

Behavior of Uranium under Conditions of Interaction of Rocks and Ores with Subsurface Water

B. I. Omel'yanenko, V. A. Petrov, and V. V. Poluektov

*Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences,
Staromonetnyi per. 35, Moscow, 119017 Russia*

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Abstract—The behavior of uranium during interaction of subsurface water with crystalline rocks and uranium ores is considered in connection with the problem of safe underground insulation of spent nuclear fuel (SNF). Since subsurface water interacts with crystalline rocks formed at a high temperature, the mineral composition of these rocks and uranium species therein are thermodynamically unstable. Therefore, reactions directed toward the establishment of equilibrium proceed in the water–rock system. At great depths that are characterized by hindered water exchange, where subsurface water acquires near-neutral and reducing properties, the interaction is extremely sluggish and is expressed in the formation of micro- and nanoparticles of secondary minerals. Under such conditions, the slow diffusion redistribution of uranium with enrichment in absorbed forms relative to all other uranium species is realized as well. The products of secondary alteration of Fe- and Ti-bearing minerals serve as the main sorbents of uranium. The rate of alteration of minerals and conversion of uranium species into absorbed forms is slow, and the results of these processes are insignificant, so that the rocks and uranium species therein may be regarded as unaltered. Under reducing conditions, subsurface water is always saturated with uranium. Whether water interacts with rock or uranium ore, the equilibrium uranium concentration in water is only $\leq 10^{-8}$ mol/l. Uraninite ore under such conditions always remains stable irrespective of its age. The stability conditions of uranium ore are quite suitable for safe insulation of SNF, which consists of 95% uraninite (UO_2) and is a confinement matrix for all other radionuclides. The disposal of SNF in massifs of crystalline rocks at depths below 500 m, where reducing conditions are predominant, is a reliable guarantee of high SNF stability. Under oxidizing conditions of the upper hydrodynamic zone, the rate of interaction of rocks with subsurface water increases by orders of magnitude and subsurface water is commonly undersaturated with uranium. Uranium absorbed by secondary minerals, particularly by iron hydroxides and leucoxene, is its single stable species under oxidizing conditions. The impact of oxygen-bearing water leads to destruction of uranium ore. This process is realized simultaneously at different hypsometric levels even if the permeability of the medium is variable in both the lateral and vertical directions. As a result, intervals containing uranyl minerals and relics of primary uranium ore are combined in ore-bearing zones with intervals of completely dissolved uranium minerals. A wide halo of elevated uranium contents caused by sorption is always retained at the location of uranium ore entirely destroyed by weathering. Uranium ore commonly finds itself in the aeration zone due to technogenic subsidence of the groundwater table caused by open-pit mining or pumping out of water from underground mines. The capillary and film waters that interact with rocks and ores in this zone are supplemented by free water filtering along fractures when rain falls or snow is thawing. The interaction of uranium ore with capillary water results in oxidation of uraninite, accompanied by loosening of the mineral surface, formation of microfractures, and an increase in solubility with enrichment of capillary water in uranium up to 10^{-4} mol/l. Secondary U(VI) minerals, first of all, uranyl hydroxides and silicates, replace uraninite, and uranium undergoes local diffusion redistribution with its sorption by secondary minerals of host rocks. The influx of free water facilitates the complete dissolution of primary and secondary uranium minerals, the removal of uranium at the sites of groundwater discharge, and its redeposition under reducing conditions at a greater depth. It is evident that the conditions of the upper hydrodynamic zone and the aeration zone are unfit for long-term insulation of SNF and high-level wastes because, after the failure of containers, the leakage of radionuclides into the environment becomes inevitable.

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INTRODUCTION

The study of the behavior of uranium in natural processes was carried out by Expedition no. 1 of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences,

Corresponding author: B.I. Omel'yanenko. E-mail: bio@igem.ru

headed by F.I. Wolfson, against the background of large-scale investigations of uranium deposits in Russia and abroad aimed at the substantiating the ore-forming role of endogenic and exogenic processes and revealing the formation mechanisms of ore-bearing solutions. The use of fission-track radiography (FR), which allows detection of even tiny tracks of migration, con-

centration, and redistribution of uranium, made a great contribution to the study of the behavior of uranium during crystallization of magmatic melts and postmagmatic hydrothermal activity, sedimentation, exogenic epigenetic transformation of rocks, and superelement alteration. Afterward, it turned out that many of the results obtained can be applied with success to safe and long-term storage and disposal of spent nuclear fuel (SNF) in underground repositories. First of all, these are the data on conditions of retention and destruction of uranium orebodies and U-bearing accessory minerals, migration and concentration of uranium in the geological medium, transition of uranium from one species to another, etc.

The recognition of the behavior of uranium in the geological medium is a necessary condition for elaboration of techniques of long-term storage and disposal of SNF. The interaction of uraninite with the geological medium is of special importance because SNF consists of more than 95% uraninite and it is precisely uraninite that is the confinement matrix for all other radionuclides. While uraninite is stable, leakage of Pu, Am, Cm, Np, Th, REE, Nb, and Zr incorporated into its lattice is ruled out. The elements that occur as nonstructural impurities (Tc, Se, I, Cs, Sr, Sn, ^{85}Kr , ^3H , ^{14}C) tend to escape uraninite by diffusion toward microfractures and intergranular sutures, where these elements accumulate. In the case of a failed fuel-element can, the gaseous radionuclides will enter the environment first, and if subsurface water is available, the nonstructural, readily soluble radioisotopes will be removed as well. The nonstructural ^{137}Cs and ^{90}Sr , which would in this case be leached from uraninite pellets and contaminate the environment, are especially hazardous over the first 500 years of SNF disposal. Therefore, irrespective of the duration of SNF storage, repository safety may be provided only by prevention of access of subsurface water to the uraninite pellets during the first 500 years, which are sufficient for a decrease in ^{137}Cs and ^{90}Sr content down to a safe level. To solve this problem, containers with a high corrosion resistance and mechanical strength are recommended.

After the decay of short- and medium-lived radionuclides, the main contribution to the radioactivity of SNF will be made by Am and Pu (98%) and, to a lesser extent, Np (~1%) and Tc (~0.7%). In the case of failed containers, natural and engineering barriers are to prevent the entry of these radionuclides into the environment and to minimize leakage of such highly mobile and long-lived isotopes as ^{14}C , ^{79}Se , ^{135}Cs , and ^{129}I . It is evident that the stability of uraninite is able to provide reliable insulation of actinides and to restrict leakage of nonstructural radionuclides.

Natural observations are of key importance for substantiation of the geochemical conditions that provide the stability of uraninite. Such observations bear information not only on the behavior of actinides in a wide range of physicochemical conditions but also on slow

processes whose results become evident only after the elapse of appreciable intervals of geologic time. Data on the behavior of uranium under conditions of uraninite instability are no less important and provide insights into the conditions under which all radionuclides that occur in SNF might pollute subsurface water. These data may also be used for forecasting of migration and concentration of other actinides, including technetium, in various geological settings. Data on uranium behavior in crystalline rocks are of special interest because precisely these rocks are the most appropriate medium for disposal of SNF and high-level wastes (HLW) in Russia.

