90529

7

Fresenius J Anal Chem (1996) 354: 763–769

© Springer-Verlag 1996

POSTER

H. Wanner · Y. Albinsson · E. Wieland

A thermodynamic surface model for caesium sorption on bentonite

NOV 2005
By

Received: 10 June 1995/Revised: 14 August 1995/Accepted: 22 August 1995

Abstract Caesium sorption on Wyoming bentonite MX-80 has been studied in solutions of NaCl, KCl, $MgCl_2$, $CaCl_2$, $NaNO_3$ and $Ca(NO_3)_2$ of concentrations varying between 0.025 and 1 mol/L, as well as in a weakly saline (I = 0.004 ml/L) and a strongly saline (I = 0.46 mol/L) natural groundwater. These experiments have been used to derive a thermodynamic model for the interaction of caesium with the bentonite surface in accordance with a surface chemical model, including acid/base reactions developed recently for montmorillonite. The sorption behaviour of caesium on bentonite can be described, within the experimental and model uncertainties, in terms of a one-site ion exchange model. The ion exchange constant obtained for the reaction $NaX + Cs^+ \leftrightarrows CsX + Na^+$ (where X represents the ion exchange sites on montmorillonite) is $\log_{10} K^0_{ex} = 1.6$. Impurities in the bentonite, influencing the concentrations of competing cations, such as Na^+, K^+, Mg^{2+} and Ca^{2+}, have a crucial impact on the sorption of caesium. This impact can be adequately quantified with the present model. The model predictions compare well with sorption data published in the open literature on both Wyoming bentonite MX-80 and other types of bentonite. Distribution coefficients from the literature obtained from both batch and diffusion experiments and varying over four orders of magnitude are reproduced and explained successfully by the model.

Introduction

The understanding of the surface reactions of heavy metals in bentonite is essential for predicting their migration behaviour and deriving site-specific distribution coefficients. Bentonite is used as a barrier material for landfills and final repositories of hazardous waste, and it is envisaged to be used in a highly compacted form in the geological isolation of high-level radioactive waste. The aim of the present study is to provide, by using caesium as a reference element, a quantitative and applicable basis for ion exchange modelling on montmorillonite as the active component of bentonites. The present study has been performed in the framework of performance assessment of radioactive waste disposal. However, we believe that its results will be useful for modelling migration of heavy metals in bentonite-containing materials in general.

H. Wanner (✉) · E. Wieland
MBT Umwelttechnik AG, Vulkanstrasse 110, CH-8048 Zürich, Switzerland

Y. Albinsson
Chalmers University of Technology, Dept. of Nucl. Chemistry, S-412 96 Gothenburg, Sweden

Experimental

Materials. The chemical properties of the Wyoming MX-80 bentonite used in the experiments are summarised in Table 1. The main impurities, which have an important impact on the porewater chemistry, especially at high bentonite/water ratios, are $CaCO_3$, $CaSO_4$ and NaCl. The latter two were derived from leaching experiments in which sulfate and chloride ions were measured in the elutriat [3]. It was assumed that these anions stem from the dissolution of soluble impurities present in the bentonite, such as $CaSO_4$ and NaCl.

Method. The K_d values for Cs^+ sorption were determined in batch-type experiments conducted in poly-carbonate tubes (15 ml). A weighed amount of untreated Wyoming MX-80 bentonite (0.1 or 1 g) was equilibrated with 10 ml of a solution containing 0.2 ml ^{137}Cs stock solution and a known concentration of the background electrolyte. In some experiments, synthetic Allard (low saline) and Äspö (high saline) groundwaters (compositions listed in Table 2) were used as background electrolyte. The activity of the ^{137}Cs stock solution was 3.3×10^7 Bq/L. The total concentration of ^{137}Cs used in the experiments ranged from 10^{-9} to 10^{-8} mol/L. After an equilibrium time of 3 and 8 days, aliquots of the supernatant were analysed for ^{137}Cs using a NaI(Tl)-detector. Each K_d value was calculated as average value from three individual samples.

14556

Table 1 Data and composition of the Wyoming MX-80 bentonite

Property	Value	Reference
Cation exchange capacity (CEC):	85 meq/100 g	Wieland et al [1]
Exchangeable cations:	81.7% Na^+	Müller-Vonmoos and Kahr [2]
	0.3% K^+	Müller-Vonmoos and Kahr [2]
	3.9% Mg^{2+}	Müller-Vonmoos and Kahr [2]
	14.1% Ca^{2+}	calculated[a]
$CaCO_3$ impurity in the bentonite	1.4% (wt)	Müller-Vonmoos and Kahr [2]
$CaSO_4$ impurity in the bentonite	0.34% (wt)	Wanner, Wersin and Sierro [3]
NaCl impurity in the bentonite	0.007% (wt)	Wanner, Wersin and Sierro [3]

[a] The value used for Ca^{2+} represents the complementary value to the measured CEC

Table 2 Compositions of the synthetic groundwaters used. These groundwaters are simplifications of the Swedish granitic reference groundwater (Allard water) and of a highly saline groundwater sampled at the Äspö site in southern Sweden.

