EXPERIMENTAL STUDY OF SORPTION OF NEPTUNIUM (V) ON KAOLINITE FROM NACL SOLUTIONS OF VARIOUS CONCENTRATIONS.

Mironenko M.V., Malikov D.A., Kulyako Yu.M., and Myasoedov B.F. (GEOKHI RAS)

The experiment was carried out in the framework of the project on experimental study of neptunium (V) sorption on clay minerals from single NaCl, KCl, $CaCl_2$, $MgCl_2$ solutions of various concentrations to obtain constants for geochemical modeling of sorption distribution of neptunium in the systems “polymineral soils – multicomponent aqueous solutions”.

The fraction of <0.001 mm of the kaolinite from the deposit near Glukhovets town, Ukraine was separated by the procedure of the sedimentation analysis. The sample was subjected to chemical and X-ray analysis. Aqueous NaCl concentrations in experiments varied within the range of 0.002 ÷ 0.3 M. Initial neptunium concentrations were 3.5×10^{-7} and 1.7×10^{-5} M. pH of solutions was approximately 7. Thermodynamic calculations showed that the dominant neptunium species in such solutions is NpO_2^+.

The suspensions of the kaolinite in Np-bearing sodium chloride solutions were prepared in plastic test-tubes. The weight portions of the kaolinite (M) were 0.1 and 0.2 g, the volume of solutions (V) was 10 мл. Test tubes were continually shaken in a shaker. Neptunium distribution coefficients $K_d = {(m_{init} - m_{equil})V} \big/ {m_{equil} M}$ were calculated based on decrease of initial aqueous neptunium concentration. The heterogeneous systems in test-tubes were centrifuged, and the dry targets were prepared from the 0.2 ml aliquots of solutions for radiometric determination of neptunium. The correction coefficients were determined experimentally to take into account alpha absorption by salt layers. To be sure of the absence of colloid forms of neptunium, we carried out additional ultra micro filtration of solutions

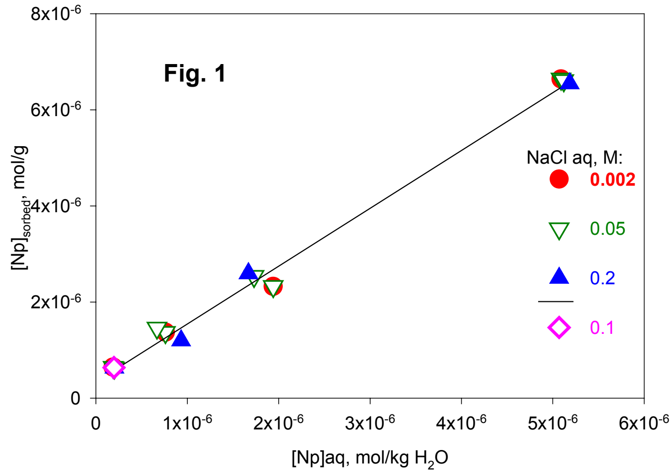


Fig. 1

Kinetics of sorption and desorption were studied. It was shown that during direct sorption equilibria established in approximately two weeks. Sorption is reversible.

The first series of the experiments was carried out after preliminary saturation of sorptive positions of the kaolinite with respect to Na^+-ions by the technique [1]. The value of distribution coefficient of neptunium for the Na-saturated kaolinite is about 10^3 ml/g, but it does not depend on aqueous sodium concentration (Fig. 1). This is why we carried out all further experiments without preliminary saturation with sodium.

