Recent research has shown that one of the main directions for increasing the extraction of uranium from difficult-to-hide ores is the use of intensifiers, which allow the most complete transfer of uranium from one valence state to another. In the article, the catalyst “M-1”, which is a compound of transition metals, is considered as an intensifier. Comparison of the kinetic dependencies of the sorption extraction of uranium by the ionites from the productive solutions of leaching of uranium-bearing ore in the presence of the “M-1” catalyst showed that they differ insignificantly. The possibility of sorption of uranium from productive solutions by natural sorbents in comparison with synthetic sorbents is investigated.

Key words: uranium, ore, leaching, sorption, catalyst

INTRODUCTION

Uranium is present in ores as part of a large number of mineral formations that differ in their physicochemical properties. According to the literature, the main uranium ores are the minerals of the tetravalent uranium: oxides (nasturan, uranium black) silicates (coffinite). The most common in the ores of almost all genetic types are simple oxides of U (IV). Minerals of hexavalent uranium are of lesser industrial importance. The use of sulfuric acid as a leaching reagent allows the extraction of only uranium (VI) compounds, since uranium compounds (IV) in sulfuric acid do not dissolve. To convert uranium (VI) to uranium (IV), oxidizers are used in industry, most often-ferric compounds. In this regard, the main problem of increasing the extraction of uranium in underground leaching is the transfer of uranium (IV) to a soluble state [1].

The method of underground well leaching finds an increasingly wide application in the development of uranium deposits, which, due to complex bedding conditions, as well as high specific investments and operating costs, can not be worked out by traditional methods.

In Kazakhstan, underground well leaching is the only effective method of uranium mining. Sulfuric acid is used as a leaching reagent [2].

Minerals of tetravalent uranium do not dissolve in sulfuric acid, unlike to hexavalent. To dissolve the minerals of tetravalent uranium in dilute solutions of sulfuric acid, leaching is conducted with the addition of oxidizing agents. It is believed that the main problem of increasing the extraction of uranium from ore during underground leaching using existing technologies is the conversion of uranium (IV) to a soluble state. Therefore, at the heart of the overwhelming majority of research works is the question of the most complete transfer of uranium compounds into a soluble state, i.e. uranium (IV) in uranium (VI) [3].

In this connection, the purpose of this work was to study the effect of the “Muhamedzhan - 1” (M-1) catalyst on uranium leaching and to assess the extent of its subsequent extraction from the resulting productive solutions.

In accordance with the complex chemical composition of uranium-containing solutions of underground well leaching and low uranium content, the most acceptable method of their processing is sorption methods, which are based on the use of ion exchange. Ion exchange has certain advantages over other methods (precipitation and extraction), since it allows to extract uranium from solutions of various concentrations [4].

In the literature, there are data on the use of natural sorbents for the extraction of uranium from productive solutions with a low content [5]. The advantages of such sorbents are their low cost. Within the framework of the present work, the possibility of sorption of uranium from productive solutions by natural zeolite and schungite in comparison with synthetic sorbents is investigated.

EXPERIMENTAL PART

Method and work technology

Experiments on the leaching of uranium ore were conducted in a thermostated reactor according to a generally accepted procedure. The maximum duration of
Sorption of uranium was carried out on the anionites Purolite A500 and Ambersep 920 in a static mode according to the procedure described in [6] from the productive solution from leaching of uranium-bearing ore. The composition of the solution is given below.

RESULTS AND ITS DISCUSSION

As mentioned above, the main task of the vast majority of research works is the question of the most complete transfer of uranium compounds into a soluble state, i.e. uranium (IV) into uranium (VI). In this connection, we chose the initial ore, in which the main mineral is U[SiO$_4$], which makes up about 95 % of the total uranium mineralization balance. Uranium-containing minerals are also represented by leucoxene, accompanying - native selenium, cobalt-nickel pyrite and sphalerite. The composition of different rocks: quartz - 70 - 80 %, feldspars - 10 - 20 %, siliceous rocks - 5 - 10 %. The average content of uranium is 0.03 %.

At the first stage of the research, the effectiveness of the M-1" catalyst’s influence on the uranium extraction degree by agitation leaching with sulfuric acid was evaluated.

The investigations were carried out in the presence of the “M-1” catalyst. Further, for comparison, in the presence of traditional oxidizing agents: ferric iron, ammonium nosulphate and sodium peroxoborate.

Preliminary studies of the catalyst “M-1” are presented in [7]. The catalyst “M-1” is a mixture of nitrates, sulfates, chlorides, bromides and iodides of transition metals (Fe, V, Cu, Mn). Data characterizing the extraction of uranium by sulfuric acid in the presence of a “M-1” catalyst are presented in Table 1.

