Modelling chemical degradation of concrete during leaching with rain and soil water types

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ARTICLE INFO

ABSTRACT

Percolation of external water through concrete results in the degradation of cement and changes the concrete pore water and solid phase composition. The assessment of long-term degradation of concrete is possible by means of model simulation. This paper describes simulations of chemical degradation of cement for different types of rain and soil water at an ambient earth surface temperature (10 °C). Rain and soil water types were derived using generic equations and measurement of atmospheric boundary conditions representative for North-Belgium. An up-to-date and consistent thermodynamic model is used to calculate the geochemical changes during chemical degradation of the concrete. A general pattern of four degradation stages was simulated with the third stage being the geochemically most complex stage involving reactions with calcium-silicate hydrates, AFm and AFt phases. Whereas the sequence of the dissolution reactions was relatively insensitive to the composition of the percolating water, the duration of the different reactions depends strongly on the percolating water composition. Major identified factors influencing the velocity of cement degradation are the effect of dry deposition and biological activity increasing the partial pressure of $CO_{2(g)}$ in the soil air phase (and thus increasing the inorganic carbon content in the percolating water). Soil weathering processes have only a minor impact, at least for the relatively inert sandy material considered in this study.

1. Introduction

Cement and concrete are typically not in thermodynamic equilibrium with the surroundings in which they are located. Because concrete used in e.g. waste conditioning and surface disposal sites is not an isolated system, infiltration and movement of solutes from the surroundings will change the concrete pore water and solid phase composition and, therefore, the solubility and sorption of contaminants (see Wang et al. [1] for an extensive review of sorption values for radionuclides and some chemotoxic elements as a function of the cement degradation stage).

Typical chemical degradation reactions are decalcification, dissolution and leaching of cement components and carbonation (Glasser et al. [2]), amongst others. These reactions induce a gradual change in the pore water composition, from typical "young" concrete pore water with a pH above 13 to more evolved pore water with a pH lower than 10. Different attempts have been made to simulate the long-term chemical degradation of concrete [3–7]. In general, at 25 °C four stages of cement degradation are identified depending on the pH and cement pore water controlling cement phases (pH-values are for 25 °C). Stage 1 has a pH larger than 12.5 with a high concentration of Na and K ions. Stage 2 has a pH of 12.5 controlled by the dissolution of portlandite

with approximately 20 mm of Ca. Stage 3 starts when all portlandite has been leached out of the cement and the pH drops from 12.5 to 10.0 when the pore water composition is buffered by different cement phases including AFt, AFm and calcium-silicate hydrates (C–S–H phases). The end of this stage is defined when all these phases are completely leached out. Stage 4 has a pH lower than 10 with calcite and aggregate minerals present. The pore water composition is then mainly influenced by the composition of the intruding water. Although the reactions within each stage, are quite independent of the composition of the intruding water, the duration of the different stages (expressed in total amount of added water) and the amount of minerals which dissolves or precipitates per kg of added water depend strongly on the composition of the infiltrating water.

The assessment of the progression of the long-term chemical degradation of cement is possible by means of model simulation. The most straightforward way is using thermodynamic equilibrium modelling coupled with transport of solution species. Such modelling approach is able to reproduce the zoning of cement degradation, as is shown by e.g. Moranville et al. [8]. A more simple approach is to use only thermodynamic equilibrium modelling with a mass-balance approach in which, after the equilibrium calculation, the cement-equilibrated pore water is replaced with a new amount of the external aggressive water but keeping the changed cement solid phase. Such type of simulation allows an in-depth analysis of the geochemical changes in both the pore water and the solid phase.

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This paper describes simulations of chemical concrete degradation using thermodynamic equilibrium modelling combined with mass-balance approach for different rain and soil water types accounting for processes like wet deposition, dry deposition, soil biological processes and soil weathering and release of major cations at ambient surface temperatures (10 °C) using a consistent thermodynamic model for cement phases at temperatures different from the standard temperature (25 °C). These calculations were done within the framework of near-surface disposal of low and intermediate-level short-lived radioactive waste in Belgium, and therefore, atmospheric boundary conditions relevant for determining rain water and soil water composition were taken representative for Belgian conditions.

2. Model approach

Chemical degradation of concrete is simulated using mass conservation and thermodynamic equilibrium laws (mass action equations) starting from 1000 cm³ of concrete at a long-term averaged atmospheric temperature (~ 10 °C, representative for Belgium, Jacques and Mallants [9]). The concrete is equilibrated with a given amount of external water (not in equilibrium with the concrete phases). After equilibration, the resulting water is replaced by a new amount of external water whereas the changed cement solid phase is kept. In this way, the changing cement pore water and solid phase composition is simulated as function of cumulative added (external) water. This approach needs (i) a consistent thermodynamic database (i.e., solubility constants of the cement minerals are calculated with a single set of aqueous species and thermodynamic constants) for aqueous species and cement phases for 10 °C, (ii) the initial concrete composition and (iii) the composition of the external water types.

