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Sorption of Sr and Cs onto Czech natural bentonite – Experiments and modelling

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INTRODUCTION

- Simple mechanistic sorption modelling was applied on the results of batch sorption experiments with Sr and Cs on the Czech natural Mg/Ca bentonite.
- Ion exchange model was based on the real characteristics of bentonite BaM. The selectivity coefficients of exchangeable cations were determined in a similar manner as in [1] and the selectivity coefficient of Sr was set to be the same as for Ca [2].
- The selectivity coefficient of Cs was chosen in accordance with literature [3] and the concentration and stability constant of the surface complex were fitted.

EXPERIMENTAL

Material:

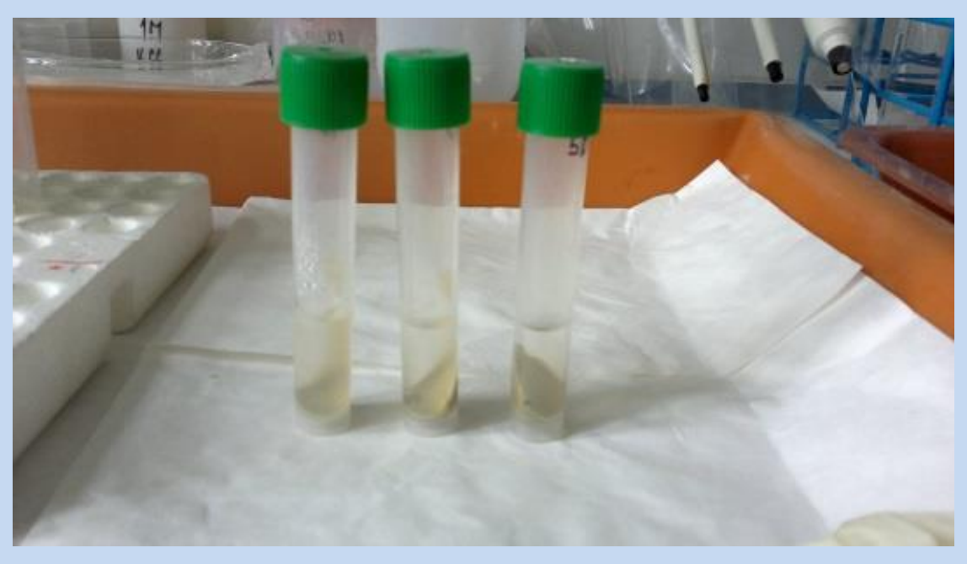
- Czech bentonite BaM (natural Mg/Ca bentonite)
- No pre-treatment or pre-equilibration with solutions
- CEC = 612 meq·kg^{-1}, specific surface area = 516 m^2·g^{-1}
- Abundances of major exchangeable cations: Mg^{2+} = 64.0 %, Ca^{2+} = 23.3 %, Na^+ = 7.1 %, K^+ = 5.5 %.

Solutions: 0.033 mol·L^{-1} $CaCl_2$, 0.1 mol·L^{-1} NaCl (I_s = 0,1 mol·L^{-1})

Sr: non-active $SrCl_2$ + radioactive tracer ^{85}Sr

Cs: non-active CsCl + radioactive tracer ^{137}Cs

Measurement: NaI(Tl) well-type gamma counter



Sorption experiments:

- Batch method: variable *m/V*, variable C_0
- Centrifugation at 966 g for 10 minutes
- Equilibrium contact time based on kinetic experiments set to 3 days for Sr and 7 days for Cs
- The average pH values at the end of experiments were 7.5 ± 0.1 in $CaCl_2$ background electrolyte and 8.0 ± 0.1 in NaCl background electrolyte.

MODELLING

Realized in PhreeqC 3, database Hatches NEA20 used for Sr and Cs speciation. The initial solution contained the selected background electrolyte and the mass of exchanger according to given solid-to-liquid ratio.

