

EXPRESS LETTER

Modeling the competition between solid solution formation and cation exchange on the retardation of aqueous radium in an idealized bentonite column

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Clays and clay rocks are considered viable geotechnical barriers in radioactive waste disposal. One reason for this is the propensity for cation exchange reactions in clay minerals to retard the migration of radionuclides. Although another retardation mechanism, namely the incorporation of radionuclides into sulfate or carbonate solid solutions, has been known for a long time, only recently has it been examined systematically. In this work, we investigate the competitive effect of both mechanisms on the transport of radium (Ra) in the near-field of a low- and intermediate level nuclear waste repository. In our idealized geochemical model, numerical simulations show that barium (Ba) and strontium (Sr) needed for Ra sulfate solid solutions also partition to the cation exchange sites of montmorillonite (Mont), which is the major mineral constituent of bentonite that is used for tunnel backfill. At high Mont content, most Ra tends to attach to Mont, while incorporation of Ra in sulfate solid solutions is more important at low Mont content. To explore the effect of the Mont content on the transport of radium, a multi-component reactive transport model was developed and implemented in the scientific software OpenGeoSys-GEM. It was found that a decrease of fixation capacity due to low Mont content is compensated by the formation of solid solutions and that the migration distance of aqueous Ra is similar at different Mont/water ratios.

Keywords: reactive transport, solid solutions, cation exchange, bentonite, radioactive waste repository, montmorillonite, OpenGeoSys, GEM-Selector

INTRODUCTION

Bentonite, comprised mainly of the clay mineral montmorillonite (Mont), is widely used in geotechnical applications to isolate hazardous wastes. In radioactive waste repositories, pure bentonite is suggested as a buffer material to seal waste canisters, while bentonite-sand mixtures are utilized as backfill for access tunnels (Nagra, 2002). The understanding of thermo-hydro-mechanical (THM) and chemical (C) processes in engineered barrier systems is of crucial importance for the long-term safety of subsurface waste repositories (Stephansson *et al.*, 2004; Wallner *et al.*, 2007; Rutqvist *et al.*, 2009). In such geotechnical systems, chemical interactions between radionuclides and clay minerals determine the retention

and possible release of radionuclides from the repository to the biosphere. Among all chemical processes, cation exchange (Reardon, 1981), surface complexation (Glynn, 2003) and the formation of solid solutions (Zhu, 2004) are considered to contribute most significantly to the retardation of radionuclides. Cation exchange reactions in bentonite, and in more general form, on clay minerals, have been well investigated (Bradbury and Baeyens, 1997; Huertas *et al.*, 2001; Fernandez *et al.*, 2004). The effect of solid solutions has also attracted some recent attention. Martin *et al.* (2003) evaluated experimentally the mobility of radium, and reported that dissolution of a (Ba,Ra)SO₄ solid solution controls the aqueous concentration of radium and barium in pore water released from nuclear waste repositories. Zhu (2004) provided a compilation of mixing parameters for Ra and Ba sulfate isostructural family. Grandia *et al.* (2008) found that the solubility of Ra in a repository environment should be in the range of 10⁻¹¹ mol/L, in the presence of (Ba,Ra)SO₄

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co-precipitation, and that it will be three orders of magnitude higher if only a pure RaSO_4 phase is considered. Shao *et al.* (2009a) numerically analyzed non-ideal aqueous-solid solution systems with both Ba–Sr–Ra carbonate and Ba–Sr–Ra sulfate formations. They concluded that the re-partitioning of radium from carbonate to sulfate may cause a strong retardation effect on Ra. A shortcoming of their study is that the cation exchange process was not considered in their reactive transport model. In this work, we further develop their model and investigate how the radium-containing solid solutions may interact with the cation exchange in bentonite, and how these interactions may influence the transport of Ra.

