

Evaluating changes of transport properties of chemically degrading concrete using a coupled reactive transport model

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Abstract. This paper presents a model to simulate chemical degradation of concrete due to leaching. The model considers simultaneously the multi-scale nature of concrete, a thermodynamic description of cement phases, and time-variable transport properties. It is implemented in the generic simulator HPI, which simulates the reactive transport in variably-saturated porous media. To illustrate the capabilities of the program, we simulate diffusive transport through concrete in contact with waters of different solution compositions (i.e., concentrations of major cations and anions and inorganic carbon contents) and use a homogenization scheme for upscaling tortuosity. The simulations show the coupled effects between geochemical state variables, transport properties, and durability criteria for cementitious materials used in near-surface radioactive waste disposal facilities.

Introduction

Cementitious materials used in near-surface radioactive waste disposal facilities have important safety functions. In the Belgian concept, two main safety functions are attributed to the cementitious materials: a) restriction of water flow through the barriers and b) retardation of radionuclide migration by chemical retention. The evolution of these safety functions is evaluated in this paper based on specific concrete durability criteria. For example, it is well known that the chemical degradation state of concrete defines the retardation factor of the radionuclides (e.g. Wang et al., 2009). One degradation mechanism, which influences concrete durability, is the process of decalcification and leaching of concrete, especially at long time frames envisaged in radioactive waste disposal (Glasser et al., 2008). This process is strongly coupled both physically and chemically because dissolution of cement phases changes transport properties, which in turn influence the progression rate of geochemical reactions. One way to understand these effects is by using coupled reactive transport codes. Recent examples of this approach are found in Moranville et al. (2004), van der Lee et al. (2008), Stora et al. (2009) and Galindez and Molinero (2010), amongst others.

This paper presents a coupled reactive transport code that considers chemical degradation of concrete during leaching and which is based on a full thermodynamic description of cement phases. Transport properties are defined as a function of geochemical state variables using a multi-scale homogenization model (in this particular case the model of Oh and Jang (2004)). Concrete leaching and selected durability criteria are estimated for diffusive transport and for three different aggressive water types: Case 1 considers the solution composition of rain water ($p\text{CO}_2 = 10^{-3.5}$ atm), Case 2 uses the solution composition of rain water adjusted for effects of dry deposition of inorganic compounds, and Case 3 utilizes the same solution composition as in Case 2, but with a higher partial pressure of CO_2 to account for the effects of microbiological activity in soil ($p\text{CO}_2 = 10^{-2.3}$ atm).

Conceptual and mathematical model of chemical concrete degradation

Conceptual model

Concrete is a multi-scale porous medium, which consists of a porous hardened cement paste with impermeable aggregate inclusions. An interfacial transitional zone (ITZ) that develops between the cement paste and the aggregates has typically larger porosity and diffusivity than the bulk cement paste. The cement paste is a

two phase system which includes capillary pores and the solid phase. Contrary to many other porous media, solid cement paste itself contains small pores, so-called gel pores in the C-S-H phase. Cement paste thus consists of two pore systems, each contributing to the diffusion of aqueous species. Especially when the capillary porosity is smaller than a given threshold value, the gel pores form an important pathway for diffusion (*e.g.*, Bejaoui and Bary, 2007). The presence of impermeable aggregates increases the tortuosity of the pore network in concrete (de Larrard et al., 2010).

The conceptual representation of concrete is illustrated in Figure 1a. Flow and transport processes and geochemical reactions are described at the continuum scale. Different phases in concrete are defined as volume fractions in a representative volume (Figure 1b). The cement paste itself consists also of four volume fractions (Figure 1c). Symbols for different volume fractions are defined in Figure 1.