Parameter	Allard groundwater, simplified [mol/L]	Äspö groundwater, simplified [mol/L]
Na^+	2.26×10^{-3}	1.31×10^{-1}
K^+	1.00×10^{-4}	1.87×10^{-4}
Mg^{2+}	1.90×10^{-4}	2.06×10^{-3}
Ca^{2+}	4.64×10^{-4}	1.10×10^{-1}
Cl^-	1.48×10^{-3}	3.40×10^{-1}
Mg^{2+}	1.90×10^{-4}	2.06×10^{-3}
SO_4^{2-}	1.00×10^{-4}	7.40×10^{-3}
SiO_2	1.39×10^{-4}	–
Alkalinity [eq/L]	1.80×10^{-3}	1.80×10^{-4}
pH	8.12	7.38
Ionic strength	4.26×10^{-3}	4.55×10^{-1}

Model development

Surface chemical model used for montmorillonite

Ion exchange reactions on fixed-charge surface sites, denoted "X sites", can be described in general terms in the following way:

$$z_B A + z_A BX_{z_B} \leftrightarrows z_A B + z_B AX_{z_A} \quad (1)$$

where A and B are exchangeable cations and z_A and z_B their charges, respectively. The conditional exchange constant is then expressed as:

$$K_{ex}^{o} = \frac{(x_A)^{z_B}(a_B)^{z_A}}{(x_B)^{z_A}(a_A)^{z_B}} \quad (2)$$

where x_A and x_B are the mole fractions of A and B, respectively, on the solid phase, and a_A and a_B are the activities of the ions A and B, respectively, in solution. K_{ex} is also called Vanselow selectivity coefficient. The activity coefficients of the ions adsorbed on the solid phase are set equal to unity. By using the mole fraction approach according to Eq. (2) we follow the recommendations of Fletcher and Sposito [4]. It should be noted, however, that several authors [5, 6] prefer the equivalent fraction approach which facilitates speciation calculations. Both the mole and equivalent fraction approaches are thermodynamically valid. Dzombak and Hudson [7] have recently commented on the different model approaches.

The investigation of the acid/base chemistry of montmorillonite resulted in the identification of variable-charge surface sites, denoted "SOH sites", whose protonation and deprotonation constants have been evaluated by using the diffuse double layer model [1, 8]. The SOH sites were found to be a factor of about 30 less abundant than the cation exchange sites.

Determination of the exchange constant of caesium

The batch experiments carried out to determine the distribution coefficient, K_d, for Cs^+ on Wyoming MX-80 bentonite are summarised in Table 3. NaCl, $NaNO_3$ and KCl solutions were used as electrolyte. Satisfactory agreement between predicted and experimental K_d values is obtained by using $\log_{10} K_{ex}^{o} = 1.6$ for Reaction (3), cf. Table 3 and Fig. 1.

$$NaX + Cs^+ \leftrightarrows Na^+ + CsX \quad (3)$$

The value of $\log_{10} K_{ex}^{o} = 1.6$ is in good agreement with values found in the literature [5, 6]. A summary of the surface chemical reactions included in the bentonite model is given in Table 4.

Testing the model

Testing of the Cs^+ exchange constant against experiments in 1:2 electrolyte solutions

Table 5 shows a comparison of the K_d values for Cs^+ sorption measured in 1:2 electrolyte solutions and calculated with the help of the model. The results are in some cases less satisfactory than those in 1:1 electrolyte solutions, especially at very low bentonite/water ratios. Our model tends to underestimate the extent of Cs^+ sorption. An explantation may be that the mole fraction model used here overrates the affinities of Ca^{2+} and Mg^{2+} to the surface sites and thus their competition with Cs^+ under certain conditions.

