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Benchmark of reactive transport modelling of a low-pH concrete / clay interface

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Abstract

Cement-based materials are key components in the barrier system of repositories for disposal of nuclear waste. Given the extremely long timespans related with geological disposal of nuclear waste, increasing the understanding of long-term performance of cementitious materials is paramount for the safety assessment. One of the alteration processes that may occur in a repository system is the interaction of cement-based materials with the surrounding host rock due to the high concentration gradients between them. These reactive transport processes can in turn impact the physical properties of cementitious materials and the interface with clayey systems. This interaction leads to complex coupled processes, which needs to be assessed by means of numerical reactive transport models. A benchmark reactive transport modelling study of the interaction between a low-pH concrete and a clay host rock (i.e. Callovo Oxfordian) is presented here. The main goal is to build confidence in the consistency of the different modelling approaches and in the application of different reactive transport codes to analyse the performance of recently developed low-pH cementitious systems. The methodology was based on the establishment of a common setup of a full reference case, building upon preliminary cases of increasing complexity. In addition, a set of sensitivity cases was simulated to test the effect of key geochemical and transport parameters on the results. The impact of porosity changes due to mineral reactions on the diffusion coefficient was also studied as a sensitivity case. The concrete used in the model corresponds to the reference low-pH concrete manufactured and characterized in the H2020 collaborative project CEBAMA. In all cases, diffusion-driven solute transport under water saturated and isothermal conditions was considered. Chemical reactions included aqueous speciation, cation exchange reactions, and mineral dissolution-precipitation both under thermodynamic equilibrium and kinetically-controlled. Different reactive transport codes were used in the benchmark (iCP, ORCHESTRA, OpenGeosys-GEM, CORE^{2D}, and MIN3P). Overall, the results show not only the high level of understanding of the governing processes but also the good agreement obtained with different codes, which is essential to demonstrate the applicability of reactive transport modelling to support safety assessment.

Keywords: Benchmark, Reactive transport modelling, low-pH concrete, cement-clay interaction, iCP, ORCHESTRA, OpenGeosys-GEM, CORE^{2D}, MIN3P

1 Introduction

CEBAMA (Cement-based materials, properties, evolution, barrier functions) is a research and innovation action granted by the EC in support of the implementation of first-of-the-kind geological repositories for nuclear waste. One of the goals of the Horizon 2020 collaborative project CEBAMA (Altmaier et al., 2017) is to improve the understanding of interaction processes between cementitious and clayey materials (i.e. bentonite, clay rocks). Different approaches were used for modelling and interpretation of experimental data generated within the project and focusing on reactive transport processes that can impact the physical properties of cementitious materials and their interface with clayey systems. Therefore, an integrated modelling study was undertaken to build confidence in the consistency of the different modelling approaches. The work consisted of benchmarking the capabilities of various reactive transport codes to simulate physical and chemical processes governing long-term interactions at the concrete-clay interface.

A large body of literature exists dealing with the modelling of cement-clay interactions. Reviews by Gaucher and Blanc (2006), Savage et al. (2007), and Bildstein and Claret (2015) are comprehensive studies of the level of knowledge and main uncertainties in this field. Many of these studies focused on the clayey system, disregarding the alteration of the cementitious barrier (Savage et al., 2002; Gaucher et al., 2004; Watson et al., 2009; Fernández et al., 2010). In those studies, the cementitious system is typically replaced by a fixed concrete porewater as a boundary condition. Other studies have focused on the prediction of the formation of an alkaline plume (e.g. Soler et al., 2011; Grandia et al., 2010; Sidborn et al., 2014), or the degradation of cementitious systems by clayey porewaters (Olmeda et al., 2017). More recently, the simultaneous interaction between clayey and cement-based materials have been given more attention (Trotignon et al., 2006; De Windt et al., 2008; Yang et al., 2008; Marty et al., 2009; Kosakowski and Berner, 2013; Soler, 2013; Liu et al., 2014; Mon et al., 2017; Samper et al., 2018). Marty et al. (2014, 2015) presented a systematic study of the interaction between a Callovo-Oxfordian clay formation and a high-pH concrete. The overall evolution sequence of ordinary Portland cement (OPC; high-pH) concrete is well-known (Miller et al., 2000; Marty et al., 2014; Olmeda et al., 2017). However, interactions of low-pH concrete with clayey materials, as studied in this paper, have been given much less attention. Thus, the goal of this study is not only to build confidence in the modelling approaches by benchmarking reactive transport codes, but also to increase the level of understanding of the alteration of low-pH cementitious materials in contact with a clayey system. A reference case was simulated considering a common framework of models and parameters, as well as a set of sensitivity cases for assessing the impact of numerical codes specificities, material variabilities, and uncertainties on the extent of alteration. In this paper, the results and main outcomes obtained with different reactive transport modelling tools are presented and the implications of the study are discussed.

The paper is structured as follows. The conceptual model is described first, together with the parameterization and the numerical implementation into the different reactive transport codes, which are also briefly presented. Then, the results of the full reference case are presented and compared. The main outcomes of the sensitivity analyses are also addressed. Finally, the conclusions of the study are highlighted.

2 Description of studied system

The studied system considers a generic concrete structure in contact with a clayey host rock at isothermal (25 °C) and fully water saturated conditions. Fickian diffusion is considered as the only solute transport mechanism in the reference case. A single diffusion coefficient for each material

domain is defined, maintaining electroneutrality of the pore solution. Both materials were considered as homogeneous and continuous porous media. It is assumed that no excavation damage zone (EDZ) is present. A one-dimensional setup in Cartesian coordinates is assumed, with a concrete thickness of 0.30 m, in contact with a large mass of claystone with a thickness of 40 m. The geometry and boundary conditions are shown in Fig. 1. Fixed concentration (Dirichlet) at the clay boundary corresponds to the initial porewater composition of the claystone.

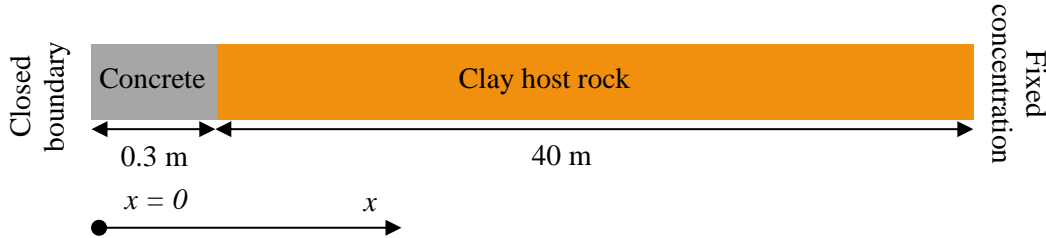


Fig. 1. Geometry and boundary conditions considered in the model.

The concrete mix corresponds to the CEBAMA reference low-pH concrete mix (Vehmas et al., 2017, 2019c), see Section 2.1 and Appendix A. The mineralogical composition of the clay host rock corresponds to the Callovo-Oxfordian claystone (COx), see Section 2.2, which is well characterised (Marty et al., 2014) and has been previously considered in a benchmark modelling study of the interface between a “high-pH” (OPC) concrete and COx (Marty et al., 2015). The effective diffusion coefficient and total porosity of the two domains are given in Table 1.

Table 1. Physical properties of the concrete and claystone domains considered in the model.

Material	Porosity	Pore diffusion coefficient (D_p , m ² /s)	Effective diffusion coefficient (D_e , m ² /s)
Low-pH concrete	0.04	$2.50 \cdot 10^{-11}$	$1.00 \cdot 10^{-12}$
COx claystone	0.18	$1.44 \cdot 10^{-10}$	$2.60 \cdot 10^{-11}$

Most of the simulation cases considered the thermodynamic database ThermoChimie version 9b0 (Giffaut et al., 2014) which contains updated data for clay minerals (Blanc et al., 2015). The version of ThermoChimie used applies the extended Debye Hückel equation to calculate activity coefficients. The main reason to select this database is that it includes data for both the cementitious and the clayey systems and it is updated. However, it does not include M-S-H phases.

2.1 Low-pH concrete model

The initial porosity of concrete adopted in the reactive transport modelling is 0.04, corresponding to the experimental value obtained by MIP (Table 1). The effective diffusion coefficient of concrete in the reference case is $1 \cdot 10^{-12}$ m²/s according to Vehmas et al. (2019c) (Table 1). The calculated mineralogical and porewater composition after 10 years of hydration has been selected as an initial condition (Appendix A). At that time, the remaining mass of unhydrated clinkers is extremely small and can be neglected, while the slag has dissolved completely. Only silica fume and quartz filler are considered in the simulations to dissolve kinetically with the pH-dependent kinetic dissolution rate of quartz, r (mol/s), proposed by Palandri and Kharaka (2004):

$$r = M_w \cdot m \cdot k \cdot A \cdot |1 - \Omega^\theta|^\eta \quad (2.1)$$

$$k = k_{25}^{nu} + \sum_i k_{25}^i \prod_j a_{ij}^{n_{ij}} \quad (2.2)$$

where M_w (g/mol) is the molar mass of the mineral, m is the total mass of the mineral (mol), k is the rate constant (mol/m²/s), A (m²/g) is the reactive surface area, Ω (-) is the mineral saturation ratio, θ and η are rate parameters (-), superscript *nu* refers to reactions under neutral conditions and

superscript i to reactions under either acid or basic conditions, and a_{ij} is the activity of a species j in reaction i . The activation energy term is equal to 1 at 25 °C and is thus not included. Table 2 specifies kinetic parameters for quartz filler and silica fume. Surface areas were estimated from the grain size distribution provided by the manufacturers. The aggregates are considered as chemically inert.

The mineralogical and porewater compositions of low-pH concrete are given in Table 3 and Table 4, respectively. A volume fraction of inert solid (aggregates and superplasticizer) is also considered in concrete with a value of 0.77477. An inert tracer with a concentration of 10^{-3} M is added to the concrete porewater to study solute transport in the system without the influence of chemical reactions. In addition, the cementitious system is characterized by surface properties, modelled through cation exchange processes. Table 5 specifies the composition of the cation exchanger in equilibrium with the initial pore solution that simulates the uptake of K and Na (exchanged with Ca) in calcium silicate hydrates (C-S-H). The selectivity coefficients are based on the Gaines-Thomas convention. Uptake of aluminium and magnesium in C-S-H is not considered in the model.

The presence of redox sensitive species (i.e. iron, sulphur) in the cementitious system might influence the redox potential of cement porewater, leading to redox potentials in the range -750 mV to -230 mV in OPC (Berner, 2002). That is the case of sulphides in slag blends, and of iron, which can sorb on C-S-H phases, substitutes Al in AFm or AFt phases, or precipitate as Ca-ferrites. With this in mind and considering that the total dissolved iron concentration does not exceed 10^{-7} M in cement paste (Berner, 2002), a redox potential (Eh) of ~ -27 mV was assumed by considering a small amount of magnetite (Table 3) and the thermodynamic equilibrium between magnetite and ferrihydrite couple at the given pH.

The secondary minerals allowed to precipitate are listed in Table 3. It is noted that the same set of secondary minerals was considered both in the concrete and COx domains. This includes the potential precipitation of quartz assuming the kinetic law defined for the COx domain (Table 7).

Table 2. Kinetic parameters for dissolution reactions in concrete (from Palandri and Kharaka, 2004).

Mineral	A (m ² /g)	M _w (g/mol)	k ₂₅ ^{nu} (mol/m ² s)	k ₂₅ ^{H+} (mol/m ² s)	n ^{H+}	θ	η
Quartz_filler	0.265	60.08	3.98107·10 ⁻¹⁴	5.12861·10 ⁻¹⁷	-0.5	1	1
SilicaFume	26.087	64.531	3.98107·10 ⁻¹⁴	5.12861·10 ⁻¹⁷	-0.5	1	1

Table 3. Mineralogical composition of low-pH concrete and COx, reaction types, secondary minerals considered, and mineral molar volumes (M_v).

