A COUPLED REACTIVE TRANSPORT MODEL FOR CONTAMINANT LEACHING FROM CEMENTITIOUS WASTE MATRICES ACCOUNTING FOR SOLID PHASE ALTERATIONS

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SUMMARY: Cementitious binders are commonly used to solidify/stabilize hazardous wastes prior to disposal in multi-barrier engineered disposal facilities or landfills. Because they are not in equilibrium with other materials in a landfill, cementitious materials usually degrade with time. Reactive transport models may be used to estimate the possible effects of changing geochemical conditions on the transport properties of the cementitious materials, the leaching of chemotoxic elements from the waste form, and alterations of the sorption properties of surrounding materials due to leaching of cement components.

1. INTRODUCTION

One particular form of waste disposed in landfills is the placement of solidified/stabilized (S/S) hazardous waste in cement-based binding materials. Cementitious materials have good physical (low porosity, low permeability) and chemical (high pH promoting in many cases low solubility, potentially high sorption) properties for contaminant containment. Landfills with such waste (which may include low-level radioactive waste) are typically complex engineered multi-barrier systems consisting of different natural and engineered materials. Cementitious materials (hardened cement paste, mortars and concrete) are characterized by elevated pH and Ca concentrations and are not in equilibrium with most other materials present in a landfill. A large range of potentially detrimental chemical reactions such as sulphate attack, decalcification, carbonation, chloride ingress (see Glasser et al. (2008) for a review) can change both the initial physical (porosity, permeability, and tortuosity) and chemical (sorption, solubility) properties of concrete. Because most of these perturbing processes are relatively slow, reactive transport models are essential to extrapolate from small-scale, short-term experimental studies to large-scale, long-term performance assessment calculations (e.g., De Windt et al., 2007).

Especially needed are reactive transport codes that integrate water flow processes with such

processes as heat transport, transport of multiple solutes and (bio)geochemical equilibrium and kinetic reactions, including mass exchange between aqueous, solid and gas phases. Integration of these different processes in one simulation code allows one to account explicitly for the interactions between transport and biogeochemical processes. The transport processes then determine the residence times available for chemical reactions and the disequilibrium between the mobile and immobile phases, whereas geochemical reactions may alter the transport properties of the porous media. In this paper we give three examples of the application of a reactive transport code (HP1) to assessments of the long-term evolution of cementitious waste forms in a landfill and the leaching of contaminants from the cementitious material. Special attention is given to interactions between the cementitious waste form and the geochemical properties of the geo- or engineered materials in contact with the cementitious materials.

2. THE HP1 COUPLED REACTIVE TRANSPORT CODE

3.1 General description of HP1

HP1 (Jacques and Šimůnek, 2005) is a coupled reactive transport code based on the HYDRUS-1D (Šimůnek et al., 2008) and PHREEQC (Parkhurst and Appelo, 1999) software packages. HYDRUS-1D is a state-of-the art model accounting for variably-saturated water flow (the Richards equation), multicomponent solute transport (the advection-dispersion equation for the aqueous phase, and the diffusion equation for the gaseous phase) and heat transport. The model allows great flexibility in defining heterogeneous porous media and unsaturated flow properties. PHREEQC is similarly a very comprehensive model for low-temperature aquatic chemistry and geochemistry. The generic nature of PHREEQC allows the inclusion of a broad range of geochemical equilibrium reactions (e.g., aqueous speciation, mineral dissolution and precipitation, exchange and surface complexation reactions, solid solution equilibrium and aqueous-gas exchange) and parallel and sequential kinetic reaction networks with user-defined kinetic rate reactions. A detailed description of HP1 and several applications are given by Jacques et al. (2006, 2008a, b). The code was embedded recently within HYDRUS-1D and is now freely available at www.pc-progress.cz.

3.2 Linking geochemical state variables to transport properties

A new feature recently included in HP1 is the possibility to change the hydraulic and transport properties as a function of evolving geochemical state variables. One typical example is the possible change in porosity and pore diffusion coefficient due to solid phase dissolution during leaching of cementitious materials. Another example is a change in hydraulic conductivity due to changing pore water composition. HP1 makes it possible to account for changes in (i) porosity (and saturated water content), (ii) the hydraulic conductivity, (iii) a hydraulic scaling factor for the pressure head, (iv) the aqueous phase and gaseous phase pore geometry factors for calculating the pore diffusion coefficient, (v) the dispersivity, (vi) the heat capacity, (vii) the heat conductivity and (viii) the heat dispersivity. HP1 for this purpose does not use any pre-defined conceptual or mathematical model to update these transport parameters, but rather uses the flexibility of an embedded BASIC interpreter which permits one to define any user-specific relation between the geochemical state variables and the transport properties.

