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INVESTIGATION OF A LITHIUM CHLORIDE EXTRACTION PROCESS FROM HYDROMINERAL RAW MATERIAL

Abstract

The purpose of the research is to create technology for processing hydromineral raw material to produce lithium salts and rare earth elements, to develop a highly efficient technology for products of lithium, lithium compounds and rare earth elements of the Aral region of Kazakhstan.

The chemical and mineralogical compositions of hydromineral raw material of the Aral region lakes have been studied by method of precipitation. The conditions for obtainment of lithium concentrates have been studied. Conditions for lithium minerals concentration and production of concentrates for lithium chloride extraction have been studied. Purification of lithium concentrates off calcium and magnesium ions and chemical composition of hydromineral raw material, effective methods of lithium precipitation in the form of lithium carbonate, its purification off Ca^{2+} , Mg^{2+} impurities by method of precipitation have been studied. The extraction methods for processing lithium-containing sediments and sorption methods of lithium extraction from brines have been studied. Water-salt systems have been studied for the directed search of effective methods for obtainment of lithium salts from brine and sediments of salt lakes.

Key words: hydromineral raw material, salt solution, sludge, lithium chloride, brine, extraction.

Introduction

Lithium is the lightest alkali metal and is considered to be the “future and strategic metal” widely used in the fields of porcelain and glass production, refrigeration engineering, metallurgy, medicine, aerospace industry, defense 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 isolation /extraction from salts will be the future trend.

From among rare metals, lithium and its compounds are widely used in the world. The annual demand for lithium is 65-70 thousand of tons. Large parts 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 isolation/extraction from specific natural waters, since the source of raw materials is groundwater which is cheap full-value raw material [1].

The largest deposits of lithium are known in granitic pegmatites of 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 mineralized waters and waters of salt lakes 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 market of lithium. 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 from solid deposits.

Methods of experiment

Currently sorption methods are widely used in applied radiochemistry: in processing the irradiated nuclear fuel (INF), isolation and separation of rare-earth (REE) and transuranic elements (TUE), as well as in the processing 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 perspective of the AXION ion-exchange materials for extraction of uranium, REE and TUE from nitrates, and also for indium extraction from waste of zinc producing units is presented.

Well-known scientists isolate/extract tantalum and niobium from concentrates by extraction method. Depending on the chosen scheme at the concentrating processing it is possible to obtain concentrates with a content of 20-45% of Nb₂O₅ and 2-4.5% of Ta₂O₅. Method of extraction from fluoride-sulphate solutions was used for isolation/ extraction and separation of niobium and tantalum. The effect of HF, H₂SO₄ consumption and other concentrate decomposition conditions on 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, concentrations of HF and H₂SO₄ on the distribution of Ta, Nb and admixtures on the extraction operations, washing and re-extraction were studied. According to 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, into the finished product - 92% and 94%, respectively.

Isolation/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). Extraction, reagent or adsorption methods are used for lithium isolation/ extraction from solutions. Electro coagulation method with soluble iron-aluminum anodes was tested [6] to obtain lithium from the thermal waters of oil fields; the degree of lithium isolation/ 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 isolation/extraction of lithium out of multicomponent solutions using chemisorption on aluminum hydroxide [7]. Lithium is precipitated using various aluminum-containing reagents: sodium hydroaluminum carbonate (SHAC), active forms of aluminum hydroxide (AHO), soluble salts of aluminum, and various composite mixtures [6].

Methods for lithium extraction/ isolation from solutions of magnesium chloride by extraction, using an extractant with iron-containing tributyl phosphate, with addition of water-insoluble carboxylic acid and re-extraction of lithium with solution of hydrochloric acid with obtainment of the target product with low concentration on lithium are known [9].

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 that lithium reserves are in the salt marshes of the Aral Sea region is mentioned in old Soviet reference books.