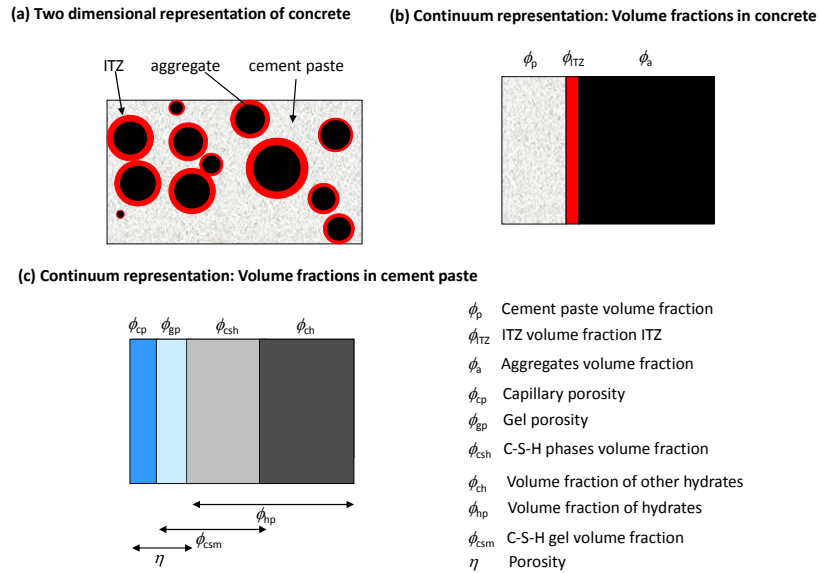


Fig. 1 Conceptual model for concrete.

Model formulation

A general formulation of the model considers variably saturated water flow (described by Richards' equation), multi-component diffusion in the gas phase (Fick's law), heat transport (Fourier's law), aqueous multi-component solute transport (advection-dispersion equation), thermodynamic geochemical equilibrium (described by mass action laws) and kinetics. Two main simplifying as-

assumptions in the general model are that electro-diffusive phenomena are neglected and, consequently, that each aqueous species has the same diffusion coefficient. In this paper, the focus is on diffusive transport under saturated, isothermal conditions, considering only thermodynamic equilibrium. The consistent thermodynamic database for cement phases CEMDATA07 (Matschei et al., 2007, Lothenbach et al., 2008) is converted into geochemical model formulations using mass action equations (Jacques, 2009). The set of equations can be found in several papers (e.g., Jacques et al. 2008, Glasser et al. 2008, amongst others). The main focus of the description of the model formulation is on the links between geochemical state variables in concrete and transport properties (porosity and pore diffusion coefficient), while accounting explicitly for the multi-scale nature of concrete.

The capillary and gel porosities are determined based on the solid phase composition. It is assumed that (i) during degradation, a net decrease in the volume of hardened cement paste corresponds to an increase in the porosity (and vice-versa), and that (ii) decalcification of the C-S-H gel itself (which is described as an ideal solid solution between jennite and tobermorite) does not change the capillary porosity (Bejaoui and Bary, 2007, Mainguy et al. 2000) except due to changes in the volume of the total amount of jennite and tobermorite. This latter assumption also implies that the ratio between the total volume of C-S-H phases and the gel porosity remains constant during chemical degradation. The porosity is updated after each geochemical calculation using the following steps: (1) The volume fraction of the hardened cement paste, ϕ_{hp} , is calculated by summing up volumes of different cement minerals. (2) The porosity, η , is obtained as $1 - \phi_{hp} - \phi_a$ (the volume of the aggregates is taken as a constant here) from the unit volume. (3) The gel porosity, ϕ_{gp} , is linked to the total volume of C-S-H phases, ϕ_{ch} , using a constant proportionality factor a^* ($=\phi_{gp}/\phi_{ch}$ at time zero). (4) The capillary porosity, ϕ_{cp} , is obtained by the difference between η and ϕ_{gp} .

The pore diffusion coefficient is obtained by multiplying the aqueous diffusion coefficient in free water, D_0 , with an overall geometry factor, T , which accounts for microscopic geometry factors such as tortuosity, connectivity, and constructivity, and for a correction factor for pore structural changes due to geochemical reactions. Several models are available to link η or ϕ_{cp} with T . Stora et al. (2010) indicated that models based on ϕ_{cp} give acceptable predictions of the ionic transport diffusivity in pure Portland-based systems. Several steps have to be taken to account for the multi-scale nature of concrete when estimating T : (1) Rescale the capillary porosity (expressed as dm^3/dm^3 concrete) to capillary porosity for the hardened cement (dm^3/dm^3 hardened cement paste). (2) Calculate the overall geometry factor of the hardened cement paste T_c . (3) Derive the overall geometry factor for concrete, T , from T_c , while accounting for the effects of the aggregates and the ITZ.

For illustrative purpose, the model approach of Oh and Jang (2004) is used below. This model was selected mainly because it is straightforward to implement into a coupled transport code (closed-form analytical expressions) and has physically interpretable parameters. A calculation of T_c is based on the general effective

medium homogenization scheme, in which the capillary porosity is the high-conductivity phase and the C-S-H phase is the low conductivity phase. This model requires two parameters: the ratio D_s/D_0 , where D_s is the diffusivity in the solid phase (C-S-H gel), and the percolation coefficient n . The calculation of the overall geometry factor using T_c is based on the composite sphere assemblage model with the assumption of impermeable aggregates. The calculation also needs two parameters: the ratio of the diffusion coefficient in the ITZ to the diffusion coefficient in the hardened cement paste, D_i/D_{hp} , and the ratio of the interface thickness to the radius of the aggregate, ε .