Allowing time-dependent flow and transport properties is particularly important when simulating the leaching of chemotoxic elements that are immobilized by solidification/ stabilization techniques in cementitious materials. Cementitious materials are multi-scale porous media that generally require relatively complex conceptual-mathematical formulations to predict changes in its transport properties during chemical degradation. For example, estimation of the

pore diffusion coefficient does not depend only on the total porosity, but also on the amount of calcium silicate hydrates (C-S-H) and the associated gel porosity. Such complex relations typically lead to conceptual uncertainty (e.g. the development and use of many different models to predict the pore diffusion coefficient of cementitious materials), thus warranting numerical codes that allow for flexible definitions of the various models.

3. EXAMPLES OF THE LEACHING OF CEMENTITIOUS MATERIALS

In this section three (hypothetical) examples are given to illustrate applications of the HP1 reactive transport model to cementitious waste forms. A first example illustrates the long-term evolution of transport properties of cementitious material subject to leaching. A second example shows the leaching of Pb from cementitious waste in contact with rain and soil water. The last example simulates the effect of leachate from a cementitious waste form on the surrounding rock materials, in this case on the sorption properties of Cs of a concrete/clay interface.

3.1 Leaching of cementitious materials during diffusive transport conditions

This example considers the situation where a small cubic concrete block (4-cm) is in contact with a constant concentration boundary at one side and a no-flow boundary at the other side. The constant concentration boundary may correspond to a water reservoir whose chemical composition does not change, or to a water-filled fracture through which water flows fast enough not to be affected by the neighboring concrete matrix. A typical example is when water is flowing around a cementitious waste form in a degraded landfill. The simulation is based on a state-of-the-art thermodynamic model (CEMDATA07, Matschei et al., 2007, which was transformed to HP1 format by Jacques, 2008) and the multi-scale model of Oh and Jang (2004) for prediction of the pore diffusion coefficient D_p [L^2T^{-1}] based on geochemical state variables (see Jacques et al., 2011, for more details). Figure 1 shows profiles of several geochemical state variables (portlandite, the C-S-H phase tobermorite, Ca and pH) and transport properties (total porosity, and the pore geometry factor D_p/D_0, where D_0 is the diffusion coefficient in pure water [L^2T^{-1}]) in case of leaching with water having a typical rain water composition. As long as portlandite is present, the pH (and the Ca concentration) is buffered by portlandite, and changes in porosity are relatively small. Note that despite the relatively small increase in porosity during portlandite dissolution (from approximately 0.10 to 0.15), there is a large increase in the pore geometry factor (from approximately 2×10^{-4} to 4×10^{-3}) since the capillary porosity becomes larger than a defined critical porosity. When portlandite is depleted, a complex sequence of cement mineral dissolution reactions takes place, involving, among others, jennite, monocarboaluminate, ettringite and tobermorite, thus altering the pore water geochemistry (as illustrated by pH and Ca concentrations; Jacques et al., 2010) and the transport properties. When all cement phases are dissolved, the porosity is increased up to approximately 0.3. The solid phase consists only of the aggregates which are assumed to be unreactive in this example.

