# QUANTITATIVE ESTIMATION OF THE DEGREE OF HEAVY METALS AND RADIONUCLIDES ADSORBTION ON THE SURFACE OF POORLY SOLUBLE OXIDES

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Migration of heavy metals and radionuclides is strongly reduced by sorption reactions on the surface of Fe (hydr)oxides. Moreover, these Fe-compounds are widespread and the most effective natural sorbents. This work deals with the comparative evaluation of adsorptive ability of three main Fe(III) minerals with respect to some divalent cations.

The conception of Sahai and Sverjensky [1, 2] is assumed *a priori* as a thermodynamic basement of our model. The $\log K^0_{298}$ values of all surface complexes (except of uranyl-ion [3]) and the properties of solid Fe phases are taken from the same papers to achieve the internal data consistency. It is caused not only by significant variability of experimental data of different investigators but it is also caused by their frequent inconsistency. This conception involves the crystallochemical approach and the Born solvation theory as a version of a single-site (all sites are considered to be energetically equivalent) triple-layer model of surface complexation. The principal point of this concept is that characteristics of the bulk solid (the Pauling electrostatic bond strength) may be projected to the surface of each solid phase.

**Table 1**

**Association constants for surface complexes and the properties of Fe (hydr)oxides**

| Reaction | $\log K^0_{298}$ Hematite | $\log K^0_{298}$ Goethite | $\log K^0_{298}$ $Fe(OH)_{3(am)}$ |
|---|---|---|---|
| $>FeOH + H^+ = >FeOH_2^+$ | 5.7 | 6.6 | 6.6 |
| $>FeOH = >FeO^- + H^+$ | -11.3 | -12.2 | -12.2 |
| $>FeO^- + Zn^{2+} = >FeOZn^+$ | - | 5.63 | - |
| $>FeO^- + Cd^{2+} = >FeOCd^+$ | - | 6.06 | - |
| $>FeO^- + Pb^{2+} = >FeOPb^+$ | - | 6.40 | - |
| $>FeO^- + UO_2^{2+} = >FeOUO_2^+$ |  | 2.56 |  |
| $>FeOH + UO_2^{2+} + H2O = >FeOUO_2OH + 2H^+$ |  | -8.0 |  |
|  | $\log K^0_{298}$ | A, $m^2/g$ | $N_s$, sites/$nm^2$ |
| $Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$ | -4.008 | 32 | 22 |
| $FeOOH + 3H^+ = Fe^{3+} + 2H_2O$ | -1.0 | 45 | 16.4 |
| $Fe(OH)_{3(am)} + 3H^+ = Fe^{3+} + 3H_2O$ | 4.891 | 600 | 11 |

**Table 2**

**Association constants for hydroxy complexes**

| Reaction | $\log K^0_{298}$ |
|---|---|
| $Zn^{2+} + H_2O = Zn(OH)^+ + H^+$ | -8.96 |
| $Cd^{2+} + H_2O = Cd(OH)^+ + H^+$ | -10.08 |
| $Pb^{2+} + H_2O = Pb(OH)^+ + H^+$ | -7.7 |
| $Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$ | -2.19 |
| $Fe^{3+} + 2H_2O = Fe(OH)_2^+$ | -5.67 |
| $Fe^{3+} + 3H_2O = Fe(OH)_3^0$ | -12.56 |
| $Fe^{3+} + 4H_2O = Fe(OH)_4^-$ | -21.6 |
| $UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$ | -5.2 |

Consequently, the model with unique type of surface complex for heavy metals is postulated (Table 1). For uranium they are $>FeOUO_2^+$ and $>FeOUO_2OH$ because of the reaction of its hydrolysis take place at rather low pH. As the acid-base properties of the sorbent surfaces should be taking into account, the reactions of protonation – deprotonation are given in Table 1 too and association constants for cation-hydroxy complexes – in Table 2. The metals uranyl-ion concentration have been chosen as low as $10^{-5}$ m to avoid the saturation of the solution with respect to all solid phases of trace elements. Preliminary calculations were carried out with the aid of WATEQ4F computer code [4].

The special chemical equilibrium code was used to solve the system of equations linking the mass action law, equations for material balance and the equation for the calculations of the total number of sites. The acidity – alkalinity was adjusted by the adding of $H_2SO_4$. The potentialities of the suggested method is demonstrated in the Fig. 1 (a – d).

