ANNOTATION

of thesis for Ph.D doctor degree
by the specialty of 6D070900 «Metallurgy»
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Sorption technology of uranium extraction from the technogenic and hydromineral raw materials by using of natural modified sorbent

Topicality of problem.

Now uranium is extracted from ores hydrometallurgical methods or by method of underground leaching. However conversion of ores by the specified methods requires considerable capital investments for receipt of uraniferous solutions. There is an opportunity to avoid expensive production and conversion of ore raw materials if to use technogenic waste of uranium chemical and metallurgical productions and hydromineral uraniferous raw materials. Liquid waste of uranium chemical and metallurgical productions contains the first tens of mg/dm^3 of uranium. Reextraction from the specified technological waste of uranium will allow to raise an ecological safety and cost efficiency of uranium productions. Quite often sources of uraniferous hydromineral raw materials in which concentration of uranium is at the level of $1 \div 8$ mg/dm^3 meet.

In Kazakhstan there are large-scale deposits of such natural materials as shungit also zeolite which, having sorption properties, can be used as a matrix for receipt of more capacious in relation to uranium of sorbents after their modification by hydroxides of metals.

Purpose of thesis work – Development of sorption technology of extraction of uranium from technogenic and hydromineral raw materials with application of the natural modified sorbents.

During the purpose achievement the **following problems** were solved:

1) the reasonable choice of natural materials for sorption extraction of uranium from solutions (by results of the analysis of references and patent researches);

2) experimental development of processes of modification and granulation of the chosen natural sorbents;

3) physical and chemical researches of sorption characteristics of the developed sorbents;

4) experimental assessment of sorption characteristics of the developed sorbents when processing technogenic and hydromineral raw materials (extent of purification of uraniferous solutions of uranium, extent of concoction of uranium in a sorbent);

5) development of technological parameters of sorption desorption of uranium

and experimental approbation of the developed sorbents in processes of extraction of uranium of technogenic and hydromineral uraniferous raw materials.

Subject of inquiry – technogenic uraniferous solutions, uranium the containing hydromineral raw materials (underground and lake waters), sorbents (zeolite, shungit, a dump phosphite and compositions on their basis) for extraction of uranium from technogenic and hydromineral raw materials.

Scientific novelty of work

1. It is established that chemical sedimentation of hydroxides of copper (II), nickel, zinc on a shungita and zeolite increases sorption properties and mechanical characteristics of a shungit and zeolite in relation to uranium in case of its extraction from the tested technogenic and hydromineral raw materials. It is shown that sorption properties and mechanical characteristics of compositions from a shungit, zeolite, a phosphite and hydroxides of copper (II), nickel and zinc are determined by a mass ratio of these components.

2. Consistent patterns of synthesis of new inorganic sorbents are determined, their physical and chemical and sorption properties are researched. Sizes of extent of ionization of ionogenic groups of a rka for developed in are determined the thesis of sorbents which constituted from 8,40 to 10,36 in case of electrometric titration of sorbents of 0,1 N KOH solution. By results of potentiometric titration it is established that the received modified sorbents are the cation exchanger capable to occlude uranium ions in the form of UO_2^{2+} and its complexes.

3. It is shown that after sorption of uranium from the technogenic and hydromineral solutions tested in the thesis uranium can be present at sorbents in the form of a 10-water magniyuranilfosfat [$Mg(UO_2)_2(PO_4)_2 \cdot H_2O$], a carbonate dropped [$UO_2CO_3$], 7-water tetrafluoride of uranium [$UF_4 \cdot 7H_2O$], and also in the form of complex phosphates dropped such as 4-water phosphate dropped [$(UO_2)_3(PO_4)_2 \cdot 4H_2O$], etc. During creation of the conditions promoting formation of the specified soyedinekniya (implementation in structure of sorbents of the corresponding components), it is necessary to expect increase in sorption reservoir on uranium.

Practical importance of work

1. Cheap raw materials are offered – shungit, zeolite and a phosphite, for receipt of the modified sorbents and their use in case of extraction of uranium from solutions.

A number of the sorbents received on the basis of use of a shungit, zeolite, a phosphite and hydroxides of copper (II), nickel, zinc is developed and offered to application. Developed sorbents are recommended for extraction of uranium from technogenic and hydromineral raw materials.

