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Cesium, strontium, europium(III) and plutonium(IV) complexes with humic acid in solution and on montmorillonite surface

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The effect of Aldrich humic acid (HA) on the mobility of ^{137}Cs, ^{85}Sr, ^{152}Eu and ^{239}Pu radionuclides was studied in Ca-montmorillonite suspensions. Verified 2-sites-2-species (2s2s) models correspond to an intensive interaction of all elements with humificated surface, what is in a remarkable contrast with the weak complexation of cesium and even strontium in solutions – the neutral ligand interaction constants β (l/mol) are log $\beta<-9.9$ and 7.56±0.21 for Cs and Sr, respectively. The result for europium complexation in solution, $\log\beta = 12.49\pm0.18$ is in a good agreement with literature data. For plutonium(IV) not only a high proton competitive constant in solution was obtained, $\log\beta = (-0.67\pm 0.32)+3\mathrm{pH}$, but also a strong chemisorption, which at high concentrations of humic acid (above 0.05 g/l) indicates the formation of bridge humate complexes of plutonium on the humificated surface. Logarithms of heterogeneous interaction constants ($\tilde{\beta}_{10}$, l/g) of the elements with surface humic acid are 4.47±0.23, 4.39±0.08, and 6.40±0.33 for Cs, Sr, and Eu(III), respectively, and the logarithm of the proton competitive constant ($\tilde{\beta}_{24}$, l/g) for Pu(IV) –3.80±0.72. Distribution coefficients of humic acid and metal humates between 0.01 g HA/l solution and montmorillonite were derived as $\log K_d(\mathrm{AH}) = -1.04\pm0.11$, $\log K_d(\mathrm{EuA}) = 1.56\pm0.11$ and $\log K_d(\mathrm{PuA}) = 2.25\pm0.04$, while the values for Cs and Sr were obtained with very high uncertainty. Speciation of the elements on montmorillonite surface is illustrated as a function of equilibrium concentration of humic acid in solution and of pH.

Introduction

In a previous paper,[1] the difference between distribution ratios of Cs and Sr ions on a free and humic acid coated ("blocked") alumosilicate surface was found to be less pronounced than expected, and no substantial complexation of the ions in solution was observed. Especially for cesium it was difficult to make the difference between the interaction with humificated surface and interactions with humic acid in solution, as reported for contaminated Chernobyl soil.[2] We decided to make a comparative study with polyvalent cations Eu^{3+} and Pu^{4+} with a regular humic acid (Aldrich)[3,4] and a well-defined montmorillonite (Jelšový potok, Slovakia),[5–8] and to verify a model describing their behavior in humic acid – alumosilicate system with a minimal number of parameters.[9] Results of the complexation of strontium and europium in solutions of this humic acid may be also compared with those of several other reports.[10–23] Unfortunately, quantitative data for plutonium(IV) are scarce and are mostly simulated by Th(IV) behavior. Generally, it is recognized that under deep underground conditions the reduction of PuO_2^{2+} to Pu^{4+} by humic acid would be very fast.[24,25] The same occurs in seawater,[26] presumably due to the presence of quinhydrone functional groups in the humic structure.[27] In the reducing conditions of a geological repository in clay[28] or in river estuary[29] plutonium is expected to be trivalent or tetravalent. A considerable effort, supported by international projects[30] is oriented towards the assessment of plutonium properties at waste disposal sites. Published data quantify plutonium in various humates-containing environmental matrices: the humic and fulvic acids of soils, sands and clays.[31–36] It was found that plutonium accumulates in the clay–high molecular weight fractions of humic acids where it remains undissolved at their organic solvent extraction.[32] On the other hand, the transport with smaller organic fractions occurs in sandy aquifers.[34] Humic acid causes considerable increase of plutonium fluxes in clay layers[28] but not in cement pore water[33] and also enables passing of colloidal particles through quartz sand.[35] Humic substances dominate actinide (thorium, uranium, plutonium and americium) speciation at pH 4–7 and concentration of humic substances above 0.1 mg/l in absence of calcium and aluminum cations, and at 3–10 mg/l in their presence.[37,38] Interaction constants for Pu(IV) with a sediment humic acid were obtained by the solvent extraction method of CHOPPIN and ALLARD[39] to be $\log\beta_1 = 9.8$ and $\log\beta_2 = 16.0$ for 1:1 and 1:2 stoichiometry. The constants for Pu(III) with a non-defined humic acid were found by MAHAJAN et al.[40] to be $\log\beta_1 = 2.8$ and $\log\beta_2 = 5.0$.

In a previous paper, the Sips isotherm for humic acid sorption, and two-site distribution model of ion sorption were found to suit well for description of mobility of cesium and strontium ions as a function of equilibrium humic acid concentration as the single variable at given pH.[1] Now, an extended 2-sites-2-species model of M^{z+} ion adsorption and chemisorption in presence of humic acid[9] was applied.

