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PHYSICAL AND CHEMICAL ASPECTS OF URANIUM EXTRACTION FROM ZONES OF RESERVOIR OXIDATION USING ULTRASONIC TECHNOLOGY

Introduction

Being in the group of actinides of the periodic system of elements by D. I. Mendeleev, the electronic structure of uranium, which determines the valency, is completed in the fifth shell from the top. Deep electrons located on the fifth electronic level, due to the large atomic radius, are less firmly bound to the nucleus and, because of this, take part in the formation of valence bonds. Differences in the energy bonds of the electrons of the uranium nucleus shells are relatively small, but still exist, and this explains the multivalency of uranium. The main valency of uranium is 4, 5 and 6. Variable valence leads to the formation of various complex compounds of uranium. Uranium mining by in-situ

This article gives physical and chemical aspects of uranium extraction from zones of reservoir oxidation using ultrasonic technology, and offers theoretical substantiation of the technology of in-situ uranium leaching in Kazakhstan. The presence of significant and well-explored uranium resources, developed uranium mining and processing facilities, as well as the current situation on the world uranium market predetermine the prospects for the development of the uranium mining industry in Kazakhstan. Host rocks of uranium localized at the fronts of reservoir oxidation zones are largely similar in terms of the chemical composition. Fe, Al, Mg, Ca, K, Na are among the most widespread petrogenic elements of rock-forming minerals. Uranium is observed in association with iron, vanadium, selenium, molybdenum, rhenium and other elements. Uranium mineralization is represented by exogenous (secondary) minerals—pitchblende and coffinite. In the general balance of uranium minerals, pitchblende is about 30% and coffinite is about 70%. Nasturan ($x\text{UO}_2 \cdot y\text{UO}_3 \cdot z$) represents an association of tetravalent uranium dioxide and hexavalent uranium trioxide with a variable composition: ($\text{UO}_2 + \text{UO}_3$)—65–85%, coffinite—tetravalent uranium silicate USiO_4 .

Keywords: physical and chemical aspects, recovery, uranium, reservoir oxidation, ultrasonic technology, theoretical substantiation, in-situ leaching, wells

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leaching through a system of wells drilled from the surface allows the most efficient exploitation of infiltration uranium deposits in reservoir oxidation zones [1–5].

Uranium forms doubly charged uranyl cations (UO_2^{2+}) in leaching in an acidic environment and uranate anions in an alkaline environment, and has a weak affinity for sulfur and a strong affinity for oxygen. As a result, simple and complex uranyl sulfate ions are formed in underground leaching solutions, depending on excess acidity. Compared to conventional mining, in-situ leaching allows uranium production at significantly lower capital and operating costs. At the same time, the efficiency of field development is largely related with the optimality of flowsheets for opening productive formations, the design of production wells used, the means of mortar lifting used, the modes of pumping solutions, etc. [1–3].

Methods

Uranium compounds are relatively well soluble, which explains uranium migration ability and formation of exogenous deposits in reservoir oxidation zones.

In solutions, uranium can exist in four valence states: U^{3+} , U^{4+} , U^{5+} , U^{6+} [1]. Aqueous solutions of salts of trivalent uranium are not very stable. Salts of tetravalent uranium form more stable solutions. Air oxygen oxidizes tetravalent uranium in aqueous solutions to hexavalent. Pentavalent uranium forms the uranyl radical (UO_2^+) in aqueous solutions in an extremely unstable form, which transforms into tetravalent and hexavalent uranium ions.

Quadrivalent uranium is slightly soluble in dilute solutions of sulfuric acid, and oxygen, permanganates, hydrogen peroxide, nitrogen-containing oxidizers, chlorine, chlorine-containing oxidants, etc. can be used for its oxidation. Industrial applications are: pyrolusite, melange, ferric iron salts, oxygen, hydrogen peroxide [2]. Compounds of hexavalent uranium are characterized by the formation of the uranyl ion UO_2^{2+} . The uranyl ion has a very high affinity for water and is hydrated in neutral solutions ($UO_2^{2+} \times 2H_2O$). Uranyl salts are highly hydrolyzed and have a pronounced acid reaction (pH 0.02M solutions of uranyl is 2.9) [1, 4, 5–10].