Table 1 Results of sulfuric acid leaching of uranium in the presence of “M-1” catalyst

<table>
<thead>
<tr>
<th>Catalyst content / g/dm$^3$</th>
<th>ORP / mV</th>
<th>Extraction U / mg/dm$^3$</th>
<th>The acid consumption ($C_{SOC}$ = 5.0 g/dm$^3$), g/g of uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>378</td>
<td>35</td>
<td>39.1</td>
</tr>
<tr>
<td>0.3</td>
<td>388</td>
<td>80</td>
<td>14.2</td>
</tr>
<tr>
<td>0.6</td>
<td>396</td>
<td>82</td>
<td>12.8</td>
</tr>
<tr>
<td>0.9</td>
<td>402</td>
<td>84</td>
<td>11.1</td>
</tr>
<tr>
<td>1.2</td>
<td>408</td>
<td>86</td>
<td>9.7</td>
</tr>
</tbody>
</table>

From the data presented, it can be seen that the use of the “M-1” catalyst in the leaching process leads to an increase in the extraction rate of uranium from the ore. The maximum increase in the concentration of uranium in the solution is observed at the site of the change in the catalyst content in the range 0 – 0.3 g/dm$^3$.

Table 2 shows the leaching of uranium-bearing ore by sulfuric acid in the presence of a catalyst in comparison with oxidants.

<table>
<thead>
<tr>
<th>Presence of catalyst or oxidizer</th>
<th>Concentration of uranium in solution / mg/dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12 h</td>
</tr>
<tr>
<td>Sulfuric acid without oxidizers and catalysts</td>
<td>35.2</td>
</tr>
<tr>
<td>The catalyst “M-1”</td>
<td>84.6</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>50.8</td>
</tr>
<tr>
<td>Ammonium Sulfate</td>
<td>48.3</td>
</tr>
<tr>
<td>Peroxoborate</td>
<td>39.2</td>
</tr>
</tbody>
</table>

It can be seen from the table that the uranium content in the leaching solution without catalyst and oxidizers was 35.2 mg/dm$^3$ after 12 hours of the experiment and increased to 38.4 mg/dm$^3$ after 48 hours after the beginning of the leaching. In the case of using traditional oxidants, an increase in uranium extraction was also observed with increasing leaching time. The use of ferric chloride during the leaching process allowed to increase the concentration of uranium in the solution from 50.8 mg/dm$^3$ for 12 hours of leaching to 58.2 mg/dm$^3$ for 48 hours, and for ammonium nitrate and sodium peroxoborate from 48.3 and 39.2 to 51.8 and 40.9 respectively. When the “M-1” catalyst was used after 12 hours of the experiment, 84.6 mg/dm$^3$ of uranium extraction was achieved, with increasing leaching time this value varies 88.3 mg/dm$^3$.

Thus, the highest concentration of uranium in the solution is achieved when the ore is leached with sulfuric acid in the presence of a catalyst and decreases in the series: the catalyst “M-1” - ferric chloride III - ammonium perchlorate - sodium peroxoborate - sulfuric acid in the absence of oxidants and catalyst.

It should be noted that the catalyst “M-1” was successfully tested under production conditions and recommended for use.

Unlike other methods, uranium sorption is characterized by the possibility of achieving high purification factors and a degree of concentration, high selectivity, the possibility of flexible regulation of selectivity by changing pH, oxidation-reduction conditions, complication, simplicity and compactness of instrumentation, and a wide variety of artificial and natural sorbents.

Sorption of uranium together with the process of leaching is a kind of indicator of its extraction from this type of raw material.

Sorption of uranium was carried out in a static mode on Purolite A500 and Ambersep 920 anion exchangers. The selected anion exchangers - strongly basic macroporous Purolite A500 anionite on the basis of styrene-divinylbenzene matrix and macroporous strongly basic anionite Ambersep 920 based on cross - linked polystyrene are effectively used in uranium mining enterprises of Kazakhstan.

In the course of the experiment, a productive solution was used from the leaching of uranium-bearing ore with sulfuric acid in the presence of the “M-1” catalyst. The concentration of uranium in the initial solution was...
88,3 mg/dm³. The kinetic dependencies of extraction of uranium from the productive solution by Purolite A500 and Ambersep 920 ion exchangers were determined in comparison. The results of the experiment are shown in Figure 1, from which it can be seen that the ion exchangers practically equally sorb uranium from the solution. The degree of extraction of uranium on ion exchanger Ambersep 920 reaches 88,3 %, Purolite A500 – 89,1 % for 8 hours of contact.

In addition, studies have shown that increasing the duration of the process over 8 hours is ineffective.

The rate of ion exchange is usually determined by diffusion processes: either by the rate of diffusion of ions inside the ionite grain (gel diffusion), or by the rate of passage of these ions through a liquid film adjacent to the grain surface (film diffusion) [8].