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Experimental

Humic acid, other chemicals and radionuclides

The studied humic acid (HA) was a commercially available sodium salt humic acid (Aldrich™), and was used without further purification. The characteristic ratio of absorbencies at 465 and 665 nm, referred to as the E_4/E_6 ratio[1] had a value of 5.0 for the humic acid used.

Strontium-85 was obtained from Dupont de Nemours (Brussels), ^{137}Cs and ^{152}Eu were products of Polatom (Otwock-Swierk). Plutonium-239 came from the Czech Institute of Metrology, Prague, as a standardized acidic solution ER25 of Pu(IV) in 2M HNO_3 with volume activity of 82.38 $kBq \cdot g^{-1}$.

All other chemicals were of AR purity grade (Lachema Brno, Czech Republic).

Montmorillonite

Monomineral, calcium homoionic montmorillonite, was isolated on a sedimentation device based on Andreasens pipette by JESENÁK[5] as a <2 μm fraction from a water suspension of bentonite Stará Kremnička-Jelšový potok (Kremnica Mts., Slovakia), main fractions (63%) consisted of 10–50 and 80–200 μm aggregated particles.[6] Its crystallochemical formula[7] is $(Si_{7.98}Al_{0.02})$ $(Al_{3.01}Fe_{0.23}Mg_{0.76})$ $(Ca_{0.37}Mg_{0.01}$ $Na_{0.02}K_{0.01})$ $O_{20}(OH)_4$. The natural content of isomorphous microelements in the finest clay fractions (<1 μm) of the original bentonite was found[8] to be about 60 ppm Ba, 100 ppm Sr, 55 ppm Y, 200 ppm La, and 180 ppm Zr.

Sorption performance

All stock solutions were prepared in demineralized water and adjusted to 0.01 $mol \cdot dm^{-3}$ NaCl to keep the ionic strength close to that of surface water.

Aqueous suspensions at a batch factor $V/m = 0.2$ l/g were prepared by sequential mixing of 20 mg of montmorillonite which was contacted with 0.01–0.1 g/l humic acid solution with the pH adjusted to 7–8, then adding 20 μl ^{85}Sr, ^{137}Cs or ^{152}Eu solution in 1M HCl, or 2 ml of ^{239}Pu in freshly diluted 0.04M HNO_3 solution. The metal chloride carrier concentration in the case of cesium and strontium was 10^{-4} $mol \cdot dm^{-3}$ and 10^{-5} $mol \cdot dm^{-3}$ for europium. The initial specific activities of radionuclide solutions before contact with sorbent were measured.

Suspensions were shaken in an end-over-end shaker for two hours at constant temperature (20±1 °C) under aerobic conditions. After separation of the solid and liquid phases by 10-minute centrifugation at 4000 rpm, the pH of the supernatant solution was measured (digital pH-meter OP-211/1 Radelkis, Hungary) and samples were withdrawn for equilibrium solution analysis.

Measurements

Humic acid in solutions was measured by a UV-VIS spectrophotometer (Specord, Zeiss Jena) in 1 cm quartz cuvettes. For spectrophotometric assessment, five values $\lambda = 270$, 285, 350, 465 and 665 nm were permanently used in present the work to inspect deviations from average HA composition in course of sorption. The wavelength 350 nm appeared the most representative analytical line.[1]

Gamma-active radionuclides were assayed by a well-type NaI(Tl) detector of an automatic gamma-spectrometric system Modumatic 5330 (Packard) or with a single-channel analyzer type NP-420 (MEV, Hungary).

Alpha-counting was performed by a silicon surface-barrier detector ULTRA™ Alpha Detector 600 (600 mm^2, 500 μm depletion depth) connected to a spectrometer 576-A-600UH™ (EG&G ORTEC Nuclear Instruments, USA) via a spectrum master multichannel buffer NS919. Spectrum was treated by Meastro II MCA emulation software A64-BI. Parallel samples were prepared by: (1) the co-precipitation and microfiltration with carrier neodymium hydroxide: 2 ml of supernatant solution was evaporated in a ceramic crucible under an infra-lamp and carefully ignited on a gas furnace to burn humic acid; the residue was dissolved in about 4 ml of 1M HCl, 50 μg of Nd was added as 0.5 g/l solution of neodymium chloride, and after precipitation with 0.5 ml of concentrated hydrofluoric acid a thin sample was prepared by filtering through a 0.2 μm/ø 25 mm polysulphonic microfilter HT-200 Tufryn™ (Gelman), and (2) calcination: 0.5 ml samples were gradually evaporated in smaller portions on a niobium planchet, and ashed at red heat.

Calculations

The SigmaPlot™ 5.0 program of Jandel Scientific based on the Marquardt algorithm of Gauss-Newton iteration of non-linear functions fitting was applied for model verification.