2.1. Thermodynamic model for cement degradation

A thermodynamic data set for cement minerals was built by Lothenbach and Winnefeld [10], Lothenbach et al. [11] and Matschei et al. [12] (CEMDATA07), consistent with the thermodynamic data in the Nagra/PSI-Thermodynamic Data Base [13]. When used in the geochemical GEMS-software [14], temperature dependencies of thermodynamic parameters are calculated with the embedded SUPCRT code [15]. The GEMS-software minimizes the Gibbs free energy of the system subject to a number of constraints (mass-balance conditions, electrical neutrality). The database can be used in other geochemical codes (e.g. PHREEQC [16] in which geochemical equilibrium is calculated based on mass action equations) at 25 °C together with the Nagra/PSI-Thermodynamic Data Base. To be used at other temperatures in PHREEQC, temperature dependencies of the aqueous species should be exactly the same as in GEMS, otherwise, the CEMDATA07 database and the Nagra/PSI database are not consistent. To simulate the chemical degradation due to leaching at a long-term average of the atmospheric temperature (taken to be 10 °C in Belgium), the equilibrium constants of all aqueous species and minerals in the model must be recalculated for this temperature. The Gibbs free energy for all species was calculated with GEMS (based on the revised Helgeson–Kirkham–Flowers equations for aqueous species or on the integration of the heat capacity function $C_p(T)$ for minerals and gases) and related to the mass action constant K_T by:

$$K_T = \exp\left(-\frac{\Delta_r G_T^{\circ}}{RT}\right) \quad (1)$$

where R is the universal gas constant, and $\Delta_r G_T^{\circ}$ is the Gibbs free energy change of a reaction at temperature T:

$$\Delta_r G_T^{\circ} = -\sum_i \nu_{ji} \Delta_f G_{T,A_i}^{\circ} \quad (2)$$

where $\Delta_f G_T^{\circ}{}_{A_i}$ is the Gibbs free energy of formation of species A_i at temperature T and ν_{ji} are the stoichiometric coefficients of the

chemical reaction. A detailed description of the conversion of the GEMS-database to a PHREEQC-database, a list of the aqueous species and minerals in the thermodynamic model and corresponding mass action constants at 10 °C are given in Jacques [17]. Note that the solubilities of Na and K in stage 1 were slightly differently treated. Alkali sulphate salts are very soluble resulting in the high Na and K concentrations, but sulphate is buffered by the formation of ettringite. Because Na- and K-controlling phases are lacking in the thermodynamic database, two surrogate phases (Na_2O and K_2O) were defined to mimic the average concentrations of Na and K in fresh ordinary Portland cement (as reported by Brouwers and van Eijk [18]).

2.2. Concrete composition and initial cement hydrates

Calculations are based on a CEM I 42.5 N composition as given in Lothenbach et al. [11] (Table 1). The concrete consists of 350 kg CEM I, 1828 kg of different calcareous aggregates and 175 of kg water per m³ of concrete (Jacques et al. [19]). Calculated equilibrium concrete pore water composition and mineral phase assemblages are given in Table 2.

2.3. Water composition

The geochemical degradation of concrete depends on the composition of the external percolated water. The sensitivity of the chemical degradation rate of concrete for water composition is evaluated by doing several simulations with different water types. Water compositions used in the simulations are given in Table 3.

The first two types of water are so-called rain water types. Type 1 is defined by assuming that the water infiltrating the concrete has the same composition as rain water. This type is indicated as Rain water — "wet only deposition" and representative values were obtained from a series of averaged yearly concentrations as measured in the Dutch 'National Precipitation Chemistry Network' (as cited in Jacques et al. [19]). The only biological process taken into account for this type of water is total nitrification of the ammonium. Another rain water variant (type 2) takes into account the bulk dry deposition in calculating its chemical composition. In this study, this so-called "Rain water — bulk deposition" is represented by long-term (1993–2002) annual averaged bulk deposition amounts measured in the open field as reported in Neirynck et al. [20]. Deposition values reported as keq/ha/year are converted to mol/kg water using the average annual precipitation surplus (= precipitation − actual evapotranspiration, [19]).

A second group of water types are those in which the rain water, prior to contacting the concrete, is flowing through soil layers resulting in composition changes due to (micro)biological respiration and soil weathering processes. Soil microbiological respiration increases the partial pressure of $CO_{2(g)}$ in the soil gas phase compared

Table 1
Oxide and phase composition of CEM I.
After [11], only the four major clinker phases are given.

Mineral	g/100 g OPC	mol/100 g OPC	Molar mass (g/mol)
CaO	62.4	1.1127	56.0794
SiO₂	18.9	0.3146	60.0843
Al₂O₃	4.4	0.0432	101.961
Fe₂O₃	2.5	0.0157	159.688
CaO(free)	0.6	0.0107	56.0774
MgO	1.4	0.0347	40.3044
K₂O	0.95	0.0101	94.196
Na₂O	0.10	0.0016	61.979
CO₂	2.1	0.0477	44.01
SO₃	3.0	0.0375	80.0652
Alite (C₃S)	58		
Belite (C₂S)	10		
Aluminate (C₃A)	7.6		
Ferrite (C₄AF)	7.5		