MODEL

Governing equations

In this work, the reactive transport of chemical components is governed by an advection-dispersion mass balance, supplemented by source/sink from chemical reactions occurring at equilibrium. These relationships are respectively (Bear and Bachmat, 1990),

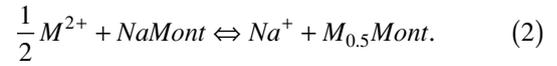
$$\begin{cases} \frac{\partial C_i}{\partial t} = -\nabla(vC_i) + \nabla(D_i \nabla C_i) + Q_i \\ \frac{\partial C_i}{\partial t} = \Gamma_i(C_1 \cdots C_m), \end{cases} \quad i = 1, 2, \dots, m, \quad (1)$$

where C_i denotes the molar concentration of the i -th species of a m multi-species system; v is the pore water velocity of groundwater flow; D_i is the diffusion-dispersion coefficient of component i ; Q_i is a source/sink term and $\Gamma_i(C_1 \cdots C_m)$ is a source/sink term of species i due to equilibrium chemical reactions with other species. The above governing equations are simulated using the multi-component reactive transport code OpenGeoSys-GEM. It employs the sequential non-iterative approach to couple the mass transport code OpenGeoSys (Wang *et al.*, 2009) with GEMIPM2K (Kulik *et al.*, 2008). For each time step, the advection-dispersion equation (ADE) is calculated first, and concentrations for each species are passed to the chemical solver, which calculates local equilibrium at each grid node. Resultant concentrations of chemical species are then passed to the subsequent time step. Details regarding code development and verification can be found in Shao *et al.* (2009a).

Representation of cation exchange processes

In reactive transport codes, cation exchange processes are usually calculated assuming that the clay mineral is represented by an X -“ligand” initially occupied with Na^+ . We implemented a more chemically plausible solid solution model of ion exchange in clay. For such a model it is

necessary to formulate each end member with exactly one negative charge per formula unit of *Mont*, according to the following exchange reaction



The corresponding equilibrium constant K_G (expressed in the Gapon convention in mole fractions) for the ideal mixing is

$$K_G = \frac{x_{M_{0.5}Mont}}{x_{NaMont}} \cdot \frac{a_{Na^+,aq}}{a_{M^{2+},aq}^{0.5}}, \quad (3)$$

where a stands for the activity of aqueous cation and x is the mole fraction of corresponding mineral end member. It is numerically the same as a Gaines-Thomas selectivity coefficient K_{GT}^c (Gaines and Thomas, 1953) or Vanselow (1932) selectivity coefficient K_V^c for the mono-to-monovalent exchange, but is related to them for mono-to-divalent exchange as

$$K_G = K_V^{0.5} = \left(K_{GT,M}^c \cdot \frac{\sum n}{2 \sum zn} \right)^{0.5}. \quad (4)$$

Here $\sum n$ is the sum of the mole amounts and $\sum zn$ is the sum of equivalents of ions present on the exchanger.

Geochemical model

The geochemical model is constructed from compositional data on FEBEX bentonite (Huertas *et al.*, 2001; Fernandez *et al.*, 2004), which contains approximately 92% smectite. In order to focus on the competition of cation exchange and solid solutions, we do not consider the redox effect in our chemical system. Therefore the smectite is represented by a pure montmorillonite formula unit (referred to as *Mont*, $[\text{MgAl}_5(\text{Si}_4\text{O}_{10})_3(\text{OH})_6]^-$) without any Fe. From this basis formula, a sodium montmorillonite with a composition of $\text{Na}[\text{MgAl}_5(\text{Si}_4\text{O}_{10})_3(\text{OH})_6]$ (referred to as *Na-Mont*) was first set up as a dependent component. Other cation-exchange components, including K, Ca, Mg, Ba, Sr, and Ra end members, were defined using exchange reactions with *Na-Mont* in form of Eq. (2). An ideal solid solution phase was composed of K-, Ca-, Mg-, Ba-, Sr-, and Ra-*Mont* as end members, and exchange coefficients were converted from K_{GT}^c values given by Fernandez *et al.* (2004). The exchange equations and corresponding coefficients are listed in Table 1.

