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4 **Reactive transport modelling of a low-pH concrete / clay interface**

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21 **Abstract**

22 Cement-based materials are key components in the barrier system and structural support of
23 repositories for disposal of nuclear waste. As such, increased understanding of their long-term
24 performance under repository conditions is paramount for the safety assessment. Quantification of
25 the impact that cement-based materials could have on the surrounding barriers and the host rock is
26 essential to assess long-term safety of the repository system. This interaction can impact the
27 physical properties of the system near the interface and needs to be assessed by means of numerical
28 modelling. A reactive transport modelling study of the interaction between a newly-developed low-
29 pH concrete and a clay host rock (i.e. Callovo Oxfordian) over 100 000 years is presented here. The
30 main goal is to build confidence in the consistency of the different modelling approaches and in the
31 application of different reactive transport codes (iCP, ORCHESTRA, OpenGeosys-GEM, CORE^{2D},
32 and MIN3P) to analyse the performance of the recently developed low-pH concrete within the
33 CEBAMA project. A common setup of a reference case was established, including
34 precipitation/dissolution reactions, redox and cation exchange processes, building upon preliminary
35 cases of increasing complexity. In addition, a set of sensitivity cases was simulated to test the effect
36 of key geochemical and transport parameters on the results, including the impact of porosity
37 changes on the diffusion coefficient and electrochemical couplings. Different reactive transport
38 codes were used in the benchmark. Overall, the results show not only the high level of
39 understanding of the governing processes but also the good agreement obtained with different
40 codes, which is essential to demonstrate the applicability of reactive transport modelling to support
41 safety assessment. The sensitivity and preliminary cases modelled show that the results obtained are
42 much more sensitive to changes to transport parameters and couplings than to the different
43 modelling tools used in each case. In addition, the impact of including or not the slow kinetics of
44 dissolution of the claystone minerals is shown to be negligible in the studied scenarios.

45
46 **Keywords:** Benchmark, reactive transport modelling, low-pH concrete, cement-clay interaction

47 **1 Introduction**

48 Cement-based materials are key components in the multi-barrier system of repositories for disposal
49 of nuclear waste (NEA, 2012). As such, increasing understanding of their long-term evolution is
50 paramount for their performance assessment. Chemical interaction between cement-based materials
51 and the surrounding host rock is one of the most important topics. Indeed, alkaline materials such as
52 concrete, widely used in such disposal, are in chemical disequilibrium when in contact with clay
53 rocks, having a circumneutral pH. This disequilibrium triggers a series of interaction processes
54 driven by mass transport between the two systems. In the long term, the interface between them is
55 subjected to various physico-chemical processes that have an impact on the chemical composition
56 of both systems and, as a result, on their physical (transport and mechanical) properties. These
57 various reactive transport processes develop over large ranges of space and time scales, which are
58 not easily accessible through an experimental approach. Thus, they need to be assessed by means of
59 numerical modelling.

60 A large body of literature exists dealing with the modelling of cement-clay interactions. Reviews by
61 Gaucher and Blanc (2006), Savage et al. (2007), and Bildstein and Claret (2015) and Savage and
62 Cloet (2018) are comprehensive studies of the level of knowledge and main uncertainties in this
63 field. One of the main open issues is related with the long-term performance of the clay host rock
64 when using recently developed low-pH concretes (e.g. Vehmas et al., 2019c). These materials were
65 developed for different applications, such as limiting the heat of hydration or the pH of the pore
66 solution (e.g. García-Siñeriz et al., 2008). They are based on the use of substantial replacements of
67 cement by supplementary cementitious materials. The Horizon 2020 collaborative project
68 CEBAMA (CEment-BASed MATERIALS, properties, evolution, barrier functions) was a research and
69 innovation action granted by the EC in support of the implementation of first-of-the-kind geological
70 repositories for nuclear waste (Altmaier et al., 2017). One of the goals of CEBAMA was to improve
71 the understanding of interaction processes between cementitious and clayey materials (i.e.
72 bentonite, clay rocks). Different approaches were used for modelling and interpretation of
73 experimental data generated within the project and focusing on reactive transport processes that can
74 impact the physical properties of cementitious materials and their interface with clayey systems
75 (Idiart, 2019). Therefore, an integrated modelling study was undertaken to build confidence in the
76 consistency of the different modelling approaches. The work consisted of benchmarking the
77 capabilities of various reactive transport codes to simulate physical and chemical processes
78 governing long-term interactions at a concrete-clay interface.

79 Many of the previous studies focused on the clayey system, disregarding the alteration of the
80 cementitious barrier (Savage et al., 2002; Gaucher et al., 2004; Watson et al., 2009; Fernández et
81 al., 2010). In those studies, the cementitious system is typically replaced by a fixed concrete water
82 as a boundary condition. Other studies have focused on the prediction of the formation of an
83 alkaline plume (e.g. Soler et al., 2011; Grandia et al., 2010; Sidborn et al., 2014), or the degradation
84 of cementitious systems by clay rock porewaters (Olmeda et al., 2017). More recently, the
85 simultaneous interaction between clayey and cement-based materials has been paid more attention
86 (Trotignon et al., 2006; De Windt et al., 2008; Yang et al., 2008; Marty et al., 2009; Kosakowski
87 and Berner, 2013; Soler, 2013; Liu et al., 2014; Mon et al., 2017; Samper et al., 2018). Marty et al.
88 (2014, 2015) presented a systematic modelling study of the interaction between a Callovo-
89 Oxfordian clay formation and a high-pH concrete. Benchmarking of reactive transport codes in that
90 geochemical system showed a good agreement of model results.

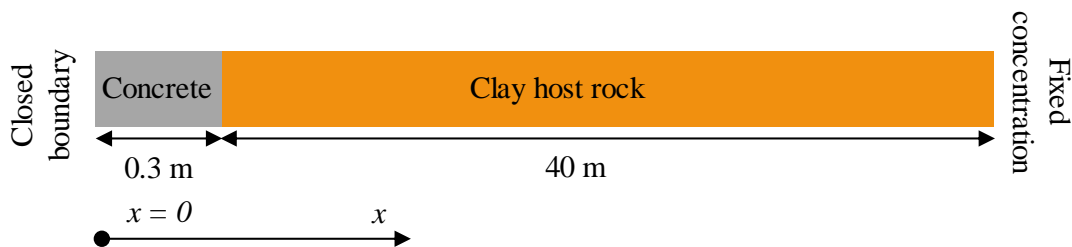
91 The overall evolution sequence of mineralogical assemblage of concrete made with ordinary
92 Portland cement (OPC; high-pH) during its chemical degradation is well-known (Miller et al., 2000;
93 Marty et al., 2014; Olmeda et al., 2017). However, interactions of low-pH concrete with clayey
94 materials, as studied in this paper, have been given much less attention. Thus, the goal of this study

95 is not only to build confidence in the modelling approaches by benchmarking reactive transport
 96 codes, but mainly to increase the level of understanding of the alteration of low-pH cementitious
 97 materials in contact with a clayey system. A reference case was simulated considering a common
 98 framework of models and parameters, as well as a set of sensitivity cases for assessing the impact of
 99 numerical codes specificities, material variabilities, and uncertainties on the extent of alteration. In
 100 this paper, the results and main outcomes obtained with different reactive transport modelling tools
 101 are presented and the implications of the study are discussed.

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

107 2 Description of studied system

108 The studied system considers a concrete structure in contact with a clayey host rock at isothermal
 109 (25°C) and fully water saturated conditions. Fickian diffusion is considered as the only solute
 110 transport mechanism in the reference case. All aqueous species have the same diffusion coefficient
 111 in free solution. A different tortuosity is assumed for each material domain, maintaining
 112 electroneutrality of the pore solution (i.e. all solutes have the same effective diffusion coefficient in
 113 one given material). Both materials were considered as homogeneous and continuous porous media.
 114 It is assumed that no excavation damage zone (EDZ) is present. A one-dimensional setup in
 115 Cartesian coordinates is assumed, with a concrete thickness of 0.30 m, in contact with a large mass
 116 of claystone with a thickness of 40 m. The geometry and boundary conditions are shown in Fig. 1.
 117 Fixed concentration (Dirichlet) at the clay host rock boundary corresponds to the initial porewater
 118 composition of the claystone.



119
 120 **Fig. 1.** Geometry and boundary conditions considered in the model.

121 The CEBAMA reference low-pH concrete is considered (Vehmas et al., 2017, 2019c), see Section
 122 2.1 and Appendix A. The mineralogical composition of the clay host rock corresponds to the
 123 Callovo-Oxfordian claystone (COx), see Section 2.2, which is well characterised (Marty et al.,
 124 2014) and has been previously considered in a benchmark modelling study of the interface between
 125 a “high-pH” (OPC) concrete and COx (Marty et al., 2015). The effective diffusion coefficient and
 126 total porosity of the two domains are given in Table 1.

127 **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	$1.44 \cdot 10^{-10}$	$2.60 \cdot 10^{-11}$

128 Most of the simulation cases considered the thermodynamic database ThermoChimie version 9b0
 129 (Giffaut et al., 2014). The main reason to select this database is that it includes consistent data for
 130 both, the cementitious and the clayey systems. Data for clay minerals and Portland cement hydrated

131 phases included in v9b0 were mainly selected from Blanc et al., (2015) and Blanc et al. (2010),
 132 respectively. Moreover, the database is under continuous development and regularly updated, so
 133 that future cement-clay interaction studies with this database can benefit from the present work.
 134 This version of the ThermoChimie database includes parameters for the extended Debye Hückel
 135 equation that is used calculate activity coefficients. ORCHESTRA and MIN3P use the Davies
 136 equation to calculate activity coefficients, which only requires the ion charges as input.

137 2.1 Low-pH concrete model

138 The concrete studied here is made by mixing water with cement, blast furnace slag, silica fume,
 139 quartz filler, superplasticizer and aggregates with the proportions specified in Appendix A (Table
 140 9). The composition of the hardened concrete can be calculated by means of thermodynamic
 141 modelling, as explained in Appendix A, starting from the raw materials. The initial porosity of the
 142 hardened concrete adopted in the reactive transport modelling is 0.04, corresponding to the
 143 experimental value obtained by MIP (Table 1). The effective diffusion coefficient of concrete in the
 144 reference case is $1 \cdot 10^{-12}$ m²/s according to Vehmas et al. (2019c) (Table 1). The mineralogical and
 145 porewater composition after 10 years of hydration simulated with thermodynamic modelling has
 146 been selected as an initial condition (see Appendix A). At that time, the remaining mass of
 147 unhydrated clinkers is extremely small and can be neglected, while the slag has dissolved
 148 completely. Only silica fume and quartz filler are considered in the simulations to dissolve
 149 kinetically with the pH-dependent kinetic dissolution rate of quartz, r (mol/s), proposed by Palandri
 150 and Kharaka (2004):

$$151 \quad r = M_w \cdot m \cdot k \cdot A \cdot |1 - \Omega^\theta|^\eta \quad (2.1)$$

$$152 \quad k = k_{25}^{nu} + \sum_i k_{25}^i \prod_j a_{ij}^{n_{ij}} \quad (2.2)$$

153 where M_w (g/mol) is the molar mass of the mineral, m is the total mass of the mineral (mol), k is
 154 the rate constant (mol/m²/s), A (m²/g) is the reactive surface area, Ω (-) is the mineral saturation
 155 ratio, θ and η are rate parameters (-), superscript nu refers to reactions under neutral conditions and
 156 superscript i to reactions under either acid or basic conditions, and a_{ij} is the activity of a species j in
 157 reaction i . The activation energy term is equal to 1 at 25°C and is thus not included. Table 2
 158 specifies kinetic parameters for quartz filler and silica fume. Surface areas were estimated from the
 159 grain size distribution provided by the manufacturers. The aggregates are considered as chemically
 160 inert.

161 The mineralogical and porewater compositions of low-pH concrete are given in Table 3 and Table
 162 4, respectively, corresponding to the results of the hydration model (Appendix A). A volume
 163 fraction of inert solid (aggregates and superplasticizer) is also considered in concrete with a value of
 164 0.7748.

165 In addition, the cementitious system is characterized by surface properties, modelled through cation
 166 exchange processes. Table 5 specifies the composition of the cation exchanger in equilibrium with
 167 the initial pore solution that simulates the uptake of K and Na (exchanged with Ca) in calcium
 168 silicate hydrates (C-S-H). More details are given in Appendix A. The selectivity coefficients are
 169 based on the Gaines-Thomas convention. Uptake of aluminium and magnesium in C-S-H is not
 170 considered in the model.

171 The presence of redox sensitive species (i.e. iron, sulphur) in the cementitious system might
 172 influence the redox potential of cement porewater, leading to redox potentials in the range -750 mV
 173 to -230 mV in OPC (Berner, 2002). That is the case of sulphides in slag blends, and of iron, which
 174 can sorb on C-S-H phases, substitutes Al in AFm or AFt phases (e.g. ettringite and
 175 monosulfoaluminate, respectively), or precipitate as Ca-ferrites. For low-pH cementitious systems,

176 no redox potentials are available. With this in mind, and considering that the total dissolved iron
 177 concentration does not exceed 10^{-7} M in cement paste (Berner, 2002), a redox potential (Eh) of ~ -
 178 27 mV was assumed here by considering a small amount of magnetite (Table 3) and the
 179 thermodynamic equilibrium between magnetite and ferrihydrite couple at the given pH.

180 The secondary minerals allowed to precipitate are listed in Table 3. It is noted that the same set of
 181 secondary minerals was considered both in the concrete and CO_x domains. This includes the
 182 potential precipitation of quartz assuming the kinetic law defined for the CO_x domain (Table 6).

