ABSTRACT

thesis for the degree of Doctor of Philosophy (PhD)
on specialty "6D072000 – Chemical technology of inorganic substances"
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"Development of new methods for obtaining compounds of some d- and p - metals by electrochemical polarization"

Relevance of the study. Inorganic metal compounds are in demand in metallurgy, electronics, medicine, and chemical technology. Compounds of titanium (III), iron (II, III), copper, lead, and many other d- and p- elements are of particular importance. There is a steady demand for such substances, necessitating improvements in their production methods with a focus on selectivity, energy reduction, and environment safety. Traditional high-temperature methods are accompanied by high reagent consumption and the formation of toxic waste. Electrochemical approaches offer an energy-efficient and controllable alternative, allowing for the synthesis of target compounds under mild conditions. Developing such methods is a relevant task with both scientific and practical significance.

The purpose of the work is to develop new methods for obtaining titanium, iron, copper, and lead compounds based on electrochemical polarization in aqueous solutions using stationary and non-stationary currents.

Research objectives:

- Investigate the electrochemical behavior of titanium through electrolysis using alternating current with bipolar electrodes and by recording voltammograms. Develop electrochemical methods for obtaining titanium dioxide, titanium (III) chloride, and sulfate.
- Investigate the electrochemical behavior of iron through electrolysis in a system of two sequentially connected electrolyzers to conduct targeted reactions during each half-cycle of alternating current and by recording voltammograms. Develop electrochemical methods for obtaining hydroxide, oxides, sulfate, and chloride of iron; investigate the possibility of oxidizing divalent iron ions to a trivalent state;
- Investigate the electrochemical behavior of copper through electrolysis using alternating current and by recording voltammograms. Develop a method for obtaining copper (II) oxide; study the process of copper (II) ions reduction, and develop fundamentally new methods for obtaining copper (I) sulfide and iodide.
- Investigate the electrochemical behavior of lead in aqueous acidic solutions through electrolysis with bipolar electrodes under alternating current of industrial frequency and by recording voltammograms; develop a method for obtaining lead (II) sulfate.

Research methods: electrolysis under polarization: alternating current of industrial frequency; cathodic pulsed current; stationary current. Electrolysis under polarization: alternating current using each half-cycle; with the use of bipolar electrodes. Method of recording voltammograms; X-ray phase analysis; scanning electron microscopy; elemental analysis.

Main provisions for defense:

1. Conducting electrolysis in aqueous acidic solutions under the influence of alternating current at industrial frequency (50 Hz) using bipolar electrodes facilitates the intense dissolution of titanium and lead, which are prone to passivation. As a result, the mass loss of electrodes for titanium increases by 1.38 times, and for lead by 2.4 times compared to electrolysis without bipolar electrodes.

2. Alternating current polarization of the "titanium-iron" electrode pair in a system of two sequentially connected electrolyzers leads to the oxidation of iron in each half-cycle of alternating current to the divalent state (Fe^{2+}). In this process, the apparent current efficiency reaches 170-180%, which is twice the performance of single-cell system.

3. Titanium (III) sulfate in acidic aqueous solutions reduces copper (II) ions to elemental copper in a highly dispersed active form. The obtained copper interacts with sodium thiosulfate or molecular iodine, producing copper (I) sulfide or copper (I) iodide, respectively. These reactions occur at room temperature, unlike traditional methods that require high temperatures (100°C and above) to obtain these compounds.

Main results of the study and justification of the novelty and importance of the obtained results

1. It has been established for the first time that after preliminary alternating current (50 Hz) or pulse polarization, spontaneous dissolution of titanium occurs, allowing the overcoming of the passive state of the metal in an acidic medium. It has been found that the application of alternating current in the range of 400-2500 A/m² on titanium bipolar electrodes leads to the destruction of the passive oxide film and the formation of Ti (III) ions. It is shown that the bipolar electrolysis scheme increases the mass loss of the electrodes by 1.38 times, indicating the effectiveness of the proposed method for dissolving metal. A similar approach is applicable to lead electrodes, which dissolve to form Pb (II) ions, and the bipolar electrolysis scheme ensures a 2.4 times increase in mass loss of the electrodes.