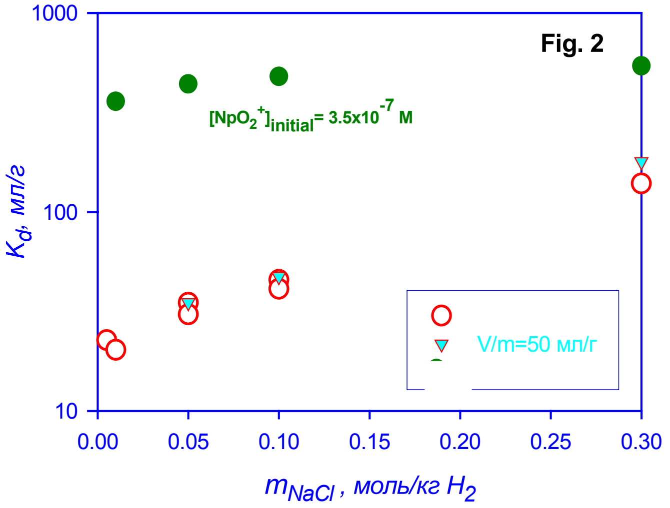


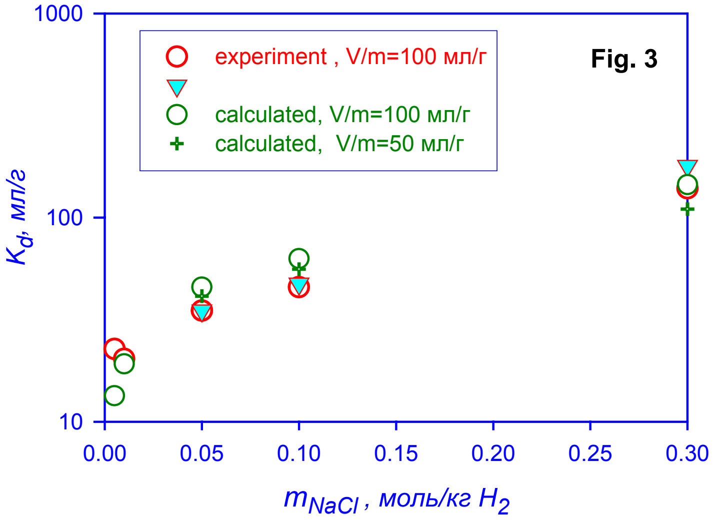
Fig. 2

The experimental isotherms of neptunium sorption on the original kaolinite from sodium chloride solutions are shown in Fig. 2 as a function of aqueous NaCl concentration. One can see that 1) neptunium distribution coefficients significantly decrease as initial neptunium content increases, which may be explained by limited sortive capacity of the kaolinite; sorption of neptunium increases as sodium chloride concentration increases, which is in contrary to NpO_2^+ - Na^+ ion exchange model.

The observed peculiarities may be described by the following ion exchange chemical reaction: $NpO_2^+ + nNa^+ + (1+n)M^+{}_{сорб.} = (NpO_2^+ nNa^+)_{сорб.} + (1+n)M^+$, where M^+ is some tentative ion formally entered for electro neutrality. In other words it is supposed that the complex $(NpO_2^+ nNa^+)_{сорб.}$ is formed on the surface of the kaolinite. The equilibrium constant of the reaction may be written as:

$$K = \frac{\left[(NpO_2^+ nNa^+)_{сорб.}\right] \cdot a_{M^+}^{(1+n)}}{m_{NpO_2^+} \cdot \gamma_{NpO_2^+} \cdot a_{Na^+}^{n} \cdot \left[M^+_{сорб.}\right]^{(1+n)}}; K^* = \frac{K_d}{\gamma_{NpO_2^+} \cdot a_{Na^+}^{n} \cdot \left[1 - \frac{(1+n)(NpO_2^+ nNa^+)_{сорб.}}{C}\right]^{(1+n)}}, \qquad (1)$$

were C is a sorptive capacity, g-eqv/kg, m, a, and γ are molalities, activities and activity coefficients of the respective ions, $K^* = K \cdot a_{M^+}^{(1+n)}$. Activity coefficients of NpO_2^+ were calculated using S.I.T. model (interaction parameter $\varepsilon(NpO_2^+, Cl^-) = 0.09$ according to [2]), activity coefficients of Na^+ were calculated by Pitzer model.



As a result of approximation of the experimental data by equation (1) the parameters of the model for above chemical reaction were estimated. ***K****=377; n=0.58; C=5.1x10^{-3} г-экв./кг. σ=1.52.

Comparison of the experimental and calculated values of Kd is shown in Fig.3. The proposed model is formal, but it has some chemical meaning, reflects specific features of sorption and describes experimental results with good enough accuracy.

Conclusions

1. Experimental study of neptunium (V) sorption on the kaolinite from sodium chloride solutions showed that distribution coefficients of neptunium increase as aqueous NaCl concentration decreases, which is in contradiction with the model of NpO_2^+ - Na^+ ion exchange.
2. The formal model of sorption of the complex ($NpO_2^+ nNa^+$) on the positions of the limited sorptive capacity of the kaolinite is proposed. Parameters of the model are estimated.

US DOE-RAS Project RG0-20100 RW40 and Project RFBR N 03-05-64284

References

1. *Wahlberg J.S. and Fishman M.J.* Absorption of cesium on clay minerals // Geological Survey Bulletin 1140-A. Washington DC, 1962.
2. Chemical thermodynamics of neptunium and plutonium. R. J. Lemire (Chaiman) // Nuclear Energy Agency. Elsevier, 2001.

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-9e.pdf
Published on July, 1, 2004