Because pore water composition for highly compacted bentonite is difficult to estimate, most available pore water

Table 1. Selectivity coefficients K_{GT}^c , equilibrium constants K_G for ion-exchange reactions, and standard Gibbs energies of end members representing the montmorillonite clay phase (-Mont stands for $[MgAl_3(Si_4O_{10})_3(OH)_6]$) at 298.15 K

End members	Reactions	K_{GT}^c *	K_G	G°_{298} (J/mol)
Na-Mont				-15908267
K-Mont	$K^+ + \text{Na-Mont} \Leftrightarrow \text{Na}^+ + \text{K-Mont}$	10.6	10.6	-15934700
Ca _{1/2} -Mont	$1/2\text{Ca}^{2+} + \text{Na-Mont} \Leftrightarrow \text{Na}^+ + \text{Ca}_{1/2}\text{-Mont}$	12.8	2.2	-15924343
Mg _{1/2} -Mont	$1/2\text{Mg}^{2+} + \text{Na-Mont} \Leftrightarrow \text{Na}^+ + \text{Mg}_{1/2}\text{-Mont}$	10.7	2.0	-15874717
Sr _{1/2} -Mont	$1/2\text{Sr}^{2+} + \text{Na-Mont} \Leftrightarrow \text{Na}^+ + \text{Sr}_{1/2}\text{-Mont}$	12.8	2.5	-15930451
Ba _{1/2} -Mont	$1/2\text{Ba}^{2+} + \text{Na-Mont} \Leftrightarrow \text{Na}^+ + \text{Ba}_{1/2}\text{-Mont}$	12.8**	2.5**	-15928924
Ra _{1/2} -Mont	$1/2\text{Ra}^{2+} + \text{Na-Mont} \Leftrightarrow \text{Na}^+ + \text{Ra}_{1/2}\text{-Mont}$	12.8**	2.5**	-15929280

*According to measurements by Fernandez *et al.* (2004).

**Assumed to be the same as for Sr.

cation profiles are extrapolated from batch extraction tests. In this work, Mont phase composition is based on the initial cation loadings reported by Fernandez *et al.* (2004). The model system includes mineral phases of Mont, quartz, kaolinite and gibbsite, together with 3.2 mMol/L of NaCl to match the chloride inventory of FEBEX bentonite. An excess atmosphere with $\log P_{\text{CO}_2}$ of -3.5 is built into the system. GEM simulation results were compared with the data from batch experiments at a solid/liquid ratio of 0.147. Initial guesses of G°_j values were first obtained from thermodynamic databases (Bechtel SAIC Company, 2004; CTD, 2009), or estimated by analytical method (Mattigod and Sposito, 1978). They are later adjusted such that trace amount of kaolinite precipitated in the presence of Mont and quartz, while Gibbsite remained undersaturated. Next, the solid/liquid ratio was varied from 0.147 to 25. The simulated pH value decreased from 8.6 to about 7.5, and dissolved Al drops from 3×10^{-7} to less than 4×10^{-8} molal at a solid/liquid ratio of 4.0. For higher solid/liquid ratios, the pore water composition is dominated by cation occupancies on clay and remained nearly constant. A more improved calibration would require comparison with measured Al concentrations, unfortunately such information was not provided by Fernandez *et al.* (2004).

Additionally, a sensitivity analysis was performed by increasing the stability of all Mont end members, i.e., decreasing their G°_{298} values simultaneously with 30 kJ/mol. In terms of aqueous primary species, only the behavior of Al was noticeably altered. Total dissolved Al decreased to 1×10^{-8} molal, while kaolinite disappeared and gibbsite remained undersaturated. The pH and other dissolved cations remained nearly unaffected. From this we conclude that the ion distribution between ion exchanger (clay) and aqueous solution is largely unaffected by the solubility of the Mont phase as long as this phase is stable relative to gibbsite and kaolinite. Hence, we accepted the G°_{298} values for Na-Mont. G°_{298} values for all

other end-members are calculated using exchange reactions with Na-Mont. The exchange coefficients and subsequent G°_{298} values are listed in Table 1.