Table 3 Measured and calculated K_d values for Cs^+ in 1 : 1 electrolyte solutions on pure Wyoming MX-80 bentonite and mixtures of 10% bentonite and 90% silica sand, respectively

b/w[a] [g/cm³]	s/w[b] [g/cm³]	Solution	K_d(meas) [m³/kg]	pH[c]	K_d(ix)[d] [m³/kg]
Pure bentonite					
0.102	0.102	1 mol/L NaCl	0.034	7.38	0.022
0.104	0.104	0.5 mol/L NaCl	0.056	7.41	0.054
0.104	0.104	0.5 mol/L $NaNO_3$	0.054	7.55	0.066
0.011	0.011	0.5 mol/L NaCl	0.080	8.81	0.055
0.104	0.104	0.05 mol/L NaCl	0.310	8.12	0.344
0.1	0.1	1 mol/L KCl	0.015	8.07	0.013
0.1	0.1	0.5 mol/L KCl	0.036	8.03	0.033
0.1	0.1	0.05 mol/L KCl	0.342	8.66	0.364
0.01	0.01	1 mol/L KCl	0.015	9.43	0.013
0.01	0.01	0.5 mol/L KCl	0.028	9.34	0.031
0.01	0.01	0.05 mol/L KCl	0.280	9.33	0.329
10% bentonite and 90% silica sand:					
0.01	0.1	1 mol/L KCl	0.001	9.30	0.001
0.01	0.1	0.5 mol/L KCl	0.003	9.10	0.003
0.01	0.1	0.05 mol/L KCl	0.020	9.30	0.033
0.0012	0.010	0.5 mol/L NaCl	0.033	9.13	0.006

[a] b/w denotes the bentonite-to-water ratio [g/cm³]
[b] s/w denotes the solid-to-water ratio [g/cm³]
[c] pH is calculated from model computation
[d] K_d(ix) is modelled with $\log K^{o}_{ex} = 1.6$ as the exchange constant for Cs^+/Na^+

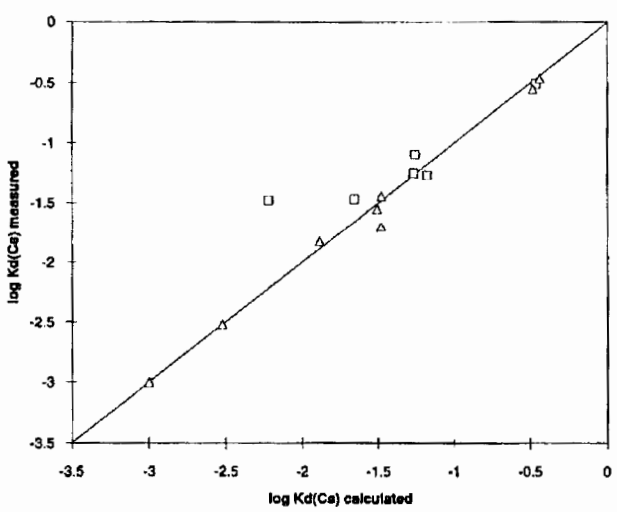

Fig. 1 Comparison of measured K_d values of Cs^+ in 1 : 1 electrolyte solutions on Wyoming bentonite MX-80 (cf. Table 2) and bentonite/sand mixtures. The experiments are carried out in NaCl and $NaNO_3$ (□) and in KCl (△) solutions

Modelling batch type experiments as a function of Cs^+ concentration

In order to verify the validity of a one-site ion exchange model for Cs^+, we carried out batch sorption experiments at Cs^+ concentrations varying between 10^{-9} and 10^{-1} mol/L. Figure 2 shows the sorption isotherm obtained in this experiment, and Table 6 presents a comparison of measured and calculated K_d values. This experiment shows that the sorption isotherm ($\log[Cs^+]_s$ vs. $\log[Cs^+]_{sln}$) is linear and has a slope of 0.95. Predicted and measured K_d values agree within a factor of two indicating that the present one-site model is adequate to describe Cs^+ sorption on montmorillonite. Site saturation is also predicted correctly by the model. It is seen from Table 6 that both the measured and predicted K_d values decrease significantly above a Cs^+ concentration of about 3×10^{-3} mol/L. This is explained by the CEC due to which 8.5×10^{-3} mol of surface sites are available per litre of water here. It should be noted that bentonite may contain up to 0.8 ppm Cs [9] which corresponds to 6×10^{-8} mol/L Cs^+ at the current bentonite/water ratio. It is thus probable that the lowest possible concentration of Cs^+ under the present conditions is 6×10^{-8} mol/L and that the three or four lowest concentrations in Table 6 do not represent total Cs^+ in solution. The results of the comparison, however, are not influenced by this apparent discrepancy.

