**ABSTRACT**
of the dissertation work of **Ulbekova Mariam Muskankovna**
on the theme: **"Development of technology of obtaining lithium salts from Kazakhstan´s hydromineral raw materials"** submitted for the degree of Doctor of Philosophy (PhD) in the educational program 6D072000 – "Chemical technology of inorganic substances"

**The relevance of the problem.** Lithium is the lightest metal with a number of unique properties. In this regard, lithium and its various compounds are widely used in highly developed countries of the world in various industries. The main areas of use of lithium products are aluminum electrolysis, batteries, medicines, the aerospace industry, glass and ceramic production, as well as the nuclear industry.

In the composition of lithium raw materials contain the minerals spodumene ($LiAlSi_2O_6$), hectorite (Na0.3 (Mg, Li)$_3$ $Si_4O_{10}(OH)_2$), petolite ($LiAlSi_4O_{10}$) and lithium micas with impurities of K, Al, etc. The extraction of lithium from mineral rocks is difficult and requires significant economic costs due to the content of impurity and associated metals, and the difficulty of accessing mineral veins. The lithium content in brines of lakes, desert basins, silts of salt lakes, seas, and salars is characterized by varying concentrations from 200 to 7000 mg/l $Li^+$, which makes exploration and resource assessment expensive. However, the extraction of lithium from natural brines requires lower costs than the extraction of lithium from solid mineral rocks. Lithium is isolated from brines by adding sodium carbonate ($Na_2CO_3$) with precipitation of $Li^+$ as $Li_2CO_3$. In the process of obtaining lithium salts from hydromineral raw materials, adsorbents in various forms of compounds were previously used. An analysis of modern lithium extraction methods has shown the advantages of selective sorption separation of lithium chloride using various aluminate sorbents.

Lithium-containing hydromineral resources of Kazakhstan are a promising material for obtaining high-demand lithium compounds in the form of chloride, carbonate, etc.

It should be noted that the lithium-containing hydromineral resources of the Aral Sea region and Lake Zhaksykylysh, according to the results of the analysis of useful components, reach Li 127.455–320.853 mg/kg in brine, Li 511.220–1125.670 mg/kg in silt sediments, and Li 403.314–1051.35 mg/l in brines.

However, existing methods for producing lithium often do not provide the necessary economic and environmental efficiency, making the development of new technologies for processing lithium-containing raw materials relevant.

The development of effective methods for the extraction and sorption of lithium chloride from local hydromineral resources will significantly reduce production costs and make Kazakhstan a competitive supplier of lithium products.

**The purpose of the research** is to develop a technology for the extraction and sorption of lithium chloride from the hydromineral resources of Kazakhstan using butyl alcohol and modified sorbents with the addition of titanium dioxide.

**Research objectives:**

– to conduct an analytical review of modern methods for the production of lithium compounds;

– to investigate the physico-chemical properties of Kazakhstan's hydromineral resources, in particular, brines of the Aral Sea and sedimentary silt deposits of Lake Zhaksykylysh, to determine their suitability as lithium sources;

– to investigate the thermodynamic and kinetic patterns of alkaline brine extraction and the sorption process using alumosilicate sorbents activated with titanium dioxide;

– to develop a sorption method for the separation of lithium on sorbents from local aluminosilicate materials modified with titanium dioxide to determine the optimal conditions and parameters for maximum extraction of lithium chloride;

– to investigate and optimize the parameters of the extraction of lithium chloride using butyl alcohol and a surfactant additive (sulfanol), under different ratios of components and process conditions.

– large-scale laboratory tests of the extraction of lithium chloride from brines with an assessment of the economic feasibility of the developed technology.

**Objects of research:**

– brines from the Aral Sea and highly mineralized water solutions containing lithium ions and other impurities;

– sorbents based on local aluminosilicate materials, acid-activated and modified with titanium dioxide for the sorption separation of lithium from hydromineral resources;

– butyl alcohol as an extractant for the extraction separation of lithium chloride from hydromineral raw materials.

**Research Methods.** To achieve the objectives of this dissertation, the following methods were used:

– Scanning electron microscopy (SEM) on a JEOL JSM 6490 LV microscope with INCA Energy 350 energy-dispersive microanalysis systems and a texture analysis system for polycrystalline samples was used to study the microstructure and elemental composition of adsorbent samples before and after adsorption.

– The lithium and alkali metal content in the initial samples and extraction products was determined by atomic absorption spectrometry (AAS) using a ContrAA 300 spectrometer. The AAS method ensures high sensitivity and accuracy of quantitative analysis.