Results and discussion

Sorption model

The basic assumptions of the "2-sites-2-species" (2s2s) model were theoretically and experimentally substantiated in our previous papers[1,9] and involve the following complexation and chemisorption equilibria (Fig. 1):

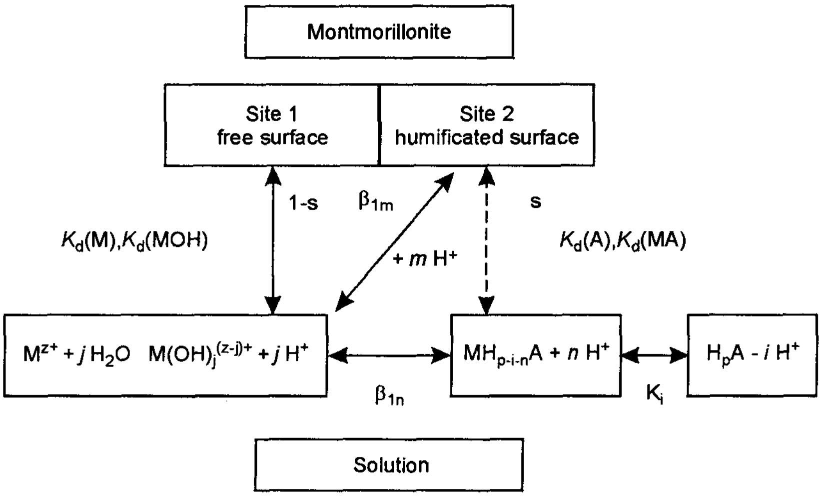

Fig. 1. "2s2s" model of metal – humic acid equilibria in solution and on surface, which were involved in modelling of complexation paramaters

Four basic equilibria: ion hydrolysis and interaction of the ions with "free" and "humificated" parts of solid surface (indicated by subscripts s1 and s2, when necessary to distinguish the two sites) the fractions of which are 1-s and s respectively. The species on the surface are given in braces.

The hydrolysis of ions,

$$M(H_2O)_x^{z+} \leftrightarrow M(H_2O)_{x-j}(OH)_j^{(z-j)+} + j\,H^+ \qquad (1)$$

which proceeds at the pH investigated maximum to the first degree ($j = 1$), the distribution of free ions between aqueous solution and solid phase,

$$M^{z+} \leftrightarrow \{M^{z+}\}, \qquad (2)$$

the distribution of hydrolyzed ions between aqueous solution and solid phase,

$$M(OH)_j^{(z-j)+} \leftrightarrow \{M(OH)_j^{(z-j)+}\}, \qquad (3)$$

and the chemisorption by complexing of ions with humificated fraction of surface,

$$M^{z+} + \{HA^{r-}\} \leftrightarrow \{MA^{u-}\} + m\,H^+. \qquad (4)$$

Now, according to the 2s2s model, the gross distribution ratio of metal can be considered as

$$D = \frac{[M^{z+}]_{s1} + [M(OH)_j^{(z-j)+}]_{s1} + [MA^{u-}]_{s2}}{[M^{z+}] + [M(OH)_j^{(z-j)+}] + [MA^{v-}]} \qquad (5)$$

For Equilibrium (1) there is hydrolysis constant

$$\beta_{0j} = \frac{[M(OH)_j^{(z-j)+}]_{s1}\, a_{H^+}^j}{[M^{z+}]} \qquad (6)$$

and for the ion distributions the partial distributions constants

$$K_d(M) = \frac{[M^{z+}]_{s1}}{[M^{z+}]} \qquad (7)$$

$$K_d(MOH) = \frac{[M(OH)_j^{(z-j)+}]_{s1}}{[M(OH)_j^{(x-j)+}]} \qquad (8)$$

To the chemisorption Equilibrium (4) corresponds a two-phase equilibrium constant (l/g),

$$\beta_{1m}^0 = \frac{[MA^{u-}]_{s2}\, a_{H^+}^m}{[M^{z+}]\Gamma} \qquad (9)$$

where the dimensionless surface concentration of humic acid Γ (g/g) can be obtained from the adsorption isotherm, e.g., the Sips isotherm,

$$\Gamma = k_1 \left(\frac{c}{k_2 + c} \right)^{n_0} = s k_1 \qquad (10)$$

where s stays for saturation degree of the surface.[1]

The best fitting constants for Aldrich acid absorption on the Jelšový potok montmorillonite at neutral pH were found[1] to be $k_1 = 0.010$ g/g, $k_2 = 5.1 \cdot 10^{-3}$ g/l, and $n_0 = 5.9$.

A sure way to find the sorption parameters of metal at zero concentration of humic acid, K_d(M) and K_d(MOH), is to investigate the distribution ratio D_0 in the absence of humic acid,

$$D_0 = \frac{K_d(\mathrm{M})[\mathrm{M}^{z+}] + K_d(\mathrm{MOH})[\mathrm{M(OH)}_j^{(z-j)+}]}{[\mathrm{M}^{z+}] + [\mathrm{M(OH)}_j^{(z-j)+}]} \qquad (11)$$

as a function of pH. However, if complexation with hydroxo ions at various pH is formalized by

$$X_{\mathrm{OH}} = \beta_{oj} a_{\mathrm{H}^+}^{-j} \qquad (12)$$

as it follows from Eq. (6), and if we use the ratio $d_0 = K_d(\mathrm{M})/K_d(\mathrm{MOH})$ then there is a new function

$$D_{10} = K_d(\mathrm{M})(1 + X_{\mathrm{OH}}/d_0) \qquad (13)$$

which can be used in evaluation of pH on free ion sorption in the model. Actually, in our case, d_0 had minor influence on the gross distribution ratio and just conventionally it was supposed to be sufficiently high (≈10), i.e., on the free alumosilicate surface the complex $\mathrm{M(OH)}_j^{(z-j)+}$ was considered to be absorbed ten times less than the more charged ion M^{z+}.