Sr: one-site ion exchange model, model parameters set according to real bentonite characteristics, selectivity coefficient set to be the same as for Ca

Cs: two-site ion exchange/surface complexation model, selectivity coefficient taken from literature [3], surface complexation sites concentration and stability constant fitted

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EXCHANGE_SPECIES
Na+ + X- = NaX
K+ + X- = KX
Ca+2 + 2X- = CaX2
Mg+2 + 2X- = MgX2
Sr+2 + 2X- = SrX2
Cs+ + X- = CsX
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SURFACE_SPECIES
Su_s + Cs+ = Su_sCs+
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Tab. 1 *Equilibrium constants and corresponding selectivity coefficients for four major exchangeable cations, strontium and cesium*

	Selectivity coefficient $K(M^{n+})/K(Na^+)$	log*K*
Na^+	1	0.00
K^+	3.10	0.49
Ca^{2+}	11.20	0.83
Mg^{2+}	12.60	0.85
Sr^{2+}	11.20	0.83
Cs^+	39.81	1.60

RESULTS

Sorption of Sr in both electrolytes showed a linear trend in the given concentration range. Mean K_d value of Sr on BaM was 11.2 ± 0.1 L·kg^{-1} in $CaCl_2$ and 33.8 ± 8.0 L·kg^{-1} in NaCl background electrolyte respectively.

In both background electrolytes, the K_d values tended to decrease with increasing *m/V*. This is probably an effect of competing cations, which are released into the solution in higher amount when the bentonite mass in the system is increased. This trend is enhanced in the NaCl background solution because Na is less competitive for Sr than Ca and therefore Sr sorption is higher when the dominant exchangeable cation is Na.
Model of ion exchange was able to predict the dependence of K_d on *m/V* in NaCl background electrolyte, the model predicted slightly lower K_d values and opposite dependence of K_d on *m/V* in $CaCl_2$ background electrolyte.

Fig. 1 *Sorption isotherms of Sr on bentonite BaM (points) in $CaCl_2$ background electrolyte (left) and NaCl background electrolyte (right) and prediction of ion exchange model (lines) for three solid-to-liquid ratios (colour differentiation).*