Mineral phases	M _v (cm ³ /mol)	Reaction type	mol/L concrete	mol/L COx
Porosity	-	-	0.04	0.18
CSH 0.8	59.29	Equilibrium	1.68022	0
Calcite	36.93	Equilibrium	0.008644	5.038
Ettringite	710.32	Equilibrium	0.011856	0
Ferrihydrite(am)	34.36	Equilibrium	0.066384	0
Hydrotalcite	227.36	Equilibrium	0.046836	0
Magnetite	44.52	Equilibrium	0.000020	0
Stratlingite	215.63	Equilibrium	0.047892	0
SilicaFume	28.06	Dissolution kinetics	0.496924	-
Quartz filler	22.69	Dissolution kinetics	1.748352	-
Quartz	22.69	Precipitation kinetics	0	9.1548
Celestite	46.25	Equilibrium	0	0.1242
Dolomite	64.3	Equilibrium	0	0.4968
Pyrite	23.94	Equilibrium	0	0.1908
Siderite	29.38	Equilibrium	0	0.198
Illite_Imt-2	139.18	Dissolution kinetics	0	1.9386
Montmorillonite-BCCa	132.48	Dissolution kinetics	0	0.495
Microcline	108.74	Dissolution kinetics	0	0.2466
Ripidolite_Cca-2	211.92	Dissolution kinetics	0	0.0738

SiO ₂ (am)	29.00	Equilibrium	0	0
Brucite	24.63	Equilibrium	0	0
CSH1.6	84.68	Equilibrium	0	0
CSH1.2	71.95	Equilibrium	0	0
C3AH6	149.52	Equilibrium	0	0
C3FH6	154.50	Equilibrium	0	0
C4AH13	269.20	Equilibrium	0	0
C4FH13	274.4	Equilibrium	0	0
Ettringite-Fe	711.80	Equilibrium	0	0
Gypsum	74.69	Equilibrium	0	0
Hemicarboaluminate	569.02	Equilibrium	0	0
Hydrotalcite-CO ₃	231.44	Equilibrium	0	0
Fe(OH) ₂ (cr)	24.48	Equilibrium	0	0
Monocarboaluminate	261.96	Equilibrium	0	0
Monosulfate-Fe	316.06	Equilibrium	0	0
Monosulfoaluminate	311.26	Equilibrium	0	0
Portlandite	33.06	Equilibrium	0	0
Pyrrhotite	18.20	Equilibrium	0	0
Saponite-FeCa	139.96	Equilibrium	0	0
Syngenite	151.63	Equilibrium	0	0

Table 4. Initial porewater composition of the fully hydrated low-pH concrete and CO_x claystone.

Variable	Low-pH concrete	CO _x claystone
pH	10.68	7.06
pe / Eh	-0.46 / -27.2 mV*	-2.84
Totals	Concentration (mol/kg water)	Concentration (mol/kg water)
Al	1.448·10 ⁻⁴	8.504·10 ⁻⁸
C	1.506·10 ⁻⁵	3.826·10 ⁻³
Ca	5.237·10 ⁻³	7.601·10 ⁻³
Cl	1.000·10 ^{-10†}	4.120·10 ⁻²
Fe	5.447·10 ⁻⁸	4.351·10 ⁻⁵
K	3.420·10 ⁻²	5.110·10 ⁻⁴
Mg	3.736·10 ⁻⁷	5.187·10 ⁻³
Na	1.910·10 ⁻²	4.008·10 ⁻²
S	3.058·10 ⁻²	1.108·10 ⁻²
Si	2.021·10 ⁻³	1.800·10 ⁻⁴
Sr	1.000·10 ^{-10†}	2.429·10 ⁻⁴
Tracer	1.000·10 ⁻³	0.000

* pe in equilibrium with magnetite/ferrihydrite(am) pair in concrete;

† Very low value considered in concrete to prevent numerical instabilities when assuming a value of 0.

Table 5. Initial exchanger composition for alkali uptake in low-pH concrete and in claystone, and thermodynamic equilibrium constants (Gaines Thomas convention). CEC = cation exchange capacity.

Concrete	Log K	mol/kg water	mol/L concrete
Ex2Ca	0.0	4.444·10 ⁻⁰¹	1.778·10 ⁻⁰²
Ex2K2	0.37	5.524·10 ⁻⁰¹	2.210·10 ⁻⁰²
Ex2Na2	0.37	1.689·10 ⁻⁰¹	6.756·10 ⁻⁰³
Total (CEC)		2.331	0.093
Claystone	Log K	mol/kg water	mol/L CO _x
CO _x 2Ca	0.7	4.744·10 ⁻⁰¹	8.540·10 ⁻⁰²
CO _x 2Mg	0.7	3.282·10 ⁻⁰¹	5.907·10 ⁻⁰²
CO _x Na	0	3.867·10 ⁻⁰¹	6.961·10 ⁻⁰²
CO _x K	1.2	7.850·10 ⁻⁰²	1.413·10 ⁻⁰²
CO _x 2Sr	0.6	1.188·10 ⁻⁰²	2.139·10 ⁻⁰³
CO _x 2Fe	0.8	2.860·10 ⁻⁰³	5.145·10 ⁻⁰⁴
Total (CEC)		2.1	0.378

2.2 Claystone model

For the Callovo-Oxfordian claystone (COx), the same physical parameters as in Marty et al. (2015) are used (porosity of 0.18 and effective diffusivity of $2.6 \cdot 10^{-11} \text{ m}^2/\text{s}$, see Table 1).

The geochemical model of the COx is largely based on the work of Marty et al. (2015), in turn relying on the model by Gaucher et al. (2009). However, the model has been adapted to the ThermoChimie v9b0 database and incorporates two additional cations in the exchanger (Fe^{2+} and Sr^{2+}). The mineralogical composition of the COx is given in Table 3. Most of the minerals are considered under thermodynamic equilibrium, except for five kinetically-controlled minerals (Table 3) based on equations (2-1) and (2-2). Among the kinetically-controlled minerals, only quartz is allowed to precipitate. The kinetic parameters are given in Table 6 and Table 7.

The initial porewater composition (Table 4) is in equilibrium with the cation exchanger composition (Table 5) using thermodynamic equilibrium constants given in the same table.

Table 6. Kinetic parameters for dissolution reactions in the COx domain (from Marty et al., 2015).

Mineral	A (m ² /g)	k_{25}^{nu} (mol/m ² s)	k_{25}^{H+} (mol/m ² s)	n^{H+}	k_{25}^{OH-} (mol/m ² s)	n^{OH-}	θ	η
Illite_Imt-2	30	$3.3 \cdot 10^{-17}$	$9.8 \cdot 10^{-12}$	0.52	$3.1 \cdot 10^{-12}$	0.38	1	1
Montmorillonite-BCCa	8.5	$9.3 \cdot 10^{-15}$	$5.3 \cdot 10^{-11}$	0.69	$2.9 \cdot 10^{-12}$	0.34	0.17	10.34
Ripidolite_Cca-2	0.003	$6.4 \cdot 10^{-17}$	$8.2 \cdot 10^{-09}$	0.28	$6.9 \cdot 10^{-09}$	0.34	1	1
Microcline	0.11	$1.0 \cdot 10^{-14}$	$1.7 \cdot 10^{-11}$	0.27	$1.4 \cdot 10^{-10}$	0.35	0.09	2.35

Table 7. Kinetic parameters for precipitation reactions.

Mineral	A (m ² /g)	k_{25}^{nu} (mol/m ² s)	θ	η
Quartz	0.05	$3.0 \cdot 10^{-12}$	4.58	0.54

2.3 Discretization

The spatial discretization was set as a compromise between spatial resolution and computation time. A simulation time of 100,000 years was considered. According to the von Neumann criterion for diffusive solute transport, the time step size should comply with the following relation:

$$\Delta t < \frac{\Delta x^2}{3 \cdot D_p} \quad (2-3)$$

where Δt (s) is the time step size, Δx is the spatial discretization (m), and D_p is the pore diffusivity (m²/s). Given the higher pore diffusivity of the COx claystone compared to concrete, the time step size is restricted by the clay domain. A finer discretization is assumed in the concrete domain and also in the first 0.1 m of the COx domain to avoid using elements of different size at the interface. The size of the elements is 0.02 m in the concrete domain ($0 \leq x \leq 0.30$), while the COx domain ($0.3 < x \leq 40.3$ m) is discretized with the following sequence: 5 x 0.02 m, 35 x 0.04 m, 10 x 0.1 m, 10 x 0.5 m, 10 x 1 m, 10 x 2 m, and 1 x 2.5 m. The temporal discretization considers a constant time step size of 0.10 years. Some of the codes used in this study have an automatic time stepping scheme. In those cases, a maximum time step size of 0.10 years was considered.

2.4 Methodology

Several preliminary cases (P1-P3) of increasing complexity were implemented and simulated step by step in different reactive transport codes (Section 2.5) to finally define the full reference case (FRC). Preliminary cases can be found in the supplementary material. Results of these cases are presented as Supplementary Material to this paper. In addition, a set of sensitivity cases was modelled with some of the reactive transport codes to assess the impact of some of key parameters and processes (S1-S3). Table 8 presents a summary of the main processes considered in each case.

In the sensitivity case S1, the concrete effective diffusion coefficient was reduced 10 times ($1 \cdot 10^{-13} \text{ m}^2/\text{s}$). This value is closer to the lowest range of experimental results obtained using HTO (Vopálka et al., 2019).

The full reference case does not consider diffusion-porosity coupling, i.e. changes in transport properties (D_e) as a result of porosity variations due to mineral volume changes. Feedback between chemical alteration and porosity and diffusivity was considered in the sensitivity case S2 using a linear relationship between porosity and diffusivity specified by equations (2-4) and (2-5):

$$D_e = D_p \phi \quad (2-4)$$

$$D_p = \tau D_w \quad (2-5)$$

with ϕ the porosity (m^3/m^3) and D_p , the pore diffusivity (m^2/s), defined as a function of a constant tortuosity factor (τ) and the diffusion coefficient in free water (D_w in m^2/s). A minimum porosity value of 0.001 is set in the entire modelled domain to prevent full clogging.

Finally, the impact of electrochemical coupling for the transport of charged species was also investigated in sensitivity case S3 and implemented in ORCHESTRA (see Section 2.5). This case considered the effects of ion specific diffusion coefficients instead of an average value as in the Fickian diffusion approach. Dissolved species are allowed to diffuse at different rates according to their diffusivities in free solution, which were selected from the phreeqc.dat database (Parkhurst and Appelo, 2013). Due to their different charges, this results in the development of local electric potential gradients. These gradients have an impact on the diffusion rate of charged ions until net charge fluxes are zero. As a result, diffusion rates of a specific ion not only depend on its own diffusion coefficient, but on the concentration gradients of all accompanying dissolved ions. For this reason, this approach is usually referred to as multicomponent transport and can be modelled using the Nernst-Planck equations (e.g. Galíndez and Molinero, 2010):

$$J_i = -D_i \left(\frac{dc_i}{dx} + z_i c_i \frac{F}{RT} \frac{d\psi}{dx} \right) \quad (2-6)$$

In equation (2-6), subscript i corresponds to variables specific of species i , J (mol/s) is the diffusive flux, D (m^2/s) is the diffusion coefficient, c (mol/L) is concentration, z is the ion valence, F is the Faraday constant (C/mol), R (J/K/mol) the constant of ideal gases, T is temperature (K), and ψ is the potential (V). During transport, the potential gradient is iteratively solved in ORCHESTRA to result in zero charge flux.

Table 8. Description of simulation cases and processes considered in this study.

ID	Description of simulation cases							
P1	Preliminary case 1: diffusion of a tracer from concrete into the clay rock							
P2	Preliminary case 2: diffusion plus cation exchange and aqueous speciation reactions							
P3	Preliminary case 3: idem case P2, and adding mineral reactions in equilibrium							
FRC	Full Reference Case: full chemical description of the system, including mineral kinetics							
S1	Sensitivity case 1: effective diffusivity of concrete reduced by 1 order of magnitude							
S2	Sensitivity case 2: porosity-diffusion coupling considered							
S3	Sensitivity case 3: electrochemical coupling (i.e. Nernst-Planck equations)							
List of simulated processes		P1	P2	P3	FRC	S1	S2	S3
Tracer diffusion		×	×	×	×	×	×	×
Aqueous species + cation exchange			×	×	×	×	×	×
Minerals in equilibrium				×	×	×	×	×
Reaction kinetics					×	×	×	×
Lower diffusion coefficient in concrete						×		
Porosity-diffusion coupling							×	
Multicomponent diffusion								×

2.5 Description of codes

Five reactive transport codes have been benchmarked: iCP, OpenGeoSys-GEM, ORCHESTRA, ParMIN3P-THCm and CORE^{2D} (Table 9).

Table 9. Reactive transport codes and numerical methods used in this study.

