

## PLUTONIUM BEHAVIOR IN DEEP ROCK REPOSITORIES OF SPENT NUCLEAR FUEL

Gaskova O.L. (IMP SB RAS), Bukaty M.B. (IGOG SB RAS)  
gaskova@uiggm.nsc.ru; fax: (3832) 33-27-92; phone: (3832)33-30-26

---

When solving the problem of the removal of transuranium radionuclides from the ecosphere, required time of isolation for which makes hundred thousands and even millions years, the geological environment is of principal value. By the moment when, probably, it will remain a unique barrier (500-1000 years), the level of safety of repository will be defined basically by intensity of migration of Pu and Am, that entering a structural lattice of uraninite ( $\text{UO}_{2(s)}$ ). The criteria of a choice of geological environments for High Level Nuclear Waste (HLNW) disposal are scientifically proved now [1]. It is established, that the main conditions of the high stability of uranium minerals are the reduced near neutral properties of underground waters or their insignificant amount in the repository area. For example, in Germany and the USA the concept of a disposal of waste products in bedded salt formations (Gorleben and Salado formations), in Sweden - in granite suite of Äspö site, in the USA - in Miocene rhyolitic tuffs (Yucca Mountain in Southern Nevada) is actively developed. According to experts opinion [2] "as a whole according to its petrophysical properties, the basic rocks are more favorable for construction of the HLNW repositories than granites, gneisses and other rocks of silicate composition".

It has been supposed in the model, that the repository of radioactive waste products is placed in the rocks of "maximum unfavorable" granite composition on [3]. In time after its dead storage there is a saturation of interstitial spaces of wall rocks by underground waters. The calculations in a 12-component system H-O-K-Na-Ca-Mg-Fe-Al-Si-S-C-Pu were carried out by GIBBS algorithm with the use of thermodynamic data bank UNITERM (the software package "HCh") [4]. For plutonium the data are taken from DB NAGRA [5].

Results of calculations have shown, that at 25°C ( $P_{\text{sat}}$ ) there is an equilibrium association of Q, Ab, Micr, Musk, Epid, Mg-chlorite, F-apatite and  $\text{CaF}_2$  Pairs of daphnite+epidote – pyrite or daphnite – pyrite or daphnite – hematite (depending on variations of the water/rock ratio and the minerals included in model) are prevailing by weight of redox sensitive components, and hence, they determine Eh in solutions. At pH of 9,4 - 10 units, values of their Eh are very close (from -0,45 up to -0,33 V). In these conditions, Pu in the solution ( $4 \cdot 10^{-11}$  mole/L) is present as  $\text{Pu}(\text{OH})_4^0$  in equilibrium with  $\text{PuO}_{2(\text{hydr,aged})}$ . In database [5] the phase of hydrous aged dioxide of Pu (IV) is designated just so. It should be noted, that in the open system (up to Eh 0,4V and  $P_{\text{CO}_2} = -3,0$  bar) the situation practically does not change.

Yucca Mountain is the unique designed repository of a long-term HLNW disposal in aerobic conditions. As there are the reliable data on water compositions from the saturated horizons directly below the repository [6], there is an opportunity to estimate possible concentration of dissolved Pu there. It turned out that the water (well J-13 at the YM) is supersaturated in relation to quartz, goethite or  $\text{Fe}(\text{OH})_3$  and Mg-chlorite. As the concentration of increases 0,5 order, hydrous montmorillonite is stable (table). Some other set of minerals "drops out" at the use of the program and DB WATEQ4F [7], specially intended to model the compositions of surface and ground waters. One is doubtless, that a great number of colloids, mainly of  $\text{SiO}_{2(\text{am})}$  or  $n\text{SiO}_2 \cdot m\text{Al}_2\text{O}_3 \cdot p\text{H}_2\text{O}$  is formed. Considerably smaller amount of  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  or smectites is produced. Concentration of Pu in the dissolved form does not exceed the value of  $4.1 \cdot 10^{-11}$  mole/L even in these mildly oxidizing conditions. This value is at the level of maximum concentration limit for the waters intended for household use.

At the same time, tests on the planned and working long-term repositories of SNF and especially experimental data on the solubility of irradiated phases of U and Pu testify to the steady concentration of  $\text{Pu} \geq 10^{-8}$  and even up to  $10^{-6}$  mole/L in the reduced conditions in waters from granite rocks [8, 9, 10, 11]. The reason of this fact, in general, is clear – the local change of the redox-potentials, arising due to  $\alpha$ -radiolysis of waters and of chloride environments, the dissolution of non- stoichiometric and amorphous phases (the radiationally induced effect interferes with their "ageing"), the mobility of Pu in the colloid form (particles of 0.001-1 microns).