In solution the complexation of ions with humic acid proceeds,

$$\mathrm{M}^{z+} + \mathrm{a\,H_pA^{r-}} \leftrightarrow \mathrm{M(H_{ap-n}A_a{}^{v-})} + \mathrm{a\,H^+} \qquad (14)$$

for which, at equilibrium concentration of humic acid h (g/l) or c (mol/l) and electrochemical activity of hydrogen ions a_{H^+} the specific (r-charged ligand) and proton competitive constant $\tilde{\beta}^r_{an}$ (l/g) or β^r_{an} (l/mol) is

$$\beta^r_{an} = \frac{[\mathrm{MA}^{\nu-}]a^n_{\mathrm{H}}}{[\mathrm{M}^{z+}](cx_r)^a} \qquad (15)$$

or the neutral ligand interaction (competitive) constant – $\tilde{\beta}^0_{an}$ (l/g) or β^0_{an} (l/mol) for the mass and molarity concentration scale, respectively:[9]

$$\beta^0_{an} = \frac{[\mathrm{MA}^{\nu-}]a^n_{\mathrm{H}^+}}{[\mathrm{M}^{z+}][\mathrm{H_pA}]^a} \qquad (16)$$

Now, combining Eq. (5) with Eqs (6)–(16) a basic equation for modeling of our results issues as

$$D = \frac{D_{10}(1-s) + sk_1\beta^0_{1m}a^{-m}_{\mathrm{H}^+}}{1 + \beta^j_{0j}a^{-j}_{\mathrm{H}^+} + \beta^0_{1n}(cx_r)^a a^{-n}_{\mathrm{H}^+}} \qquad (17)$$

Auxiliary parameters for Aldrich humic acid were obtained from partial dissociation values of pK in the paper of ALEXIO[4] while the proton exchange capacity obtained for europium by MOULIN[41] was adopted (Table 2). The data for radionuclide hydrolysis were chosen from literature[42,43] as well.

The mathematical fitting of parameters (constants and stoichiometric coefficients) at the highly non-linear function of distribution ratios is sensitive to the initial parameters setting and constraints. Both individual and constrained, and at the end mutual and unconstrained fitting for the integer stoichiometric constants (a, m, n) was applied to the data treatment, to avoid local minima. Because of the strong correlation existing between the $\tilde{\beta}^0_{am}$ and $\tilde{\beta}^0_{an}$ constants, the unknown parameter $\tilde{\beta}^0_{an}$ was replaced by the dimensionless ratio

$$K_{mn} = \frac{\tilde{\beta}^r_{an}}{\tilde{\beta}_{am}} \qquad (18)$$

Table 1. Auxiliary radionuclide parameters

	$\mathrm{Cs^+}$	$\mathrm{Sr^{2+}}$	$\mathrm{Eu^{3+}}$	$\mathrm{Pu^{4+}}$
pH interval	7.0	7.0	6.8÷7.2	2.5÷3.2
log β_{01}	$-\infty$	–13.18	–9.30	–1.51
$\mathrm{X_{OH}}$	0	$6.6\cdot10^{-7}$	$3.2\cdot10^{-3} \div 2.0\cdot10^{-2}$	9.8÷49
D_{10}, l/kg	$(6.3\pm1.0)\cdot10^2$	$(1.25\pm0.06)\cdot10^3$	$(4.178\pm0.002)\cdot10^4$	$(8.98\pm0.02)\cdot10^4$

Table 2. Auxiliary Aldrich acid parameters. Calculated values according to dissociation constants by Reference 4. Proton exchange capacity (PEC): $3\cdot10^{-3}$ mol/g [38]

pH	2.5	3.2	6.8	7.0	7.3
1–α ($\mathrm{x_0}$)	0.885	0.601	$4.78\cdot10^{-7}$	$1.15\cdot10^{-7}$	$1.19\cdot10^{-8}$
log(1–α)	–0.053	–0.221	–6.32	–6.94	–7.92
$\mathrm{x_3}$	$1.65\cdot10^{-7}$	$1.41\cdot10^{-5}$	0.707	0.675	0.557
log $\mathrm{x_3}$	–6.78	–4.85	–0.151	–0.171	–0.254
<i>	0.12	0.41	3.0	3.2	3.3
r ($\mathrm{i_{max}}$)	0	0	3	3	3
$\mathrm{x_r}$	0.885	0.601	0.707	0.675	0.557
log $\mathrm{x_r}$	–0.053	–0.221	–0.151	–0.171	–0.254

From this ratio, as follows from the ratio of Eqs (9) and (16), the relation between distribution ratio of humic acid, K_d(HA), and metal humate, K_d(MA) can be obtained as

$$K_{mn} = \frac{a_{\mathrm{H}^+}^{(n-m)} K_d(\mathrm{HA})}{K_d(\mathrm{MA})} \tag{19}$$

where K_d(HA) can be replaced by the Γ/c ratio from a linear part of the sorption isotherm – Eq. (10). Conditionally, it was done for $c = 0.01$ g/l, when $K_d(\mathrm{HA}) = 9.06 \cdot 10^{-2}$ l/g at pH 7.0 and $I = 0.01$.