Reactive transport code	Numerical method
iCP	Finite Elements
OGS-GEM (OpenGeoSys-GEM)	Finite Elements
ORCHESTRA	Finite Volumes
CORE ^{2D}	Finite Elements
MIN3P	Finite Volumes

iCP version 1.5 (interface COMSOL-PHREEQC) couples two standalone simulation codes, the general-purpose finite element software COMSOL Multiphysics® version 5.3 and the geochemical simulator PHREEQC version 3 (Parkhurst and Appelo, 2013). The interface is intended to maximize the synergies between the two codes, providing a numerical platform that can efficiently simulate a wide range of multiphysics problems coupled with geochemistry (Nardi et al., 2014). iCP is written in Java and uses the IPhreeqc C++ dynamic library and the COMSOL Java-API. The coupling approach is based on the operator-splitting (OS) technique with a sequential non-iterative approach (SNIA). Conservative solute transport equations are solved in COMSOL, coupled with other physical processes, if required. In turn, the equilibrium and kinetic chemical reactions are solved by PHREEQC. iCP has been extensively used in geosciences, for instance for long-term performance of engineered barriers for nuclear waste (e.g. Idiart et al., 2019).

OpenGeoSys-GEM (OGS-GEM) is an open-source code for simulation of thermo-hydro-mechanical-chemical processes in porous media that couples the OpenGeoSys V5 framework with the GEMS3K thermodynamic solver (Kosakowski and Watanabe, 2014). It is based on an object-oriented Finite-Element-Method concept (Kolditz et al., 2012). Fluid flow and mass transport equations are solved by OpenGeoSys based on a standard finite element formulation. The geochemical thermodynamic solver GEMS3K uses the Gibbs-Energy-Minimization (GEM) method for calculation of local/partial equilibria in complex heterogeneous multicomponent-multiphase systems (Kulik et al., 2013). Mass transport and chemical reactions are solved with a SNIA. The advantage of the GEM solver compared to conventional Law-of-Mass-Action (LMA) solvers is the availability of several equations of state which allows to conserve mass and volume balances for mixtures of gas, liquid and solid phases.

OpenGeoSys-GEM has been applied extensively to investigate very complex geochemical reactions to assess the long-term geochemical evolution of materials and interfaces in deep geological repositories (Cloet et al., 2018; Kosakowski and Berner, 2013; Kosakowski and Watanabe, 2014; Poonoosamy et al., 2018).

ORCHESTRA (Objects Representing CHEmical equilibrium and TRANsport) is written in Java (Meeussen, 2003). In ORCHESTRA, all model equations are provided as run-time input, which means that equations can be defined directly in input files in text format. It is also possible to use predefined definitions (objects) from a standard object file (e.g. reactions, minerals, diffusion, etc.). ORCHESTRA has a GUI for defining chemical equilibrium systems, able to read PHREEQC format thermodynamic databases. This makes ORCHESTRA a flexible tool for combining standard chemical / transport models with user defined/modified parts. This approach was followed in the transport modules, where standard objects (e.g. for diffusion) were combined with user defined expressions for feedback between porosity and tortuosity and even for implementing the effect of electric potentials on diffusion (Nernst-Planck). For the present benchmark study, coupling between the chemical equilibrium and transport module was organized via an OS with a SNIA. The transport equation is solved using the finite volume (FV) method, which requires mass changes to be defined in terms of fluxes between (well-mixed) cells. The FV approach is automatically mass-conservative and very suitable for parallel processing. With the FV methods output is only available at the centres of the mixed cells, which can be observed in the calculated concentration profiles. Kinetic reactions were calculated simultaneously with the transport equation, using the same time-step. ORCHESTRA has been used to study solute transport in cement (Sarkar et al., 2010) or cement/clay interaction (Marty et al., 2015).

ParMIN3P-THCm is the parallelized version of MIN3P-THCm, a general-purpose multicomponent reactive transport code to simulate coupled hydrogeological, thermal, and biogeochemical processes in subsurface domains with variable water-saturated conditions. While the reactive mass transport is solved by the direct substitution approach (DSA), the code uses the global implicit approach (GIM) with adaptive time stepping to solve the multicomponent advection-dispersion equations and the geochemical reactions (Mayer et al., 2002; Mayer and MacQuarrie, 2010). Spatial discretization is based on the FV method and allows conducting simulations in one, two, and three spatial dimensions. A hybrid MPI and OpenMP programming approach is implemented in ParMIN3P-THCm with a domain decomposition method based on PETSc libraries (Su et al., 2017).

CORE^{2D} is a finite element code for saturated and unsaturated water flow, heat transport and multicomponent reactive solute transport under both local chemical equilibrium and kinetic conditions in heterogeneous and anisotropic media (Samper et al., 2009; Samper et al., 2011). It uses the sequential iteration approach (SIA) to solve for chemical reactive solute transport. The iterative cycle is repeated until prescribed convergence criteria are met. The flow and transport equations are solved with Galerkin triangular finite elements and an Euler scheme for time discretization. The chemical formulation is based on ion association theory and uses an extended version of Debye-Hückel equation (B-dot) for the activity coefficients of aqueous species. CORE^{2D} has been widely used to model laboratory and in situ experiments (Zheng et al., 2011), the interactions of corrosion products and bentonite (Lu et al., 2011) and the long-term geochemical evolution of repositories in granite and clay (Samper et al., 2016; Mon et al., 2017; Samper et al., 2018).

3 Results and discussion

The results of the full reference case (FRC) and 3 sensitivity cases are presented and discussed in this section. Supplementary data is provided separately, including the results of the preliminary simulation cases P1 to P3.

3.1 Full reference case (FRC)

The geochemical evolution of the system of the FRC is presented by means of spatial distribution profiles after 100,000 years of interaction. Comparison of results include porewater composition, exchanger evolution and mineralogical changes of the concrete and claystone domains. The simulations presented in this section were modelled using iCP, ORCHESTRA, MIN3P, OGS-GEM and CORE^{2D}. However, it is noted that the CORE^{2D} model did not consider the minerals under kinetically-controlled precipitation/dissolution. The overall evolution of the system is detailed below.

3.1.1 Porewater evolution

Spatial profiles of aqueous components and solution properties after 100,000 years are presented in Fig. 2 and Fig. 3. Some species present important concentration gradients between concrete and clay porewaters, governed by equilibrium (or kinetic laws) with different sets of minerals and cation distribution in the exchangers. This is the case for Al, C, Mg, Fe, Sr, or Si. On the other hand, other species show small variations between concrete and clay due to their null or limited role in solid-liquid interaction, at least after 100,000 years. This is the case for Cl, K, S, or Na. Cl has no interaction with mineral phases or exchanger composition, thus acting as a tracer. Sulphate diffuses out of the concrete domain, triggering ettringite dissolution in concrete and favouring celestite precipitation at both sides of the interface due to the ingress of Sr from the claystone. However, after 100,000 years, the concentration gradient between concrete and claystone has practically vanished. Due to the complexity of the system, it is not easy to clearly identify direct links between all aqueous concentrations and mineral phases. For instance, aluminium concentration decreases in the centre part of the concrete domain due to hydrotalcite precipitation in that region (Fig. 6). Changes in ionic strength of the system are small and agree well between the different codes (Fig. 3).

The pH profile is a suitable indicator of chemical alteration. On the concrete side, pH values after 100,000 years present a maximum value of 10.5 in the innermost 13 cm in concrete, in equilibrium with C-S-H with Ca:Si of 0.8 (Fig. 3). The decrease from the initial value (~10.7) is due to alkali (K) diffusion to the clay. pH decreases linearly to 10 at $x=21$ cm and then drops to ~7.3 towards the interface. On the COx side, pH changes are almost negligible, with a value of ~7.3 at the interface decreasing to its initial value towards the right boundary (~7.1). Thus, the maximum increase is predicted at the interface and is equal to ~0.2 pH units.

After 100,000 years, the redox conditions (pe) of COx remain practically unaffected ($E_h \sim -170$ mV) and controlled by the presence of the accessory minerals pyrite (FeS_2), celestite (SrSO_4) and siderite (FeCO_3) and the precipitation of small amounts of magnetite (Fe_3O_4) in a reactive front of ~1 m from the interface. Contrarily, an important redox gradient of between -170 mV and 190 mV is established over half of the concrete thickness (0.15 m) mainly due to the pH decrease close to the claystone. This change in pH promotes the dissolution of the iron (III) phase ferrihydrite ($\text{Fe}(\text{OH})_3$) and the precipitation/dissolution of the Fe(II)/Fe(III) phase magnetite controlling the Fe(II)/Fe(III) ratio in solution and the redox of concrete. The maximum value of 190 mV at half of the concrete thickness decreases again to its initial value of 30 mV along 7 cm due to changes in the solid phases controlling the pH of the pore solution (i.e. C-S-H gel or hydrotalcite). Finally, weakly reducing conditions (E_h value of 30 mV) are kept constant in the unaltered zone of concrete.

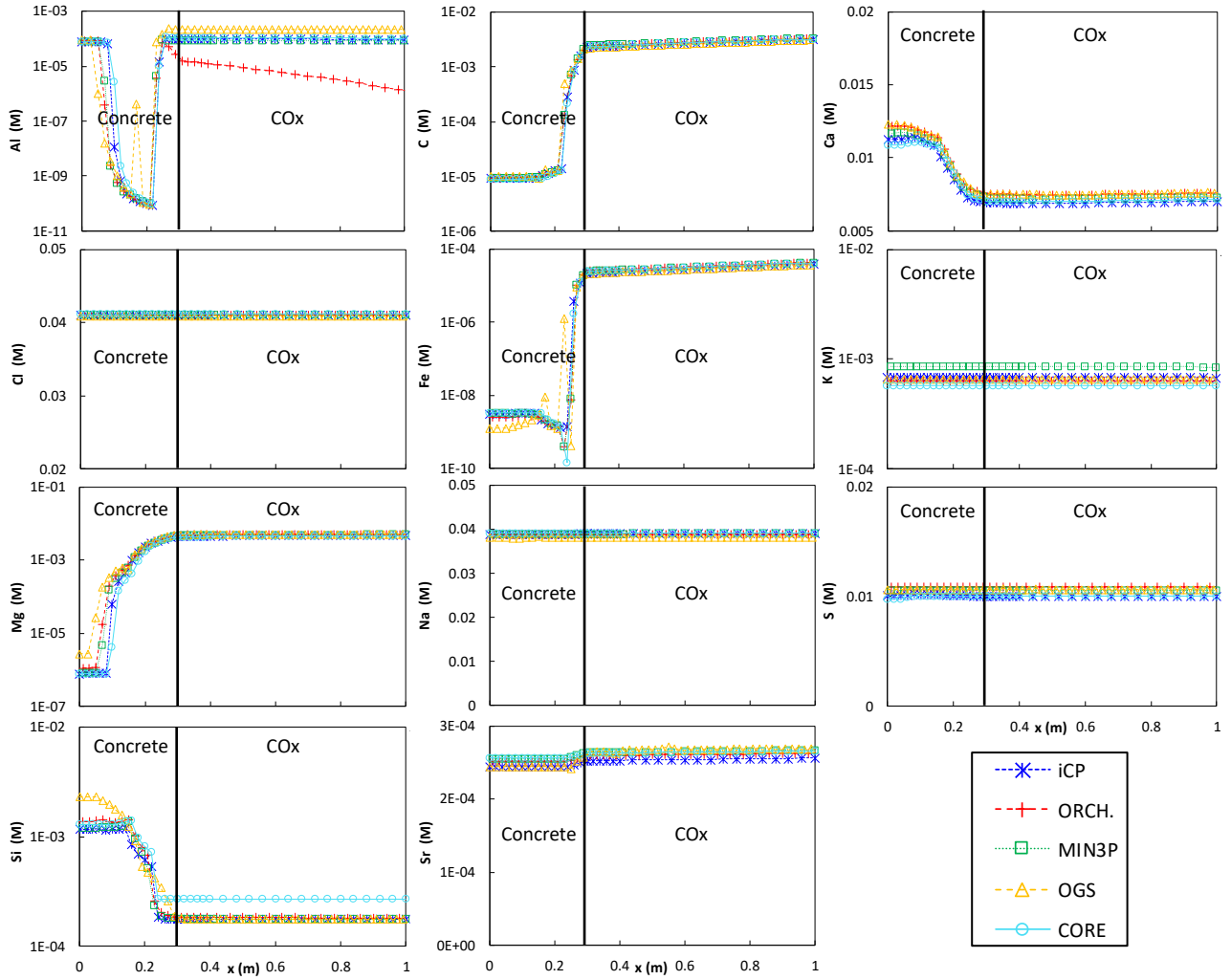


Fig. 2. Total aqueous species concentration (M) profiles at 100,000 years obtained with *iCP*, *ORCHESTRA*, *MIN3P*, *OGS-GEM*, and *CORE^{2D}*.

