

Physico-chemical peculiarities of uranyl ion accumulation by rutile

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Hydrated rutile exhibits a high adsorption activity with respect to water-soluble forms of uranium – the uranyl ion (UO_2^{+2}). Sorption isotherms obtained at pH 3.5 and 5.5 and 8–9 are described using the Langmuir equation. The calculated value of the limiting amount of sorption was 170 mg/m^2 at pH up to 5.5, with increasing pH to 8 it was 1.2 mg/m^2 . The sorption behavior of uranium on the mineral sorbent – rutile is determined by: on the one hand, the values of pH, concentration of uranium (U(VI)), and on the other hand, the different surface groups on the surface of rutile, the quality of the pore space and the presence of different types of structural defects.

Key words: radionuclides, sorption, geochemical barriers, rutile

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To determine the factors influencing the migration behavior of uranium in the environment, it is necessary to investigate the interaction of soluble forms of the radionuclide with the surface of the host rock and the colloidal particles in the liquid phase. In the landscape migration of chemical elements, including water-soluble forms of uranium, the geochemical barriers where migration decreases and concentration takes place are important. In studying the mobility of radioactive elements in surface conditions, a lot of attention paid to the sorption properties of the barriers on the basis of various natural minerals. One of the natural sorbents is rutile, which along with the clay minerals is often part of the soil absorbing complex. Hydrated rutile exhibits a high adsorption activity with respect to water-soluble forms of uranium – the uranyl ion (UO_2^{+2}). The purpose of this work is to evaluate the sorption parameters of rutile as an adsorbent for uranium.

The object of the study is a suspension of rutile, consisting of 75% of natural rutile (solid phase 20 mesh) and of 25% of water.

The samples of natural rutile was ground to a size of 20–30 μm . According to X-ray data, the sample under study corresponded to the rutile phase. Crystal-chemical formula calculated on the two oxygen atoms was the following: $(\text{Ti}_{0.973} \text{V}_{0.016} \text{Fe}_{0.007} \text{Cu}_{0.008} \text{Si}_{0.006} \text{Al}_{0.004} \text{Ca}_{0.002})_{1.014} \text{O}_2$.

Experiments on the sorption were conducted of a wide range of pH (from 1.5 to 10) at 20 ± 1 °C. Uranium solutions were prepared from uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Experiments on the sorption were conducted with the active magnetic stirring. Separation of the liquid phase from the solid was carried out in a centrifuge at 13–15 thousand rev/min. Uranium concentration was determined by a laser spectrometer "Angara". Thermal analysis of samples was performed on derivatograph «Paulik-J», phase composition was controlled by X-ray diffraction method on diffractometer DRON-3. EPR studies performed on radiospectrometer «Kadiopan» SE/X254. Measurements of surface area and pore size were performed on ASAP-2400 ("Micromeritics", USA) on the adsorption of nitrogen at 77°K. Before measuring the samples were heated up to 300°C in dynamic vacuum ($2 \cdot 10^{-3}$ Torr) during 12 hours. The adsorption isotherms were analyzed by BET.

Previously it was found that the efficiency of immobilization of uranium in rutile is caused by the peculiarities of its surface-active functional groups which depend on the pH of the solution, as well as by the presence of various types of irregularities in the structure. The study of sorption in the pH range from 1.5 to 9 showed a significant dependence on the acidity of the process. For example, at pH < 3.5 0.5–1 % of uranyl sorbed. With increasing pH values from 3.5 to 5.5, the rates of sorption increase dramatically (up to 45–57 %) (table. 1). The increase in pH to 8–9 leads to a further increase in the amount of uranium sorbed by the surface of rutile.

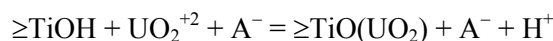
The study of sorption kinetics showed that the mobile equilibrium of dilute solutions of uranium (10^{-4} – 10^{-5} M), that is with a low degree of saturation of the surface of rutile, is reached within 20 minutes of the experiment. Increasing the concentration of uranium in solution leads to an increase in

time required to reach equilibrium, which indicates a high degree of saturation of chemically active surface groups by uranyl ions, as well as increasing participation in the process of sorption of the surface of the pore space. This is indicated by the change in volume of micropores from 0.08 sm^3/g to 0.11–0.23 sm^3/g , and the diameter of micropores varies from 76 to 115–165 Å. Sorption isotherms obtained at pH 3.5 and 5.5 and 8–9 are described using the Langmuir equation. The calculated value of the limiting amount of sorption was 170 mkg/m^2 at pH up to 5.5, with increasing pH to 8 it was 1.2 mg/m^2 .

Table 1. Dependence uranyl ion sorption on pH of the solution and the rutile specific surface

pH	Sorption uranyl ion, %	Specific surface, m^2/g
4.0	3	40.8
4.3	8	45.2
4.5	21	46.0
5.0	40	46.4
5.3	60	47.0
5.5	85	49.3
6.0	92	54.2
7.0	99	58.0
8.0	100	60.1

X-ray structure analysis of rutile in the crystallographic directions (110) and (001) showed that the ions of U (VI) associated with atoms in the direction of the rutile (110). The oxygen atoms related to the surface of rutile in an acidic environment often remain protonated after the sorption of uranium and do not participate actively in the further process. And the rutile surface areas that are not protonated, on the contrary, absorb uranium by the reaction of:



At low pH uranium in solution present in the form of UO_2^{+2} , and on the surface of rutile $\geq\text{TiOH}_2^+$ groups of atoms dominate. At values of pH > 5.5 the solution contains $\text{UO}_2(\text{OH})^+$ or $(\text{UO}_2)(\text{OH})_5^+$ complexes, and on the surface of rutile surface groups occur, where TiO-form is dominated. After contact with rutile the complexes are fixed: TiOUO_2OH and $\text{TiO}(\text{UO}_2)_3(\text{OH})_5$, it is evidenced by the shift of the absorption bands in the optical adsorption spectra (232, 443 and 610 sm^{-1}) compared with the initial sample of rutile (232, 447 and 613 sm^{-1}).

Another important contribution to understanding the mechanism of uranium immobilization by rutile, is the study of the role of surface defects in the structure. This is particularly important in the study of landscape uranium migration, where, under the influence of various environmental factors not only a refinement of rutile with a significant increase of specific surface area (from 0.8 to 36 m^2/g) occurs, but also the appearance of deep structural defects. By the method of thermal analysis on DTA curves during heating of samples of natural rutile at the 400–7000K, exothermic effects appeared that are absent in standard samples of rutile. Evaluation of peak areas showed the thermal effect equal to 26 kJ/mol . However, during the interaction with the uranyl ion, the effect is reduced due to the redox interaction. Thus, by the EPR method the appearance of trivalent titanium in the reaction was reported: $e^- + \text{Ti}^{4+} = \text{Ti}^{3+}$. In such a way the local destruction of the oxygen cage, the appearance of titanium atoms in the crystal lattice intersite space leads to an increase in the number of paramagnetic chemically active states. It is resulted in an increase of sorption capacity of rutile with respect to uranium.

Thus, the sorption behavior of uranium in the mineral sorbent – rutile is determined by: on the one hand, the values of pH, concentration of uranium (U(VI)), and on the other hand, the different surface groups on the surface of rutile, the quality of the pore space and the presence of different types of structural defects.