The leaching of chemotoxic elements from solidified wastes hence is influenced by the dynamic water composition (this since precipitation or sorption of many elements depends strongly on the pore water geochemistry) and the evolving transport properties. The effects depend also strongly on the composition of the boundary solution. Figure 1 shows the result of a simulation with a soil water composition in which the partial pressure of $CO_{2(g)}$ is approximately one order of magnitude larger than that of rain water. Leaching of cement minerals is retarded compared to leaching with rain water due to calcite precipitation near the interface. However, the soil water itself is more aggressive towards dissolution of cement minerals as can be seen from the faster advance of the low pH (pH ~ 4) front into the waste.
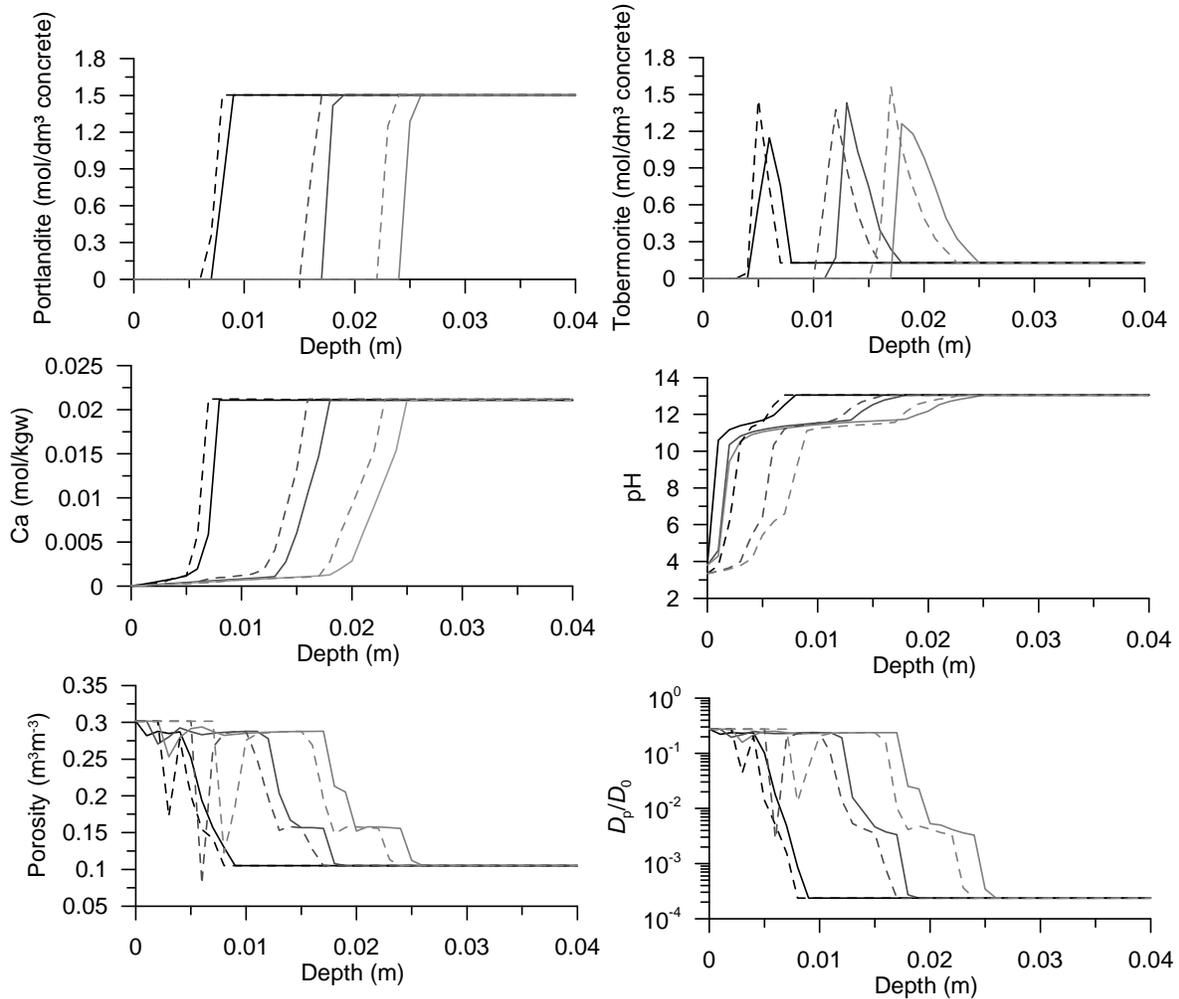
Figure 1. Profiles of different geochemical state variables in concrete after 50 (black), 150 (dark grey) and 300 (light grey) years during diffusive leaching with rain water (full line) or soil water (dashed line).

3.2 Pb leaching from a cementitious waste form

A second example simulates the leaching of Pb from its cementitious waste form. Pb leaching in cementitious environments at high pH is controlled by precipitation/dissolution reactions (Martens et al., 2010). The thermodynamic model for Pb leaching described by Martens et al. (2010) is combined here with the cement leaching model of the previous example. The solubility of Pb exhibits a typical amphoteric behaviour with a minimum solubility at a pH of about 10 (Mallants et al., 2008). Figure 2 shows the solid phase Pb profile of a cementitous waste form after 20 years of leaching with two different types of water (rain water and soil water). In case of soil water, Pb is leached only from the outer cement shell. There is also a small decrease in Pb at 9 – 10 mm. The profile for leaching with soil water is different. First, the location of the slight decrease in solid Pb is somewhat closer to the cement/water interface. The previous example also showed that the portlandite dissolution front moved slower in case of soil water (due to calcite precipitation). Next, Pb is precipitating near the cement/water interface. This coincides with the calcite precipitation zone discussed in the previous example. The pH is then buffered at

