Solubility of Uranium Dioxide during Underground Disposal of Radioactive Wastes and Spent Nuclear Fuel

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Abstract

The problem of reliable prediction of the safety of burial of the spent nuclear fuel in the environmental components is connected with the reliability of quantitative models describing solubility/precipitation of uranium dioxide $UO_2(s)$ as the major component, depending on a number of physicochemical parameters, such as temperature, E_h–pH, salt composition and concentration of electrolyte solutions. In the present paper we report on the free Gibbs' energy of formation of this phase and the accompanying complexes in the solutions of different composition. The reported values of Gibbs' energy allow reliable model reproduction of the experimental results on solubility and the concentrations of dissolved uranium observed in nature. In addition, the reasons that may cause local non-equilibrium fluctuations of the concentrations of this element under the conditions conjugated with the radioactive decay of short- and medium-lived isotopes are discussed.

INTRODUCTION

The main requirement for burial of radioactive wastes (RW) is their reliable isolation from the ecosphere for the entire period of their potential danger for humans (reasonable standards stipulate for the isolation warranted for 10 000 years). The first years of the development of nuclear industry were characterized by substantial underestimation of the danger connected with RW. However, during the last fifty years the way from pouring the liquid waste directly into a river net (Mayak Plant near Chelyabinsk) to the development of high-tech and expensive procedures of waste processing, storage and final burying has been passed. A direct method of burying liquid radioactive wastes (LRW) in deep-seated water-bearing layers with slowed-down water exchange exists. This method is actively used at the Siberian Chemical Plant (Tomsk), Mining and Chemical Plant (Krasnoyarsk) and the Research Institute of Atomic Reactors (Dimitrovgrad). Along with this, modern requirements of the International Nuclear Power Agency provide a compulsory transfer of LRW into the solidified form (in order to do this, the wastes are concentrated and introduced into a conserving matrix). The most promising way to remove all the kinds of RW from the ecosphere is to bury them in the Earth's interior. As examples, we should mention an actively developing concept: burying in salt mines (Gorleben salt formation) in Germany, in granites (Äspö site) in Sweden, in Miocene rhyolite tuff of the Yucca Mountain (in Southern Nevada) or in permafrost rocks of geographically remote grounds in the USA. However, due to the limited period of action of the engineering barriers or definite

circumstances (emergency conditions), it is possible that the RW starts to interact with natural mineralized water including ground water, pore solutions, seawater or salt liquors, a kind of which is cryopag − water of the permafrost zones with negative temperature.

The main solid phase (about 95 %) of the spent nuclear fuel (SNF) is uranium dioxide UO_2(s). When aqueous solutions penetrate into the damaged underground repositories, their content will get dissolved thus supplying uranium into the geosphere, though in the case of conservation of reducing conditions the solubility of uranium will stay limited. Prognostic estimations of the solubility and forms of existence of U compounds under the prevailing chemical conditions of the burying medium, and finally of further safety of SNF storage, may be made with the help of multiparameter thermodynamic models using either of numerous computer software blocks. However, the dependence of thermodynamic properties of the UO_2(s) phase and its modifications on the degree of crystallinity is not very thoroughly studied yet.

URANIUM CONCENTRATION LIMITS UNDER REDUCING CONDITIONS

Uranium (IV) included in natural compounds as U^{4+} cation forms simple and complex oxides, silicates, titanates. The most widespread natural mineral uraninite UO_{2+x} (0.01 < x < 0.25) is a chemical and structural analogue of uranium dioxide of the fuel matrix of a nuclear reactor. The experience of investigation of uranium deposits which occurred under definite geological conditions in the Earth's interior for many million years showed that highly intact state of uranium accumulations is due to the reducing environment in the sites of uranium localization where U(IV) is immobile. However, it is necessary to stress that the major part of industrial ores of uranium deposits is represented by superfine concretions of mixed oxides related to the group of pitchblende. According to the data of chemical analyses of natural samples, the oxygen coefficient x in their average structural formula can vary within a broad range from 0.16 to 0.92 [1]. The question

concerning uranium transport in solutions from which the industrial ores had been formed was recently discussed in [1]. In application to the subject under consideration, it may rephrased as follows: What phases determine uranium concentrations observed under the conditions of underground RW repositories?

