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Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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NEWS

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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STUDYING THE PROCESS OF LITHIUM CHLORIDE EXTRACTION FROM THE BRINE

Abstract. The purpose of the research is to create a technology for processing the hydromineralic raw materials of Kazakhstan for the production of lithium salts and rare earth elements, the development of a highly efficient technology for obtaining lithium, lithium compounds and rare earth elements of the Aral region.

The study of Chemical and mineralogical compositions of hydromineral raw materials of lakes of the Aral region are studied by the method of deposition. Conditions of receiving lithium concentrates are studied. Conditions concoction of lithium minerals and receiving concentrates for extraction chloride of lithium are studied. Cleaning of lithium concentrates from ions of calcium and magnesium and chemical composition of the hydromineral raw materials, the effective methods of precipitating lithium in the form of lithium carbonate, its purification from the impurities of Ca^{2+} , Mg^{2+} by the precipitation method are studied. Extraction methods for processing lithium-containing precipitates and sorption methods for extracting lithium from brines are studied. Water-salt systems have been studied for the directed search for effective methods for obtaining lithium salts from brine and saline lake precipitation.

Key words: hydromineralic raw materials, salt solution, sludge, lithium chloride, rare earth elements.

The lightest alkali metal - lithium, which is considered to be "future and strategic metal" is widely used in the fields of porcelain and the production of glass, refrigeration, metallurgy, medicine, aerospace, military industry, atomic energy, electronics, alloys and batteries, etc. Lithium resources exist in nature either in solid ores or in liquid brines. However, the limited reserves of solid lithium ores and high costs associated with its extraction indicate that the extraction of lithium from salt salts will be a future trend.

In the world from rare metals treat widely used lithium and its connections. Annual requirement of lithium makes 65-70 thousand tons. The most part of lithium about 80% in natural waters are concentrated. Therefore foreign countries: the USA, Chile, Italy, Japan, etc. constantly conduct researches on extraction of lithium from concrete natural waters since the raw source underground waters is cheap full-fledged raw materials [1].

The most large-scale deposits of lithium are known in granite pegmatites of natro-lithium type since lithium in the nature intimately associates with sodium (owing to similarity of power characteristics of ions of lithium and sodium), especially in fields of a residual crystallization. However, in recent years the increasing value is gained by fields of sedimentary type and underground salt waters and waters of salty lakes [2,3].

Now the leaders of the world market are FMC Lithium Division from the USA and SQM from Chile, each of which controls 30% of the world market for lithium. In South America, this metal is mined in the bottom of a dried-up salt lakes. The extraction of REE from brine and solid deposition in the focus of numerous works [4,6].

Currently, the sorption methods are widely used in applied radiochemistry: in the processes of reprocessing of irradiated nuclear fuel (SNF), the allocation and separation of rare earth (REE) and transuranic elements (TUE) and in the processing of liquid radioactive waste (LRW). The synthesized ion exchange materials AXION series (Am, Pu) represent the gel of the phosphorus-nitrogen-containing ion-exchange polymers that have high selectivity in relation to ions of REE and TUE in strongly acidic environments. The high potential of the AXION ion-exchange materials for the extraction of uranium, REE and TUE from nitric acid media, and also for extracting indium from waste zinc production is shown.

Famous scientists extract tantalum and niobium from concentrates by extraction method. Depending on the selected scheme on the enrichment redistribution it is possible to obtain concentrates with a content of 20-45% Nb₂O₅ and 2-4.5% Ta₂O₅. For isolation and separation of niobium and tantalum the method of extraction from fluoride - sulfate solutions was used. The influence of consumption of HF and H₂SO₄ and other terms of the decomposition of the concentrate in the enumeration Ta, Nb and accompanying elements in solution, the effect of the ratio of volumes of organic and water phases V_v:V_w, HF and H₂SO₄ concentrations on the distribution of Ta, Nb and impurities on the operations of extraction, washing and stripping. By results of researches the schematic diagram is offered [5]. As the extractant used the octanol - 1. According to this scheme, the planned extraction of Ta and Nb in solution during the decomposition of the concentrate of at least 95 and 98%, respectively, in the finished products of 92 and 94%.