Testing of the Cs^+ sorption model against batch sorption measurements from the literature

The vast majority of batch sorption experiments of Cs^+ from the literature cannot be simulated with a predictive model, because the solid phases and the water compositions are insufficiently characterised. In order to test our model, only those experiments are considered for which sufficient information is provided on the type of solution used and the bentonite composition. Soluble impurities play an important role, especially if the solution is poorly mineralised. Table 7 presents a selection of published K_d values obtained from batch experiments for montmorillonite and for various bentonites. Significant deviations between the

Table 4 Reactions and parameters of the surface chemical model for bentonite

Surface reaction	Mass law equation	$\log_{10} K^{o}$
$SOH_2^+ \leftrightarrows SOH + H^+$	$K_{a1}^{int} = \frac{(SOH)\{H^+\}}{(SOH_2^+)} \exp\left(\frac{-F\Psi}{RT}\right)$	− 5.4 [1, 8]
$SOH \leftrightarrows SO^- + H^+$	$K_{a2}^{int} = \frac{(SO^-)\{H^+\}}{(SOH)} \exp\left(\frac{-F\Psi}{RT}\right)$	− 6.7 [1, 8]
$K^+ + NaX \leftrightarrows KX + Na^+$	$K_{ex}^{o} = \frac{(x_{KX})(a_{Na})}{(x_{NaX})(a_K)}$	0.26 [4]
$Cs^+ + NaX \leftrightarrows CsX + Na^+$	$K_{ex}^{o} = \frac{(x_{CsX})(a_{Na})}{(x_{NaX})(a_{Cs})}$	1.6 [this study]
$Mg^{2+} + 2NaX \leftrightarrows MgX_2 + 2Na^+$	$K_{ex}^{o} = \frac{(x_{MgX_2})(a_{Na}^2)}{(x_{NaX}^2)(a_{Mg})}$	0.13 [3]
$Ca^{2+} + 2NaX \leftrightarrows CaX_2 + 2Na^+$	$K_{ex}^{o} = \frac{(x_{CaX_2})(a_{Na}^2)}{(x_{NaX}^2)(a_{Ca})}$	0.21 [3]

Site density TOT-SOH: 2.8×10^{-5} mol/g
Site density TOT-X: 85.0 meq/100 g

Table 5 Measured and calculated K_d values for Cs^+ in 1 : 2 electrolyte solutions on pure Wyoming MX-80 bentonite and mixtures of 10% bentonite and 90% silica sand, respectively

b/w[a] [g/cm³]	s/w[b] [g/cm³]	Solution	K_d(meas) [m³/kg]	pH[c]	K_d(ix)[d] [m³/kg]
Pure bentonite					
0.104	0.104	0.25 mol/L $CaCl_2$	0.053	6.61	0.033
0.103	0.103	0.25 mol/L $Ca(NO_3)_2$	0.047	6.61	0.052
0.103	0.103	0.025 mol/L $CaCl_2$	0.183	7.39	0.205
0.010	0.010	0.25 mol/L $CaCl_2$	0.148	7.15	0.031
0.1	0.1	1 mol/L $MgCl_2$	0.036	6.96	0.021
0.1	0.1	0.5 mol/L $MgCl_2$	0.045	7.05	0.030
0.1	0.1	0.05 mol/L $MgCl_2$	0.117	7.72	0.113
0.01	0.01	1 mol/L $MgCl_2$	0.084	7.54	0.021
0.01	0.01	0.5 mol/L $MgCl_2$	0.089	7.62	0.029
0.01	0.01	0.05 mol/L $MgCl_2$	0.150	8.09	0.085
0.01	0.01	Allard water	1.0	9.53	2.03
0.18	0.18	Äspö water	0.172	7.16	0.076
10% bentonite and 90% silica sand:					
0.01	0.1	1 mol/L $MgCl_2$	0.015	7.00	0.0003
0.01	0.1	0.5 mol/L $MgCl_2$	0.018	7.31	0.0014
0.01	0.1	0.05 mol/L $MgCl_2$	0.025	8.01	0.008
0.0011	0.010	0.25 mol/L $CaCl_2$	0.093	7.90	0.003
0.018	0.20	Äspö water	0.030	7.45	0.008

[a], [b], [c], [d] as in Table 3

predicted and measured K_d values are observed for the experiments reported by Wahlberg and Fishman [10]. It should be mentioned, however, that the composition of the solid phase in these experiments is not well known.