DISTRIBUTION OF URANIUM IN IGNEOUS ROCKS

Uranium is supplied to the Earth's crust along with magmatic melts, where this element is dissolved as U(IV). The comparison of U contents in igneous rocks, especially in volcanic glasses, shows that magmatic melts of similar bulk compositions may markedly (approximately by an order of magnitude) differ in U concentrations. The ordinary granitic melts contain $\sim n \times 10^{-4}\%$ U, whereas the melts with $n \times 10^{-3}\%$ U or more should be regarded as U-bearing. Crystallization of melts leads to the fractionation of uranium. In the case of fast crystallization, the major amount of uranium is dispersed in the glassy groundmass, while phenocrysts of rock-forming minerals are almost free of uranium. In the case of slow crystallization, uranium is gradually accumulated in the residual melt to a still higher degree while ore-forming minerals are crystallizing. When the main body of the magmatic melt is crystallized, U-bearing accessory minerals (zircon, monazite, apatite, allanite, britholite, etc.) start to grow. In some cases, the uranium concentration in the residual melt may reach a level that corresponds to the conditions of uraninite formation. In holocrystalline rocks, the major amount of uranium is contained in accessory minerals. Sporadic uranium atoms dispersed in rock-forming minerals, dotty segregations of U atoms as nuclei of accessory minerals, grain boundaries enriched in uranium, and U-bearing fluid inclusions are of subordinate importance (Omel'yanenko et al., 1983). In the general case, as soon as igneous rocks have crystallized, they are involved in low-temperature interaction with subsurface water, where the mineral composition of rocks and uranium species therein becomes unstable. A tendency to replacement of high-temperature mineral assemblages with low-temperature minerals and to the redistribution of uranium between solid phases to establish equilibrium in the subsurface water-rock system arises inevitably, and it is important to answer the question of what happens to uranium while igneous rocks interact with subsurface water. The behavior of radioactive minerals that retain U, Th, and REE is of special interest. Each such mineral, to a certain extent, may be regarded as a natural analogue of an

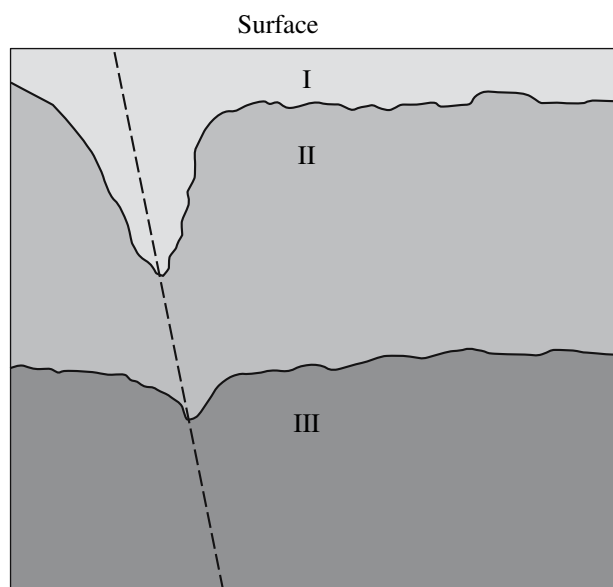


Fig. 1. Hydrochemical zoning of subsurface water in massifs of crystalline rocks. (I) Zone of active water exchange, oxygen-bearing fresh water; (II) zone of hindered water exchange, near-neutral and reducing conditions, brackish water; (III) zone of very hindered water exchange, slightly alkaline and reducing conditions, strongly saline water and brine. The configuration of zones in the vertical section is controlled by faults.

SNF and HLW repository. If uraninite is a confinement matrix for SNF in any case, confinement matrices of the actinide fraction of HLW may be created on the basis of other minerals (pyrochlore, zirconolite, monazite, brookite, etc.). In this regard, it is extremely important to assess the degree of stability of these minerals in the water–rock system and their ability to retain U, Th, and REE as imitators of artificial actinides at the depths of expected disposal of SNF and HLW (0.3–1.5 km). All these minerals were formed at a high temperature and are related to magmatic activity. For many millions of years after their crystallization, they were affected by low-temperature subsurface water. The results of this effect are controlled largely by the chemical properties of subsurface water. These properties also exert an influence on the migration of radionuclides and their removal from a repository into the environment.

CHEMICAL PROPERTIES OF SUBSURFACE WATER OF CRYSTALLINE MASSIFS

The solubility and speciation of uranium in a water solution depend on Eh, pH, the composition and concentration of complex-forming ions, temperature, and salinity. The main factor that determines the chemical properties of subsurface water is its interaction with host rocks. The longer the interaction, the greater the difference of subsurface water in composition and properties from fresh water that is supplied from the surface. The composition and properties of water in the

upper hydrodynamic zone do not correspond to the stability conditions of magmatic or metamorphic silicates and aluminosilicates. The oxygen-saturated, slightly acid (pH ~5.7) surface water penetrates along fractures and interacts with minerals of rocks for a long time. Every new portion of water makes a contribution to the decomposition of a specific mineral and the rock as a whole. The slightly acid character of rainwater is determined by the occurrence of dissolved carbon dioxide. The intensity of alteration of minerals may increase if organic acids are present in the soil. As the interaction with rocks proceeds, the pH of the water increases. The reactivity of water is gradually lost with depth. Therefore, the most intense chemical weathering occurs near the ground surface, where the reactivity of the solution is maintained by the supply of new portions of rainwater.

The rate of reactions of hydrolytic decomposition of minerals is widely variable. Mg–Ca silicates (olivine, pyroxene, amphibole, biotite) are replaced first; then plagioclase; and finally, potassium feldspar. Light micas and quartz are the most stable. The oxidation of minerals containing Fe, Mn, and Ti facilitates their transformation into hydroxides. The mantles of weathering largely composed of clay minerals and corresponding to equilibrium composition are products of weathering that lasted for many thousand years. With increasing depth, weathered rocks begin to consist of products of transitional grades of supergene alteration and relict minerals of endogenic rocks. The development of secondary minerals is controlled by tectonic fractures. The weathering of rocks increases their permeability and gives rise to the formation of zones characterized by free water exchange. The thickness of such zones depends on the topography, climate, and the composition and structure of rocks. Generally, the thickness of the zone of free water exchange varies from a few meters to several tens of meters. Oxygen that is contained in water, as a rule, has no time to be consumed in oxidation in a zone of free water exchange, and thus oxidizing conditions are constantly maintained in this zone.

The intensity of water exchange generally decreases with depth. The duration of water–rock interaction increases, the mineralization of water grows, and the proportion of masses in the water–rock system shifts toward the rock. As a result, the vertical hydrochemical zoning of subsurface water develops, being expressed in an increase in the mineralization, alkalinity, and reducing ability of subsurface water with depth (Fig. 1).

Zones of (1) active, (2) hindered, and (3) extremely hindered water exchange are formed. In zone 1, subsurface runoff participates in exchange with the surface; in zone 2, subsurface runoff is hindered and water exchange is slowed; and in zone 3, subsurface runoff develops only on the scale of geologic time. The hydrochemical and hydrodynamic zonings of rock massifs are interrelated (Kravtsov and Shvets, 1992; Kiryukhin et al., 1993). The longer the interaction of subsurface

water with rock, the greater the percentage of dissolved oxygen consumed for oxidation and the lower the Eh. A decrease in Eh below -100 mV at a depth of a few tens of meters is a common phenomenon related to the occurrence of ferrous ions in rock. In general, the aggregate of hydrochemical data indicates that subsurface water acquires reducing properties below a certain depth in any geological medium. The depth of subsurface water with positive Eh depends on the content of reductants in rocks, their permeability, the intensity of water exchange, climate, and the elevation of the surface above the regional and local base levels. The lower boundary of oxygen-bearing water in crystalline massifs is extremely uneven, and its shape displays the distribution of rocks with different permeability. Oxygen-bearing water penetrates most deeply along tectonic zones composed of brecciated, foliated, and severely fractured rocks. The maximum depth of penetration (down to 1000 m) of water with positive Eh is typical of mountainous foldbelts composed of rocks devoid of organic matter. In ancient fold systems, the depth of fresh water is controlled by the surface topography. For example, as has been established in Sweden, in granitic plutons, the Eh of water is lower than -100 mV at a depth below 100 m (Neretnieks, 1986).

With saturation with cations, subsurface water acquires near-neutral or slightly alkaline properties. The pH of subsurface water becomes higher with increasing basicity of the host rock. Calcite as a metamorphic mineral or a product of hydrothermal activity is abundant in rocks. In the zone of free exchange, calcite, as a rule, is leached, and this reaction results in alkalization of subsurface water. In the zone of hindered water exchange, calcite is commonly stable. The pH of subsurface water under equilibrium with calcite is ~ 8.4 . The pH of subsurface water from the zone of hindered water exchange is close to this value.

These and many other data on the properties of subsurface water in crystalline massifs allow us to draw the following conclusions: (1) in the general case, the intensity of water exchange in fractured crystalline rock decreases with depth; (2) under conditions of long-term interaction with aluminosilicate rocks, water acquires near-neutral–slightly alkaline and reducing properties; and (3) the upper boundary of water with the above properties is determined by the intensity of water exchange and may be located at a depth of a few tens of meters to 500 m from the ground surface.