The mathematical model with all transport equations, geochemical equilibrium calculations, and feedbacks of geochemical state variables on transport properties was implemented in the generic transport code HP1 (Jacques et al., 2006, 2008). This code is flexible enough to implement in a straightforward way different conceptual models for updating porosity and transport properties. The model of Oh and Jang (2004) is used here as an illustration.

Description and parameterization of simulation scenarios

As an example, a purely diffusive transport problem for a 4-cm long concrete core with a constant concentration boundary condition at one side and a no-flow boundary condition at the other side is presented. Such boundary conditions correspond to a water reservoir, in which the chemical composition does not change (upstream boundary), or a water-filled fracture, in which water in contact with the concrete matrix flows fast enough not to be affected by interactions with concrete (downstream boundary).

Concrete used in the simulation is based on the CEM I ordinary Portland cement (OPC), the composition of which was described by Lothenbach et al. (2008). 350 g of OPC and a water-cement ratio of 0.47 are used to produce 1 dm³ of concrete. The initial volume fraction of the hydrated cement paste, ϕ_{hp} , is obtained by the thermodynamic equilibrium model. Volume fractions of the capillary and gel porosities are calculated using the model of Powers and Brownnyard (1947) with the parameters reported in Taylor (1997). The initial ratio of 0.88 between the gel porosity and the volume fraction of the C-S-H phase is used as an estimate for a^* . Physical transport parameters are as follows: the initial effective saturated hydraulic conductivity accounting for macro cracks is 3.41×10^{-12} m/s (Seetharam et al. 2011), the dispersivity is 1.0×10^{-3} m (Seetharam et al. 2011), and the aqueous diffusion coefficient D_0 is 9.61×10^{-10} m/s (at 10°C). Parameters of the model of Oh and Jang (2004), representative of OPC, are taken from this reference: $D_s/D_0 = 2 \times 10^{-4}$, $n = 2.7$, $D_i/D_{hp} = 6$ and $\varepsilon = 0.005$. The latter is based on the average ITZ thickness of 30 μm and the representative aggregate size of 6000 μm .

Diffusive transport calculations are carried out for three types of water in contact with concrete (see *Introduction*). Jacques et al. (2010) showed, based on

flush-type¹ simulations, that the water composition has a significant effect on the rate of concrete chemical degradation: soil water (Case 3) is the most aggressive while rain water (Case 1) is the least aggressive.

All results are presented as a function of the Boltzmann transform $\lambda = x t^{-0.5}$ (x is distance and t is time). Consequently, concentration profiles at different times should collapse to a single curve for a purely diffusive transport process (i.e., according to the Fick's second law). The degradation process of decalcification and leaching is simulated for up to 900 years.

Chemical degradation fronts for diffusive transport conditions

Detailed discussion of Case 1

Figure 2 shows selected geochemical variables and transport properties at two times of 300 and 600 years. Various curves normalize fairly well to a single curve with respect to λ , except for the maximum values, which differ somewhat between different profiles. Normalized curves for the shorter time differ somewhat from those for the longer time because a certain travel distance is required before a steady propagation front is obtained (probably due to the change in transport properties during degradation). Figure 3 (λ versus the travel depth) indicates that about 10 mm is needed to obtain constant values of λ for this set of parameters. Also note that concentration and property profiles at the end of the simulation are different because of the effects of the no-flow boundary condition.

Analysis of normalized concentration profiles allows an interpretation of the sequence of mineralogical changes. Portlandite is completely depleted at $\lambda \sim 1.4$ mm/year^{0.5} (i.e., the portlandite depletion front is at a depth of 14, 28, and 42 mm after 100, 400, and 900 years, respectively). As long as portlandite is present, most geochemical variables (such as Ca and pH) are buffered and changes in porosity are small. Notice that despite the relatively small increase in porosity during portlandite dissolution, there is a large increase in T because the capillary porosity becomes larger than the critical porosity. Between the depletion of portlandite (at $\lambda \sim 1.4$ mm/year^{0.5}) and tobermorite (at $\lambda \sim 1$ mm/year^{0.5}), a complex series of dissolution/precipitation reactions occurs in concrete (dissolution of jennite, monocarboaluminate, ettringite, and tricarboaluminate, and precipitation/dissolution of strätlingite and tobermorite). These reactions gradually increase porosity and tor-

