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1 **Predicting long-term geochemical alteration of wellbore cement in a generic geological CO₂**
2 **confinement site: tackling a difficult reactive transport modeling challenge**

3
4 Fabrizio GHERARDI ¹, Pascal AUDIGANE ², Eric C. GAUCHER ²

5 ¹ CNR - Istituto di Geoscienze e Georisorse, Via Moruzzi 1, I-56124 Pisa, Italy

6 ² BRGM, 3 Avenue C.Guillemin, F-45060 Orléans, France

7
8 **1. Abstract**

9
10 The safety of the future CO₂ geological storage is largely dependent on the integrity of existing
11 surrounding wells. Well integrity is of major concern in confinement sites where the number of
12 abandoned wells is particularly high, such as it often occurs in depleted gas and/or oil fields. The
13 degradation of the cement filling of these wells is a key issue to insure the confinement of the CO₂.
14 Laboratory experiments are unable to produce data for long periods of interaction; therefore,
15 numerical modeling stands as a powerful means to predict the long-term evolution of the cement
16 plugs, and to assess well integrity and leakage risk for the confining system. We thus present the
17 results of a set of numerical simulations that predict the evolution of fluid chemistry and mineral
18 alteration in the cement of an idealized abandoned wellbore at the top of the Dogger aquifer in Paris
19 Basin, France, where CO₂ geological disposal is currently under consideration. A continuum-based
20 reactive transport formulation has been adopted which accounts for multi-component reactivity
21 under water saturated and diffusion-controlled mass transfer conditions. Simplified two-
22 dimensional models have been applied to simulate the complex geochemical interactions occurring
23 at the interfaces between cement, aquifer and caprock domains. The simulations predict a two-stage
24 evolution of the cement porous matrix, after interaction with acid fluids from reservoir: (i) a first,
25 “clogging” stage, characterized by a decrease in porosity due to calcite precipitation, and (ii) a
26 second stage of porosity reopening, related to the disappearance of primary cement phases, and the
27 re-dissolution of secondary minerals, such as zeolites. Overall, the interaction with acid fluids
28 causes a severe mineralogical alteration of the cement and the development of a carbonated, low-
29 porosity layer near the reservoir interface. As the caprock imposes a high partial pressure of CO₂,
30 some mineralogical alteration of the cement is promoted also at the interface with the caprock. This
31 pattern of reaction results in a large increase in porosity that might lead to the formation of vertical
32 ascent route for reservoir fluids.

33
34 Keywords: reactive transport modeling; CO₂ geological storage; cement; caprock; Paris Basin

35

36 2. Introduction

37

38 In recent years, many studies in subsurface carbon dioxide (CO₂) storage in geological formations
39 have been performed to evaluate the leakage risks connected to the different storage options under
40 consideration (saline aquifers, depleted gas and oil reservoirs, unminable coal seams; e.g., among
41 many others, Bachu et al., 2007, 1994; Gaus et al., 2005; Bachu, 2000; Hitchon et al., 1999; Freund
42 and Omerod, 1997; Holloway, 1997). Laboratory experiments and studies on artificial and natural
43 analogues of cement/rocks interactions indicate that long-term wellbore integrity is a crucial aspect
44 to be investigated when assessing the impact of CO₂ geological storage (IPCC 2005, 2008). One of
45 the most relevant issues is whether the petrophysical and geochemical properties of the host rocks
46 and sealing materials (i.e. caprock and cement of wellbores) will remain constant over long periods
47 of time (hundreds to thousands of years). Abandoned wells are a major concern because of the
48 inherent high reactivity of cements. When CO₂ encounters a well without proper plugging, it will
49 tend to migrate upwards due to buoyancy force. This rising plume chemically interacts with aquifer,
50 caprock and cement minerals predominantly through the wetting aqueous phase, which has low pH
51 and high mineral dissolution potential, due to the solubilization of high amounts of CO₂. The
52 interaction between these fluids and the rocks through which they migrate is expected to alter the
53 initial minerals and lead to the formation of secondary minerals, resulting in changes in physical
54 and chemical properties of the system. Possible leakage may occur through preferential flow
55 pathways along rock-cement and casing-cement interfaces, or through degraded materials because
56 of mechanical failure and/or chemical degradation of rocks, wellbore casings and/or cementitious
57 materials. Recent laboratory experiments and field observations show evidences about the type of
58 geochemical modifications induced in the cement after exposure to CO₂ (see among many others
59 Duguid and Scherer, 2010; Rimmelé et al., 2008; Jacquemet et al., 2008; Carey et al., 2007;
60 Kutchko et al., 2007). A large part of these results are specific to T,P and geochemical conditions of
61 the experiments and/or of the field observations, and they are not directly usable outside these
62 conditions to infer possible evolutionary scenarios in other sites under consideration for CO₂
63 geological confinement. In addition, laboratory experiments are unable to produce data for long
64 periods of interaction. Numerical modeling is then the only effective means to predict the long term
65 evolution of the cement plug and to evaluate the integrity of wellbore systems designed to prevent
66 fluids from escaping the sequestration reservoir.