The specific features of migration and concentration of uranium in the geological medium are largely controlled by its variable valence. Therefore, the major factors that affect the behavior of uranium are those that facilitate its transition from one valence state to another. First of all, this is the occurrence of reductants in host rock and the chemical properties of subsurface water, mainly Eh. Owing to the great difference in the chemical properties of U(IV) and U(VI), the effect of Eh of solutions on uranium behavior in the geological

medium is crucial. In the context of the general variations in subsurface water chemistry with depth, it is expedient to consider the behavior of uranium separately for conditions where rocks are affected by (1) mineralized subsurface water that occurs in the zone of hindered water exchange and is characterized by near-neutral–slightly alkaline and reducing properties; (2) poorly mineralized subsurface water that occurs in the zone of active water exchange and is characterized by near-neutral–slightly acid and oxidizing properties; and (3) oxygen-rich surface and capillary waters acting in the zone of aeration above the water table.

BEHAVIOR OF URANIUM UNDER REDUCING CONDITIONS

According to general hydrochemical zoning, subsurface water within the depth range of the expected location of underground repositories (0.5–1.5 km) should be characterized by near-neutral–slightly alkaline and reducing properties (pH 7–9). The mineralogical indication of reducing conditions is the overall stability of minerals containing a ferrous component (pyrite, biotite, amphibole, magnetite, chlorite, epidote, etc.) and U(IV) minerals. Due to the low temperature, the subsurface water is far from equilibrium with high-temperature minerals of crystalline rocks. Nevertheless, with the exception of cases of superposition of a hydrothermal process, these minerals, as a rule, retain their initial composition and structure and in the case of routine petrographic examination are described as unaltered. Minerals from blocks of poorly permeable rocks only slightly affected by tectonic deformation are distinguished by the best preservation. The results of isotopic investigations show that the isotopic systems of such minerals are undisturbed and may be used for age determination. It is evident that the interaction of minerals with subsurface water is extremely sluggish, especially in poorly permeable zones, and commonly does not lead to appreciable alteration. Nonetheless, while characterizing a mineral as unaltered, one must keep in mind that this definition is conditional. As a matter of fact, no absolutely unaltered minerals exist in nature. Even in zones with a very low permeability, minerals are constantly influenced by solutions that occur as the thinnest films in microfractures, micropores, intergranular sutures, and cleavage planes. The occurrence of a water solution facilitates the establishment of equilibrium with subsurface water. The examination of minerals at high magnification (optical and electron microscopy, FR, etc.) shows that this process results in the formation of micro- and nanoparticles of secondary minerals.

The study of minerals with FR convincingly indicates that uranium species in rocks formed at a high temperature become unstable at a low temperature. The share of absorbed uranium and presumably REE and Th increases at the expense of other species. The enrichment of secondary minerals in uranium as a

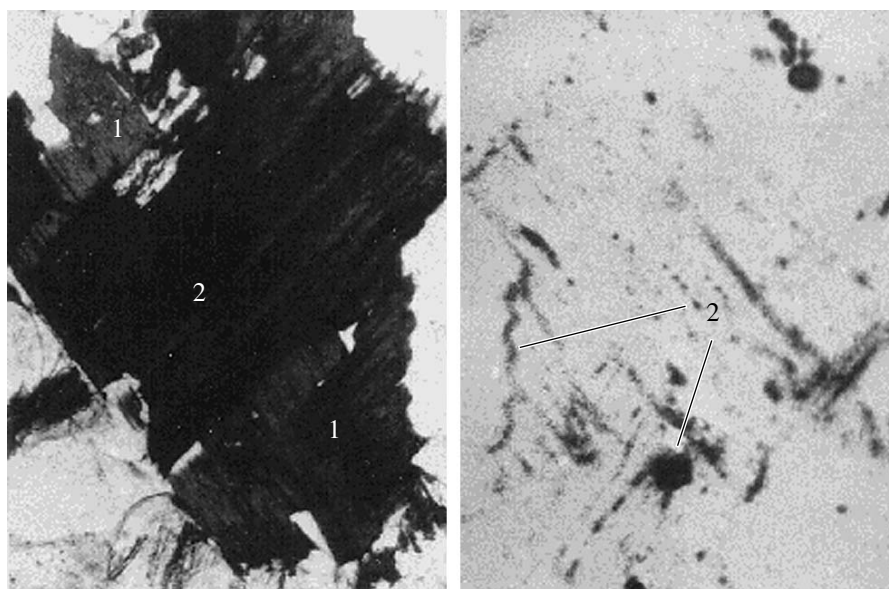


Fig. 2. Diffusion redistribution of uranium in biotite (1) and its accumulation in secondary minerals (2): leucoxene, Fe oxides, and chlorite. Transparent polished thin section on the left and lavsan detector on the right. Magn. 50.

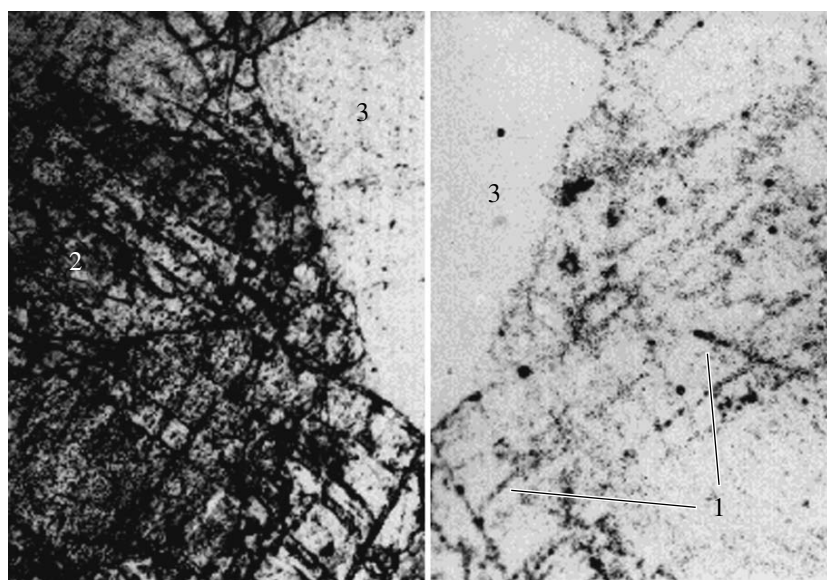


Fig. 3. Concentration of uranium in microfractures (1) within microcline (2); quartz (3) does not contain uranium. Transparent polished thin section on the left and lavsan detector on the right. Magn. 50.

result of diffusion redistribution in Fe- and Ti-bearing minerals is evident (Fig. 2). The increase in the relative amount of absorbed uranium is especially distinct in zones of elevated fracturing and cataclasis, where minerals actively interact with subsurface water. Uranium concentrates at the surface of minerals and in fractures, so that its distribution directly reflects the textural pattern of tectonite (Fig. 3). In such areas, uranium is redistributed not only within the host mineral but also between different mineral grains.

In general, the available data cast no doubt that, under reducing conditions at the depths of expected disposal of SNF and HLW, uranium species formed at a high temperature turn out to be unstable. A tendency toward replacement of high-temperature mineral assemblages with low-temperature minerals and transition of uranium to the most stable absorbed form that corresponds to the equilibrium in the water-rock system inevitably arises. At the same time, in assessing the scale of alteration of primary minerals and the redistribution of uranium therein, it should be admitted that