¹ A flush-type reaction path simulation calculates equilibrium between aqueous and solid phase during different steps (or water-cycles). After each step, an increment of unreacted fluid is added to the system displacing the existing fluid and leaving the reacted minerals in place. Such a type of simulation is also called a mixing-flow reaction in chemical engineering.

tuosity. At $\lambda \sim 1 \text{ mm/year}^{0.5}$, T increases by about three orders of magnitude. Note also that hydrotalcite precipitation at $\lambda \sim 0.18 \text{ mm/year}^{0.5}$ causes a decrease in the overall geometry factor T .

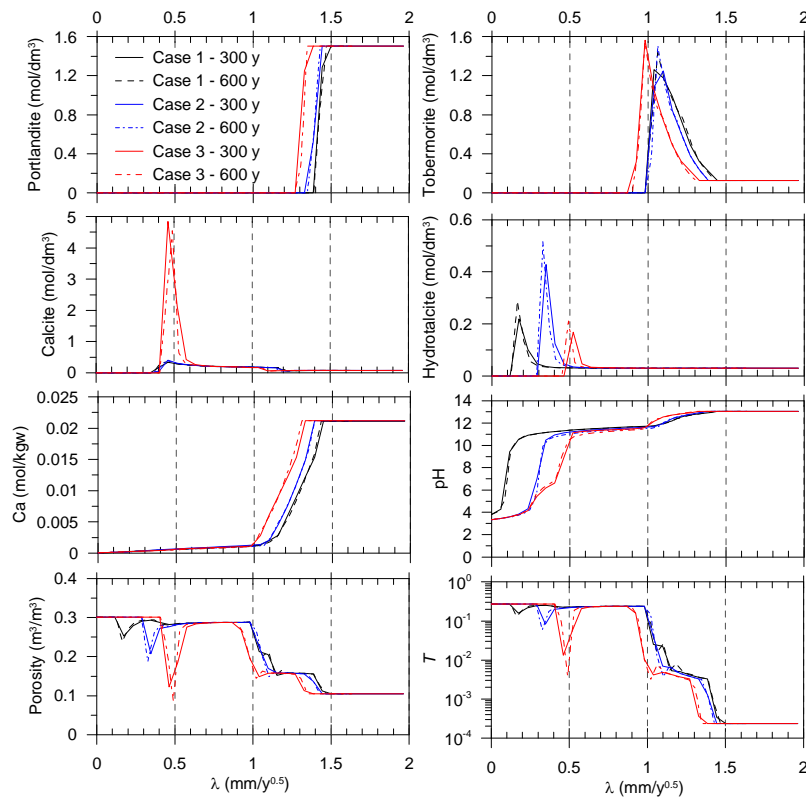


Fig. 2 Normalized profiles of several geochemical and physical state variables during diffusive leaching of a concrete core for three different types of water (reactions progress from right to left).

Comparison of results for different water compositions

Figures 2 and 3 also compare geochemical changes in concrete caused by different inflow water types. Depletion fronts of portlandite and C-S-H move slower in Case 3 than in the other two cases, which is contrary to the findings based on the

flush-type simulations of Jacques et al. (2010). In the continuum-type simulations discussed here, a large porosity decrease due to calcite precipitation is simulated for Case 3 (at $\lambda \sim 0.5$ mm/year^{0.5}, Figure 2), which further retards the degradation front velocities in concrete. However, the more aggressive nature of water in Case 3 still produces faster dissolution of calcite and hydrotalcite at λ smaller than 0.5 mm/year^{0.5}, which results in lower pH values at lower λ compared to the other two cases. As in Jacques et al. (2010), dissolution fronts in Case 2 are intermediate to those in Cases 1 and 3.

