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Research paper

Coupled transport-reaction modeling of the long-term interaction between iron, bentonite and Callovo-Oxfordian claystone in radioactive waste confinement systems

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ABSTRACT

Appropriate geological disposals are required to manage the high level and intermediate level long lived radioactive waste. Several concepts have been developed in a number of nations. In France, different concepts have been investigated successively with time by Andra: either the steel waste package for vitrified waste was separated from the host rock (Callovo-Oxfordian (COx) claystone) by a bentonite engineered barrier or in the actual design, is in direct contact with the COx claystone. The long term interactions of the geological groundwater and steel overpack with the bentonite and/or claystone barriers were carried out by using the Kirmat 1D reactive transport code. Three different modeling approaches with the (T, t) conditions expected in the repository were implemented to (i) investigate the influence of the surface area of the primary minerals and the diffusion coefficient on the evolution of the iron–bentonite system and to (ii) compare the reactivity of the iron–bentonite and iron–COx claystone systems.

For the iron–bentonite interactions, the simulated results showed significant differences depending on the different hypotheses used to calculate surface areas for minerals. When different sizes of mineral particles are assumed to estimate the surface areas of primary minerals, the system explored a larger change in porosity and more intense mineralogical modifications in the zone close to the bentonite/steel overpack interface. This result is likely related to the lower diffusion of aqueous corrosion products through the bentonite barrier. The comparison between iron–bentonite and iron–COx claystone interactions confirmed a clear different behavior of reactivity. For the iron–bentonite the alteration concerns two zones in direct contact with the geological groundwater and steel overpack but for the iron–COx claystone the mineralogical modifications are predicted to occur in the whole medium. The mineralogical evolution of the COx claystone barrier is mainly impacted by the dissolution of primary minerals, especially for total transformation of interstratified illite/smectite (I-Sm) and formation of secondary minerals such as illite and berthierine-Fe^{II}. The modeling results obtained from the sensitivity test showed a significant impact of the diffusion parameter on the evolution of the COx barrier, especially the changes in pH, porosity and the mineralogical modification of the zone in contact with the steel container.

1. Introduction

Appropriate geological disposals are required to manage the high level and intermediate level long live radioactive waste, more specifically vitrified waste. Several concepts for the waste confinement have been developed in a number of countries (Baldwin et al., 2008): Concept from SKB (Sweden) and Posiva (Finland) in granite, from Nagra (Switzerland) in Opalinus clay, from Ondraf in Boom clay, and from Andra in the COx claystone. In these disposal concepts, bentonite is generally selected as an engineered barrier material since it has some interesting specific properties such as an extremely low permeability, small pore size, high swelling pressure, and high ion exchange capacity (Wilson et al., 2011; Dohrmann et al., 2013). A thorough knowledge about the long term performance of bentonite is needed to support the design of the geological disposal facility. However, there are still limited studies investigating the long term iron–bentonite interactions (Montes-H et al., 2005b; Bildstein et al., 2006; Marty et al., 2010; Savage et al., 2010b; Lu et al., 2011). There are even much less works performing the long term iron–COx claystone interactions (Bildstein et al., 2006).

For Andra concept of nuclear waste disposal in a deep geological repository in the Callovo-Oxfordian formation (Haute-Marne, Meuse, France), different designs have been investigated successively with time: either the steel waste package was separated from the clay host rock by a bentonite engineered barrier or, in the present design, is in direct contact with the COx claystone. Due to radioactive activity of

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the waste and after closing of the repository, the temperature at the surface of the waste package is expected to increase up to a maximum of 100 °C. The clay barriers, in contact with the geological medium on one side and with the steel overpack on another side will evolve. Experiments have been conducted over short to medium timescales (e.g., Guillaume et al., 2003, 2004; Lantenois et al., 2005; Perronnet et al., 2007; Schlegel et al., 2008, 2010; Mosser-Ruck et al., 2010) to identify the mechanisms and the mineral phases involved in the transformation processes. It is still difficult to follow the transformation at the interface between clay and steel with experiments only. Therefore, to provide the necessary background information to underpin the above designs, it is important to use modeling approach to investigate the long term interactions between steel components and clay barriers.

Previous studies supported by Andra were devoted to the predictive behavior of a bentonite barrier (Montes-H et al., 2005b; Marty et al., 2010). In these works the authors considered that the primary minerals had the same particle size and hence the same value of the reactive surface area for each particle, estimated by using a geometrical model. This simple hypothesis may have a great impact on the long term simulated evolution of the iron–bentonite since various authors have reported that the reactive surface area is one of the most sensitive parameters (Savage et al., 2002; Bildstein et al., 2006).

In this current study, we will compare the results obtained from the iron–bentonite and iron–COx claystone. Firstly, the iron–bentonites with the different hypotheses for the reactive surface area of the primary minerals are compared to investigate how significantly the reactive surface area may influence the long term evolution of this system. Secondly, the present work focuses on the comparison between the iron–bentonite and iron–COx claystone interactions to determine if the reactivities at the interface with the steel overpack are comparable and to evaluate the impact of diffusion on the evolution of the iron–COx claystone system.

2. Material and method

2.1. The Kirmat code

2.1.1. Kinetics of mineral reaction

The simulations were carried out with the reactive transport code Kirmat (Gérard et al., 1998). It has been already applied in different works investigating the long-term performance of the engineered bentonite system for radioactive waste confinement (Montes-H et al., 2005b; Marty et al., 2010). In order to easily understand the kinetic and thermodynamic data presented in the next section, the main equations containing the most important parameters will be briefly described.