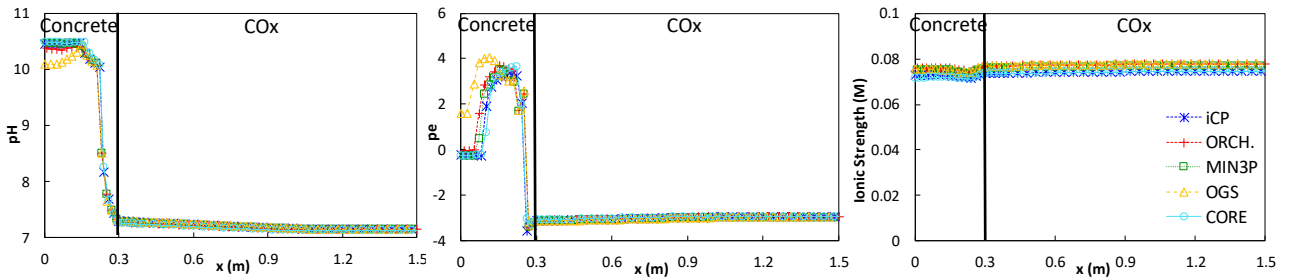


Fig. 3. pH, pe, and ionic strength profiles at 100,000 years obtained with *iCP*, *ORCHESTRA*, *MIN3P*, *OGS-GEM*, and *CORE^{2D}*.

3.1.2 Cation exchanger composition

The exchanger composition of concrete is shown in Fig. 4. After 100,000 years, K^+ concentration in the concrete exchanger decreases from $5.52 \cdot 10^{-1}$ to $\sim 10^{-4}$ M due to alkali release to the claystone, resulting in an increase in Na^+ and Ca^{2+} (Fig. 4). In the clay, the exchanger at 100,000 years shows a perturbation from the interaction with concrete even far from the interface (Fig. 5). The main cation exchange reaction in the clay is the increase in K^+ from concrete leaching at the expense of a local decrease in Ca^{2+} , Na^+ and Fe^{2+} . In turn, the concentrations of all other cations show small changes. This is in agreement with the results of Marty et al. (2015) for a high-pH concrete – COx interface.

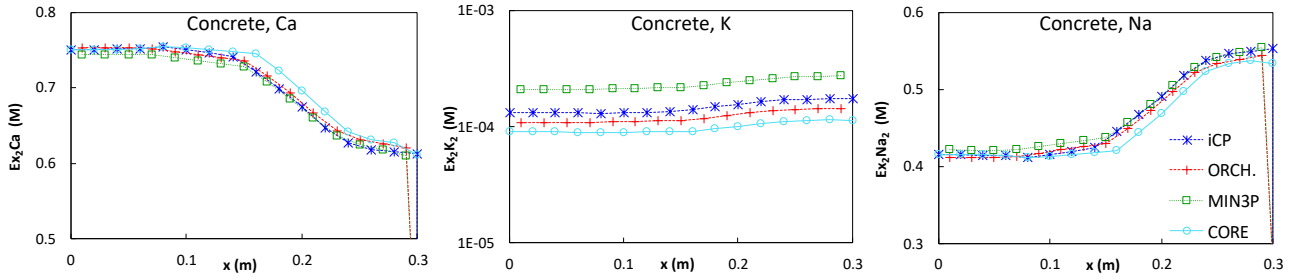


Fig. 4. Cation concentration (M) profiles in concrete exchanger at 100,000 years obtained with iCP, ORCHESTRA, MIN3P and CORE^{2D}.

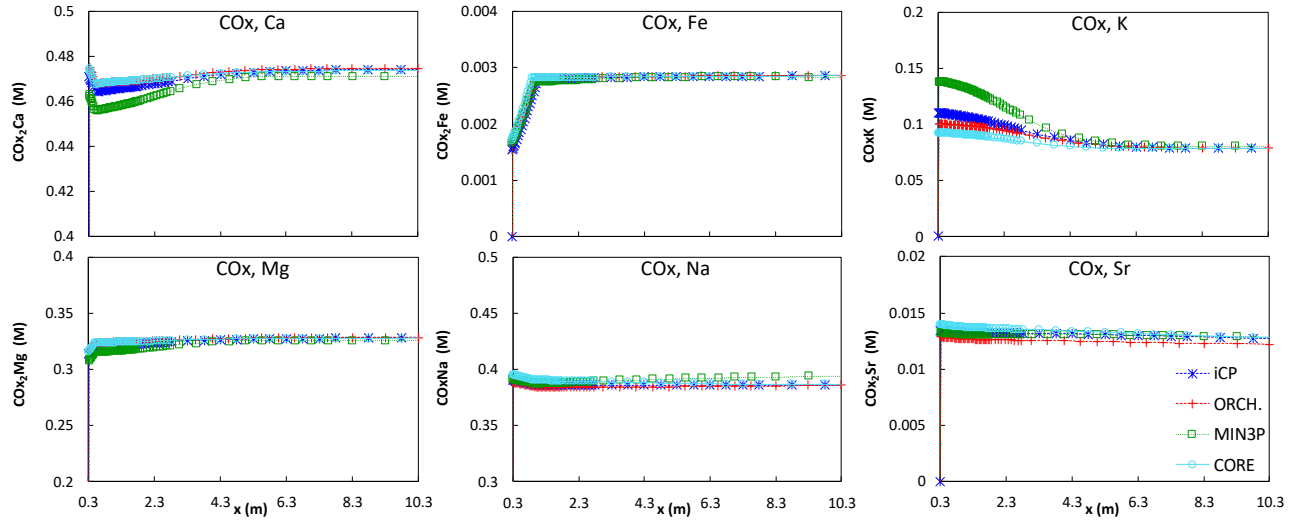


Fig. 5. Cation concentration (M) profiles in clay exchanger at 100,000 years obtained with iCP, ORCHESTRA, MIN3P and CORE^{2D}.

3.1.3 Mineralogical changes

Fig. 6 and Fig. 7 present the distribution profiles of mineral phases after 100,000 years of interaction. The mineral degradation sequence is consistent with previous studies (e.g. Gaucher and Blanc, 2006; Savage, 2011; Marty et al., 2015). After 100,000 years, the extent of the alteration front is about 15 cm in concrete (characterized by the dissolution of the C-S-H gel) and 20 cm in the claystone (characterized by dolomite depletion).

This includes dissolution of C-S-H, ettringite, hydrotalcite, strätlingite, and ferrihydrite in concrete with precipitation of brucite and calcite, and reprecipitation of hydrotalcite. In the claystone, the main changes are the dissolution of dolomite and siderite and precipitation of calcite and quartz.

Hydrotalcite and ettringite dissolve completely next to the interface and reprecipitate at the degradation front (Fig. 6). Brucite and Fe-Ca saponite are predicted to form in concrete as secondary phases, while quartz (as a result of C-S-H dissolution and consequent release of Si), magnetite, celestite and calcite precipitate at both sides of the interface. A clear geochemical disturbance is the formation of calcite in concrete and clay close to the interface. Calcite precipitates due to the changes in solubility: in concrete, due to the ingress of dissolved carbonate from the COx; in the claystone, due to the diffusion of dissolved calcium and hydroxyl ions from concrete. Calcite is the main phase responsible for porosity clogging in concrete. Quartz filler (Fig. 6) and silica fume (not shown), the two kinetically-controlled mineral phases in concrete, partially dissolve at around $x = 23$ cm.

Degradation in the claystone is characterized by the dolomite and siderite distribution profiles (Fig. 7). Dolomite is depleted in the first 0.2 m near the interface, and partially dissolves in the next 0.6 m. In turn, siderite completely dissolves in the first 1.1 m, favouring pyrite and magnetite precipitation.

Considering the C-S-H gel and dolomite as reference minerals for concrete and CO_x degradation, respectively, the concrete degradation front extends over half of its thickness (0.15 m), while in the clay the front is at 0.2 m after 100,000 years. Montmorillonite, illite, microcline, and ripidolite concentrations (not shown) remain virtually unchanged after 100,000 years of interaction with the low-pH concrete. This can be explained by their very slow dissolution kinetics at pH < 10.5.

The FRC case does not consider changes in transport properties (porosity and diffusion coefficient) due to mineral volume changes. Thus, no coupling with transport properties or water mass is taken into account. The evolution of porosity in this uncoupled case can still be computed from mineral volume fractions as a post-process of the simulations. These results are presented in Fig. 7. On the concrete side, porosity remains unaltered in the innermost 5 cm. As the degradation front approaches, an increase in porosity is predicted, with values of ~0.10 between $x = 0.15$ m and $x = 0.22$ m. However, as geochemical interaction proceeds, porosity decreases mainly due to calcite and brucite precipitation. Negative values are predicted near the interface, showing porosity clogging. On the clay side, porosity decreases over 0.5 m from the interface, although noticeable changes are only predicted for the closest 3 to 7 cm, with values down to 0.12 at the interface.

Overall, the results of the FRC are very similar to case P3 without kinetically-controlled minerals (see Supplementary Material), supporting the comparison of the FRC results of iCP, ORCHESTRA and MIN3P with the P3 results of CORE^{2D}. Including kinetically-controlled mineral phases is, for this particular case, not a key factor. Primary kinetically-controlled minerals in the clay (montmorillonite, illite, microcline and ripidolite) remain unaffected for 100,000 years. In concrete, silica fume and quartz filler are only dissolving locally and are replaced by quartz precipitation. One of the conclusions is that kinetically-controlled minerals do not play an important role in this case.

The results obtained with the different reactive transport codes for mineral concentration profiles are in good agreement, especially for concrete degradation. In the clay domain, dolomite dissolution fronts agree well between different codes, while mineral profiles show slight differences when comparing iron-bearing minerals (magnetite, siderite and pyrite).

Some discrepancies between OGS-GEM and other reactive transport codes can be found, especially in the cementitious system. This is due to the following differences in the implementation of this code. First, Thermochimie database is not available in a version that can be used in Gibbs Energy Minimization method (GEM). Thus, in OGS calculations a modified version of the Thermoddem database (Blanc et al., 2012) was used. However, it was checked that calculated values of Gibbs energy and entropy from both databases typically deviate by less than 10 J/mol. Second, OGS-GEM calculates the liquid phase volume based on volume balance for each cell, even if porosity is not coupled with the diffusion coefficient. In the other codes, a constant liquid phase volume was considered in the FRC. Finally, cation exchange reactions based on Gaines-Thomas convention are used in other codes, while OGS uses an ideal solid-solution implementation based on Vanselow convention.

The results are consistent with previous studies addressing concrete/clay interaction (e.g. Gaucher et al., 2006; Savage et al., 2007; Marty et al., 2014) and with recent experimental results obtained within CEBAMA (e.g. González-Santamaría et al., 2019; Mäder et al., 2017.)

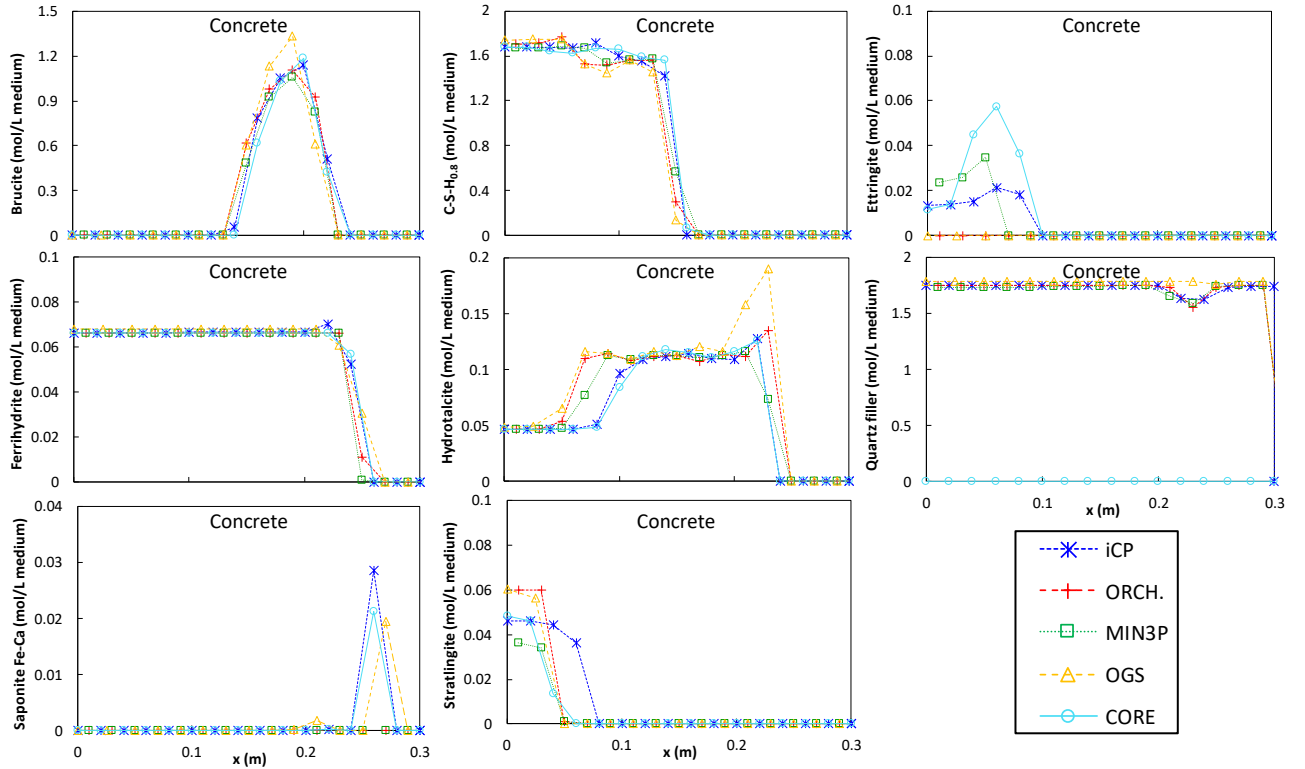


Fig. 6. Mineral phase profiles (in mol/L medium) in the concrete domain at 100,000 years, obtained with iCP, ORCHESTRA, MIN3P, OGS-GEM, and CORE^{2D}.

