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The Adsorption of Radionuclides on Bitumen

Part I: Strontium

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Abstract

The adsorption of $^{85}Sr^{2+}$ on bitumen emulsions with well characterized surfaces was studied as function of pH and ionic strength of the equilibrium solution. The bitumen/solution interface is negatively charged due to the deprotonation of weakly acidic carboxyl groups present at the surface. The surface group density is calculated to be $1.37 \cdot 10^{18}$ groups/m^2 and the deprotonation behaviour can be fairly well desribed by the Ionizable Surface Group Model with a $pK_H = 6.6$.

Sr^{2+} adsorbs on the bitumen by an outer sphere complexation reaction in which one surface carboxyl group is involved in the adsorption of one Sr^{2+}-ion. The adsorption depends on the ionic strength and pH of the contact solution. The higher the ionic strength, the lower the adsorption. Sorption increases with increasing pH due to the deprotonation of carboxyl groups.

In a cementitious environment, Sr^{2+} adsorption on bitumen is negligible due to the strong competition of Na^+, K^+ and Ca^{2+} present in the cement pore water.

Introduction

Bitumen is used world wide as a matrix for incorporating low level and intermediate level radioactive waste mainly because of its good leach resistant properties. When the matrix also has a significant adsorption capacity, this can be regarded as an additional positive effect which contributes to the retention of radionuclides in the near field of a repository. It is interesting for the safety assessment studies to know whether or not radionuclides do adsorb on the matrix.

The adsorption of radionuclides on bitumen has not received much attention in the past [1 – 3] and almost no information on the adsorption mechanisms is available. This work describes the adsorption of Sr^{2+} on bitumen emulsions in which the particles have well characterized surface properties as a function of pH, ionic strength and the presence of complexing ligands.

Materials and methods

Preparation and conditioning of the bitumen emulsion

About 10 g of bitumen (Mexphalt 80/100) were placed in a 500 ml flask. Approximately 400 ml of a 10^{-3} M NaOH (pH = 11) were added and the mixture heated to 80 – 90 °C and then stirred vigorously at 24000 rpm for 5 minutes by a high speed mixer (Ultra-Turrax, T-25; Janke and Kunkel, IKA). After cooling to room temperature, the emulsion was poured in an Erlenmeyer flask and left standing overnight.

A 50 ml aliquot of the emulsion was placed in a dialysis bag (Dialysis Tubing-Visking, Medicell London) and equilibrated with 10^{-3} M NaOH containing different $NaClO_4$ concentrations. The solutions were replaced 4 times at intervals of about 2 hours. After the fourth replacement, the conditioned bitumen emulsion was filtered through a 40 µm nominal pore size nylon membrane (Nytal, nylon monofilament). The filtered solution was used for adsorption experiments, dry weight determination, particle size analysis and surface group density measurements.

Dry weight determination

10 ml of the bitumen emulsion were placed in a preweighted petri-dish and dried at 50 °C for 24 hours. After correction for the presence of salts, the dry weight was calculated.

Particle size analysis

The particle size distribution of the emulsion was measured with a Coulter-Multisizer (Coulter Electronics Limited). The Coulter Counter determined the number and size of particles suspended in an electrically conducting liquid by forcing the suspension through a small aperture having an immersed electrode on either side. As a particle passes through the aperture, the resistance between the electrodes changes and produces a voltage pulse whose magnitude is proportional to the particle size. Isoton(II) was used as the conducting fluid and an orifice tube of 50 µm was selected, which has a measurement range from 1 to 30 µm. The apparatus was calibrated by latex particles with a nominal diameter of 5.8 µm. Size distributions for particles smaller than 1 µm were determined with a laser diffraction particle size distribution analyzer (Horiba LA-500). This apparatus had a measurement range from 0.1 µm to 200 µm. The specific surface area (SSA) was calculated from the size distributions assuming the particles to be spherical.

Surface group density determination

The functional group density was determined by the adsorption of $Co(NH_3)_6^{3+}$ on the bitumen surface. This technique has recently be used successfully to determine the functional group capacity of humic acids [4] and in previous studies to measure the cation exchange capacities of metal oxides [5], clay minerals [6] and polyacrylic acids [7].

$Co(NH_3)_6^{3+}$ is stable in aqueous solutions between pH 2 and 12. It adsorbs only due to Coulombic interaction and a charge reversal due to over-equivalent adsorption is excluded [5]. The negative charge on the surface is almost completely neutralized by the electrostatically adsorbed $Co(NH_3)_6^{3+}$. One mole of adsorbed $Co(NH_3)_6^{3+}$ represents three moles of negative charges on the surface [4, 5, 7]. $Co(NH_3)_6^{3+}$ can therefore be used very well to determine the functional group density on bitumen under conditions where they are completely dissociated (high pH).