All salts are characterized by incomplete dissociation into ions.

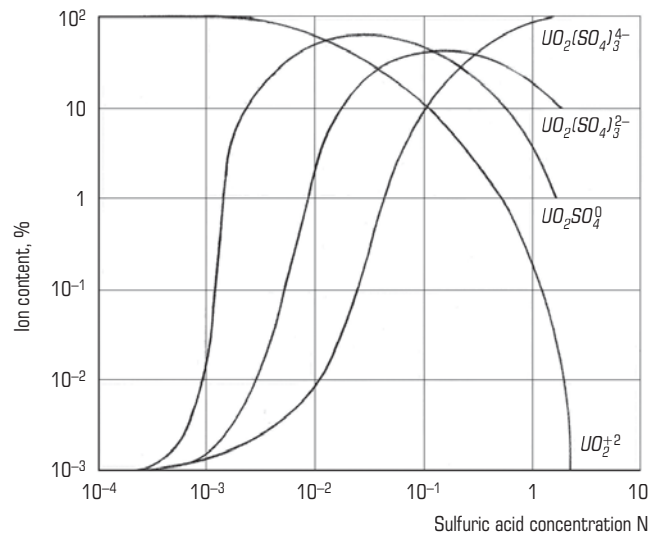
In a sulfate medium, the uranyl ion is a strong complexing agent. In weakly acidic solutions with pH = 1–2, trisulfate and disulfate complex ions are formed $[UO_2(SO_4)_3]^{4-}$ and $[UO_2(SO_4)_2]^{2-}$.

In sulfate solutions, the ratio of simple and complex uranium ions depends on the excess acidity of the solution, the content of sulfate ions in it, and the concentration of uranium (Figure). For hexavalent uranium, the formation constants of the main complex ions in leaching solutions are [2, 6]:

- for the uranyl cation UO_2^{2+} 5.0–6.5;
- for a neutral molecule of uranyl sulfate $UO_2SO_4^0$ – 50–96;
- for the anion of uranyl disulfate $[UO_2(SO_4)_2]^{2-}$ – 20–900;
- for the uranyl trisulfate anion $[UO_2(SO_4)_3]^{4-}$ – 2500.

The analysis of the graph (see Fig.) shows that an increase in the acidity of the solution from pH = 3–3.5 to pH = 2–2.5 leads to a decrease in the content of the uranyl cation and, due to an increase in the content of sulfate ions, to a sharp increase in the complex ions of uranyl sulfate in the solution with the transition from a neutral molecule $UO_2SO_4^0$ to an anion of uranyl disulfate and uraniumtrisulfate.

A further increase in acidity (up to pH = 0.5–0.3) leads to a decrease in the content of $UO_2SO_4^0$ and $[UO_2(SO_4)_2]^{2-}$, since in acidic solutions at pH < 2–1.5 the most stable form of uranium is the



Ionic composition of uranium compounds in sulfuric acid solutions at different acidity

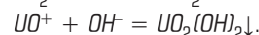
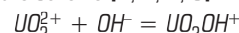
uranyl trisulfate anion $[UO_2(SO_4)_3]^{4-}$. If the solution is raised again to pH > 2.5, polymerization of ions occurs with the formation of tri- and disulfate uranyl dimer $[UO_2O_5(SO_4)_3]^{4-}$, $[UO_2O_5(SO_4)_2]^{2-}$, due to hydrolysis of complex ions, which leads to a significant increase in the capacity of anion exchangers [4, 7, 8].

Therefore, it is advisable to start uranium leaching in a mild mode at pH > 2.5 (H_2SO_4 3.0–5.0 g/l), increasing the concentration in the uranyl sulfate solution to 50–60%. Then, it is advised to increase the acidity of the solution to pH = 1.5–1.0 (H_2SO_4 10–15 g/l) and bring it to pH = 0.5–0.3 (H_2SO_4 20–25 g/l), concentrating uranium in solution for uranyl trisulfate up to 95–100%. Then, at the outlet, it is required to quench the solution with soda to an acidity of pH = 2.5–4.0, thereby facilitating the formation of well-sorbed uranyldimer trisulfate ions as much as possible.

