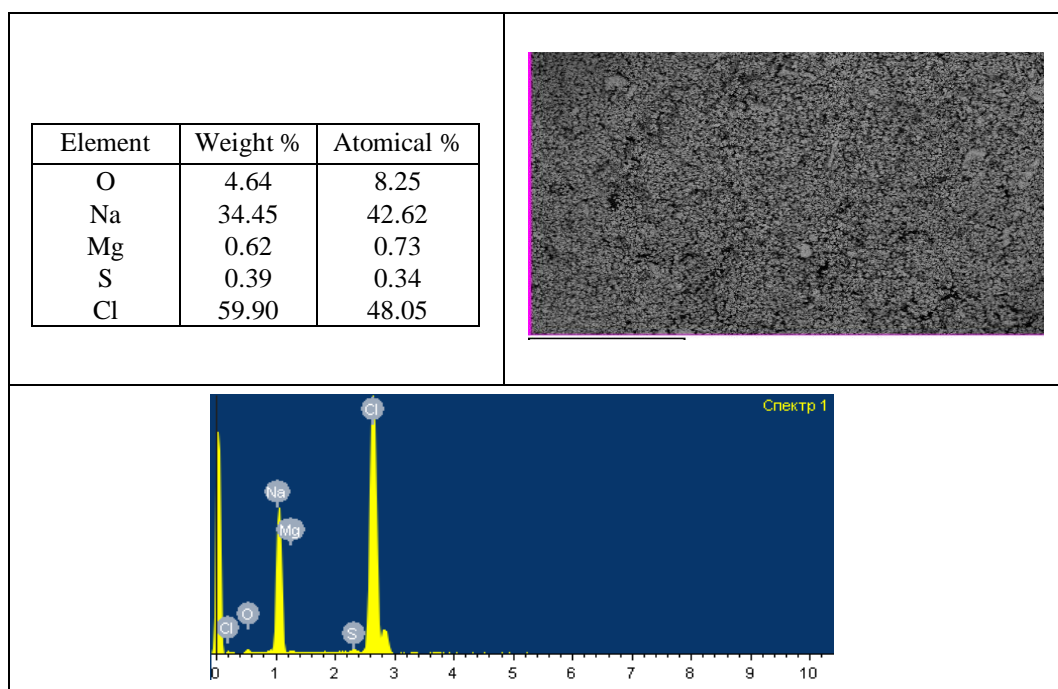


Fig. 3. Elemental analysis of the precipitate obtained from the brine of salt lakes of the Aral Sea region

From Fig. 3 it is seen that the precipitate mainly consists of sodium and chlorine and of a small amount of magnesium and sulfur.

V. CONCLUSION

Thus, the data obtained enable to produce valuable products of lithium chloride and cooking salt from the brine of the Aral Sea saline lakes. At that as the volume of brine increases at a fixed rate of flow of butyl alcohol extractant and time, the degree of lithium extraction gradually decreases from 96.9% to 83.9%. With a fixed rate of flow of brine (10 ml) and volume of extractant (30 ml) and with an increase of extraction duration, the degree of lithium extraction gradually increases. With a duration from 10 min to 15 min, it is 96.7%, and with an increase in time up to 30 min the degree of lithium extraction from then on decreases to 88.7%.

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