An adsorption isotherm of $Co(NH_3)_6^{3+}$ on bitumen was determined. 20 ml aliquots of the bitumen emulsion, conditioned in 10^{-3} M NaOH (pH=11), were placed in teflon centrifuge tubes (Oak Ridge Type, 50 ml) and different volumes of a solution containing 10^{-4} M $Co(NH_3)_6^{3+}$ and 10^{-3} M NaOH were added. The volume in each centrifuge tube was then made up to 30 ml by 10^{-3} M NaOH. The mixtures were shaken end-over-end for 24 hours at room temperature. After equilibration, the solutions were centrifuged at 11000 g (Heraeus Sepatech, Biofuge 17S) for 30 minutes. The clear supernatant was analyzed for Co by ICP-AES. The amount of $Co(NH_3)_6^{3+}$ adsorbed was calculated from the difference in Co concentration before and after equilibrium.

Adsorption of $^{85}Sr^{2+}$

20 ml aliquots of the bitumen emulsion, conditioned in 10^{-3} M NaOH and containing different concentrations of $NaClO_4$ in the range 10^{-3} M and $9 \cdot 10^{-3}$ M, were transferred to the 50 ml teflon centrifuge tubes. 5 ml of the equilibrium solution, spiked with $^{85}Sr^{2+}$, were added. The final Sr^{2+} concentration was 10^{-10} M. The mixtures were shaken end-over-end for 24 hours whereafter phase separation was performed by centrifugation at 11000 g for 30 minutes. 2 ml of the clear supernatant were sampled and analyzed for ^{85}Sr by liquid scintillation counting (Packard, Tricarb 2250 CA) using Instagel (Packard) as the scintillation cocktail. The amount of Sr^{2+} adsorbed was calculated from the difference in concentration before and after equilibrium.

To study the pH dependency of the Sr^{2+}-adsorption, bitumen emulsions were equilibrated in dialysis bags at different pH values between 7 and 11. Because of the low buffering capacity of the bitumen emulsion, $5 \cdot 10^{-4}$ M TRIS (Tris(hydroxymethyl)-aminomethane) was used to buffer the pH in the range 7 to 8.6. Beyond pH 9, the pH was adjusted with NaOH to the desired value. The ionic strength of the solutions was fixed at 0.001 M. The same adsorption procedure was used as described earlier.

The effect of complexing substances on the adsorption of Sr^{2+} on bitumen was studied by adding NTA (nitrilotriacetic acid) to the liquid phase. The concentration of NTA was varied from 10^{-6} M to 10^{-4} M. The total Na^+ concentration amounted to $1.5 \cdot 10^{-3}$ M and the pH was fixed at 11. The adsorption was performed in the same way as described above.

Results and discussion

The emulsification described previously yields bitumen-in-water emulsions with 0.2–0.3% dry matter content. The particle diameter ranges from 0.1 to 30 μm, resulting in a specific surface area of 3.5–4.5 m^2/g.

The negative surface charge of the bitumen is caused by the deprotonation of carboxyl groups at the bitumen/water interface. The electric properties of the interface can be explained by the Ionizable Surface-Group Model [8]. A brief description of the model is given here.

For the deprotonation reaction of a carboxyl group on a surface:

$$RCOOH \rightleftharpoons RCOO^- + H^+ \quad (1)$$

the deprotonation constant is given by:

$$K_H = \frac{\{RCOO^-\}[H^+]_s}{\{RCOOH\}} \quad (2)$$

where $[H^+]_s$ is the concentration of hydrogen ions close to the surface in mol/l. The concentration of protonated and deprotonated groups on the surface is expressed as groups/cm^2. The concentration of H^+ on the surface $[H^+]_s$ is related to the bulk H^+ concentration $[H^+]_b$ by the Boltzmann equation:

$$[H^+]_s = [H^+]_b \exp(-Y_0) \quad (3)$$

where Y_0 is the reduced surface potential, defined as

$$Y_0 = \frac{e\psi_0}{kT}$$

with: e = elementary charge ($1.6 \cdot 10^{-19}$ C)
ψ_0 = surface potential (V)
k = Boltzmann constant ($1.38 \cdot 10^{-23}$ JK^{-1})
T = absolute temperature (K).

As the potential ψ_0 is negative for bitumen, the term $\exp(-Y_0) > 1$, and this implies that the hydrogen ion concentration on the surface is higher than the hydrogen ion concentration of the bulk solution, or, the surface pH is lower than the solution pH. This phenomenon has been investigated and described earlier by Danielli [9]. The difference in pH between surface and bulk solution can amount to several pH units. For instance, when the surface potential ψ_0 equals -200 mV, the pH of the surface is 4 pH units lower than the pH of the bulk solution. Weakly acidic functional groups at solid-liquid interfaces display an apparently acidic character arising from, and determined in magnitude by, the electrical potential ψ_0 generated upon ionization of the interface. As a result, the dissociation of the weakly acidic surface groups will only be complete at higher pH values in solution than would be the case for a monomeric weak acid in solution [10].