Testing of the Cs^+ sorption model against diffusion measurements

The extent of retardation of Cs^+ in compacted bentonite, a material envisaged to isolate high-level nuclear waste repositories from the surrounding geosphere, can only be measured indirectly via diffusion measurements. The interpretation of measured values of the apparent diffusivity, D_a, in terms of K_d is possible if the pore diffusivity, D_p, which represents the hypothetical case of zero sorption, is known:

$$D_a = \frac{\varepsilon}{\varepsilon + K_d \rho_d} D_p \tag{4}$$

ε is the porosity and ρ_d the dry density of the bentonite. The K_d value in Eq. (4) depends on the chemical conditions in the compound bentonite. Prediction of K_d is possible using the ion exchange model of Table 4. The verification of Eq. (4) then requires certain assumptions: It is assumed that ε can be calculated from the dry density, ρ_d, and the specific density ($\rho_s = 2700$ kg/m³), $\varepsilon = 1 - \rho_d/\rho_s$, and that D_p of Cs^+

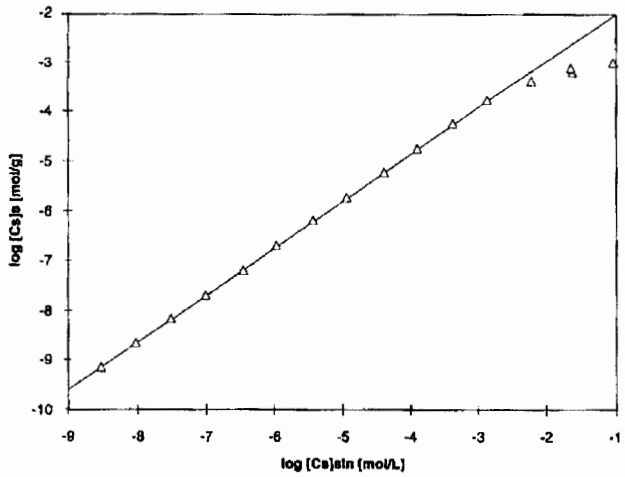

Fig. 2 Sorption isotherm of ^{137}Cs on Wyoming MX-80 bentonite. Background electrolyte is 0.1 mol/L NaCl, bentonite/water ratio = 0.01 g/mL

Table 6 Measured and calculated K_d values on Wyoming MX-80 bentonite as a function of ^{137}Cs concentration; bentonite/water ratio = 0.01 g/mL, background electrolyte: 0.1 mol/L (Cs, Na)Cl

Cs^+ concentration [mol/L]	K_d (measured) [m^3/kg]	pH[c]	K_d(ix)[d] [m^3/kg]
1E-1	0.010	9.15	0.009
3E-2	0.030	9.08	0.035
1E-2	0.072	9.09	0.116
3E-3	0.124	9.14	0.220
1E-3	0.133	9.17	0.262
3E-4	0.133	9.18	0.277
1E-4	0.140	9.18	0.281
3E-5	0.152	9.18	0.283
1E-5	0.158	9.18	0.284
3E-6	0.167	9.18	0.284
1E-6	0.188	9.18	0.284
3E-7	0.200	9.18	0.284
1E-7	0.222	9.18	0.284
3E-8	0.224	9.18	0.284
1E-8	0.231	9.18	0.284
1E-9[a]	0.309	9.37	0.511

[a] The background electrolyte is 0.05 mol/L NaCl here, rather than 0.1 mol/L NaCl
[c], [d] As in Table 3

can be set equal to D_a of HTO (assuming unretarded diffusion of tritiated water [25]). The assumption of unretarded diffusion of HTO may be questioned, because water, and hence HTO, always interacts with mineral surfaces. However, HTO is the least retarded of the radionuclides measured in diffusion experiments in bentonite [20], and this observation was the basis for our assumption. In addition, interactions not taken

Table 7 Batch K_d values for Cs^+ on bentonite from the literature, compared with K_d values predicted with the present ion exchange model

Solid phase	CEC[a] [meq/100 g]	Solid/water ratio [g/cm^3]	Water type[b]	K_d(rep)[c] [m^3/kg]	K_d(ix)[d] [m^3/kg]	Ref.
Montmorillonite No. 11	n.r.	0.010	0.2 M NaCl	0.8	0.180	[10]
	n.r.	0.010	0.2 M KCl	0.2	0.106	
	n.r.	0.010	0.2 M $MgCl_2$	1	0.036	
	n.r.	0.010	0.2 M $CaCl_2$	0.9	0.034	
	n.r.	0.010	0.002 M NaCl	20	4.01	
	n.r.	0.010	0.002 M KCl	20	4.20	
	n.r.	0.010	0.002 M $MgCl_2$	8	2.79	
	n.r.	0.010	0.002 M $CaCl_2$	4	2.55	
Montmorillonite No. 21	n.r.	0.010	0.2 M NaCl	0.3	0.180	[10]
	n.r.	0.010	0.2 M KCl	0.2	0.106	
	n.r.	0.010	0.2 M $MgCl_2$	0.2	0.036	
	n.r.	0.010	0.2 M $CaCl_2$	0.3	0.034	
	n.r.	0.010	0.002 M NaCl	10	4.01	
	n.r.	0.010	0.002 M KCl	20	4.20	
	n.r.	0.010	0.002 M $MgCl_2$	1	2.29	
	n.r.	0.010	0.002 M $CaCl_2$	2	2.55	
Montmorillonite	87	0.033	0.03 N $CaCl_2$	0.22	0.117	[11]
	87	0.033	0.03 N $NaHCO_3$	1.56	0.919	
	87	0.033	0.03 N NaCl	1.12	0.79	
Bentonite	72	0.05	nat. GW	1.57	1.75	[12]
	72	0.10	nat. GW	1.42	1.27	
Resadiye clay	n.r.	0.010	nat. GW[e]	3.5	2.75	[13]
Kunipia-F	108	0.001	distilled water	3.4	3.31	[14]

