Sorption recovery of rhenium and uranium from sulfuric acid solutions of underground leaching of polymetallic raw materials

Vatsura Fedor Yaroslavovich

Abstract. The relevance of the topic of the dissertation work is due to the need to provide the domestic raw material base with compounds of critically important rare metals – rhenium and uranium, which can be obtained by the sorption method from sulfuric acid solutions of underground leaching of polymetallic ores. Rhenium-containing superalloys are used in the aerospace industry, uranium – for the manufacture of fuel elements for nuclear reactors. The predicted production of rhenium in Russia should increase by ~8 times over 10 years, uranium – ~1.5 times. A significant part of Russian uranium ores (~50%) is processed by the borehole in-situ leaching (IS) method using sulfuric acid. From the resulting dilute solutions, uranium is extracted by the sorption method using pyridine and strongly basic anion exchangers with trimethylammonium or diethanolamine ionogenic groups. Solutions of underground leaching of ores from the Khiagda ore field (Buryatia, JSC Khiagda) are characterized by a low temperature of 4–10 °C. Improving the sorption of uranium is associated with the search for an anionite with higher equilibrium and kinetic parameters when operating under such temperature conditions. Uranium ores processed by the IS method are distinguished by their polymetallic nature: they contain scandium and other rare earth elements, rhenium, molybdenum, and vanadium. In URFU them. the first President of Russia B.N. Yeltsin, along with the developed method for extracting uranium on a macroporous pyridine anion exchanger, a technology was introduced for obtaining scandium fluoride from solutions that had previously undergone uranium sorption (Dalmatovskoye deposit, Dalur JSC). Due to the lack of traditional raw materials sources of rhenium in Russia - molybdenum and copper sulfide ores, IS solutions are promising for mining in order to obtain rhenium. Information on the sorption of rhenium from uranium-containing low-temperature solutions is practically absent. The available technological schemes for the associated extraction of rhenium, as a rule, include the operation of liquid extraction of rhenium from the resulting eluates. The processing of eluates by the sorption method with the use of impregnates containing amine seems to be topical.

The main goal of the present work is to obtain the sorption characteristics of pyridine anion exchangers in the recovery of rhenium and uranium, as well as amine-containing impregnates for concentrating rhenium with approbation of the selected anion exchanger for sorption from productive sulfuric acid solutions of underground leaching of polymetallic ores.

The main tasks were: obtaining equilibrium, kinetic and dynamic characteristics of the sorption of rhenium and uranium by pyridine anion

exchangers, including the implementation of the process at low temperature; obtaining impregnates containing a tertiary amine, and studying their characteristics in the extraction of rhenium; approbation of the gel pyridine anion exchanger selected in the work for the recovery of rhenium from IS solutions of complex ores (JSC Dalur); conducting laboratory and semi-industrial tests of a gel pyridine anion exchanger for extracting uranium from productive solutions of ores (JSC Khiagda) with the issuance of data for calculating the dimensions of equipment for industrial testing and a feasibility study for the transition of the enterprise to work with this sorbent.

Scientific novelty.

1. It has been established that a gel anion exchange resin with functional groups of N-methylpyridinium nitrogen has a higher capacity for uranium during sorption from sulfuric acid solutions with a temperature of 4–8 °C compared to the capacity of the mixture of anion exchangers based on the AMP resin.
2. For the first time, the uranium kinetic characteristics of a gel anion exchanger with N-methylpyridinium nitrogen groups at low temperatures (4, 8 and 15 °C) were determined: half-sorption time ($1.62 \cdot 10^4$, $1.50 \cdot 10^4$ and $1.32 \cdot 10^4$ s), rate constants ($9.56 \cdot 10^{-3}$, $6.97 \cdot 10^{-3}$ and $6.56 \cdot 10^{-3}$ $g \cdot mg^{-1} \cdot min^{-1}$), effective diffusion coefficients ($3.6 \cdot 10^{-13}$, $3.9 \cdot 10^{-13}$ and $4.4 \cdot 10^{-13}$ m^2/s).
3. It has been established that the kinetic data on the sorption of uranium by a gel anion exchanger with pyridinium functional groups and rhenium impregnate based on trialkylamine from sulfuric acid solutions are described by a pseudo-second order model.
4. The value of the apparent activation energy of sorption of uranium by a gel anion exchanger with pyridinium groups (12.7 ± 0.5 kJ/mol) indicates the occurrence of sorption from solutions with a low temperature in the external diffusion region.

The practical significance of the work.

1. The possibility of extracting rhenium with VPA G2.4 gel anion exchanger from productive solutions of IS of polymetallic ores of the Dalmatovskoye deposit (JSC Dalur) with a sorption degree of 92.4% is shown.
2. A block diagram of the extraction of rhenium with concentration at the second stage of sorption from the circulating solutions of IS with an impregnate based on a tertiary amine (K-TAA) is proposed.
3. Semi-industrial tests of sorption extraction of uranium by VPA G2.4 gel anion exchanger from productive IS solutions of ores (JSC Khiagda) were carried out at a pilot plant. The capacity of the gel anion exchanger for uranium is ~3.0 times higher compared to the one used above, which makes it possible to recommend the sorbent chosen in the work for improving the sorption technology of underground leaching of uranium, carried out at low temperatures.
4. Data on the calculation of the dimensions of equipment for conducting industrial tests of uranium sorption from productive solutions of in-situ leaching

and a feasibility study for the transition of JSC Khiagda to work with VPA G2.4 gel anion exchanger were issued.

Defense Provisions.

1. Sorption characteristics of pyridine anion exchangers in the recovery of rhenium and uranium from sulfuric acid solutions.
2. Results of mathematical processing of equilibrium, kinetic and dynamic data on the sorption of rhenium and uranium by the selected pyridine anion exchanger from sulfuric acid solutions.
3. Sorption characteristics of the K-TAA impregnate during the extraction of rhenium from sulfuric acid solutions.
4. Results of approbation of rhenium sorption by gel anion exchanger VPA G2.4 from productive solutions of borehole underground leaching of polymetallic ores of the Dalmatovskoye deposit (JSC Dalur).
5. Results of tests on a pilot plant for sorption of uranium by a gel anion exchanger VPA G2.4 from productive solutions of borehole underground leaching of polymetallic ores of the Khiagda ore field (JSC Khiagda).