The surface charge of the bitumen is given by:

$$\sigma_0 = -e \cdot \{\mathrm{RCOO}^-\} \tag{4}$$

and the total surface density of functional groups (N_s, groups/cm^2) is:

$$N_s = \{\mathrm{RCOO}^-\} + \{\mathrm{RCOOH}\}. \tag{5}$$

The surface charge (σ_0, C/cm^2) can thus be written as:

$$\sigma_0 = \frac{-eN_s}{1 + ([\mathrm{H}^+]_b/\mathrm{K_H})\exp(-Y_0)}. \tag{6}$$

The surface charge has to be neutralized by the charge in the diffuse electrical double layer (σ_d, C/cm^2):

$$\sigma_0 = -\sigma_d. \tag{7}$$

The charge density in the diffuse double layer can be related to the surface potential by applying the Gouy-Chapman theory:

$$\sigma_d = -(8n\varepsilon kT)^{1/2} \sinh(zY_0/2) \tag{8}$$

with: n = number of counter ions per unit volume (cm^{-3})
z = valency of the counter ions
ε = permittivity of the medium (CV^{-1}cm^{-1}).

Combination of equations (6) and (8) provides an explicit relationship between surface charge and surface potential as a function of pH$_b$, the salt concentration and the amount of functional groups N_s on the surface:

$$\mathrm{pH_b} = -Y_0/2.303 + \mathrm{pK_H} - \log\left(\frac{\theta}{\sinh(zY_0/2)} - 1\right) \tag{9}$$

where $\theta = \dfrac{-eN_s}{(8n\varepsilon kT)^{1/2}}$.

This relationship enables the surface potential at a given pH$_b$, ionic strength and functional group density to be calculated. The corresponding σ_0 can be obtained by applying equation (8), assuming that $\sigma_0 = -\sigma_d$. Figure 1 displays the relationship between the level of dissociation α and the bulk pH$_b$ as a function of the salt concentration in the solution for a functional group density on the surface of $1.37 \cdot 10^{18}$ groups/m^2, with α:

$$\alpha = -\frac{\sigma_0}{e \cdot N_s}. \tag{10}$$

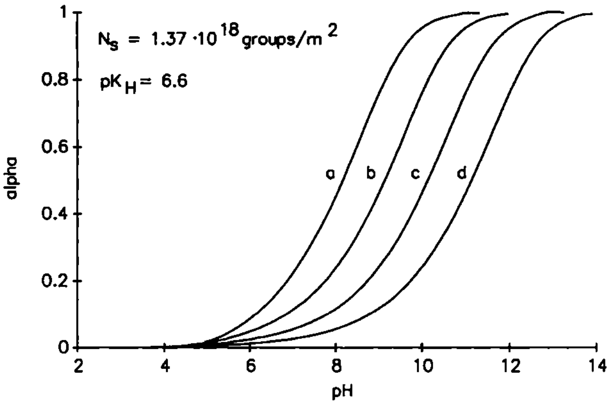

Fig. 1. Deprotonation of surface carboxyl groups on bitumen as a function of pH. Surface group density: $1.37 \cdot 10^{18}$ groups/m^2; pK$_H$=6.6. a) I=0.1 M; b) I=0.01 M; c) I=0.001 M; d) I=0.0001 M.

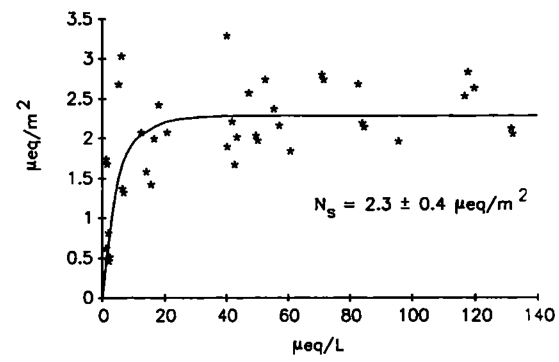

Fig. 2. Adsorption isotherm of $\mathrm{Co(NH_3)_6^{3+}}$ on bitumen at pH=11 (NaOH 10^{-3} M, T=20°C). N_s=2.3±0.4 µeq/m^2= $1.37 \cdot 10^{18}$ groups/m^2.

It is clear that the deprotonation behaviour of the carboxyl groups is complex and depends strongly on the surface group density and ionic strength of the medium.

Figure 2 shows the adsorption isotherm of $\mathrm{Co(NH_3)_6^{3+}}$ on bitumen. The adsorption isotherm shows a maximum adsorption level of 2.3±0.4 µeq/m^2. This corresponds to a carboxyl group density of $1.37 \cdot 10^{18}$ groups/m^2. From Fig. 1 we can see that at pH=11 and I=0.001 M, not all the carboxyl groups have been deprotonated. Adsorption of $\mathrm{Co(NH_3)_6^{3+}}$, however, causes the surface potential to become less negative with the consequence that a complete deprotonation occurs at a pH value lower than shown in Fig. 1. The maximum adsorption level of $\mathrm{Co(NH_3)_6^{3+}}$ thus represents the surface group density. The value of the functional group density given here is in good agreement with those reported in the literature [8]. The latter values, however, were not determined directly but were estimated by modelling experimental results of electrophoretic movement of bitumen particles.

