

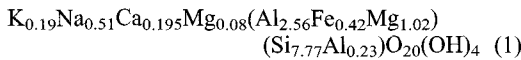
Modelling the dissolution behaviour of a clayey barrier

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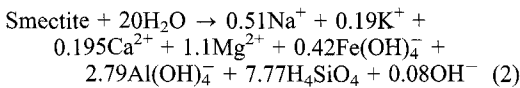
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The experimentally determined rate law of smectite dissolution is used to model the chemical evolution of the backfilling material in the multibarrier system designed to storage nuclear waste as is employed in the undergoing FEBEX experiment located in the Grimsel area (ENRESA, 1995). We assume that a zone of fractures is originated in the backfilling material in order to create a possible scenario in which the ground-water circulating throughout the granite host rock might dissolve the clayey material. Also an important consideration is done by assuming that the backfilling material contains together with smectite an small amount of minor silicates proper of bentonite rocks such as quartz, muscovite and albite.

The used smectite is a mixed-layer illite/montmorillonite (I/M) with 10 per cent illite from the Neogene Cabo de Gata volcanic deposit (Almería, Spain), and its structural formula is expressed as



The stoichiometric dissolution rate of the smectite under alkaline conditions (pH = 8.8) and various degrees of saturation state, expressed as ΔG_r , at 80°C has been measured by means of flow-through experiments. The overall dissolution reaction taking place is given by



and the dissolution rate law is expressed as

$$R_{\text{smect}} = (-88.7 \pm 8) \times 10^{-13} (\text{mol m}^{-2} \text{s}^{-1}) [1 - \exp(0.5 \times 10^{-6} g^4)] \quad (3)$$

where $g = \Delta G_r/RT$, and ΔG_r is the Gibbs free energy

TABLE 1. k_i values ($\text{mol m}^{-2} \text{s}^{-1}$) at 298, and n_{H^+} and n_{OH^-} values for smectite, muscovite, albite and quartz

	k_{H^+}	k_7	k_{OH^-}	n_{H^+}	n_{OH^-}	n	p
Smectite	$10^{-10.5}$	$10^{-13.6}$	$10^{-14.70}$	0.38	-0.22	0.1	13
(TST)	"	"	"	"	"	1.0	1.0
albite	$10^{-10.0}$		$10^{-14.75}$	0.49	-0.30	0.4	14
muscovite	$10^{-11.37}$	$10^{-12.82}$	$10^{-14.95}$	0.38	-0.22	0.3	13
quartz	$10^{-13.38}$	$10^{-13.38}$	$10^{-13.38}$	0	0	1.0	1.0

of the overall reaction.

Calculations

The algorithm employed in the reactive transport code RETRASO (Saaltink *et al.*, 1997) solves simultaneously for multicomponent reactions and advective transport in one and two dimensions, and uses kinetic formulation for mineral dissolution and precipitation reactions. One dimension is based on a finite differences scheme whereas a finite elements scheme is used for two dimensional calculations.

Mathematical formulation of dissolution/precipitation rate laws is expressed as

$$\frac{dc_i}{dt} = \sum_{m=1}^{N_m} \nu_{mi} \cdot e^{-\frac{E_{app}}{RT}} \left(k_{\text{H}^+} a_{\text{H}^+}^{n_{\text{H}^+}} + k_7 + k_{\text{OH}^-} a_{\text{H}^-}^{-n_{\text{OH}^-}} \right) A_m (g_m^n - 1)^p \quad (4)$$

where A stands for the reactive surface area of mineral m , and the mineral constant rate values k and exponents n and p are given in Table 1.

Apparent activation energy values of 15 kcal mol⁻¹ for smectite and muscovite (Lasaga, 1984), and 14.3 and 17 kcal mol⁻¹ for albite and quartz respectively (Knauss and Wolery (1989), Rimstidt and Barnes (1980)) are used to compute k values at 80°C.

Darcy velocity values of ground-water at the Grimsel emplacement depending on the degree of rock fracturation ranging between 0.032 and 0.1 m any⁻¹ are used in the simulations.