A significant part of lithium is found in lakes and lake slimes, ground waters, in sea water (1.5-10.5 wt. %). In the process of obtaining lithium salts from hydromineral raw material, inorganic and organic sorbents were used formerly, depending on lithium content in various forms of compounds. Isolation/extraction of lithium from complex mineral compounds was not always resolved successfully because of the low degree of lithium isolation into the commercial product.

The brine volume of the Southern and Northern Basin of Zhaksykylysh lake contains 40-60mg/l of Lithium (not more than 0.2% of Mg²⁺, not more than 0.4% of Ca²⁺, not more than 1.2% of SO₄²⁻), in slimes the content significantly exceeds and amounts 60-120mg/kg. In addition, the enrichment

of brine to the required quality of lithium concentrate is necessary. The available reserves of hydromineral raw material (lakes and lake muds, brine and saline deposits) in the Aral region provide 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.

Results and discussion

Brine of salt lakes of the Aral Sea region is used for the experiment, the composition of brine is presented in Table 1.

Table 1- Composition of the Zhaksykylysh field brine *

Number of sample	Sample 1	Sample 2	Sample 3	Sample 4
Li, mg/kg	262.50	259.25	312.94	280.28
B, mg/kg	101.93	87.40	749.75	700.58
Na, mg/kg	70639.89	68056.06	89061.57	82418.29
Mg, mg/kg	23513.36	22467.09	43707.03	39545.03
Ca, mg/kg	2110.24	1898.49	3536.85	2361.25
S, mg/kg	4314.42	4080.36	10058.80	5429.23
Fe, mg/kg	620.17	682.79	1424.15	581.04

*brine selected from different trajectories of the field

From the data in table 1, it follows that lithium content in the sample fluctuates within the limits of 128.38-263.50 mg/kg and rare-earth elements are almost insignificant.

For the experiment, a sample of the brine is averaged out, an aliquot is selected (table 2) and placed in a 100 ml 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. White precipitate, consisting of sodium chloride, falls out at the alcohol-water interface in the process of mixing with the use of anhydrous butanol.

After the predetermined time (table 2), the sample is put into a separating funnel, where after the separation of butanol and water, the lower aqueous layer is discharged. The alcohol layer is stripped to dryness in vacuum (water-jet air pump). The residual matter is “dried” off butanol traces in a drying oven at the temperature of 130°C.

The obtained precipitate was studied in an ICP device to determine lithium content, and 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 Table 2 and 3 and shown in Figure 1, 2 and 3.

Table 2 – Change in precipitation yield depending on the brine volume

V, ml	m, g	Time of extraction, min	Degree of LiCl extraction, %
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 2 it can be seen that with an increase in the brine volume at 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 till 83.9% with the increase of the brine flow rate up to 50 ml.

Later, brine extraction was carried out in the time interval of 10-30 minutes. The results of the experiment are presented in table 3.

Table 3 – Dependence of the degree of lithium chloride extraction on the process time

No.	V _{sample} , ml	V _{extragent} , ml	Time of extraction, min	m, g	Degree of LiCl extraction, %
1	10	30	10	0.33	86.9
2	10	30	15	0.48	96.7
3	10	30	20	0.47	95.9
4	10	30	25	0.42	92.6
5	10	30	30	0.36	88.7

From data of table 3 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 duration of 10 minutes, the degree of lithium extraction is 86.95, at 15 minutes it is 96.7%, and at further time equal to 30 minutes the degree of lithium extraction decreases and is 88.7%. It means that the highest degree of lithium extraction is reached during 15 minutes. At the same time at first the mass yield of the brine precipitate increases, then with increase of extraction time, the mass yield of the precipitate decreases.

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. 1 presents the elemental analysis of precipitate.