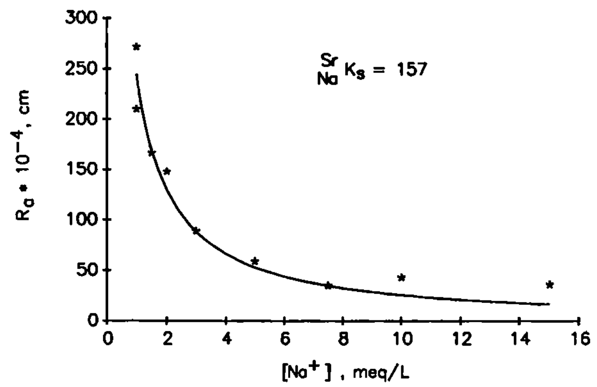

Fig. 3. Adsorption of Sr^{2+} on bitumen as a function of the Na^+ concentration in the liquid phase at pH = 11. *: experimental points, —: calculated from equation (22).

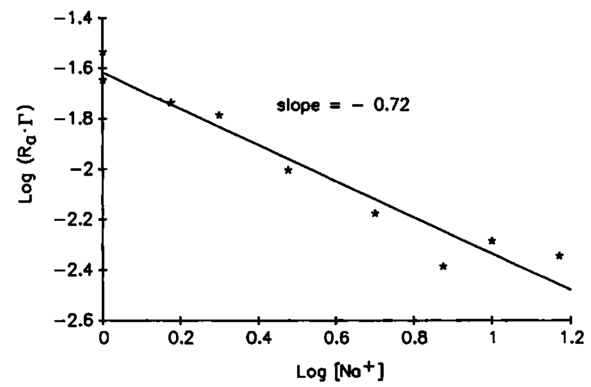

Fig. 4. Log-log plot of $K^{Sr}{}_a \cdot \Gamma$ as a function of m_{Na}. *: experimental points; —: regression analysis.

Figure 3 shows the adsorption of $^{85}Sr^{2+}$ as function of the Na^+ concentration in the equilibrium solution at a pH = 11. The concentration ratio (R_a^{Sr}, cm) decreases with increasing Na^+ concentration. The concentration ratio is defined as:

$$R_a^{Sr} = \frac{\text{Sr adsorbed}}{\text{Sr in solution}} = \frac{\mu\text{mol Sr/cm}^2}{\mu\text{mol Sr/cm}^3}. \tag{11}$$

Initially, the adsorption of Sr^{2+} was assumed to be an ion exchange process. The heterovalent ion exchange reaction can be written as follows:

$$2\overline{Na^+} + Sr^{2+} \rightleftharpoons \overline{Sr^{2+}} + 2Na^+. \tag{12}$$

The selectivity coefficient is defined by:

$$^{Sr}_{Na}K_c = \frac{z_{Sr} \cdot [Na^+]^2 \cdot \gamma_{Na}^2}{z_{Na}^2 \cdot [Sr^{2+}] \cdot \gamma_{Sr}} \tag{13}$$

with: z_{Sr} and z_{Na} = fractional occupancy of the surface by Sr^{2+} and Na^+

$[Sr^{2+}]$ and $[Na^+]$ = concentration of Sr^{2+} and Na^+ in solution (µmol/cm^3)

$\overline{Na^+}$ and $\overline{Sr^{2+}}$ = amount of Na^+ and Sr^{2+} adsorbed (µmol/cm^2)

γ_{Na} and γ_{Sr} = activity coefficient of Na^+ and Sr^{2+} in solution.

Since we are dealing with a system containing a macroelectrolyte Na^+ and a trace element Sr^{2+}, the composition of the bitumen surface does not change significantly when Sr^{2+} adsorbs. The activity coefficient ratio of the adsorbed species is constant and is included in the $^{Sr}_{Na}K_c$ value [11]. The aqueous activity coefficient ratio can be calculated from the extended Debye-Hückel [12] theory and is denoted by Γ in the subsequent equations. The term z_{Sr} can be replaced by $\overline{Sr}$/CEC:

$$^{Sr}_{Na}K_c = \frac{\overline{Sr}/CEC \cdot [Na^+]^2}{z_{Na}^2 \cdot 2 \cdot [Sr^{2+}]} \cdot \Gamma \tag{14}$$

with $\Gamma = \gamma_{Na}^2/\gamma_{Sr}$ and CEC is the amount of deprotonated carboxyl groups or the actual cation exchange capacity.

The factor 2 in equation (14) is introduced because the concentration of Sr^{2+} on the surface is expressed on equivalent basis.