The methods of extraction of uranium from technogenic and hydromineral raw materials based on use of the sorbents developed in the thesis are created and offered

to application.

2. Value of exchange capacity for the developed sorbents which constituted respectively 1,07÷6,75 and 12,40÷95,19 of uranium mg on 1 g of a sorbent that allows to approach the choice of technology of sorption of uranium from technogenic and hydromineral raw materials are established. Settlement content of uranium in developed sorbents after their use for sorption of uranium from model uranium solutions constituted 1,23÷8,69 of % of masses.

It is shown that the inorganic sorbents received during the dissertation researches are characterized by sorption reservoir on uranium, comparable to that for the organic pitches applied in case of sorption of uranium from solutions from a stage of underground and hydrometallurgical leaching of uranium from ores. This characteristic of the sorbents received in work allows recommending them for technological approbation of sorption of uranium from the specified solutions.

The possibility of desorption of uranium from the sorbent received in the course of sorption of uranium from model solution (as eluent sodium carbonate solution was used 1M) is shown. Uranium desorption degree from a sorbent in eluate 80,4% is reached.

3. Technological parameters of sorption of uranium from the solution imitating waste solution of uranium production of JSC UMP, on granules of the modified shungit in dynamic conditions of sorption are determined. Results of these researches showed a possibility of receipt of the modified shungit saturated on uranium with content of uranium of 3,97% that corresponds to uranium ore of a grade of I ("very rich ore"). This result is provided due to sorption of uranium on granules of the sorbent received from the mix of a shungit, hydroxide of copper (II) and hydroxide of nickel taken in a mass ratio 16: 1: 4.

The technological mode of sorption of uranium from the solution modeling waste solution of uranium production of JSC UMZ, with use of the modified coarse-grained shungit in dynamic conditions of sorption is offered. Results of researches showed a possibility of receipt of the sorbent saturated on uranium with content of uranium of 6,35% that corresponds to uranium ore of a grade of I ("very rich ore"). The achieved result is provided due to sorption of uranium on chemically activated by sulfuric acid shungit fineness +0,5–1,0 mm, modified by zinc hydroxide (the mass relation shungit: zinc hydroxide in the modified sorbent constitutes 7: 1).

It is established that sorption of uranium from waste solution of JSC UMZ in dynamic conditions with use of the sorbents developed in the thesis with guarantee provides the % of masses saturated to 1,86÷5,29 on uranium of sorbents if the size of a specific expense of a sorbent on sorption constitutes about 0,011÷0,027 and less than a kg on 1 g of uranium in waste uraniferous solution of JSC UMP. It is determined that sorption of uranium from waste solution of JSC UMP (radioactive

effluent) in dynamic conditions with use of the sorbents developed in the thesis with guarantee provides purification of the specified waste solution of uranium before its content no more than three mg/dm^3 (waste liquids) if the size of a specific expense of a sorbent on sorption constitutes about 0,024÷0,600 of kg on 1 g of uranium in waste uraniferous solution of JSC UMP.

It is established that sorption of uranium from waste solution of JSC UMP in static conditions with use of a shungit, zeolite and a phosphite with guarantee provides the % of masses saturated to 0,55÷2,34. on uranium of sorbents if the size of an udelkny expense of a sorbent on sorption constitutes about 0,026÷0,125 and less than a kg on 1 g of uranium in waste uraniferous solution of JSC UMP. It is determined that sorption of uranium from waste solution of JSC UMZ (radioactive effluent) in static conditions with use of a shungit, zeolite and a phosphite with guarantee provides purification of the specified waste solution of uranium before its content no more than three mg/dm^3 (waste liquids) if the size of a specific expense of a sorbent on sorption constitutes about 0,083÷0,260 of kg on 1 g of uranium in waste uraniferous solution of JSC UMP.

The found values of a specific expense of sorbents on sorption of uranium from waste uraniferous solution of JSC UMZ, allow approaching the choice of hardware registration of processes of sorption of uranium of the specified solution reasonably.

The uranium desorption mode from the developed sorbents used for extraction of uranium from uraniferous waste solutions of JSC UMP providing uranium desorption degree to % ~99 is offered.

The possibility of increase in an ecological safety and cost efficiency of uranium chemical and metallurgical production of JSC UMP by sorption additional recovery of uranium from waste solutions of this production is established.