183 Two potentially relevant groups of phases for the studied system (i.e. low-pH concrete) that are not
 184 included in the current version of the thermodynamic database are the group of Magnesium-
 185 Silicate-Hydrates (M-S-H phases) and C-(A)-S-H phases. During the course of this work,
 186 thermodynamic data for the mentioned phases were reported in Lothenbach et al. (2019) and Roosz
 187 et al. (2018). Formation of M-S-H phases at the interface between low-pH concrete and a claystone
 188 has been recently identified as one of the relevant alteration processes (e.g. Dauzeres et al., 2016;
 189 Mäder et al., 2017). The sink of Mg in the cementitious system is considered by other Mg-bearing
 190 phases, namely brucite and hydrotalcite. Due to significantly higher molar volume M-S-H phases
 191 compared to other Mg-bearing phases, the impact on porosity could be non-negligible. Partial
 192 substitution of Al for Si in C-S-H, so-called C-(A)-S-H phases, is also not accounted for in the
 193 model. Instead, strätlingite, an Al-bearing cement hydrate is predicted to form during hydration
 194 (Appendix A).

195 **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

196 **Table 3.** Mineralogical composition of low-pH concrete after 10 years of hydration and CO_x, reaction types,
 197 and secondary minerals considered. All reactions considered in thermodynamic equilibrium unless
 198 otherwise stated.

Mineral phases	mol/L concrete	mol/L CO _x
CSH 0.8	1.68022	0
Calcite	0.008644	5.038
Ettringite	0.011856	0
Ferrihydrite(am)	0.066384	0
Hydrotalcite	0.046836	0
Magnetite	0.000020	0
Stratlingite	0.047892	0
SilicaFume [†]	0.496924	-
Quartz filler [†]	1.748352	-
Quartz [*]	0	9.1548
Celestite	0	0.1242
Dolomite	0	0.4968
Pyrite	0	0.1908
Siderite	0	0.198
Illite_Imt-2 [†]	0	1.9386
Montmorillonite-BCCa [†]	0	0.495
Microcline [†]	0	0.2466
Ripidolite_Cca-2 [†]	0	0.0738
SiO ₂ (am)	0	0
Brucite	0	0
CSH1.6	0	0
CSH1.2	0	0
C3AH6	0	0
C3FH6	0	0
C4AH13	0	0

C4FH13	0	0
Ettringite-Fe	0	0
Gypsum	0	0
Hemicarboaluminate	0	0
Hydrotalcite-CO ₃	0	0
Fe(OH) ₂ (cr)	0	0
Monocarboaluminate	0	0
Monosulfate-Fe	0	0
Monosulfoaluminate	0	0
Portlandite	0	0
Pyrrhotite	0	0
Saponite-FeCa	0	0
Syngenite	0	0
† Dissolution kinetics; * precipitation kinetics		

199 **Table 4.** Initial porewater composition of the low-pH concrete after 10 years of hydration and CO_x
200 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	$1.448 \cdot 10^{-4}$	$8.504 \cdot 10^{-8}$
C	$1.506 \cdot 10^{-5}$	$3.826 \cdot 10^{-3}$
Ca	$5.237 \cdot 10^{-3}$	$7.601 \cdot 10^{-3}$
Cl	$1.000 \cdot 10^{-10†}$	$4.120 \cdot 10^{-2}$
Fe	$5.447 \cdot 10^{-8}$	$4.351 \cdot 10^{-5}$
K	$3.420 \cdot 10^{-2}$	$5.110 \cdot 10^{-4}$
Mg	$3.736 \cdot 10^{-7}$	$5.187 \cdot 10^{-3}$
Na	$1.910 \cdot 10^{-2}$	$4.008 \cdot 10^{-2}$
S	$3.058 \cdot 10^{-2}$	$1.108 \cdot 10^{-2}$
Si	$2.021 \cdot 10^{-3}$	$1.800 \cdot 10^{-4}$
Sr	$1.000 \cdot 10^{-10†}$	$2.429 \cdot 10^{-4}$
Tracer	$1.000 \cdot 10^{-3}$	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.

201 **Table 5.** Initial exchanger compositions for alkali uptake in low-pH concrete and in claystone, and
202 thermodynamic equilibrium constants (Gaines Thomas convention). CEC = cation exchange capacity.
203
204

Concrete	Log K	mol/kg water	mol/L concrete
Ex2Ca	0.0	$4.444 \cdot 10^{-01}$	$1.778 \cdot 10^{-02}$
Ex2K2	0.37	$5.524 \cdot 10^{-01}$	$2.210 \cdot 10^{-02}$
Ex2Na2	0.37	$1.689 \cdot 10^{-01}$	$6.756 \cdot 10^{-03}$
Total (CEC)		2.331	0.093
Claystone	Log K	mol/kg water	mol/L CO _x
COx2Ca	0.7	$4.744 \cdot 10^{-01}$	$8.540 \cdot 10^{-02}$
COx2Mg	0.7	$3.282 \cdot 10^{-01}$	$5.907 \cdot 10^{-02}$
COxNa	0	$3.867 \cdot 10^{-01}$	$6.961 \cdot 10^{-02}$
COxK	1.2	$7.850 \cdot 10^{-02}$	$1.413 \cdot 10^{-02}$
COx2Sr	0.6	$1.188 \cdot 10^{-02}$	$2.139 \cdot 10^{-03}$
COx2Fe	0.8	$2.860 \cdot 10^{-03}$	$5.145 \cdot 10^{-04}$
Total (CEC)		2.1	0.378

205 2.2 Claystone model

206 For the Callovo-Oxfordian claystone (CO_x), the same physical parameters as in Marty et al. (2015)
207 are used (porosity of 0.18 and effective diffusivity of $2.6 \cdot 10^{-11}$ m²/s, see Table 1).

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

215 The initial porewater composition (Table 4) is in equilibrium with the cation exchanger composition
 216 (Table 5) using thermodynamic equilibrium constants given in the same table (Gaucher et al.,
 217 2009).

218 **Table 6.** Kinetic parameters for dissolution reactions in the COx domain (from Marty et al., 2015) and for
 219 quartz precipitation.

Mineral	A (m^2/g)	k_{25}^{nu} ($\text{mol}/\text{m}^2/\text{s}$)	k_{25}^{H+} ($\text{mol}/\text{m}^2/\text{s}$)	n^{H+}	k_{25}^{OH-} ($\text{mol}/\text{m}^2/\text{s}$)	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
Quartz (precipitation)	0.05	$3.0 \cdot 10^{-12}$	-	-	-	-	4.58	0.54

220 2.3 Discretization

221 The same spatial discretization was used in all the 1D models implemented in all the codes. A finer
 222 discretization was assumed in the concrete domain and also in the first 0.1 m of the COx domain to
 223 avoid using elements of different size at the interface. The size of the elements is 0.02 m in the
 224 concrete domain ($0 \leq x \leq 0.30$), while the COx domain ($0.3 < x \leq 40.3$ m) is discretized with the
 225 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
 226 2.5 m. The total number of elements is 60. This discretization was set as a compromise between
 227 spatial resolution and computation time. A simulation time of 100,000 years was considered.
 228 According to the von Neumann criterion for diffusive solute transport, the time step size should
 229 comply with the following relation:

$$230 \Delta t < \frac{\Delta x^2}{3 \cdot D_p} \quad (2-3)$$

231 where Δt (s) is the time step size, Δx is the spatial discretization (m), and D_p is the pore diffusivity
 232 (m^2/s). Given the higher pore diffusivity of the COx claystone compared to concrete, the time step
 233 size is restricted by the clay domain. The temporal discretization considers a constant time step size
 234 of 0.10 years. Some of the codes used in this study have an automatic time stepping scheme. In
 235 those cases, a maximum time step size of 0.10 years was considered.

236 2.4 Methodology

237 Several preliminary cases (P1-P3) of increasing complexity were implemented and simulated step
 238 by step in different reactive transport codes (Section 2.5) to finally define the full reference case
 239 (FRC). A description of the preliminary cases and the results obtained can be found as
 240 Supplementary Material to this paper. In addition, a set of sensitivity cases was modelled with some
 241 of the reactive transport codes to assess the impact of some of key parameters and processes (S1-
 242 S3). These cases are based on the FRC. Table 7 presents a summary of the main processes
 243 considered in each case.

244 In the sensitivity case S1, the concrete effective diffusion coefficient was reduced 10 times ($1 \cdot 10^{-13}$
245 m^2/s). This value is closer to the lowest range of experimental results obtained using HTO (Vopálka
246 et al., 2019) and considers the fact that the diffusion coefficient decreases with time with continued
247 hydration (e.g. Vehmas et al., 2019c).

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

$$252 \quad D_e = D_p \phi \quad (2-4)$$

$$253 \quad D_p = \tau D_w \quad (2-5)$$

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

257 Finally, the impact of electrochemical coupling for the transport of charged species was also
258 investigated in sensitivity case S3 and implemented in ORCHESTRA (see Section 2.5). This feature
259 is also available in MIN3P but could not be simulated due to limited resources. This case
260 considered the effects of ion specific diffusion coefficients instead of an average value as in the
261 Fickian diffusion approach. Dissolved species are allowed to diffuse at different rates according to
262 their diffusivities in free solution, which were selected from the phreeqc.dat database (Parkhurst and
263 Appelo, 2013). Due to their different charges, this results in the development of local electric
264 potential gradients. These gradients have an impact on the diffusion rate of charged ions until net
265 charge fluxes are zero. As a result, the diffusion rate of a specific ion not only depends on its own
266 diffusion coefficient, but on the concentration gradients of all accompanying dissolved ions. For
267 this reason, this approach is usually referred to as multicomponent transport and can be modelled
268 using the Nernst-Planck equations (e.g. Galíndez and Molinero, 2010):

$$269 \quad J_i = -D_i \left(\frac{dc_i}{dx} + z_i c_i \frac{F}{RT} \frac{d\psi}{dx} \right) \quad (2-6)$$

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

275 **Table 7.** 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								×

276 **2.5 Description of codes**

277 Five reactive transport codes have been benchmarked: iCP, OpenGeoSys-GEM, ORCHESTRA,
 278 ParMIN3P-THCm and CORE^{2D} V5. Their main features are summarized in Table 8 and detailed
 279 below.

280 **Table 8.** Relevant features of reactive transport codes used in this study.

Code name	Spatial discretization	Time stepping scheme	Coupling approach for RT	Chemical equilibrium approach	Aqueous activity coefficient	TDB
iCP	FEM	Pres.	SNIA	LMA	eDH	ThermoChimie
OGS-GEM	FEM	Aut.	SNIA	GEM	eDH	Thermoddem (modified)
ORCHESTRA	FVM	Pres.	SNIA	LMA	Davies	ThermoChimie
CORE ^{2D} V5	FEM	Pres.	SIA	LMA	eDH	ThermoChimie
MIN3P	FVM	Aut.	GIA	LMA	Davies	ThermoChimie

FEM: finite element method; FVM: finite volume method; Pres.: prescribed; Aut.: automatic; SNIA: sequential non-iterative approach; SIA: sequential iterative approach; GIA: global implicit approach; LMA: law-of-mass action, GEM, Gibbs energy minimization method; eDH: Extended Debye-Hückel

281 iCP version 1.5 (interface COMSOL-PHREEQC) couples two standalone codes, the general-
 282 purpose software COMSOL Multiphysics® version 5.3 and the geochemical simulator PHREEQC
 283 version 3 (Parkhurst and Appelo, 2013). The interface provides a numerical platform to simulate a
 284 wide range of multiphysics problems coupled with geochemistry (Nardi et al., 2014). iCP is written
 285 in Java and uses the IPhreeqc C⁺⁺ dynamic library and the COMSOL Java-API. The coupling
 286 approach is based on the operator-splitting (OS) technique. Conservative solute transport equations
 287 coupled with other physical processes are solved by COMSOL, while equilibrium and kinetic
 288 chemical reactions are solved by PHREEQC. iCP has been extensively used in geosciences and for
 289 long-term performance of engineered barriers for nuclear waste (e.g. Idiart et al., 2019).

290 OpenGeoSys-GEM (OGS-GEM) is an open-source code for simulation of thermo-hydro-
 291 mechanical-chemical processes in porous media that couples the OpenGeoSys V5 framework with
 292 the GEMS3K thermodynamic solver (Kosakowski and Watanabe, 2014). It is based on an object-
 293 oriented Finite-Element-Method concept (Kolditz et al., 2012). Fluid flow and mass transport
 294 equations are solved by OpenGeoSys. The geochemical thermodynamic solver GEMS3K is used

295 for calculation of local/partial equilibria in complex heterogeneous multicomponent-multiphase
296 systems (Kulik et al., 2013). OpenGeoSys-GEM has been applied extensively to investigate very
297 complex geochemical reactions to assess the long-term geochemical evolution of materials and
298 interfaces in deep geological repositories (Cloet et al., 2018; Kosakowski and Berner, 2013;
299 Kosakowski and Watanabe, 2014; Poonoosamy et al., 2018).

300 ORCHESTRA (Objects Representing CHEmical equilibrium and TRANsport) is written in Java
301 (Meeussen, 2003). In ORCHESTRA, all model equations are provided as run-time input, which
302 means that equations can be defined directly in input files in text format. It is also possible to use
303 predefined definitions (objects) from a standard object file (e.g. reactions, minerals, diffusion, etc.).
304 ORCHESTRA has a GUI for defining chemical equilibrium systems, able to read PHREEQC
305 format thermodynamic databases. This makes ORCHESTRA a flexible tool for combining standard
306 chemical / transport models with user defined/modified parts. This approach was followed in the
307 transport modules, where standard objects (e.g. for diffusion) were combined with user defined
308 expressions for feedback between porosity and tortuosity and even for implementing the effect of
309 electric potentials on diffusion (Nernst-Planck). Kinetic reactions were calculated simultaneously
310 with the transport equation, using the same time-step. ORCHESTRA has been used to study solute
311 transport in cement (Sarkar et al., 2010) or cement/clay interaction (Marty et al., 2015).