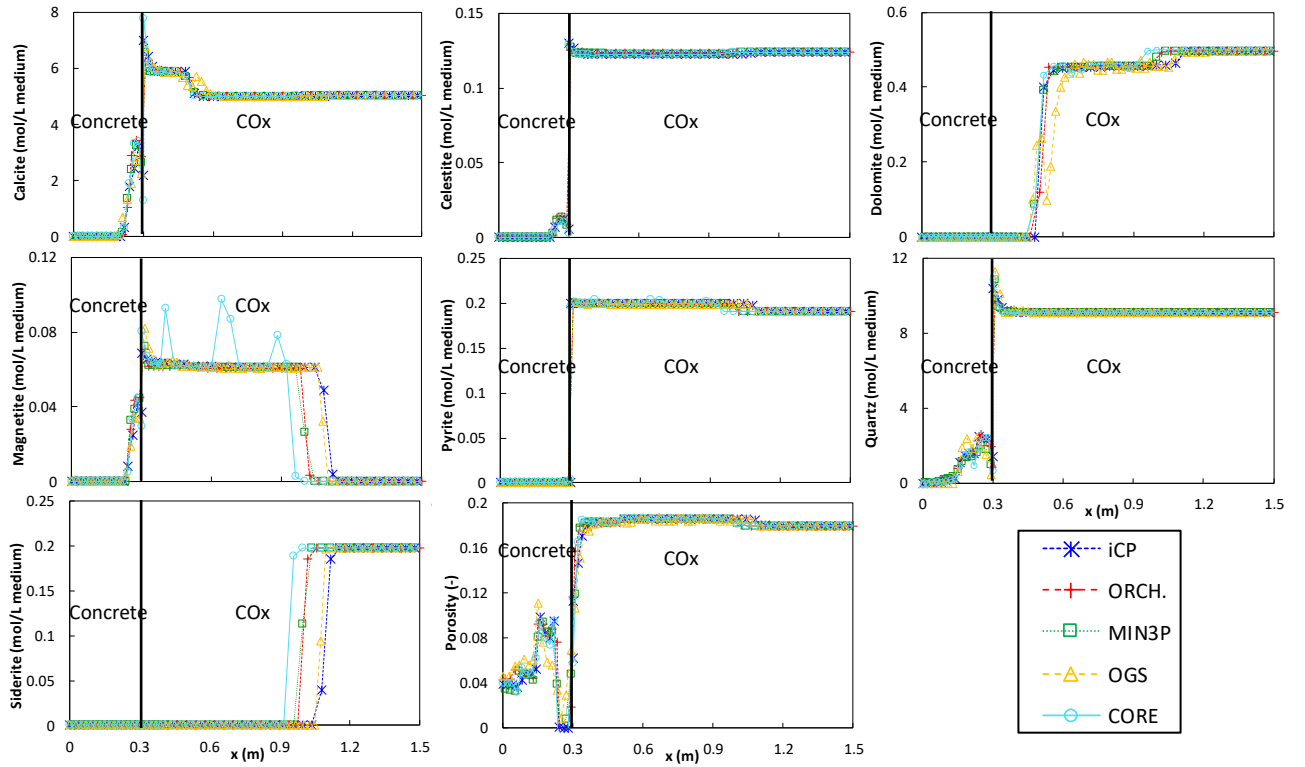


Fig. 7. Mineral phases (in mol/L medium) and porosity (-) profiles in concrete and clay domains at 100,000 years, obtained with iCP, ORCHESTRA, MIN3P, OGS-GEM, and CORE^{2D}.

3.2 Reduced concrete diffusion coefficient

A sensitivity case (S1) assuming a lower diffusion coefficient of concrete was simulated with MIN3P, CORE^{2D} and iCP. A constant effective diffusion coefficient of $1 \cdot 10^{-13} \text{ m}^2/\text{s}$ was assumed for the concrete barrier, which is one order of magnitude lower than for the FRC. Fig. 8 shows the porosity, pH and mineralogical distribution profiles at 100,000 years obtained with the three codes. Moreover, the results are compared with the FRC (iCP model results). The results of the three codes for S1 case show a very good agreement. As expected, the level of alteration at a given time is much more limited in this case compared to the FRC due to the reduced concrete diffusivity. Porosity clogging is not predicted to occur even after 100,000 years, and changes are only noticeable over a distance of 0.10 m from the interface. In the concrete domain, pH is lower than 10.5 only close to the interface (4 cm), where C-S-H gel dissolves. This contrasts with the 15 cm degradation front of the FRC. Overall, the degradation sequence is qualitatively consistent with that of the FRC but occurs over a much longer time scale.

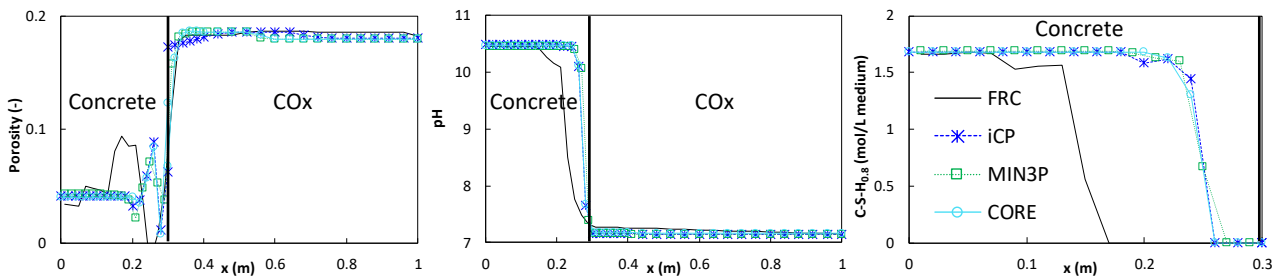


Fig. 8. Distribution profiles of porosity (-), pH and C-S-H_{0.8} concentration (mol/L medium) at 100,000 years. Results of iCP, MIN3P and CORE^{2D} for S1 and of FRC (with iCP).

3.3 Coupling mineral volume changes with transport properties

This sensitivity case (S2) considers the effect of mineral volume changes due to precipitation/dissolution processes on the transport properties, i.e. porosity and diffusion coefficient. The effective diffusion coefficient was chosen to depend linearly on porosity changes, see equations (2-4) and (2-5). A minimum porosity value of 0.001 is assumed to avoid complete clogging, corresponding to a minimum effective diffusion coefficient of $2.5 \cdot 10^{-14} \text{ m}^2/\text{s}$. Four codes were used in this case: iCP, ORCHESTRA, OGS-GEM and CORE^{2D}. The differences between these models lie firstly, in the description of mineral reactivity. Kinetically-controlled mineral phases were not included in the CORE^{2D} model. However, as shown for the FRC model setup, only a very small impact is expected due to this simplification. Secondly, the OGS-GEM model considers a fully coupled update of porosity, based on the actual volumetric fluid to solid ratio calculated by the chemical solver.

Fig. 9 presents the results of the four simulations together with the FRC results (iCP model results) for comparison purposes. Two variables are used as indicators of the level of alteration: porosity, which reflects the mineral volume changes, and pH. The mineralogical evolution sequence is similar as the FRC and is not repeated here. Calcite precipitation (not shown) near the interface is the main process responsible of the reduction of porosity to the residual value of 0.001. Porosity clogging is predicted after 50,000 years in iCP and ORCHESTRA (Fig. 9), virtually stopping further geochemical interaction. Concrete degrades to a less extent compared to the FRC, even before porosity clogging. Porosity decreases at a relatively slower rate in CORE^{2D}, although differences are not significant. The reasons for this discrepancy are still not clear.

The temporal porosity changes calculated by OGS-GEM are distinctively different from the other codes, since no porosity clogging is predicted after 100,000 years. This could be due to the inherent difference in the porosity update formulation based on the fluid to solid ratio. As porosity decreases

due to mineral precipitation, the volume of reacting fluid also decreases. Thus, the amount of minerals that can precipitate in the next time step also decreases. As a result, the clogging of porosity is delayed. Changes in pH (Fig. 9) are more limited than the FRC after 100,000 years due to porosity clogging. On the COx domain, pH remains below 7.2 even at the interface. In concrete, dissolution of C-S-H is also more limited in this case, with the degradation front at 5 cm from the interface in iCP and ORCHESTRA. In turn, CORE^{2D} and OGS-GEM results show a much smaller impact compared to the FRC results (Fig. 9), which is due to the relatively lower rate of porosity decrease. The reasons for the lower pH in part of the concrete domain predicted by OGS-GEM are not completely understood yet but could be related to the description of cation exchange on C-S-H in this code.

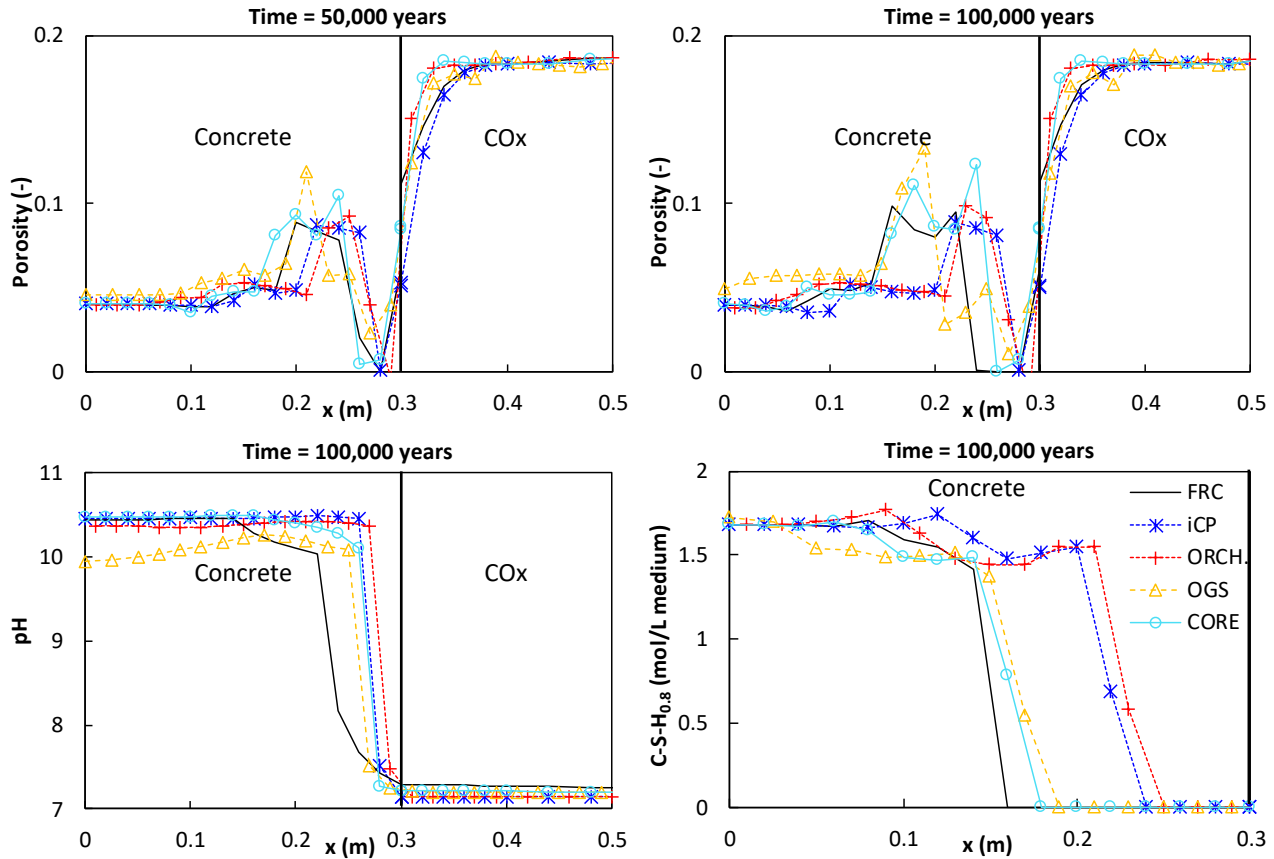


Fig. 9. Distribution profiles of porosity (-) at 50,000 and 100,000 years, and of pH and C-S-H gel with Ca/Si = 0.8 (in mol/L medium) at 100,000 years. Results for FRC (iCP results) and models coupling porosity with effective diffusion coefficient using iCP, ORCHESTRA and CORE^{2D}.