67 Simulating reactive fluid flow and transport under these conditions is a challenging task because of
68 the complexity of multiphase fluid flow, water-gas-rock and fracture matrix interaction
69 mechanisms, and difficulties dealing with the heterogeneous physical and chemical properties of the

70 medium. Additional difficulties stem from the inherent chemical complexity of the investigated
71 system, related to the concomitant migration of two compositionally different plumes: an acidic, C-
72 rich plume propagates from the reservoir upwards into the seal, whereas an alkaline pulse, caused
73 by the equilibration of local groundwater with cement minerals, diffuse into the adjacent caprock
74 and the underlying reservoir.

75 The objective of this paper is to investigate, by numerical modeling, the long-term durability of the
76 cement of the pre-existing wells of a generic site for CO₂ geological storage in the Paris Basin
77 (France). The target reservoir is hosted in the Middle Jurassic (Dogger) regional aquifer, in the
78 centre of the Paris Basin, at a depth of 1500-2000 m. The Dogger aquifer, already exploited for
79 geothermal and petroleum resources, is mainly composed of carbonates. Sedimentary studies (Rojas
80 et al., 1989) have shown that the most permeable horizons of the Dogger aquifer correspond to
81 high-porosity layers of oolitic limestones which still retain, or even increase, their initial porosity by
82 mechanical fracturing and/or chemical dissolution. Recently, several French research projects have
83 been conducted to investigate the potential of this system for carbon dioxide geological storage
84 purpose. The “PICOREF” project (*Pilote pour l’Injection de CO₂ dans les Réservoirs géologiques,*
85 *En France, 2006-2008*) aimed, in particular, at developing a methodology of site selection for CO₂
86 geological storage in deep saline aquifers and studying the injection of CO₂ in specific contexts of
87 the Paris Basin (Brosse et al., 2007). The “GeoCarbone-Injectivity” and “GeoCarbone Integrity”
88 projects have been funded by the French National Agency of Research (ANR, see [http://www-anr-](http://www-anr-co2.cea.fr)
89 [co2.cea.fr](http://www-anr-co2.cea.fr)). The main goal of the “GeoCarbone-Injectivity” project was to develop a methodology
90 to understand and predict the injectivity evolution of a CO₂ well during the injection operations in
91 saline aquifers (Lombard et al., 2007), while the project “GeoCarbone Integrity” provided an
92 integrated approach to evaluate sealing efficiency (Fleury, 2007). One work package of this project
93 is dedicated to numerical modeling assessment of cap rock integrity (Bildstein et al., 2009).

94 In a very similar fashion, our study aims at providing preliminary estimates of the geochemical
95 processes occurring at the interface between (i) reservoir, (ii) cement and (iii) caprock porous
96 formations under isothermal, water-saturated and diffusively-controlled mass transfer conditions
97 with a specific attention on long term well cement integrity. The aim of the simulations is to provide
98 a sort of reference scenario for the processes likely occurring at the top of the injection target
99 reservoir over a time span of 1000 years, which lies reasonably in the middle of the range (hundreds
100 to thousands of years) required for long-term integrity modeling of geological CO₂ sequestration
101 (IPCC 2005, 2008, Gaus et al., 2008). The present simulations are prototypical in nature because no
102 specific information is available on cement mineralogy and pore water chemistry of the abandoned
103 wells in the Paris Basin. In contrast, field and laboratory data are available to constrain the initial

104 hydraulic and geochemical conditions for reservoir and caprock domains. The effect of highly
105 uncertain parameters, such as tortuosity, or intrinsically variable initial conditions, such as the initial
106 chemical composition of porewaters, has been assessed by performing a set of different simulations
107 with selected parameters calibrated on the basis of experimental data or numerical results of
108 previous simulations.

109

110 **3. Modeling approach**

111

112 All calculations were performed with the TOUGHREACT code, a comprehensive, publicly
113 available reactive transport simulator for multiphase systems (Xu et al., 2004). The modeling of
114 reactive transport is based on space discretization by means of integral finite differences
115 (Narasimhan and Witherspoon, 1976), and is carried out by using a sequential non iterative
116 approach. The chemical transport is solved on a component basis, and the resulting concentrations
117 obtained from the transport are substituted into the chemical reaction model. The system of
118 chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration. Full
119 details on numerical methods are given in Xu and Pruess (2001) and Xu et al. (2006).

