Business from technology

Cation Exchange in Montmorillonite

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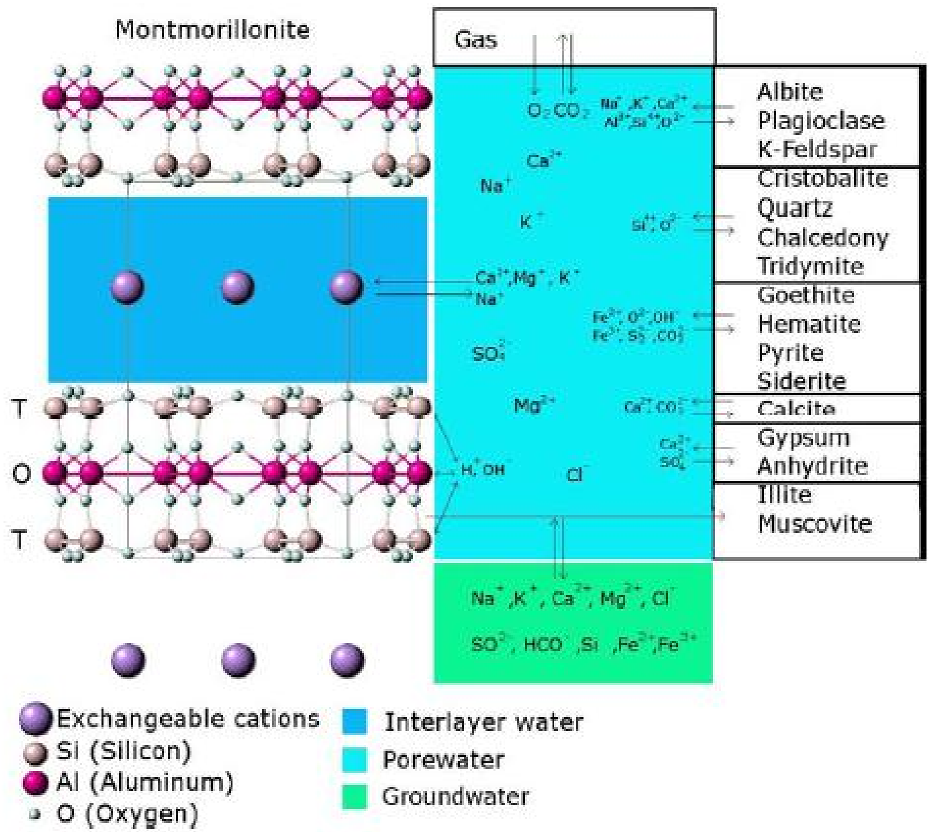
Introduction 1/2

- Spent nuclear fuel rods are places inside copper canisters deep into the bedrock.
- Each Canister will be separated from the bedrock by a bentonite clay layer (buffer).
- The spent nuclear fuel produces heat the first 10000 year time period which can affect the cation-exchange behaviour. Thus, for the long-term modelling of the chemical processes in the buffer, the cation-exchange selectivity coefficients have to be known at different temperatures.
- During this project we will clarify if the cation exchange selectivity of montmorillonite changes significantly and how the selectivity coefficients behave in different temperatures.

Introduction 2/2

- Montmorillonite layers have permanent negative charge (CEC).
- The cation form affects to properties of montmorillonite (swelling, structure, etc.).
- In KBS-3 concept max T is 90°C
- The selectivities have mostly been studied at room temperature.
- Thus we need data from higher temperatures also.



Experiments 2011, 1/2

- MX-80 bentonite from Wyoming (USA) was purified to Na-montmorillonite.[1)]
- This was done to avoid unnecessary complexes and mineral reactions
- 1g of Na-montmorillonite was allowed to react approximately 30ml of $NaClO_4^{-}/Ca(ClO_4^{-})_2$ solution using 0.01 eq/l cation normality in centrifugal tubes.
- Three temperatures 25, 50 and 75 ^{o}C was used
- Every test series include five Na/Ca ratios with two parallel samples.
- The tests were shaken with digital incubator for five days.
- At the end of the tests, the centrifugal tubes were centrifuged and the separated solution was ultra filtered with 10kDa filters for the analysis.