312 ParMIN3P-THCm is the parallelized version of MIN3P-THCm, a general-purpose multicomponent
313 reactive transport code to simulate coupled hydrogeological, thermal, and biogeochemical processes
314 in subsurface domains with variable water-saturated conditions (Mayer et al., 2002; Mayer and
315 MacQuarrie, 2010). A hybrid MPI and OpenMP programming approach is implemented in
316 ParMIN3P-THCm with a domain decomposition method based on PETSc libraries (Su et al., 2017).

317 CORE^{2D} V5 is a code for saturated and unsaturated water flow, heat transport and multicomponent
318 reactive solute transport under both local chemical equilibrium and kinetic conditions in
319 heterogeneous and anisotropic media (Samper et al., 2009; Samper et al., 2011). The flow and
320 transport equations are solved with Galerkin triangular finite elements and an Euler scheme for time
321 discretization, while the chemical formulation is based on ion association theory. CORE^{2D} has been
322 widely used to model laboratory and in situ experiments (Zheng et al., 2011), the interactions of
323 corrosion products and bentonite (Lu et al., 2011) and the long-term geochemical evolution of
324 repositories in granite and clay (Samper et al., 2016; Mon et al., 2017; Samper et al., 2018).

325 **3 Results and discussion**

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

329 **3.1 Full reference case (FRC)**

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

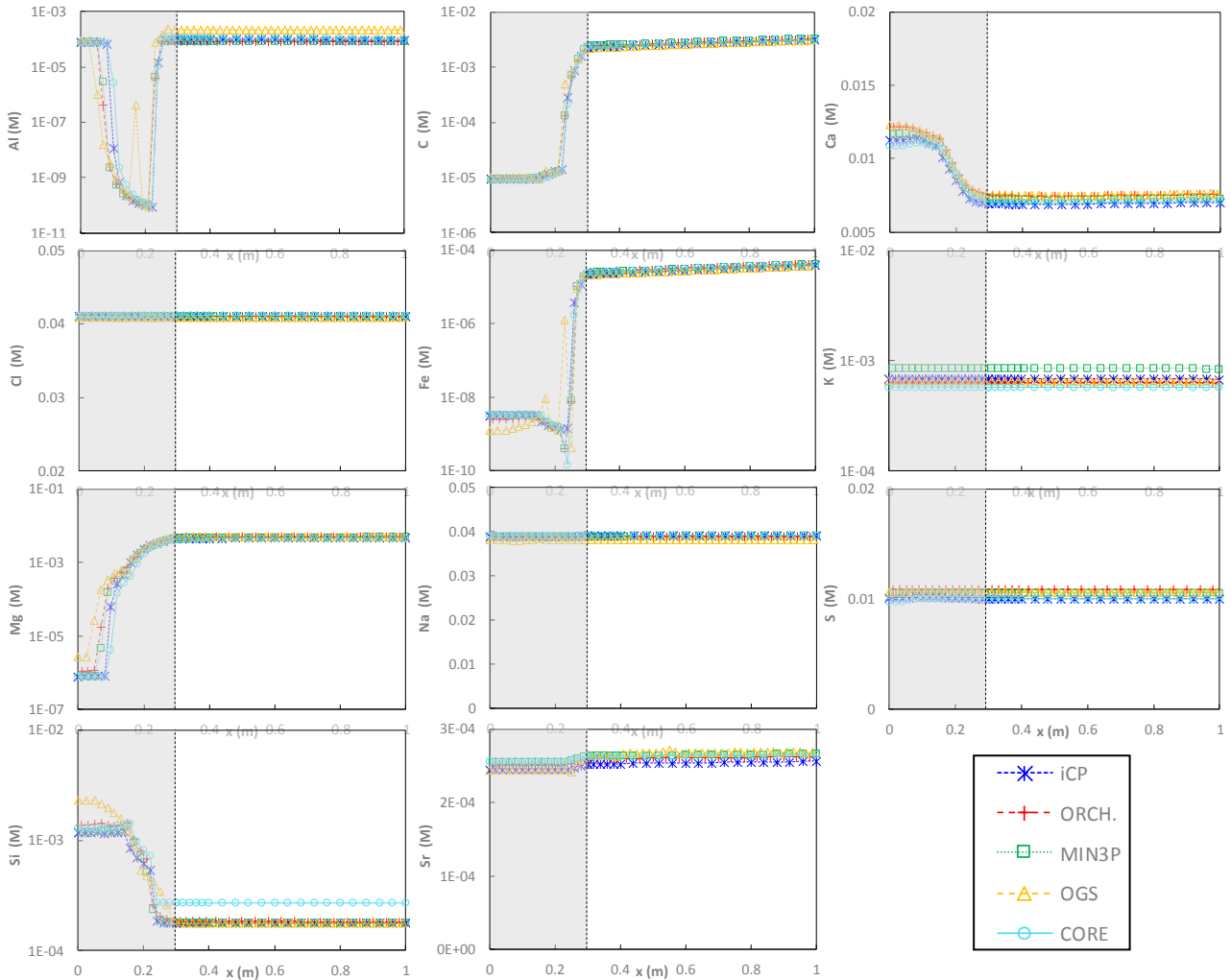
337 3.1.1 Porewater evolution

338 Spatial profiles of aqueous components and solution properties after 100,000 years are presented in
339 Fig. 2 and Fig. 3. Some species present important concentration gradients between concrete and
340 clay porewaters, governed by equilibrium (or kinetic laws) with different sets of minerals and cation
341 distribution in the exchangers. This is the case for Al, C, Mg, Fe, Sr, or Si. Significant Mg and C
342 concentration gradients drive diffusion of these species from the claystone to the concrete, where
343 Mg precipitates as brucite and hydrotalcite (Fig. 6), while calcite formation near the interface is the
344 main sink of C (Fig. 7). In turn, Si diffuses from the concrete to the claystone, coupled to the
345 dissolution of C-S-H (Fig. 6), the formation of quartz (Fig. 7) and the decrease in pH in the
346 degraded concrete region. Ca also diffuses out of the concrete structure throughout the simulation,
347 also driving the dissolution of cement hydrates (C-S-H, ettringite, strätlingite, see Fig. 6).

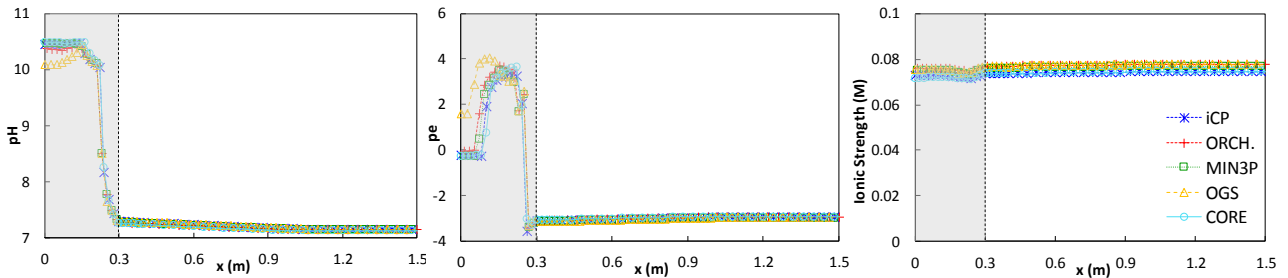
348 On the other hand, other species show small variations between concrete and clay due to their null
349 or limited role in solid-liquid interaction, at least after 100,000 years. This is the case for Cl, K, S
350 (mainly as sulfate), or Na. Cl has no interaction with mineral phases or exchanger composition, thus
351 acting as a tracer. Sulphate diffuses out of the concrete domain, triggering ettringite dissolution in
352 concrete and favouring celestite precipitation at both sides of the interface due to the ingress of Sr
353 from the claystone. However, after 100,000 years, the concentration gradient between concrete and
354 claystone has practically vanished. Aluminium concentration decreases in the centre part of the
355 concrete domain due to hydrotalcite precipitation in that region (Fig. 6). Changes in ionic strength
356 of the system are small and agree well between the different codes (Fig. 3).

357 The pH profile is a suitable indicator of chemical alteration. On the concrete side, pH values after
358 100,000 years present a maximum value of 10.5 in the innermost 13 cm in concrete, in equilibrium
359 with C-S-H with Ca:Si of 0.8 (Fig. 3). The decrease from the initial value (~10.7) is due to alkali
360 (K) diffusion to the clay. The pH decreases linearly to 10 at $x=21$ cm and then drops to ~7.3
361 towards the interface. On the CO_x side, pH changes are almost negligible, with a value of ~7.3 at
362 the interface decreasing to its initial value towards the right boundary (~7.1). Thus, the maximum
363 increase is predicted at the interface and is equal to ~0.2 pH units.

364 After 100,000 years, the redox conditions (pe) of CO_x remain practically unaffected (Eh ~ -170
365 mV) and controlled by the presence of the accessory minerals pyrite (FeS₂), celestite (SrSO₄) and
366 siderite (FeCO₃) and the precipitation of small amounts of magnetite (Fe₃O₄) in a reactive front of
367 ~1 m from the interface. Contrarily, an important redox gradient of between -170 mV and 190 mV
368 is established over half of the concrete thickness (0.15 m) mainly due to the pH decrease close to
369 the claystone. This change in pH promotes the dissolution of the iron (III) phase ferrihydrite
370 (Fe(OH)₃) and the precipitation/dissolution of the Fe(II)/Fe(III) phase magnetite controlling the
371 Fe(II)/Fe(III) ratio in solution and the redox of concrete. The maximum value of 190 mV at half of
372 the concrete thickness decreases again to its initial value of -30 mV along 7 cm due to changes in
373 the solid phases controlling the pH of the pore solution (i.e. C-S-H gel or hydrotalcite). Finally,
374 weakly reducing conditions (Eh value of -30 mV) are kept constant in the unaltered zone of
375 concrete.



376
 377 **Fig. 2.** Total aqueous species concentration (M) profiles at 100,000 years obtained with *iCP*, *ORCHESTRA*,
 378 *MIN3P*, *OGS-GEM*, and *CORE^{2D}*.
 379

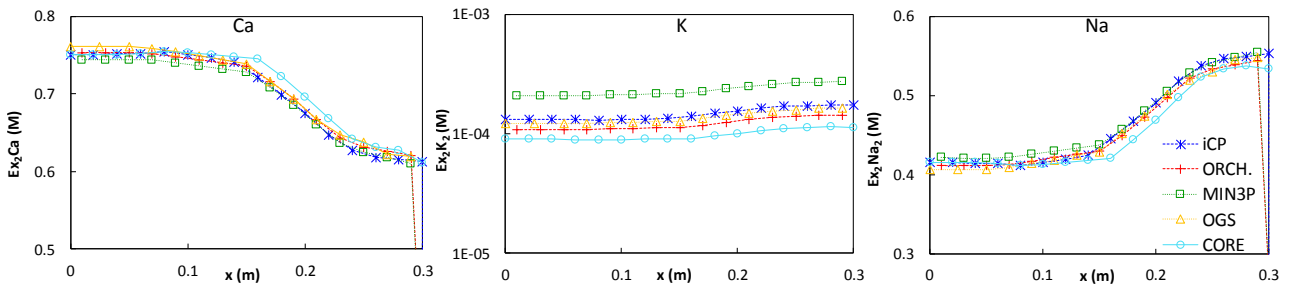


380
 381 **Fig. 3.** *pH*, *pe*, and ionic strength profiles at 100,000 years obtained with *iCP*, *ORCHESTRA*, *MIN3P*, *OGS-*
 382 *GEM*, and *CORE^{2D}*.

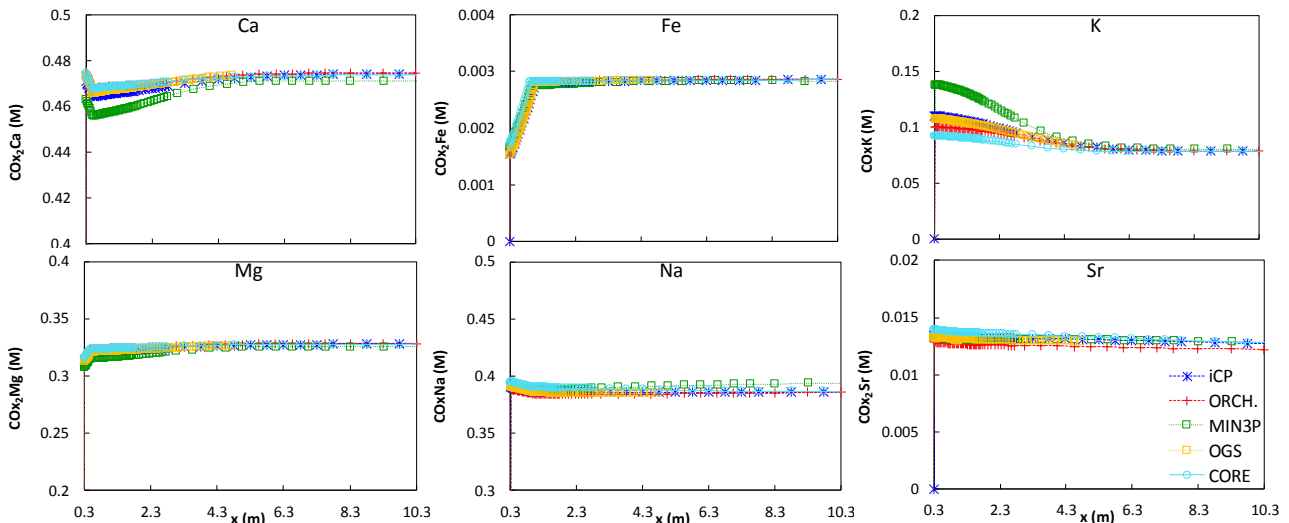
383 3.1.2 Cation exchanger composition

384 The exchanger composition of concrete is shown in Fig. 4. After 100,000 years, K^+ concentration in
 385 the concrete exchanger decreases from $5.52 \cdot 10^{-1}$ to $\sim 10^{-4}$ M due to alkali release to the claystone,
 386 resulting in an increase in Na^+ and Ca^{2+} (Fig. 4) with respect to the initial concentrations (Table 5).
 387 In the clay, the exchanger at 100,000 years shows a perturbation from the interaction with concrete
 388 even far from the interface (Fig. 5). The main cation exchange reaction in the clay is the increase in
 389 K^+ from concrete leaching at the expense of a local decrease in Ca^{2+} , Na^+ and Fe^{2+} . In turn, the

390 concentrations of all other cations show small changes. This is in agreement with the results of
 391 Marty et al. (2015) for a high-pH concrete – CO_x interface.
 392



393
 394 **Fig. 4.** Cation concentration (*M*) profiles in concrete exchanger at 100,000 years obtained with *iCP*,
 395 *ORCHESTRA*, *MIN3P*, *OGS-GEM*, and *CORE*^{2D}.
 396



397
 398 **Fig. 5.** Cation concentration (*M*) profiles in clay exchanger at 100,000 years obtained with *iCP*,
 399 *ORCHESTRA*, *MIN3P*, *OGS-GEM*, and *CORE*^{2D}.

