ANNOTATION

dissertation work on the topic:
“OBTAINING MODIFIED SORBENTS ON THE BASIS OF NATURAL RAW MATERIALS FOR URANIUM EXTRACTION”

submitted for the degree of Doctor of Philosophy (PhD)
specialty 8D07204 - "Metallurgical Engineering"

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Goal of the work.

The purpose of the dissertation work is to develop a technology for modifying natural minerals — shungite and zeolite — using industrial waste materials in order to obtain efficient modified sorbents for uranium extraction from liquid radioactive waste (LRW), characterized by enhanced sorption capacity and low production cost.

Research objectives

– results of physicochemical studies of Kusmurun zeolite, Koksu shungite, and phosphorus production slag;
– a methodology for synthesizing solid-phase extractants based on natural minerals, organic reagents, and polyacrylamide;
– results of sorption and physicochemical studies of the modified sorbents;
– a method for activating phosphorus slag;
– a procedure for impregnating natural minerals with the activated modifier;
– results of studies on the sorption and physicochemical properties of natural minerals modified with phosphorus slag;
– results of scaled-up laboratory testing of the technology for modifying natural minerals and extracting uranium using modified sorbents.

Based on the research work carried out, the presented methods and tasks to be solved in this dissertation work are aimed at achieving the overall goal.

The objects of research are:

Kusmurun zeolite, Koksu shungite, and phosphorus production slag.

Methods for modernizing facilities:

- Using X-ray diffraction analysis (XRD), infrared (IR) spectroscopy, and mineralogical and petrographic analysis with a LEICA DM2500P microscope, as well as scanning electron microscopy with energy-dispersive X-ray analysis on a JEOL JXA-8230 electron microprobe, it was established that activation of phosphorus slag in a carbonate medium leads to the breakdown of mineral phases and the formation of new compounds — analcime, calcite, and iron oxides — resulting in an increased number of active sites on the sorbent surface.

- When activating phosphorus slag in a sodium chloride (NaCl) medium, the amorphous glassy phase is retained, while Fe, Mg, Al, and Si ions are released from the structure, which promotes the formation of pores and structural defects, enhancing the sorption capacity of the modified sorbent.

- It was found that during the impregnation (apprêtage) of zeolite and shungite with activated slag and polyacrylamide, a composite polymer–mineral matrix is formed, ensuring uniform distribution of the modifier and anchoring of functional groups such as P=O, P–OH, and Si–OH.

- Experimental results demonstrated that the obtained solid-phase extractant-type sorbents provide an increase in sorption capacity for uranium from 0.2 to 38 mg/g, with uranium extraction efficiency reaching up to 98.7% under static conditions.

- The study showed that the sorption of uranium on the modified sorbents follows the Langmuir isotherm, indicating monolayer adsorption on a homogeneous surface without significant interaction between adsorbed molecules.

Methods for studying objects

The main research and analytical methods used in this dissertation include:

- Critical analysis of patent and scientific literature sources;
- A set of modern analytical techniques, including:

1. Chemical analysis of sorbents and model solutions — using titrimetric methods and quantification of uranium and iron concentrations with an optical emission spectrometer with inductively coupled plasma (ICP-OES), Optima 8300 DV (PerkinElmer, USA);
2. X-ray diffraction analysis (XRD) — conducted using a D8 Advance diffractometer (Bruker AXS GmbH) to determine the phase composition of natural and modified materials;
3. Infrared spectroscopy (IR) — used to identify functional groups and assess structural changes in sorbents before and after modification;
4. Scanning electron microscopy (SEM) — performed using a LEICA DM2500P microscope equipped with energy-dispersive X-ray spectroscopy (EDS) to examine surface morphology and the distribution of the modifier within the sorbent structure.

Basic provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense

– results of physicochemical studies of Kusmurun zeolite, Koksu shungite, and phosphorus production slag;

– methodology for synthesizing solid-phase extractants based on natural minerals, organic reagents, and polyacrylamide;

– results of sorption and physicochemical studies of the modified sorbents;

– method for activating phosphorus slag;

– method for impregnating (apprêtage) natural minerals with the activated modifier;

– results of studies on the sorption and physicochemical properties of natural minerals modified with phosphorus slag;

– results of scaled-up laboratory tests of the technology for modifying natural minerals and extracting uranium using the modified sorbents;

– results of techno-economic assessments of the developed technology.

