REMEDIATION OF ARTIFICIAL WATER BASINS OF URANIUM ENTERPRISES

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Annotation
In the given paper the technology of one of the stages of slurry storage basins conservation - cleaning decantates from slurry storage basins of uranium production, which reduces uranium content to the value below the MPC level (0.1 mg / L) is proposed.

The process of galvanochemical treatment of decantates from slurry storage basins of uranium enterprises is considered. The main features of the galvanochemical treatment are determined. Comparison with direct alkalization of the decantate is made.

This research work will be useful for nuclear industry workers involved in preservation and radioactive waste management, as well as for scientists working on environmental safety and at engineering complexes processing all types of waste.

Key words: decantates from slurry storage basins, uranium, radionuclides, galvanic couple, galvanochemical treatment.

Introduction
Today the majority of enterprises of atomic industry neutralize industrial wastewaters containing nonferrous, heavy, and radioactive metals and discharge the resulting slurries into open slurry storage basins. Basins for accumulation of liquid radioactive waste (LRW) are potentially hazardous, because in the course of their operation radionuclides migrate beyond the storage basin. Furthermore, accidents at protecting and filtering dams can lead to considerable pollution of the adjacent territories and of underground and surface waters. The life of slurry storage basins is limited. The Environmental Safety section of the Concept of the Development of the Atomic Industry in the Period of up to 2010 indicates that it is necessary to develop measures for step-by-step conservation and liquidation of radioactive slurry storage basins and to construct industrial complexes for reprocessing of all kinds of wastes [1].

Here we suggest a process for one of the steps of conservation of slurry storage basins: treatment of the decantates from slurry storage basins of uranium production to decrease the uranium concentration below the MPC level (0.1 mg l⁻¹).

Experimental
In our experiments of treatment of the decantate from slurry storage basins of a uranium enterprise (the decantate composition is given below), we performed both direct alkalization and galvanochemical treatment. In the initial decantate and in the filtrate after the treatment, we determined $U_{tot}$ by the procedure from [2-7], using Arsenazo III as indicator. The galvanic sludge precipitates were examined by thermal
gravimetric and X-ray phase analysis and by IR spectroscopy.

Thermal gravimetric analysis of galvanic sludge samples were performed with an SDT Q600 combined thermal analyzer in the temperature range 20-1000°C in a nitrogen atmosphere. X-ray diffraction patterns were taken with a DRON-3M diffractometer (CuKα radiation). The IR spectra of galvanic sludge samples in KBr pellets were recorded with a Nicolet 5700 IR Fourier spectrometer in the range 400-4000 cm⁻¹ at room temperature.

Composition (mg ¹⁻) of the decantate from the slurry storage basin of the Novosibirsk Plant of Chemical concentrates, Joint-Stock Company

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>11.9-21.9</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>320-350</td>
</tr>
<tr>
<td>Na⁺</td>
<td>375-445</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>50-55</td>
</tr>
<tr>
<td>Li⁺</td>
<td>6.1-7.8</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1345-1520</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>11.9-21.9</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>320-350</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>375-445</td>
</tr>
<tr>
<td>F⁻</td>
<td>50-55</td>
</tr>
<tr>
<td>Dry residue</td>
<td>6.1-7.8</td>
</tr>
<tr>
<td>pH</td>
<td>1345-1520</td>
</tr>
<tr>
<td>To</td>
<td>7.1-7.8</td>
</tr>
</tbody>
</table>

In the course of operation of slurry storage basins, the discharged alkaline industrial wastewaters undergo acidification due to dissolution of atmospheric carbon dioxide. Acidification of decantates leads to partial dissolution of the precipitate and to an increase in the uranium concentration.

An interesting approach is alkalization of the decantate from slurry storage basins to decrease the uranium concentration via formation of both insoluble uranium compounds and a precipitate (calcium and magnesium hydroxides, calcium carbonate) acting as uranium collector. Treatment of basins with calcite-containing reagents to decrease their acidity was reported in [3].

Experiments on capturing uranium by the forming precipitate were performed as follows. The decantate from a slurry storage basin, containing 0.393 mg l⁻¹ Utot, was treated with lime milk [10% Ca(OH)₂] in the pH range 7-13. The results of the experiment are shown in Fig. 1.

Efficient trapping of uranium is attained by alkalization of the decantate to pH > 12.9, which corresponds to complete precipitation of magnesium hydroxide (pH 12.4) [4]. In the process, the decantate
from a slurry storage basin exhibits pronounced properties of a buffer solution.