Table 1 shows the composition of underground water in Swedish granites [2], fresh water of the exploited water-bearing layers of one of the Siberian grounds of LRW burying, liquors of saliferous mass of the Siberian Platform, which is considered as a promising ground to make underground repositories of solidified highly active wastes (HAW); the most typical compositions of sodium and magnesium liquors used in the experiments on the solubility of non-irradiated (non-exposed) UO_2(s) are also shown [3, 4]. For the selected compositions, uranium concentrations were measured under the indicated physicochemical parameters (E_h, pH) of solutions. One can see that they vary from ~10^{-7} to 10^{-9} mol/l, or from several tens to several tenths mg/l.

Several best known experimental studies of the solubility of UO_2(s) phase showed substantial scattering of its values depending on the strictness of controlling reducing-oxidizing conditions, the degree of phase crystallinity, the presence of micro-amount of the oxides of U(VI). The authors of [5] measured solubility of UO_2(c) within temperature range 100−300 °C and discovered that statistically it is independent of temperature and pH (pH ≥ 4) and is equal to $10^{-10}-10^{-9}$ mol/l H_2O. Therefore, it is quite reasonable to assume the reaction

$$UO_2(c) + 2H_2O = U(OH)_4^0 \qquad (1)$$
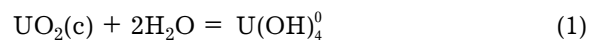
with the formation of a neutral complex; for this reaction, log $K_{s,4}^0 = -9.47 \pm 0.56$.

The authors of [6] studied the solubility of UO_2(c) within the temperature range 300−600 °C in the solutions of different compositions; their oxidative status was controlled by buffers: haematite − magnetite and Ni−NiO. Those authors also concluded that the solubility of this phase in water is almost independent of temperature and kind of buffer; it is log $K_{s,4} = -9 \pm 0.5$. The fact that the

TABLE 1

Concentrations of the components of uranium-containing solutions of different types, mol/l

Component	Underground water Äspö site [2]	Fresh water [4]	Liquors [4]	Liquors [3]	
				NaCl	MgCl$_2$
HCO_3^-	$1.13 \cdot 10^{-3}$	$4.426 \cdot 10^{-3}$	0.0138	–	–
Na^+	$51.3 \cdot 10^{-3}$	$1.435 \cdot 10^{-3}$	2.13	6.036	0.48
K^+	$0.16 \cdot 10^{-3}$	$0.141 \cdot 10^{-3}$	0.486	0.037	0.57
Ca^{2+}	$18.5 \cdot 10^{-3}$	$0.6 \cdot 10^{-3}$	1.712	0.021	0
Mg^{2+}	$1.23 \cdot 10^{-3}$	$0.395 \cdot 10^{-3}$	0.355	0.018	4.21
Fe_{tot}	$5.86 \cdot 10^{-6}$	–	–	–	–
F^-	$0.14 \cdot 10^{-3}$	–	–	–	–
Cl^-	$85.4 \cdot 10^{-3}$	$0.180 \cdot 10^{-3}$	6.7	6.036	8.84
Br^-	$0.199 \cdot 10^{-3}$	–	–	–	–
I^-	$1.3 \cdot 10^{-6}$	–	–	–	–
PO_4^{3-}	$3.8 \cdot 10^{-8}$	–	–	–	–
SO_4^{2-}	$2.76 \cdot 10^{-3}$	–	$8.75 \cdot 10^{-3}$	0.058	0.32
NH_4^+	$0.018 \cdot 10^{-3}$	$0.019 \cdot 10^{-3}$	–	–	–
SiO_2	$0.068 \cdot 10^{-3}$	–	–	–	–
U_{tot}	$1.93 \cdot 10^{-9}$	$5 \cdot 10^{-9}$–$1.7 \cdot 10^{-9}$	$4.66 \cdot 10^{-9}$	$2.8 \cdot 10^{-7}$	$3.1 \cdot 10^{-7}$
pH	7.9	7.99–6.44	7.0–7.3	7.7	4.7
E_h, mV	−280	−53	−100...−200	0−60	0−60

solubility of uraninite is independnet of temperature, as it follows from [5, 6], is important for estimations of the concentrations of radionuclides under the conditions of HAW repositories where temperature rise is connected only with the decay of wastes.

The authors of [8] determined the solubility of the amorphous $UO_2(am)$ phase at a temperature of 25 °C experimentally. The rate constant of reaction (1) differs from that for the crystal phase by five orders of magnitude; it is log $K_{s,4} = -4.4 \pm 0.4$; solubility is independent of pH within the range 5.5−10.