Extraction of lithium from hydromineral raw materials is a necessary and relevant task in view of limitation of ore stocks (the main reserves of lithium are revealed as accompanying fields of tantalum, niobium, tungsten and tin). For release of lithium from solutions use extraction, reagent or adsorptive methods. For its receiving from thermal waters of oil fields the electrothermic coagulation method with soluble iron-aluminum anodes [6], extent of extraction of lithium of 70,5% is tested. The received results showed high efficiency and insignificant power consumption of process. However, it demands further completion. In particularly, the issues of thickening, filtration and disposal allocated to the lithium-containing precipitate. Continue work on the isolation of lithium from multicomponent solutions by chemisorption on the aluminium hydroxide [7]. Deposition of lithium is carried out using a variety of aluminum-containing reagents: hydroaluminate sodium (HAUS), active forms of aluminium hydroxide (AGO), soluble salts aluminum, various composite mixes [8].

There are known methods for extracting lithium from solutions of magnesium chloride by extraction using an extractant with iron-containing tributyl phosphate, with the addition of water-insoluble carboxylic acid and re-extraction of lithium, with a solution of hydrochloric acid to obtain the desired product with a low concentration of lithium [9].

A large deposit with proven reserves of lithium is in the East Kazakhstan – Kalba ridge, where the mountains of the Altai pass into the coaching staff. However, theoretically a larger lithium deposit must be in the Aral region – at the bottom of the dried sea. The information that there are lithium reserves in the salt marshes of the Aral Sea region is mentioned in the old Soviet reference books.

The considerable proportion of lithium are in lakes and lake oozes, underground waters, in ocean water (1,5·10⁻⁵ mass. %). In the course of receiving lithium salts from hydromineral raw materials inorganic and organic sorbents depending on the content of lithium in various form connection were applied earlier. Extraction of lithium from complex mineral compounds not always decided successfully because of low extent of extraction of lithium in marketable products.

The volume of brine in the southern and Northern basin of the lake Zhaksykylysh lithium 40-60mg/l (Mg₂⁺ not more than 0.2%, Ca₂⁺ is not more than 0.4%, SO₄²⁻ - not more than 1.2%), silt content significantly exceeds and is 60-120mg/kg. in addition, the required enrichment of the brine to the required quality lithium concentrate is needed. Available reserves of hydromineral raw materials (lakes and lacustrine silts, brine and saline deposits) in the Aral sea region provide annual demand for lithium.

The technological basis for use of mineral resources available in the Aral region will be developed taking into account features of this hydromineral raw materials, scheduled chemical upgrading of equipment to ensure the integrated use of raw materials waste-free technology.

Thus, a detailed study of all of the above processes of the proposed technology, of course, is relevant, and obtain new results on the solubility in the system LiCl - NaCl – Na₂SO₄ – H₂O and REE (La, Pr, Nd, Er, Hf, Ta) with regard to the influence of impurities in hydromineral raw materials and determine the optimal conditions, the flow rate of the extractant, temperature and time of sorption process lithium and REE determines the scientific novelty of the research.

For the experiment, a brine of salt lakes of the Aral region is used, the composition of which is presented in table 1.

Table 1 – Composition of the brine of the Zhaksykylysh deposit*

Sample number	30-1.	30-2.	30-3.	30-4.
Li7 mg/kg	263.50279	311.94302	128.38595	142.01970
B11 mg/kg	102.93350	750.75133	95.18996	225.84787
Na23 mg/kg	70639.89147	89061.56736	75962.03229	83489.99644
Mg24 mg/kg	23513.35944	43707.03329	17750.59646	19025.78142
Al27 mg/kg	24.84001	237.44130	16.68423	9.90388
La139 mg/kg	0.00512	0.02087	0.00479	0.00237
Ce140 mg/kg	0.00768	0.02087	0.00479	0.00949
Pr141 mg/kg	0.00256	0.00522	0	0
*Brine selected from various trajectories of the deposit.				