3.4 Electrochemical coupling

This sensitivity case (S3) was performed with ORCHESTRA. Multicomponent diffusion can have noticeable impacts in systems containing ions with very different diffusion coefficients. For instance, cementitious systems with hyperalkaline porewater contain large concentrations of OH⁻ ions which have a higher diffusion coefficient than other ions. The faster OH⁻ ions are likely to induce a local potential gradient which in turn affects the diffusion of other ions.

The effect of multicomponent diffusion in the present study can be observed as the development of an electric potential gradient over the cement-clay interface (Fig. 10). The resulting potential difference (ca. 7 mV) leads to a reduction of the diffusion rate of OH⁻ from concrete (and all other accompanying anions) and enhances transport of anions from the claystone towards the concrete. For cations, the potential gradient has the opposite effect. To illustrate this, Fig. 10 shows the enhanced

transport from the clay towards concrete of Cl^- , a non-reactive anion in this case, by comparing the same simulation with and without the electric potential gradient effect. However, for reactive substances, such as protons (or pH) the effect is much smaller, as shown in Fig. 10. Although the effect of the electrochemical coupling is clearly visible in the simulation, the impact of the evolving electric potential gradients on the effective ion diffusion rates is probably small in comparison with other uncertainties. Finally, results in terms of porosity distribution show that the effect of the potential gradient on mineral precipitation and dissolution is negligible (Fig. 10), at least after 1,000 years.

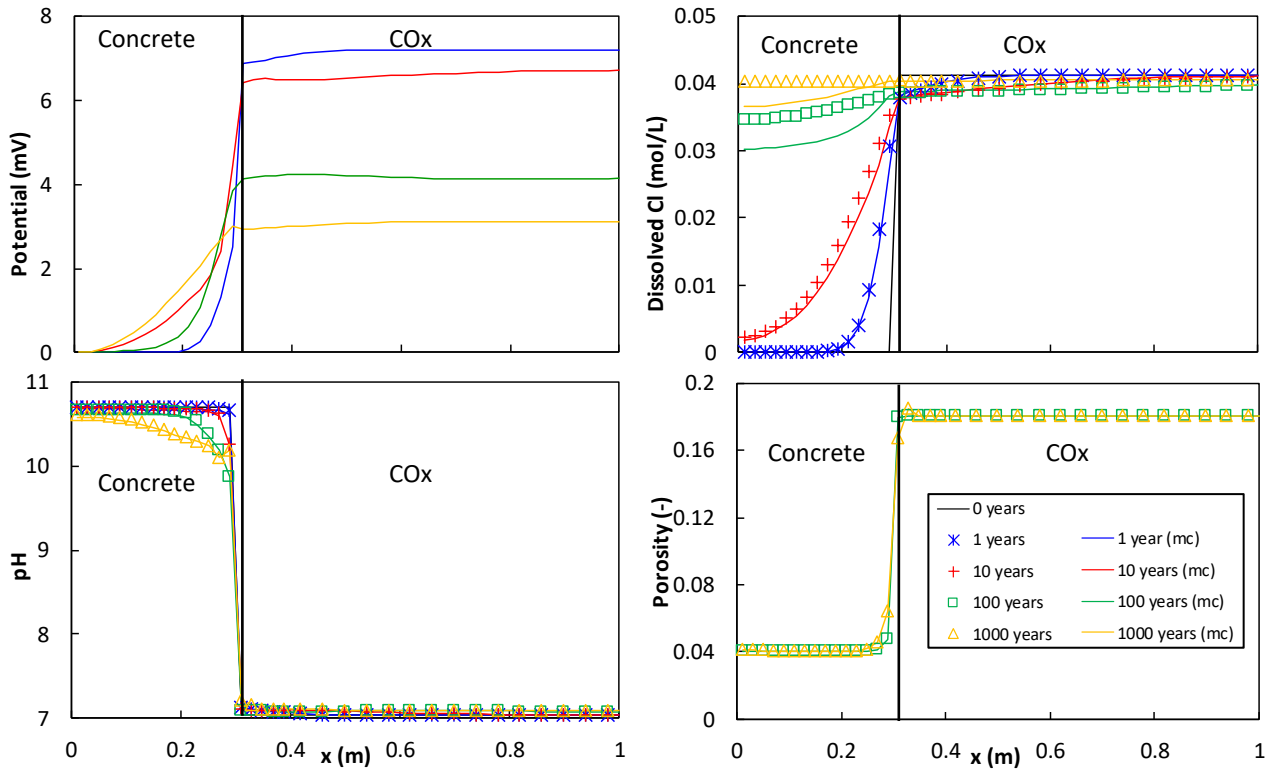


Fig. 10. Electric potential (mV), dissolved chloride (mol/L), pH, and porosity distribution profiles at 0, 1, 10, 100 and 1,000 years. Results for ORCHESTRA with (mc) and without accounting for potential/charge effects.

4 Conclusions

The results of the benchmark modelling study presented in this paper show that different reactive transport codes can be successfully used to study the interaction between a low-pH concrete and a claystone. The geochemical evolution of the concrete/clay system obtained with every code used in this benchmark is essentially the same despite of differences between modelling approaches (numerical methods, activity correction models, etc.). In all modelled cases, the differences observed between models do not have significant consequences on the description of the governing processes and system evolution. The impact of keys parameters, such as the diffusion coefficient of concrete, electrochemical couplings, and especially the coupling between geochemical and transport parameters, has also been assessed. The impact of including or not the slow kinetics of dissolution of the claystone minerals is shown to be negligible in the studied system. This is in part due to the low-pH nature of the cementitious system, but also to the relatively small concrete volume considered. As a general conclusion, the sensitivity and preliminary cases modelled in this study show that the results obtained are much more sensitive to changes in the model setup (transport parameters, couplings) than to the different modelling tools used in each case.

This study has served to build confidence in the representation of this complex system with reactive transport modelling tools used within the Horizon 2020 project CEBAMA when simulating the long-term behaviour of low-pH cementitious systems. The results show not only the high level of understanding of the governing processes, but also a good agreement between codes, which is essential to demonstrate the applicability of these numerical tools in safety assessments.

A subject for future research concerns the simultaneous modelling of cement hydration with reactive transport processes and water transport at the concrete/clay interface. This may be important for concrete mixes with low water-to-binder ratio, as is the case of the studied system. In these systems, the water used for cement hydration partly comes from the claystone, which may have an impact on the resulting phase assemblage. The role of solid solutions to represent cement hydrates, such as C-S-H with lower Ca:Si ratio than 0.8, C-A-S-H, or M-S-H could also be explored. Another challenging aspect is the assessment of more realistic couplings between mineral volume changes and their impact on the concrete microstructure and ultimately on its transport properties. Upscaling of pore-scale models of cementitious systems to the macroscopic scale could be a potential way forward.

Acknowledgements

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5 Appendix A – modelling the hydration of low-pH concrete

Characterization of the composition of hardened concrete after curing requires the hydration of the mix to be modelled. The hydrated composition is then used as initial condition in reactive transport models. To model hydration, the methodology developed by Lothenbach and Winnefeld (2006) and Lothenbach et al. (2008) was followed. The model is based on coupling a set of kinetic reactions of dissolution of the mix components with thermodynamic calculations. This Appendix describes the cement hydration model as well as the main results in terms of phase assemblage of the cement hydrates, total porosity, and porewater composition.

Cement hydration modelling was performed with PHREEQC v3 (Parkhurst and Appelo, 2013) using the thermodynamic database ThermoChimie v9b0 (Giffaut et al., 2014), similar to the full reference case. Note that C-A-S-H or M-S-H phases are not included in the thermodynamic database, while the lowest Ca:Si ratio of the C-S-H model is 0.8. Data of the composition of the raw materials available from CEBAMA (Vehmas et al., 2017, 2019b) and from literature (SKB, 2014) were used as input to the model. The composition of the CEBAMA reference concrete mix is detailed in Table 10. More details can be found in Vehmas et al. (2017, 2019a, 2019c). The stoichiometry of the clinker phases (alite, belite, aluminat, and ferrite), silica fume (SF) and Blast Furnace Slag (BFS) are based on their oxide composition determined experimentally (Table 11).

Table 10. Composition of CEBAMA reference concrete mix. Data from Vehmas et al. (2016, 2018, 2019c). Density values from material manufacturers.

Component	Amount (kg/m ³ _{conc})	Density (kg/m ³)	Volume fraction (-)
CEM I 42.5	105	3100	0.0339
Silica fume	110	2300	0.0478
Blast furnace slag	65	2900	0.0224
Quartz filler	116	2650	0.0438
Aggregates			
0/1 mm	168	2600	0.0646
0/8 mm	770	2600	0.2962
8/16 mm	532	2600	0.2046
16/32 mm	396	2600	0.1523
Superplasticizer	16.8	1200	0.0140
Water	120	1000	0.1200
Total	2399		0.9996

Table 11. Oxide composition of the components of the CEBAMA reference mix used in the model.

Oxide	Mw (g/mol)	CEM I ^a (wt. %)	SF ^b (wt. %)	BFS ^c (wt. %)
CaO	56.08	64	1.46	41.5
SiO ₂	60.08	21	93.1	32.8
Al ₂ O ₃	101.96	3.5	1.44	10.6
SO ₃	80.06	2.2	0.47	1.4
MgO	40.30	0.7	0.88	8.29
Fe ₂ O ₃	159.69	4.6	0.91	0.81
K ₂ O	94.20	0.62	1.73	0.62
Na ₂ O	61.98	0.07	-	0.62
CO ₂	44.01	2.2	-	-
MnO	70.94	-	-	0.42
TiO ₂	79.87	-	-	2.04
SrO	103.62	-	-	0.05
V ₂ O ₅	181.88	-	-	0.09
ZrO ₂	123.22	-	-	0.03
Total		98.89	99.99	99.27

^aCEM I 42.5 MH/SR/LA produced by CEMENTA AB (Anläggningscement) (SKB, 2014). ^bSF from Vhemas et al. (2019), ^cBFS measured at VTT (Finland).

Cement hydration is assumed to occur under atmospheric conditions at 25°C and 100% relative humidity (i.e. unlimited supply of water for hydration). Redox reactions are not considered in the simulation. Empirical expressions of dissolution rates of clinker phases follow from Parrot and Killoh (1984). The dissolution rate of the BFS is taken from Schöler et al. (2017), while those of SF and quartz filler correspond to that of quartz from Palandri and Kharaka (2004). The latter is based on a pH-dependent transition-state-theory formulation. The specific surface areas of the BFS, SF, and quartz filler are either specified directly by the providers or derived from their particle size distribution. Apart from these kinetically-controlled reactions, all other chemical reactions are considered under thermodynamic equilibrium. The aggregates and superplasticizer are considered as chemically inert. The alkali uptake in C-S-H phases (Na⁺ and K⁺) is considered using a cation exchange model, with a cation exchange capacity (CEC) that depends on the concentration of C-S-H phases and their Ca/Si ratio. On the other hand, aluminium and magnesium uptake in C-S-H is not

considered in the simulations. Finally, calcium aluminosilicate hydrate (C-A-S-H) or magnesium silicate hydrate (M-S-H) phases are not included in the thermodynamic database used in the hydration model.