Results and discussion

During leaching, reaction of a solvent with rock-forming minerals forms mobile geochemical barriers (acid-base and redox) with alternating acts of dissolution and precipitation of uranium due to changes in pH and Eh of the medium. At the same time, acids are spent not only and not so much on uranium leaching, but on the dissolution of rock-forming minerals, reaching tens and hundreds of kilograms per kilogram of uranium in real conditions. The main acid-intensive minerals are carbonates (calcium, dolomite, magnesite) and some types of clay minerals.

Due to the consumption of H_2SO_4 for the reaction with rock-forming minerals, its concentration front moves much more slowly than if only uranium was leached. At the same time, the concentration front of dissolved uranium tends to overtake the acid front, but this does not happen, since with a decrease in the acidity of the solution at the concentration acid front, uranium is hydrolyzed and redeposited according to the scheme [1, 2, 7, 9]:



In this case, the acid concentration front plays the role of a mobile alkaline barrier. Then, when new portions of acid approach, the

redeposited substance dissolves again, i.e. the reaction goes in the opposite direction. Repeated steps lead to an increase in H_2SO_4 concentration on the moving barrier up to the saturation concentration.

It is not possible to determine the spatio-temporal position of the geochemical barrier under the conditions of underground leaching by calculation methods. Changes in the pH and Eh parameters, and ionic composition are controlled only in observation wells and at the outlet from pumping-out wells.

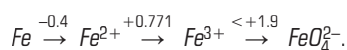
There are no models of the in-situ leaching process related to thermodynamics toward the spatio-temporal control over redox processes of uranium leaching in the deposits of reservoir oxidation zones. Creation of a generalized mathematical model of in-situ leaching control for these conditions remains an extremely complex and perhaps yet unsolvable task.

As is known, ISL efficiency is directly related to concentration of potential-determining components of the system:

$$E = E_o + \frac{0,059}{n} \lg \frac{|O_k|}{|B_o|}$$

From the point of view of potential-determining systems, the association of uranium and iron is of the greatest interest in these deposits. The reaction between uranium and iron in an acidic environment proceeds in the direction of uranium oxidation and iron reduction.

Oxidation potentials for iron:



In turn, at Eh + 0.35*v*, tetravalent uranium transforms into a hexavalent hydrated oxide $UO_2(OH)_2$ and then at Eh + 0.407*v*, into a hexavalent doubly charged uranyl cation UO_2^{2+} .

Oxidation of uranium with the participation of ferric ions proceeds by the reaction $UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+}$, where uranium is oxidized to the hexavalent form, and iron is reduced to the divalent form.

In real conditions of in-situ uranium leaching, in addition to iron ions, the solution always contains other cations of variable valence and ions that affect the ISL efficiency. However, the role of these ions in ISL stabilization, compared with iron ions, is insignificant. Iron ions play the role of catalysts for the uranium oxidation process.

In the process of in-situ leaching, complex formation has a great influence on the change in the oxidizing environment. In acid leaching, except for uranyl sulfate complexes; UO_2SO_4 ; $[UO_2(SO_4)_2]^{2-}$, $[UO_2(SO_4)_3]^{4-}$, about half of calcium, magnesium, manganese binds to sulfate complexes $CaSO_4$, $MgSO_4$, $MnSO_4$. Up to 80% of aluminum and over 90% of iron bind into sulfate complexes $FeSO_4^+$, $Fe(SO_4)_2$, $AlSO_4^+$, $Al(SO_4)_2^-$.

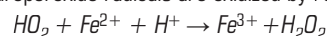
The proportion of simple ions decreases with an increase in the total concentration of sulfate sulfur in the solution, pH and Eh change, and the content of free SO_4 ions decreases. Complexation causes a shift in the acidity of the in-situ leaching solution at geochemical barriers towards an increase in the pH value, and in order to maintain the process of oxidation and dissolution of uranium, it is necessary to increase the consumption H_2SO_4 .