From the data in table 1, it is clear that the lithium content in the sample varies within the range 128.38-263.50 mg/kg, and the rare earth elements are almost insignificant.

To conduct the experiment, the brine sample is pre-averaged, an aliquot is taken (table 2) is placed in a 100 ml flask mounted on a magnetic stirrer with a speed controller (set at 600 rpm) after butyl alcohol of 30 ml is added. The sample is stirred for a given time consisting of a layer of alcohol and water. During the mixing process, when using anhydrous butanol at the alcohol-water phase boundary, a white precipitate consisting of sodium chloride precipitates.

After a given time (table 2), the sample is transferred to a separating funnel, where after separation of butanol and water, the lower water layer is drained. The alcohol layer is evaporated to a dry state in a vacuum (water-jet pump). The residue is "dried" from traces of butanol in a drying oven at a temperature of 130°C.

The resulting precipitate was investigated on the ISP device for the lithium content and the degree of lithium extraction was calculated from the results obtained. The sediment was studied with the SEM instrument. The results of the experiment are given in table 2 and 3 and are shown in figure 1, 2 and 3.

Table 2 – Change of sediment yield depending on the volume of brine

V of sample, ml	m, gr.	Extraction time, min	Extraction degree 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 in table 2, it is seen that with the increase in the volume of brine at a constant flow rate of butyl alcohol extractant and time, the degree of lithium extraction gradually decreases. At the rate of brine 10 ml. the degree of extraction of lithium is 96,9%, with the increase of brine flow up to 50 ml., the degree of extraction of lithium is reduced to 83.9%. Figure 1 shows the mass output from the volume of the extracted brine.

Figure 1 shows that under the same conditions, the weight of the precipitate changes with the change in the volume of extracted brine. The higher the consumption of brine, the less the mass of the sediment. When extracting 10 ml of brine, the yield of the precipitate is 0.3498 g, and when extracted 50 ml of brine – the precipitate yield is 0.3031 g.

Subsequently, brine extraction was performed in the time interval 10-30 min. The results of the experiment are given in table 3.

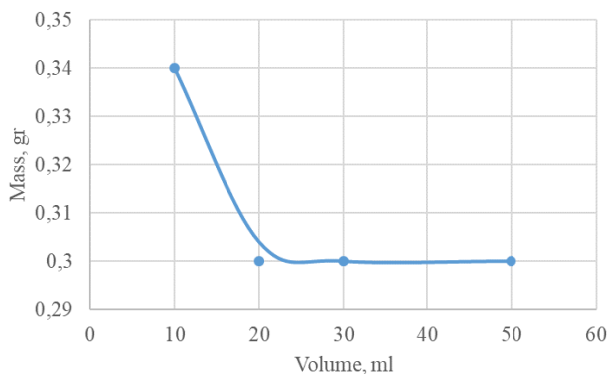


Figure1 – The mass output from the volume of the extracted brine

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

№	V of sample, ml	Vof extractant, ml	Extraction time, min	m, g.	Extraction degree of LiCl, $\%$
23-1	10	30	10	0,32183	86,9
23-2	10	30	15	0,47845	96,7
23-3	10	30	20	0,47080	95,9
23-4	10	30	25	0,42264	92,6
23-5	10	30	30	0,36393	88,7

From the data in table 3 it follows that at a constant flow rate of 10 ml of brine and 30 ml of extractant, and with an increase in the duration of extraction, the degree of lithium extraction gradually increases. With a runtime of 10 min the degree of extraction of lithium is 86,95, when the runtime 15 min the degree of extraction of lithium is 96,7%, and in further time of 30 min. the degree of extraction of lithium is reduced and is 88.7%. The greatest degree of lithium extraction is achieved by a time of 15 min. At the same time, the mass of the precipitate from the brine increases from the beginning, then with an increase in the extraction time, the mass of the precipitate decreases. Figure 2 shows the precipitation output from time.