The dissolution of a mineral is influenced by different factors. The most important factors include the aqueous solution composition (in particular pH), the mineral surface area available for dissolution, the degree of saturation of the solution with respect to mineral, and the temperature. The dissolution rate of a mineral is written in Kirmat as:

$$r_d = \mathrm{k_d} S_m^{eff} \alpha_{H^+}^n \left(1 - \left(\frac{\mathrm{Q_m}}{\mathrm{K_m}}\right)^{\mathrm{n_1}}\right)^{\mathrm{n_2}} \quad (1)$$

where $\mathrm{k_d}$ is the dissolution rate constant (mol $\mathrm{m^{-2}}$ $\mathrm{year^{-1}}$), S_m^{eff} is the reactive surface area of mineral m ($\mathrm{m^2\ kg^{-1}\ H_2O}$), $\alpha_{H^+}^n$ is the activity of proton, $\mathrm{n_1}$ and $\mathrm{n_2}$ are exponents depending on the pH of the solution, $\mathrm{Q_m}$ is the ion activity product of mineral m, $\mathrm{K_m}$ is the thermodynamic equilibrium constant of the hydrolysis reaction of mineral m at given temperature and pressure.

Similarly, the precipitation of a mineral can also be described by using a kinetic approach. The Kirmat code describes the precipitation rate of a mineral according to the following expression:

$$\mathrm{r_p} = \mathrm{k_p} S_m^{eff} \left[\left(\frac{\mathrm{Q_m}}{\mathrm{K_m}}\right)^{\mathrm{p}} - 1\right]^{\mathrm{q}} \quad (2)$$

where $\mathrm{k_p}$ is the kinetic rate constant of precipitation (mol $\mathrm{m^{-2}}$ $\mathrm{year^{-1}}$), p and q are experimental values describing the dependence of the reaction on the saturation state.

However, in the literature there are much less kinetic data available for the precipitation reactions than for kinetic dissolution reactions. This arises from the fact that experiments investigating the precipitation process of a mineral are facing the difficulty of the detection of small amounts of secondary phases among dominating primary ones. The control of precipitated amounts as a function of time remains a real challenge for future experimental studies.The relationship of the effective diffusion coefficient ($\mathrm{D_{eff}}$) to the porosity is expressed as:

$$\mathrm{D_{eff}} = \mathrm{D_0}(\omega)^{\mathrm{C_m}-1} \quad (3)$$

where $\mathrm{D_0}$ is the diffusion coefficient of solute in free water, ω is the porosity, $\mathrm{C_m}$ is the cementation factor.

2.1.2. Feedback effect

The Kirmat code can also account for the feedback effects of the chemical and mineralogical evolutions on the variation of porosity. Calculation of the spatial and temporal changes in porosity in each grid cell is based on the balance of dissolved and precipitated minerals in that cell. The porosity at the increment n is determined as follows:

$$\omega^n = 1 - \left[\frac{\mathrm{S}\Delta\mathrm{x}\left(1-\omega^{n-1}\right) + Bv^n}{\mathrm{S}\Delta\mathrm{x}}\right] \quad (4)$$

where ω^n and ω^{n-1} are the porosity at the increments n and n-1, respectively; S is the grid cell surface in contact with the adjacent cell ($\mathrm{m^2}$); Δx is the cell length (m); Bv^n is the volume balance of all minerals at the increment n ($\mathrm{m^3}$).

2.1.3. Description of the corrosion rate

To our knowledge, very few modeling studies exist in the area of iron–clay interactions (e.g., Montes-H et al., 2005b; Bildstein et al., 2006; de Combarieu et al., 2007; Samper et al., 2008; Marty et al., 2010; Savage et al., 2010b; Lu et al., 2011; Ngo et al., accepted for publication). Modeling of steel corrosion in contact with clay based on mathematical models for prediction of on-going corrosion kinetics would be a challenging task, taking into account the variety of influencing parameters. This needs a thorough knowledge of the evolution of corrosion with time. It is comprehensible that corrosion of steel in contact with clay is a complex electrochemical process strongly dependent on environmental factors and properties of the metal and clay (Chainais-Hillairet and Bataillon, 2008; Bataillon et al., 2010; 2012). Recently, a critical review (King, 2009) has reported that the corrosion rate of steel in conditions relevant for nuclear waste disposal was found to decrease with time. The decrease in corrosion rate is partly due to the presence of the preformed film of corrosion product (e.g., $\mathrm{Fe_3O_4}$ and $\mathrm{FeCO_3}$). In addition, the presence of other elements such as $\mathrm{Fe^{2+}}$ and partial pressure $\mathrm{H_2}$ has little effect as well. King (2009) also concluded that the mean long term corrosion rate of steel in saturated bentonite will not exceed 3 μm/year and there is good evidence that actual corrosion rate should be much lower.

It is found from the literature that in reactive-transport modeling, iron corrosion is taken into account with two simplified approaches (i) a constant rate during the numerical calculation (Bildstein et al., 2006; de Combarieu et al., 2007; Samper et al., 2008; Savage et al., 2010a) or (ii) a corrosion rate depending on a term of affinity (Montes-H et al., 2005b; Marty et al., 2010; Lu et al., 2011). The latter approach describes the corrosion process similarly to the kinetic dissolution of a primary mineral, which also means that the corrosion of steel depends on the kinetic constant, the reactive surface and the saturation index of iron in the system. Even though this simple approach is still far from the complexity of the corrosion process (Chainais-Hillairet and