The dissolution of the clinker, binder components, and quartz filler are shown as a function of time in Fig. 11, together with the precipitation of cement hydrates, in terms of volume fraction (m^3 per m^3 of concrete). An almost complete dissolution of the clinker phases and BFS occurs within the first 100 days. On the other hand, SF rapidly dissolves at the beginning, but after 100 days it slows down significantly. This is due to the drop in pH of the pore solution until reaching a constant value in equilibrium with C-S-H phases that form with a Ca:Si ratio of 0.8. Finally, dissolution of quartz filler is very limited, due to the lower surface area compared to silica fume (see Table 2). The final phase assemblage is composed of unhydrated SF, C-S-H with Ca:Si ratio of 0.8, strätlingite (Al-bearing phase), ettringite (sulphate-bearing phase), and ferrihydrite (Fe-bearing phase).

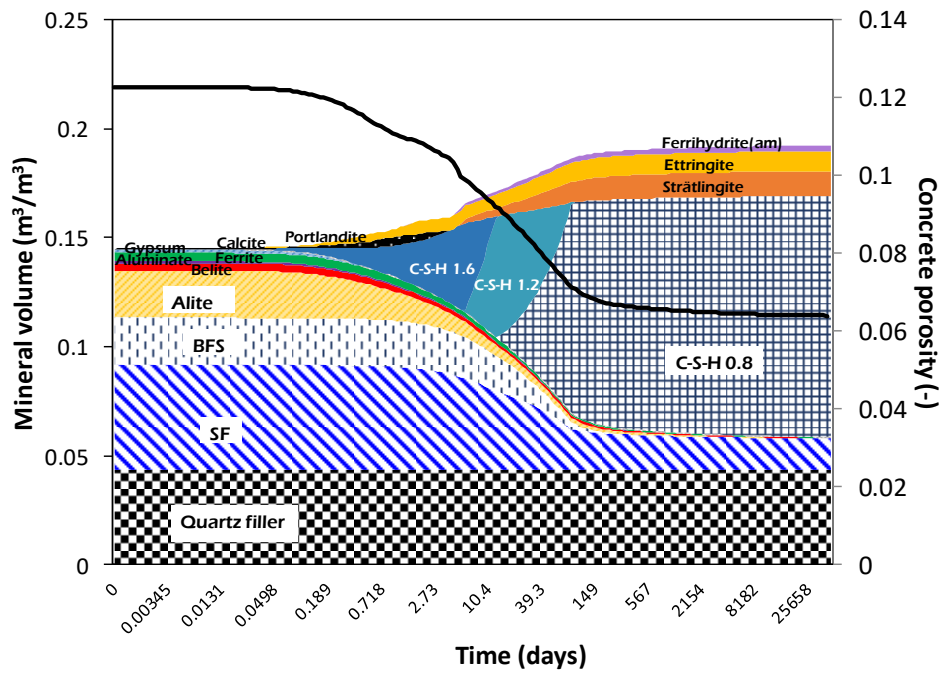


Fig. 11. Dissolution of the clinker and binder phases, precipitation of main cement hydrates (volume fraction in %) and concrete porosity (-) as a function of hydration time (in days). The black solid line corresponds to porosity.

The evolution of porewater composition and pH is shown in Fig. 12. The pH of the pore solution fluctuates between 12.5 and 13 at hydration times < 10 days. This short period is followed by large variations in pH until reaching a value of ~ 10.7 at long hydration times. The evolution of the Ca:Si ratio of the C-S-H has a large impact on the pH of the pore solution as portlandite is already dissolved after 5 days. The two abrupt changes in pH at 10-12 days and 80-100 days correspond to changes in the Ca:Si ratio of C-S-H, from 1.6 to 1.2, and from 1.2 to 0.8.

The alkali uptake in the C-S-H phases is also influenced by the pH of the pore solution. Mg^{2+} and Fe^{3+} concentrations in the aqueous solution remain low ($< 10^{-6}$ M) and are controlled by the presence and the low solubility of hydrotalcite and ferrihydrite, respectively. In turn, sulphate concentration remains below $3 \cdot 10^{-2}$ M, controlled by ettringite solubility, while the aluminium concentration is controlled by strätlingite solubility. At $\text{pH} \leq 10.7$, the dissolution of SF and quartz filler is significantly lowered, and the system virtually reaches equilibrium. In fact, changes observed between hydration times of 10 years, 100 years or 1,000 years are extremely small.

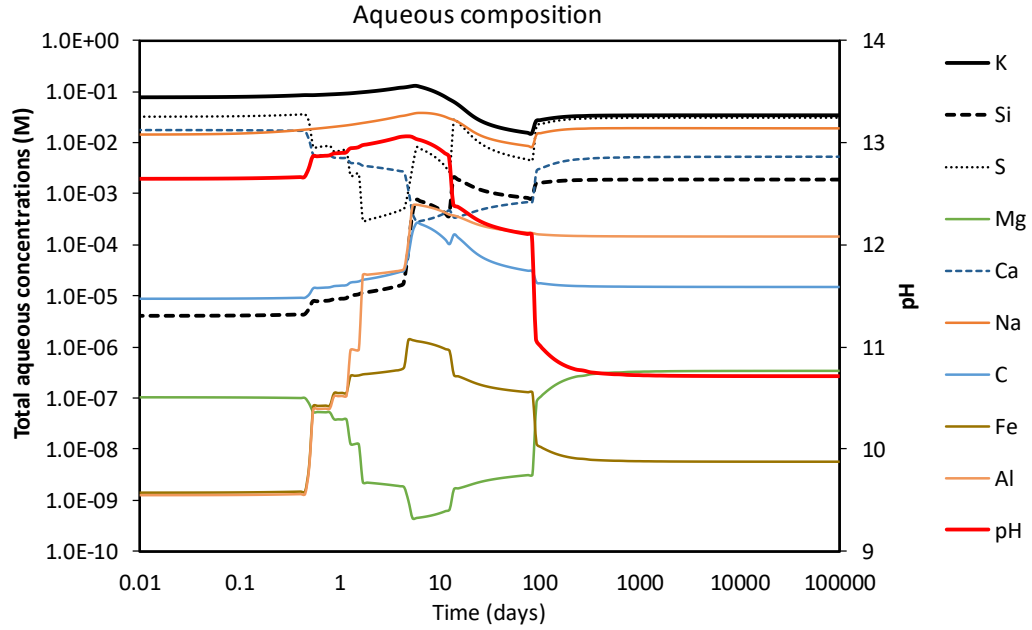


Fig. 12. Evolution of aqueous composition and pH as a function of hydration time.

The total porosity, denoted as ϕ_{tot} and calculated with equation (A.1), is shown as a function of hydration time in Fig. 11. The value of total porosity after long hydration times is around 0.063. This value is relatively larger than the value obtained experimentally using mercury intrusion porosimetry (MIP), i.e. 0.038 (Vehmas et al., 2019b, 2019c) and smaller than the one measured by the kerosene method or calculated considering the grain density (Vehmas et al. 2019c).

$$\phi_{tot} = \frac{V_{b,0} + V_{w,0} - V_{b,t} - V_{hyd,t}}{V_{b,0} + V_{w,0} + V_{aggr} + V_{sp}} \quad (A.1)$$

In equation (A.1), V stands for volume (litre) and subscripts b , w , hyd , $aggr$, and sp stand respectively for unhydrated binder, water, cement hydrates, aggregates, and superplasticizer (considered inert), respectively, while subscripts 0 and t refer to initial values and values at time t .

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7 Supplementary material

7.1 Results of preliminary cases

7.1.1 P1: Tracer diffusion (without considering geochemistry)

Case P1 studied the diffusion of a non-reactive and uncharged tracer from the concrete domain towards the clay host rock in the setup presented in Fig. 1 and Table 1 and the same spatial discretization than the FRC. The initial tracer concentration in the concrete and claystone pore solutions is 1 and 0 mM, respectively (Table 4). A closed boundary condition is imposed on the left and a tracer concentration of 0 on the right. For completeness, two additional reactive transport codes were used, namely PHAST (Parkhurst et al., 2010) and NPS (Damiani et al., 2019).

Fig. 13 shows the concentration profiles obtained with several codes at different times. Diffusion of the tracer towards the claystone has the effect of decreasing its concentration in concrete as a function of time. Good comparison between six codes is found for the tracer diffusion. After 100 years, slightly lower concentrations can be found in the concrete domain with MIN3P.

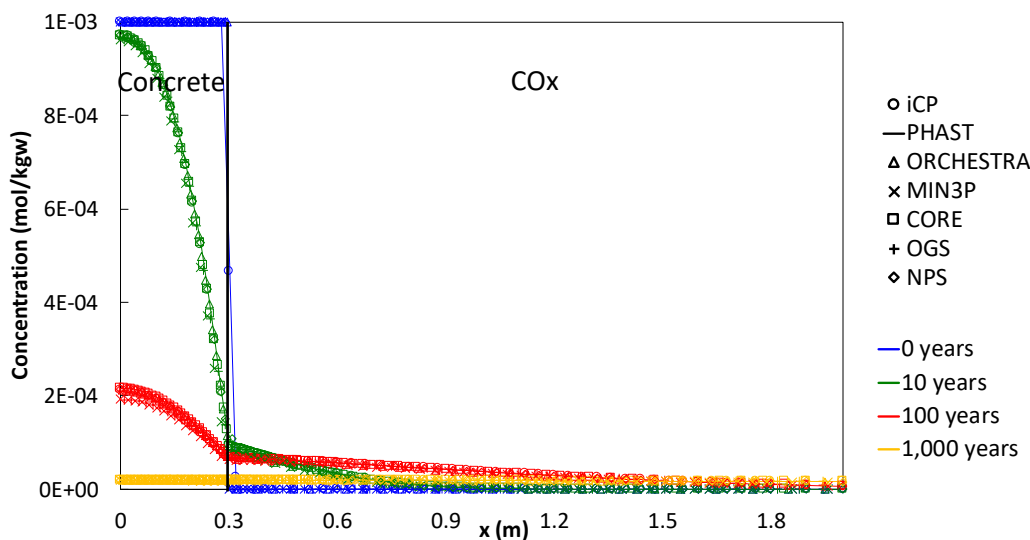


Fig. 13. Comparison of tracer concentration profiles over 2.1 m (in mol/kg water) at 0, 10, 100 and 1,000 years obtained with iCP, PHAST, ORCHESTRA, CORE^{2D}, MIN3P, OGS-GEM and NPS.

7.1.2 P2: Aqueous species and cation exchange

Case P2 is equivalent to the FRC but without any primary or secondary minerals, i.e. only the aqueous solutions and cation exchange reactions are considered. The goal was to benchmark the implementation of cation exchange reactions before implementing mineral reactions. Concrete/clay interaction is thus limited to porewater diffusion and cation exchange in thermodynamic equilibrium. This case was simulated with iCP, MIN3P, OGS-GEM and CORE^{2D}. Results after 1,000 years of interaction centred on the first meter of the studied system are presented from Fig. 14 to Fig. 16. Concrete exchanger concentrations of Ca²⁺, K⁺ and Na⁺ at 1,000 years (Fig. 14). K⁺ release (initial concentration of 0.55 mol/L) to concrete porewater driven by diffusion towards the claystone is the main process. This decrease in K⁺ fraction in the exchanger is compensated by an increase in Na⁺

(initial concentration of 0.17 mol/L), diffusing from the claystone, and in Ca^{2+} . Ca^{2+} concentration remains unchanged at $x = 0$ (initial concentration of 0.45 mol/L). Na^+ and Ca^{2+} concentrations changes in the exchanger maintain a similar Ca/Na ratio in the concrete exchanger. Overall, good agreement between codes is found, with slight differences in the results of MIN3P. In turn, Fig. 15 shows the composition of the exchanger within the first meter of claystone. Potassium diffusion from concrete results in an important concentration increase in the clay exchanger. As a consequence, all other cation concentrations are reduced.

Total dissolved calcium and potassium distribution profiles at 1,000 years show the in-diffusion into concrete of the former from the clay and the out-diffusion of the latter (Fig. 16). After 1,000 years, only small variations are observed in the pH profile (Fig. 16), with values between 7.1 and 7.2 for the two materials (initial pH is 10.68 and 7.06 for concrete and clay, respectively). As the clayey domain has a much larger volume (~ 130 times) than the concrete one, pH tends to the clay initial values in the system. Differences in porewater between codes can be directly linked with the differences observed in the exchanger compositions.