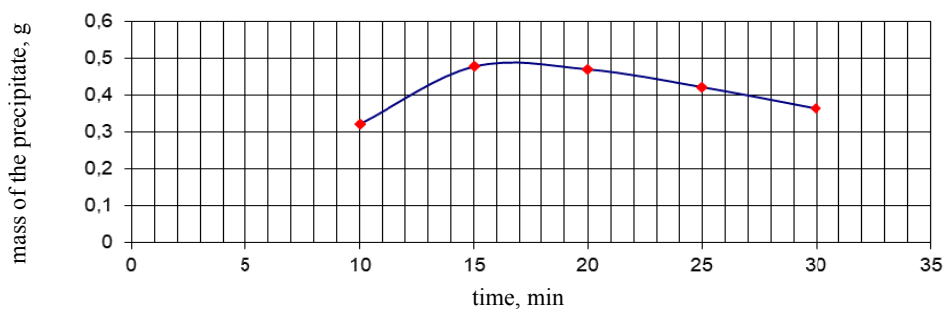


Figure 2 – The mass output from the volume of the extracted brine

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

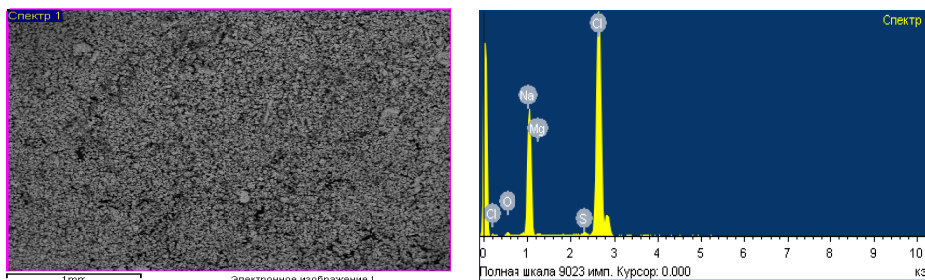


Figure 3 – Elemental analysis of the precipitate obtained from the brine of salt lakes in the Aral region

From figure 2 it is seen that at a time 10 min, the mass of the precipitate is 0,32183 g, and at 15 min. the mass of the precipitate is 0,47845, then the time from 20 min. up to 30 min. the mass of the precipitate is reduced and is equal to 0,36393 g. i.e. the output mass and the degree of extraction of lithium are reduced at the same time. The precipitate may consist of lithium chloride salt and sodium. To determine the composition of the precipitate after the separation of lithium chloride, the separated mass was investigated with SEM. Figure 3 shows the elemental analysis of the precipitate.

It is seen from figure 3 that the precipitate consists mainly of sodium and chlorine and a small amount of magnesium and sulfur.

Conclusion. Thus, the data obtained allow to receive valuable products of lithium chloride and table salt from the brine of the salt lakes of the Aral sea region. At the same time, with the increase in the volume of brine at a constant flow rate of butyl alcohol extractant and time, the degree of lithium extraction gradually decreases from 96.9% to 83.9%. With a constant consumption of brine 10 ml. and extractant volume of 30 ml. and with increasing the duration of extraction, the degree of lithium extraction gradually increases. If the duration from 10 min. to 15 min. is 96,7%, and in the future with the increase of time up to 30 min. the degree of lithium extraction is reduced and is 88.7%.

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ТҰЗДЫ ЕРТІНДІДЕН ЛИТИЙ ХЛОРИДІН БӨЛІП АЛУ ПРОЦЕССИН ЗЕРТТЕУ

Аннотация. Зерттеу мақсаты – тұзды көлдердің тұзды ертінділерінен литий хлоридін алу процесін зерттеу және Қазақстанда литий тұздары мен сирек кездесетін элементтерді өндіру үшін гидроминералды шикізатты өңдеу технологиясын жасау. Литий концентраттарын кальций мен магний иондарынан тазарту процесі және гидроминералды шикізаттың химиялық құрамы зерттелді. Литийді литий карбонаты түрінде тұндыру ең тиімді әдіс. Құрамында литийі бар тұнбаларды өңдеудің экстракциялық әдістері және литийді ертінділерден алудың сорбциялық әдістері зерттелген. Тұзды және тұзды көл шөгінділерінен литий тұзын алудың тиімді әдістерін іздестіру үшін су-тұз жүйелері зерттелді. Арал маңындағы көлдердің гидроминералды шикізатының химиялық және минералогиялық құрамы тұндыру әдісімен зерттелді.

