

## SORPTION OF $\text{UO}_2^{2+}$ ON CALCIUM CARBONATE

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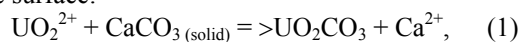
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Uranium migrates in biosphere mainly in aqueous medium. It presents there in the form of  $\text{UO}_2^{2+}$  ion and its complex compounds, with except for anaerobic conditions. Sorption processes serve the main factor, that control uranium contents in natural waters. A large number of research considered sorption of uranium(VI) on various natural materials. Besides that, many problems remain deficiently investigated. In particular, it relates to sorption of uranium (IV) on calcium carbonate – one of the major rock-forming mineral in the Earth's crust. Reference [1] notes, that sorption of uranium(VI) on calcium carbonate depends linearly upon the value of ratio between activities of  $\text{UO}_2^{2+}$  and  $\text{Ca}^{2+}$  in solution according to the reaction, which proceeds on a solid phase surface:



where a ">" symbol designates surface complex, that hosts sorbed uranium. However, the reaction (1) equilibrium constant was determined by the authors [1] with insufficient accuracy ( $\lg K_{U(VI)} = 5.12 \pm 0.53$ ), that confines application of gained results to applied research in uranium geochemistry and environmental science.

The proposed paper is aimed in specifying the value of equilibrium constant for reaction of  $\text{UO}_2^{2+}$  sorption on calcium carbonate. It includes also recognizing of how relation between masses of solid phase and solution affects the reaction. Some data [2] indicate, that characteristics of sorption equilibrium depend on this relation.

Calcium carbonate (calcite) of high purity with specific surface of  $0.0235 \text{ m}^2/\text{g}$  was used in experiments. Experiments embraced two runs with different concentrations of dissolved calcium. The first run was performed on initial solutions, which contained 2 mM of  $\text{HNO}_3$  and 2-10  $\mu\text{M}$  of uranium(VI). The second run operated with initial solutions, in which calcium nitrate was additionally introduced at 20 mM level of concentrations. Each run consisted of experiments performed under two values of mass ratio solid/solution: 1 to 67, and 1 to 200, respectively.

Weighted samples of calcium carbonate (1-3 g) were placed into cone flasks. After that 200 ml of initial solution were added to each flask. Open samples were intensively mixed during 4-6 hours for complete removal of excess  $\text{CO}_2$ , that originates due to  $\text{CaCO}_3$  reaction with nitric acid. Removal of  $\text{CO}_2$  was controlled via solution pH transition to a steady value. Reaction of  $\text{CaCO}_3$  with  $\text{HNO}_3$  increased  $\text{Ca}(\text{NO}_3)_2$  concentrations by 1 mM. As a result, the total content of dissolved calcium amounted for the first run and for the second run 1 and 21 mM, corre-

spondingly. Simultaneously, mass of  $\text{CaCO}_3$  after its partial dissolution decreased in all experiments by 0.02 g, i.e. not more than by 2% from the initial sample weight (1-3 g). After removal of  $\text{CO}_2$  samples were closed, and were intensively mixed during two months. Preliminary kinetic experiments showed, that sorption attained equilibrium in 1-2 weeks. After exposition time finished, samples were filtered through dense paper filter. Values of pH and residual concentration of uranium(VI) were determined in filtrate applying potentiometry and colorimetry with arsenazo III, correspondingly.

Experimental results indicate, that values of specific sorption ( $\Gamma_{U(VI)}$ ,  $\mu\text{mol U/g}$ ) rise linearly with increase in equilibrium concentration of dissolved uranium ( $[\text{U(VI)}]$ , mM), not depending on mass relation between solid phase and solution. Relatively, proportional coefficient  $k$  for the regularity

$$\Gamma_{U(VI)} = k [\text{U(VI)}] \quad (2)$$

decreases with growth of calcium contents in solution: when calcium concentration is equal to 1 mM  $k=0.0066$ , but when calcium concentration is equal to 21 mM  $k=0.0053$ . Dependence of uranium(VI) sorption from calcium concentration in solution was recognized as well in reference [1]. According to the results presented there, the value of specific sorption is a function of ratio between activities of  $\text{UO}_2^{2+}$  and  $\text{Ca}^{2+}$  ions.

