Model abstraction addressing long-term simulations of chemical degradation of large-scale concrete structures

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Abstract. This paper presents a methodology to assess the spatial-temporal evolution of chemical degradation fronts in real-size concrete structures typical of a near-surface radioactive waste disposal facility. The methodology consists of the abstraction of a so-called full (complicated) model accounting for the multicomponent-multiscale nature of concrete to an abstracted (simplified) model which simulates chemical concrete degradation based on a single component in the aqueous and solid phase. The abstracted model is verified against chemical degradation fronts simulated with the full model under both diffusive and advective transport conditions. Implementation in the multiphysics simulation tool COMSOL allows simulation of the spatial-temporal evolution of chemical degradation fronts in large-scale concrete structures.

Introduction

Cementitious materials used in low-level radioactive waste disposal have in general important safety functions. In the case of near-surface disposal in Belgium, safety functions attributed to the near-field cementitious materials are i) limitation of water flow through the near field and ii) retardation of radionuclide migration by chemical retention.

Chemical degradation of concrete and the link with time-dependent hydraulic and transport properties can be modelled with relatively complex models integrating variably-saturated flow, multicomponent advective-dispersive solute transport, equilibrium or kinetic degradation including aqueous speciation calculations, pure phase and (ideal / non-ideal) solid solutions, microstructural representations of concrete (to link geochemical state variables to capillary and gel porosity) and formulations for updating hydraulic (permeability) and transport (pore diffusion...
coefficient) properties (e.g. Moranville et al. (2004), van der Lee et al. (2008), Stora et al. (2009) Galindez and Molinero (2010), and Jacques et al. (2011), amongst others). However, because the relatively high computational demands of such integrated model, it is extremely intricate to perform simulations at realistic spatial (~10³ m³ and larger) and temporal (several 10⁴ years) scales for a representative geometrical configuration (spatial distribution of different concrete types, cracks, etc.).

Not all details on the spatial-temporal evolution of the pore water composition, solid phase composition and local transport properties are required for long term safety assessment of a waste repository. A general characterization of the chemical degradation state of the cementitious materials is in many cases sufficient. In some cases, a distribution coefficient for radionuclides is defined for different degradation states of concrete (e.g. four degradation states in the study of Wang et al. 2009). When the spatial distribution of the degradation state of concrete at a given time is known, other properties, such as radionuclide sorption, are adapted accordingly. As such, a simplified model should be derived from the full geochemical model in such a way that the simplified model is still able to simulate key features of the full model. We prefer to refer to the simplified model as the abstracted model to underscore that the goal of model abstraction (simplification) is a reduction of model complexity while maintaining the validity of the simulation results with respect to the questions that the simulation is being used to address (Frantz, 2002). One of the most commonly used abstraction methods in the concrete literature is the reduction of the complex cement chemistry to a single aqueous component (typically Ca) and a single solid phase (typically Ca in the solid phase) (e.g. Gérard 1996, Mainguy et al. 2000, Yokozeki et al. 2004, Bejaoui and Bary 2007, amongst others). Although this modelling approach is, in some cases, compared with or derived from experimental data, publications addressing direct comparison with a fully coupled reactive transport model accounting for the full geochemistry of cementitious materials and coupling between changes in geochemical state variables and transport properties are scarce to the authors’ knowledge.

This paper presents a model abstraction methodology for simulating the chemical degradation fronts within large scale cementitious structures (several m³). Firstly, the full model and the model abstraction are discussed. Secondly, the implementation of the abstracted model in a transport code is verified against full reactive coupled simulations under diffusive and advective transport conditions. In the last section, an example of the simulation of the progress of degradation fronts in a large cracked concrete structure is given.

Model abstraction of decalcification and leaching of concrete

The key question in this example is to obtain the spatial-temporal evolution of the chemical degradation states in concrete. The abstracted model should thus provides sufficient information for the estimation of the propagation of chemical deg-
radiation fronts. Two degradation fronts are of particular interest: (i) the end of the so-called chemical degradation state II which is defined by portlandite depletion, and (ii) the end of the so-called chemical degradation state III which is defined by depletion of the C-S-H phases (Wang et al. 2009). The model abstraction consists of two steps: (i) defining a full complex model, and (ii) based on the simulation results of the full model, an abstracted model is derived which accounts for the key processes without a significant loss in accuracy.

