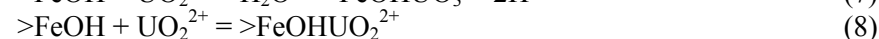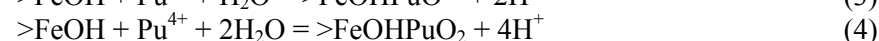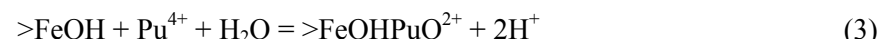# ADSORPTION OF U(VI) AND PU(IV, V) ONTO FERRIC OXYHYDROXIDES

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As a rule, concentrations of natural and "anthropogenic" actinides in the environment are low enough, but even this quantity may be destructive for the biosphere owing to the chemical and/or radiation impact. Therefore, in the systems in which these elements are microcomponents (without forming their own phases) a reliable quantitative prediction of their transport is impossible without taking into consideration the adsorption onto widespread sedimentary Fe(III) oxyhydroxides of $Fe_2O_3 \cdot H_2O_{(am)}$, hematite $\alpha\text{-}Fe_2O_3$ and goethite $\alpha\text{-}FeOOH$ type.

For the purpose of radionuclide adsorption modeling, the Gibbs free energy minimization computer code "HCh" [1] was used in combination with a simple non-electrostatic surface complexation approach [2]. Within the scope of this approach, the surface protonation/deprotonation and complexation with actinide reactions for iron oxides can be described by equations of the following form:

$$>FeOH + H^+_{aq} = >FeOH_2^+ \qquad (1),$$
$$>FeOH = >FeO^- + H^+_{aq} \qquad (2).$$

$$>FeOH + Pu^{4+} + H_2O = >FeOHPuO^{2+} + 2H^+ \qquad (3)$$
$$>FeOH + Pu^{4+} + 2H_2O = >FeOHPuO_2 + 4H^+ \qquad (4)$$

$$>FeOH + PuO_2^+ = >FeOHPuO_2^+ \qquad (5)$$
$$>FeOH + PuO_2^+ + H_2O = >FeOHPuO_3^- \qquad (6)$$

$$>FeOH + UO_2^{2+} + H_2O = >FeOHUO_3 + 2H^+ \qquad (7)$$
$$>FeOH + UO_2^{2+} = >FeOHUO_2^{2+} \qquad (8)$$

where $>FeOH$ is a functional group on the surface of iron oxide and Pu^{4+}, PuO_2^+ and UO_2^{2+} are aqueous species that sorb onto the surface to form complexes with the stehiometry suggested by [2, 3, 4, 5, 6].

For the calculations with the aid of the "HCh" code the following admissions have been made:
1) With the assumption of a "conditional insolubility" of Fe(III) phases at 25°C and in the near neutral solutions, the passing of the respective reactions was "suppressed", i.e. all solid phases besides those concerned with the surface $>FeOH$ functional group were withdrawn.
2) Zero value was allocated for the free energy of $>FeOH$ and another values were calculated using the constants of equations (1 – 8) from Table 1.
3) The non-electrostatic model assumes that electrical charge at mineral surfaces does not effect surface complexation of ions which form intersphere complexes. Therefore, adsorption is only a function of concentration of surface $>FeOH$ functional group and chemistry of solution.
4) The concentration of $>FeOH$ functional group was calculated by formula:

$$N_{tot} = N_s \cdot A \cdot C_s \cdot 1/N_A \cdot 10^{18}, \qquad (9)$$

where N_s (site/nm^2) is the total number of sites, A is the specific surface area (m^2/g), C_s is the concentration of solid mineral in the aqueous dispercion (g/l), N_A – is Avogadros number $(6,02252 \cdot 10^{23})$, and the factor 10^{18} converts nm^2 to m^2.

The free energy of formation of U- and Pu-species was compiled according to [7, 8].

Rather good correspondence of calculated and experimental values was achieved as a result (Fig. 1, 2). In the following simulations systematic calculations will be carried out in the systems with variable concentrations of microcomponents (radionuclides) and basic electrolyte ions including carbonate ion.

Table 1.

Surface complexation reaction constants for iron (III) oxyhydroxides according to [1, 9].

№ $_{reac}$	1	2	3	4	5	6	7	8
logK	7.29	-8.93	9.25*	-1.29	4.79	-10.66	-3.05	6.63

* this value was selected to fit experimental data of [2] instead 6.93.
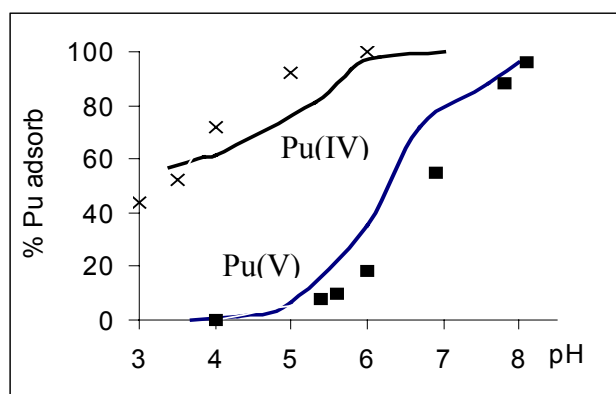
Fig. 1. Calculated adsorption of Pu (IV and V) on α-FeOOH (solid lines) in comparison with experimental data from [3] (crosses and squares). The lines represent the data fit using total Pu(IV) = 10^{-11} mole/l, 0.5g/l of solid and its specific surface area is 50 m^2/g.
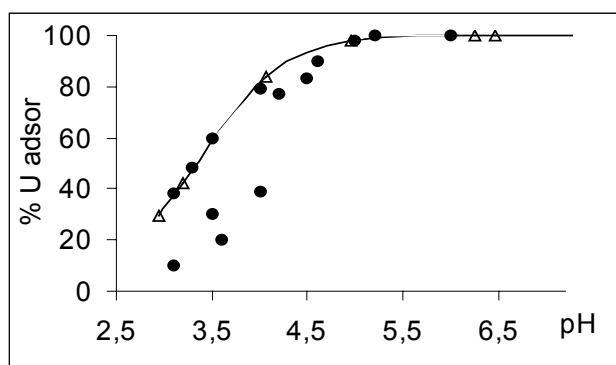

Fig. 2. Calculated adsorption of U(VI) on $Fe_2O_3 \cdot H_2O_{(am)}$. (triangles on the line) in comparison with experimental data from [5] (points). The line represents the data fit using total U(IV) = 10^{-5} mole/l, 1g/l of solid and its specific surface area is 600 m^2/g.

Preliminary results using the non-electrostatic model indicate that the iron oxyhydroxide surfaces can significantly reduce the U(VI) mobility even at pH = 4. At the same pH value, only 2% of PuO_2^+ (basic valence form of Pu in surface environment) is connected with the surface of α-FeOOH.. Plutonyl ion leaves a solution almost entirely only at pH 7 - 8. If the reduction of Pu(V) to Pu(IV) occurred in solution [3] or in the reduced environment, the removal of 60-70% of Pu(IV) could be expected.

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