SORPTION OF PLUTONIUM (IV) ON THE PLYMINERAL SAND FROM ACID SODIUM NITRATE SOLUTIONS. RESULTS OF THE MODEL EXPERIMENT

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The goal of the experiment was estimation of the scale of plutonium sorption from acid sodium nitrate solutions in view of injections of liquid radioactive waste in deep strata as well as for understanding of the nature of plutonium (IV) sorption.

The real polymineral sand was picked out from the productive strata. The mineral composition of the sand is as follows (weight %): quartz - 55–65, feldspars (albite, microcline, plagioclase) - 10–20, micas (muscovite and biotite) - 2–10, clay (montmorillonite, kaolinite, illite) – up to 15, Ca, Mg carbonates - 0.5–3, heavy fraction - <1. Concentration of $NaNO_3$ in solutions varied from 0.005 to 1 M. Concentration of HNO_3 was about ~ 0.1 M (pH=1.2). Initial aqueous plutonium (IV) contents were $3\cdot10^{-7}$ and $1.3\cdot10^{-6}$ M. Thermodynamic calculation on the basis of the data from [1] shows that at specified acidity the hydroxide complex $Pu(OH)_2^{2+}$ dominates (Fig.1).

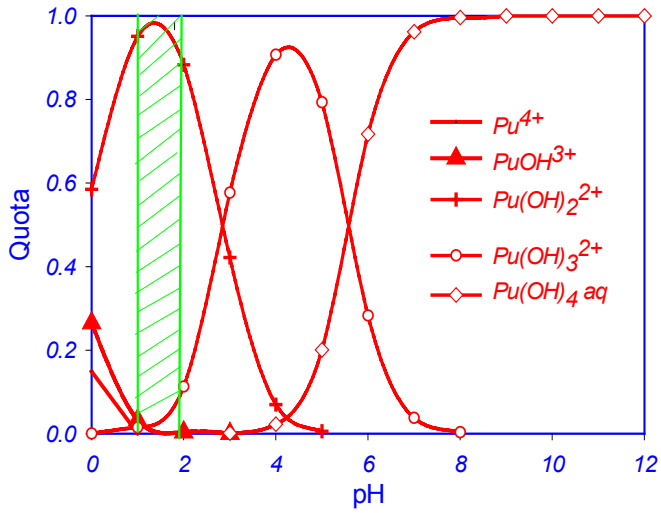

Fig. 1. Speciation of Pu(IV) as function of pH.

Weight portions of the sand (M) were equal to 1 g, volumes of solution (V) – 10 ml. The test tubes were continuously shaken during the experiments. Distribution coefficients $K_d = \frac{(m_{init} - m_{equil})V}{m_{equil}M}$ were calculated based on decrease of plutonium concentration in aqueous solutions. The heterogeneous systems in test-tubes were centrifuged, and the dry targets were prepared for radiometric determination of plutonium from the 0.2 ml aliquots of solution. The kinetic controls of the sorption process as well as the control of pH change were carried out. Plutonium concentrations in solutions stopped to change approximately in 8-14 days (Fig. 2). pH values slowly increased apparently as a result of interaction of the acid with minerals of the sand (Fig. 3).

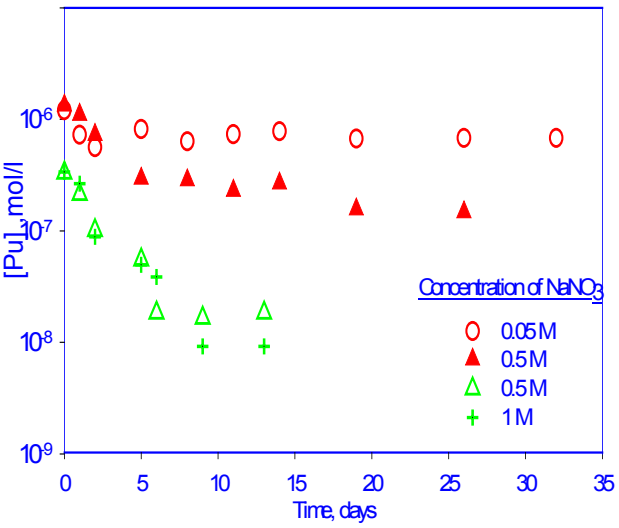

Fig. 2. Kinetics of plutonium (IV) sorption on polymineral sand

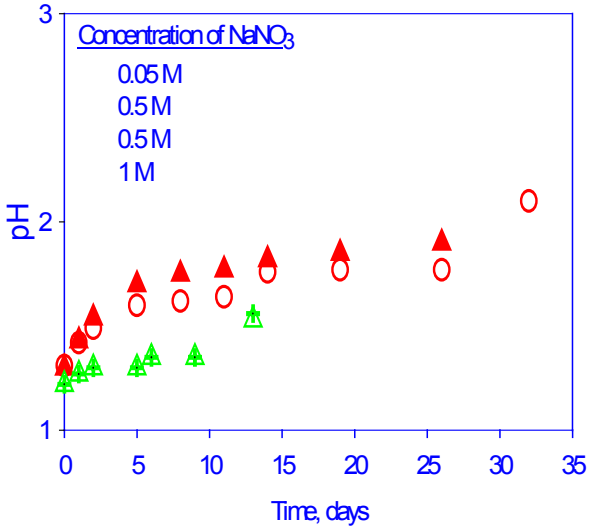

Fig. 3. Change of pH in time

The obtained distribution coefficients are shown in Fig. 4 as a function of sodium nitrate concentration. One can see that 1) plutonium sorption increases as increase of $NaNO_3$ content, which is in contradiction with the model of $Pu(OH)_2^{2+}$ - Na^+ competitive ion exchange; 2) distribution coefficients of

plutonium decrease as it's initial concentration increases, that can be explained by the limited sorptive capacity of the sand.