After calibrating the Mont phase model, four non-ideal solid solutions, (Ca,Ba,Sr)CO₃, (Ra,Ba,Sr)CO₃, (Ra,Ba,Sr)SO₄ and (Ra,Sr,Ba)SO₄, were added to the definition of the chemical system. We assumed that Ba and Sr tend to form separate solid solution phases, while calcium is distributed between calcite and gypsum in the presence of sulfate. The CaSO₄ containing solid solutions were excluded from the present setup. Instead, the Ra-Ba-Sr sulfate system was set as two solid solution phases, one mainly celestite-RaSO₄ and another mainly barite-RaSO₄. Gypsum, magnesite and quartz were included as pure mineral phases. Details regarding the chemical system definition are provided in a separate Excel file (see supporting information Shao *et al.*, 2009b). During pre-processing, bentonite is usually exposed to the air, and the bentonite pore water alkalinity is then controlled by the partial pressure of CO₂. To reflect this, the system is maintained in equilibrium with atmospheric air so that the $\log P_{\text{CO}_2}$ value is consistent at -3.5. With this setting, our calculated pH value (7.51) is similar to the one measured by Fernandez *et al.* (2004). A different $\log P_{\text{CO}_2}$ value would be required to represent a closed and fully saturated repository (e.g., to -2.2 for typical groundwater). In FEBEX bentonite, the initial bentonite (solid)/liquid ratio is 19 kg/kg (Fernandez *et al.*, 2004). However, bentonite can be mixed with different proportions of sand for backfilling the access tunnels. This also results in a change of the solid/liquid ratio. For example, the tunnel backfilling material may contain 80 wt. % of sand and 20 wt. % of bentonite (that contains 75% Mont) for the dry material. At a porosity of 0.3, the solid/liquid ratio for Mont/water is about 1.35. In our model, we fix the amount of water at 1 kg, and scale the given amount of Mont proportionally. Total system volume is conserved through the addition of quartz, thus representing different propor-

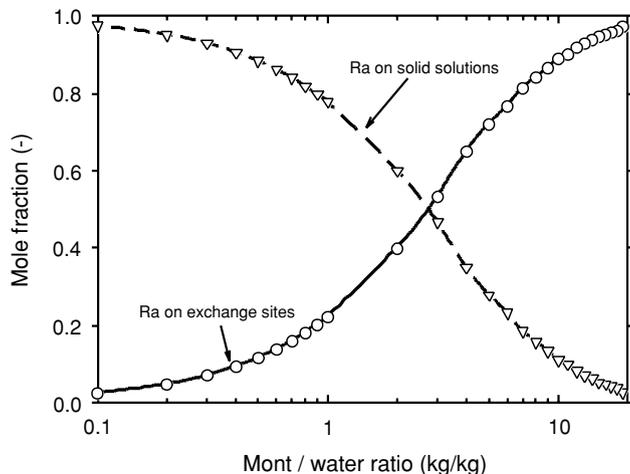


Fig. 1. Influence of Mont/water ratio on the radium distribution among cation exchange sites and solid solution formations.

tions of sand in the Mont-sand backfill. The Mont/water ratio was gradually lowered from 19 to 0.1, but with 2×10^{-7} M of Ra^{2+} remaining in the system. The Ra distribution between sulfate solid solutions and Mont phase was calculated in order to investigate the influence of clay content on retention mechanisms of Ra.

Model geometry and numerical setup

To demonstrate the impact of competition between the two mechanisms on the transport of mobile radium, we considered a simplified 5 m long one-dimensional column model, representing a tunnel connected to an intermediate level radioactive waste repository. Sensitivity analyses were conducted to ensure appropriate spatial and temporal discretizations. For a constant time step setting, grid sizes of 0.05, 0.025, and 0.0125 m were tested, with no observable influence on the radium profile. Therefore we have chosen a spatial discretization of 0.05m. On the other hand, an inappropriate choice of the time step size has a much bigger impact on the penetration depth of radium. An improperly calibrated time step (too large) results in overestimation of transport distance for radium. After several tests, we found that, at the conditions investigated here, the simulation result converges accurately for time steps equal to or smaller than 1×10^6 s (11.6 days). If we accept that time step size is governed theoretically by a relationship of the form $\Delta t = A \cdot \Delta x^2 / D_e$, where D_e is effective diffusion coefficient, then these results suggest A is approximately 0.1 for the conditions explored here. Therefore, all of our reactive transport simulations adopt this setting.