400 3.1.3 Mineralogical changes

401 Fig. 6 and Fig. 7 present the distribution profiles of mineral phases after 100,000 years of
 402 interaction. The mineral degradation sequence is consistent with previous studies (e.g. Gaucher and
 403 Blanc, 2006; Savage, 2011; Marty et al., 2015). After 100,000 years, the extent of the alteration
 404 front is about 15 cm in concrete (characterized by the complete dissolution of the C-S-H gel) and 20
 405 cm in the claystone. In fact, there are two distinct zones in the CO_x domain: one strongly altered,
 406 whose extension can be characterized by complete dolomite depletion (~20cm), and another one,
 407 less disturbed, corresponding to minor mineral alteration, whose extension coincides with that of
 408 porosity changes (~50cm, Fig. 7).

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

412 Hydrotalcite and ettringite dissolve completely next to the interface and reprecipitate at the
 413 degradation front (Fig. 6). Brucite and Fe-Ca saponite are predicted to form in concrete as
 414 secondary phases, while quartz (as a result of C-S-H dissolution and consequent release of Si),
 415 magnetite, celestite and calcite precipitate at both sides of the interface. A clear geochemical
 416 disturbance is the formation of calcite in concrete and clay close to the interface. Calcite precipitates
 417 due to the changes porewater composition: in concrete, due to the ingress of dissolved carbonate

418 from the CO_x; in the claystone, due to the diffusion of dissolved calcium and hydroxyl ions from
419 concrete. Calcite is the main phase responsible for porosity clogging in concrete. Quartz filler (Fig.
420 6) and silica fume (not shown), the two kinetically-controlled mineral phases in concrete, partially
421 dissolve at around $x = 23$ cm.

422 Degradation in the claystone is characterized by the dolomite and siderite distribution profiles (Fig.
423 7). Dolomite is depleted in the first 0.2 m near the interface, and partially dissolves in the next 0.6
424 m. In turn, siderite completely dissolves in the first 1.1 m, favouring pyrite and magnetite
425 precipitation. Considering the C-S-H gel and dolomite as reference minerals for concrete and CO_x
426 degradation, respectively, the concrete degradation front extends over half of its thickness (0.15 m),
427 while in the clay the front is at 0.2 m after 100,000 years. Montmorillonite, illite, microcline, and
428 ripidolite concentrations (not shown) remain virtually unchanged after 100,000 years of interaction
429 with the low-pH concrete. This can be explained by their very slow dissolution kinetics at $\text{pH} <$
430 10.5.

431 The FRC case does not consider changes in transport properties (porosity and diffusion coefficient)
432 due to mineral volume changes. Thus, no coupling with transport properties or water mass is taken
433 into account. The evolution of porosity in this uncoupled case can still be computed from mineral
434 volume fractions as a post-process of the simulations. These results are presented in Fig. 7. On the
435 concrete side, porosity remains unaltered in the innermost 5 cm. As the degradation front
436 approaches, an increase in porosity is predicted, with values of ~ 0.10 between $x = 0.15$ m and $x =$
437 0.22 m. However, as geochemical interaction proceeds, porosity decreases mainly due to calcite and
438 brucite precipitation. Negative values are predicted near the interface, showing porosity clogging.
439 On the clay side, porosity decreases over 0.5 m from the interface, although noticeable changes are
440 only predicted for the closest 3 to 7 cm, with values down to 0.12 at the interface.

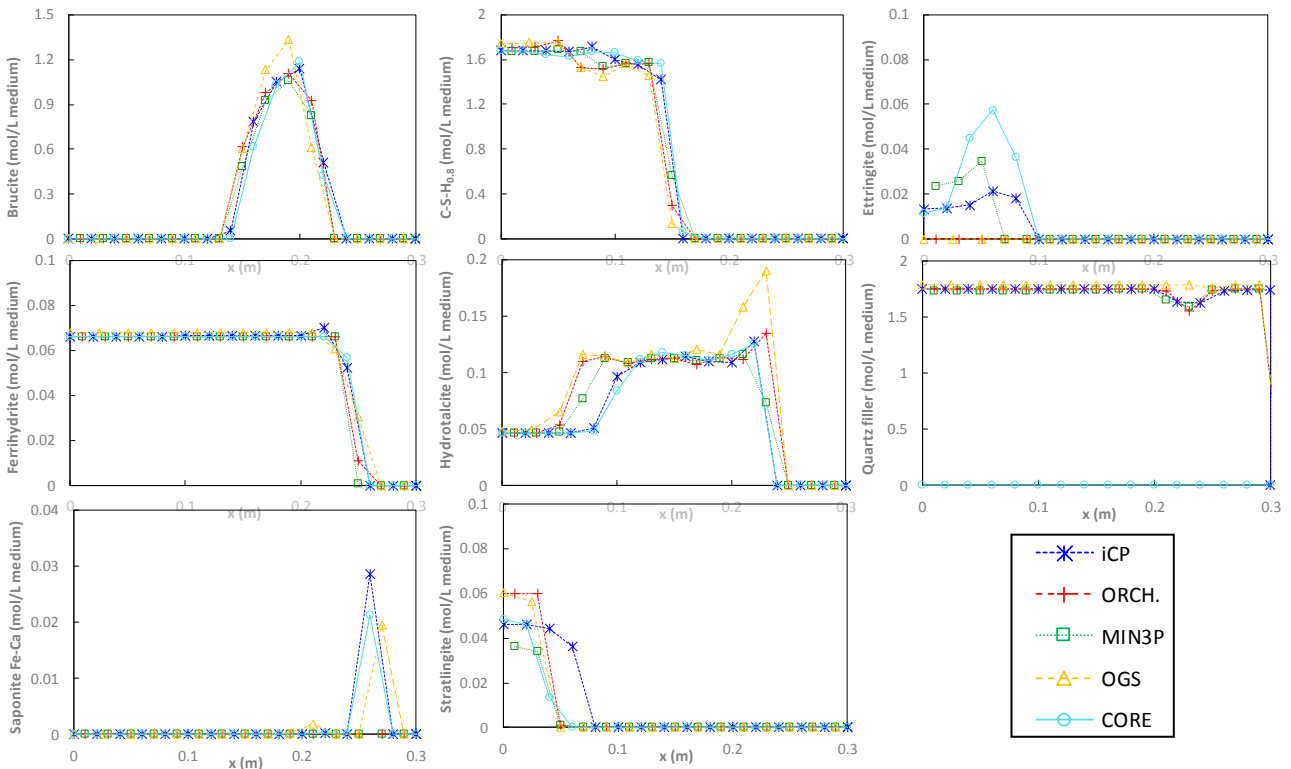
441 Overall, the results of the FRC are very similar to case P3 without kinetically-controlled minerals
442 (see Supplementary Material), supporting the comparison of the FRC results of iCP, ORCHESTRA
443 and MIN3P with the P3 results of CORE^{2D}. Including kinetically-controlled mineral phases is,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

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

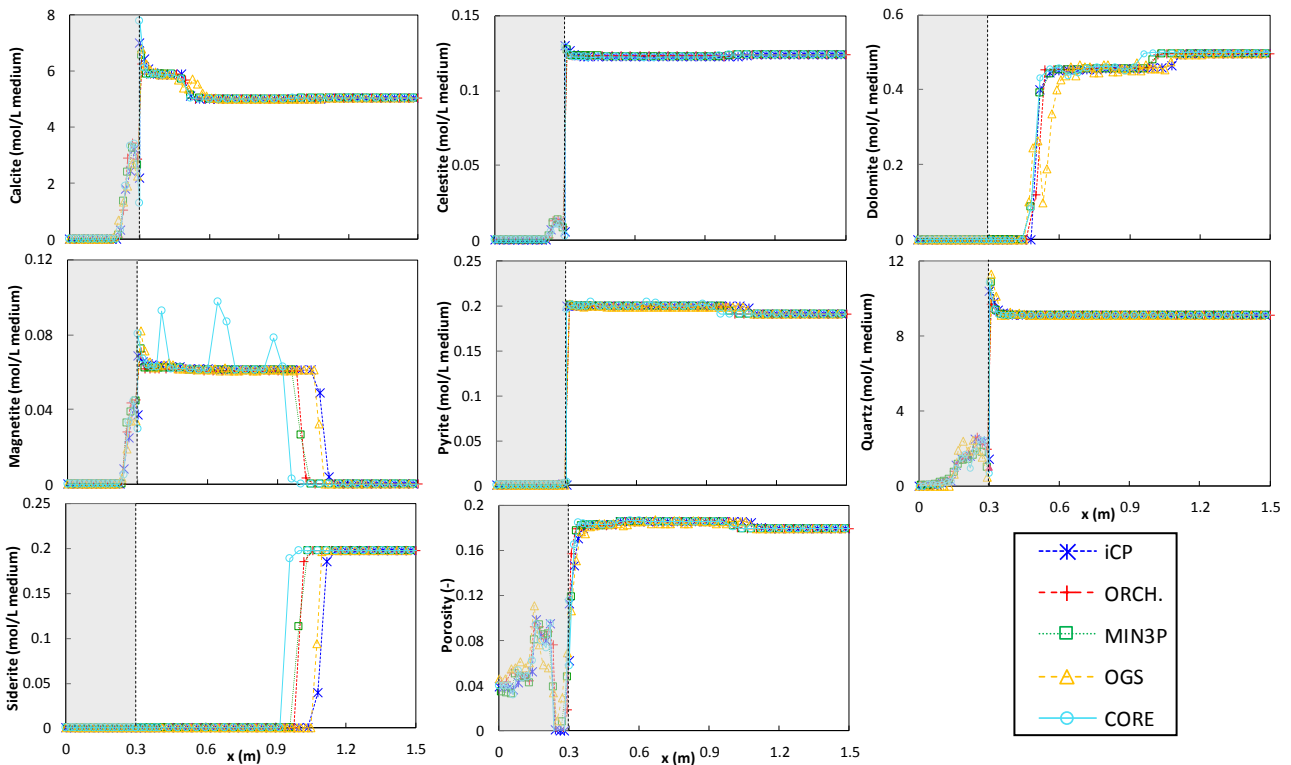
452 Some discrepancies between OGS-GEM and other reactive transport codes can be found, especially
453 in the cementitious system. This is due to the following differences in the implementation of this
454 code. First, ThermoChimie database is not available in a version that can be used in Gibbs Energy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

463 The results are consistent with previous studies addressing concrete/clay interaction (e.g. Gaucher et
464 al., 2006; Savage et al., 2007; Marty et al., 2014). Recent experimental results obtained within
465 CEBAMA (e.g. Cuevas et al., 2018; González-Santamaría et al., 2019; Mäder et al., 2017; Vhemas

466 et al., 2019c) also show qualitative agreement, e.g. in the decalcification of concrete, formation of
 467 calcite and Mg-rich phases near the interface.
 468



469
 470 **Fig. 6.** Mineral phase profiles (in mol/L medium) in the concrete domain at 100,000 years, obtained with
 471 *iCP*, *ORCHESTRA*, *MIN3P*, *OGS-GEM*, and *CORE^{2D}*.
 472

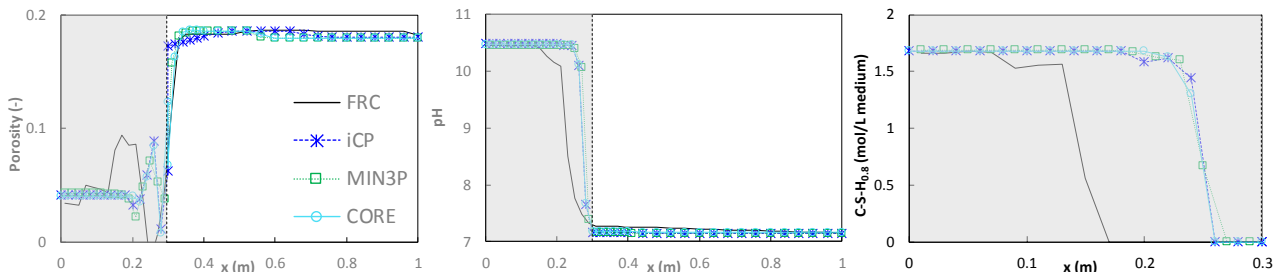


473
 474 **Fig. 7.** Mineral phases (in mol/L medium) and porosity (-) profiles in concrete and clay domains at 100,000
 475 years, obtained with *iCP*, *ORCHESTRA*, *MIN3P*, *OGS-GEM*, and *CORE^{2D}*.

