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Reactive transport model and apparent K_d of Ni in the near field of a HLW repository in granite

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ABSTRACT

Current performance assessment models for radionuclide migration through the near field of high-level radioactive waste repositories often rely on the assumption of a constant K_d for sorption. The validity of such assumption is evaluated here with a reactive transport model for Ni^{2+} in the near field of a repository in granite. Model results show that Ni^{2+} sorbs mainly by surface complexation on weak sorption sites. The apparent K_d of Ni^{2+}, K_d^a, depends on the concentration of dissolved Ni and pH and is constant only when the concentration of dissolved Ni is smaller than 10^{-6} mol/L. The results of the sensitivity runs show that K_d^a is sensitive to the water flux at the bentonite–granite interface, the effective diffusion of the bentonite and the concentration of weak sorption sites of the bentonite. The competition of other nuclides such as Cs^+ on Ni^{2+} sorption is not important. Corrosion products, however, affect significantly the sorption of Ni^{2+} on the bentonite. The model with a constant K_d does not reproduce the release rates of Ni^{2+} from the bentonite into the granite. A model with a variable K_d which depends on the concentration of dissolved Ni^{2+} and pH may provide an acceptable surrogate of the multicomponent reactive transport model for the conditions of the repository considered in our model. Simulations using the K_d-approach were performed with GoldSim based on the interpolation in the pH and concentration table, while the reactive transport model simulations were performed with CORE^{2D} which incorporates multisite surface complexation.

1. Introduction

Current performance assessment models for radionuclide migration through the near field of a high-level radioactive waste (HLW) repository usually rely on simplifying assumptions such as the use of a constant K_d for nuclide sorption and "the limited solubility" for nuclide precipitation (Bethke and Brady, 2000; USEPA, 1999). But the distribution of aqueous species depends strongly on the chemical conditions, especially pH and the concentrations of complexing ligands such as carbonate ions (Curtis et al., 2006; Davis et al., 2004). Although the effects of changes in the chemical conditions on the solubility of radionuclides usually can be calculated in a straightforward manner, the consequences of variable chemical conditions on adsorption and the choice of the appropriate K_d value are more complex (Curtis et al., 2004; Davis et al., 2004; Kohler et al., 1996; USEPA, 1999). Testing the validity of the constant K_d has been limited by: (1) the lack of nuclide surface complexation and cation exchange data and (2) the unavailability of computer codes which could handle simultaneously the migration, sorption and precipitation of radionuclides and the geochemical evolution of the near field. Laboratory experiments performed in recent years have provided substantial data and understanding on the mechanisms of nuclide sorption. Thermodynamic sorption models based on cation exchange (Bolt, 1982; Fletcher and Sposito, 1989; Gaines and Thomas, 1953) and surface complexation mechanisms (Davis and Kent, 1990; Hayes et al., 1991; Sposito, 1984; Stumm and Morgan, 1981) provide the framework for evaluating and predicting the contribution of sorption reactions to radionuclide migration. Instead of the K_d approach often used in performance assessment studies, the way begins to open to methods capable of calculating sorption values specific to different geochemical scenarios. Accounting for competitive sorption in repository safety analyses also becomes a possibility (Bradbury and Baeyens, 2005).

The structural components of the fuel assembly are made of Inconel (INC-718) and stainless steel (SS-304) which contain nickel (ENRESA, 2001b). Nickel release will be controlled by the degradation of these alloys under repository conditions. Although

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these alloys are very resistant to corrosion, usually a short duration of 1000 years is assigned to them in safety assessment exercises (ENRESA, 2001a). Nickel is a transition metal of the tenth group which is often found in the +2 oxidation state in aqueous and solid states. The solubility of Ni can be controlled either by $NiCO_3(s)$ or $Ni(OH)_2(s)$, depending on the pH of the system. Ni solubility is a matter of controversy. There are discrepancies among the reported solubilities and the solid phase controlling Ni solubility. Reported solubility constants for $NiCO_3(s)$ range from $1.0 \times 10^{-11.2}$ to $1.0 \times 10^{-6.82}$ (Duro et al., 2006). Ni solubility decreases an order of magnitude when pH increases from 6 to 7 while $NiCO_3(s)$ is the solid phase controlling Ni solubility. The concentration of dissolved Ni^{2+} is the largest for pH < 7.5 (Mattigod et al., 1997). Pfingsten et al. (2011) studied the influence of Fe^{2+} competition on the sorption and migration of Ni^{2+} in MX-80 bentonite. They adopted a Ni^{2+} solubility of 3.5×10^{-5} mol/L for pH=7.25. The mobility and availability of Ni^{2+} in soils depend primarily on the sorption on clay silicates, manganese, iron, and aluminum oxides (Ticknor, 1994; Tiller et al., 1984; Trivedi and Axe, 2001). Ni^{2+} sorption on the bentonite may occur via cation exchange and surface complexation (Lazarevic et al., 2010; Yang et al., 2009b). The sorption of Ni^{2+} is endothermic (Ijagbemi et al., 2010; Lazarevic et al., 2010; Zhang et al., 2010) and depends on pH, ionic strength, humic acid, temperature and the concentrations of other dissolved ions (Doménech and Duro, 2008; Fan et al., 2009; Hu et al., 2010; Yang et al., 2009b). Ni^{2+} sorption via surface complexation (SC) is strongly nonlinear and depends nonlinearly on pH. Ni^{2+} sorption increases with pH regardless of temperature (Bhattacharyya and Gupta, 2007; Boonfueng et al., 2006; Tertre et al., 2005; Zhang et al., 2010). Bradbury and Baeyens (1997a,b, 1999) found that the Ni^{2+} sorption is constant and occurs only via cation exchange for pH < 5. At high pH, on the other hand, SC is stronger and the effect of ionic strength becomes less relevant (Boonfueng et al., 2006; Bradbury and Baeyens, 1997b). Ni^{2+} uptaken by SC occurs on at least two types of pH-dependant sites. Ni^{2+} sorption at low radionuclide concentrations is strong and linear and occurs on a relatively small number of sites with a high binding affinity. These are the so-called “strong sites”. For intermediate concentrations of Ni^{2+} the sorption is non-linear because sorption takes place on a second set of sites which have a larger concentration but a weaker binding constant. These are the so-called “weak sites”. For the conditions of a radioactive waste repository, the sorption of Ni^{2+} is governed by surface complexation on the edge surface sites (Bradbury and Baeyens, 1997a,b, 1999, 2005; Ijagbemi et al., 2010; Lazarevic et al., 2010; Montavon et al., 2006; Yang et al., 2009a; Zhang et al., 2010). Here we report the posibility of using the K_d models for Ni^{2+} with a reactive transport model considering multisite surface complexation. The paper starts by describing the conceptual and numerical models. Then, model results are presented for the base run and the sensitivity runs. Competition effects are then evaluated. Finally, the results of the constant and variable K_d models performed with GoldSim are compared to those of the reactive transport model. The paper ends with the main conclusions.