Within a waste repository, the hydraulic gradient is usually flat and the bentonite has a very low hydraulic conductivity (up to 5.0×10^{-11} m/s), so that transport of

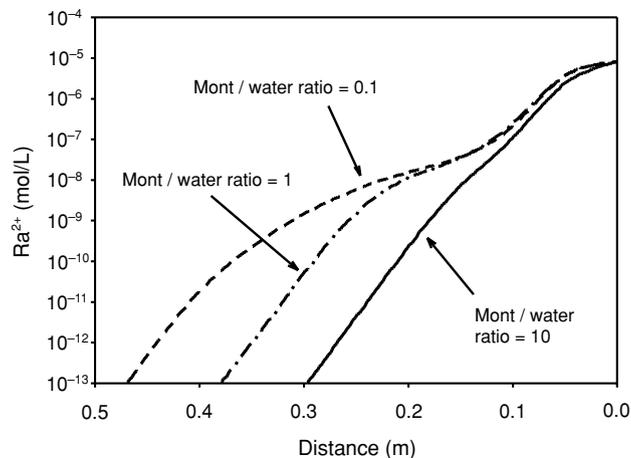


Fig. 2. Aqueous phase radium profile after 1000 years, with clay content adjusted by Mont/water ratio of 10, 1.0 and 0.1 kg/kg.

aqueous species in the tunnel will be dominated by diffusion. We used for all species the same effective diffusion coefficient of 2.0×10^{-10} m²/s. With a cation accessible porosity of 0.12 for a highly compacted bentonite (Nagra, 2002), the pore diffusion coefficient for all mobile chemical components is set to 1.7×10^{-9} m²/s. The temperature and pressure were assumed to be 25°C and 1 bar, respectively. The imposed chemical boundary condition is a constant radium concentration, representing the leakage of the radionuclides out of the waste matrix at the right end of the tunnel backfill. The source term, i.e., aqueous concentration of Ra^{2+} , was fixed at 1.0×10^{-6} mol/L. Such a radium concentration can be estimated in the cement backfill material for intermediate level waste (Nagra, 2002). To keep the model simple, the radioactive decay of radium was not considered.

RESULTS

Figure 1 depicts the partitioning of Ra between the ion exchanger and solid solutions subject to the amount of clay in the system (in terms of the Mont/water ratio). At a Mont/water ratio of 19, bentonite is in a compacted form, which is used to seal the high level waste canister. Cation exchange sites in the Mont phase attract most of the Ba and Sr in the system so that, while carbonate and sulfate are abundant in the aqueous phase, insufficient Ba and Sr restrains the formation of Ra sulfate solid solutions. Sufficient Ba and Sr remain for sulfate formation only when the Mont/water ratio is lowered to approximately unity. Despite the fact that the limited clay content lowers the total amount of Ra bound in the Mont phase, the sulfate solid solutions compensate for this and provide a secondary fixation mechanism. When the ratio

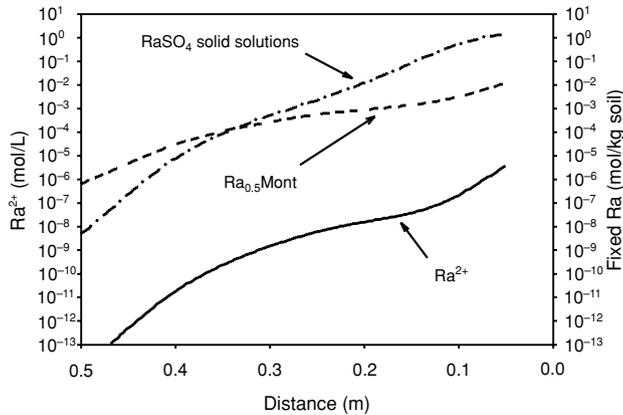


Fig. 3. Amount of Ra distributed between sulfate solid solutions, clay cation exchange, and pore water. Simulation results after 1000 years, at Mont/water ratio of 0.1.

is about 0.1, only a minor proportion of Ra is retained in the montmorillonite, and the incorporation in sulfate solid solution becomes the major retardation mechanism for the transport of radium.