Since $z_{Na} = 1$ at trace level occupancy of Sr^{2+} and $\overline{Sr}/(2 \cdot [Sr^{2+}]) = R_a^{Sr}$ (cm), equation (14) can be written as:

$$^{Sr}_{Na}K_c(z_{Sr} \rightarrow 0) = \frac{R_a^{Sr} \cdot [Na^+]^2}{CEC} \cdot \Gamma \tag{15}$$

or

$$R_a^{Sr} \cdot \Gamma = \frac{^{Sr}_{Na}K_c \cdot CEC}{[Na^+]^2} \tag{16}$$

$$\log(R_a^{Sr} \cdot \Gamma) = \log {}^{Sr}_{Na}K_c + \log CEC - 2 \cdot \log[Na^+]. \tag{17}$$

In case of a pure ion exchange process, the log-log plot of $R_a^{Sr} \cdot \Gamma$ as a function of $[Na^+]$ yields a straight line with a slope −2. Figure 4 represents such a log-log plot. The slope of the straight line equals −0.72 instead of −2. As this is close to −1, it can be concluded that 1 mol of Na^+ is exchanged by 1 mol of Sr^{2+}. This observation thus suggests that the adsorption of Sr^{2+} on bitumen is not a stoichiometric ion exchange process, but has a specific interaction character.

If we assume that the reaction of Sr^{2+} with the bitumen surface (carboxyl group) can be written as:

$$RCOONa + Sr^{2+} \rightleftharpoons RCOOSr^+ + Na^+ \tag{18}$$

then

$$^{Sr}_{Na}K_s = \frac{\{RCOOSr^+\} \cdot [Na^+] \cdot \gamma_{Na}}{\{RCOONa\} \cdot [Sr^{2+}] \cdot \gamma_{Sr}}. \tag{19}$$

Since we are dealing with trace amounts of Sr^{2+}, the composition of the surface does not change significantly when Sr^{2+} adsorbs. The surface charge and potential are completely determined by the pH and the Na^+ concentration in solution. Consequently, {RCOONa} equals the actual CEC of the bitumen. As $R_a^{Sr} = \{RCOOSr^+\}/[Sr^{2+}]$, equation (19) takes the form:

$$ {}^{\mathrm{Sr}}_{\mathrm{Na}}K_s(z_{\mathrm{Sr}} \rightarrow 0) = \frac{R_a^{\mathrm{Sr}} \cdot [\mathrm{Na}^+]}{\mathrm{CEC}} \cdot \Gamma \tag{20} $$

and

$$ R_a^{\mathrm{Sr}} = \frac{{}^{\mathrm{Sr}}_{\mathrm{Na}}K_s \cdot \mathrm{CEC}}{[\mathrm{Na}^+] \cdot \Gamma} \tag{21} $$

where $\Gamma = \gamma_{\mathrm{Na}}/\gamma_{\mathrm{Sr}}$.

Fig. 1 shows that the deprotonation of the surface carboxyl groups depends strongly on the ionic strength below pH = 13. Consequently, the CEC cannot be considered to be constant. Since $\mathrm{CEC} = \alpha \cdot \mathrm{CEC}_{\max}$, equation (21) is modified in:

$$ R_a^{\mathrm{Sr}} = \frac{{}^{\mathrm{Sr}}_{\mathrm{Na}}K_s \cdot \alpha \cdot \mathrm{CEC}_{\max}}{[\mathrm{Na}^+] \cdot \Gamma} \tag{22} $$

where: α = degree of dissociation.

The value of α can be calculated for specific pH and I values by applying equation (7), (8), (9) and (10).

The solid line in Fig. 3 shows a least square fit of the experimental R_a^{Sr} (cm) by equation (22). The value of ${}^{\mathrm{Sr}}_{\mathrm{Na}}K_s$ was derived from this least square fit and equals 157 ± 7. The intrinsic deprotonation constant ($\mathrm{pK_H}$) to calculate α was 6.6 and the $\mathrm{CEC}_{\max}$ was taken 2.3 $\mu\mathrm{eq/m^2}$. The experimental data can be reasonably good described by equation (22). In the model it has been assumed that one carboxyl group reacts with one Sr^{2+} ion to form a surface complex (or surface ion-pair). As the adsorption depends on the Na^+ concentration in solution, the complex is an outer-sphere complex. This means that the complex formation is caused by an electrostatic attraction between ligand and metal atom, both of which conserve their hydration sphere [13]. The Sr^{2+} ion is thus still located in the diffuse part of the double layer and not in the Stern layer.

Evidence for a complexation reaction with one surface carboxyl group only is provided by the surface group density. The functional group density is calculated to be $1.37 \cdot 10^{18}$ groups/m^2 or 1.37 groups/nm^2. One carboxyl group is thus localized on a surface of 0.7 nm^2. The mean distance between adjacent carboxyl groups equals ±0.9 nm, which corresponds to 4 C−C bonds. This distance is too large to allow a chelation reaction with two carboxyl groups.

