ABSTRACT

on dissertation for the Doctor of Philosophy degree (PhD) on specialty 6D072000 – "Chemical technology of inorganic substances"

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"Optimization the conditions of electrochemical refining of crude indium of Kazakhstan**"**

General description of the work. The thesis work is devoted to the electrorefining of rough indium, produced in Kazakhstan with additional purification of the refining electrolyte by sorption and cementation stages.

Urgency of Research

Obtaining high purity indium is a complex technological task that requires the use of complex technological schemes, including both physical and chemical cleaning methods. One of the main methods for producing high-purity indium is the method of electrochemical refining. To achieve this goal and solve the problems of the project it is necessary to use a set of modern physical and chemical methods of research and analysis. Electrolysis is a universal method of purification of metals, both from metal and non-metallic impurities. This method is characterized by high performance, the ability to automate the process and the simplicity of hardware design. Demand for India has increased in the last two decades due to increased consumption of this metal in the electronics industry. The main form of indium used in the manufacturing industry is indium tin oxide (ITO). The main end use of ITO is the production of LCD monitor and TV screens, which is about 70% of the total produced in India, and another 25% are used in led lighting.

Currently, there is no alternative to India in any of these areas, and all substitutes have much worse properties. Therefore, the development and modernization of methods of electrochemical refining of indium in order to obtain high purity metal from domestic raw materials are very relevant. This will eliminate the dependence of our Republic on imports of high-purity India from its producing countries, will open up new opportunities for the growth of economic and social level of Kazakhstan to join the 50 most developed countries in the world.

The **research objective** is to increase the purity of refined indium based on the selection of optimal electrolysis conditions and the use of an electrolysis unit with additional purification of the electrolyte.

In order to achieve this objective, the following tasks are considered:

• Finding the optimum temperature and electrolyte concentration during electrodeposition of indium;

• Reducing the content of some impurity metals when using complexing additives;

• Determination of the optimal values of current density and interelectrode distance corresponding to the minimum energy consumption and maximum current efficiency;

• Calculation of the sorption characteristics of chitosan in electrolytes containing impurity metals;

• Creation of a cell with cementation and sorption sections to increase the purity of cathode deposits;

• Electrorefining of indium and analysis of indium cathodic deposits.

The research object is the rough indium produced by the JSC "KazZinc" in the city of Ust-Kamenogorsk.

The research subject is the content of impurity metals in refined indium.

Scientific novelty.

• For the first time, optimal values of temperature, current density, supporting electrolyte concentration have been established during electrorefining of domestic rough indium;

• For the first time, complex-forming additives DTPA and tartaric acid were used to increase the separation coefficients of impurity metals.

• An electrolysis cell was created with pre-purification of the electrolyte as it passes through the cementation and sorption sections.

• For the first time during electrorefining of indium, chitosan with high sorption properties was used as a sorbent.

• Determination of the sorption characteristics of chitosan was carried out by the DPV method.

Practical relevance of the research

The work carried out in the framework of projects on the electrochemical purification of indium, funded by the MES RK, is among the studies on the rational use of natural resources, the creation of non-waste technologies and industries. The Republic of Kazakhstan has significant reserves of polymetallic raw materials, which is the basis for creating breakthrough technologies for its processing. India, produced by Kazzinc JSC, is exported to various countries of the world. Variation of electrolysis parameters, electrolyte concentration, temperature, current density, use of additional grouting and sorption purification of the refining electrolyte allow optimizing the technology of electrochemical purification of domestic rough indium. In this work, chitosan with a high sorption capacity, easily regenerated and environmentally friendly, was used for the first time as a sorbent during the purification of the electrolyte refining. The theoretical significance of this work lies in the possibility of using the results obtained in the development of new advanced technologies for the electrochemical purification of high-purity metals.

Main findings

1. The effect of temperature on the electrical reduction of indium in chloride electrolytes on a titanium electrode was investigated and the optimum temperature was determined.

2. The effect of impurity metals on the electroplating of indium was investigated. Under the chosen conditions, the distribution coefficients of impurity metals and indium were calculated, and it was proved that this value increases in the presence of diethylenetriaminepentaacetic acid and tartaric acid.

3. An electrolytic refining of indium with varying interelectrode distances and current densities was carried out and their optimal values were determined corresponding to the minimum energy consumption.

4. The sorption properties of chitosan in chloride electrolytes containing cadmium, copper, and lead ions have been studied. The content of the investigated metals before and after the sorption was determined by the method of differential pulse voltammetry (DPV). The amount of sorbed metal and the removal efficiency are calculated for all studied impurities. Using the sorption isotherms of Langmuir and Freindlich, experimental results were worked out, from which the maximum regression value was obtained corresponding to the Langmuir isotherm.

5. In order to reduce the content in the electrolyte of impurities that contaminate cathode deposits, an electrolysis cell with separated cathode and anode spaces has been designed, allowing the anolyte to pass through the external circulation through the cementation and sorption chambers.

6. Electrorefining of the rough indium in the constructed cell was performed using an indium sponge during the cementation process and chitosan as a sorbent in the sorption process. Cathodic deposits were analyzed by ICP-OES and ICP-MS for the content of impurity metals. Thus, the use of additional purification of the electrolyte will significantly reduce the content of impurity metals, the purity of the cathode sediment was 99.9998%.

7. The calculations of material and energy balances in the electrochemical refining of indium. A process schematic diagram has been developed for electrochemical purification of rough indium in Kazakhstan.

Estimation of the completeness of the objective solutions

The objectives and tasks set in the thesis are completely solved:

- The effect of temperature on the electroplating of indium on the titanium cathode in chloride solutions was studied and the optimal mode was determined;
- The influence of impurity metals on the electrodeposition of indium and the effect of complexing additives on them;
- The influence of the construction parameters of the electrolyzer on the energy consumption of the electrolysis process was studied;
- The sorption properties of chitosan sorbent, first used for the purification of electrolyte refining, were identified;
- Electrolysis was carried out with preliminary electrolyte purification, including cementation and sorption, and high-purity indium samples were obtained.

Development of recommendations and initial data on the specific use of results.

It has been established that the degree of purity of indium produced in Kazakhstan can be enhanced by electrorefining using a preliminary electrolyte purification stage by cementation and sorption, and a semi-industrial laboratory

unit is developed in which electrolysis will be carried out. This method was proposed by Kazzinc JSC (Ust-Kamenogorsk), which produces rough indium.

The interrelation of the subject of the thesis work and research works and various State programs. The dissertational work was performed at the Department of Analytical, Colloidal Chemistry and Technology of Rare Elements of Al-Farabi Kazakh National University and at the Center for Physical and Chemical Methods of Research and Analysis, RSE named after Al-Farabi Kazakh National University "Development of technology and pilot plant for electrochemical production of pure indium from polymetallic and industrial raw materials of Kazakhstan" (state registration number 0115RK02243).

Contribution made by the defender of the thesis: theoretical justification of the goal and objectives, review of research results, processing of produced experimental data and preparation of publication on the basis thereof.

Approbation of practical results. The main results of dissertation were reported and discussed:

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- **Publications**

The key content of the work was published in 12 scientific journals including 5 articles in journals on the list Supervisory Committee of the Ministry of Education and Science of the Republic of Kazakhstan, 2 article in journal Scopus database, 5 theses of reports in international and republican scientific and practical conferences and symposia.

Thesis Work Structure and Scope

The thesis work consists of introduction, 4 parts and conclusion. The scope of the thesis work is 109 pages and 162 references were used at preparation of the thesis work.