The results of data fitting are presented in Figs 2–5, and the interaction constants found for various stoichiometric constants postulated are collected in Tables 3–5. The data which were completed at a bad convergence and/or high uncertainty are placed in parentheses.

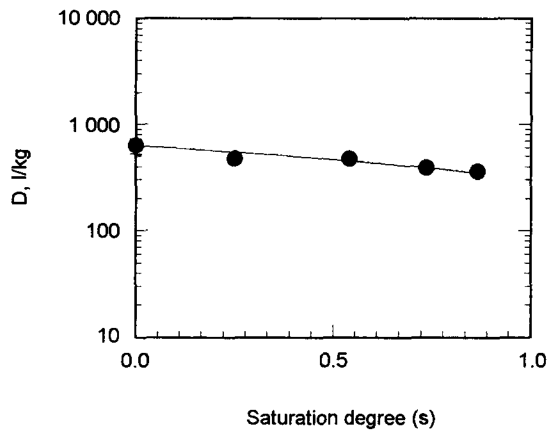

Fig. 2. Distribution ratio of cesium as a function of saturation degree of montmorillonite by humic acid (pH 7.0, $I = 0.01$); • experimental data; solid line: model calculation (Table 6)

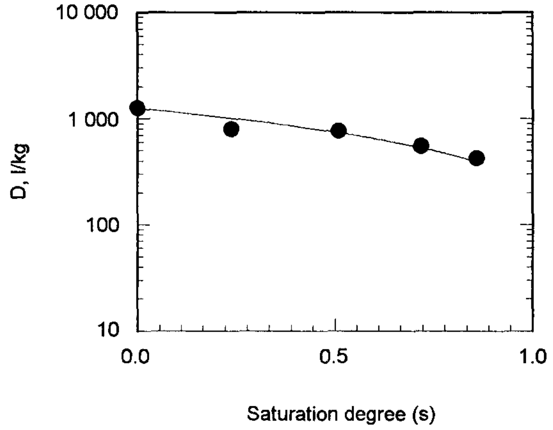

Fig. 3. Distribution ratio of strontium as a function of saturation degree of montmorillonite by humic acid (pH 7.0, $I = 0.01$); • experimental data; solid line: model calculation (Table 6)

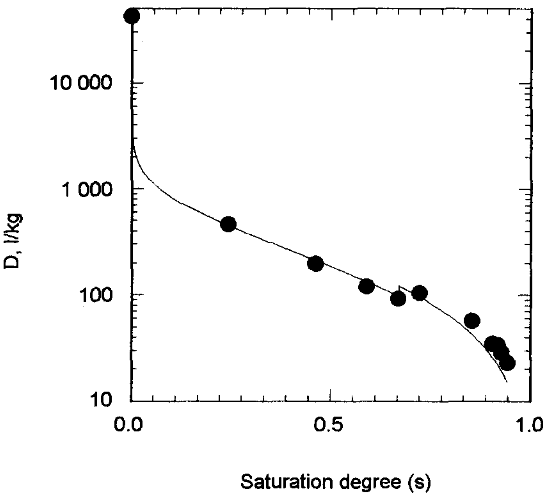

Fig. 4. Distribution ratio of europium(III) as a function of saturation degree of montmorillonite by humic acid (pH 6.8–7.3, $I = 0.01$); • experimental data; solid line: model calculation (Table 6)

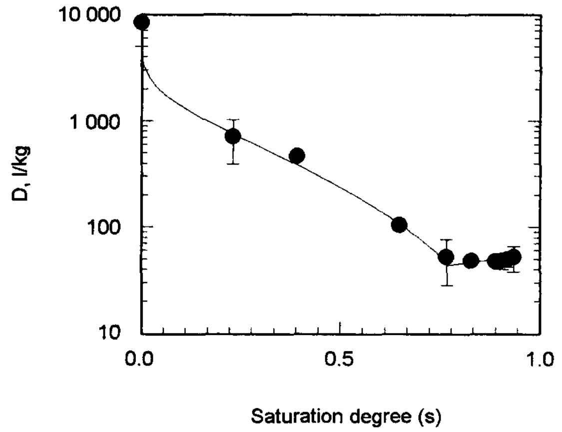

Fig. 5. Distribution ratio of plutonium(IV) as a function of saturation degree of montmorillonite by humic acid (pH 2.5–3.2, $I = 0.05$); • experimental data; solid line: model calculation (Table 6)

