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Abstract

Dissertation topic: "Development of the Process for Recovering High-Purity Lithium Compounds from Aqueous Tail Solutions of the Facilities for Recycling of Lithium Hydrogen-Containing Materials."

Relevance of the research: Today lithium metal, lithium compounds, as well as materials and products manufactured on their basis have wide practical application. Extensive technological use of lithium and growing amounts of lithium-containing products make it necessary to put in place industrial processing of lithium-containing materials to enable lithium recycling.

The process of treatment of lithium-containing materials implies generation of highly concentrated lithium-containing aqueous solutions including various chemical and mechanical impurities, apart from the main component. In all areas of lithium application, the main requirement is chemical purity and, as a consequence, the main condition for the use of secondary lithium is its deep purification and removal of all specified impurities.

The main specific feature of processing of recyclable lithium-containing raw material, as opposed to lithium recovery from natural lithium raw material, is that the main component of aqueous solutions is lithium, while the impurities are found in relatively small quantities, constituting no more than 1–2 % of lithium weight. Consequently, it is more technically and economically advantageous to remove impurities without extracting the bulk of lithium.

Another feature of the production facilities involved in processing of secondary lithium raw material is the use of relatively small tonnage equipment for the process. Therefore, the process of lithium purification must be implemented with the use of simple process equipment with the possibility for fully automated control of the processes.

Until recently, deep chemical purification of lithium was carried out with the use of an electrochemical method with a mercury cathode. It is evident that this process is not compliant with present-day requirements to environmental and industrial safety and cannot be proposed for processing of lithium-containing materials.

Development of a state-of-the-art technology with a high level of technical and economic performance that meets the present-day environmental requirements is quite a challenging task. This is due to the fact that lithium and impurities in the initial lithium-containing raw material are found in various phase and dispersion states, such as ions, colloids, insoluble particles with a varied degree of dispersion. Therefore, deep purification of lithium from all specified impurities requires the use of various chemical and physical-and-chemical processes, such as precipitation, mechanical and membrane filtration, sorption, extraction and others. For development of the

most efficient technology for processing of secondary lithium raw material it is necessary to thoroughly study the forms of both lithium, as the main component, and all the impurities present in aqueous solutions.

Taking into account the current level of technological development, the dissolved forms of impurities can be most efficiently removed using a sorption method based on selective extraction of impurities in presence of prevailing amount of lithium. At present, micro- and ultrafiltration methods are becoming more widely used for removal of colloid and finely dispersed particles. However, until recently the above-mentioned methods have practically not been used for processing of aqueous lithium-containing solutions with complex chemical composition and particle-size distribution.

Therefore, the research area of this thesis focused on development of a process for recovery of high-purity lithium compounds from reusable raw material, i.e. lithium-containing aqueous tail solutions of the facilities for recycling of lithium hydrogen-containing materials, which satisfies present-day technical-and-economic and environmental requirements, is of quite immediate importance and relevance.

The research objective is to develop the process for recovery of high-purity lithium compounds from aqueous lithium-containing tail solutions of the facilities for recycling of lithium hydrogen-containing materials.

The research tasks:

1. To determine the forms of impurities of alkaline, alkaline-earth and transition metals, aluminum and silicon present in aqueous lithium-containing tail solutions of lithium hydroxide.
2. To propose and experimentally test methods of lithium purification from all specified impurities depending on their phase and dispersion states.
3. To develop a process flow diagram for recovery of high-purity lithium carbonate and lithium chloride from aqueous lithium-containing tail solutions.
4. To test the developed process under laboratory conditions, to determine optimal conditions for all stages of the process and to perform lithium material balance.
5. To study corrosion resistance of various structural materials in typical process media and to select the materials suitable for manufacturing of the main process equipment.
6. Based on the obtained results to draw up a statement of work for designing of a pilot facility for processing of aqueous lithium-containing tail solutions to produce high-purity lithium carbonate and lithium chloride.

Scientific novelty of the research:

1. Distribution of trace impurities of alkaline, alkaline-earth and transition metals, aluminum and silicon in the course of carbonation of lithium hydroxide solutions and thermal decarbonation of lithium hydrocarbonate solutions has been studied for the first time.

2. A method of filtration with the use of ceramic ultrafiltration membranes for purification of lithium-containing solutions from impurities in finely dispersed and colloid state has been proposed.

3. Sorption of various metal impurities from lithium hydrocarbonate solutions has been studied. It has been demonstrated that iminodiacetate chelate cationites are most efficient for deep integrated purification of $LiHCO_3$ from impurities.

4. Conditions for producing $LiCl \cdot H_2O$ phase and its thermal dewatering with generation of anhydrous lithium chloride have been identified.

5. Corrosion resistance of various structural materials has been tested for the first time in saturated lithium chloride solution at its boiling temperature. A conclusion has been made on high corrosion resistance of zirconium metal and titanium alloy VT1-0 (rus. BT1-0) under specified conditions.

Practical significance of the research:

1. The method of in-process control of carbonation of lithium hydroxide solution based on measurements of the electrical conductivity and pH level of the solution was developed. Values of the above-mentioned parameters that are necessary for monitoring of the carbonation completeness were estimated.

2. The method of purification of lithium-containing solutions from finely dispersed and colloid particles of impurities with the use of ultrafiltration ceramic membranes was proposed.

3. The process flow diagram for the production of high-purity lithium carbonate and lithium chloride from aqueous lithium-containing tail solutions was developed.

4. The statement of work for the designing of the pilot facility for processing of aqueous lithium-containing tail solutions for the purpose of producing high-purity lithium carbonate and lithium chloride was drawn up on the basis of the research findings. Types and characteristics of the main process equipment of the pilot facility were determined.

5. The main units of the pilot facility for processing of aqueous lithium-containing tail solutions were manufactured and delivered to FSUE Mayak PA in accordance with the statement of work.