– X-ray fluorescence analysis (XFA) was used to study the elemental composition of hydromineral raw materials and extraction products. XRD makes it possible to quickly and accurately determine the concentrations of elements in complex multicomponent mixtures.

– The physical - mechanical strength of the sorbents was measured using an ultrasonic hardness tester TKM-459.

– The specific surface area of dispersed materials is determined by the PSX-K device (Russia). It allows you to measure the specific surface area in the range of 100-50000 $cm^2/g$, the average mass size of powder particles is 0.1–250 microns with an average measurement error of ± 1.5%.

– The degree of lithium chloride release was calculated as the ratio of the lithium salt content in the initial brine to the lithium salt content in the final solution after adsorption, multiplied by 100%.

–The HSC Chemistry software complex was used to calculate changes in thermodynamic properties (enthalpy, entropy, Gibbs free energy) under various conditions for the isolation and production of lithium compounds. Thermodynamic modeling allows us to determine the equilibrium distribution of elements and compounds in the studied systems.

– Determination of kinetic parameters of lithium extraction - the rate and mechanism of chemical reactions during the extraction process was performed using the Rotinyan–Drozdov equation.

– For mathematical planning of the sorption separation of lithium chloride from brines of the Aral Sea region using sorbents based on Darbaza bentonite clay and titanium oxide, the rotatable planning method of the second order was used. The adequacy of the equations was checked by the Fisher criterion (F-criterion).

**The main provisions of the thesis submitted for defense:**

– results of physico-chemical and physico-mechanical studies of the preparation of sorbents based on bentonites activated with sulfuric acid 0.1M, 0.5M, 1.8M, in a ratio of 2:1 and modified with titanium oxide in an amount of 20-27% contribute to the reduction of alkaline and basic oxides. With an increase in the molarity of the acid and the bentonite: titanium oxide ratio of 100:10, 100:20, 100:30, 100:40, the lithium to titanium ratio (R = n (Li)) / n (Ti) was maintained at 1.98-2.05. After heat treatment at a temperature of $1000^0$C for 60 minutes, the mechanical strength of the sorbents reaches 5.25 MPa, the specific surface area is 1560 $cm^2$/g.

– the results of thermodynamic and kinetic studies to determine the probability of lithium carbonate formation reactions from lithium oxide, hydroxide, and chloride having negative Gibbs energy values from -42.401kJ/mol to -253.20kJ/mol in the range of 298-1898 KJ. The "apparent" activation energy of 1.91–27.68 kJ/mol calculated according to the Rotinyan-Drozdov equation is a criterion for the feasibility of the process of lithium chloride release with diffusion limitation.

– experimentally confirmed conditions of sorption extraction of lithium on modified aluminosilicate sorbents in the temperature range of 40-50°C, flow rate of the studied liquid of 2.1-2.3 l/min, humidity of 42-48 g/$m^3$, duration of 70-90s ensured the degree of extraction of lithium chloride of up to 87-90%.

– for the first time, within the framework of the COMSOL Multiphysics® numerical model for the extraction of lithium from brines, the influence of brine velocity in the range of 0.1–0.5 m/s on the pressure drop in a fixed bed of adsorbent and the increase in hydrodynamic resistance at velocities of 0.3–0.5 m/s was quantitatively determined.

– results of large-scale laboratory studies of LiCl extraction from brines using butanol and sulfanol, in a brine:butanol:sulfanol ratio of 1:3:0.017 and a 15–20 min regime, providing an extraction degree of 96.8–98.9%, as well as temperature ranges of 25–35°C with quantitative extraction ranges of 87.2–98.9%;

– calculations of economic indicators of the advantages of sorption and extraction of lithium chloride.

**The main results of the study.** The main theoretical research results are focused on the use of technology for the isolation of lithium chloride by sorbents based on local aluminosilicate minerals modified with titanium oxide. The proposed technology for processing hydromineral lithium-containing brine is fundamentally different from existing global analogues, in that for the first time lithium compounds will be produced in Kazakhstan using new sorbents based on local bentonites. The use of cheap multifunctional sorbents helps to reduce unit costs for the production of commercial lithium products.

To ensure the complexity, a waste-free technology of alkaline extraction of brines of the Aral Sea region with butyl alcohol mixed with sulfanol has been developed, which contributes to the maximum yield of the final product.