Литийдің дәлелденген қорлары бар ірі кен орны Қазақстанның шығысында - Қалба жотасында және Арал теңізі аймағында - құрғатылған теңіз түбінде орналасқан. Литийдің едәуір бөлігі көлдер мен көлдердің шөгінділерінде жер асты сулары мен теңіз суында (1,5–10,5%) болатындығы анықталды. Жақсықылыш көлінің оңтүстік және солтүстік бассейндерінің тұздықтарының көлеміндегі литийдің құрамы 40-60 мг/л (Mg^{2+} - 0,2% артық емес, Ca^{2+} - 0,4% артық емес, SO_4^{2-} - 1,2% артық емес), ал оның шөгінділердегі құрамы әлдеқайда жоғары және 60-120 мг/кг құрайды. Литий тұздарын гидроминералды шикізаттан алу кезінде, қосылыстың әртүрлі формаларындағы литийдің құрамына байланысты бұрын бейорганикалық және органикалық сорбенттер қолданылған. Күрделі минералды қосылыстардан литийді алу әрдайым сәтті шешілмеді, өйткені литийді товарлы өнім түрінде алу деңгейі төмен болды. Тұз ертіндісін литий концентратының қажетті сапасына дейін байыту керек. Арал аймағындағы гидроминералды шикізаттың (көлдер мен көл сулары, тұздар мен тұзды батпақтар) қоры литийге деген жылдық қажеттілікті қамтамасыз етеді.

Литий минералдарын концентрациялау және литий хлоридін экстракциялау үшін концентраттар дайындау шарттары зерттелді. Бутил спиртінің экстрагенті мен уақытты тұрақты тұтыну кезінде, тұзды мөлшердің жоғарылауымен литий экстракциясының деңгейі біртіндеп төмендейтіні анықталды. 10 мл. тұздықты тұтынған кезде, литийді экстракциялау дәрежесі 96,9% құрайды, тұздықты тұтыну мөлшері 50 мл. дейін артқанда, литийді экстракциялау дәрежесі 83,9% дейін төмендеді. Тұздықты үнемі тұтыну және экстракция көлемінің жоғарылауы кезінде, экстракцияның ұзақтығының артуымен литийдің экстракция дәрежесі біртіндеп артады. Ұзақтығы 10 минут ішінде литийдің шығарылу деңгейі 86,95, ал 15 минутта - 96,7% құрайды, одан әрі 30 минутқа дейін жоғарылағанда, литийдің шығарылу деңгейі төмендейді және 88,7% құрайды. Литий экстракциясының ең жоғары дәрежесіне 15 минут ішінде қол жеткізіледі. Сонымен қатар бір мезетте, алдымен тұзды ертіндіден алынған тұнба массасының шығымы артады, содан кейін өндіру уақыты ұлғаюымен тұнба массасының шығымдылығы төмендейді.

Түйін сөздер: гидроминералды шикізат, тұз, тұнба, литий хлориді, сирек кездесетін элементтер.

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ИЗУЧЕНИЕ ПРОЦЕССА ЭКСТРАКЦИИ ХЛОРИДА ЛИТИЯ ИЗ РАССОЛА

Аннотация. Цель исследования заключается в изучение процесса экстракции хлорида лития из рассола соленых озер и создании технологии переработки гидроминерального сырья Казахстана на продукцию солей лития и редкоземельных элементов. Исследован процесс очистки литиевых концентратов от ионов кальция и магния и химического состава гидроминерального сырья. Эффективными методами осаждения лития в виде карбоната лития является метод осаждения. Исследованы экстракционные методы переработки литийсодержащих осадков и сорбционные методы извлечения лития из рассолов. Изучены водно-солевые системы для направленного поиска эффективных способов получения литиевых солей из рапы и осадков соленых озер. Изучены химические и минералогические составы гидроминерального сырья озер Аральского региона методом осаждения.