[a] Cation exchange capacity, "n.r." = not reported
[b] M = mol/L, N = eq/L, nat. GW = natural groundwater
[c] K_d values reported by the authors
[d] K_d(ix) is modelled with $\log K^{\circ}_{ex} = 1.6$ for the Cs^+/Na^+ exchange
[e] The charge is not balanced in the composition of the groundwater reported

Table 8 Results of diffusion experiments of Cs^+ from the literature and comparison of derived K_d values with predicted K_d values using the ion exchange model of the present study

Solid phase	ρ_d [kg/m^3]	Water type	D_a [m^2/s]	K_d(rep)[a] [m^3/kg]	D_p[b] [m^2/s]·10^{-10}	K_d[c] [m^3/kg]	K_d(ix)[d] [m^3/kg]	Ref.
MX-80	2000	Allard water	1.4 to 2·10^{-12}	0.13 to 0.19	2.5	0.019 to 0.027	0.024	[15]
MX-80	2000	Allard water	2.4·10^{-12}		2.5	0.015	0.024	[16]
MX-80	2030	1.2 M NaCl	6.5·10^{-13}	0.05	2.4	0.055	0.004	[17]
	1980	0.6 M NaCl	6.9·10^{-13}	0.09	2.6	0.056	0.007	
	1870	0.2 M NaCl	8.5·10^{-13}	0.21	2.9	0.055	0.015	
	1910	0.02 M NaCl	3.5·10^{-13}	0.85	2.8	0.125	0.025	
	1940	0.003 M NaCl	2.5·10^{-13}	1.80	2.7	0.166	0.026	
MX-80	2105[e]	Allard water	5·10^{-13}		2.2	0.052	0.021	[18]
MX-80	2000	Allard water	3·10^{-12}		2.5	0.012	0.024	[19]
Kunigel-V1	400	distilled water	1.8·10^{-11}		17	0.204	0.574	[20]
	800		1.4·10^{-11}		11	0.066	0.205	
	1400		7.8·10^{-12}		5.2	0.024	0.073	
	2000		5.2·10^{-12}		2.5	0.007	0.018	
MX-80	2000	Allard water	2.5·10^{-12}		2.5	0.015	0.024	[21]
10/90 MX-80/ silica sand	2000	Allard water	5·10^{-12}		2.5	0.007	0.005	[22]
MX-80	2000	Äspö water	3.2·10^{-12}		2.5	0.012	0.009	[21]
10/90 MX-80/ silica sand	2000	Äspö water	6.5·10^{-12}		2.5	0.006	0.0008	[21]
Avonlea clay[f]	1250	high salinity	4.5·10^{-11} to 2.5·10^{-10}		6.2	0.001	0.038 to 0.008	[23]
	1750	low salinity	2·10^{-12}		3.4	0.034	0.051	
Kunipia-F	200	distilled water	1.5·10^{-11}	0.430	22	0.680	0.954	[14]
	400		1.1·10^{-11}	0.158	17	0.332	0.461	
	600		7.9·10^{-12}	0.098	14	0.222	0.263	
	800		5.9·10^{-12}	0.057	11	0.157	0.154	
	1000		4.4·10^{-12}	0.041	8.4	0.120	0.136	
	1200		3.7·10^{-12}	0.025	6.6	0.083	0.110	
	1400		2.2·10^{-12}	0.022	5.1	0.080	0.080	
	1600		1.4·10^{-12}	0.018	4.1	0.074	0.069	
	1800		7.9·10^{-13}	0.016	3.2	0.074	0.035	
	2000		3.9·10^{-13}	0.016	2.5	0.083	0.017	