Short-term experiments [9] aimed at determination of the solubility of the amorphous phase of uranium oxide in NaCl solutions (0.03−1 mol/kg) showed that for pH > 5 it is approximately equal to 10^{-8} mol/l, while for pH 4−5 it is 10^{-6} mol/l H_2O.

The authors of [10] described experiments in 0.1 M $NaClO_4$ solutions within pH range 2−12. In the experiments lasting for 7 days and involving uranium supersaturation procedure, uranium concentration in solution was 10^{-8} mol/l; according to the data of diffraction analysis, the precipitated solid phase is represented by $UO_2(am)$. Nevertheless, an increase in the duration of experiments to 14 and 28 days revealed a decrease in the equilibrium concentrations log [U] = −8.7 ± 0.8, which coincides with the results of experiments carried out using the solubility method; the diffraction peaks of the solid precipitate became more intensive and clear during ageing.

THERMODYNAMIC DATABASE

On the basis of the above-listed data, one may conclude that the solubility of uranium dioxide $UO_2(s)$ in the system $UO_2(s)-H_2O$ can be determined with sufficient reliability to be log $K_{s,4} = -9 \pm 1$ for pH > 4, assuming that within this range the whole uranium dissolved is present as the fourth hydroxo complex $U(OH)_4^0$. The sub-index "s" instead of "c" or "am" means uncertainty of the degree of crystallinity of the solid phase; however, large interval of accuracy (±1) allows taking into account the solubility of both the amorphous and crystalline species. The question is to decide which value should be taken for $UO_2(s)$ to

TABLE 2

Free energies of formation of the initial forms in solution and uranium-containing components [7, 11]

Component	$\Delta_f G_m^0$, kJ/mol	Component	$\Delta_f G_m^0$, kJ/mol
U^{4+}	−529.860	UOH^{3+}	−763.918
UO_2^{2+}	−952.551	$U(CO_3)_5^{6-}$	−3364.092
H_2O	−37.140	$U(CO_3)_4^{4-}$	−2842.567
Cl^-	−131.217	UCl_3^+	−670.895
CO_3^{2-}	−527.917	$UO_2(CO_3)_2^{2-}$	−2105.080
$UO_2(s)$*	−1004.140*	$UO_2(CO_3)_3^{4-}$	−2659.597
$U_3O_8(c)$	−3369.481	UO_2Cl^+	−1084.738
$U(OH)_4^0$	−1427.048	$UO_2Cl_2^0$	−1208.706

* The data from [11], since in [7] the value (−1031.8 ± 1.0) kJ/mol is given for the crystal phase and (−1003.6 ± 4.37) kJ/mol for the amorphous modification.

calculate $\Delta_f G_m^0$ of the $U(OH)_4^0$ complex according to reaction (1). Since an answer to this question is far from being unambiguous (Table 2), the authors of [11] recommend to use additionally the experimental data reported in [12] about a more important system $UO_2(s)-H_2O-CO_2$. Under the conditions chosen in [12], involving rather high concentration of carbonate ion (1 M Na_2CO_3), the predominant complex is $U(CO_3)_5^{6-}$, which is confirmed by means of spectroscopy (UV-vis-IR and XAS). In this case, using the rate constants of reactions (2)–(6) and the required $\Delta_f G_m^0$ values for the main components (see Table 2) we obtain:
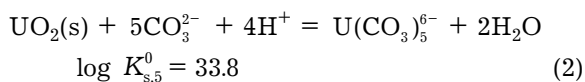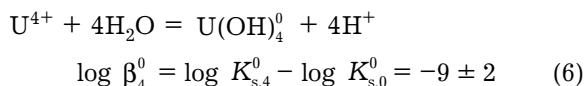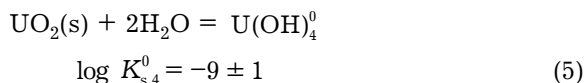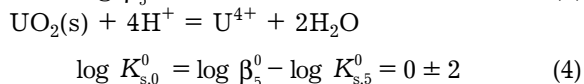
$$UO_2(s) + 5CO_3^{2-} + 4H^+ = U(CO_3)_5^{6-} + 2H_2O$$
$$\log K_{s,5}^0 = 33.8 \qquad (2)$$

$$U^{4+} + 5CO_3^{2-} = U(CO_3)_5^{6-}$$
$$\log \beta_5^0 = 34.1 \pm 1.0 \qquad (3)$$
$$UO_2(s) + 4H^+ = U^{4+} + 2H_2O$$
$$\log K_{s,0}^0 = \log \beta_5^0 - \log K_{s,5}^0 = 0 \pm 2 \qquad (4)$$
$$UO_2(s) + 2H_2O = U(OH)_4^0$$
$$\log K_{s,4}^0 = -9 \pm 1 \qquad (5)$$
$$U^{4+} + 4H_2O = U(OH)_4^0 + 4H^+$$
$$\log \beta_4^0 = \log K_{s,4}^0 - \log K_{s,0}^0 = -9 \pm 2 \qquad (6)$$