Composition from well J-13 at the YM site [6] and quantity of precipitated minerals

Species, mmole/L	Species, mmole/L	Minerals, % parameters ("HCh")	Minerals, Saturation Indexes(SI)* ("WATEQ4F")
Na <sup>+</sup> 1.99	F <sup>-</sup> 0.11	SiO <sub>2</sub> , 96.5	Allophane (a, p) ±0.4
K <sup>+</sup> 0.129	Cl <sup>-</sup> 0.20	FeOOH 0.3	[Al(OH) <sub>3</sub> ] <sub>(1-x)</sub> [SiO <sub>2</sub> ] <sub>x</sub>
Li <sup>+</sup> 0.009	NO <sub>3</sub> <sup>-</sup> 0.14	Mg-chlorite 3.2	Halloysite
Ca <sup>++</sup> 0.324	SO <sub>4</sub> <sup>2-</sup> 0.19	traces of montmoril.	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O -0.044
Mg <sup>++</sup> 0.083	SiO <sub>2</sub> 1.02	PuO <sub>2</sub> (hydr. aged)-,	Silica gel SiO <sub>2(am)</sub> +0.025
Mn <sup>++</sup> >0.0001	HCO <sub>3</sub> <sup>-</sup> 2.1	Eh = 430 mV,	Chalcedony SiO <sub>2</sub> +0.559
Fe <sup>2+/3+</sup> >0.001	PH = 7.4	log f <sub>O<sub>2</sub></sub> = -23.5	Calcite CaCO <sub>3(cr)</sub> -0.776
Eh = 430 mV		pH = 7.6	Ferrihydrite +1.5

\* SI = 0±0.3 means near-equilibrium saturation

Thermodynamic modelling allows us to carry out more detailed simulations. According to [9], near the surface of SNF in the same waters of [6], the oxidizing potential will be ~600mV. It means the intensive dissolution of PuO<sub>2(s)</sub> and increase of concentration of PuO<sub>2</sub>(CO<sub>3</sub>)<sup>-</sup> species with a small share of Pu(VI) carbonate complexes up to **3·10<sup>-9</sup> mole/L**. The redox conditions displaced by environment already at a distance (or after a time) imply that these complexes appear in a unstable condition of oxidation and are the source of formation of PuO<sub>2</sub>·nH<sub>2</sub>O<sub>(am)</sub> nanoparticles. In fact, general technique of preparation of colloids in laboratory, for example, just consists in creation of locally supersaturated solution that leads to forming of germs of the pre-solid phase with physical interface. The subsequent coagulation and growth should result in the drop of concentration in the solution and the size of particles increase [12]:

$$\log K_{sp}^0 (\text{particle size } d) = -58 \pm 1 + 23/d \text{ (nm)},$$

where  $K_{sp}^0$  is a solubility constant according to [5]. However, the given equation has no relation to the duration of this process, but there are data, that, for example, for Th (IV) within 100-400 days the size of particles has not been changed [13]. It is quite possible, that metastable steady state conditions Pu(OH)<sub>4(aq)</sub> ⇌ PuO<sub>2</sub>·2H<sub>2</sub>O<sub>(am)</sub> is established in the solution and formation of pseudocolloids, i.e. a capture of plutonium by other colloid particles usually represented by clay minerals, silica gels, (hydr)oxides of iron, chlorite, etc., follows the mechanism of adsorption of the first and co-precipitation the second.

At the same time, experimental data [12] evidently testify that the capture of Pu is reduced in hematite >> siliceous colloids > montmorillonite series (equal concentration of colloid particles). Their amount can be easily estimated in the calculations similar to those given in the table. Besides, iron (hydr)oxides hold Pu tightly, but silicon and montmorillonite release it easily at change of environmental conditions. Thus, the role of the petrochemical composition of host rocks can be also considered from this point of view.

*Financial support by the RFBR (grants № 02-05-64623 u 03-05-64548)*

## References

1. Underground disposal of radioactive nuclear wastes. 1981. The basic management. Vienna: IAEA, 56 p.
2. Laverov N.P., Omelyanenko B.I., Velichkin V.I. 1994. Geocology. №6. p.3.
3. Bogatkov O.A., Kosireva L.V., Sharkov E.V. 1987. Average chemical compounds of magmatic rocks. M.: Nedra, 152 p.
4. Shvarov Yu.V. 1999. Geochemistry. №4. p.431.
5. NAGRA/PSI Chemical Thermodynamic Data Base 01/01, Technical report 02-16, 2002.
6. Harrar J.E., Carley J.F., Isherwood W.F., Raber E. 1990. Report of the Committee to review the use of J-13 well water in Nevada nuclear waste storage investigations.
7. Ball J.W., Nordstrom D.K. User's manual for WATEQ4F, with revised thermodynamic database. U.S. Geological Survey, 1991.

8. *Runde W., Conradson S.D., Efurud D.W., et al.* 2002. *Appl. Geochem.* 17, p.837.
9. *Finn P.A., Hoh J.S., Wolf S.F. et al.* 1996. *Radiochim Acta.* 75. p.65.
10. *Amosov P.V.* 2002. *Geoecology.* №6. p.506.
11. *Laverov N.P., Omelyanenko B.I., Yudintsev S.V.* 2003. *Geology of ore deposits.* 45. №1. p.3.
12. *Fanghanel Th., Neck V.* 2002. *Pure Appl. Chem.* 74, N10. p.1985.
13. *Bitea C., Muller R., Neck V., Walter C., Kim J.I.* 2002. *Proc. E-MRS Spring Meeting, Symp. Colloid, Strasbourg, France.*

---

*Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22) 2004  
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004  
URL: [http://www.scgis.ru/russian/cp1251/h\\_dgggms/1-2004/informbul-1\\_2004/geoecol-5e.pdf](http://www.scgis.ru/russian/cp1251/h_dgggms/1-2004/informbul-1_2004/geoecol-5e.pdf)  
Published on July, 1, 2004*

*© Herald of the Department of the Earth Sciences RAS, 1997-2004  
All rights reserved*