If the process is limited by diffusion in the film (film kinetics), the following simplified formulas are used:

\[ \ln(1-F) = \frac{-3D^{3/2}C}{\pi^{1/2}} \cdot \sigma^{1/2} \cdot t \]

where, F - degree of achievement of equilibrium in fractions, %;

\[ D \] - constant rate of ion exchange, s⁻¹;

\[ C \] - concentration of the solution, g/l;

\[ \sigma \] - the thickness of the film, cm;

\[ t \] - time, s;

\[ \lambda \] - the distribution coefficient.

To determine the limiting stage of the uranium sorption process, the dependence “ln (1-F) on t” was constructed and shown in Figure 2.

In Figure 2 confirms the predominance of gel kinetics in this region.

Experiments on the influence of temperature were carried out in the interval of 15 - 45 °C in a thermostated reactor. Figure 3 shows the degree of extraction of uranium as a function of temperature on Purolite A500 and Ambersep 920 anion exchangers.

It follows from the figure that the temperature has a positive effect on the sorption of uranium. With an increase in temperature to 45 °C, the uranium recovery rate rises: on the ioniser Ambersep 920 up to 91,6 %, Purolite A500 up to 95,7 %. However, the temperature of the solutions should not be more than 50 - 60 °C, because when heated above this temperature, the destruction of the sorbent grains, the cleavage of the active groups and, as a consequence, the decrease in the capacity of the resin, is possible. Based on the studies carried out, the values of the activation energy and the diffusion coefficients of uranium were calculated. The results are shown in Table 3.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>T / K</th>
<th>Diffusion coefficient / cm²/s</th>
<th>Activation energy / kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite A500</td>
<td>298</td>
<td>6,338·10⁻⁹</td>
<td>6,94</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>8,574·10⁻⁹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>8,015·10⁻⁹</td>
<td></td>
</tr>
<tr>
<td>Ambersep 920</td>
<td>298</td>
<td>2,649·10⁻¹</td>
<td>1,53</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>1,086·10⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1,73·10⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

It follows from the table that the calculated values of the diffusion coefficients of uranium are of the order of 10⁻⁹ - 10⁻¹¹ m²/s and indicate a diffusion mechanism inside. The calculated activation energies for uranium sorption on Purolite A500 and Ambersep 920 anionites are characteristic for a mixed external and internal diffusion process type.
During the research, sorption extraction of uranium was tested with natural sorbents. Chemical composition of schungite, %: C - 10; SiO₂ - 26.0; Al₂O₃ - 6.5; Fe₂O₃ - 3.8; MgO - 2.5; CaO - 13.5; Na₂O - 0.6.

The results of uranium sorption from productive solutions are presented in Table 4.

Table 4 Results of sorption of uranium from productive solutions

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Uranium content / mg/dm³</th>
<th>The extraction of U into the sorbent / %</th>
<th>Content of U in the sorbent / % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shungite</td>
<td>0.85</td>
<td>90,9</td>
<td>0.193</td>
</tr>
<tr>
<td>Zeolite</td>
<td>0.97</td>
<td>90,1</td>
<td>0.165</td>
</tr>
</tbody>
</table>

It states in the table that the degree of extraction of uranium by natural sorbents is quite comparable with the synthetic ones (the ratio of solid to liquid equals (S : L) for synthetic sorbents 1 : 500, and for natural sorbents 1 - 1,2 : 25), but their sorption capacity is low. The main disadvantage of synthetic sorbents is their high cost, and therefore, the use for uranium sorption from solutions with low concentrations (usually for pre-extraction) is unreasonable. To extract uranium from productive solutions, or from liquid waste of uranium chemical-metallurgical industries, it is more profitable to use natural sorbents. However, due to the low sorption capacity, their use is limited. At present, we are working to increase the sorption capacity of natural ion exchangers for uranium.

CONCLUSION

The technology of uranium mining by the method of borehole underground leaching mainly uses aqueous solutions of mineral acids or salts of alkali metal carbonates. From the practice of conducting the process of underground uranium leaching, it follows that the choice of the type of solvent for the working (leaching) solutions depends on the form of the uranium mineralization, the material composition of the ores and host rocks, and on the chemical nature of the uranium minerals.

When poorly soluble uranium ores containing mainly tetravalent uranium by sulfuric acid is leached, the main task is the most complete oxidation of uranium (IV) to uranium (VI). Uranium (IV) in sulfuric acid is insoluble. In this connection, the study of the effect of new intensifiers on the process of uranium leaching is of great interest.

The influence of “M-1” catalyst on uranium leaching from persistent uranium-containing ore is studied and its advantage over traditional oxidants is shown. Sorption methods are used to extract uranium from productive solutions. The concentration of uranium on Purolite A500 and Ambersep-920 ion exchangers and natural sorbents - zeolite and shungite was studied. In view of the low cost of natural sorbents, their priority use is considered for the extraction of uranium from productive solutions and liquid waste of uranium chemical and metallurgical industries.

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REFERENCES


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