Figure 2 shows the concentration profile for aqueous Ra^{2+} after 1000 years. The shape and extension of the profiles are similar at three different Mont/water ratios of 0.1, 1.0, and 10 kg/kg. The aqueous radium concentrations is lowered by 2~3 orders of magnitude, as soon as it diffuses into the column. Both sulfate and Mont solid solutions provide the capacity to fix radium. Figure 3 shows the amount of radium in solution and on both types of fixation sites, at a Mont/water ratio of 0.1. The sulfate solid solution provides the major fixation capacity, due to the low Mont content in the solid phase. These results agree well with the case study presented by Martin *et al.* (2003), where Ra transport was monitored in a sandy/gravel aquifer contaminated by leakage from a mining waste deposit.

DISCUSSIONS

In order to simulate cation exchange reactions, models based on the Law of Mass Action (LMA) such as PhreeqC (Parkhurst and Appelo, 1999, Xie *et al.*, 2004) and MINSORB (Bradbury and Baeyens, 1997) are often used. In such models, the real stoichiometry of clay minerals (Al, Mg, Si, H and O) is usually not included, and is replaced by “sorption site capacities”. However, the GEM-Selektor package based on Gibbs Energy Minimization simplifies the thermodynamic consideration of cation exchange reactions in the form of solid solutions with full stoichiometry of the clay mineral, whose solubility can be calibrated according to cation profiles measured in batch extraction tests. In the experiment of Fernandez *et*

al. (2004), it was observed that the measured aqueous concentrations of K, Mg, Ca and Sr increase together with the S/L ratio (table 5 in their paper), while the pH of the aqueous solution decreased accordingly. These phenomena are both qualitatively reproduced in our model.

In this work, the equilibrium exchange constant for Ra was assumed to be the same as for Sr. To test the sensitivity of this parameter, we decreased the stability of the exchange component $\text{Ra}_{1/2}\text{Mont}$, by increasing its G°_{298} value 7000 J/mol (17 times weaker K_G). This correction is well above the range of selectivity coefficients for alkali earth cations on montmorillonite (Benson, 1982; Bruggenwert and Kamphorst, 1979). However, the model result basically remains the same and the trend in Fig. 1 is intact, suggesting that it is the availability of Ba, Sr, and sulfate in competition with the availability of clay ion exchange sites that govern the formation of solid solutions, rather than a particular value of the exchange constant of radium on montmorillonite. Therefore, the distribution of Ra among the clay ion exchange and the sulfate solid solution is far more influenced by the Mont/water ratio than by the value of cation exchange constant.

A comparison of the Ra profile in Fig. 2 with previous results (Shao *et al.*, 2009a) shows that the mobility of aqueous radium is considerably lower if cation exchange reactions in addition to solid solution formation is considered. Even with a limited amount of clay (Mont/water ratio of 0.1 in Fig. 3), Ra^{2+} can penetrate less than 1.5 m into the column after 1000 years. The Ra profile shown in Fig. 2 suggests that the diminishing fixation capacity of the Mont phase can be compensated for by incorporation into sulfate solid solution. However, the chemical system presented here is simplified. In a real bentonite-sand mixture, it is possible that some portion of carbonate and sulfate will be unavailable to solid solution formation and that the cation exchange reactions may be influenced by the competition with other cations.

SUMMARY

In this work, the impact of competition between the cation exchange on montmorillonite and the formation of sulfate solid solutions on the retardation of radium is investigated. Both mechanisms are built in an idealized geochemical model and simulation shows that both of them can fix the mobile radium into the solid phase. The distribution of radium in sulfate solid solutions is mainly influenced by the amount of Ba and Sr available, which can also undergo cation exchange on clay minerals like montmorillonite. At high clay content, the cation exchange dominates the whole system and is the major process that retards the transport of Ra, whereas at low clay content, the incorporation in sulfate solid solutions fixes most of the Ra.

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