Element	Weight %	Atomic %
O	4.64	8.25
Na	34.45	42.62
Mg	0.62	0.73
S	0.39	0.34
Cl	59.90	48.05

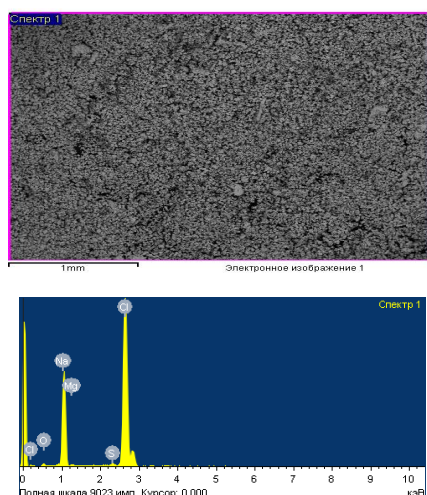


Fig. 1 - Elemental analysis of the precipitate obtained from brine of salt lakes of the Aral Sea region.

From Fig. 1 it is seen that the precipitate mainly consists of sodium and chlorine and a small amount of magnesium and sulfur.

Conclusion

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

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ГИДРОМИНЕРАЛДЫ ШИКІЗАТТАН ЛИТИЙ ХЛОРИДІН АЛУ ПРОЦЕСІН ЗЕРТТЕУ

Түйін

Зерттеудің мақсаты-литий тұздары мен сирек жер элементтерін алу үшін гидроминералды шикізатты өңдеу технологиясын жасау, Қазақстанның Арал өңірінің литий, литий қосылыстары мен сирек жер элементтерін өндірудің жоғары тиімді технологиясын жасау.

Арал өңірі көлдерінің гидроминералды шикізатының химиялық-минералогиялық құрамы жауын-шашын әдісімен зерттелді. Литий концентраттарын алу шарттары зерттелді. Литий минералдарының концентрациясы және литий хлоридін алу үшін концентраттар алу шарттары зерттелді. Литий концентраттарын кальций мен магний иондарынан тазарту және гидроминералды шикізаттың химиялық құрамы, литий карбонаты түріндегі литий жауын-шашынының тиімді әдістері, оны Ca^{2+} , Mg^{2+} қоспаларынан жауын-шашын әдісімен тазарту зерттелді. Құрамында литий бар шөгінділерді өңдеудің экстракция әдістері және тұзды ерітінділерден литий алудың сорбциялық әдістері зерттелді. Тұзды көлдердің тұзды ерітінділері мен шөгінділерінен литий тұздарын алудың тиімді әдістерін мақсатты түрде іздеу үшін су-тұз жүйелері зерттелді.

Кілттік сөздер: гидроминералды шикізат, тұз ерітіндісі, тұнба, литий хлориді, тұзды ерітінді, экстракция.

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ИССЛЕДОВАНИЕ ПРОЦЕССА ИЗВЛЕЧЕНИЯ ХЛОРИДА ЛИТИЯ ИЗ ГИДРОМИНЕРАЛЬНОГО СЫРЬЯ

Аннотация

Целью исследований является создание технологии переработки гидроминерального сырья с получением солей лития и редкоземельных элементов, разработка высокоэффективной технологии получения продуктов из лития, соединений лития и редкоземельных элементов Аральского региона Казахстана.

Методом осаждения изучен химический и минералогический состав гидроминерального сырья озер Приаралья. Изучены условия получения литиевых концентратов. Изучены условия обогащения литиевых минералов и производства концентратов для извлечения хлорида лития. Изучены очистка литиевых концентратов от ионов кальция и магния и химический состав гидроминерального сырья, эффективные методы осаждения лития в виде карбоната лития, его очистка от примесей Ca^{2+} , Mg^{2+} методом осаждения. Изучены экстракционные методы переработки литийсодержащих осадков и сорбционные методы извлечения лития из рассолов. Для направленного поиска эффективных методов получения солей лития из рассолов и отложений соленых озер были изучены водно-солевые системы.

Ключевые слова: гидроминеральное сырье, солевой раствор, осадок, хлорид лития, рассол, экстракция.