a value of about 10, giving the lowest solubility of Pb. Lastly, the zone of complete Pb depletion is slightly larger for soil water as compared to rain water. The previous example showed that the zone of low pH (high Pb solubility) is moving faster in case of soil water.
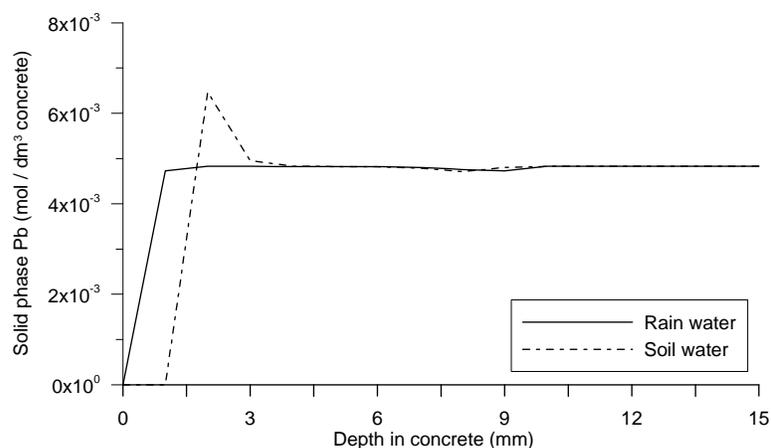

Figure 2. Solid phase Pb profiles after 20 years leaching of cementitious waste during diffusive transport conditions.

3.3 Cesium transport in a cement – clay system

The last example simulates the effect of leachates from a cementitious waste barrier on the sorption properties of the host rock. The example considers deep disposal of high-level radioactive waste. A cementitious barrier is placed between the waste (e.g. vitrified waste or cemented) and the geological host formation (e.g. a clay rock with low permeability). For this example we used properties of the concrete and the host clay formation for the Belgian reference case (for disposal of high-level waste in Boom Clay – Mallants et al. 2001). Cesium is assumed to be released from the waste matrix at a constant release rate and migrates through the cementitious barrier to the Boom Clay. All transport processes are diffusion dominated. At the same time, the cementitious materials interact with the Boom Clay, which leads to changes in the pore water chemistry and the solid phase composition of both the cementitious barrier and the Boom Clay. A general description of these processes, typically called alkaline plume interactions, can be found in Gaucher and Blanc (2006). Wang et al. (2010) discussed issues specific for the Belgian case. Of particular interest here is the so-called illitization of montmorillonite and the precipitation of zeolites (both processes occur in the clay zone). Illite and zeolites both have important sorption potentials for cesium. For this particular example we used the three-site cation exchange model of Bradbury and Baeyens (2000) for Cs sorption on illite (validated for Boom Clay by Maes et al. (2008)) and the cation exchange model of De Windt et al. (2004) for Cs sorption on zeolites. Sorption in the concrete is neglected here since it is much lower than sorption on illite (Wang et al., 2009). Figure 3 shows the simulation results for a 1.5-m thick cementitious barrier in contact with Boom Clay. To illustrate the effect of alkaline interactions between Boom Clay and cementitious pore water, two simulations were performed: Case 1 for which we did not account for the effect of the alkaline plume on Cs sorption on Boom Clay, and case 2 accounting for the effect of the alkaline plume.

As long as Cs is released in the concrete (i.e., < 20000 years), concentrations in the concrete part are equal and relatively high (no sorption of Cs on the concrete). In the Boom Clay, the concentration drops two or three orders of magnitude due to sorption on illite (and scolecite for case 2) (Figure 3a). Large differences can be observed between the two cases. The migration of