The research was carried out at the "Pyrometallurgy of Non-Ferrous Heavy Metals" Laboratory of the JSC "Institute of Metallurgy and Ore Beneficiation" (IMiO), Almaty.

Justification of the need for research and work

In the context of the rapid development of nuclear energy and the expansion of the uranium mining sector in Kazakhstan, the task of efficient uranium extraction from liquid radioactive waste (LRW) and low-concentration productive solutions has become particularly relevant. A significant volume of these solutions is generated as a result of in-situ leaching (ISL) — the primary method of uranium extraction in Kazakhstan, which accounts for over 40% of global production. The uranium concentration in both natural and industrial waters can range from 0.01 to 10 mg/dm^3, requiring the use of highly efficient yet economically viable sorbent materials.

In global practice, synthetic ion-exchange resins are widely used; however, their high cost, import dependency, and difficulties in disposal limit their large-scale application. At the same time, natural sorbents such as zeolites and shungite offer good chemical stability and are readily available in Kazakhstan, but their low sorption capacity (typically 0.2–0.5 mg/g) restricts their use without preliminary modification.

One of the promising approaches to enhancing the efficiency of natural sorbents is their modification using industrial waste, particularly phosphorus production slags, which are by-products from the production of yellow phosphorus. These slags contain wollastonite, known for its sorption properties, as well as phosphorus-containing compounds that have the potential to interact with uranyl anions. However, without proper activation and anchoring onto the surface of natural minerals, these properties cannot be fully utilized.

Addressing these challenges will enable the development of a technology for producing effective and low-cost sorbents suitable for use in nuclear industry facilities, which is of significant importance from both ecological and economic perspectives.

Description of the main results of the study

Chapter 1 provides an overview of the problem of uranium-containing liquid waste disposal, evaluates the current state of the uranium industry, and highlights the relevance of using natural sorbents for extracting uranium from low-concentration productive solutions. The necessity of modifying natural minerals to improve their sorption performance is substantiated, along with the rationale for selecting

phosphorus production slag as an affordable industrial modifier.

Chapter 2 presents the physicochemical characterization of natural minerals — Kusmurun zeolite and Koksu shungite — as well as phosphorus slag. Their chemical composition, morphology, specific surface area, porosity, and structure are determined. Wollastonite ($CaSiO_3$) is identified as the main component of the slag, with inherent sorption properties.

Chapter 3 introduces a method for activating phosphorus slag in carbonate (Na_2CO_3) and chloride (NaCl) media. It is shown that activation in a carbonate environment leads to the breakdown of mineral structures and the formation of new phases (analcime, calcite, iron oxides), while chloride activation preserves the amorphous phase but causes the removal of Fe, Mg, Al, and Si ions, leading to defect formation and enhanced porosity.

Chapter 4 explores various approaches to modifying natural minerals, including impregnation with activated phosphorus slag and polyacrylamide. Solid-phase extractants were synthesized and characterized. The influence of modification conditions on sorbent structure, modifier distribution, and the formation of functional groups such as P=O, P–OH, and Si–OH was investigated.

Chapter 5 presents the results of sorption experiments. It was established that sorbents modified with phosphorus slag and polyacrylamide show a significant increase in uranium sorption capacity — from 0.2 to 38 mg/g, with a uranium extraction efficiency of up to 98.7%. The sorption process follows the Langmuir isotherm. Desorption studies using Na_2CO_3 demonstrated a uranium recovery rate of up to 70%.

Chapter 6 describes the scaled-up laboratory trials, confirming the stability of the sorption characteristics of the modified sorbents. Optimal process parameters were determined: sorption time of 2–3 hours, pH around 7, and solid-to-liquid ratio of 1:50. It was observed that modified shungite remains effective for reuse, while zeolite may require regeneration.

Chapter 7 presents the techno-economic assessment of the proposed technology. The analysis confirms significant economic benefits due to the use of low-cost industrial waste, the elimination of expensive synthetic ion-exchange resins, and the simplicity of the technological scheme.