1. H. Tributh and G.A. Lagaly, “Aufbereitung und Identifizierung von Boden- und Lagerstättentonen. I. Aufbereitung der Proben im Labor“. (GIT-Fachzeitzschrift für das Laboratorium 30, 1986) pp. 524-529.

Experiments 2011, 2/2

- Perhlorate backround was chosen because it does not form complexes.
- The concentration of sodium and calcium was determined using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry).
- CEC was determined using copper-triethylenetetramine (0.96meq/g)
- After analyses, it was found out that the amount of cations was higher than in original solutions (Donnan exlusion effect).
- This had to be condisered in the calculations.

Used equations

- The Donnan exclusion effect which caused the increase of cation concentration in the supernatant was taken into account by using an effective volume for the solution after centrifugation

$$\left(2c_{\mathrm{Ca}}^{\mathrm{i}}+c_{\mathrm{Na}}^{\mathrm{i}}\right)V_{\mathrm{total}}=\left(2c_{\mathrm{Ca}}^{\mathrm{e}}+c_{\mathrm{Na}}^{\mathrm{e}}\right)V_{\mathrm{effective}}$$

- Amount of sodium and calcium in the montmorillonite was calculated with mass balance equation:

$$2\left(c_{\mathrm{Ca}}^{\mathrm{i}}V_{\mathrm{total}}-c_{\mathrm{Ca}}^{\mathrm{e}}V_{\mathrm{effective}}\right)=\beta_{Ca}(CEC\cdot m_{\mathrm{montmorillonite}}) \qquad \beta_{Ca}+\beta_{Na}=1$$

- The cation exchange reaction in montmorillonite was:

$$2\mathrm{NaX}+\mathrm{Ca}^{2+}\rightleftharpoons 2\mathrm{Na}^{+}+\mathrm{CaX}_2$$

- The Selectivity efficients were calculated according to:

$$K_{\mathrm{Ca\backslash Na}}=\frac{\beta_{\mathrm{Ca}}\gamma_{\mathrm{Na}^+}^2 m_{\mathrm{Na}^+}^2}{\beta_{\mathrm{Na}}^2\gamma_{\mathrm{Ca}^{2+}} m_{\mathrm{Ca}^{2+}}}$$

Results 1/2

Table I. Experimental data on Na^+/Ca^{2+} exchange at 25 ºC, 50 ºC and 75 ºC on Na-montmorillonite in 0.1M perchlorate solution.

Temp	Initial c_{Na} [mmol/l]	Initial c_{Ca} [mmol/l]	Analyzed c_{Na} [mmol/l]	Analyzed c_{Ca} [mmol/l]	q_{Na} [eq/kg]	q_{Ca} [eq/kg]	$K_{Ca/Na}$
25	88.24	5.26	104.39	1.62	0.736	0.227	4.48
25	67.84	15.02	91.34	6.36	0.420	0.543	6.46
25	48.55	25.23	73.95	14.22	0.273	0.690	5.73
25	28.82	35.94	56.55	24.08	0.195	0.767	4.35
25	9.94	45.50	39.36	32.44	0.116	0.847	4.95
50	86.97	5.16	100.04	1.58	0.739	0.223	4.19
50	68.17	16.18	91.34	7.24	0.404	0.559	6.51
50	48.83	25.60	73.95	14.47	0.270	0.692	5.91
50	29.18	35.81	56.55	23.95	0.199	0.763	4.31
50	9.79	46.07	40.23	34.93	0.139	0.824	3.38
75	87.61	5.14	100.04	1.57	0.744	0.219	4.22
75	68.20	15.34	91.34	6.49	0.412	0.551	7.05
75	48.72	25.62	78.29	14.72	0.245	0.718	8.55
75	29.41	35.84	60.90	24.08	0.151	0.811	9.50
75	9.73	46.11	40.89	34.93	0.125	0.837	4.49