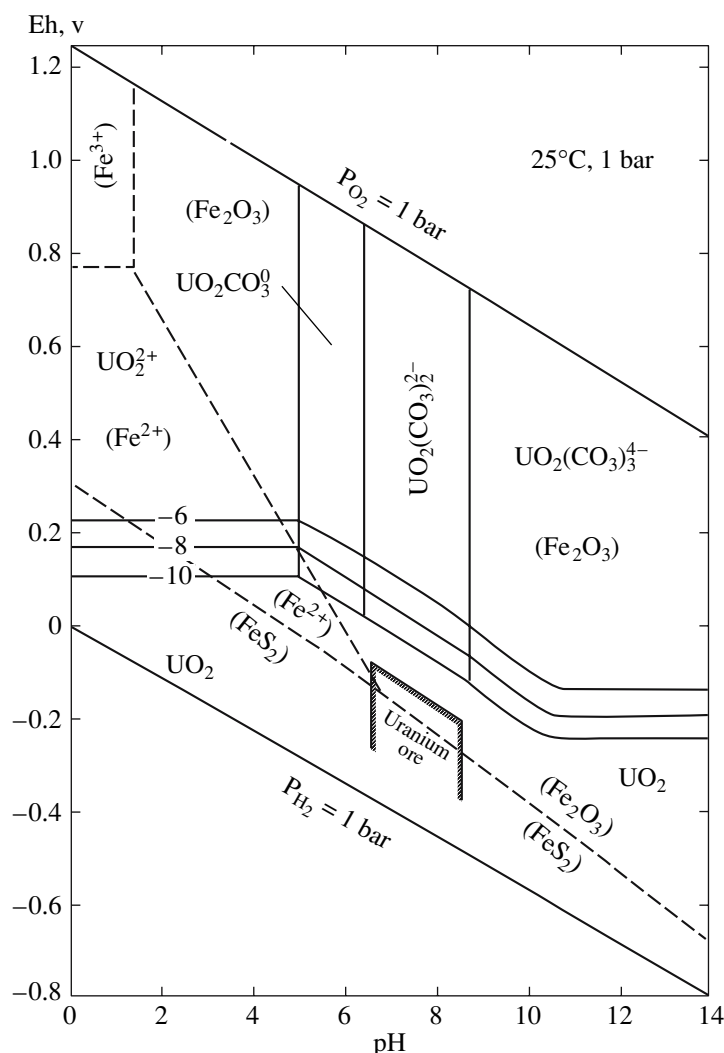


Fig. 4. The Eh–pH diagram of the U–C–O–H system and a part of the Fe–S–O–H system, after Brookins (1988). Activities of dissolved particles are 10^{-6} , 10^{-8} , 10^{-10} U, 10^{-3} C, 10^{-6} Fe, and 10^{-3} S. The selected area is the Eh–pH region of subsurface water in equilibrium with unoxidized uranium ore.

this alteration in blocks with low permeability is negligible and such rocks are commonly identified as unaltered. The diffusion redistribution of uranium with its transition into absorbed form is detected rather distinctly in Fe- and Ti-bearing minerals (biotite, titanomagnetite, titanite, amphibole, etc.). However, uranium redistribution in the rock as a whole and especially its removal are not established. As concerns uraninite and potential confinement matrices based on zirconolite, monazite, pyrochlore, britholite, zircon, and other minerals, it should be admitted that they will be in nonequilibrium conditions in underground depositories and these conditions will stimulate their alteration with recovery of uranium, thorium, and REE and their transition into absorbed form. However, natural observations show that, under reducing conditions, the rates of these reactions are so low that their results may be neglected and these minerals may be accepted as virtu-

ally stable. The low rates of reactions are explained by the low temperature, the low water/rock ratio, and the absence of water flow in some domains. In zones of high permeability, the intensity of secondary mineral formation and transition of uranium into an absorbed form increases and in principle may lead to appreciable results. Thus, even under reducing conditions, highly permeable zones are not favorable for disposal of SNF and HLW.

It is fundamentally important that, despite the relatively low uranium content in rocks (10^{-5} – 10^{-3} wt %), the amount of this element is quite sufficient for saturation of subsurface water under reducing conditions. In water solutions, U(IV) has a very low migration ability due to the formation of poorly soluble hydroxide,



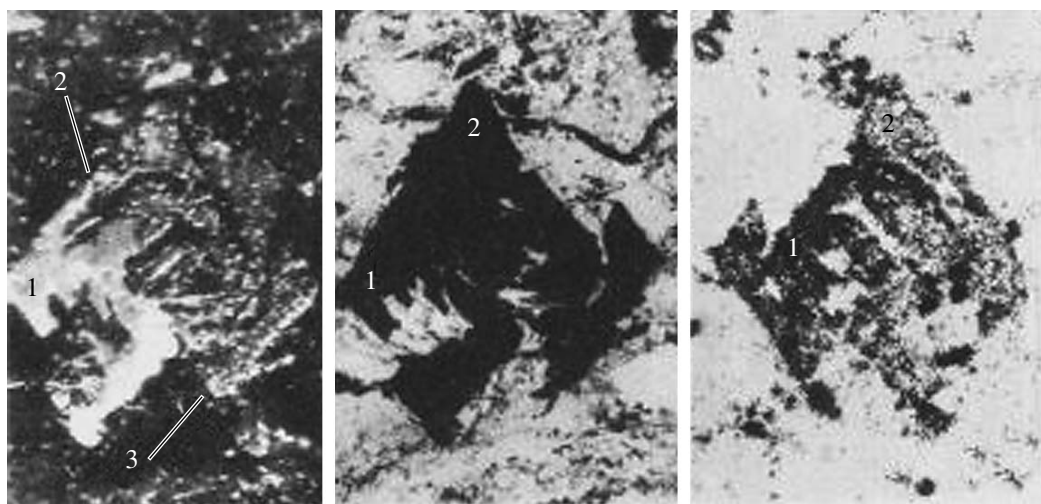


Fig. 5. Sorption of uranium by leucoxene (1) and pyrite (2) pseudomorphs after amphibole. The sample was taken at a distance of 1 m from a uranium orebody at the Ishim deposit, northern Kazakhstan. A view of a pseudomorph under oblique illumination on the left and in transmitted light in the center, and lavsan detector on the right. Magn. 50.

The solubility product of $[\text{U}(\text{OH})_4]$ approximately equals 10^{-52} . Therefore, under reducing conditions, subsurface water is always saturated with uranium. Owing to the low solubility under near-neutral and reducing conditions, the equilibrium uranium concentration in subsurface water is not higher than 10^{-8} mol/l. It makes no difference whether subsurface water interacts with rock or uranium ore. The equilibrium U concentration near orebodies or at a distance from them is virtually the same. In water from an orebody that contains 40% U at the Cigar Lake deposit in Canada, the U concentration does not differ from the background value of 10^{-8} mol/l (Cramer, 1986). Experiments on solubility of uraninite under near-neutral and reducing conditions yielded a similar U concentration in the equilibrium solution (Johnson and Shoesmith, 1988; Red'kin et al., 1989). It may be stated that the published data on higher concentrations of uranium in subsurface water are either related to oxidizing conditions or to the total contribution of dissolved and colloidal species.

Owing to the saturation of subsurface water with uranium, uranium ore is practically insoluble under reducing conditions. It has been established that the main amount of uranium in ore concentrates in oxides. As a rule, the orebodies are localized in highly permeable zones composed of cataclasites, intensely fractured and brecciated crystalline or water-saturated sedimentary rocks. This implies that uranium minerals in orebodies mostly occur in immediate contact with subsurface water. Nevertheless, even in highly permeable areas, numerous cases of virtually perfect preservation of uranium orebodies are known. Their age often reaches hundreds of millions of years. It is doubtless that the main cause of uranium dioxide stability is the near-neutral and reducing properties of subsurface water (Fig. 4).

It should be emphasized that uranium in orebodies is not absolutely inert under reducing conditions. As in rocks, diffusion redistribution with transition of a part of uranium into absorbed form continuously proceeds in ore and nearby, with formation of a secondary dispersion halo. Accumulation of uranium in minerals with high sorption capacity is distinctly recorded by FR (Fig. 5). At the same time, it should be noted that the intensity of diffusion redistribution is extremely low and it may be detected only owing to the great duration of geological processes. In summary, diffusion redistribution cannot exert an appreciable effect on leakage of uranium from uraninite ore and, hence, from SNF.

BEHAVIOR OF URANIUM UNDER OXIDIZING CONDITIONS

Oxygen-saturated rainwater is characterized by slightly acid properties (pH ~ 5.7) due to the effect of dissolved carbon dioxide ($P_{\text{CO}_2} = 10^{-3.5}$ bar).

Therefore, rainwater generally is not equilibrated with crystalline rocks. The stability of rock-forming minerals interacting with such water decreases in the series quartz–light mica–potassium feldspar–sodic plagioclase–biotite–amphibole–pyroxene–calcic plagioclase–olivine. Leaching bases from these minerals, the rainwater is alkalized and transfers the bases to groundwater and then to sites of water discharge. The intensity of leaching increases when the soil and subsoil water is enriched in organic acids. Kaolin is the final product of weathering. In most cases, the process does not reach the stage of complete leaching and products of initial and transitional grades of weathering are retained in the zone of interaction with oxygen-bearing water.