The reactive surface area value of the smectite is the most difficult physical parameter to be controlled. In the simulations this value has been determined to be as

$$A_{\text{min}} = \frac{2\theta}{b} \quad (5)$$

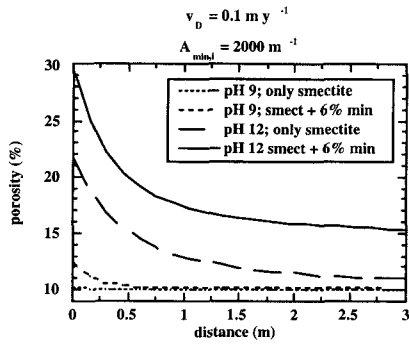


FIG. 1. Comparison of porosity evolution depending on both pH and the 6 % content of associated silicates together with smectite in the backfilling material.

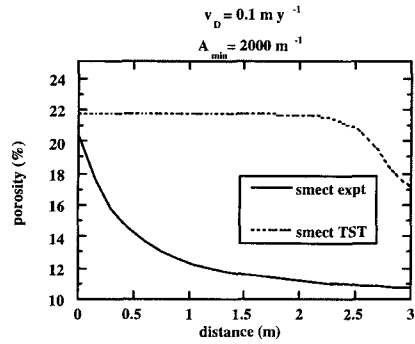


FIG. 2. Comparison of porosity decrease along the fracture as different smectite rate law is used in the modelling at pH 12.1.

where b is the distance between fracture planes, and θ is the porosity in the backfilling material. Assuming that the originated porosity in the fractured zone is 0.1 (10 %), and the distance b ranges between 1 i 0.1 mm, then A_{min} equals 200 o 2000 ($m^2 \text{ min } m^{-3} \text{ rock}$), respectively.

The mineral dissolution effect on the porosity change is obtained from variations of volume mineral fraction of n minerals as is expressed as follows

$$\theta = 1 - \sum_{m=1}^n \chi_m V_{mol,m} \quad (6)$$

where χ_m is the molal mineral fraction per m^3 of material, and $V_{mol,m}$ is the molal volume of mineral m . As the mineral dissolution takes place, the respective χ decreases, and the porosity increases.

In the Grimsel granite the ground-water pH value is 9.0. When the ground-water previously passes through a concrete plug (FEBEX experiment design) the pH becomes as high as 12.5 because of the major concrete component portlandite. Chemical equilibrium composition of water respect to smectite is taken as an initial condition in the different scenarios.

Results and discussion

Simulations run up to 10,000 years at constant temperature (80°C) are done to study porosity changes in the clayey material due to the ground-water circulation along a fracture. An important effect in the porosity change becomes the ground-water pH reacting with the minerals making up the backfilling material. For pH values close to 7 ($6.7 \leq \text{pH} \leq 9$) dissolution rate of smectite does not produce a significant porosity increase (less than 10.15%) (Fig. 1). However, as the pH becomes hyper alkaline (12.1)

dissolution rate of smectite increases considerably producing a consequent increase of porosity (29%) (Fig. 1). Solution saturation state is responsible of the porosity decrease along the fracture. As the dissolution of smectite takes place according to the form of the dissolution rate dependency on solution saturation state (eq. 4), the reacting water becomes less undersaturated respect to smectite and equilibrium is approached decreasing the porosity.

As an amount of 6 % of common minerals of Cabo de Gata bentonitic rocks (Linares, 1993), such as quartz, albite, and muscovite, is present in the material, the increase of the initial porosity reaches 29 % (Fig. 1) at pH 12.1.

Moreover, the porosity profile in Fig. 2 shows that porosity decrease along the fracture is affected by the particular function of mineral dissolution rate dependency used in the modelling. For example, calculations based on smectite dissolution rate law predicted by the transition state theory yield different porosity evolution compared to that found out by the experimental data (see Table 1).

Knowledge of the form of dissolution rate laws, that is the dependence of dissolution rate on the degree of solution saturation state, is a very important variable to correctly predict porosity changes.

References

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