2. It has been shown for the first time that when the "titanium-iron" electrode pair is polarized with alternating current at industrial frequency in a specially designed setup of two sequentially connected electrolyzers, the oxidation of iron proceeds in each half-cycle of alternating current to the divalent state. This occurs with an apparent current efficiency of 170-180%, meaning the iron dissolves twice as intensively as when polarized in a single electrolyzer. As a result of additional experiments, a method for obtaining iron (III) sulfate has been developed. Experiments have first demonstrated the possibility of oxidizing iron (II) ions to the trivalent state using a solid-phase oxidizer – powdered lead dioxide.

3. It has been established for the first time that titanium (III) sulfate is capable of reducing copper (II) ions in acidic aqueous solutions at room temperature, producing finely dispersed elemental copper powder with exceptionally high reactivity. It has been shown for the first time that freshly produced active copper can react with inorganic reagents – sodium thiosulfate or molecular iodine to produce Cu_2S and CuI, respectively. The technological novelty lies in the development of a one-step method for producing copper (I) sulfide and copper (I) iodide, which does not require heating, aggressive oxidizers, or multi-stage processes. The method is characterized by

reactions occurring in an aqueous medium, at room temperature, without the formation of toxic by-products, and it differs from known synthesis methods conducted at high temperatures with the participation of alkali metal salts and strong reducing agents. The technology has the potential to be adapted for green chemistry processes, copper waste recycling, and the recovery of non-ferrous metals in industry.

Theoretical and practical significance of the results

The results obtained in this study expand the understanding in the field of electrochemistry, particularly regarding the behavior of titanium, iron, copper, and lead in aqueous solutions under the influence of non-steady currents and the use of a bipolar electrolysis scheme. The high efficiency of bipolar electrodes under alternating current electrolysis of industrial frequency has been established for the first time.

The possibility of synthesizing titanium hydroxide, dioxide, chloride, and sulfate under alternating current polarization of both monopolar and bipolar titanium electrodes has been demonstrated. Electrochemical methods for obtaining iron compounds in various oxidation states (hydroxides, oxides, sulfate, chloride) have been developed, along with a technical solution to utilize each half-cycle of the alternating current to intensify the iron dissolution process.

Methods for obtaining copper (I) iodide and sulfide using pre-synthesized titanium (III) sulfate, a strong reducing agent, have been developed. Additionally, a method for producing lead (II) sulfate under alternating current polarization using a bipolar electrolysis scheme has been developed. The resulting compounds have practical value and can be used in various industries and fields, including electronics, organometallic synthesis, and the creation of materials for special purposes.

Compliance with development directions or state programs

This thesis is closely related to the project titled “Development of electrochemical methods for obtaining inorganic pigments for the paint and coatings industry based on secondary metallurgical raw materials”, IRN AR 08856929, carried out with grant funding for scientific and technical projects for the years 2020-2022 under the priority: “Rational use of natural resources, including water resources, geology, processing, new materials and technology, safe products, and structures”.

Publications

The main results of the dissertation research have been published in 25 scientific works, namely: in one monograph, two articles in scientific journals, which, according to the Scopus and Web of Science databases, have percentiles of 44 and 27, quartiles Q2 and Q4; in four articles in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Higher Education and Science of the Republic of Kazakhstan; in one article in the International Scientific and Practical Journal “Global Science and Innovation 2020: Central Asia”; in ten articles and abstracts in collections of international conferences held abroad and in nearby foreign countries, one Eurasian patent, one patent for invention of the Republic of Kazakhstan, and five patents for utility model of the Republic of Kazakhstan were obtained.

Description of the doctoral student’s contribution to the preparation of each publication

1. Bayeshova A., Bayeshov A., Zhumabay F., Osińska M., Łęska B. Electrochemical dissolution of titanium under alternating current polarization to obtain its dioxide // Open Chemistry 2024; 22: 20240104. https://doi.org/10.1515/chem-2024-0104 received May 2, 2024 – conducting experiments, collecting literature, processing results, description, formatting.