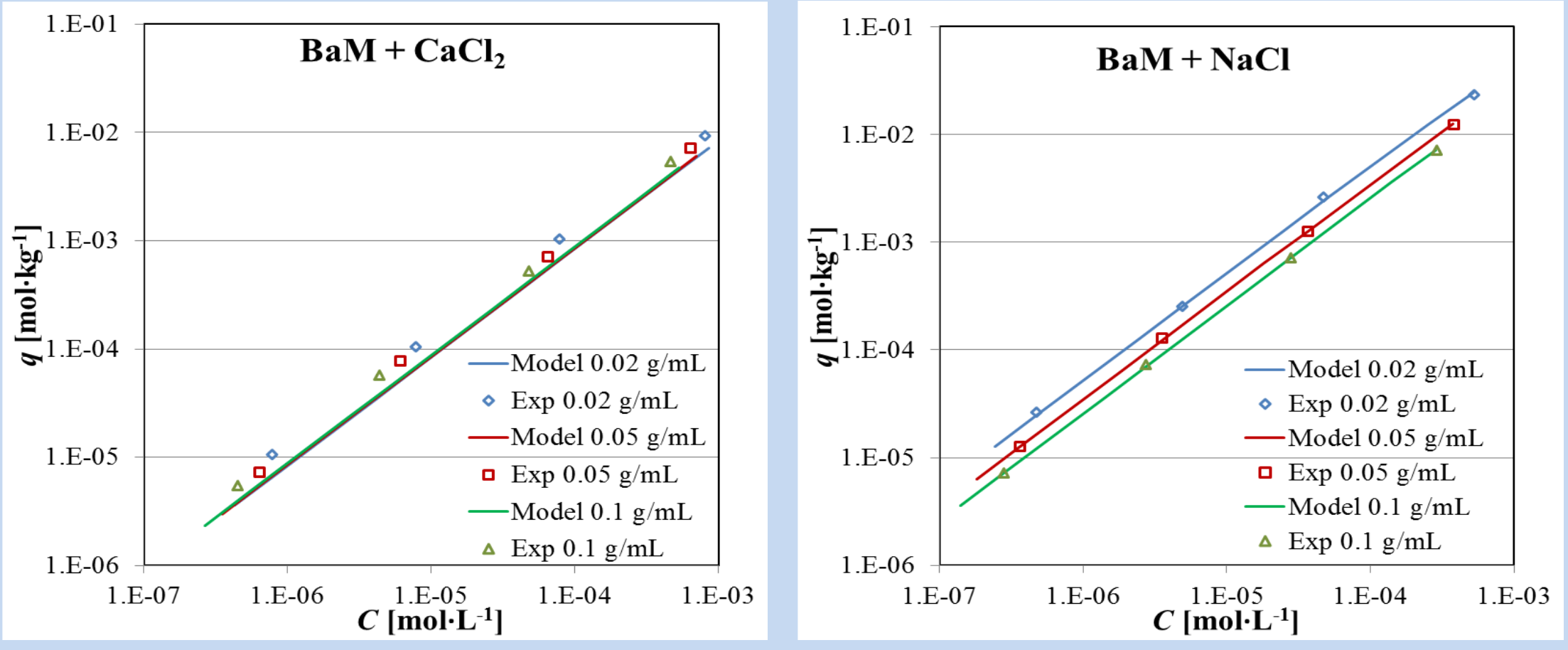
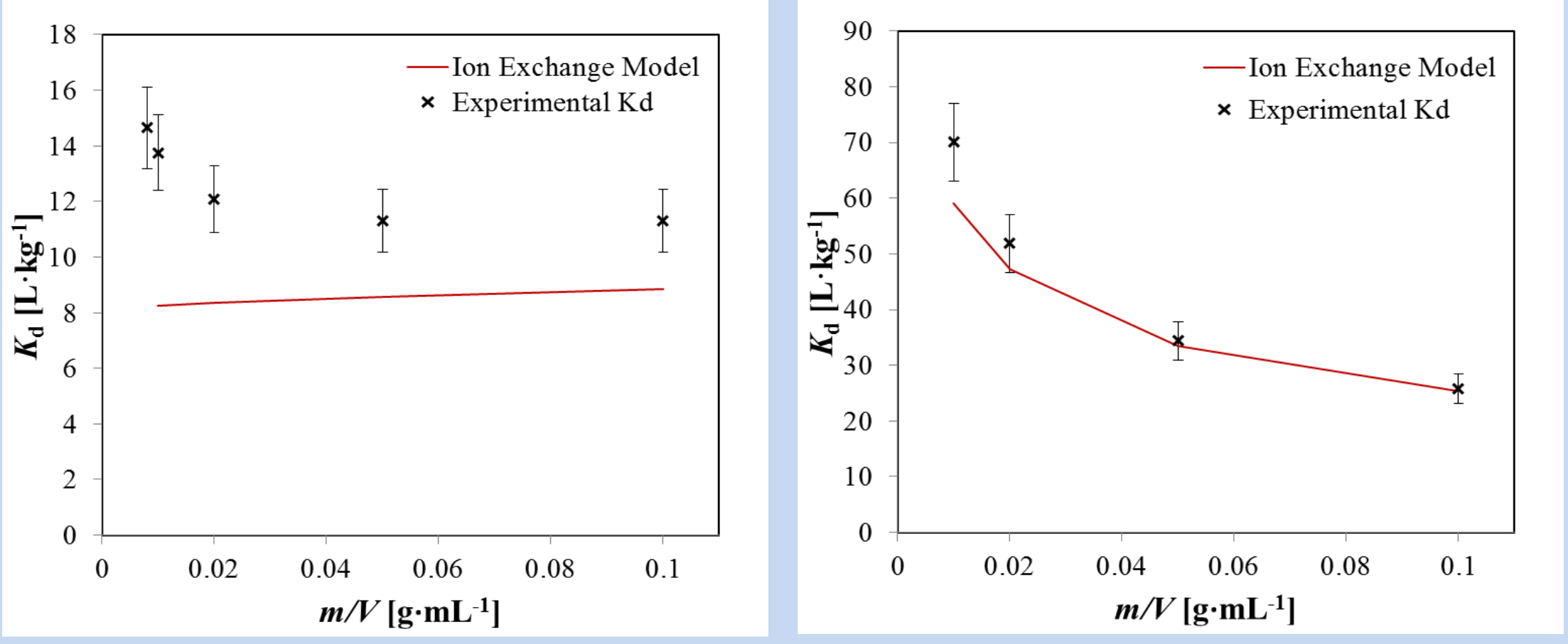
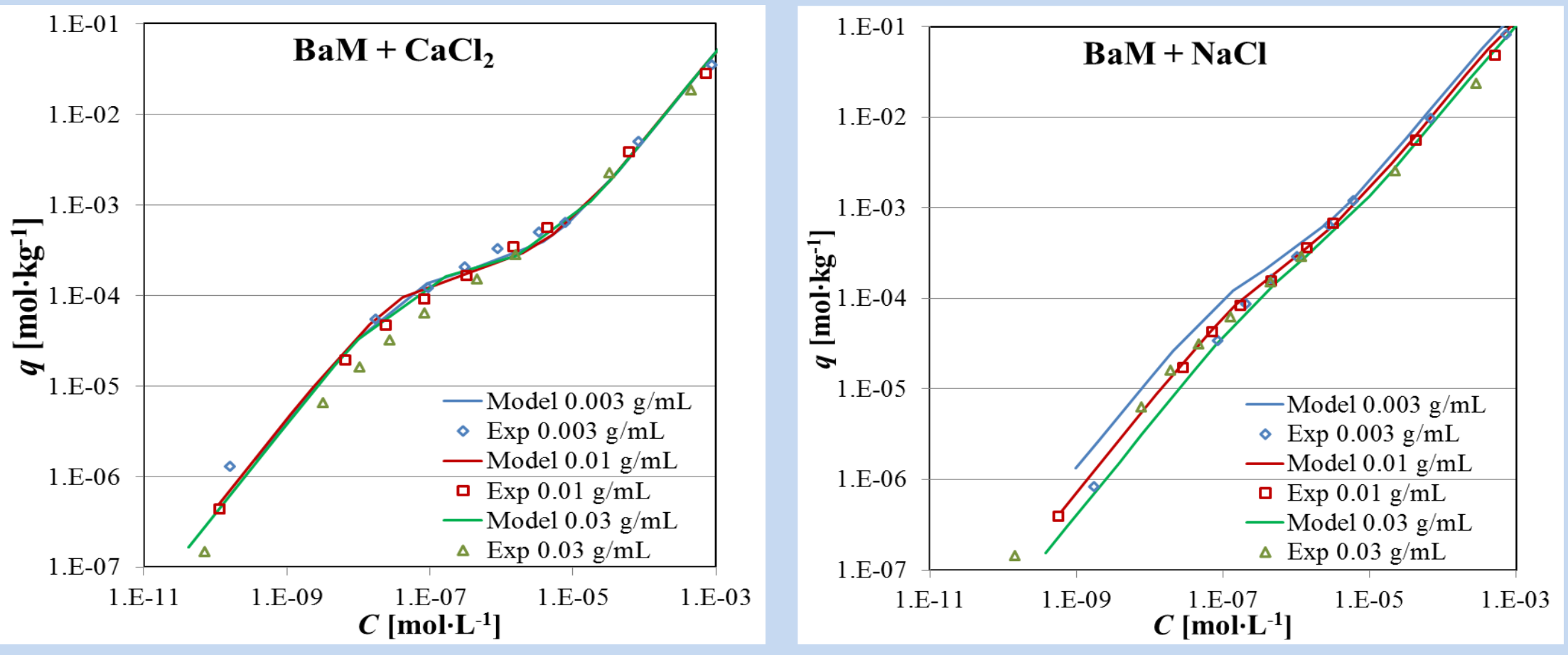