**Full model**

Leaching of concrete is simulated based on a mechanistic and process-based model. Water flow and multicomponent transport are described by Richards’ and the advective-dispersive transport equation, respectively. Equilibrium between the concrete pore water composition and solid phase composition is calculated with a thermodynamic model accounting for aqueous speciation, activity corrections, and the different mineral phases. A state-of-the-art thermodynamic model is used (CEMDATA07, Matschei et al., 2007, Lothenbach et al., 2008). To adapt transport properties (porosity, pore diffusion coefficient, and hydraulic conductivity), the multi-scale nature of concrete is taken into account by considering gel porosity in the C-S-H phase, capillary porosity, the interfacial transition zone and the effect of aggregates. In this particular model, the analytical model of Oh and Jang (2004) was used. The model is implemented in the flexible reactive transport code HP1 (Jacques et al. 2006, 2008). Details on the conceptual and mathematical model can be found in Jacques et al. (2011). The derivation of the abstracted model is based on leaching calculations during diffusive transport conditions using a constant concentration boundary condition (with a typical rain water composition) in a 4-cm long concrete core (see also Jacques et al. 2011).

**Abstracted model formulation**

The complex geochemistry involved in leaching and decalcification of cementitious materials is reduced by accounting only for one aqueous component and one solid phase component. The Ca concentration is taken as the aqueous component whereas the total Ca in the cement solid phase of the hardened cement paste (not in the aggregates) is taken as the solid phase component with the latter the driving variable. The relations between the aqueous and solid phase Ca are taken from the full model at three spatial locations (10, 20, and 30 mm). As shown in Jacques et al. (2011), about 10 mm of travel distance was needed to obtain more or less stable dissolution and precipitation waves.
Fig. 1 Abstracted relations between (a) solid Ca and aqueous Ca concentration, (b) porosity and solid Ca concentration, and (c) the ratio of the pore diffusion coefficient and the free aqueous diffusion coefficient $D_p/D_0$ and solid Ca concentration based on simulated relations with the full model. The solid Ca is only Ca in the hardened cement paste and not in the calcareous aggregates.
From Figure 1a, it is clear that this relation is not univocal at all depths. A piecewise-polynomial function was used to capture the main relations between the solid-phase Ca and the other variables. At high solid Ca concentrations (above approximately 2.39 mol/dm³), the aqueous Ca concentration is determined by the solubility of a single mineral (portlandite). Also, at low solid Ca concentrations, aqueous Ca concentration remains constant over a broad range of solid Ca concentrations indicating again that its concentration is controlled by minerals with a fixed composition (a C-S-H phase with a fixed Ca/Si ratio of 0.833).

The porosity (Figure 1b) is not uniquely defined as a function of the Ca solid content (e.g., at a Ca solid content of approximately 1.25 or 1.75 mol/dm³) due to complex precipitation and dissolution patterns (see also Jacques et al. 2011). Nevertheless, the relation between aqueous and solid phase Ca is described by a single piece-wise curve in the abstracted model. In the full model, porosity is calculated as the sum of the capillary porosity (derived from the change in the total volume of minerals) and the gel porosity (derived from the amount of C-S-H phases). Because this information is not available in the abstracted model, the porosity must also be related to e.g. the Ca in the solid phase by an abstracted relation (see Figure 1b). Three parts are distinguished: (i) at solid Ca concentrations larger than approximately 2.39 mol/dm³, a linear relation exists because it corresponds with the dissolution of a single mineral (portlandite). (ii) At solid Ca concentrations smaller than approximately 1.25 mol/dm³, again a linear relation exist which corresponds to the dissolution of a C-S-H with fixed stoichiometry. (iii) In between, there is a complex sequestration of dissolution and precipitation reactions which was captured by a polynomial curve. Similarly, the geometry factor relating the free aqueous diffusion coefficient to the concrete pore diffusion coefficient needs information on capillary porosity. Figure 1c shows the abstracted relation for the geometry factor as a function of Ca in the solid phase.

The derived abstracted model is evaluated in terms of the output of interest, i.e., the end of the chemical degradation state II (defined by the complete dissolution of portlandite) and the end of the chemical degradation state III (defined by the complete dissolution of the C-S-H phase). These end points are again formulated in terms of total solid Ca as 2.39 and 0.19 mol Ca / dm³ for the end of state II and III, respectively.

**Verification of the abstracted model**

The abstracted model is verified by comparison of the profiles of Ca in the solid phase at different depths as a function of time for the full and abstracted model. The full model is implemented in the reactive transport code HP1. The abstracted model is implemented in the multiphysics simulation tool COMSOL Multiphysics (2008). A first verification is done for pure diffusive transport conditions using a horizontal 4-cm long concrete core with a constant concentration boundary condition at one side and a closed boundary condition at the other (identical to the simu-
lation used for the model abstraction). The abstracted model duplicates the solid Ca profiles rather well (Fig. 2). The propagation of the portlandite dissolution front also corresponds well with the full geochemical model, whereas the C-S-H depletion front in the abstracted model is a little bit ahead of that of the full model, but the difference in time remains constant throughout the simulation. There was a significant gain in computational time: the full model requires more than 3 days, whereas the abstracted model was finished within 15 minutes.