Results

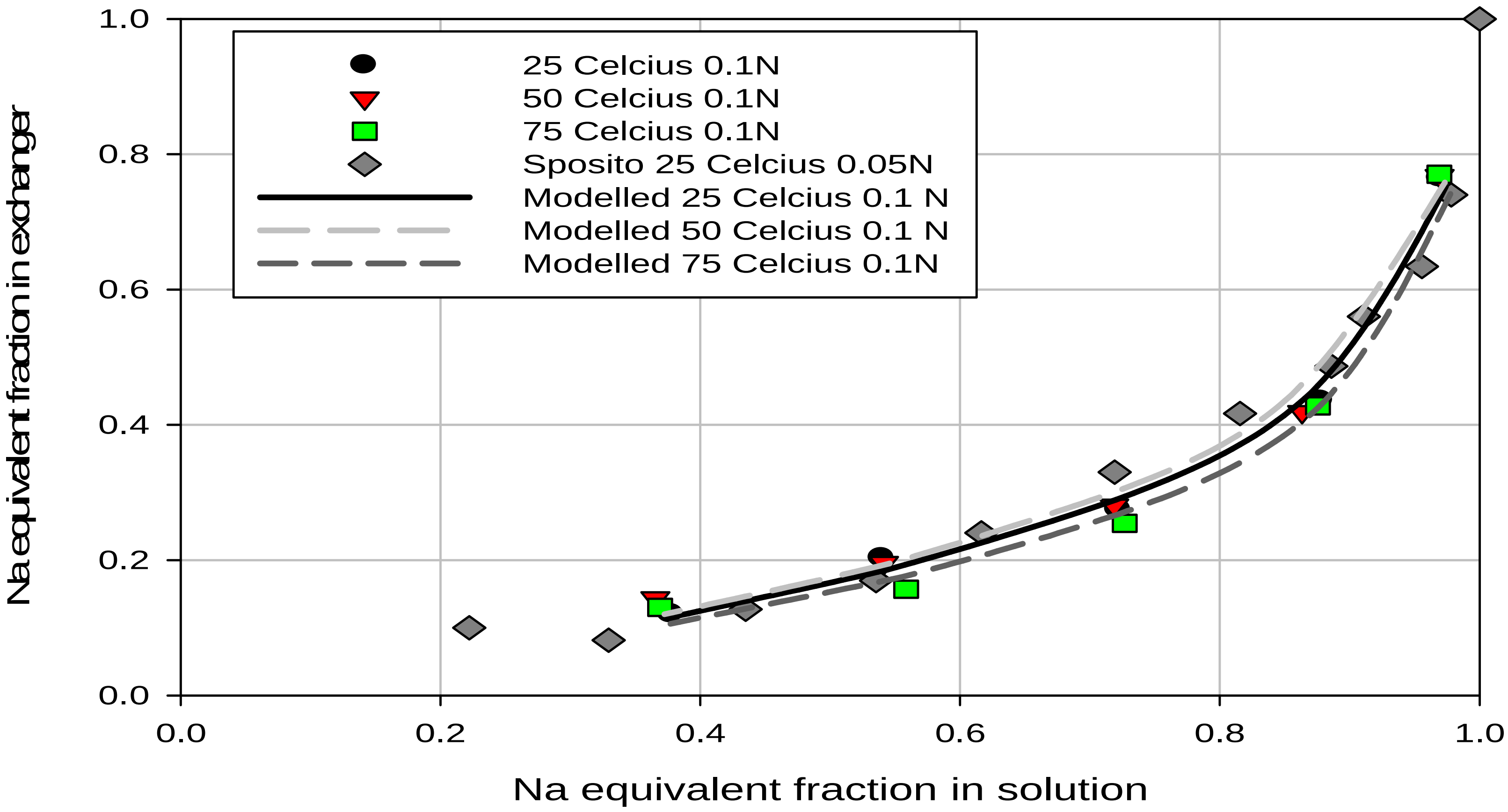


Figure 1. Exchange isotherm of Na^+ on Na-montmorillonite in perchlorate background for Na-Ca exchange.

Conclusion

- The exchange of Na-montmorillonite can be characterised by Gaines-Thomas Selectivity coefficients that are independent of the exchanger composition for example with PHREEQC.
- Experimental results were in good agreement with the earlier studies
- The results showed tendency to take more calcium inside montmorillonite at 75^{o}C
- Temperature seems to affect to selectivities and thus more experiments is needed to confirm these results and get the selectivities for high temperatures also for Mg and K.

Future work

- To make more experiments with Na/Ca-montmorillonite to confirm the results and get the selectivity coefficients at high temperatures.
- To develop the experimental results further (analyze the clay slurry in addition to supernatant).
- To make the experiments for non-compated bentonite without centrifugation to avoid the electrokinetic effects
- To make the experiments also for compacted material (long term experiments)
- To test the selectivities also for Mg and K.

Thanks