[a] K_d values reported by the authors as derived from the diffusivities
[b] Pore diffusivity, D_p, of Cs^+ estimated by analogy with the diffusivity of HTO
[c] Derived from measured D_a and from the estimated D_p (referred to as "log K_d measured" in Fig. 3).
[d] K_d(ix) is modelled with $\log K^o_{ex} = 1.6$ for the Cs^+/Na^+ exchange
[e] This is the correct dry density of the solid used in the experiments, as remeasured recently [24]. The porosity is estimated to 0.25
[f] For the calculation of D_p it is assumed that the solid behaves like pure bentonite with porosities of 50% for ρ_d = 1250 kg/m^3 and 35% for ρ_d = 1750 kg/m^3. "High salinity" is assumed to be represented by Äspö groundwater and "low salinity" by Allard groundwater

into account for HTO can be expected to occur also for Cs and other species, and they therefore cancel out to some extent. The approach requires a further adjustment: Agreement between the parameters in Eq. (4) can only be obtained by reducing the CEC from 85 to 10 meq/100 g in the ion exchange model [24], otherwise the predicted K_d values turn out too high. This effect has been observed by other authors, but there is no agreement in the mechanistic interpretations. Some authors propose a surface diffusion mechanism for cations explaining the higher D_a values than expected from K_d prediction [25], others [26] apply a surface interaction model affecting in essence the value of D_p (increase for cations, decrease for anions), or even others [27] apply an empirical scaling factor for K_d depending essentially on the value of the dry density. Table 8 shows that, in the light of our simplifying assumptions, the result of the comparison is encouraging. The K_d values predicted with the present ion exchange model agree well with those derived from the diffusion experiments.

Conclusions

The sorption behaviour of caesium in bentonite and related clay minerals is described successfully by the use of a one-site ion exchange model using $\log K^o_{ex} = 1.6$ for the Cs^+/Na^+ exchange. The K_d values from diffusion experiments can be simulated with the same model

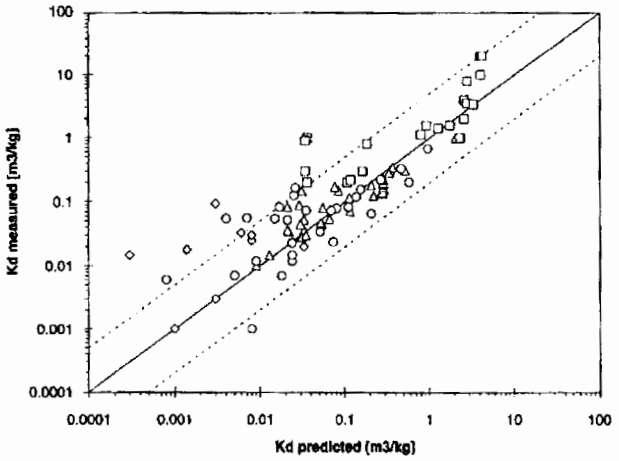

Fig. 3 Comparison of measured and predicted values of all the data reported in Table 3, 5, 6, 7 and 8. The full line indicates coincidence between model and experiment, and the range within the dotted lines contains 90% of the points. △: batch K_d's (this study) on MX-80; ◇: batch K_d's (this study) on 10/90 bentonite/sand; □: batch K_d's from the literature; ○: K_d's from diffusion experiments

by assuming that the available CEC of compacted bentonite is reduced to 10 meq/100 g, and by using the apparent diffusivity of tritiated water as pore diffusivity of Cs^+. Figure 3 presents an overview of the measurements vs. predictions of all K_d's (more than 100 values) considered in the present study. 90% of the K_d values are predicted correctly within a factor of $\pm$ 5 (cf. dotted lines in Fig. 3). Significant deviations are noted for 10/90 bentonite/sand mixtures with $MgCl_2$ and $CaCl_2$ as background electrolyte. They may be due to experimental uncertainties or modelling errors, e.g., the mole fraction appraoch using a dependence of the ion exchange constants on the level of exchange.

Uncertainties exist in the amounts of soluble impurities in the bentonite and in the evaluation of the diffusion parameters. Future investigations should therefore focus on a complete chemical characterisation of the solid phases and the chemically active impurities. For modelling purposes in compacted bentonite it is recommended to develop an integrated sorption/diffusion database system containing both surface chemical mechanisms and diffusion mechanisms.

Acknowledgements Financial support by the Swedish Nuclear Fuel and Waste Management Co. (SKB) is gratefully acknowledged.