476

477 3.2 Reduced concrete diffusion coefficient

478 A sensitivity case (S1) assuming a lower diffusion coefficient of concrete was simulated with
479 MIN3P, CORE^{2D} and iCP. A constant effective diffusion coefficient of $1 \cdot 10^{-13} \text{ m}^2/\text{s}$ was assumed
480 for the concrete barrier, which is one order of magnitude lower than for the FRC. Fig. 8 shows the
481 porosity, pH and mineralogical distribution profiles at 100,000 years obtained with the three codes.
482 Moreover, the results are compared with the FRC (iCP model results). The results of the three codes
483 for S1 case show a very good agreement. As expected, the level of alteration at a given time is
484 much more limited in this case compared to the FRC due to the reduced concrete diffusivity.
485 Porosity clogging is not predicted to occur even after 100,000 years, and changes are only
486 noticeable over a distance of 0.10 m from the interface. In the concrete domain, pH is lower than
487 10.5 only close to the interface (4 cm), where C-S-H gel dissolves. This contrasts with the 15 cm
488 degradation front of the FRC. Overall, the degradation sequence is qualitatively consistent with that
489 of the FRC but occurs over a much longer time scale.



490

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

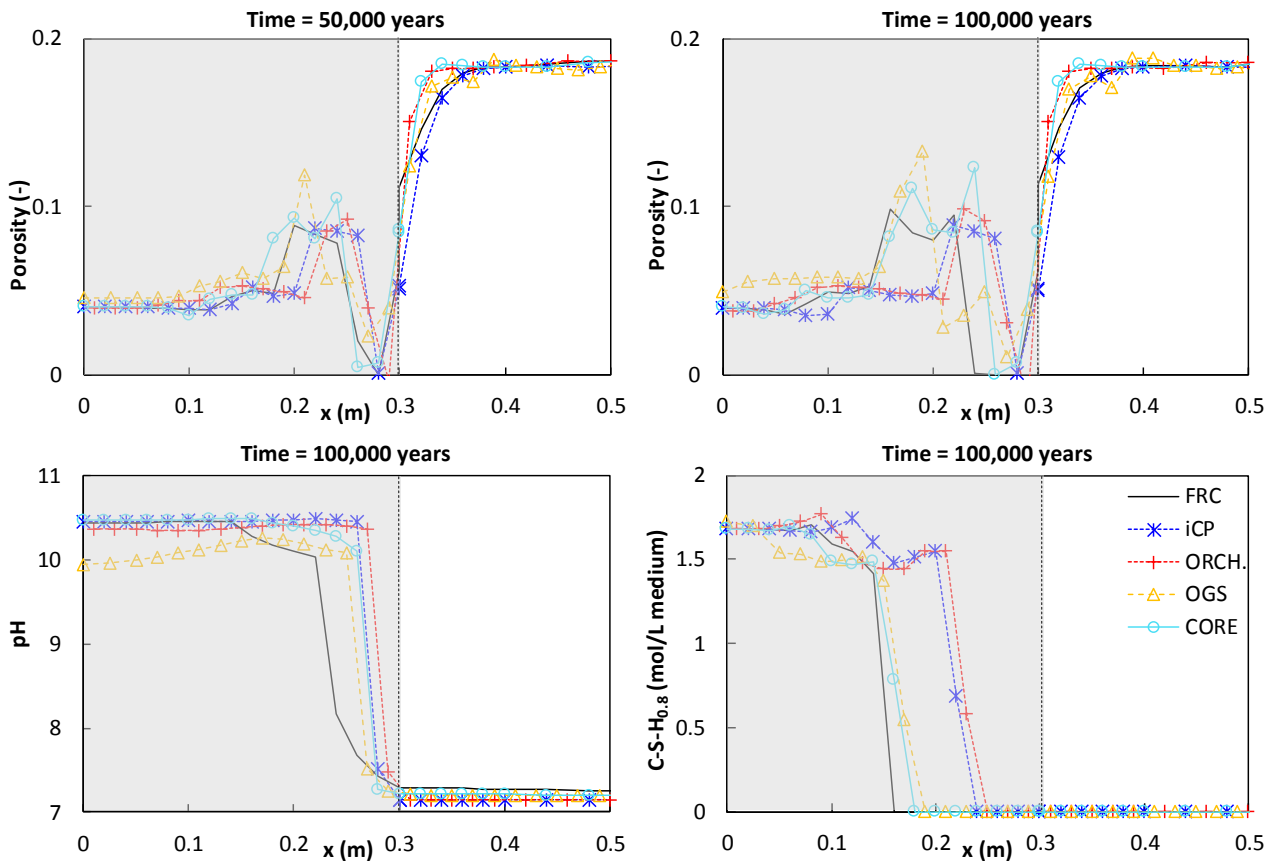
493 3.3 Coupling mineral volume changes with transport properties

494 This sensitivity case (S2) considers the effect of mineral volume changes due to
495 precipitation/dissolution processes on the transport properties, i.e. porosity and diffusion coefficient.
496 This coupling has been previously studied for simple geochemical systems by Xie et al. (2015) and
497 Poonosamy et al. (2018). The effective diffusion coefficient was chosen to depend linearly on
498 porosity changes, see equations (2-4) and (2-5). Other forms of couplings between porosity and
499 diffusivity were simulated as part of this study and the results can be found in Idiart and Laviña
500 (2019). A minimum porosity value of 0.001 is assumed to avoid complete clogging, corresponding
501 to a minimum effective diffusion coefficient in the low-pH concrete of $2.5 \cdot 10^{-14} \text{ m}^2/\text{s}$. Four codes
502 were used in this case: iCP, ORCHESTRA, OGS-GEM and CORE^{2D}. MIN3P also includes this
503 porosity coupling feature but could not be used for S2 due to a lack of resources. The differences
504 between these models lie firstly, in the description of mineral reactivity. Kinetically-controlled
505 mineral phases were not included in the CORE^{2D} model. However, as shown for the FRC model
506 setup, only a very small impact is expected due to this simplification. Secondly, the OGS-GEM
507 model considers a fully coupled update of porosity, based on the actual volumetric fluid to solid
508 ratio calculated by the chemical solver.

509 Fig. 9 presents the results of the four simulations together with the FRC results (iCP model results)
510 for comparison purposes. Two variables are used as indicators of the level of alteration: porosity,
511 which reflects the mineral volume changes, and pH. The mineralogical evolution sequence is
512 similar to the FRC and is not repeated here. Calcite precipitation (not shown) near the interface is
513 the main process responsible for the decrease of porosity to the residual value of 0.001. Porosity
514 clogging is predicted after 50,000 years in iCP and ORCHESTRA (Fig. 9), virtually stopping

515 further geochemical interaction. Concrete degrades to a less extent compared to the FRC, even
 516 before porosity clogging. Porosity decreases at a relatively slower rate in CORE^{2D}, although
 517 differences are not significant. The reasons for this discrepancy are still not fully clear.

518 The temporal porosity changes calculated by OGS-GEM are distinctively different from the other
 519 codes, since no porosity clogging is predicted after 100,000 years. This could be due to the inherent
 520 difference in the porosity update formulation based on the fluid to solid ratio. As porosity decreases
 521 due to mineral precipitation, the volume of reacting fluid also decreases. Thus, the amount of
 522 minerals that can precipitate in the next time step also decreases. As a result, the clogging of
 523 porosity is delayed. Changes in pH (Fig. 9) are more limited than in the FRC after 100,000 years
 524 due to porosity clogging. On the COx domain, pH remains below 7.2 even at the interface. In
 525 concrete, dissolution of C-S-H is also more limited in this case, with the degradation front at 5 cm
 526 from the interface in iCP and ORCHESTRA. In turn, CORE^{2D} and OGS-GEM results show a much
 527 smaller impact compared to the FRC results (Fig. 9), which is due to the relatively lower rate of
 528 porosity decrease. The reasons for the lower pH in part of the concrete domain predicted by OGS-
 529 GEM are not completely understood but could be related to the description of cation exchange on
 530 C-S-H in this code.



531
 532 **Fig. 9.** Distribution profiles of porosity (-) at 50,000 and 100,000 years, and of pH and C-S-H gel with Ca/Si
 533 = 0.8 (in mol/L medium) at 100,000 years. Results for FRC (iCP results) and models coupling porosity with
 534 effective diffusion coefficient using iCP, ORCHESTRA, OGS-GEM, and CORE^{2D}.

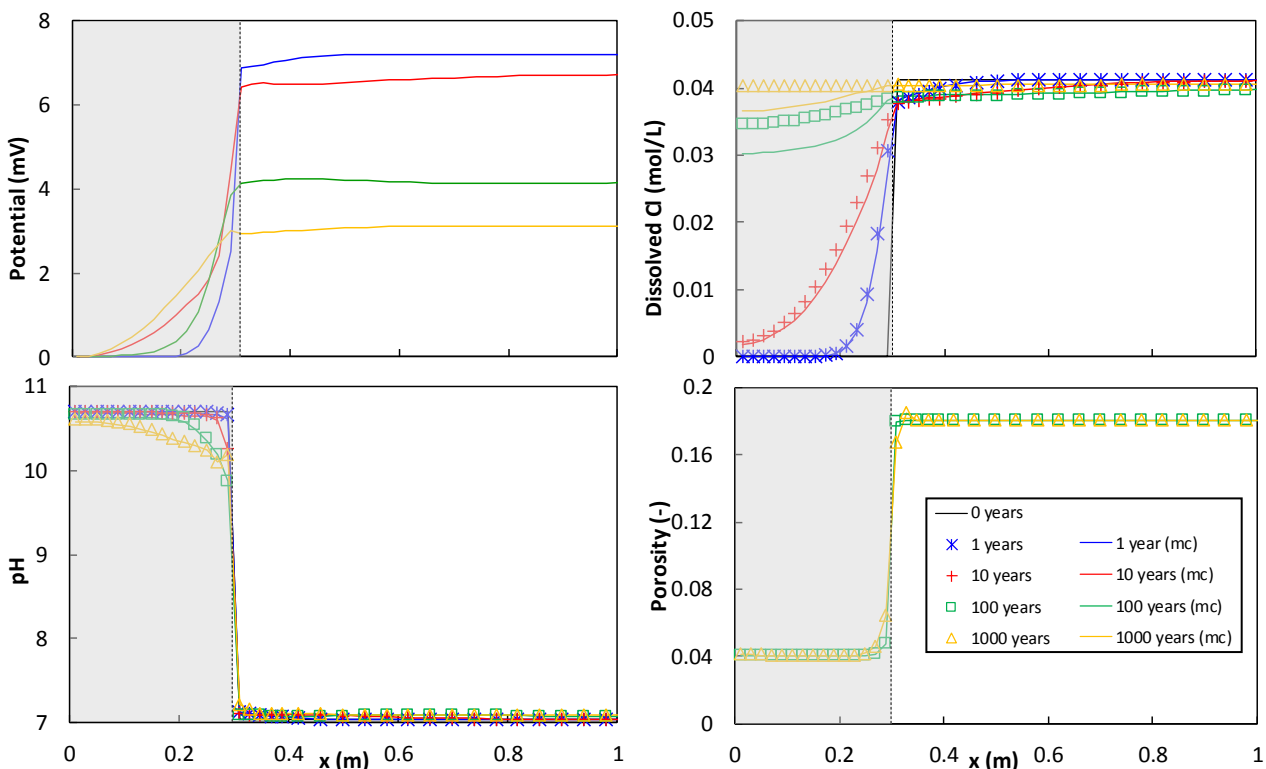
535 3.4 Electrochemical coupling

536 This sensitivity case (S3) was performed with ORCHESTRA. Multicomponent diffusion can have
 537 noticeable impacts in systems containing ions with very different diffusion coefficients. For
 538 instance, cementitious systems with hyperalkaline porewater contain large concentrations of OH⁻

539 ions which have a higher diffusion coefficient than other ions. The faster OH^- ions are likely to
540 induce a local potential gradient which in turn affects the diffusion of other ions.

541 The effect of multicomponent diffusion in the present study can be observed as the development of
542 an electric potential gradient over the cement-clay interface (Fig. 10). The resulting potential
543 difference (ca. 7 mV after 1 year) leads to a reduction of the diffusion rate of OH^- from concrete
544 (and all other accompanying anions) and enhances transport of anions from the claystone towards
545 the concrete. For cations, the potential gradient has the opposite effect. To illustrate this, Fig. 10
546 shows the enhanced transport from the clay towards concrete of Cl^- , a non-reactive anion in this
547 case, for which the effect of the induced potential gradient on diffusion is most clearly observed
548 when comparing the same simulation with and without the electric potential gradient effect.
549 However, for reactive substances, such as protons (or pH) the effect is much smaller, as shown in
550 Fig. 10. For ions that are in equilibrium with solid phases, concentration gradients are constrained
551 with mineral precipitation/dissolution fronts, so that differences between their aqueous
552 concentrations using both diffusion models are negligible.

553 The results show furthermore that the electric potential gradient decreases over time because of the
554 lowering of concentration gradients. This implies that the effect of electric potentials on diffusion
555 will also decrease over time, which is illustrated by the small differences between the model results
556 with and without taking into account potential/charge effects. Although the effect of the
557 electrochemical coupling is clearly visible, the impact of the evolving electric potential gradients on
558 the effective ion diffusion rates is probably small in comparison with other uncertainties. Finally,
559 results in terms of porosity distribution show that the effect of the potential gradient on mineral
560 precipitation and dissolution is negligible (Fig. 10), at least after 1,000 years.