In addition to the hydroxo and carbonate complexes, U(IV) forms the only weak chloride complex UCl^{3+}. The reaction rate constant was taken from [7]:
$$U^{4+} + Cl^- = UCl^{3+} \quad \log \beta_1^0 = 1.27 \pm 0.13 \qquad (7)$$

Thermodynamic modeling was carried out by minimizing free Gibbs' energy of the system with the help of the software complex HCh [13] including the database of thermodynamic parameters of the solid phases and components of solution UNITHERM supplemented with the matched values for specific U-containing minerals and components of solution. The involved $\Delta_f G_m^0$ values for uranium phases calculated with the help of equation
$$\Delta_r G_m^0 = (-\ln 10)RT \log K^0 \qquad (8)$$
are listed in Table 2.

A simple method of approximations of the theory of specific interactions was used to calculate ionic activity coefficients [14]:

$$\log \gamma_i = -\frac{z_i^2 A \sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \sum_k \varepsilon_{(i,k)} I_m m_k \qquad (9)$$

where $A = 0.5092$ $(kg/mol)^{1/2}$ for 25 °C and a pressure of 1 bar, $\varepsilon_{(i,k)}$ is a parameter of
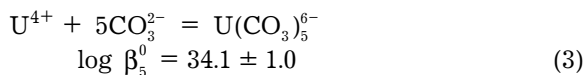
TABLE 3

Parameters of specific interactions of ions $\varepsilon_{(i,k)}$ in NaCl solution, calculated ionic acitivity coefficients and water activity

Concentration		Na^+-Cl^-	Na^+-OH^-	H^+-Cl^-	$UCl^{3+}-Cl^-$	$UO_2Cl^+-Cl^-$	a_{H_2O}
mol/kg	mol/l						
0.1	0.1	0.7830	0.7848	0.7994	0.1113	0.7759	1.0
1	0.98	0.6704	0.6860	0.8247	0.0290	0.6114	0.97
2	1.92	0.6705	0.7068	1.0216	0.0326	0.5614	0.93
3	2.82	0.6996	0.7497	1.3028	0.0477	0.5307	0.89
4	3.69	0.7335	0.8043	1.6804	0.0774	0.5075	0.85
5	4.51	0.7736	0.8680	2.1802	0.1323	0.4881	0.81

Note. The $\varepsilon_{(i,k)}$ coefficient for Na^+-Cl^-, Na^+-OH^-, H^+-Cl^-, $UCl^{3+}-Cl^-$, and $UO_2Cl^+-Cl^-$ pairs is 0.03, 0.04, 0.12, 0.295, and −0.01, respectively.

specific interactions between i and k ions. Summing is carried out over all k ions present in the solution. The program for calculating the ionic activity coefficients (γ_i) and $\varepsilon_{(i,k)}$ parameters were taken from [15]. Table 3 shows the calculated activity coefficients, the double concentration scale for chloride solutions, since their molal (taken for calculations) and molar (determined analytically) concentrations differ substantially. For UO_2Cl^+, the $\varepsilon_{(i,k)}$ parameter was taken from [16]; for UCl^{3+} in NaCl solution, on the basis of analysis of the data on the interaction of other multi-charged cations and due to the absence of accurate estimations, it was accepted to be two times smaller (0.295) than that in $NaClO_4$ solution (0.59 ± 0.1). Changes in the ionic force of solution have almost no effect on the activity of neutral complexes like $U(OH)_4^0$. The HCh software complex is not intended to model concentrated solutions; activity coefficients are calculated in this software automatically according to the third approximation of Debye−Hückel. However, by organizing the files with filename extension .stg it allows us to introduce the required γ_i calculated using another method. We did this.