120 Simplified geometries with hydraulically and geochemically homogeneous media have been taken
121 into consideration, and fully saturated (i.e. aqueous phase saturation, $S_1=1.0$) and isothermal
122 conditions at 75°C assumed throughout our calculations. These highly idealized conditions provide
123 a reasonable approximation to average field conditions far from CO₂ injection areas in the Paris
124 Basin, at the top of the Dogger reservoir (Figure 1). Previous simulations have indicated that a
125 supercritical CO₂ bubble is likely expected to occur in the first 5 m around the injection well after
126 10 years injection, and that this zone is surrounded by a two-phase zone of about 650 m (André et
127 al., 2007).

128 Model implementation has been carried out in stages of increasing complexity. We started from
129 geometrically simplified systems, i.e. 0- and 1-dimensional models, to explore the sensitivity with
130 respect to different space discretizations, initial mineralogy and chemical composition of pore
131 waters. Nearly equilibrated, steady-state geochemical systems were created by running batch
132 simulations, and the resulting mineralogical and pore water chemical compositions used as initial
133 conditions for the 1-D and 2-D simulations. Simplified 1-D models have been preliminary used to
134 investigate the processes occurring at reservoir-cement, reservoir-caprock and caprock-cement
135 interfaces. Space and time discretization of the 2-D model results from a compromise between
136 computation time, simulation time, grid spacing and numerical stability. Numerical stability has
137 been achieved through von Neumann analysis (Hindmarsh et al., 1984) by enforcing small

138 maximum time-step increments, variable between 5×10^4 to 1×10^3 s depending on initial conditions
139 and geometry. Maximum simulation times were typically in the order of few to several days (up to a
140 maximum of about 15 days) on a 3.6 MHz CPU. The results of a 2-D reference case will be
141 presented in the next sections.

142

143 **3.1. Geometry**

144

145 In an attempt to keep the implementation of the model as simple as possible, a two-dimensional,
146 idealized Cartesian grid has been arranged to reproduce a vertical cross-section of a heterogeneous
147 porous medium sampled in proximity of the interfaces between cement, caprock and reservoir
148 domains (Figure 2). This section is drawn through the axis of a hypothetical abandoned well, and
149 because of the symmetry of the model, only half of the domain has been modeled. The grid extends
150 horizontally 5 m from the axis of the abandoned well and vertically 10 m from the top of the
151 reservoir. A 2 m-thick reservoir with large-volume blocks at the bottom is placed below cement and
152 caprock domains so as to guarantee an almost infinite supply of chemicals from the carbon-rich,
153 low-pH waters likely permeating the reservoir after massive injection of CO_2 at depth. The reservoir
154 is further discretized into 8 layers between the interface with cement and caprock domains (at the
155 top) and this large volume (at the bottom of the model), in order to account for possible
156 geochemical variations induced in the reservoir by the diffusion of alkaline and near-neutral fluids
157 coming from the cement filling and the cap rocks, respectively. A refined spatial discretization,
158 with internodal distances of 0.05 m, is adopted near the interfaces to better resolve concentration
159 gradients between the different rock domains. A coarser spacing is applied in the rightmost part
160 (along the horizontal direction, far from cement-caprock interface) and in both the uppermost and
161 lowermost parts of the grid (along the vertical direction, far from reservoir-caprock interface). In
162 these zones, the maximum internodal distance slowly increases up to 0.75 and 1.76 m along the
163 vertical and horizontal directions, respectively. This non-uniformly spaced cartesian grid responds
164 to the double need to keep the highest resolution localized where the highest concentration gradients
165 occur, i.e. near the interfaces, and to reduce the computation cost of the simulations (by reducing
166 the total number of cells). Exploratory, simplified simulations (only unreactive aqueous tracers¹
167 have been allowed to propagate all over the modeled domain to reduce simulation times) with
168 uniform and non-uniform grids confirmed that the choice of increasingly larger blocks with
169 increasing distances from the interfaces does not cause any appreciable dispersion effect. Selected

¹ Aqueous tracers are unreactive chemical components characterized by negligible molecular weight and molar volume. In our model, a fictitious chemical component, with initial concentration of 10^{-6} mol $\text{kg}_{\text{H}_2\text{O}}^{-1}$, has been used as aqueous tracer for each of the three rock domains considered in the simulations.