For cesium, no significant interaction occured if cesium ions with humic acid was obtained in humic acid (Table 5, Fig. 2) and the controversial data published for investigation of Chernobyl soil decontamination[2] are probably caused by retention of cesium on humificated surface, which we characterized in a previous paper.[1]

For strontium and europium, at the pH interval used, the model (Table 5, Figs 3 and 4) corresponds to interaction of the ions with the 3-charged humic acid anion both in solution and on the humificated surface, at pH close to 7,

$$\mathrm{M}^{z+} + \mathrm{H}_{p-3}\mathrm{A}^{3-} \leftrightarrow \mathrm{MH}_{p-3}\mathrm{A}^{(3-z)-} \tag{20}$$

Table 3. Metal – humic acid interaction constants for a 2s2s model with maximal proton competition ($n = z$)

	Cesium	Strontium	Europium	Plutonium
m	1	2	3	4
n	1	2	3	4
j	0	1	1	1
r	3	3	3	0
a	1	1	1	1
log $\tilde{\beta}_{am}$	–2.53±0.23	–9.62±1.02	–13.27	–3.43±0.80
log K_{mn}	<–23	–5.46	–2.98±0.10	–2.79
log $\tilde{\beta}^{r}_{1n}$	<–7.2	<–13.8	<7.66	–6.22±0.35
log β^{r}_{1n}	<–23.5	<–12.6	–13.73	–3.70±0.80
log β^{0}_{10}	<–16.8	<–5.8	–7.56÷–6.06	–3.70
$1/n$ log β^{0}_{10}	<–16.8	<–2.9	–2.52÷–2.02	–0.95
log K_d(MA)	(22)	4.4	1.94±0.10	1.75±0.03

Table 4. Metal – humic acid interaction constants for a 2s2s model with partial proton competition ($n = z–1$) – the best model for plutonium behavior at $a = 2$ (Fig. 5)

	Cesium	Strontium	Europium	Plutonium
m	1	2	3	4
n	0	1	2	3
j	0	1	1	1
r	3	3	3	0
a	1	1	1	2
log $\tilde{\beta}_{am}$	–2.53±0.90	–9.61±1.02	–14.29	–3.49±0.72
log K_{mn}	(–15)	(1.63)	4.44±0.01	–3.80±0.04
log $\tilde{\beta}^{r}_{1n}$	<0.44	<–6.8	<–5.5	–3.80±0.32
log β^{r}_{1n}	<–14.3	<–5.5	<–7.3	–0.67±0.32
log β^{0}_{10}	<–7.6	<1.3	–1.16÷0.34	–0.67±0.32
$1/n$ log β^{0}_{1n}	<–7.6	<0.65	–0.40÷0.11	–0.17±0.32
log K_d(MA)	(6.3)	(–9.7)	(–12.28)	2.25±0.04

Table 5. Metal – humic acid interaction constants for a 2s2s model with ligand charge neutralization ($m = n = 0$) – the most consistent model for Cs^+, Sr^{2+}, and Eu^{3+} behavior (Figs 2–4)

	Cesium	Strontium	Europium	Plutonium
m	0	0	0	0
a	0	0	0	0
j	0	1	1	0
r	3	3	3	3
a	1	1	1	1
log $\tilde{\beta}_{am}$	4.47±0.23	4.39±0.08	6.40±0.33	0.65±0.15
log K_{mn}	(–24)	–6.1	–2.60±0.11	9.78±0.06
log $\tilde{\beta}^{r}_{1n}$	<–0.18	<0.21	3.80±0.18	10.43±0.09
log β^{r}_{1n}	(–16.7)	0.80±0.21	6.32±0.18	12.95±0.09
log β^{0}_{10}	(–9.9)	7.56±0.21	12.49÷13.99	17.58÷19.68
$1/n$ log β^{0}_{10}	(–9.9)	3.78	4.16÷4.66	4.39÷4.92
log K_d(MA)	(23)	(5)	1.56±0.11	–10.82±0.06

Table 6. Resume of the best fit for the 2s2s model interaction constants (Figs 2–5) based on the auxiliary parameters of Tables 1 and 2

Element	m	a	$\log \tilde{\beta}_{am}$, l/g	n	I, mol/l	$\log \beta^0_{1n}$, l/mol	$1/z \log \beta^0_{10}$	K_d(MA), l/g
Cesium	0	1	4.47±0.23	0	0.01	<–9.88	<–9.88	–
Strontium	0	1	4.39±0.08	0	0.01	7.56±0.21	3.78	–
Europium	0	1	6.40±0.33	0	0.01	12.49±0.18	4.16	1.56±0.11
Plutonium	4	2	–3.80±0.72	3	0.05	–0.67±0.32	–	2.25±0.04
Plutonium				0	0.05	6.83÷8.93	1.70÷2.23	