Justification of the novelty and importance of the results obtained

The novelty of the research lies in the use of activated phosphorus slag in the technology for modifying natural sorbents (zeolite and shungite) intended for the extraction of uranium from low-concentration uranium-containing solutions. The proposed approach allows for minimal raw material costs and eliminates the need for expensive chemical reagents during the modification process.

The new scientific results are as follows:

– For the first time, using X-ray phase analysis, IR spectroscopy, and scanning electron microscopy (SEM), it has been established that the activation of phosphorous slag in a carbonate medium leads to the formation of new crystalline phases—analcime, calcite, and iron oxides—resulting in an increase in the number

of active centers on the sorbent surface and enhancing its sorption capacity.

– New data have been obtained on the formation of the porous and amorphous structure of phosphorous slag during activation in a chloride medium (NaCl), including the removal of Fe, Mg, Al, and Si ions involved in the structure, which promotes defect formation and increases sorption capacity.

– It has been established that the sorption capacity of natural sorbents (zeolite and shungite) after modification with activated phosphorous slag and polyacrylamide increases from 0.2 mg/g to 38 mg/g, with uranium extraction efficiency reaching 98.7%.

– It has been demonstrated that the uranium sorption process on modified sorbents follows the Langmuir isotherm, indicating a monolayer adsorption mechanism on the surface active sites.

Technological novelty of research:

A technology for modifying natural sorbents (zeolite and shungite) using pre-activated phosphorous slag has been proposed. This approach is distinguished by the use of readily available industrial byproducts and does not require complex structural modifications to existing purification systems.

Two methods for activating phosphorous slag—in carbonate and chloride media—have been developed and tested. These methods enable the formation of different types of active centers, thereby allowing control over the selectivity of sorption with respect to uranium and iron. The use of polyacrylamide as a binding and stabilizing agent ensured the mechanical strength of the resulting sorbents.

A key technological advantage is that the developed modified sorbents achieve high uranium recovery rates (up to 98.7%) from low-concentration solutions while reducing the cost of the sorption material. This makes the proposed technology promising for large-scale implementation in Kazakhstan’s uranium industry.

Compliance with areas of scientific development or government programs

The dissertation topic aligns with the priority research direction "Ecology, Environmental Protection, and Sustainable Natural Resource Management" and falls under the specialized scientific field "Advanced Processing of Mineral and Organic Resources" of the National Scientific Council under the Government of the Republic of Kazakhstan.

The research area corresponds to the "Engineering and Technology; Materials Engineering; Metallurgy" classification in the Scientific Fields Classifier.

The dissertation research was conducted within the framework of a program-targeted funding project (2020–2022) under the topic: "Development of Methods for Modifying Natural Sorbents for Uranium Extraction Using Industrial Byproducts" (Grant No. AP08856246).

Author's personal contribution

The author's personal contribution consists of conducting a comprehensive set of experimental studies on the modification of natural sorbents (zeolite and shungite) using activated phosphorus slag. This included performing laboratory experiments

as detailed in the dissertation, developing experimental methodologies, participating in industrial trials, and analyzing and presenting the results in the form of publications, scientific presentations at international conferences, and a patent.

Approbation of the work

Based on the materials of the dissertation work, 8 printed works have been published, of which 3 articles are in international peer-reviewed scientific journals included in the Scopus/Web of Science databases:

1. Kenzhaliyev B, Surkova T, Berkinbayeva A, Amanzholova L, Mishra B, Abdikerim B, Yessimova D. Modification of Natural Minerals with Technogenic Raw Materials. Metals. 2022; 12(11):1907. Scopus: Q2, percentile 76. Web of Science: Q2

2. Surkova TYu, Abdikerim BE, Berkinbayeva AN, Azlan MN, Kassymova G.K. Obtaining modified sorbents based on natural raw materials of Kazakhstan and research of their properties. Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources. 2022;322(3):23-32. Web of Science: Q3