2. Conceptual and numerical models

2.1. Reference concept

The Spanish reference concept for a spent-fuel repository in granite envisages the emplacement of carbon-steel canisters in 500 m long horizontal drifts excavated at a depth of 500 m in a granite formation by tunnel boring. Canisters are disposed in cylindrical disposal cells built with blocks of compacted bentonite having a dry density of 1700 kg/m^3 to achieve a final dry density of 1600 kg/m^3. The bentonite blocks are initially unsaturated with a gravimetric water content of 14%. The disposal drifts have a diameter of 2.4 m. The dimensions of an individual “cell” corresponding to a single canister are shown in Fig. 1 (ENRESA, 2005; Samper et al., 2010). The volume of voids of each canister is estimated to be 0.5 m^3.

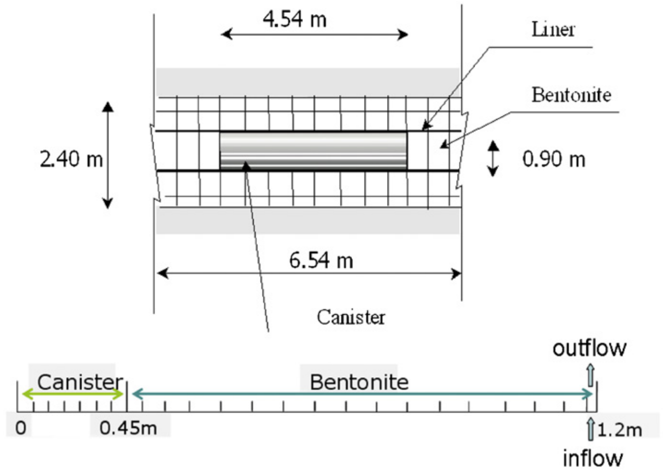

Fig. 1. Dimensions of an individual disposal cell and the sketch of the 1D axisymmetric model (Samper et al., 2010).

2.2. Conceptual model

Canister failure due to steel corrosion is estimated to occur after several thousands of years. After canister failure, the canister cavity will fill with the bentonite pore water. Then, radionuclides will be released into the water and later will diffuse into the bentonite buffer. The model in this paper simulates the geochemical evolution and radionuclide migration after the canister has failed so that water can fill all the voids within the canister. According to ENRESA (2005, 2006) the bentonite barrier will become fully water-saturated after less than 50 years for the Spanish reference concept. The thermal pulse will dissipate in 10^4 years (ENRESA, 2001a). The numerical simulation starts after canister failure and once the thermal pulse has gone. Therefore, calculations are performed by assuming isothermal (25 °C) and water-saturated conditions. The model does not account for the corrosion of the liner in Fig. 1.

Given the low hydraulic conductivity of the bentonite, diffusion is the dominant transport process in the bentonite which has a porosity equal to 0.407 (ENRESA, 2006; Samper et al., 2008b). All dissolved chemical species are assumed to have the same effective diffusion of 4.07×10^{-11} m^2/s which is the value used in the BENIPA project (BENIPA, 2003). A flux of 0.06 L/year per canister is used for the boundary condition at the bentonite/granite interface as indicated in Fig. 1 (Samper et al., 2010).

The geochemical model considers the following geochemical reactions: aqueous complexation, acid-base, redox, dissolution/precipitation of calcite, goethite, gypsum, magnetite, quartz and siderite, cation exchange of Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+} and Ni^{2+} and protonation/deprotonation by surface complexation. The chemical system is defined in terms of the following primary species: H_2O, $O_2(aq)$, H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, HCO_3^-, Cl^-, Ni^{2+}, SO_4^{2-}, Ni^{2+} and $SiO_2(aq)$. Pore waters in the canister and the bentonite are assumed to have initially the same chemical composition (Samper et al., 2008a) which is controlled by mineral dissolution/precipitation at chemical equilibrium (calcite and quartz), proton SC and cation exchange. A discussion of the