The intensity of supergene alteration of rocks distinctly wanes with depth, although the total thickness of

weathered rocks varies widely. As follows from the multifold increase in thickness within fault zones, permeability is the main factor that controls the thickness of weathered rocks. The pigmentation of fracture walls by iron hydroxides, which practically do not penetrate into the rock matrix, is the first indication of effects exerted by oxygen-bearing water. Close to the surface, iron hydroxides replace Fe-bearing minerals and fill microfractures. Still higher, the weathering results in the formation of a disintegration zone that consists of rock fragments partially replaced with phyllosilicates (montmorillonite, chlorite, various mixed-layer silicates, kaolinite) and titanium and iron hydroxides. The disintegration zone is characterized by high permeability and active exchange with the surface. At the level of the disintegration zone and at higher levels, mineral particles are washed out by the water flow and removed to the discharge sites. Approaching the surface, the intensity of weathering increases and eventually the zone of disintegration gives way to the zone of argillic alteration with a gradual upward increase in the relative amount of clay minerals; kaolinite becomes the major clay mineral.

It is principally important that oxygen-bearing water, while affecting the Fe- and Ti-bearing minerals, decomposes them, beginning from the formation of tiny particles of iron hydroxides and earthy aggregates of secondary titanium minerals and iron hydroxides defined as leucoxene. Iron hydroxides and, particularly, leucoxene are characterized by exceptionally high sorption capacity with respect to actinides and REE. Iron hydroxides and, especially, leucoxene in the form of dispersed dusty particles, sinters, crusts, coatings, and close intergrowths with clay minerals are ubiquitous products of chemical weathering. Thus, the general tendency of weathering is removal of mobile elements along with relative enrichment in the least mobile elements, primarily, Al, Fe, and Ti. It should be emphasized that phyllosilicates (chlorite, montmorillonite, and various mixed-layer minerals), which are able to absorb Cs and Sr, are formed under the effect of oxygen-bearing water along with iron hydroxides and leucoxene, which are sorbents of U, Th, Pu, Am, Cm, and REE.

In light of the problem under consideration, it is important to note that two opposite tendencies develop during interaction of subsurface water with rock under oxidizing conditions: on the one hand, removal of many chemical elements from rock, and, on the other hand, the formation of minerals with high sorption capacity, which are able to retain various elements, including radionuclides, in absorbed form. As concerns the safety of SNF and HLW repositories, the first tendency is obviously negative, while the second tendency is positive.

Under oxidizing conditions, subsurface water is commonly undersaturated with uranium as a precondition of its leaching from rocks and ores. The solubility product of $[\text{UO}_2(\text{OH})_2]$ is 30 orders of magnitude higher than that of $[\text{U}(\text{OH})_4]$. This difference deter-

mines a much higher migration ability of U(VI) in comparison with U(IV). However, because of insufficient duration of interaction with rocks, the oxygen-bearing water has no time to become saturated with uranium before discharge. Therefore, the U concentration in subsurface water under oxidizing conditions is usually much lower than the equilibrium value and approaches 10^{-7} mol/l, i.e., is an order of magnitude higher than under reducing conditions. However, the UO_2^{2+} ion is not a major U(VI) species in subsurface water. Owing to the susceptibility of U(VI) to complexation, complex uranyl compounds with various anions are the main migration species. The most probable transport species are $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, $[\text{UO}_2(\text{CO}_3)_2]^{2-}$, $[\text{UO}_2(\text{CO}_3)]^0$, and less frequently $[\text{UO}_2(\text{SO}_4)_2]^{2-}$. Therefore, the U concentration in subsurface water strongly depends on the concentration of the $(\text{CO}_3)^{2-}$ ion. For water equilibrated with calcite at a concentration of $(\text{CO}_3)^{2-} \approx 10^{-5}$ mol/l, the equilibrium U concentration in the water interacting with rocks approximately equals 10^{-5} mol/l (Liu and Neretnieks, 1999). However, the U content in natural water is commonly lower than this value.

The FR examination of weathered rocks showed that absorbed uranium is a single stable species. All other uranium species are extremely sensitive to the impact of oxygen-bearing water. Star-shaped segregations of uranium atoms disappear rather rapidly, followed by uranium segregations at grain boundaries and, finally, by dispersed uranium atoms in rock-forming minerals. The accessory U-bearing minerals (zircon, apatite, monazite, etc.) are the most resistant with respect to leaching of uranium. A special study has shown that, in most cases, the outer zones of zircon grains from unaltered granite are markedly enriched in uranium, whereas the outer zones of zircons from weathered granite are always depleted in uranium relative to the inner zones (Fig. 6). The complete dissolution of zircon is achieved only in the kaolin mantle of weathering. The following steps in alteration of zircon have been established: marginal zones of grains are corroded, microfractures appear and gradually widen, zircon grains disintegrate into fragments separated by kaolinite, and then these fragments diminish in size up to complete dissolution (Eliseeva and Omel'yanenko, 1987).

The absence of obvious removal of uranium from rocks in the course of weathering was a surprising result. The range of U contents in weathered rocks is appreciably wider than in unaltered rocks; however, the average contents do not show a significant difference. The tendency for all uranium species to be converted into absorbed form is expressed extremely clearly. The sorption of uranium by leucoxene is especially active (Fig. 7). As concerns the total amount of absorbed uranium in products of weathering, the leading role undoubtedly belongs to the ubiquitous iron hydroxides.

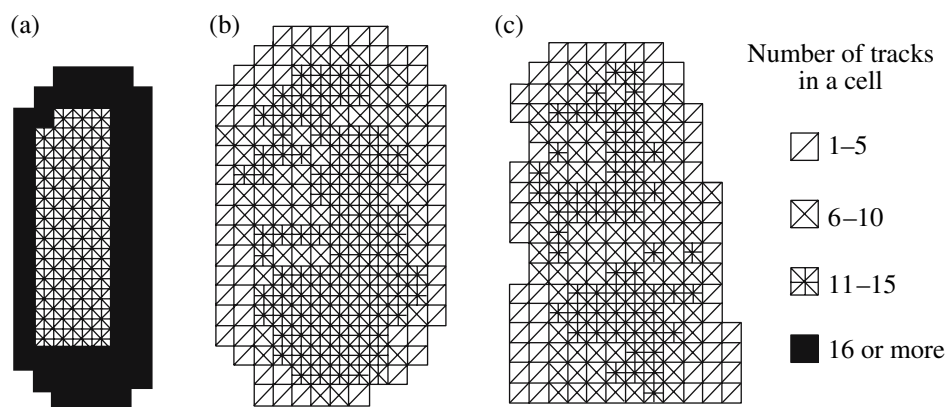


Fig. 6. Uranium distribution in zircons from (a) unaltered, (b) weathered, and (c) intensely weathered granites.

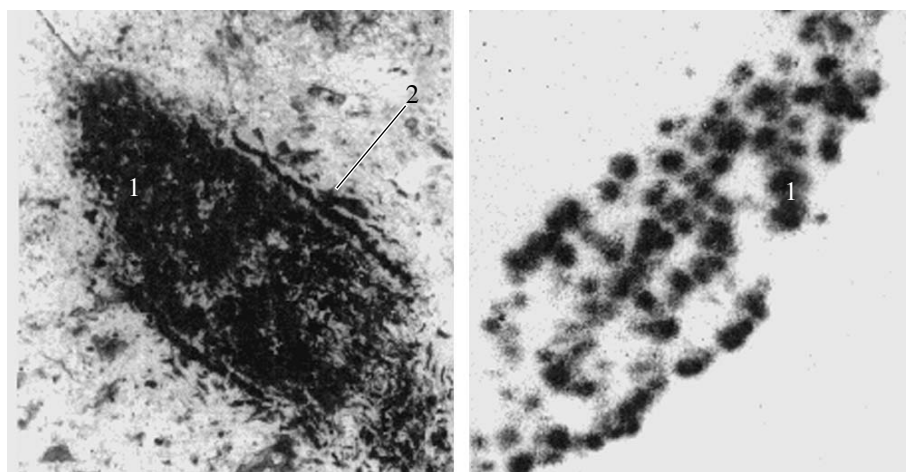


Fig. 7. Uranium distribution in weathered amphibole. Virtually all uranium is concentrated in leucoxene and iron hydroxide pseudo-morphs (1) after amphibole (2). Transparent polished thin section on the left and lavsan detector on the right. Magn. 50.