![Solid calcium profiles](chart.png)

**Fig. 2** Comparison of the solid Ca profiles and the ends of chemical degradation state II and III between the full and abstracted model during diffusive transport conditions.
Fig. 3 Comparison of the solid Ca profiles, the end of chemical degradation state II and III (top) and the water flux (bottom) between the full and abstracted model during advective transport conditions.
A second verification considers a saturated advective-dispersive transport problem in a 10-cm long vertical concrete column. The hydraulic conductivity is arbitrarily put two orders of magnitude larger than in the diffusive case to obtain the advective flow conditions \((3.41 \times 10^{-12} \text{ m/s}} \) versus \(3.41 \times 10^{-10} \text{ m/s} \) for the diffusive and the advective case, respectively). The upper boundary condition for water flow is constant zero head. The calculated water flux through the concrete core is also an output variable of interest. Fig. 3 shows the solid Ca profiles at selected depths and the water flux through the 10-cm long core for the full and the abstracted model. The portlandite dissolution front (i.e. until end of State II) is perfectly described by the abstracted model. Also the C-S-H depletion front and the water flux are represented in an acceptable way. The only significant difference between the full and abstracted model is found in water flux at times larger than 1000 years. The abstracted model simulates a faster dissolution of the residual Ca in the solid phase compared to the full model. Consequently, the water flux through the concrete core increases faster compared to the full model.

It is important to say that this type of verification does not ensure that the abstracted model performs always as good as in the two examples above. However, the abstracted model was tested for a large range of Ca concentrations (and chemical degradation states) and flow regimes (pure diffusive case and an advective-dispersive transport case). Additional comparisons were made at other hydraulic conductivities up to \(4.1 \times 10^{-9} \text{ m/s} \) (results not shown). In all cases, the spatial-temporal evolution of the output variables of interest (end of degradation state II and III) were well simulated with the abstracted model compared to the full model. Nevertheless, further validation might be warranted including e.g. more complex flow and transport domains (including cracks).

**Decalcification of a large structure**

The abstracted model is next applied to real structures present in surface disposal facilities based on the design for the Belgian low-level radioactive waste disposal facility at Dessel. Two examples are presented here. The first structure is a roof structure with cracks perpendicular to rebar due to chemical shrinkage and rebar corrosion, and some through-going cracks due to shrinkage in fiber reinforced concrete. The so-called postulated crack network is shown as the solid lines in Fig. 4. The second structure is the monolith which is a concrete caisson in which the radioactive waste is grouted. Again, after some time, a postulated crack network will be present. The chemical degradation states are simulated by the abstracted model using COMSOL Multiphysics. Also chemical state I (high Na and K concentration) and state IV (basically only calcareous aggregates are left) are indicated, although the precise location is less accurately defined.

Water infiltrates at the top boundaries into the cracks leading to regions of preferential chemical degradation. At the right hand-side of the monolith, the leaching is controlled by diffusive processes. Chemical degradation progresses
somewhat faster in the cracks compared to the uncracked regions. Variable sorption parameters (as a function of the chemical degradation state) can be linked to these spatial-temporal variation of the chemical degradation of cementitious components in the near-field of a surface disposal facility (e.g., Perko et al. 2011).

Fig. 4 Spatial distribution of chemical degradation fronts in a roof (top) and monolith (bottom) concrete structure with cracks (solid lines) simulated with the abstracted model.
Summary and Outlook

The paper presents an abstraction methodology for a chemical degradation model of concrete subject to decalcification and leaching. In the model abstraction approach, basically, a so-called full model is simplified in such a way that the resulting abstracting model is still able to represent well the key variables of interest. The full model for chemical degradation is a multicomponent reactive transport model including a state-of-the-art thermodynamic database for the full cement chemistry and a multi-scale model for relating geochemical state variables to transport properties. The abstracted model uses only one component in the aqueous and solid phase. Relations between the Ca in the solid phase and Ca in the aqueous phase, total porosity and the pore diffusion coefficient based on the full model are the backbone of the abstracted model. The abstracted model was implemented in the multiphysics simulation tool COMSOL Multiphysics and verified for diffusive and advective transport conditions. The abstracted model can be used to simulate chemical degradation fronts in real-scale concrete structures used in surface disposal facilities.

Note that it is important to validate the full model with experimental data and/or simulation results from microstructural simulations which was not done in the current study. Nevertheless, the abstraction methodology still applies when the full model is changed.

Further development is aimed towards the application of radionuclide transport coupled with the concrete degradation. Radionuclide migration is affected by the change of physical properties (determined by the degradation model) and also by the evolution of sorption properties of degrading concrete.

Acknowledgement and Disclaimer

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References

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