References

1. Wieland E, Wanner H, Albinsson Y, Wersin P, Karnland O (1994) A surface chemical model of the bentonite/water interface and its implications for modelling the near-field chemistry in a repository for spent fuel. SKB technical report TR 94-26, Stockholm, Sweden
2. Müller-Vonmoos M, Kahr G (1983) Mineralogische Untersuchungen von Wyoming-Bentonit MX-80 und Montigel. Nagra technical report 83-12, Baden, Switzerland
3. Wanner H, Wersin P, Sierro N (1992) Thermodynamic modelling of bentonite-groundwater interaction and implications for near-field chemistry in a repository for spent fuel. SKB technical report TR 92-37, Stockholm, Sweden
4. Fletcher P, Sposito G (1989) Clay Minerals 24:375–391
5. Benson LV (1982) Environ Geol 4:23–29
6. Bruggenwert MGM, Kamphorst A (1982) Survey of experimental information on cation exchange in soil systems, Chapter 5. In: Bolt GH (ed) Soil chemistry. Elsevier, Amsterdam, pp 141–203
7. Dzombak DA, Hudson RJM (1995) Ion exchange: The contributions of diffuse layer sorption and surface complexation, Chapter 3. In: Huang CP, O'Melia CR, Morgan JJ (eds) Aquatic chemistry: interfacial and interspecies processes. Advances in chemistry, Series 244. American Chemical Society, Washington, DC, pp 59–94
8. Wanner H, Albinsson Y, Karnland O, Wieland E, Wersin P, Charlet L (1994) Radiochim Acta 66/67:157–162
9. Snellman M, Uotila H, Rantanen J (1987) Mat Res Soc Symp Proc 84:781–790
10. Wahlberg JS, Fishman MJ (1962) Geol Survey Bull 1140-A:A1-A30
11. Mucciardi AN, Booker IJ, Orr EC, Cleveland D (1978) Statistical investigation of the mechanics controlling radionuclide sorption. In: WISAP Task 4, 2nd Contractor Meeting Proc PNL-SA-7352
12. Wolfsberg K (1978) Sorption-desorption studies of Nevada Test Site. Alluvium and leaching studies of nuclear test debris. Los Alamos Scientific Laboratory, Informal Report LA-7216-MS, UC-11
13. Erten HN, Aksoyoglu S, Hatipoglu S, Göktürk H (1988) Radiochim Acta 44/45:147–151
14. Miyahara K, Ashida T, Kohara Y, Yusa Y, Sasaki N (1991) Radiochim Acta 52/53:293–297
15. Torstenfelt B, Allard B, Andersson K, Kipatsi H, Eliasson L, Olofsson U, Persson H (1983) Radionuclide diffusion and mobilities in compacted bentonite. KBS TR 83–34, Stockholm, Sweden
16. Torstenfelt B, Allard B (1986) Migration of fission products and actinides in compacted bentonite. SKB TR 86–14, Stockholm, Sweden
17. Muurinen A, Rantanen J, Penttilä-Hiltunen P (1986) Mat Res Soc Symp Proc 50:617–624
18. Albinsson Y, Forsyth R, Skarnemark G, Skålberg M, Torstenfelt B, Werme L (1990) Mat Res Soc Symp Proc 176:559–565
19. Albinsson Y, Andersson K, Börjesson S, Allard B (1993) Diffusion of radionuclides in concrete/bentonite systems. SKB technical report TR 93–29, Stockholm, Sweden
20. Sato H, Ashida T, Kohara Y, Yui M (1993) Mat Res Soc Symp Proc 294:403–408
21. Albinsson Y (1993) Diffusion and sorption of Cs in bentonite/bentonite-sand mixtures. Internal Report KK930803, Chalmers University of Technology, Gothenburg, Sweden, draft of August 1993
22. Albinsson Y, Engkvist I (1991) Rad Waste Manage Nucl Fuel Cycle 15(4):221–239
23. Cheung SCH, Gray MN (1989) Mat Res Soc Symp Proc 127:677–681
24. Wanner H, Albinsson Y, Wieland E (1994) An ion exchange model for the prediction of distribution coefficients of caesium in bentonite. SKB technical report TR 94-10, Stockholm, Sweden
25. Muurinen A (1994) Diffusion of anions and cations in compacted bentonite. PhD thesis, VTT Publications Nr 168, Technical Research Centre of Finland, Espoo, Finland
26. Sato H, Yui M, Yoshikawa H (1995) Diffusion behaviour for Se and Zr in sodium-bentonite. Mat Res Soc Symp Proc (in press)
27. Oscarson DW, Hume HB, King F (1994) Clays and Clay Minerals 42(6):731–736