561
562 **Fig. 10.** Electric potential (mV), dissolved chloride (mol/L), pH, and porosity distribution profiles at
563 0, 1, 10, 100 and 1,000 years. Results for ORCHESTRA with (mc) and without accounting for
564 potential/charge effects.

565 **4 Conclusions**

566 The results of the presented modelling study show that different reactive transport codes can be
567 used to quantify the geochemical interaction between a low-pH concrete and a claystone to
568 essentially obtain the same results, despite of inherent differences between modelling approaches.
569 In all modelled cases, the differences observed between models do not have significant
570 consequences on the description of the governing processes and system evolution. This builds
571 confidence in the application of reactive transport codes used within the CEBAMA project to
572 simulate the long-term behaviour of low-pH cementitious systems to be used for disposal of
573 radioactive waste, which is essential for the safety cases (Duro et al., 2019). The impact of key
574 parameters, such as the diffusion coefficient of concrete, electrochemical couplings, and especially
575 the coupling between geochemical and transport parameters, has also been assessed. The impact of
576 including or not the slow kinetics of dissolution of the claystone minerals is shown to be negligible
577 in the studied system. This is in part due to the low-pH nature of the cementitious system, but also
578 to the relatively small concrete volume with respect to the clay rock volume considered in the
579 models. As a general conclusion, the modelling results of sensitivity and preliminary cases show
580 that the system is much more sensitive to changes in the model setup (transport parameters,
581 couplings) than to the different modelling tools used in each case.

582

583 A subject for future research concerns the simultaneous modelling of cement hydration with
584 reactive transport processes and water transport at the concrete/clay interface in a partially saturated
585 system. This may be important for concrete mixes with low water-to-binder ratio, as is the case of
586 the studied system. The role of solid solutions to represent cement hydrates, such as C-S-H with
587 lower Ca:Si ratio than 0.8, C-A-S-H, or M-S-H could also be explored. A last issue is the
588 assessment of more realistic couplings between mineral volume changes and their impact on the
589 microstructure and transport properties.

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599 **5 Appendix A – modelling the hydration of low-pH concrete**

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

607 Cement hydration modelling was performed with PHREEQC v3 (Parkhurst and Appelo, 2013)
608 using the thermodynamic database ThermoChimie v9b0 (Giffaut et al., 2014), similar to the full
609 reference case. Note that the lowest Ca:Si ratio of the C-S-H model is 0.8. Data of the composition

610 of the raw materials available from CEBAMA (Vehmas et al., 2017, 2019b) and from literature
 611 (SKB, 2014) were used as input to the model. The composition of the CEBAMA reference concrete
 612 mix is detailed in Table 9. More details can be found in Vehmas et al. (2017, 2019a, 2019c). The
 613 stoichiometry of the clinker phases (alite, belite, aluminite, and ferrite), silica fume (SF) and Blast
 614 Furnace Slag (BFS) are based on their experimentally-determined oxide composition (Table 10).

615 **Table 9.** Composition of CEBAMA reference concrete mix. Data from Vehmas et al. (2016, 2018, 2019c).
 616 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

617

618 **Table 10.** Oxide composition of the components of the CEBAMA reference mix used in the model.

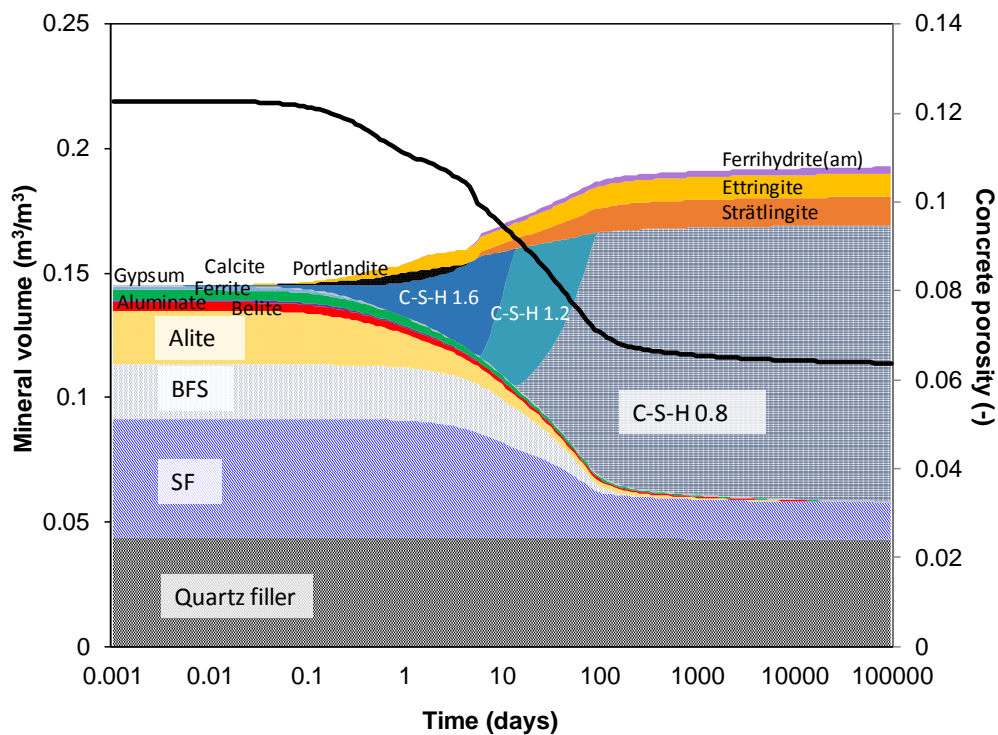
Oxide	Mw (g/mol)	CEM I ^a (wt. %)	SF ^b (wt. %)	BFS ^c (wt. %)
CaO	56.08	64	1.46	41.5
SiO ₂	60.08	21	93.1	32.8
Al ₂ O ₃	101.96	3.5	1.44	10.6
SO ₃	80.06	2.2	0.47	1.4
MgO	40.30	0.7	0.88	8.29
Fe ₂ O ₃	159.69	4.6	0.91	0.81
K ₂ O	94.20	0.62	1.73	0.62
Na ₂ O	61.98	0.07	-	0.62
CO ₂	44.01	2.2	-	-
MnO	70.94	-	-	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 (Anl ggningscement) (SKB, 2014). ^bSF from Vehmas et al. (2019), ^cBFS measured at VTT (Finland).

619 Cement hydration is assumed to occur under atmospheric conditions at 25°C and 100% relative
 620 humidity (i.e. unlimited supply of water for hydration). Redox reactions are not considered in the
 621 simulation. Empirical expressions of dissolution rates of clinker phases follow from Parrot and
 622 Killoh (1984). The dissolution rate of the BFS is taken from Sch ler et al. (2017), while those of SF
 623 and quartz filler correspond to that of quartz from Palandri and Kharaka (2004). The latter is based
 624 on a pH-dependent transition-state-theory formulation. The specific surface areas of the BFS, SF,
 625 and quartz filler are either specified directly by the providers or derived from their particle size

626 distribution. Apart from these kinetically-controlled reactions, all other chemical reactions are
 627 considered under thermodynamic equilibrium. The aggregates and superplasticizer are considered
 628 as chemically inert. The alkali uptake in C-S-H phases (Na^+ and K^+) is considered using a cation
 629 exchange model based on Missana et al. (2017), with a cation exchange capacity (CEC) that
 630 depends on the concentration of C-S-H phases and their Ca/Si ratio (Hong and Glasser, 1999). On
 631 the other hand, aluminium and magnesium uptake in C-S-H is not considered in the simulations.
 632 Finally, calcium aluminosilicate hydrate (C-A-S-H) or magnesium silicate hydrate (M-S-H) phases
 633 are not included in the thermodynamic database.

634 The dissolution of the clinker, binder components, and quartz filler are shown as a function of time
 635 in Fig. 11, together with the precipitation of cement hydrates, in terms of volume fraction (m^3 per
 636 m^3 of concrete). An almost complete dissolution of the clinker phases and BFS occurs within the
 637 first 100 days. On the other hand, SF rapidly dissolves at the beginning, but after 100 days it slows
 638 down significantly. This is due to the drop in pH of the pore solution until reaching a constant value
 639 in equilibrium with C-S-H phases that form with a Ca:Si ratio of 0.8. Finally, dissolution of quartz
 640 filler is very limited, due to the lower surface area compared to silica fume (see Table 2). The final
 641 phase assemblage is composed of unhydrated SF, C-S-H with Ca:Si ratio of 0.8, strätlingite (Al-
 642 bearing phase), ettringite (sulphate-bearing phase), and ferrihydrite (Fe-bearing phase). The
 643 minerals determined experimentally in the hydrated system are unreacted SF and quartz, C-S-H
 644 with a Ca:Si ratio between 0.5 and 0.7, C-A-S-H phases with an Al:Si ratio of 0.05, ettringite, and
 645 small amounts of BFS and clinker phases, while absence of portlandite was experimentally
 646 confirmed (Vehmas et al., 2019c).

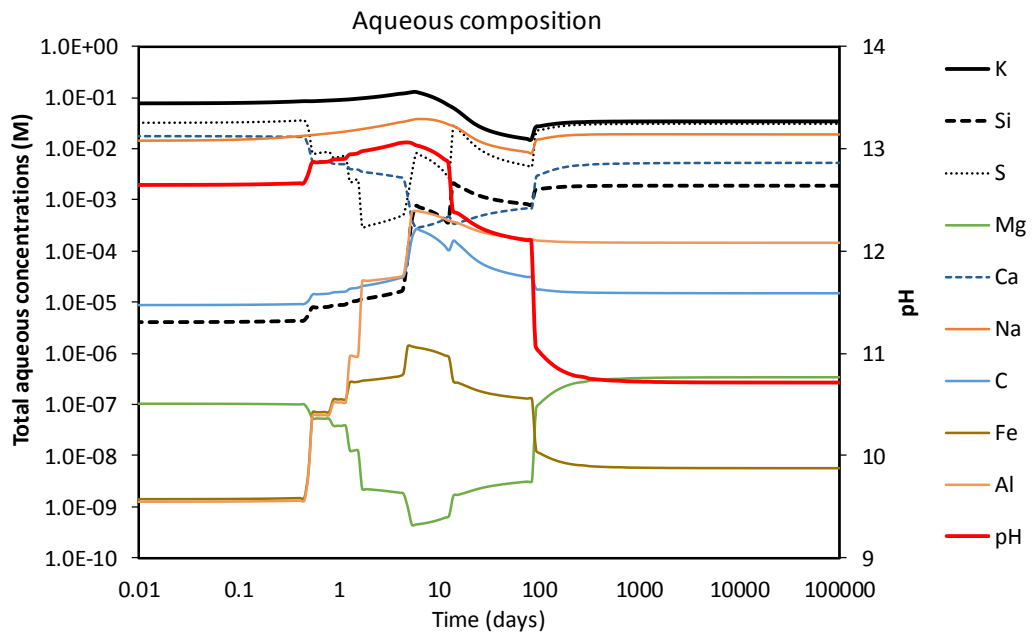


647
 648 **Fig. 11.** Dissolution of the clinker and binder phases, precipitation of main cement hydrates (volume fraction
 649 in %) and concrete porosity (-) as a function of hydration time (in days). The black solid line corresponds to
 650 porosity.

651 The evolution of porewater composition and pH is shown in Fig. 12. The pH of the pore solution
 652 fluctuates between 12.5 and 13 at hydration times < 10 days. This short period is followed by large
 653 variations in pH until reaching a value of ~ 10.7 at long hydration times. The evolution of the Ca:Si
 654 ratio of the C-S-H has a large impact on the pH of the pore solution as portlandite is already

655 dissolved after 5 days. The two abrupt changes in pH at 10-12 days and 80-100 days correspond to
 656 changes in the Ca:Si ratio of C-S-H, from 1.6 to 1.2, and from 1.2 to 0.8. The values obtained
 657 experimentally using the ex-situ leaching method (Alonso et al., 2012) are slightly higher beyond
 658 100 days of hydration, between 11.3 and 11.7 (Vehmas et al., 2019c).

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



666
 667 **Fig. 12.** Evolution of aqueous composition and pH as a function of hydration time.

668 The total porosity, denoted as ϕ_{tot} and calculated with equation (A.1), is shown as a function of
 669 hydration time in Fig. 11. The value of total porosity after long hydration times is around 0.063.
 670 This value is relatively larger than the value obtained experimentally using mercury intrusion
 671 porosimetry (MIP), i.e. 0.038 (Vehmas et al., 2019b, 2019c) and smaller than the values measured
 672 with the kerosene method (0.125) or calculated considering the grain density (0.128) (Vehmas et al.
 673 2019c).

674
$$\phi_{tot} = \frac{V_{b,0} + V_{w,0} - V_{b,t} - V_{hyd,t}}{V_{b,0} + V_{w,0} + V_{aggr} + V_{sp}} \quad (A.1)$$

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

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923 7 Supplementary material

924 7.1 Thermodynamic data of minerals

925 **Table 11.** Thermodynamic data from ThermoChimie database (Giffaut et al., 2014) and molar volumes (M_v)
926 of minerals (from Thermoddem database, Blanc et al., 2012).