However, taking into account the fact that in the process of repeated circulation of sulfuric acid solutions between pumping and injection wells, up to 0.05 mol/l and more ferrous sulfate $FeSO_4$ in the divalent form (Fe^{2+}) accumulates in the circulating solutions, in-situ leaching can be maintained at the required level without additional consumption

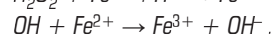
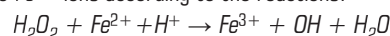
of sulfuric acid and other oxidizing reagents. For this, attention should be paid to the effects of the chemical action of ultrasound.

It is known that the kinetics of sonochemical reactions in liquid media (water, solutions) is determined by the rate of formation and consumption of radicals.

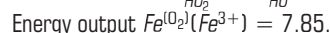
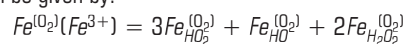
It can be assumed that under ultrasonic impact on circulating solutions of in-situ leaching in the cavitation mode, water molecules, passing into an excited state [1, 7, 9–13], split into *H*, *OH* radicals, ionize with the formation of hydrated electrons e_{aq}^- and then, in the presence of dissolved oxygen, transform into HO_2 , O_2^- and *OH* and H_2O_2 . The formed hydroperoxide radicals are oxidized by Fe^{2+} :



moreover, the formed hydrogen peroxide H_2O_2 will additionally oxidize two Fe^{2+} ions according to the reactions:



The equation for the chemical-acoustic yield of Fe^{3+} , in this case, can be given by:



Conclusions

This article describes the physical and chemical aspects of uranium extraction from the zones of reservoir oxidation using ultrasonic technology and theoretically substantiates the in-situ uranium leach technology for uranium deposits in Kazakhstan. In comparison with the known works in this area of knowledge, the proposed study on innovative technologies for exploitation of hydrogenous uranium deposits is important for extraction of minerals in complex mining and geological conditions not only in Kazakhstan, but also in other mining regions of the world [1, 2, 8, 14–18].


The result of these studies is the development of technology for in-situ leaching of uranium in Kazakhstan. To implement the ultrasonic method of acid-free enhancement of in-situ leach solutions in industrial conditions, complex facilities and high specific power of ultrasound are not required. Ultrasonic impact on the in-situ leaching solution can be carried out in settling tanks using submersible magnetostrictive transducers with a flat radiating surface and a frequency of up to 50 kHz, at a power consumption of 0.4 to 4 kW, or directly in sorption columns using ring magnetostrictive transducers operating at frequencies from 4 to 400 kHz and power consumption from 2.5 to 10 kW, produced by the Taganrog and Tallinn machine-building plants.

When applying ultrasound to sorption columns, a double effect can be obtained—the intensification of sorption of uranium and the oxidation of Fe^{2+} to Fe^{3+} , to increase the efficiency of leach solutions fed from sorption columns and to injection wells.

The use of ultrasonic technology to increase the oxidation potential of the in-situ leaching circulating solution can significantly reduce the cost of sulfuric acid at uranium leaching facilities and significantly reduce the cost of uranium production.

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PROCESSING TECHNOLOGY FOR FERRUGINOUS QUARTZITE OF OKOLOVO DEPOSIT

Introduction

Ferruginous quartzite of Okolovo deposit is a promising source of raw materials for mining and processing. The commercial reserves are estimated as 145.4 Mt at the contents of $Fe_{\text{magnetic}} = 8.0\text{--}26.1\%$ and $Fe_{\text{total}} = 15.0\text{--}31.7\%$. In terms of processability, ferruginous quartzite belongs to the categories of readily grindable and easy minerals [1]. The deposit is composed of 11 sheet-like ore bodies of variable thickness, with feathering-out or thin schistosity, and with replacement of ferruginous quartzite by gangue with

The article describes mineralogical and technological studies of ferruginous quartzite of Okolovo deposit. A signature of the mineral composition of ferruginous quartzite from this deposit is a noticeable predominance and diversity of silicate minerals as against quartz. The presence of low metallic and non-metallic materials in quartzite dictates their extraction in the process of ore pretreatment.

The promising trend in processing of ferruginous quartzite of Okolovo deposit is combination of pretreatment and deep concentration. The technological research has proved feasibility of obtaining a high-quality product suitable for metallization using the recommended technology.

Keywords: ferruginous quartzite, magnetite, hematite, martite, quartz, dry magnetic separation, wet magnetic separation, grindability

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