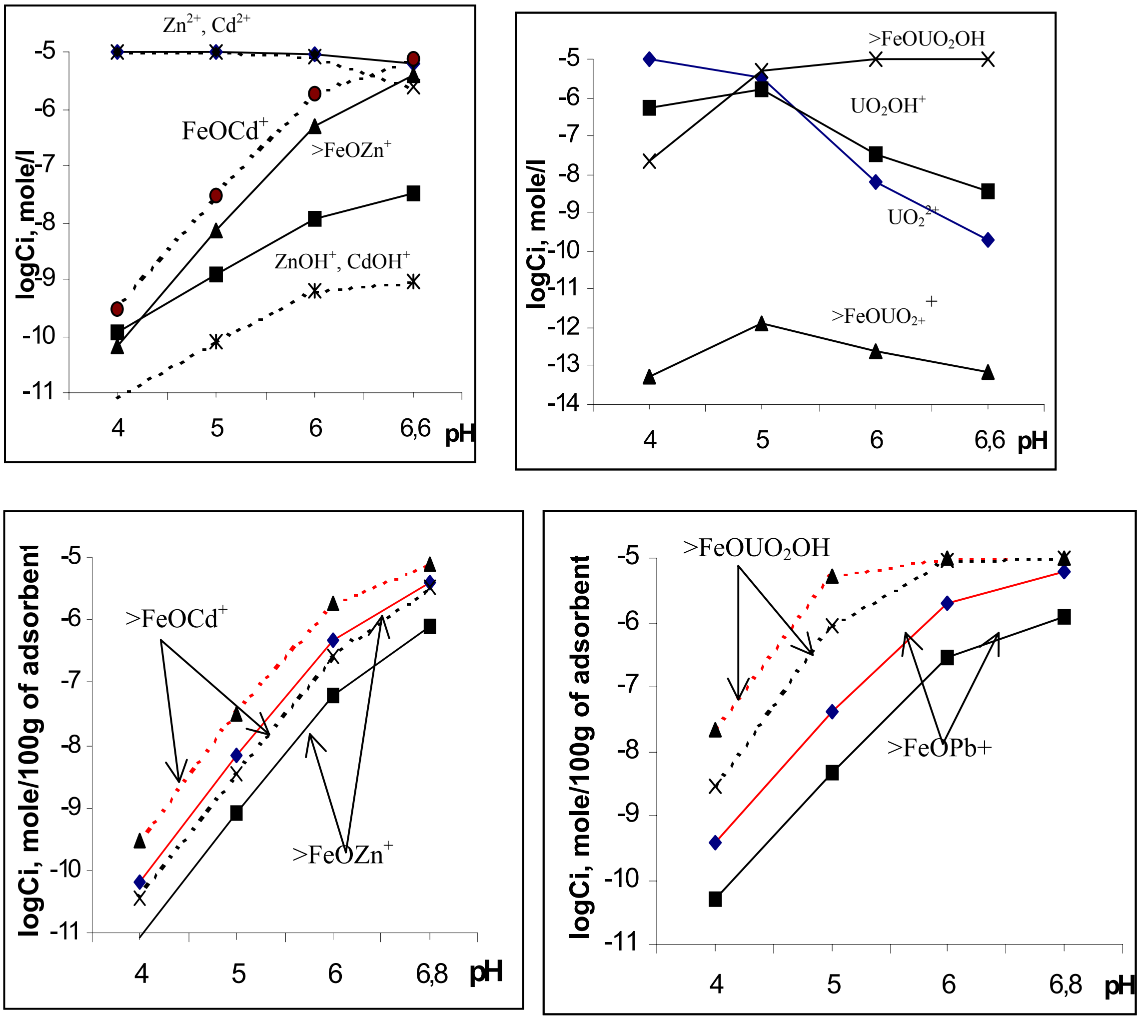

**Fig.1.** Variation of species concentrations in aqueous solution and on the surface as a function of pH. Total metal concentration was $10^{-5}$ mole/l, total solid concentration was 100 g/l.
a – for Cd (dotted line) and Zn (solid line) on the $Fe(OH)_{3(am)}$;
b – for $UO_2^{2+}$ taking into consideration the presence of neutral and charged complexes on the $Fe(OH)_{3(am)}$;
c – for the surface complexes of Cd (dotted line) and Zn (solid line) on the $Fe(OH)_{3(am)}$ (red colored lines) and on the FeOOH (black colored lines);
d – for the dominant uranium surface complex (dotted line) and for Pb (solid line) on the $Fe(OH)_{3(am)}$ (red colored lines) and on the FeOOH (black colored lines).

## References

1. *Sahai N., Svergensky D.A.* 1997. Geochim. et Cosm. Acta. V.61, N 14, P.2801-2826.
2. *Sahai N., Svergensky D.A.* 1997. Geochim. et Cosm. Acta, V.61, N 14. P.2827-2848.
3. *Ball J.W., Nordstrom D.K* 1991. User's manual for WATEQ4F, with revised thermodynamic database and test cases. US Geological Survey, Menlo Park, California.
4. *Hsi C.-K.D., Langmuir D.* 1985. Geochim. et Cosm. Acta. V.49. P.1931-1941.