Fig. 2 *Experimental K_d values of Sr on bentonite BaM in in $CaCl_2$ background electrolyte (left) and NaCl background electrolyte (right) and ion exchange model prediction.*



Sorption isotherm of Cs was non-linear with distribution coefficients being higher in lower range of Cs total concentration (up to 1×10^{-6} − 1×10^{-5} mol·L^{-1}).
Below this concentration, the irreversible sorption mechanism on specific sites, which are present in low concentration in clay material, is dominant, whereas in higher Cs total concentration range, this effect is superimposed by ion exchange on layer sites of clay minerals [4].

Fig. 3 *Sorption isotherms of Cs on bentonite BaM (points) in $CaCl_2$ background electrolyte (left) and NaCl background electrolye (right) and prediction of ion exchange/surface complexation model (lines) for three solid-to-liquid ratios (colour differentiation).*



In general, sorption of Cs is lower in NaCl electrolyte, because Na^+ is relatively stronger competitor for Cs^+ than Ca^{2+}.
The selectivity coefficient of Cs taken from literature [3] was found satisfactory.
Surface sites concentration was fitted and the value was 0.2 meq·kg^{-1} which is 0.03 % of the concentration of ion exchange sites. Stability constant of surface complexation reaction was also fitted and they differed in each electrolyte used with values log*K* = 10.5 in case of $CaCl_2$ and log*K* = 7.8 in case of NaCl.

CONCLUSION

- One-site ion exchange model fitted Sr sorption data adequately and was able to predict the observed K_d dependence on solid-to-liquid ratio.
- Two-site ion exchange/surface complexation model for Cs sorption simulated the dual sorption mechanism of Cs adequately, thus the predictive ability was lower due to the fact that the protonation of edge sites or competition with Na ion was not taken into account.

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