This conclusion is also supported by the observation that the stability constants of complexes of bicarboxylic acids and metals decrease with increasing distance between the two carboxylic groups. As soon as the carboxyl groups are separated by two or more C-atoms, the stability constant is low ($\log K = 2$) and changes little with increasing distance [14].

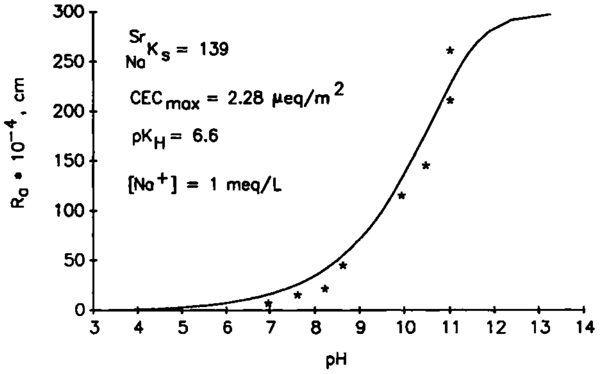

Fig. 5. Adsorption of Sr^{2+} on bitumen as function of pH at I = 0.001 M. ∗: experimental points; — : calculated from equation (22).

Figure 5 shows the adsorption of Sr^{2+} on bitumen (R_a^{Sr}) as a function of the pH of the liquid phase. As expected, the adsorption is lower for lower pH values. The solid line in Fig. 5 shows the variation of R_a^{Sr} as a function of pH as calculated from equation (22). The value of ${}^{\mathrm{Sr}}_{\mathrm{Na}}K_s$ was derived from this least square plot and equals 139 ± 8. There is a good agreement between the calculated and experimental values. A good fit value of the deprotonation constant $\mathrm{pK_H}$ for the experimental data in Figure 5 was found to be 6.6. This is somewhat greater then the typical values of 4.5 to 4.8 quoted in the literature for surface carboxyl groups and the $\mathrm{pK_H}$ value of 4.5 calculated by Takamura and Chow [8] for carboxyl groups on bitumen. A reasonable explanation for this difference cannot be given at the moment because no information is available on the nature and chemical environment of the carboxyl groups on the bitumen surface. A value of 6.6, on the other hand, is not an implausible value. The $\mathrm{pK_H}$ values observed for the carboxyl groups of different compounds in solution have a Gaussian distribution, exhibiting values from 0.5 to 8.5 [15].

As soon as competing complexation reactions (hydrolysis, ion pair formation, complexation with humic acids and organics such as EDTA, DTPA, NTA ...) occur in the liquid phase, the above model must be extended to account for their influence.

Assume that the following 1 : 1 complexation reaction takes place in the liquid phase:

$$ \mathrm{Sr}^{2+} + \mathrm{L}^{2-} \rightleftharpoons \mathrm{SrL}. \tag{23} $$

The stability constant of the complex is defined as:

$$ K_{\mathrm{SrL}} = \frac{[\mathrm{SrL}]}{[\mathrm{Sr}^{2+}][\mathrm{L}^{2-}]}. \tag{24} $$

The total concentration of Sr is:

$$ \begin{aligned} [\mathrm{Sr}]_{\mathrm{tot}} &= [\mathrm{Sr}^{2+}] + [\mathrm{SrL}] && (25) \\ &= [\mathrm{Sr}^{2+}] + K_{\mathrm{SrL}} \cdot [\mathrm{Sr}^{2+}] \cdot [\mathrm{L}^{2-}] && (26) \\ &= [\mathrm{Sr}^{2+}](1 + K_{\mathrm{SrL}} \cdot [\mathrm{L}^{2-}]). && (27) \end{aligned} $$

Hydrolysis of Sr^{2+} can be neglected. At a pH of 11, 99.6% of the Sr is present as Sr^{2+} and only 0.4% as $\mathrm{Sr(OH)}^+$.

As shown previously, the adsorption of Sr^{2+} can be described by:

$$ {}^{\mathrm{Sr}}_{\mathrm{Na}}K_s = \frac{\{\mathrm{RCOOSr}^+\} \cdot [\mathrm{Na}^+]}{\{\mathrm{RCOONa}\} \cdot [\mathrm{Sr}^{2+}]} \cdot \Gamma. \tag{28} $$

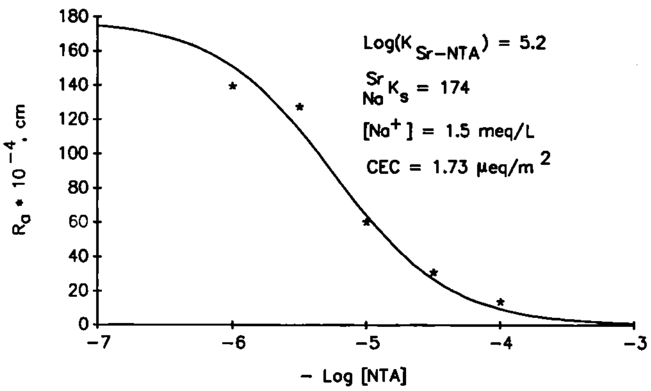

Fig. 6. Adsorption of Sr^{2+} on bitumen at pH = 11 and I = 0.0015 M as a function of [NTA] in the liquid phase. *: experimental results; — : calculated from equation (30).