MODELING RESULTS

Thermodynamic calculations showed that the whole uranium dissolved in the water of Swedish granites is present as a complex $U(OH)_4^0$. The solutions are in equilibrium with dolomite, fluorite, montmorillonite, and the

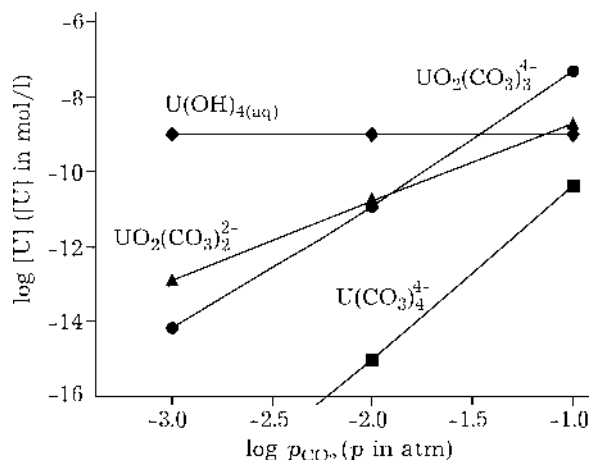Fig. 1. Concentrations of complexes of U(IV) and U(VI) in solutions depending on the partial pressure of CO_2 at 25 °C and a pressure of 1 atm.

calculated pH (7.56) is close to the measured value 7.9. However, an increase in uranium concentration in the fresh water of the Siberian ground of LRW disposal (E_h = ~53 mV) is connected with the appearance of carbonate complexes of uranyl ion: $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. In order to establish their role under oxygen-free conditions for negative Eh (log f_{O_2} = −70 atm), partial pressure of CO_2 in the system was sequentially increased to 0.1 atm, which corresponds to 4.87 10^{-2} mol/l HCO_3^- at pH 7.41. A comparison between the concentration curves (Fig. 1) shows that even under these conditions the carbonate complexes of U(VI) can make a substantial contribution into the solubility of $UO_2(s)$. As it was correctly stated in [1], geochemical significance of the high strength of complex uranyl ions involves

TABLE 4

Uranium concentrations in NaCl solutions for different values of reduction-oxidation potential in equilibrium with $UO_2(s)$ and $UO_{2.67}$, mol/l

Concentration of NaCl, mol/l	U_{tot}	UO_2Cl^+	$(UO_2)_3(OH)_7^-$	$(UO_2)_4(OH)_7^+$	pH	E_h, mV	log f_{O_2}
0.1	$9.54 \cdot 10^{-10}$	$4.97 \cdot 10^{-18}$	–	–	6.9 ± 0.2	−210 ± 10	−70
1.0	$9.29 \cdot 10^{-10}$	$7.52 \cdot 10^{-17}$	–	–			
3.0	$8.50 \cdot 10^{-10}$	$4.96 \cdot 10^{-16}$	–	–			
5.0	$7.46 \cdot 10^{-10}$	$1.49 \cdot 10^{-15}$	–	–			
5.0	$7.22 \cdot 10^{-9}$	$9.40 \cdot 10^{-10}$	–	–	6.75	93	−50
5.0*	$5.79 \cdot 10^{-6}$	$3.0 \cdot 10^{-8}$	$2.54 \cdot 10^{-8}$	$8.51 \cdot 10^{-7}$	7.25	285	−35

*The data for $UO_{2.67}$.

first of all a substantial decrease in the redox potential necessary for their reduction to the tetravalent state.

The results of calculation of the solubility of $UO_2(s)$ in chloride sodium solutions with variable concentration are shown in Table 4. One can see that under the oxygen-free conditions (negative E_h) even in the case of increased NaCl concentration the calculated concentration of dissolved uranium dioxide remains at a level of 10^{-9} mol/l. The contribution from UCl^{3+} is insignificant; weak chloro complexes of uranyl, unlike its carbonate complexes, are unable to change the situation. This relates to neutral reducing solutions, while for acidic (0.1 M $HClO_4$) artificial liquors predominance of the first and second chloro complexes of hexavalent actinides was proved by means of spectrophotometry [16].

An elevation of the redox potential of the system to 93 mV also does not allow obtaining agreement with the experimental data of [3]: uranium concentrations in equilibrium with $UO_2(s)$ remain substantially below $3 \cdot 10^{-7}$ mol/l. Their sharp increase was obtained only under weakly oxidative conditions in equilibrium with the U_3O_8 phase ($UO_{2.67}$) modeling mixed oxides. Under these conditions (see Table 4), even polynuclear complexes of the UO_2^{2+} cation appear. It is necessary to stress that the unexposed phase used in [3] at first contained $UO_{2.7}$ on the surface (XPS measurements), which caused rapid dissolution even under reducing conditions maintained by hydrogen flow and by the Pt catalyst. Uranium concentration in solution decreased gradually and reached the steady state after 20–25 days. After the experiment, the surface of the dissolving phase was identified as $UO_{2.1}(s)$.