The results of thermodynamic studies of possible reactions of the proposed technology based on calculations of Gibbs energy change in the range of 298-1898K showed the possibility of lithium carbonate formation with the participation of lithium oxides, hydrates, sulfates and chloride. This is evidenced by negative Gibbs energy values from -32.82 to -280.5 kJ/mol. Thermodynamic modeling of the working systems $Al_2O_3$ -0,5$SiO_2$– $TiO_2$ – $O_2$ (1); $Al_2O_3$–2$SiO_2$–$TiO_2$-$O_2$ (2) in the temperature range of 290–1898K showed stable formation of $3Al_2O_3 \cdot 2SiO_2$ up to 45% at a temperature of 1000°C. In the range of 200°C, decomposition of $Al_2O_3 \cdot 2SiO_2$ is observed, facilitating the formation of $Al_2O_3 \cdot TiO_2$ up to 55%. In system (2), an increase in $SiO_2$ to 2 moles leads to a sharp increase in $Al_2O_3$ to 99% due to the decomposition of $Al_2O_3 \cdot 2SiO_2$. In the high-temperature region, up to 63% $3Al_2O_3 \cdot 2SiO_2$ and 84% $Al_2O_3 \cdot TiO_2$.are formed.

IR spectrometric analysis of sorbents based on bentonite clay modified with titanium oxide revealed a broad absorption band characteristic of Si–O–Al covalent bonds in the range of 547–995 $cm^{-1}$ and less intense peaks corresponding to Si–O–Ti in the range of 1114–1431 $cm^{-1}$.

Mathematical planning of extraction conditions, such as temperature, duration of the process and the ratio of reagents, allowed us to determine the optimal parameters that ensure a high degree of lithium extraction. In particular, the degree of lithium extraction reached 98.9% when using optimal concentrations of butanol and sulfanol 1:3:0.017, as well as a process duration of 10-35 minutes. At a temperature of 25°C and a process duration of 10-40 minutes, the degree of lithium release is 87.2–95.95%. At 30°C, the degree of release reaches 88.4–98.9%, and at 35°C — 92.6–97.9%.

**Substantiation of the novelty and significance of the results obtained.** In the dissertation, for the first time for the studied hydromineral raw materials of the Aral Sea region, the patterns of sorption-extraction isolation of lithium chloride are substantiated.

IR spectrometric and X-ray fluorescence analysis confirmed the theoretical properties of the prepared sorbents based on bentonite modified with titanium oxide. IR spectrometric analysis of the sorbent with 20% $TiO_2$ after heat treatment at 800°C revealed a broad range of oscillations at 547.78–995.27 $cm^{-1}$

characteristic of the covalent Si-O-Al bonds of montmorillonite. After heat treatment, less intense oscillations of waves at 1431, 18-1504,48 $cm^{-1}$ of the Si-O valence bonds appeared. The $TiO_2$ content provides a specific sorbent surface and adsorption sites that facilitate the binding of lithium ions.

The results of physico-mechanical studies of sorbents with different ratios of titanium oxide additives, heat-treated at a temperature of 800°C and lasting 60 minutes, showed that with the addition of 20-27% $TiO_2$, sorbents have high physico-mechanical properties and specific surface area. These figures are confirmed by an increase in the average diameter of the granules from 15.9 to 18.5 mm. At the same time, the mechanical strength of the granules reaches 5.29-5.3 MPa.

According to thermodynamic calculations of Gibbs energy in the range of 298-1898 K, the processes are directed towards the production of target lithium compounds; at the same time, the calculated $\Delta G$ at 1798 K, equal to -42.401 kJ/mol, corresponds to the reaction of formation of lithium carbonate from its oxide and -280.5 kJ/mol to the formation of lithium carbonate from its chloride. Positive Gibbs energy changes of 460 kJ/mol and 68 kJ/mol for the formation of titanium chloride and lithium titanate are thermodynamically impossible.

For a system involving an aluminosilicate matrix and $TiO_2$, the redistribution of aluminosilicates into phases of the $Al_2O_3$–$2TiO_2$ type has been established.

The results of mathematical planning of sorption isolation of lithium chloride by the method of rotable planning of the second order showed the influence of variable factors - humidity 45-89%, flow rate 2.3-3.9 l/min, temperature 30-50°C to maximize the release of lithium chloride. Under these conditions, the release of lithium chloride increases from 87 to 90% with a gas dynamic capacity of 252 mEq./g and lithium chloride content in brine of 1000 mg/l at a linear rate of 0.25 minutes.

Kinetic studies of the extraction of lithium chloride from brines using butyl alcohol allowed us to determine the parameters affecting the efficiency of the process. The application of the Rotinyan–Drozdov equation revealed that the degree of lithium chloride release is significantly affected by the temperature, flow rate, and humidity of the brine.