The observed peculiarities may be formally described by the following chemical reaction: $Pu(OH)_2^{2+} + nNa^+ + (2+n)M^+_{copб.} = (Pu(OH)_2^{2+} nNa^+)_{copб.} + (2+n)M^+$, where M^+- some tentative ion entered by us for electro neutrality. In other words it is supposed that the complex $(Pu(OH)_2^{2+} nNa^+)_{copб.}$ is formed on the surface of mineral sorbents. The equilibrium constant of the reaction may be written as:

$$K = \frac{\left[(Pu(OH)_2^{2+} nNa^+)_{copб.}\right] \cdot a_{M^+}^{(2+n)}}{m_{Pu(OH)_2^{2+}} \cdot \gamma_{Pu(OH)_2^{2+}} \cdot a_{Na^+}^n \cdot \left[M^+_{copб.}\right]^{(2+n)}}; K^* = \frac{K_d}{\gamma_{Pu(OH)_2^{2+}} \cdot a_{Na^+}^n \cdot \left[1 - \frac{(2+n)\cdot(Pu(OH)_2^{2+} nNa^+)_{copб.}}{C}\right]^{(2+n)}},$$

were C is a sorptive capacity, g-eqv/kg, m, a, and γ are molalities, activities and activity coefficients of the respective ions, $K^* = K \cdot a_{M^+}^{(2+n)}$. Activity coefficients of the complex $Pu(OH)_2^{2+}$ were calculated using S.I.T. model (interaction parameter $\varepsilon_{Pu(OH)_2^{2+},NO_3^-}$ was taken as equal to 0.3 by analogy with $\varepsilon_{Pu(OH)_2^{2+},ClO_4^-}$ [1]), activity coefficients of Na^+ were calculated by Pitzer model.

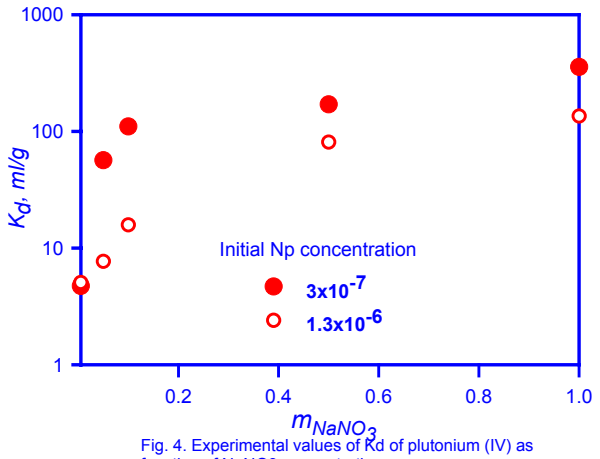

Fig. 4. Experimental values of Kd of plutonium (IV) as function of NaNO3 concentration

As a result of approximation of the experimental values of the plutonium distribution coefficients by the equation the values of the parameters of the proposed model have been estimated. K^*=433; n=0.88; C=7x10^{-5} g-eqv./kg

The calculated by the model distribution coefficients in comparison with experimental ones are shown in Fig. 5. Authors understand that the model is formal, but it has some chemical meaning and adequately reflects peculiarities of the experimental data on plutonium sorption.

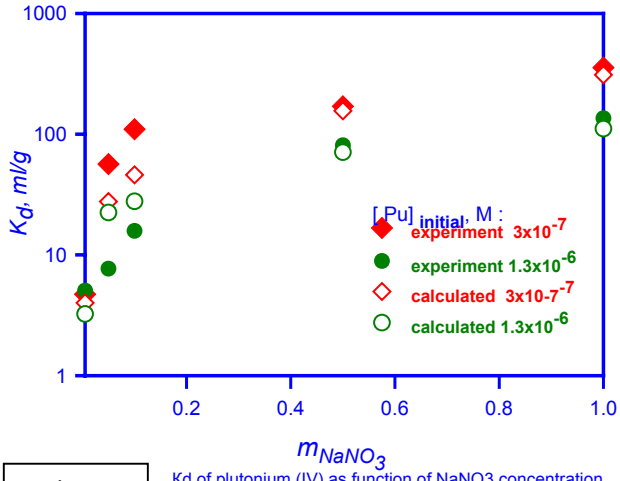

Fig. 5. Kd of plutonium (IV) as function of NaNO3 concentration

Conclusions

1. As a result of experimental study of Pu (IV) sorption on the polymineral sand from acid NaNO3 solutions Kd of plutonium were determined. It was shown that distribution coefficients increase as sodium concentration increases, which is in contradiction with the model of $Pu(OH)_2^{2+}$ - Na^+ competitive ion exchange;

2. The formal model of the sorption of the complex ($Pu(OH)_2^{2+}$ nNa+) on the limited sorptive capacity was proposed to describe experimental data. The parameters of the model such as equilibrium constant of the reaction, the stoichiometric coefficient n, and sorptive capacity of the sand have been calculated.

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Reference

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