Assessment of selected concrete durability measures

To assess the long term durability of concrete in a near-surface radioactive waste repository, different durability criteria are defined to quantify the fulfillment of safety functions of concrete in the safety concept. As an illustration, two chemical and two mechanical/physical criteria are selected here. As concrete chemically degrades due to leaching, its sorption capacity for radionuclides changes with time. For example, Wang et al. (2009) attributed different retardation factors to different chemical degradation states. The end of chemical degradation states II (portlandite depletion) and III (C-S-H or tobermorite depletion) can be quantified from the front progressions once λ has reached a constant value (Figure 3). Mechanical/physical failure of concrete is defined when either pH drops below a value of 9-10 (depassivation of reinforcement bars and corrosion initiation) or a given amount of portlandite is leached from a load bearing concrete component (e.g., one assumption that the failure may occur when 33% of portlandite has leached out (Walton et al. 1990)). The latter can be derived from the portlandite front as $t^{0.5} = c_f L / (0.5(B_u + B_l))$, where t is the time of the failure, c_f is the percentage of portlandite that can dissolve (33%), L is the thickness of the concrete wall, and B_u and B_l are the upper and lower values of λ for the linear part in the portlandite normalized profiles. Table 1 gives an overview of the assessment of different durability criteria. As seen from the table, the calculations suggest that the mechanical failure of a 120-mm thick concrete wall is more likely due to portlandite leaching than due to the initiation of corrosion of reinforcement bars as the rate of decalcification front is much faster than the rate of reduction in the pH. Note that the latter statement is only true for a fully saturated condition as in the above example calculations. It is to be further noted that the durability criteria at these smaller scales (4 cm in this instance) may be different compared to large-scale structures due to heterogeneities and time dependent boundary conditions that exists at the larger scale. Nevertheless, these types of simulations allow a functional evaluation of different model elements, such as parameters, mathematical models of T , and boundary conditions.

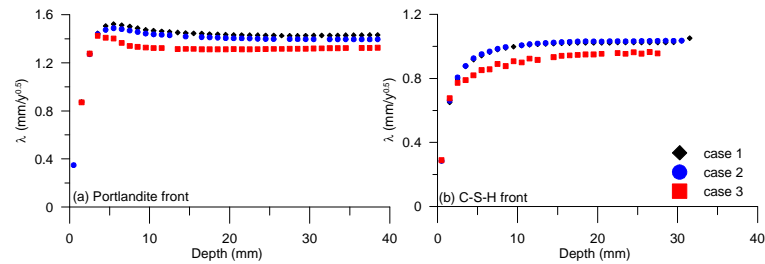


Fig. 3 The Boltzmann variable λ for (a) portlandite and (b) tobermorite (C-S-H) depletion fronts as a function of the travel depth in the concrete core for three different water types.

Summary and Outlook

Leaching and decalcification is one chemical degradation process of cementitious materials, which influences the long term durability of concrete in low level radioactive waste repositories. One way to assess this process is to use a multi-component reactive transport model, combined with a state-of-the-art thermodynamic database for cement phases, and a multi-scale representation of concrete for estimation of transport properties. In this paper, one possible homogenization scheme was implemented in the generic coupled transport code HP1 and leaching under diffusive transport conditions with three differently aggressive water types was simulated. Besides obtaining a phenomenological understanding of coupled chemical and physical effects on chemical degradation of concrete, different durability criteria were estimated, which are relevant for a near-surface repository. Since the complex model for cementitious materials was implemented into a generic code HP1, we can carry out in the future sensitivity and uncertainty analyses of parameters and conceptual models (e.g., homogenization schemes), evaluate effects of other transport conditions (advective-dispersive transport), and assess relative importance of other degradation mechanisms (e.g. carbonation).

Table 1 Overview of durability criteria.

End of chemical degradation state II	Front velocity (mm/year^{0.5})
Case 1	1.40
Case 2	1.35
Case 3	1.28
End of chemical degradation state III	Front velocity (mm/year^{0.5})
Case 1	0.95
Case 2	0.95
Case 3	0.8
33% of portlandite leached	Years till the mechanical failure of the 120-mm thick wall
Case 1	808
Case 2	867
Case 3	962
pH below 9 to 10	Front velocity (mm/year^{0.5})
Case 1	0.12
Case 2	0.33
Case 3	0.50

Acknowledgement and Disclaimer

This work has been performed as part of the project on disposal of category A waste – short-lived low and intermediate level waste (LILW-SL) – that is carried out by ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and enriched Fissile Materials.

The findings and conclusions in this paper are those of the authors and do not necessarily represent the official position of ONDRAF/NIRAS. The work presented in this paper was more particularly carried out as preparatory work to a future license application file for a near surface disposal facility at Dessel to be submitted by ONDRAF/NIRAS to the FANC. Therefore, the results in this paper have not yet undergone regulatory review nor approval by the FANC. Furthermore, it is not excluded that further developments and refinements of the work presented in this paper will be included in the future license application file.

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