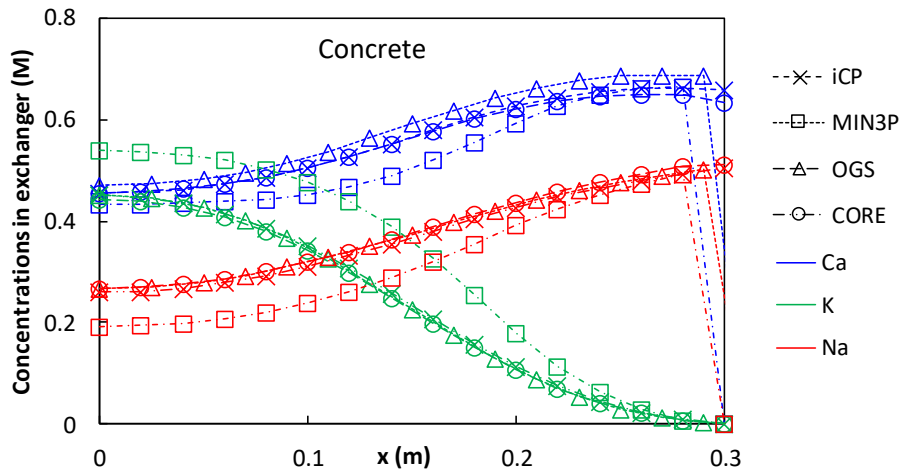


Fig. 14. Cation concentration (M) profiles in concrete exchanger at 1,000 years obtained with iCP, MIN3P, OGS-GEM and CORE^{2D}.

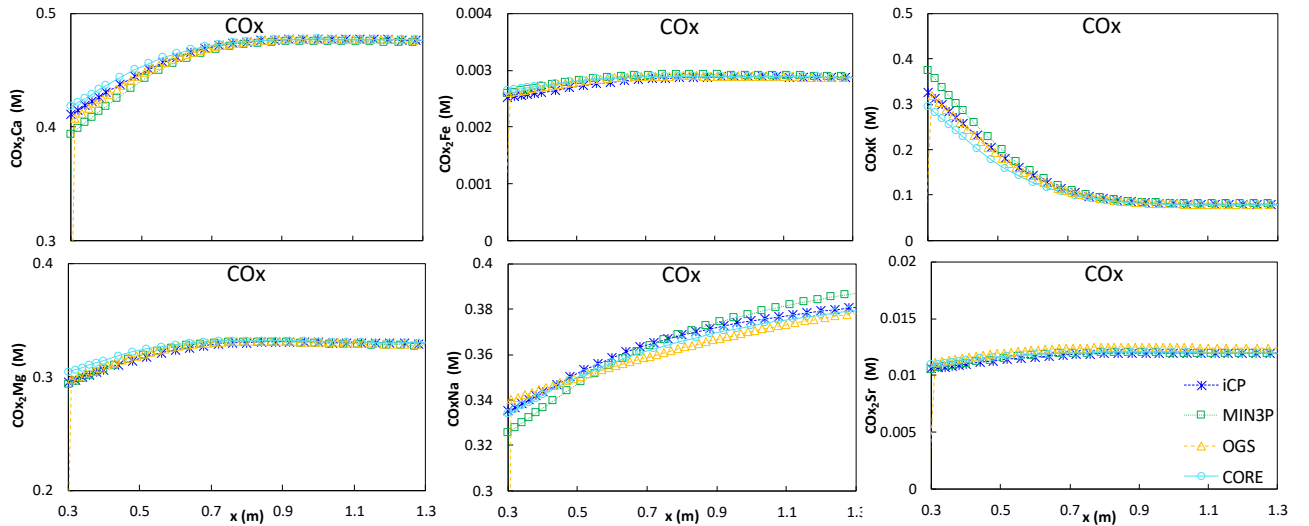


Fig. 15. Cation concentration (M) profiles in COx exchanger at 1,000 years obtained with iCP, MIN3P, OGS-GEM and CORE^{2D}.

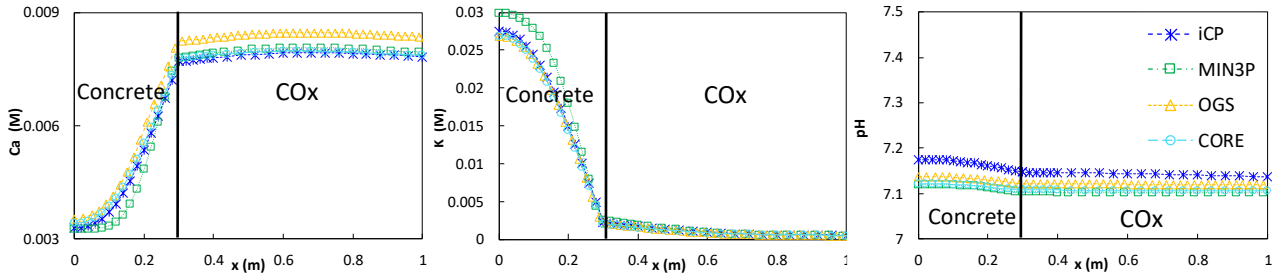


Fig. 16. Total aqueous concentrations (M) and pH profiles at 1,000 years obtained with iCP, MIN3P, OGS-GEM and CORE^{2D}.

7.1.3 P3: Minerals in equilibrium

The setup of case P3 is equivalent to the FRC but without accounting for the kinetically-controlled minerals. The only exception is quartz, which is included in case P3 as secondary phase in thermodynamic equilibrium in both materials, although in the FRC it was considered as a kinetically-controlled mineral. Quartz is expected to form in the model when the C-S-H gel dissolves. This case was simulated with iCP, MIN3P and CORE^{2D}. It is to note that in MIN3P, mineral reactions can only be simulated using kinetic rates. Thus, fast kinetic rates ($1 \cdot 10^{-9}$ mol/L_{medium}/s) were considered for all minerals to mimic thermodynamic equilibrium conditions. The results after 100,000 years are presented in terms of pH and porosity (Fig. 17) and mineral profiles (Fig. 18 and Fig. 19). The results of CORE^{2D} are the same as those included in the FRC comparison.

Overall, a very good agreement is observed between the results obtained with the different codes, with very small differences in pH and porosity profiles. However, the sensitivity of the system to iron is noticeable in the magnetite and siderite profiles.

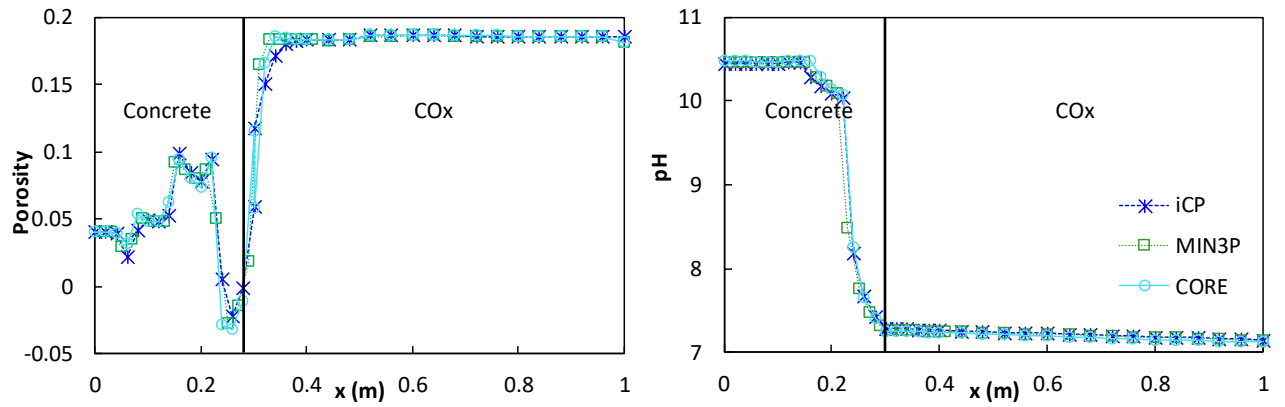


Fig. 17. Porosity and pH distribution profiles at 100,000 years obtained with iCP, MIN3P and CORE^{2D}.

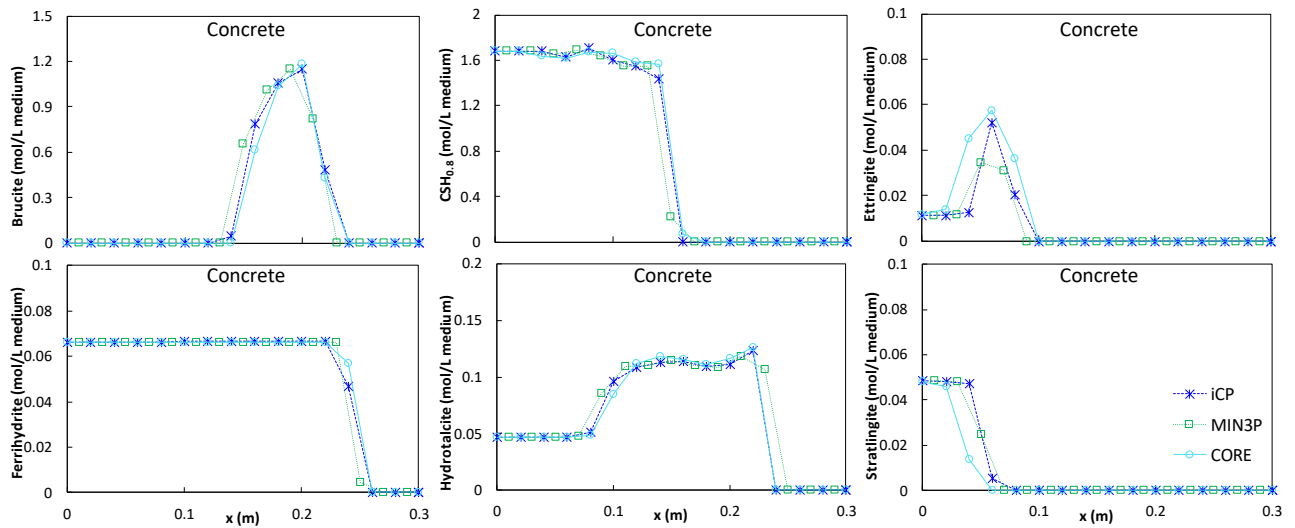


Fig. 18. Mineral phase profiles (in mol/ L medium) in the concrete domain at 100,000 years, obtained with iCP, MIN3P and CORE^{2D}.

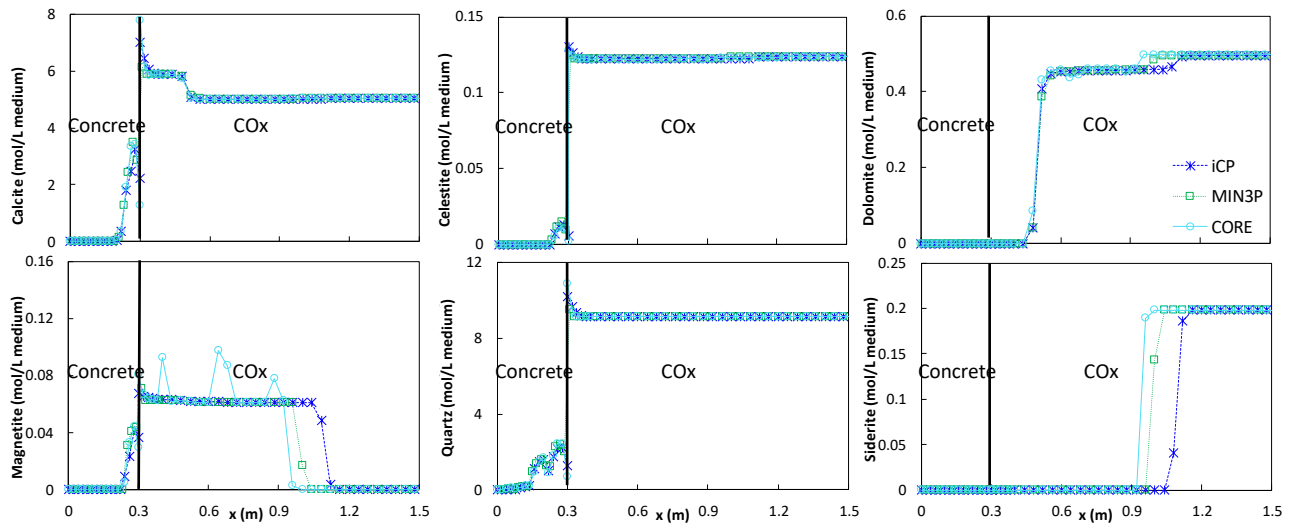


Fig. 19. Mineral phase profiles (in mol/ L medium) in concrete and clay domains at 100,000 years, obtained with iCP, MIN3P and CORE^{2D}.