The removal of uranium from rocks is strictly detected only by formation of white kaolin, which is practically devoid of iron hydroxides. When the products of weathering contain iron hydroxides and leucoxene, the U concentration therein is quite comparable with that in unaltered rocks. The absorbed uranium species is predominant.

In contrast to the extremely sluggish transition of uranium to the absorbed form under reducing conditions, this process develops spontaneously under oxidizing conditions, and its products may often be detected in rocks from mines where oxygen-bearing water circulated for only a few years. It may be stated that the rate of uranium transition into the absorbed form under oxidizing conditions is orders of magnitude higher than under reducing conditions. The primary Fe- and Ti-bearing minerals readily react to oxidizing conditions as well. Iron hydroxides and leucoxene replace these minerals from their margins and fill cleavage planes and microfractures therein. The results of FR examination testify to the absence of such natural rocks

where iron hydroxides and leucoxene are not enriched in uranium. Thus, these minerals are a reliable barrier that prevents removal of uranium from rocks affected by oxygen-bearing water.

The effect of oxygen-bearing water on uranium ore-bodies inevitably results in their destruction. The rate of this process depends on the intensity of water exchange; the surface of interaction; and the chemical composition of subsurface water, especially as concerns Eh, pH, and concentrations of carbonate and sulfate ions. The occurrence of sulfides in host rocks exerts a great effect on the rate of uranium ore destruction. When the content of sulfides is rather high, sulfuric acid solutions intensify the removal of uranium. The highest U concentrations in subsurface water, attaining 10^{-2} mol/l, were established in sulfuric acid drip from uranium ore. Although the oxidation of sulfides requires somewhat higher Eh values than the oxidation of uranium minerals does, the dissolution of uraninite under natural conditions in the presence of pyrite is noted in exceptional cases. In near-neutral oxygen-bearing water interacting

with uranium ore, the U concentration reaches 10^{-4} mol/l (Liu and Neretnieks, 1999) but rather rapidly falls to 10^{-6} mol/l at a short distance from the orebody. These figures are approximate and may vary in specific cases of water–ore interaction.

The essence of the interaction in the rock–subsurface water–uraninite system is most evident under conditions of active or very hindered water exchange. Under conditions of active water exchange, new portions of oxygen-rich water are progressively supplied to uraninite, facilitating formation of uranyl ions or complexes in line with the reaction



The most probable U(VI) species in oxygen-bearing water are $[\text{UO}_2\text{CO}_3^0]$, $[\text{UO}_2(\text{CO}_3)_2^{2-}]$, and $[\text{UO}_2\text{SO}_4^0]$, while the deposits are enriched in sulfides. Due to the active water exchange, the saturation of subsurface water with uranium is not reached. Because of this, the interaction of uraninite with oxygen-bearing water must be accompanied by removal of uranium from the orebody. The uranium passing into subsurface water may be converted into the most stable absorbed form with formation of a secondary dispersion halo; migrate along with the descending water flow in the region of reducing conditions, where it will be redeposited in a zone of secondary enrichment; and be removed to the discharge site. Which of these mechanisms will dominate depends on the direction and velocity of water flow and the sorption capacity of rocks. Natural observations show that a wide halo of elevated U contents related to the absorbed form is always retained at the site of uranium ore destroyed by weathering. The residual U concentrations commonly do not exceed a few hundredths of weight percent.

Tentative estimates of the possible rate of dissolution of natural uraninite may be deduced from experimental results. At a partial oxygen pressure of 0.2 atm, a concentration of carbonate ion equal to 0.0002 mol/l, a temperature of 25°C, and pH 8, the rate of uraninite dissolution in a running solution is 2.55 mg/m²/day (Steward and Gray, 1994). If the concentration of carbonate ion is increased to 0.02 mg/l, the temperature to 75°C, and pH to 10, the rate of dissolution rises to 77.4 mg/m²/day. Taking into account geologic time, it is hardly probable that a uraninite orebody will be preserved even at the minimum rate of dissolution under conditions of active water exchange.

The complete dissolution of uraninite ore with halos of elevated U contents related to the absorbed form being left behind is quite possible in territories of dissected topography and intense water exchange. However, at most deposits, the alteration of uranium ore under the influence of oxygen-bearing water is established only in the upper portion of orebodies. Permeability of rocks is the main factor that controls the extent of retention and alteration of the primary ore.

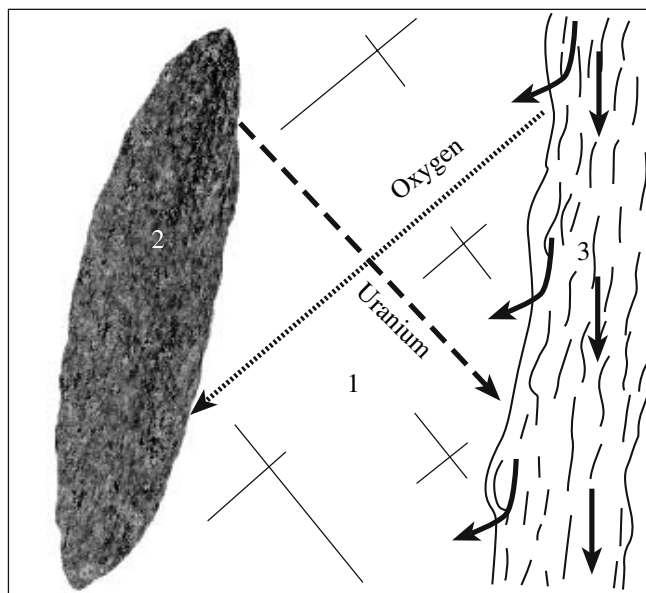


Fig. 8. Diffusion mass exchange between running oxygen-bearing water and uranium ore through a zone of low-permeable rock with stagnant water: a conceptual scheme. (1) Zone of diffusion mass exchange in low-permeable rock, (2) uranium ore, (3) fissure filled with oxygen-bearing water. Arrows indicate the direction of decrease in oxygen and uranium concentrations in pore water.

Precisely because of the extremely nonuniform permeability of ore-bearing rocks, one may observe both primary ore and products of its alteration up to the complete dissolution of all uranium minerals at the same deposit and at the same hypsometric level.

The role of this factor is illustrated by a conceptual scheme of diffusion mass exchange between oxygen-bearing water flowing through a fissure and uranium ore occurring at a certain distance away from it (Fig. 8). The fissure and the uranium ore are separated by a block of rock with a low permeability. The water solution that fills microfractures and pores is a medium of diffusion mass exchange between the running water and the uranium ore. It is evident that the minimum oxygen concentration in the water will be maintained at the boundary with the uranium ore, where oxygen is consumed for oxidation of uraninite, while the maximum concentration will be retained in the running water that fills the fissure. As a result, the counter diffusion of oxygen and uranium through the zone of stagnant water arises. The first reaction with consumption of oxygen will be the oxidation of uraninite with formation of UO_{2+x} in zone of interaction, where the highest x value may reach unity. Taking into account experimental results, it may be stated that oxidation should increase the solubility of uraninite owing to loosening of the surface and formation of microfractures. The gradient of U concentration formed between uraninite and the fissure with intense water exchange will facilitate transfer of uranium in the direction opposite the direc-

tion of oxygen diffusion. The gradients of uranium and oxygen concentrations in stagnant subsurface water create favorable conditions for uraninite oxidation, precipitation of uranyl minerals on the surface of uraninite and nearby, sorption of uranium by minerals of host rocks, transfer of uranium into the zone of active water exchange and its removal from orebodies along with subsurface water, and redeposition of the leached uranium at deeper levels distinguished by lower Eh values with formation of a secondary enrichment zone. U(IV) minerals (coffinite and ningyosite) are characteristic of the secondary enrichment zone and may indicate that oxidation gives way to reduction.