Mineral phases	M_v (cm^3/mol)	Formula	Log K
CSH 0.8	59.29	$\text{Ca}_{0.8}\text{SiO}_{2.8}:1.54\text{H}_2\text{O} = 0.8\text{Ca}^{+2} - 1.6\text{H}^+ + 1\text{H}_4(\text{SiO}_4) + 0.34\text{H}_2\text{O}$	11.05
Calcite	36.93	$\text{CaCO}_3 = 1\text{Ca}^{+2} + 1\text{CO}_3^{-2}$	-8.48
Ettringite	710.32	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}:26\text{H}_2\text{O} = 6\text{Ca}^{+2} + 2\text{Al}^{+3} - 12\text{H}^+ + 3\text{SO}_4^{-2} + 38\text{H}_2\text{O}$	56.97
Ferrihydrite(am)	34.36	$\text{Fe}(\text{OH})_3 = 1\text{Fe}^{+3} - 3\text{H}^+ + 3\text{H}_2\text{O}$	2.54
Hydrotalcite	227.36	$\text{Mg}_4\text{Al}_2(\text{OH})_{14}:3\text{H}_2\text{O} = 4\text{Mg}^{+2} + 2\text{Al}^{+3} - 14\text{H}^+ + 17\text{H}_2\text{O}$	73.74
Magnetite	44.52	$\text{Fe}_3\text{O}_4 = 2\text{Fe}^{+3} + 1\text{Fe}^{+2} - 8\text{H}^+ + 4\text{H}_2\text{O}$	10.41
Stratlingite	215.63	$\text{Ca}_2\text{Al}_2\text{SiO}_3(\text{OH})_8:4\text{H}_2\text{O} = 2\text{Ca}^{+2} + 2\text{Al}^{+3} - 10\text{H}^+ + 1\text{H}_4(\text{SiO}_4) + 11\text{H}_2\text{O}$	49.66
SilicaFume	28.06		-
Quartz filler	22.69	$\text{SiO}_2 = 1\text{H}_4(\text{SiO}_4) - 2\text{H}_2\text{O}$	-3.74
Quartz	22.69	$\text{SiO}_2 = 1\text{H}_4(\text{SiO}_4) - 2\text{H}_2\text{O}$	-3.74
Celestite	46.25	$\text{Sr}(\text{SO}_4) = 1\text{Sr}^{+2} + 1\text{SO}_4^{-2}$	-6.62
Dolomite	64.3	$\text{CaMg}(\text{CO}_3)_2 = 1\text{Ca}^{+2} + 1\text{Mg}^{+2} + 2\text{CO}_3^{-2}$	-17.12
Pyrite	23.94	$\text{FeS}_2 = 1\text{Fe}^{+2} + 2\text{HS}^- - 1\text{H}_2\text{O} + 0.5\text{O}_2$	-58.78
Siderite	29.38	$\text{Fe}(\text{CO}_3) = 1\text{Fe}^{+2} + 1\text{CO}_3^{-2}$	-10.80
Illite_Imt-2	139.18	$(\text{Na}_{0.044}\text{K}_{0.762})(\text{Si}_{3.387}\text{Al}_{0.613})(\text{Al}_{1.427}\text{Fe}_{0.292}\text{Fe}_{0.084}\text{Mg}_{0.241})\text{O}_{10}(\text{OH})_2 = 0.241\text{Mg}^{+2} + 0.762\text{K}^+ + 0.044\text{Na}^+ + 0.292\text{Fe}^{+3} + 0.084\text{Fe}^{+2} + 2.040\text{Al}^{+3} - 8.452\text{H}^+ + 3.387\text{H}_4(\text{SiO}_4) - 1.548\text{H}_2\text{O}$	11.54
Montmorillonite-BCCa	132.48	$\text{Ca}_{0.17}\text{Mg}_{0.34}\text{Al}_{1.66}\text{Si}_4\text{O}_{10}(\text{OH})_2 = 0.17\text{Ca}^{+2} + 0.34\text{Mg}^{+2} + 1.66\text{Al}^{+3} - 6\text{H}^+ + 4\text{H}_4(\text{SiO}_4) - 4\text{H}_2\text{O}$	4.20
Microcline	108.74	$\text{KAlSi}_3\text{O}_8 = 1\text{K}^+ + 1\text{Al}^{+3} - 4\text{H}^+ + 3\text{H}_4(\text{SiO}_4) - 4\text{H}_2\text{O}$	0.05
Ripidolite_Cca-2	211.92	$(\text{Mg}_{2.964}\text{Fe}_{1.712}\text{Fe}_{0.215}\text{Al}_{1.116}\text{Ca}_{0.011})(\text{Si}_{2.633}\text{Al}_{1.367})\text{O}_{10}(\text{OH})_8 = 0.011\text{Ca}^{+2} + 2.964\text{Mg}^{+2} + 0.215\text{Fe}^{+3} + 1.712\text{Fe}^{+2} + 2.483\text{Al}^{+3} - 17.468\text{H}^+ + 2.633\text{H}_4(\text{SiO}_4) + 7.468\text{H}_2\text{O}$	61.35
SiO ₂ (am)	29.00	$\text{SiO}_2 = 1\text{H}_4(\text{SiO}_4) - 2\text{H}_2\text{O}$	-2.71
Brucite	24.63	$\text{Mg}(\text{OH})_2 = 1\text{Mg}^{+2} - 2\text{H}^+ + 2\text{H}_2\text{O}$	17.10

CSH1.6	84.68	$\text{Ca}_{1.6}\text{SiO}_{3.6} \cdot 2.58\text{H}_2\text{O} = 1.6\text{Ca}^{+2} - 3.2\text{H}^+ + 1 \text{H}_4(\text{SiO}_4) + 2.18\text{H}_2\text{O}$	28.00
CSH1.2	71.95	$\text{Ca}_{1.2}\text{SiO}_{3.2} \cdot 2.06\text{H}_2\text{O} = 1.2\text{Ca}^{+2} - 2.4\text{H}^+ + 1 \text{H}_4(\text{SiO}_4) + 1.26\text{H}_2\text{O}$	19.30
C3AH6	149.52	$\text{Ca}_3\text{Al}_2(\text{OH})_{12} = 3 \text{Ca}^{+2} + 2 \text{Al}^{+3} - 12 \text{H}^+ + 12 \text{H}_2\text{O}$	80.32
C3FH6	154.50	$\text{Ca}_3\text{Fe}_2(\text{OH})_{12} = 3 \text{Ca}^{+2} + 2 \text{Fe}^{+3} - 12 \text{H}^+ + 12 \text{H}_2\text{O}$	72.39
C4AH13	269.20	$\text{Ca}_4\text{Al}_2(\text{OH})_{14} \cdot 6\text{H}_2\text{O} = 4 \text{Ca}^{+2} + 2 \text{Al}^{+3} - 14 \text{H}^+ + 20 \text{H}_2\text{O}$	103.65
C4FH13	274.4	$\text{Ca}_4\text{Fe}_2(\text{OH})_{14} \cdot 6\text{H}_2\text{O} = 4 \text{Ca}^{+2} + 2 \text{Fe}^{+3} - 14 \text{H}^+ + 20 \text{H}_2\text{O}$	95.16
Ettringite-Fe	711.80	$\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} = 6 \text{Ca}^{+2} + 2 \text{Fe}^{+3} - 12 \text{H}^+ + 3 \text{SO}_4^{-2} + 38 \text{H}_2\text{O}$	54.55
Gypsum	74.69	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 1 \text{Ca}^{+2} + 1 \text{SO}_4^{-2} + 2 \text{H}_2\text{O}$	-4.61
Hemicarboaluminate	569.02	$\text{Ca}_6\text{O}_6 \cdot \text{Al}_4\text{O}_6 \cdot \text{CaCO}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 21\text{H}_2\text{O} = 8 \text{Ca}^{+2} + 4 \text{Al}^{+3} - 26 \text{H}^+ + 1 \text{CO}_3^{-2} + 35 \text{H}_2\text{O}$	173.20
Hydrotalcite-CO ₃	231.44	$\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O} = 4 \text{Mg}^{+2} + 2 \text{Al}^{+3} - 12 \text{H}^+ + 1 \text{CO}_3^{-2} + 14 \text{H}_2\text{O}$	50.86
Fe(OH) ₂ (cr)	24.48	$\text{Fe}(\text{OH})_2 = 1 \text{Fe}^{+2} - 2 \text{H}^+ + 2 \text{H}_2\text{O}$	12.76
Monocarboaluminate	261.96	$(\text{CaO})_3\text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 10.68\text{H}_2\text{O} = 4 \text{Ca}^{+2} + 2 \text{Al}^{+3} - 12 \text{H}^+ + 1 \text{CO}_3^{-2} + 16.68\text{H}_2\text{O}$	70.30
Monosulfate-Fe	316.06	$\text{Ca}_4\text{Fe}_2(\text{SO}_4)(\text{OH})_{12} \cdot 6\text{H}_2\text{O} = 4 \text{Ca}^{+2} + 2 \text{Fe}^{+3} - 12 \text{H}^+ + 1 \text{SO}_4^{-2} + 18 \text{H}_2\text{O}$	66.05
Monosulfoaluminate	311.26	$\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 6\text{H}_2\text{O} = 4 \text{Ca}^{+2} + 2 \text{Al}^{+3} - 12 \text{H}^+ + 1 \text{SO}_4^{-2} + 18 \text{H}_2\text{O}$	73.07
Portlandite	33.06	$\text{Ca}(\text{OH})_2 = 1 \text{Ca}^{+2} - 2 \text{H}^+ + 2 \text{H}_2\text{O}$	22.81
Pyrrhotite	18.20	$\text{Fe}_{0.87}\text{S} = 0.87\text{Fe}^{+2} - 0.74\text{H}^+ + 1 \text{HS}^- - 0.13\text{H}_2\text{O} + 0.065\text{O}_2$	-11.18
Saponite-FeCa	139.96	$\text{Ca}_{0.17}\text{Mg}_2\text{FeAl}_{0.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2 = 0.17\text{Ca}^{+2} + 2 \text{Mg}^{+2} + 1 \text{Fe}^{+2} + 0.34\text{Al}^{+3} - 7.36\text{H}^+ + 3.66\text{H}_4(\text{SiO}_4) - 2.64\text{H}_2\text{O}$	26.55
Syngenite	151.63	$\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} = 1 \text{Ca}^{+2} + 2 \text{K}^+ + 2 \text{SO}_4^{-2} + 6 \text{H}_2\text{O}$	-7.45

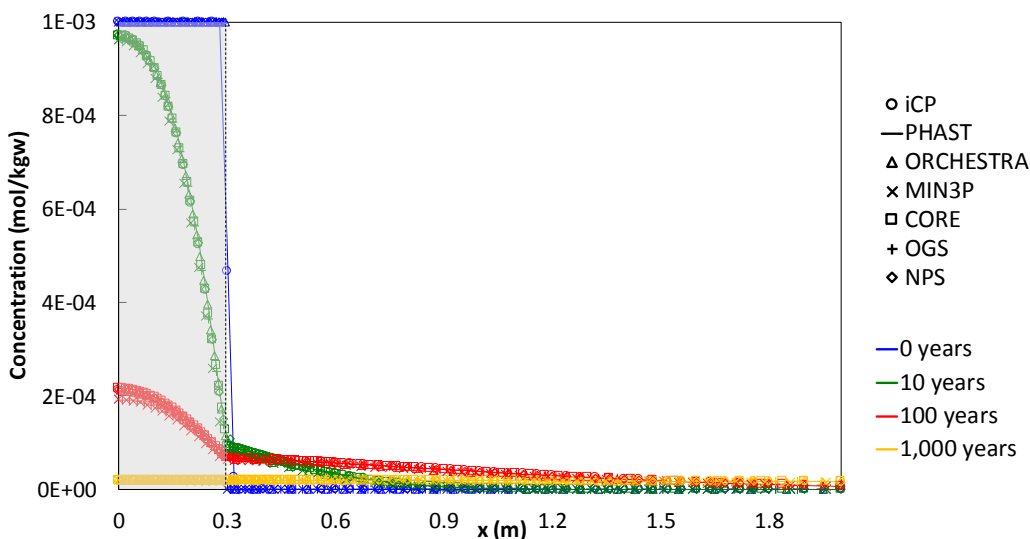
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928 7.2 Description and results of preliminary cases

929 7.2.1 P1: Tracer diffusion (without considering geochemistry)

930 Case P1 studied the diffusion of a non-reactive and uncharged tracer from the concrete domain
 931 towards the clay host rock in the setup presented in Fig. 1 and Table 1 and the same spatial
 932 discretization than the FRC. The initial tracer concentration in the concrete and claystone pore
 933 solutions is 1 and 0 mM, respectively (Table 4). A closed boundary condition is imposed on the left
 934 and a tracer concentration of 0 on the right. In addition, two alternative reactive transport codes
 935 were included in the comparison, namely PHAST (Parkhurst et al., 2010) and NPS (Damiani et al.,
 936 2019).

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



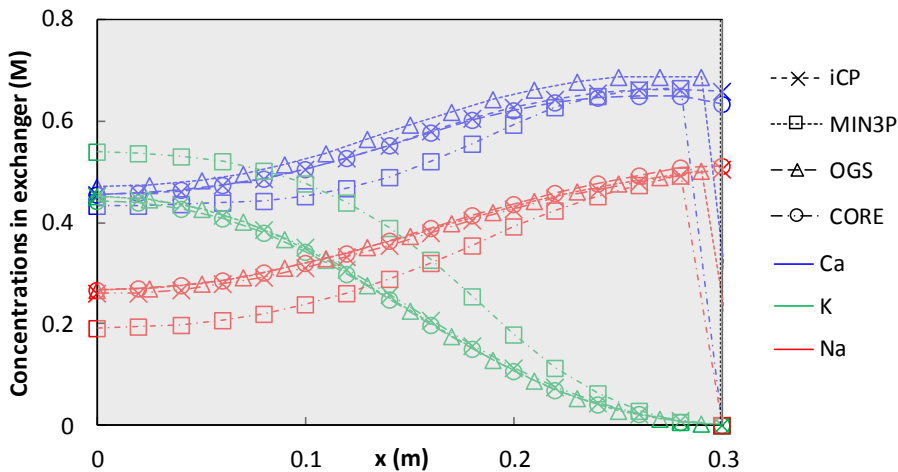
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942 **Fig. 13.** Comparison of tracer concentration profiles over 2.1 m (in mol/kg water) at 0, 10, 100 and 1,000
 943 years obtained with iCP, PHAST, ORCHESTRA, CORE^{2D}, MIN3P, OGS-GEM and NPS.