Table 1. Overview of $^{Sr}_{Na}K_s$ values obtained from different experiments

Experiment	$^{Sr}_{Na}K_s$	$\log ^{Sr}_{Na}K_s$
Variable [Na$^+$]	157±7	2.20
Variable pH	139±8	2.14
NTA	174±9	2.24

$$\text{With: } [Sr^{2+}] = \frac{[Sr]_{tot}}{(1 + K_{SrL}[L^{2-}])}$$

$$\{RCOONa\} = CEC$$

$$\text{and } \{RCOOSr^{2+}/[Sr]_{tot} = R_a^{Sr}$$

equation (28) takes the form:

$$^{Sr}_{Na}K_s = \frac{R_a^{Sr} \cdot [Na^+]}{CEC/(1 + K_{SrL} \cdot [L^{2-}])} \cdot \Gamma \tag{29}$$

$$R_a^{Sr} = \frac{^{Sr}_{Na}K_s \cdot CEC_{max} \cdot \alpha}{[Na^+] \cdot (1 + K_{SrL} \cdot [L^{2-}]) \cdot \Gamma}. \tag{30}$$

Figure 6 shows the adsorption of Sr^{2+} (expressed as R_a^{Sr}) as a function of the NTA concentration in solution. NTA forms 1:1 complexes with Sr^{2+} with a stability constant of log K = 5.0 (I = 0.1 M) [14]. The adsorption experiments were carried out at pH = 11 and a Na^+ concentration of 0.0015 M. The value of the stability constant of NTA with Sr^{2+} equals 5.2 at this ionic strength. At pH = 11, 76% of the carboxyl groups are deprotonated so that the CEC has a value of 1.73 μeq/m^2.

The figure clearly demonstrates the inhibiting effect of NTA on the adsorption of Sr^{2+}. The solid line in Fig. 6 represents a least square fit of R_a^{Sr} as function of NTA as calculated from equation (30). Equation (30) describes the experimental results well. This is in fact not surprising since equation (30) forms the basis of the Schubert method for the determination of stability constants of complexes [16]. The $^{Sr}_{Na}K_s$ was derived from the least square fit and equals 174±9.

Equation (30) is a general equation which describes the adsorption of Sr^{2+} as a function of pH, ionic strength and the concentration of complexing ligands in solution. Depending on the chemical conditions, equation (30) can be simplified.

Table 2. Composition of a standard Portland cement water SPP [17]

Parameter	Cement SPP
Temperature [°C]	25
pH	13.2
Ionic strength [M]	0.23
E_h (mV)	+139
Na^+ [M]	6.52×10^{-2}
K^+ [M]	1.61×10^{-1}
Mg^{2+} [M]	1.00×10^{-5}
Ca^{2+} [M]	2.25×10^{-3}
Fe_{tot} [M]	1.00×10^{-5}
Al [M]	2.00×10^{-4}
Alkalinity [N]	2.31×10^{-1}
SiO_2 [M]	2.00×10^{-4}

The values of $^{Sr}_{Na}K_s$ obtained from the different experiments are summarized in Table 1. The values are very similar and it can be concluded that a value of 160 (log K = 2.2) characterizes the adsorption of Sr^{2+} in presence of Na^+ and K^+. In case of Ca^{2+} as counter-ion, the value of $^{Sr}_{Ca}K_s$ is expected to be ±1 because of the similar chemistry of both Sr^{2+} and Ca^{2+}. Complexes of carboxylic acids with Ca^{2+} and Sr^{2+} show similar stability constants [14].

Equation (30) can be used to calculate the adsorption (R_a^{Sr}) of Sr^{2+} on bitumen under near field conditions (cementitious environment). If it is assumed that the bitumen is in contact with a cement pore water having the composition as given in Table 2 [17], then all carboxyl groups are deprotonated ($\alpha = 1$) so that the CEC value attains its maximum value of 2.3 μeq/m^2. The hydrolysis reaction of Sr^{2+} becomes more important at this high pH (Sr^{2+}: 80%); $Sr(OH)^+$: 20%) but can be neglected because Sr^{2+} is still the dominant species. Equation (30) is thus reduced to its most simple form:

$$R_a^{Sr} = \frac{^{Sr}_{Na}K_s \cdot CEC_{max}}{[Na^+] \cdot \Gamma}. \tag{31}$$

The $^{Sr}_{Na}K_s$ is expected to be the same as $^{Sr}_{K}K_s$, so that equation (31) can be written as

$$R_a^{Sr} = \frac{^{Sr}_{Na,K}K_s \cdot CEC_{max}}{([Na^+] + [K^+]) \cdot \Gamma}. \tag{32}$$

The activity coefficient ratio Γ is equal to 2.45 at an ionic strength of 0.22 M. A mean value of 160 for $^{Sr}_{Na}K_s$ was taken. This value, of course, is a maximum value operating at trace levels of Sr^{2+}. At higher concentrations of Sr^{2+}, the value of $^{Sr}_{Na}K_s$ is expected to be lower since interaction of Sr^{2+} with less specific surface groups might occur when the loading of the bitumen surface with Sr^{2+} increases. The subsequent calculations thus represent the maximum R_a^{Sr} value that can be expected.