Under the reducing conditions of actual repositories and pilot plants of RW disposal, an increase in total concentrations of radionuclides dissolved in liquors in the near-field zone is believed to be connected with local changes in redox potentials arising due to a-radiolysis of water and also chloride media and the dissolved N_2. As it was shown in [17], the solubility of $PuO_2(am)$ in 4.36 M NaCl solutions in the experiments at the 110th day of equilibrium establishment is substantially higher than that after 7 days. At the same time, in 4.92 M $NaClO_4$ solutions we did not observe any

increase in solubility, which is likely to be connected with the transformation of a part of NaCl into NaOCl. Additional experiments in 0.02 M NaOCl solutions showed that as early as after 2 days only 30 % of Pu(IV) remains in solution, while 22 % is present in the form of Pu(V) and 48 % in the form of Pu(VI).

The formation of hypochlorite ion ClO^- which proceeds according to reaction (10) was proved in spectroscopic studies [18].

The most significant changes in the spectra of the irradiated liquors (dose: 120–216 kGy) were observed within the range 220–300 nm (UV-vis absorption spectrum). Besides the oxidizing properties, the hypochlorite ion is able to form stable complexes with plutonium (VI) [19]; however, the absence of constants for uranium (VI) does not allow us to take into account their effect on the solubility of $UO_2(s)$.

The authors of [17] also studied the kinetics of reduction of Pu(V) in alkaline media with hydrogen peroxide which is formed by radiolysis in highly active LRW. In addition, there are confirmations of the formation of H_2O_2 by means of photolysis of the organic material in natural water, so, this process can actively affect the environmental behaviour of actinides with variable valence. The reduction of PuO_2^+ by hydrogen peroxide is described by the following equation of the rate of proceeding reaction:

$$R = (3.59 \pm 1.79) \cdot 10^{-9} \text{ min}^{-1}$$
$$\times [Pu(V)] [H_2O_2] [H^+]^{-1} \qquad (11)$$

Starting from this equation one may calculate that in deep seawater, where the usual H_2O_2 content is 10^{-7} M and pH is 8, 50 % of PuO_2^+ will be reduced within 55 years, while under the conditions of burying of HAW at pH 11 (in the presence of MgO) and H_2O_2 concentration equal to 0.001 mol/l this will require only 4 min.

Along with this, we showed in [4] that the change in geochemical situation and in particular the change in chemical composition of water is observed only in the vicinity of the injection wells. As a rule, at a distance of 100–200 m the differences from the natural background are insignificant; they do not go out of the limits of requirements to the composition of water for household and drinking purposes.

CONCLUSIONS

1. The values of free Gibbs' energy accepted in the present work for the formation of $UO_2(s)$ phase and $U(OH)_4^0$ allow reliable modeling of the behaviour of dissolved uranium under reducing conditions which are considered as promising ones for the arrangement of underground repositories of RW. At the same time, the calculated solubility in the system $UO_2(s)-H_2O$ should be considered as minimal one, because it is known that actinides in the lowest state of oxidation (+4) form stable organic complexes. In this case, the solubility of uranium may increase.

2. The presence of carbon dioxide in underground water ($E_h \leq 0$) in the amounts characteristic of underground water of different regions ($f_{CO_2} = 10^{-2}-10^{-3.5}$ atm) should not promote an increase in the concentration of dissolved uranium; however, an increase in f_{CO_2} to 10^{-1} atm leads to the appearance of stable carbonate complexes of uranyl ion: $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$.

3. We did not discover any significant influence of an increase in the concentration of chloride ion on the solubility of $UO_2(s)$ due to an increase of the ionic force of solutions or due to the formation of chloro complexes.

4. Overshoots of the content of dissolved actinides observed directly near the injection wells and conserving matrices can be connected with other reasons, not with those factors that are taken into account when modeling thermodynamic equilibria (in particular, possible reasons may be active radiolysis of water and chloride solutions initiated by radioactive decay of short- and medium-lived radionuclides).

5. Extreme redox sensitivity of uranium causes the appearance of mixtures of non-stoichiometric oxides in the zones of its deposition; the stability of these oxides can hardly be predicted with high accuracy. However, within the time comparable even with the duration of laboratory experiments, uranium concentrations are leveled to a value determined by the phase which is stable exactly under the buffering conditions of the geochemical environment.

Acknowledgements

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