The linear nature of the dependence of the degree of lithium chloride release confirms the applicability of the Rotinyan–Drozdov equation to this system. The results of the activation energy calculation in the range of 1.91–27.68 kJ/mol characterize the process in the diffusion region.

The three—dimensional dependence of the degree of sorption of lithium chloride on the proposed sorbent showed that with a decrease in brine moisture, the degree of lithium extraction is up to 90%.

A numerical model of the sorption plant has been developed that takes into account an increase in the brine velocity from 0.1 to 0.5 m/s, which contributes to an increase in the hydrodynamic resistance of the porous layer and an increase in the pressure drop to 600 Pa, as well as to the formation of flow turbulence zones before entering the adsorbent.

Based on the theoretical and experimental results of the extraction of lithium-containing brines with butyl alcohol, extensive laboratory tests have been confirmed, and the material balance and economic efficiency of the technology have been calculated.

The research results are confirmed by 3 utility model patents of the Republic of Kazakhstan (No. 3657 dated 21.10.2017, No. 4959 dated 22.05.2020, No. 5326 dated 28.08.2020).6 by the act of integrated laboratory tests (No. 22 dated January 13, 2026) and the acts of introducing research results into the educational process (No. 217, 218, dated December 24, 2024).

**Compliance with scientific development directions or government programs.** The dissertation work was carried out within the framework of the research plan of the Department "Technology of inorganic and petrochemical productions" of the M. Auezov South Kazakhstan University for 2021-2025 on the topic GB NIR-21-03-02 "Development of new promising technologies and improvement of traditional technologies for obtaining inorganic products, environmentally friendly fertilizers and plant growth stimulants based on mineral raw materials and man-made waste".

**The doctoral student's personal contribution to the preparation of each publication.**

According to the research results within the framework of the dissertation, 17 scientific papers have been published, including 3 patents for a utility model of the Republic of Kazakhstan, 2 articles in scientific publications recommended by the authorized body (Committee for Quality Assurance in Science and Higher Education RK), 5 articles in peer-reviewed scientific publications indexed in the Scopus/Web of Science database, 10 articles in international journals, and also in the collections of international scientific conferences. According to the results of the research, two acts of implementation of the results in the educational process were obtained Acts No.217, No.218 dated 24.12.2024.

1. The article “Development prospects of new technologies of lithium-containing products” published in the journal “ARPN Journal of Engineering and Applied Sciences”, experiments and analyses of the obtained products for lithium content and premiums were conducted, with the presentation of graphical dependencies and tabular data.

2. The article "Mathematical Modeling of Sorptive Extraction of Lithium Chloride from Lithium-containing Brine of the Aral Sea Region" published in the journal "The open chemical engineering – Sharjah, U.A.E." conducted experimental studies of sorption separation of lithium chloride from brines, with the design of the data obtained in the form of large-scale graphical dependencies.

3. The article "Investigation of the Process of Agglomeration of Phosphorites Using Phosphate-Siliceous Shales and Oil Sludge" published in the journal "The open chemical engineering – Sharjah, U.A.E." conducted the identification and description of physico–chemical analyses of the initial and obtained products, the design of volume graphs of decarbonization dependencies.

4. The article "Studies of Physico–Chemical Bases and Optimization of Environmentally Safe Technology of Lead Production Waste Recycling" published in the Journal of Ecological Engineering - Lublin, she etched graphical dependencies of Gibbs energy changes by reactions and constructed large-scale graphical dependencies of metal release.

5. The article "Process of Obtaining Sorbents from Bentonite and Refractory Clays Using Industrial Waste," published in the Oriental Journal of Chemistry, Bhopal prepared 18 reactions for calculating thermodynamic parameters and presented the data in graphs and tables.

6. The article "Mathematical Modeling of the Process of Obtaining Sorbents for Phosphorus Extraction from Sludge," published in the journal "Bulletin of KazNITU named after K.I. Satpayev," she studied the physical and mechanical properties of sorption materials and presented graphical data.

7. The article "Mathematical description of the process of sorption wastewater treatment of chemical industries" published in the journal "Bulletin of KBTU", conducted research on sorption purification with data processing in the form of large-scale graphical dependencies.

**The structure and scope of the dissertation.** The volume of the thesis is 122 pages, includes 42 tables and 52 figures. The dissertation work consists of an introduction, 5 chapters, a conclusion, a list of 116 references, and 4 appendices.