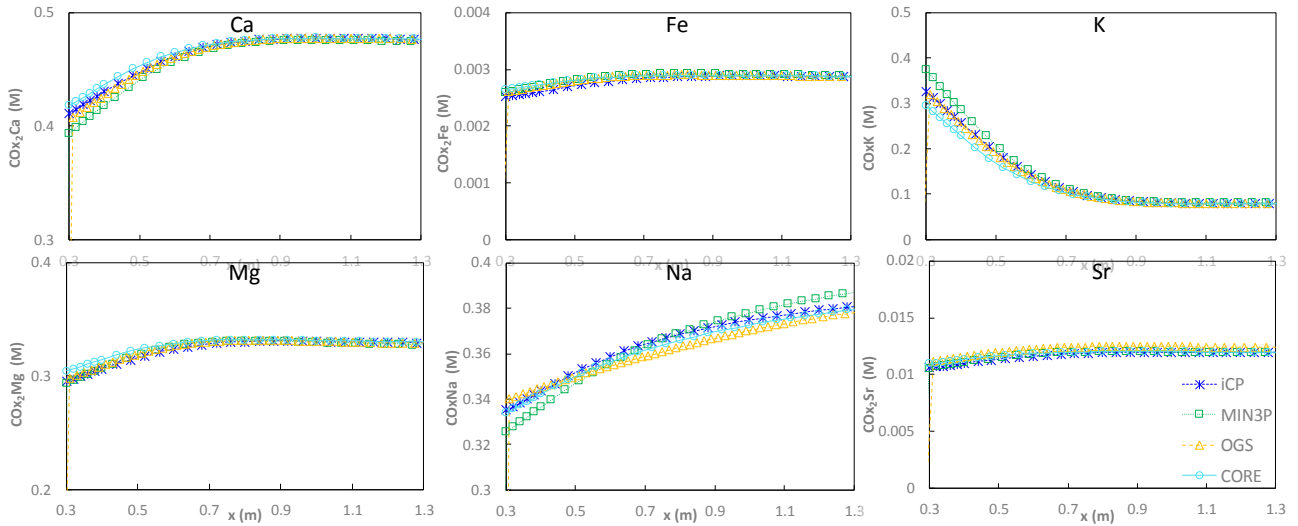
944 **7.2.2 P2: Aqueous species and cation exchange**

945 Case P2 is equivalent to the FRC but without any primary or secondary minerals, i.e. only the
 946 aqueous solutions and cation exchange reactions are considered. The goal was to benchmark the
 947 implementation of cation exchange reactions before implementing mineral reactions. Concrete/clay
 948 interaction is thus limited to porewater diffusion and cation exchange in thermodynamic
 949 equilibrium. This case was simulated with iCP, MIN3P, OGS-GEM and CORE^{2D}. Results after
 950 1,000 years of interaction centred on the first meter of the studied system are presented from Fig. 14
 951 to Fig. 16. Concrete exchanger concentrations of Ca²⁺, K⁺ and Na⁺ at 1,000 years (Fig. 14). K⁺
 952 release (initial concentration of 0.55 mol/L) to concrete porewater driven by diffusion towards the
 953 claystone is the main process. This decrease in K⁺ fraction in the exchanger is compensated by an
 954 increase in Na⁺ (initial concentration of 0.17 mol/L), diffusing from the claystone, and in Ca²⁺. Ca²⁺
 955 concentration remains unchanged at x = 0 (initial concentration of 0.45 mol/L). Na⁺ and Ca²⁺
 956 concentrations changes in the exchanger maintain a similar Ca/Na ratio in the concrete exchanger.
 957 Overall, good agreement between codes is found, with slight differences in the results of MIN3P. In
 958 turn, Fig. 15 shows the composition of the exchanger within the first meter of claystone. Potassium
 959 diffusion from concrete results in an important concentration increase in the clay exchanger. As a
 960 consequence, all other cation concentrations are reduced.

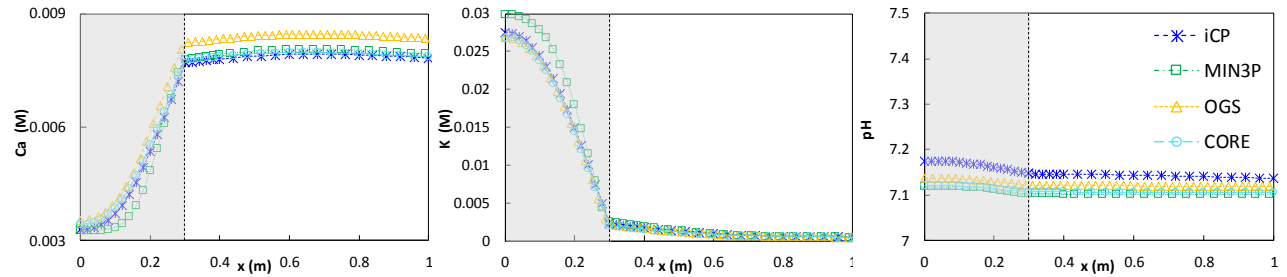
961 Total dissolved calcium and potassium distribution profiles at 1,000 years show the in-diffusion
 962 into concrete of the former from the clay and the out-diffusion of the latter (Fig. 16). After 1,000
 963 years, only small variations are observed in the pH profile (Fig. 16), with values between 7.1 and
 964 7.2 for the two materials (initial pH is 10.68 and 7.06 for concrete and clay, respectively). As the
 965 clayey domain has a much larger volume (~130 times) than the concrete one, pH tends to the clay
 966 initial values in the system. Differences in porewater between codes can be directly linked with the
 967 differences observed in the exchanger compositions.



968 **Fig. 14.** Cation concentration (M) profiles in concrete exchanger at 1,000 years obtained with iCP, MIN3P,
 969 OGS-GEM and CORE^{2D}.
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972
973 **Fig. 15.** Cation concentration (M) profiles in CO_x exchanger at 1,000 years obtained with *iCP*, *MIN3P*,
974 *OGS-GEM* and *CORE^{2D}*.
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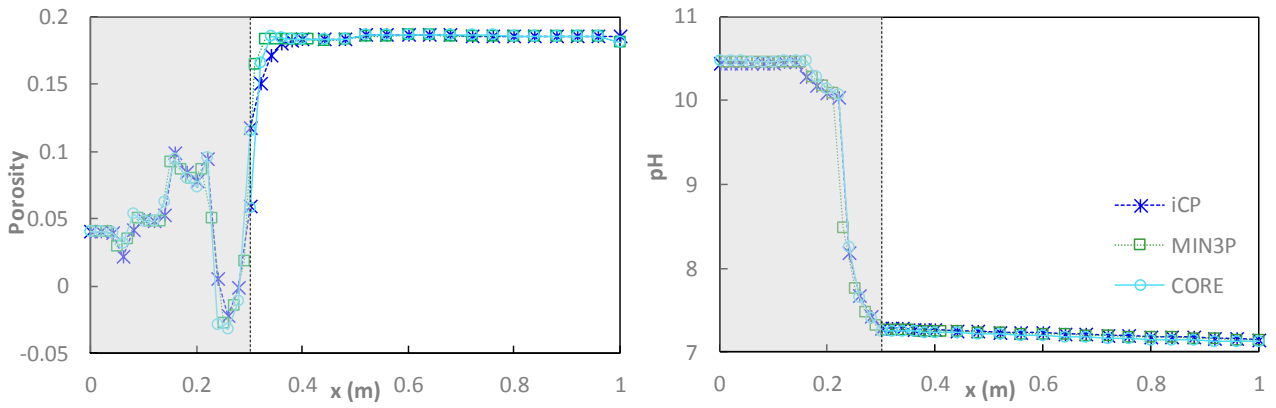


976
977 **Fig. 16.** Total aqueous concentrations (M) and pH profiles at 1,000 years obtained with *iCP*, *MIN3P*, *OGS-*
978 *GEM* and *CORE^{2D}*.

979 7.2.3 P3: Minerals in equilibrium

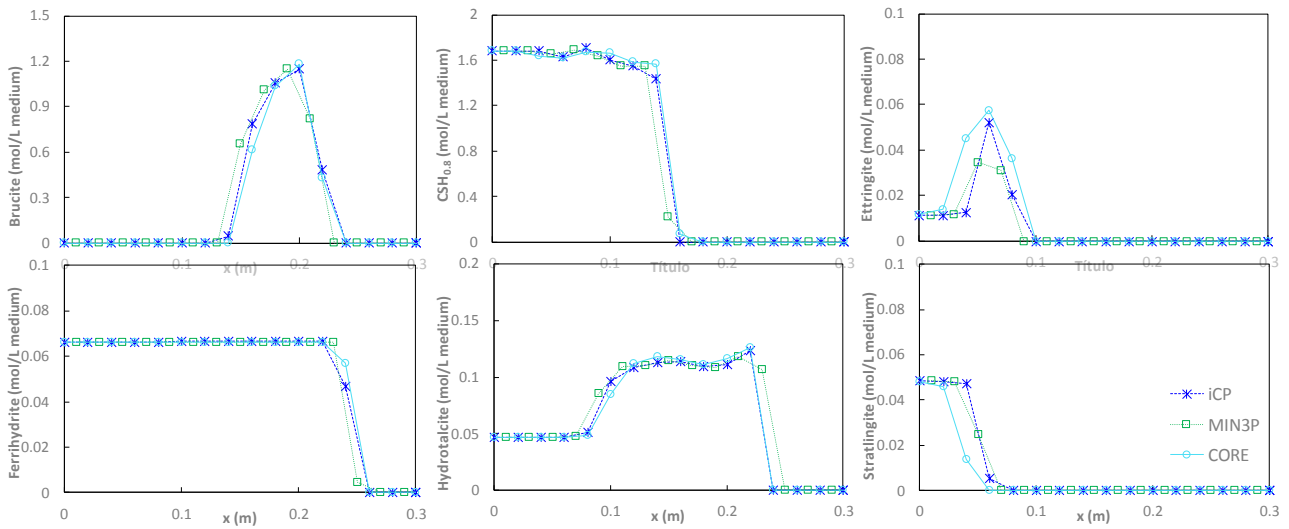
980 The setup of case P3 is equivalent to the FRC but without accounting for the kinetically-controlled
981 minerals. The only exception is quartz, which is included in case P3 as secondary phase in
982 thermodynamic equilibrium in both materials, although in the FRC it was considered as a
983 kinetically-controlled mineral. Quartz is expected to form in the model when the C-S-H gel
984 dissolves. This case was simulated with *iCP*, *MIN3P* and *CORE^{2D}*. It is to note that in *MIN3P*,
985 mineral reactions can only be simulated using kinetic rates. Thus, fast kinetic rates ($1 \cdot 10^{-9}$
986 $\text{mol/L}_{\text{medium}}/\text{s}$) were considered for all minerals to mimic thermodynamic equilibrium conditions.
987 The results after 100,000 years are presented in terms of pH and porosity (Fig. 17) and mineral
988 profiles (Fig. 18 and Fig. 19). The results of *CORE^{2D}* are the same as those included in the FRC
989 comparison.

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



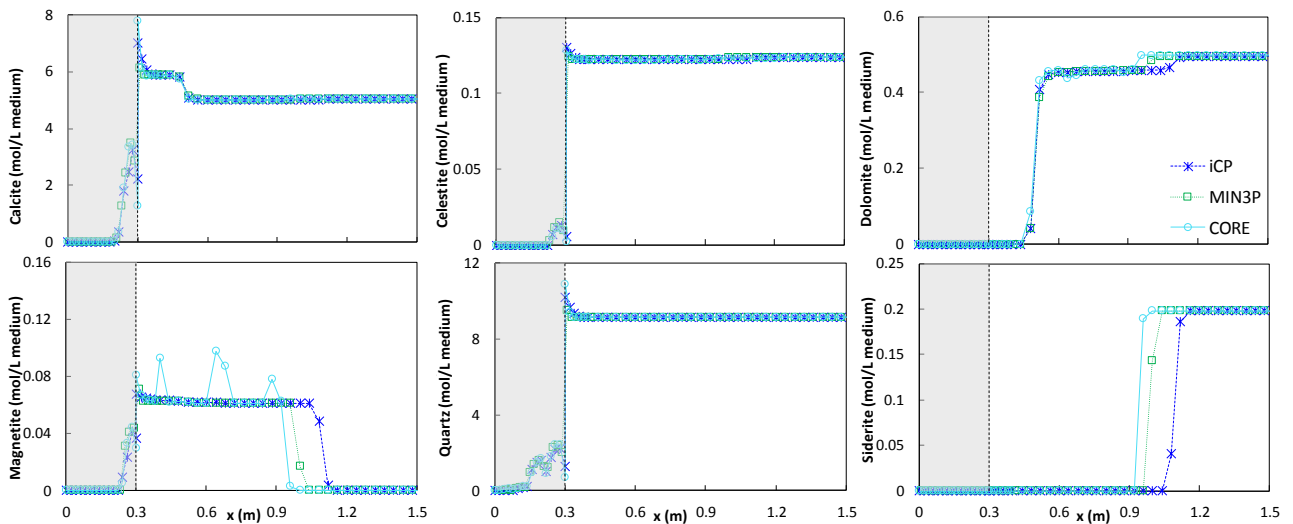
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Fig. 17. Porosity and pH distribution profiles at 100,000 years obtained with *iCP*, *MIN3P* and *CORE*^{2D}.



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



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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}.