2. Bayeshova A.K., Bayeshov A., Zhumabay F.M. On the Dissolution of a Copper Electrode with the Production of Copper (II) Oxide During Alternating Current Polarization in a Sulfate Electrolyte // Portugaliae Electrochimica Acta, 42. – 2024. – P. 273-283 – conducting experiments, collecting literature, processing results, description, formatting, editing.

3. Bayeshova A.K., Kongyratbay A.M., Zhumabay F.M., Bayeshov A., Leska B. Obtaining of lead (II) sulfate by polarization of bipolar lead electrodes with alternating current // "Bulletin of Karaganda University". Chemistry Series. – 2019. – No. 4(96). – P. 83-91 – conducting experiments, collecting literature, processing results, description.

4. Bayeshova A.K., Zhumabay F.M., Abukasova A.B., Bayeshov A. Development of a new method for obtaining copper (I) iodide // Bulletin of the L.N. Gumilyov Eurasian National University. Chemistry. Geography. Ecology series. – 2019. – No. 1(126). – P. 8-15 – conducting experiments, collecting literature, processing results, description.

5. Bayeshova AK, Bayeshov A., Zhumabay FM Shakenova M.Sh. Iron sulfates production being polarized by the direct and alternating current // Complex Use of Mineral Resources. – 2019. – No. 4. – P.57-63 – conducting experiments, collecting literature, processing results, description, formatting, editing.

6. Bayeshova A.K., Bayeshov A.B., Zhumabay F.M., Kadirbayeva A.S. Dissolution of iron in a sodium chloride solution under polarization with alternating current // Complex use of mineral raw materials. – 2021. – No. 3 (318). – P. 51-61– conducting experiments, collecting literature, processing results, description, formatting, editing.

7. Bayeshova A.K., Bayeshov A., Zhumabay F.M. Monograph. "Electrochemical synthesis of compounds of some d- and p -metals under alternating current polarization" // Almaty: Publishing House "Zhibek zholy". – 2022. – collecting and reviewing literature data, organizing and summarizing experimental results related to the behavior of metals such as titanium, copper, iron, and lead.and formatting the documents for publication.

8. Baeshova A.K., Baeshov A., Zhumabay F.M. Method for producing titanium dioxide / Eurasian Patent for Invention No. 042064, published on 30.12.2022.

9. Bayeshova A.K., Bayeshov A., Zhumabay F.M., Tazhibaeva A.Sh. Chemical process for producing univalent copper sulfide / Patent for Invention of the Republic of Kazakhstan No. 36190, Bulletin No. 17 dated 28.04.2023.

10. Bayeshov A., Bayeshova A.K., Zhumabay F.M., Shakenova M.Sh. Method for producing sulphate of trivalent iron / Patent for utility model of the Republic of Kazakhstan No. 4329, Bulletin No. 9 dated 27.09.2019.

11. Bayeshov A., Bayeshova A.K., Turlybekova M.N., Abduvaliyeva U.A., Zhumabay F.M., Abukasova A.B. Chemical method of obtaining copper (I) iodide /

Patent for utility model of the Republic of Kazakhstan No. 3829, Bulletin No. 14 dated 05.04.2019.

12. Bayeshova A.K., Bayeshov A., Bayeshova S.A., Myrzabekov B.E., Zhumabay F.M. Method of ferrous ion oxidation / Patent for utility model of the Republic of Kazakhstan No. 4604, Bulletin No. 22 dated 14.01.2020.

13. Bayeshova A.K., Bayeshov A., Zhumabay F.M. Method for producing titanium dioxide / Patent for utility model of the Republic of Kazakhstan No. 6326, Bulletin No. 47 dated 26.11.2021.

14. Bayeshova A.K., Bayeshov A., Konyratbay A.M., Zhumabay F.M., Method of obtaining lead (II) sulfate / Patent for utility model of the Republic of Kazakhstan No. 4261, Bulletin No. 33 dated 29.08.2019.

In works 8-14 – conducting experiments, performing a patent search, processing the results, preparing the patent application, and formatting the document for submission.

Volume and the structure of the thesis

The dissertation consists of an introduction, literature review, 6 chapters, and a conclusion. The list of references includes 195 sources, among which are references to publications co-authored by the PhD student. The content of the work is 150 pages, containing 75 figures and 21 tables, and appendices.