The most efficient and cost-saving method of wastewater treatment, as noted by UNESCO, is galvanochemical method. This method was suggested for treatment of the decantate from slurry storage basins to remove uranium without strong alkalization [5, 6]. The method is based on anodic dissolution of iron in the galvanic couple Fe–C owing to internal electrolysis, with continuous formation of precipitates of hydrated iron polyforms (galvanic sludge) in the volume of the solution being treated.

The major advantages of the galvanochemical method are simplicity and reliability, highly efficient removal of nonferrous, heavy, and radioactive metals from highly saline water systems, the use of metal working wastes as galvanic packing, the possibility of combining with other treatment methods, magnetic properties of precipitates, and high performance [5].

For the treatment of the decantate from a slurry storage basin, we used a laboratory vibration coagulator of vertical type having the productive capacity of up to 50 l h–1, with the Fe (St.3)–C (graphite) galvanic couple [7]. The decantate was treated as follows.

After pH adjustment at 20°C, the decantate was fed to the vibratory galvanic coagulator, which was followed by pH adjustment and separation of the galvanic sludge precipitate by filtration.

In our experiments we studied how pH of the decantate, contact time, and vibration frequency affect the amount of the generated iron and the residual uranium concentration. We found that, by varying pH of the initial and treated decantate, it is possible to control the generation of the galvanic sludge precipitate and the uranium concentration in the filtrate.

The residual concentration of uranium correlates with the content of the galvanic sludge precipitate. To attain MPC of $U_{tot}$ (0.1 mg l$^{-1}$) at the initial $U_{tot}$ concentration of 0.393 mg l$^{-1}$ and adjustment with lime milk, it is necessary to generate no less than 0.5 g l$^{-1}$ of the galvanic sludge precipitate (treatment time $\tau = 5$ min). When the amount of the galvanic sludge precipitate exceeds 1.6 g l$^{-1}$, the uranium recovery is virtually complete.

The phase separation is satisfactory: complete clarification is attained within 20 min (rough clarification, within 2–3 min). Introduction of Praestol 2530 flocculant substantially improves the process parameters (phase separation time ~10 min). The precipitates have magnetic properties and can be removed by magnetic separation.
Fig. 3. IR spectra of galvanic sludge precipitates obtained by processing of the decantate with various uranium concentrations, mg l\(^{-1}\): (1) 0 (initial), (2) 5, (3) 10, and (4) 30.

Figure 2 shows the results of thermal analysis of the galvanic sludge obtained by treatment of the decantate containing 30 mg l\(^{-1}\) U. Exothermic processes are recorded in the interval 200-400°C. These processes are associated with the decomposition of uranyl carbonate compounds and hydrated iron polyforms. At 690°C, an endothermic effect is observed in the DTA curve. It is associated with the decomposition of intermediate uranium compounds and formation of uranium dioxide.

Figure 3 shows the IR spectra of galvanic sludges obtained by treatment of decantate samples with different uranium contents.

In the IR spectrum of the initial galvanic sludge, there is a broad band of stretching vibrations ν(OH) with a maximum at 3346 cm\(^{-1}\) and a band with a maximum at 572 cm\(^{-1}\), characteristic of Fe\(_2\)O\(_3\) [8]. In the IR spectra of galvanic sludges containing uranium, the stretching vibration band ν(OH) changes shape, and the vibrations characteristic of Fe\(_2\)O\(_3\) gradually disappear.

It is known [9] that, in the presence of excess carbonate ions in solutions, uranyl ion forms a very stable uranyl tricarbonate complex [UO\(_2\)(CO\(_3\))\(_3\)]\(^{4-}\) (K\(_{st}\) = 2 × 10\(^{18}\)). The decantate from a slurry storage basin contains a large amount of carbonate ions (see above). Therefore, it can be assumed that uranium occurs in the solution in the form of this complex compound. The fact that the IR spectra of galvanic sludge samples contain bands with maxima at 1439-1440 and 1123-1143 cm\(^{-1}\), belonging to the absorption of carbonate ions, counts in favor of this assumption.

X-ray phase analysis showed that the major phases in the initial precipitates of hydrated iron polyforms are magnetite, goethite, and γ-FeOOH. In the X-ray diffraction pattern of the galvanic sludge obtained by treatment of the decantate containing 30 mg l\(^{-1}\) U, we detected the phases of magnetite, lepidocrocite, iron carbonate, and others (Fig.4).

**Conclusion**

Our results show that the contact of hydrated iron with uranium decantates involves a chemical reaction with the formation of new chemical compounds.

The developed galvanochemical treatment process can be used for treatment of the decantate from a slurry storage basin, of surface and mine waters, and of uranium-containing process solutions. Direct
alkalization of the decantate from a slurry storage basin is not efficient because of high reagent consumption.