By results of work for extraction of uranium from waste solutions of uranium production of JSC UMP hardware schemes of processes of sorption desorption of uranium with use of cascades of columns or settlers are recommended.

4. The possibility of deep purification of underground water from uranium when using of the developed sorbents in static conditions of sorption is shown, and also a possibility of receiving a sorbent with the settlement content of uranium of 1,3% of masses.

It is shown that modification of a shungit and zeolite hydroxides of copper (II) and nickel allows to receive ionites with the increased sorption capacity in relation to the uranium ions which are contained in the tested underground water (in static conditions of sorption). Increase in sorption capacity of a shungit fineness of -0,1 mm in relation to uranium is reached by his modification by hydroxides of copper (II) and nickel at a mass ratio shungit: hydroxide of copper (II): nickel hydroxide, equal 16 :

1: 4. Increase in sorption capacity of zeolite fineness of -0,1 mm in relation to uranium is reached by his modification by hydroxides of copper (II) and nickel at a mass ratio zeolite: hydroxide of copper (II): nickel hydroxide, equal (14÷16): 1: 4.

The granulated compositions the shungit containing of the sorbents received with use of their modification by hydroxides of copper (II), nickel and zinc providing deep purification of the tested underground water of uranium in the dynamic mode of sorption are developed (binding material at data acquisition of sorbents the waterless phosphite was). When using as the zinc sulfate solution modifier with concentration of zinc of 31,42 g/dm3 sorbent granules from this solution, the mechanoactivated shungit and the calcinated phosphite with their mass ratio 1 are received: 1: 1, the uranium % ~99 providing sorption from the tested underground water. In dynamic conditions of sorption concentration of uranium in a phase of a sorbent of 0,3 % of masses is reached., what is comparable to the content of uranium in uranium ores of a grade III ("average ore").

By results of work for extraction of uranium from underground water hardware schemes of processes of sorption desorption of uranium with use of the cascade of columns are recommended.

5. By results of experiments on sorption extraction of uranium in static conditions of sorption from Lake Alakol water, poor on uranium, with use of a powdery shungit fineness of -0,1 mm it is established that upon transition of uranium from this water in the specified sorbent volume concoction of uranium in ~160000 of times is reached. At the same time received after sorption shungit has the settlement content of uranium of 0,12 % of masses, what corresponds to the content of uranium in ore of a grade IV ("ordinary ore").

6. The possibility of expansion of mineral resources of uranium by involvement in processing of uraniferous technogenic and hydromineral raw materials is shown.

The provisions submitted to defense

1) methods of receipt of sorbents for extraction of uranium from technogenic and hydromineral raw materials;

2) methods of sorption extraction of uranium from technogenic and hydromineral raw materials with use of the received sorbents and methods of their conversion after saturation by uranium.

Work was performed at "Chemistry, Metallurgy and Enrichment" department of EKSTU, "Rare Metals and Nanomaterials" and "Physical and Colloidal Chemistry" departments UrFU, in JSC UMP, with participation of Kazzink LLP and ALS KazLab LLP.

Approbation of work, publications.

Materials of work are provided in 23 papers published in Kazakhstan, the near

and far abroad. In the editions recommended by CCES of MES of the RK for the publication of materials of theses 8 articles are published (including 1 article in the periodical of the Russian Academy of Sciences entering the Scopus database). Materials of the thesis are published in collections of the International scientific conferences – 15 reports, including 2 individual reports (without coauthors). Two patent decisions from Federal Institute of Industrial Property of Russia are received. On the examination in Federal Institute of Industrial Property of Russia 3 requests for the invention. The certificate on passing of the "Technology of Extraction a Beryllium, a Lithium and Uranium from Mineral and Technogenic Raw Materials" project of the first round of "STARTUPTOUR 2016" to the nominations "Industrial Technology and Materials" (the founder of the nomination is Skolkovo Foundation, Russia) and in the nomination "The Technology Solution of a Problem of Extraction of Rare Metals from Mineral and Technogenic Raw Materials" is received (the founder of the nomination Autonomous Cluster Fund "Park of Innovative Technologies", Kazakhstan). Diploma of top division in nomination «The best young scientist» in the Republic youth competition of innovative projects «NURINTECH» is received (the founder of the competition is «Ner Otan» party).