When comparing the neutral ligand interaction constants (l/mol) published in literature for Aldrich humic acid: with our result for Eu(III), $\log \beta^0_{10} = 12.49 \pm 0.18$, the latter is more close to the data of TAKAHASHI[12] for a paddy-soil humic acid and the land or sea water ($\log \beta^0_{10} = 12.10 \div 14.30$ at pH 7–8, $I = 0.02$–0.7), but much higher than the values obtained for Aldrich humic acid by dialysis,[10] by ion exchange,[21] and also by ultrafiltration.[19] The reason may be in the adjusting of the original Aldrich humic acid by removing the low-molecular, dialyzable fractions,[10] and also due to the eventual equilibrium shift during the prolonged dialysis. For the ion exchange technique,[21] the covering of the ion exchanger surface by humic acid may exert considerable influence.

	pH	Ionic strength, mol/l	$\log \beta^0_{10}$	Reference
Sr(II)	4.5–5		3.22	10
Sr(II)			3.50±0.20	16
Eu(III)	3.75	0.1	8.86±1.72	18
Eu(III)	4.5	0.1	6.2	10
Eu(III)	5–6	0.1	4.5	19
Eu(III)	6.0	0.01	7.5	21
Pu(IV)				Unknown

Plutonium behavior significantly differs from europium in the region of relatively high humic acid concentrations (above 0.05 g/l). A definite plateau occurs (compare Figs 5 and 4), completely opposite to the expectation that strong complexation in solution will decrease the distribution ratio at the high degree of montmorillonite surface covering by humic acid. Such behavior can be explained in a bridge (1:2) complex formation on surface, at low pH (2.5–3):

$$Pu(OH)^{3+} + 2\{H_pA\} \leftrightarrow \{PuH_{p-5}A_2\} + 4H^+ + H_2O \quad (21)$$

In solution the "normal" competitive interaction prevails,

$$Pu^{4+} + H_pA \leftrightarrow PuH_{p-3}A^+ + 3H^+, \quad (22)$$

which is undistinguishable from a parallel equilibrium

$$Pu(OH)^{3+} + H_pA \leftrightarrow PuH_{p-4}A + 3H^+ + H_2O. \quad (23)$$

The corresponding two-phase stability constant (l/g, when c remains in g/l units) is

$$\tilde{\beta}^0_{24} = \frac{[MA_2]_{s2} a^4_{H^+}}{[M]\Gamma c(1-\alpha)} \quad (24)$$

where $1-\alpha \equiv x_0$ is the undissociated fraction of humic acid. Distribution coefficient of plutonium humate, which in correspondence with Eq. (18) is

$$K_d(PuA) = K_{43} a^{-1}_{H^+} \Gamma \quad (25)$$

indicates that plutonium(IV) humate is bound to the montmorillonite surface for a one order of magnitude (in the distribution constant terms) higher than humic acid itself.

The data are summarized in Table 6.

Conclusions

The "2-sites-2-species" model of radionuclide humates distribution between aqueous solutions containing humic acid provides consistent interaction constants of polyvalent elements with humic ligands in solution and on the alumosilicate (montmorillonite) surface. It seems to be a reasonable compromise between the interaction constants in solution and those in water – clay – humic acid systems, that can be used for radionuclide mobility assessment in the environment. A special attention deserves its applicability to a more peculiar complexation and distribution of plutonium(IV).

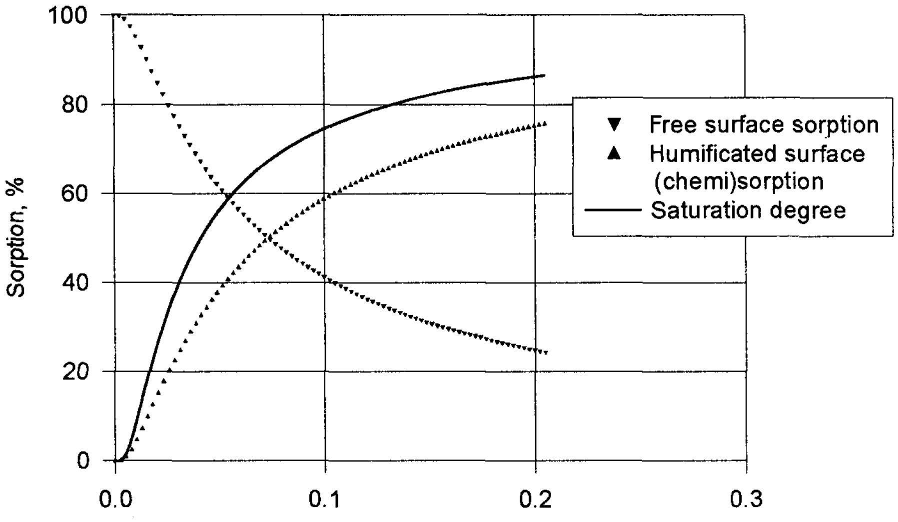

Fig. 6. Fractions of cesium on montmorillonite surface saturated by humic acid, as a function of equilibrium humic acid concentration (g/l) in solution, pH 7.0