The value of R_a^{Sr} is calculated to be:

$$R_a^{Sr} = \frac{160 \cdot 2.28 \cdot 10^{-4}}{226.2 \cdot 2.45} = 7 \cdot 10^{-5} \text{ cm.}$$

Taking the effect of Ca^{2+} into account, the predicted R_a^{Sr} value is $< 10^{-4}$ cm. It may therefore be concluded that in a cementitious environment, Sr^{2+} exhibits negligible small sorption on the bitumen due to competitive effects of Na^+, K^+ and Ca^{2+} present in the cement pore water.

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References

1. Burnay, S. G.: Sorption effects in the leaching of ^{137}Cs from organic matrix waste forms. AERE R 12421 DOE/RW/87.083, August 1987.
2. Hietanen Raija, Alaluusua Maarit, Jaakkola Tino: Sorption of Cesium, Strontium, Iodine, Nickel and Carbon in mixtures of concrete, crushed rock and bitumen. Report YJT-85-38, 1985.
3. Alaluusua Maarit, Hakanen Martti: Sorption of Cesium, Strontium, Cobalt and Technetium in mixtures of concrete, crushed rock and bitumen. Report YJT-87-10, 1987.
4. Maes, A., van Elewijck, F., Vancluysen, J., Tits, J., Cremers, A.: Cobaltihexammine as an index cation for measuring the cation exchange capacity of humic acids. Proceedings of the International Symposium on Humic Substances in the Aquatic and Terrestrial Environment, Linkoping, Sweden, August 21–23, 1989. In Press in Lecture Notes in Earth Sciences.
5. Dalang, F.: Zur Adsorption von Kationen an die Metalloxid-Wasser-Grenzfläche: Die Adsorption von robusten Kobaltkomplexen. Ph. D. Thesis, Diss. Nr. 5916, ETH Zürich, Switzerland 1977.
6. Morel, R.: Etudes expérimentales des phénomènes d'échange sur differentes minéraux argileux. Ann. Agron. **6**, 5–90 (1975).
7. Eldridge, R. J., Treloar, F. E.: Binding of counterions to polyacrylate solutions. J. Phys. Chem. **74**, 1446–1449 (1970).
8. Takamura, K., Chow, R. S.: The Electric Properties of the Bitumen/Water Interface, Part II: Application of the Ionizable Surface-Group Model. Colloids Surf. **15**, 35–48 (1985).
9. Danielli, J. F.: The Relations between Surface pH, Ion Concentrations and Interfacial Tension. Proc. R. Soc. London, Ser. B, **122**, 155–174 (1937).
10. Stone-Masui, J., Watillon, A.: Characterization of Surface Charge on Polystyrene Latices. J. Colloid Interface Sci. **52**, 479–503 (1975).
11. Diamond, R. M., Whitney, D. C.: Resin selectivity in dilute to concentrated aqueous solutions. In: *Ion exchange*, Volume I, (J. A. Marinsky, ed.), Marcel Dekker, In., New York 1966.
12. Novozamsky, I., Beek, J., Bolt, G. A.: Chemical Equilibria. In: *Soil Chemistry, A: Basic elements* (G. Bolt and M. Bruggenwert, eds.), Elsevier Scientific Publishing Company. Amsterdam-Oxford-New York 1978.
13. Buffle, J.: *Complexation Reactions in Aquatic Systems: an Analytical Approach*, 1st ed., Ellis Horwood Limited 1988, p. 692.
14. Sillen, L. G., Martell, A. C.: *Stability constants of metal-ion complexes*, Special Publication 25, Chemical Society, Burlington House, W1 London 1971.
15. Perdue, E. M., Reuter, J. H., Parrish, R. S.: A Statistical Model of Proton Binding by Humus. Geochim. Cosmochim. Acta **48**, 1257–1263 (1984).
16. Van Loon, L. R., Kopajtic, Z.: Complexation of Cu^{2+}, Ni^{2+} and UO_2^{2+} by radiolytic degradation products of bitumen, PSI report no. 66, Würenlingen and Villigen, Switzerland 1990.
17. Anderson, K.: Transport of radionuclides in Water/Mineral systems. Ph. D. Thesis, ISBN 91-7032-105-1, Chalmers University, Goteborg 1983.