In another case, uraninite ore occurs in a zone of active circulation of oxygen-bearing water undersaturated not only with uraninite but also with uranyl minerals. As a result, uraninite can undergo complete dissolution. Uranium that has passed into subsurface water may be absorbed by minerals of host rocks with formation of a dispersion halo, removed from the zone of interaction to the site of discharge, and redeposited at lower levels in the zone of low Eh in the form of various U(IV) minerals. Eventually, only a halo of elevated U contents provided by absorbed forms will be retained at the spot of the primary ore.

The extreme variants considered above illustrate the interaction of uranium ore with oxygen-bearing water under conditions where mass exchange is realized by diffusion through a block of poorly permeable rocks with stagnant water and in a zone of intense water exchange. These extreme situations, if they arise, pertain to local areas. In the main body of mineralized rocks, the interaction of uraninite ore with subsurface water occurs under conditions of hindered filtration of water through microfractures and intergranular space. The real process is a combination of infiltration and diffusion mass exchange with variable contributions of these mechanisms at different points of the geological medium. In one area, the destruction of primary ore with removal of uranium by subsurface water is predominant; in another area, the primary ore is replaced with secondary uranyl minerals; and in a third area, the leached uranium is precipitated at the redox barrier. In the general case, the tendency to removal of uranium that is prevalent near the surface changes with depth to the formation of secondary uranyl minerals and then to redeposition of the leached uranium in secondary enrichment zone. Accumulation of uranium in host rocks in absorbed form is an indispensable phenomenon accompanying any mechanism of interaction of uranium ore with oxygen-bearing water at every level.

The formation of a zone of uranyl minerals is an important result of interaction of oxygen-bearing water with uranium ore. The high uranyl concentration in subsurface water that is necessary for realization of this process is reached under the conditions of primary ore oxidation and hindered water exchange. The diversity of uranyl minerals is controlled by the mineralic com-

position of the oxidation zone and the composition of the primary ore, host rocks, and subsurface water. Water-bearing oxides with variable proportions of UO_3 and H_2O , occasionally with additional alkali and alkali earth elements, are the most abundant phases replacing primary uranium ore. Schoepite $[\text{UO}_3 \cdot 2\text{H}_2\text{O}]$, compreignacite $[(\text{Na},\text{K})_2[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}]$, and becquerelite $[\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}]$ serve as examples. Clarkeite, curite, fourmarierite, welsendorfit, and urgite are typical of the oxidation zone. Uranium silicates (soddyite $[(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}]$, uranophane and β -uranophane $[\text{Ca}(\text{UO}_2)(\text{SiO}_3\text{OH})_2(\text{H}_2\text{O})_5]$, sklodowskite $[\text{Mg}(\text{UO}_2)(\text{SiO}_3\text{OH})(\text{H}_2\text{O})_4]$, etc.) are often formed together with hydroxides. Diverse phosphates and, to a lesser extent, arsenates, vanadates, and molybdates are characteristic as well. In the case of hindered water exchange, the main mass of uranium that passes into subsurface water is fixed in secondary uranyl minerals, which may be of economic importance. The conditions of hindered water exchange are advantageous for sorption of uranium by minerals of host rocks, and the secondary dispersion halo may be much larger in size than the zone of uranyl mineralization. In areas subject to weathering, halos of elevated U contents related to absorbed forms are commonly used as a guide for prospecting of deep-seated primary ore.

The data on sorption of uranium by host rocks in the course of oxidation of primary uranium ore are of exceptional importance for the safe disposal of SNF and HLW because these data show that the absorbed form is the single stable uranium species in this case. The fast drop in the concentration of uranium in oxygen-bearing water apart from uranium ore ($<10^{-5}$ mol/l) is largely caused by sorption. The weathering that results in destruction of primary uranium ore is at the same time accompanied by formation of secondary minerals with a high sorption capacity. The sorption of uranium actively opposes its removal by oxygen-bearing water. It may be suggested that, in the case where SNF and HLW are affected by oxygen-bearing water, a similar mechanism of fixation of elements within a restricted body of rocks will be applicable to other absorbed radionuclides. Intense water exchange, in which U-bearing water has no time to react with minerals of host rocks, is an unfavorable factor. This scenario is most probable under conditions of dissected topography.

As a rule, interaction of water solutions with uranium ore occurs simultaneously at different hypsometric levels and under conditions of nonuniform permeability. The general tendency is a decrease in intensity of water exchange with depth. However, permeability of rocks appreciably varies in the lateral direction as well. Therefore, at the same hypsometric level, areas of complete dissolution of all uranium minerals are combined with areas with abundant uranyl minerals and relict primary uranium ore.

BEHAVIOR OF URANIUM IN THE AERATION ZONE

The aeration zone comprises the rocks that are situated above the water table. Depending on the amount of precipitation during different periods, the water table shifts. The thickness of the aeration zone depends on climate, the roughness of the topography, the permeability of rocks, and other factors. The variety of conditions characterizing interaction in the water-rock system is a distinguishing feature of the aeration zone. Broadly speaking, two types of conditions are recognized.

The first type comprises the greater part of the period of interaction in water-rock systems and is characterized by the presence of three constituents: rocks affected by weathering to a certain extent, capillary and film waters that are contained in rocks, and air and water vapor that fill fractures.

The second type of conditions is distinguished by filling of fissures with free water during rains or thawing of snow; the free water penetrates into aquifers via the aeration zone. Thus, this type of conditions is characterized by penetration of slightly acid (pH ~5) fresh oxygen-bearing water into fissures instead of air. Under intermediate conditions, an insufficient amount of precipitation does not ensure the complete filling of fissures with free water. As a result, in some periods, both air and free water can co-occur in fissures. In most cases, irrespective of the frequency of free water supply, the high humidity steadily maintained in the aeration zone facilitates oxidation. Let us consider the processes that proceed under both types of extreme conditions.

The following reactions are highly probable under conditions of the first type:

- equilibrium is established between capillary water and rocks with respect to pH by leaching of bases from rocks with shifting of this parameter in the liquid phase toward the near-neutral-slightly alkaline level;

- replacement of primary minerals of rocks with secondary supergene minerals in the course of hydration reactions;

- oxidation of Fe(II) that occurs in rocks with formation of iron hydroxides;

- oxidation of uranium that occurs in rocks and transition of all uranium species to the single absorbed form.

The most important feature of the aforementioned reactions is that they proceed at a very low water/rock ratio. As a result, the pH of capillary water that corresponds to its equilibrium with rocks is reached rather quickly, decelerating the formation of secondary supergene minerals. At the same time, Eh of capillary water is maintained at a high level owing to the presence of air, facilitating the completion of ferrous ion oxidation and the conversion of uranium into the absorbed form. A U concentration in the liquid phase of $\sim 10^{-6}$ mol/l in equilibrium with the absorbed form of uranium seems to be the most probable. Diffusion mass transfer under conditions of the first type is undoubtedly prevalent.

Natural observations show that time is the critical factor that determines the degree of reaction completion in the aeration zone.

The principal difference of the conditions of the second type is filling of fissures with fresh, slightly acid (pH ~5.7) free water that contains oxygen. This water is not in equilibrium with either host rocks or capillary water. The following reactions are the most probable under conditions of the second type:

- interaction of free water with capillary and film waters that changes their properties toward a decrease in pH and the concentrations of bases and uranium;

- oxidation of Fe(II) with participation of both capillary and fresh waters;

- leaching of bases and uranium from rocks by free water;

- washing out of dispersed mineral phases from rocks by free water and transfer of these phases to subsurface water in the form of suspended or colloidal particles.

Under conditions of the second type, the reactions proceed at a much higher water/rock ratio in comparison with conditions of the first type. A substantial deviation of the pH of free water from equilibrium with rock intensifies the replacement of primary minerals with secondary minerals and leaching of uranium from rock. The degree of completion of the reactions depends on the duration of fissure filling with free water and the permeability of rock (more precisely, on the area involved in the interaction between free water and rock). As a result of interaction with free water, the capillary water becomes able to interact more actively with host rocks. Irrespective of the presence or absence of free water, all reactions in the aeration zone proceed at a high Eh. This circumstance is advantageous for complete oxidation.