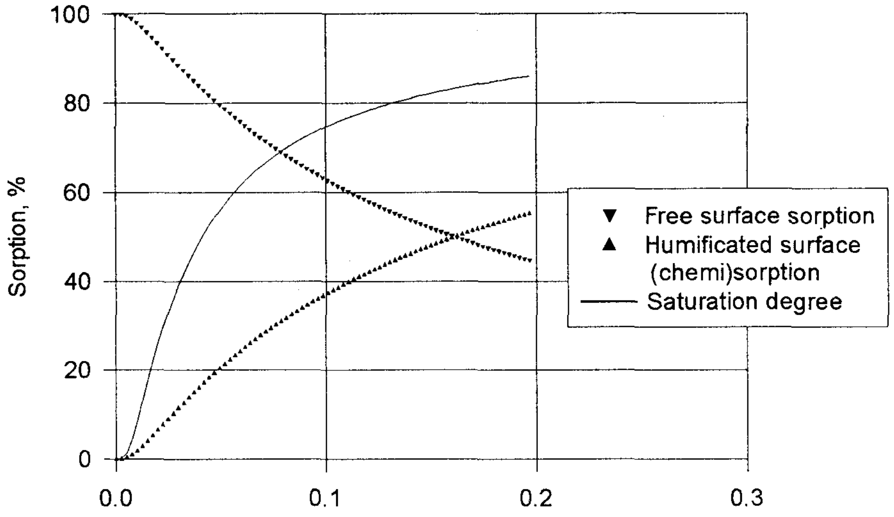

Fig. 7. Fractions of strontium on montmorillonite surface saturated by humic acid, as a function of equilibrium humic acid concentration (g/l) in solution, pH 7.0

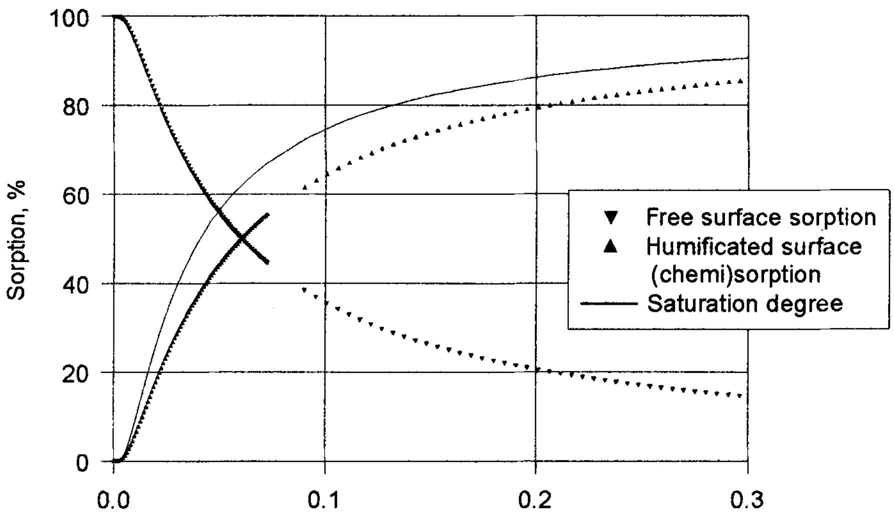

Fig. 8. Fractions of europium(III) on montmorillonite surface saturated by humic acid, as a function of equilibrium humic acid concentration (g/l) in solution

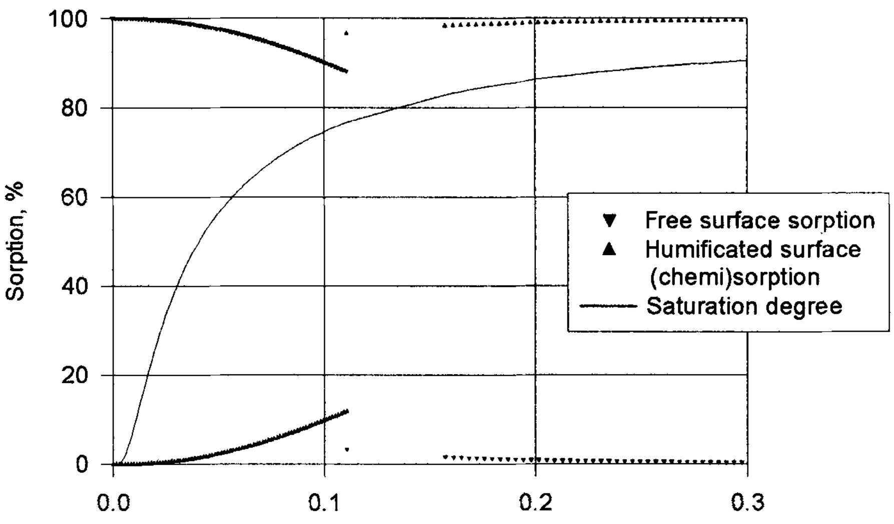

Fig. 9. Fractions of plutonium(IV) on montmorillonite surface saturated by humic acid, as a function of equilibrium humic acid concentration (g/l) in solution

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