Cs for case 2 is much more retarded compared to case 1 (Figure 3a-c). This is also indicated by the ratio of the adsorbed and aqueous concentrations (Figure 3d). For case 1, the ratio changes between 2000 at the concrete/Boom Clay boundary (relatively high Cs concentrations) to about 26000 at 25 cm and further away from the boundary (low Cs concentrations). The latter value corresponds to the situation of maximum sorption on the initial amount of illite in the Boom Clay. In contrast, the ratio is almost always larger than 26000 for case 2. The high value near the concrete/Boom Clay boundary (about 70000) is caused by precipitation of scolecite and illite (results not shown). The drop in the ratio (starting at about 20 cm up to 50 cm) coincides with a decrease in illite further away from the concrete/Boom Clay interface. However, this decrease in illite is compensated by precipitation of scolecite (results not shown), thereby keeping the sorption of Cs in altered Boom Clay relatively high.
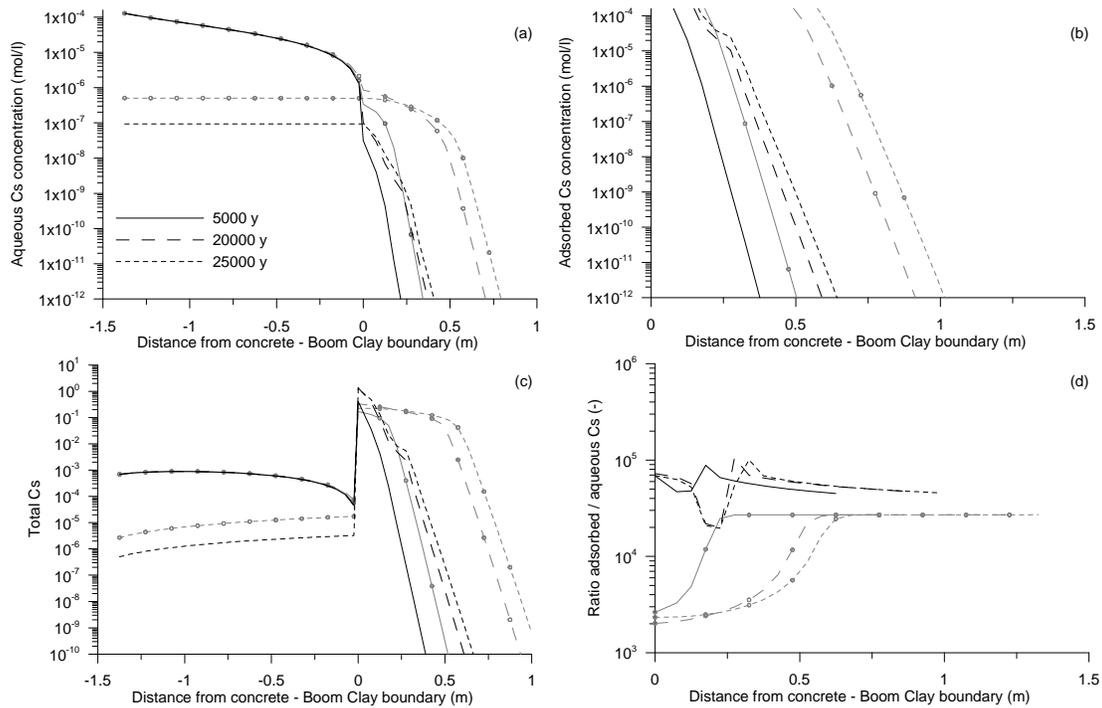

Figure 3. Simulation of Cs migration for case 1 (gray lines with circles, no alkaline plume interactions) and case 2 (black lines, alkaline plume interactions) for (a) aqueous Cs concentration, (b) adsorbed Cs concentration, (c) total Cs content, and (d) the ratio of adsorbed over aqueous Cs.

The alkaline plume was found to have a positive effect on the retardation of Cs on Boom Clay. This result is of course not transferable to other radionuclides or heavy metals. The properties of Cs contributing to this positive effect are (i) no solubility-limiting or other pH-dependent properties and (ii) the strong affinity to illite which is formed at some locations during the alkaline plume interactions.

Although this example is not specific for landfill conditions, similar configurations in which cementitious waste forms are in contact with impermeable clay liners may be present in some landfills. The key point here is that different geo-engineered layers in a landfill can interact and may change the hydraulic and solute transport properties and the sorption of elements.

5. SUMMARY

This paper illustrated the interactions of cementitious waste forms with other geo- and engineered materials in disposal sites using an advanced reactive transport code and a state-of-the-art thermodynamic database for cement minerals. One specific process is leaching of typical cement components to the surroundings. This causes changes both in the pore water and solid phase geochemistry and in the transport properties of the cementitious waste form. This evolution affects the leaching of chemotoxic elements from the waste form. The cement components may also alter the materials surrounding the cement, such as a clay liner around the cement. At the same time, the surrounding cover materials may influence also the degradation and leaching of the cementitious material itself as was shown by comparing leaching influenced by rain and soil water.

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