Крупное месторождение с доказанными запасами лития находится в восточном Казахстане – в Калбинском хребте и в Приаралье – на дне высохшего моря. Установлено, что значительная часть лития находится в озерах и озерных илах, подземных водах, в морской воде (1,5-10,5 масс.%). Рассол Южного и Северного бассейна озера Жаксыкылыш содержат 40-60 мг/л лития (Mg^{2+} - не более 0,2%, Ca^{2+} - не более 0,4%, SO_4^{2-} - не более 1,2%), в илах содержание составляет 60-120 мг/кг.

В процессе получения литиевых солей из гидроминерального сырья ранее применялись неорганические и органические сорбенты в зависимости от содержания лития в различной форме соединения. Извлечение лития из комплексных минеральных соединений не всегда решалось успешно из-за низкой степени извлечения лития в товарный продукт.

Необходимо обогащение рассола до требуемого качества литиевого концентрата. Имеющиеся запасы гидроминерального сырья (озерах и озерных илах, рапах и солончаковых отложениях) в Аральском регионе обеспечивают годовую потребность в литии.

Для проведения эксперимента пробу рапы предварительно усредняют, отбирают аликвоту помещают в колбу на 100 мл установленную на магнитную мешалку с регулятором оборотов (установить на 600 об/мин) после добавляют экстрагент-бутиловый спирт в количестве 30 мл. Пробу, состоящую из слоя спирта и воды, перемешивают в течение заданного времени. В процессе перемешивания при использовании безводного бутанола на границе фаз спирт-вода выпадает белый осадок, состоящий из хлорида натрия.

После заданного времени пробу переносят в делительную воронку, где после разделения бутанола и воды нижний водный слой сливают. Спиртовой слой упаривают до сухого состояния в вакууме (водоструйный насос). Остаток «досушивают» от следов бутанола в сушильном шкафу при температуре 130 °С.

Результаты исследования показали, что чем больше расход рапы, тем меньше масса осадка. Полученный осадок исследовали на приборе ИСП на содержание лития и по полученным результатам считали степень экстракции лития. Осадок исследовали на приборе РЭМ. При экстракции 10 мл рапы выход осадка составляет 0,3498 г., а при экстракции 50 мл рапы - выход осадка составляет 0,3031 г. Процесс экстракции хлорида лития проведен в интервале времени 10-30 мин. Полученные данные показали, что при постоянном расходе рапы 10 мл. и объеме экстрагента 30 мл с увеличением продолжительности экстракции степень экстракции лития постепенно возрастает. При продолжительности 10 мин степень экстракции лития составляет 86,95, при 15 мин. составляет 96,7%, а в дальнейшем времени 30 мин. степень экстракции лития уменьшается и составляет 88,7%. Наибольшая степень экстракции лития достигается при времени 15 мин. Одновременно выход массы осадка из рапы сначала возрастает, затем с увеличением времени экстракции выход массы осадка уменьшается.

Изучены условия концентрирования литиевых минералов и получение концентратов для экстракции хлорида лития. Установлено, что с увеличением объема рапы при постоянном расходе экстрагента бутилового спирта и времени степень экстракции лития постепенно уменьшается. При расходе рассола 10 мл степень экстракции лития составляет 96,9%, с увеличением расхода рассола до 50 мл степень экстракции лития снижается до 83,9%. При постоянном расходе рассолов и объема экстрагента, с увеличением продолжительности экстракции, степень экстракции лития постепенно возрастает.

Установлено, что увеличение продолжительности экстракции от 10 мин до 15 мин приводит к увеличению степени экстракции хлорида лития и составляет 96,7%, в дальнейшем при повышении времени до 30 минут степень экстракции хлорида лития уменьшается до 88,7%. Наибольшая степень экстракции лития достигается за время 15 минут. Одновременно выход массы осадка из рассола сначала возрастает, затем с увеличением времени экстракции выход массы осадка уменьшается.

Ключевые слова: гидроминеральное сырье, рассол, ил, хлорид лития, редкоземельные элементы.

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