Based on our experimental data, linear increase of uranium(VI) specific sorption with growth of ratio between activities of  $\text{UO}_2^{2+}$  and  $\text{Ca}^{2+}$  ions in solution was established (fig. 1). The increase is described by the common equation for all experiments:

$$\Gamma_{U(VI)} = K \frac{a_{\text{UO}_2^{2+}}}{a_{\text{Ca}^{2+}}}, \quad (3)$$

where  $\Gamma_{U(VI)}$  is specific sorption for a unit of sorbite mass,  $\text{mol U/g CaCO}_3$ ;  $\alpha_{\text{UO}_2^{2+}}$  and  $\alpha_{\text{Ca}^{2+}}$  are activities of  $\text{UO}_2^{2+}$  and  $\text{Ca}^{2+}$  ions, respectively;  $K$  is proportional coefficient, equal to  $0.0401 \pm 0.0039 \text{ mol/g}$ . If sorption is referred to a unit of sorbite surface, equation of dependence looks as follows:

$$\Gamma'_{U(VI)} = K' \frac{a_{\text{UO}_2^{2+}}}{a_{\text{Ca}^{2+}}}, \quad (4)$$

where  $\Gamma'_{U(VI)} = \Gamma/S$  is specific sorption for a unit of sorbite surface,  $\text{mol U/m}^2$ ,  $S$  is specific surface of  $\text{CaCO}_3$ , equal to  $0.0235 \text{ m}^2/\text{g}$ ,  $K'$  is proportional coefficient, equal to  $1.71 \pm 0.16 \text{ mol/m}^2$ .

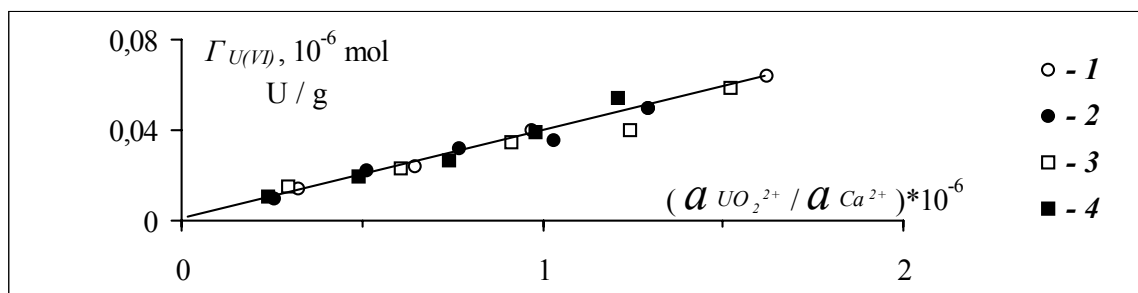


Fig. 1. Dependence of uranium(VI) specific sorption from ratio between activities of  $\text{UO}_2^{2+}$  and  $\text{Ca}^{2+}$  ions: **1** is 1 mM  $\text{Ca}(\text{NO}_3)_2$ , solid / solution ratio 1: 200; **2** is 21 mM  $\text{Ca}(\text{NO}_3)_2$ , solid / solution ratio 1: 200; **3** is 1 mM  $\text{Ca}(\text{NO}_3)_2$ , solid / solution ratio 1: 67; **4** is 21 mM  $\text{Ca}(\text{NO}_3)_2$ , solid / solution ratio 1: 67

The sorption value was determined in reference [1] as mol fraction of uranium in surface phase:

$$\chi_{U(VI)} = \frac{[>\text{UO}_2\text{CO}_3]}{[>\text{UO}_2\text{CO}_3] + [>\text{CaCO}_3]} \approx \frac{[>\text{UO}_2\text{CO}_3]}{[>\text{CaCO}_3]} = K_{U(VI)} \frac{a_{\text{UO}_2^{2+}}}{a_{\text{Ca}^{2+}}} \quad (5)$$

where  $K_{U(VI)}$  is sorption equilibrium constant, equal to  $10^{5.12 \pm 0.53}$ . According to [1], for pure calcite  $[>\text{CaCO}_3] = 8.31 \cdot 10^{-6} \text{ mol/m}^2$ . When uranium(VI) concentrations in solution are at low level,  $[>\text{UO}_2\text{CO}_3] \ll [>\text{CaCO}_3]$ , so the  $\Gamma'_{U(VI)}$  value in equation (4) may be expressed in terms of parameters for equation (5):

$$\begin{aligned} \Gamma'_{U(VI)} &= [>\text{CaCO}_3] K_{U(VI)} \frac{a_{\text{UO}_2^{2+}}}{a_{\text{Ca}^{2+}}} = \\ &= (0.32 \div 3.71) \frac{a_{\text{UO}_2^{2+}}}{a_{\text{Ca}^{2+}}} \end{aligned} \quad (6)$$

Comparison of equations (4) and (6) shows, that the value of proportional coefficient  $K'$ , that were gained in our experiments ( $1.71 \pm 0.16 \text{ mol/m}^2$ ), is in a good agreement with the value range  $0.32 \div 3.71 \text{ mol/m}^2$  referenced by [1].

1. Carroll S. A., Bruno J. // *Radiochim. Acta*. 1991. Vol. 52/53. P. 187–193.
2. McKinley J. P., Jenne E. A. // *Environ. Sci. Technol.* 1991. Vol. 25. P. 2082–2087.