The behavior of uranium orebodies in the aeration zone requires special consideration. In the general case, orebodies are formed with the participation of subsurface water or hydrothermal solutions at a depth of hundreds of meters to a few kilometers from the surface and below the water table, i.e., under reducing hydrochemical conditions. As a result of uplifting of a geological block accompanied by erosion, an orebody may find itself in either the zone of circulation of oxygen-bearing water or in the aeration zone. Because the rate of uplifting is commonly not great (a few millimeters per year), the orebodies should be affected by oxygen-bearing subsurface water for a long time before appearing in the aeration zone. It is hardly probable that the primary uranium ore will be retained in this case.

It is much more probable that primary uranium ore is found in the aeration zone due to man-made subsidence of the water table. Such a situation is commonly created by open-pit mining of deposits and/or active pumping out of water from underground mines. As a result, a cone of depression arises, the level of subsurface water drops, and primary ore is found in the aeration zone.

For example, this situation may be observed in the Tulukui open pit in the southeastern Transbaikalian region.

As in the case of rocks, uranium minerals will continually experience the effects of capillary and film waters, oxygen in the air, and water vapor. Owing to the high Eh, uranium will tend to be oxidized to U(VI). The following reactions are the most probable in the course of interaction of primary uranium ore with capillary water and air in the presence of water vapor:

oxidation of uraninite accompanied by loosening of the grain surface, formation of microfractures, and an increase in solubility;

dissolution of uraninite with a rise in U concentration in capillary water to $\sim 10^{-4}$ mol/l;

replacement of uraninite with secondary minerals of U(VI), largely with uranyl hydroxides and silicates;

local diffusion redistribution of uranium and its accumulation in minerals of host rocks as absorbed species.

The above reactions are distinguished by local development in small areas of ore minerals and adjacent sites. Due to the small amount of the liquid phase participating in reactions, the scale of interaction is rather limited. The concentration of U(VI) in capillary water brought in equilibrium with uraninite is $\sim 10^{-4}$ mol/l. This estimate is based on experimental results for uraninite and SNF solubility under oxidizing conditions in natural waters of various composition (Quinones et al., 1999).

The filling of fissures with free water substantially changes the conditions of interaction with uranium ore. In the presence of free water, the following reactions are the most probable:

interaction of free water with capillary water accompanied by depletion of the latter in uranium and an increase in its reactivity;

dissolution of both primary and secondary ore minerals in the areas of intense water exchange with partial removal of uranium to the site of discharge and partial sorption by host rocks resulting in the formation of secondary dispersion halos.

The following reactions are probable in areas that are characterized by nonuniform water exchange:

oxidation of primary uranium minerals; precipitation of uranyl minerals within and near the zones of primary uranium mineralization;

dissolution of ore minerals and removal of uranium into the region of intense water exchange; accumulation of uranium in host rocks as absorbed species;

redposition of the leached uranium at deeper levels with formation of a secondary enrichment zone.

The interaction of water solutions with uranium ore in the aeration zone eventually leads to destruction of orebodies and formation of secondary halos of absorbed uranium in their place. The main cause of the ore destruction is a sporadic supply of oxygen-rich water into the aeration zone; this water is sharply

undersaturated with uranium minerals (both U(IV) and U(VI)). Only absorbed uranium is able to withstand leaching from rock by oxygen-bearing water.

CONCLUSIONS

(1) The rock and U-bearing minerals that occur in nature are continually affected by subsurface water. Minerals formed at a high temperature and all uranium species therein become thermodynamically unstable at a low temperature. The results of interaction in the subsurface water-rock system depend on the hydrochemical properties of water, especially as concerns Eh and pH. The variable valence of uranium is the major factor that controls the behavior of this chemical element. The high mobility of U(VI) in comparison with U(IV) determines the dependence of uranium mineral stability on redox conditions.

(2) Hydrochemical properties of subsurface water in crystalline rock massifs vary with depth, forming a vertical hydrochemical zoning expressed in a downward increase in mineralization, alkalinity, and reducing ability. Under conditions of hindered water exchange and long-term interaction with host rocks, subsurface water acquires near-neutral and reducing properties. Under such conditions, the interaction with minerals is extremely sluggish, especially in poorly permeable zones, and is expressed in the formation of micro- and nanoparticles of secondary minerals.

(3) Under low-temperature reducing conditions, the slowly proceeding diffusion redistribution of uranium results in enrichment in absorbed uranium at the expense of all other uranium species. The products of secondary alteration of Fe- and Ti-bearing uranium minerals are the major sorbents of uranium. Uraninite, zirconolite, monazite, pyrochlore, britholite, and other U-bearing minerals occur for millions of years under conditions that stimulate recovery of uranium and its conversion into absorbed form. However, the rates of reactions under reducing conditions are negligibly low and these minerals may be regarded as practically stable.

(4) Despite the relatively low uranium content in rocks (10^{-5} – 10^{-3} wt %), subsurface water under reducing conditions is always saturated with uranium. Whether subsurface water interacts with rock or uranium ore, the equilibrium uranium concentration in subsurface water is not higher than 10^{-8} mol/l. At contacts with uranium orebodies, diffusion redistribution of uranium with its partial transition into the absorbed form proceeds continuously under reducing conditions and results in the formation of a secondary dispersion halo. The intensity of this process is extremely low, and its results are detected only owing to the long duration of geologic processes.

(5) Within the depth interval of the expected location of SNF and HLW repositories (0.5–1.5 km), subsurface water is characterized by near-neutral–slightly alkaline properties. Under such conditions, uraninite is

virtually insoluble. This fact is important for the safe long-term storage and disposal of SNF consisting of more than 95% uraninite, which also serves as a confinement matrix for all other radionuclides. The disposal of SNF in massifs of crystalline rocks at a depth below 500 m gives a reliable guarantee of its high stability.

(6) Under oxidizing conditions in the upper hydrodynamic zone, the slightly acid water continually interacts with minerals of endogenic rocks, which are replaced with phyllosilicates; quartz; and Fe, Ti, and Mn hydroxides. Under these conditions, subsurface water is, as a rule, undersaturated with uranium and it may be leached from rocks and ores. However, uranium is commonly not removed from rocks but absorbed by secondary minerals, particularly, by iron hydroxides and leucoxene. The rate of conversion of all other uranium species into an absorbed form under oxidizing conditions is higher by orders of magnitude than in a reducing environment. The depletion of rocks in uranium is distinctly detected only in white kaolin clay as a final product of chemical weathering virtually free of iron hydroxides.

(7) The interaction of oxygen-bearing water with uranium ores unavoidably leads to their destruction. This process occurs simultaneously at different hypsometric levels and under conditions of nonuniform permeability both vertically and horizontally. In connection with this, in ore-bearing zones, along with segments of complete dissolution of all uranium minerals, zones with wide development of uranyl minerals and relics of primary uranium ores may be present.

(8) Uranium that has passed into subsurface water may be removed to sites of discharge, redeposited at lower levels with formation of secondary enrichment zones, or gained in host rocks as absorbed species. The contribution of each process depends on the specific geological setting. A wide halo of elevated uranium contents formed as a result of sorption is always retained at the site of ore destroyed by weathering.

(9) In the aeration zone, capillary and film waters supplemented by free water that moves along fissures during rains and thawing of snow participate in interaction with rocks and ores. The interaction of rocks with capillary water occurs at a very low water/rock ratio and is expressed in hydration reactions, oxidation of iron to Fe(III) and uranium to U(VI), and transition of the latter into the absorbed form. The interaction of capillary water with uranium ore results in oxidation of uraninite; an increase in its solubility; loosening of the surface of this mineral; formation of microfractures therein; an increase in the U concentration in capillary water to $\sim 10^{-4}$ mol/l; replacement of uraninite with secondary U(VI) minerals, first of all, with uranyl hydroxides and silicates; and local diffusion redistribution of uranium with its accumulation in the absorbed form in minerals of host rocks. The influx of free water gives rise to the dissolution of primary and secondary uranium minerals, the removal of uranium along with free water, and its partial deposition in the absorbed form and redeposition at lower hypsometric levels.

(10) The probability of retention of primary uranium ore in the aeration zone arising as a result of natural geologic processes is very low due to the destroying effect of oxygen-bearing water. Uranium ore commonly turns out to occur in the aeration zone owing to man-made subsidence of the water table related to open-pit mining and/or pumping out of water from underground mines.

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