3. B.K. Kenzhaliyev, T.Yu. Surkova, B.E. Abdikerim, A.N. Berkinbayeva,Ye.B. Abikak, Z.D. Dosymbayeva. Research on sorption properties of phosphoric production slag-waste // Metallurgija. – 61. – 2022. - № 1. – P. 209-212. Croatia, Zagreb, ISSN 0543-5846, SJR IF-0,779, Scopus percentile 37, Q3. Web of Science: Q4

4. Bagdaulet K. Kenzhaliyev, Tatiana Yu. Surkova, Ainur N. Berkinbayeva, Zamzagul D. Dosymbayeva, Ainur A. Mukhanova, Bekzat E. Abdikerim. Development of a method of modifying a natural sorbent for uranium extraction // Journal of Chemical Technology and Metallurgy, 55, 5. – 2020. – P. 1041-1046. Bulgaria, Sofia. ISSN 1314-7471, IF - 0.81, Scopus percentile 38, Q3

5. B.K. Kenzhaliyev,, T.Yu. Surkova, A.N. Berkinbayeva, Z.D. Dosymbayeva, B.E. Abdikerim. Revisiting the Kazakhstan natural sorbents modification // Metallurgija. – 59. – 2020. - № 1, 2. – P. 117-120, Croatia, Zagreb, ISSN 0543-5846, SJR IF-0,779, Scopus percentile 37, Q3. Web of Science: Q4

6. Abdikerim B.E., Kenzhaliyev B.K., Surkova T.Yu., Didik N., Berkinbayeva A.N., Dosymbayeva Z.D., Umirbekova N.S. Uranium extraction with modified sorbents // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu. 2020. № 3 (314), pp. 84-90., Almaty, Kazakhstan, ISSN 2224-5243. Web of Science: Q3

Proceedings of international scientific and practical conferences:

1. Abdikerim, B.E., Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., & Dosymbayeva, Z.D. (2021). Uranium sorption by organo-mineral material based on shungite. *Proceedings of Satpayev Readings "Satpayev Readings - 2021"*, Section "Innovative Technologies for Implementation in the Metallurgical Industry of the Republic of Kazakhstan", 1289-1293.

2. Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., Dosymbayeva, Z.D., Chukmanova, M.T., & Abdikerim, B.E. (2018). Study of zeolites from Northern

Kazakhstan. Report No. 1. Proceedings of the International Scientific-Practical Conference on Efficient Technologies for Production of Non-Ferrous, Rare, and Noble Metals, Almaty, September 27-29, 2018, 293-296.

3. Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., Dosymbayeva, Z.D., Chukmanova, M.T., & Abdikerim, B.E. (2019). Study of zeolites from Northern Kazakhstan. Report No. 2. Proceedings of the XXIV International Scientific-Technical Conference "Scientific Foundations and Practice of Processing Ores and Technogenic Raw Materials", Yekaterinburg, April 9-12, 2019, 132-137.

4. Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., Dosymbayeva, Z.D., Yesimova, D.M., & Abdikerim, B.E. (2021). On methods of modifying natural minerals. Proceedings of the International Practical Internet Conference "Challenges of Science", Almaty, November 15-22, 2021.

5. Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., Dosymbayeva, Z.D., Abdikerim, B.E., & Bektenov, N.A. (2020). Organo-mineral synthesis based on natural shungite in Kazakhstan. Modern Science, *5*(3), [Specify pages if available].

6. Abdikerim, B. (2020). Research of organo-mineral sorbents based on shungite from Kazakhstan. Proceedings of the International Conference on Engineering, Technology and Vocational Education (ICETVE 2020), November 7, 2020.

Patents:

1. Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., Dosymbayeva, Z.D., Chukmanova, M.T., & Abdikerim, B.E. (2019). Patent for invention "Method of uranium extraction by sorption" (Patent No. 2019/0116.1, No. 34401). [Kazakhstan].

2. Kenzhaliyev, B.K., Surkova, T.Y., Berkinbayeva, A.N., Abdikerim, B.E., Yesimova, D.M., Abikak, E.B., & Bektaev, M.E. (Year). Patent for invention "Method of uranium extraction from aqueous solutions" (Patent No. [Number]). [Kazakhstan].

The total personal participation of the author amounted to 80%.