170 relevant parameters on grid geometry are shown in Table 1. Eleven observation points have been
171 used to analyze the simulation results (Figure 2B). The mesh element CEM-01 is part of the cement
172 domain and is located at the reservoir-cement interface. It is directly connected to the RES-01
173 element which is part of the reservoir domain. The CEM-02 element is connected to the CEM-01
174 element in the Z direction. In a similar fashion, elements CEM-03, CEM-04 and RES-02 illustrated
175 the reservoir-cement interface where cement, reservoir and caprock domains are in contact.
176 Elements CAP-01, part of the caprock domain, and element RES-03 part of the reservoir domain
177 are used for the understanding of the interactions at the caprock-reservoir interface. Element CAP-
178 02 is connected to the CAP-01 element in the Z direction. Finally, elements CEM-05 and CAP-03
179 are used for the analysis of the geochemical reactivity occurring at the caprock-cement interface in
180 the upper part of the simulated area. A no-flux boundary condition applies to the borders of the
181 model. Our simulations are focused on a hypothetical abandoned well plugged with cement, and
182 then any possible chemical effect induced by the corrosion or the degradation of the steel of the
183 casing (e.g. Hope et al., 1985; Alonso et al., 2000; Glass and Buenfeld, 1997; Hausmann, 1967) is
184 not taken into account.

185

186 **3.2. Initial geochemical system**

187

188 Geology, petrophysical and geochemical characteristics of the Dogger aquifer, in the Paris Basin,
189 have been extensively investigated in the past (Rojas et al., 1989). The Paris Basin is a Late Tertiary
190 intracratonic basin with a diameter of 600 km and a maximum thickness of 3000 m, bordered by
191 Palaeozoic massifs (Vosges to the east, Armorican Massif to the west, Central Massifs to the south,
192 Ardennes in the northeast). The reservoir is hosted in limestones and dolomite-bearing formations.
193 The most permeable part of the aquifer is represented by oolitic and bioclastic limestones
194 predominantly made of carbonates (up to 85% by vol.) and minor alumino-silicates (albite, K-
195 feldspar) and clays (Rojas et al., 1989). Several large aquifers are present at depths that are being
196 exploited for potable supply and geothermal purposes. Maximum temperatures range up to 85 °C at
197 a maximum depth of -1900 m below sea level in the central part of the Basin, some 20 km east of
198 Paris.

199 The geochemistry of this aquifer has been extensively investigated by means of isotope, noble gas
200 and hydrochemical studies (Michard and Bastide, 1988; Criaud et al., 1989; Coudrain-Ribstein and
201 Gouze, 1993; Matray et al., 1994; Azaroual et al., 1997; Marty et al., 2003). Pore waters have
202 different salinities ranging between 5 to 35 g kg_{H₂O}⁻¹. An aqueous solution with a chemical
203 composition similar to that of Fontainebleau waters (Michard and Bastide, 1988), but higher total

204 salinity (ionic strength, IS, of about $0.3 \text{ mol kg}_{\text{H}_2\text{O}}^{-1}$ instead of about $0.1 \text{ mol kg}_{\text{H}_2\text{O}}^{-1}$), has been
205 preliminary considered as representative of the average initial conditions in the reservoir, before
206 CO_2 injection at depth. Following André et al. (2007), zero- and mono-dimensional models have
207 been successively run using this water and a simplified primary mineralogy to evaluate the
208 geochemical effects induced by the injection of CO_2 at depth. The modified mineralogy and a new
209 chemical composition of the pore water, characterized by the lowest pH values calculated during
210 these simulations, have been then used to initialize the 2-D models (Tables 2 and 3).

211 The caprock of the site is represented by a clay-rich formation of Callovian-Oxfordian age
212 (“Callovian-Oxfordian argillite” or “COx formation”) which is also expected to play the role of
213 geological barrier for deep nuclear waste disposal in another location. This formation has a
214 thickness of about 100-150 m and it extends all over the Paris Basin. A large number of physical
215 property measurements and geochemical analyses performed in the framework of the French
216 National Radioactive Waste Management Agency (ANDRA) Meuse/Haute Marne underground
217 research laboratory scientific programme (Delay et al., 2007; Landais, 2006) are available to
218 constrain the initial conditions of our model.

219 Mineralogy and pore water chemistry of Callovian-Oxfordian argillites has been thoroughly
220 investigated by experimental methods and numerical simulations (Sammartino et al., 2003;
221 Vieillard et al., 2004; Gaucher et al., 2004a; 2006; 2009; Leroy et al., 2007; Vinsot et al., 2008).

222 The Callovian-Oxfordian argillite is a complex mineral assemblage predominantly composed of
223 phyllosilicates, silicates, carbonates and S-bearing minerals (Claret et al., 2002; Claret et al., 2004;
224 Gaucher et al., 2004a). Clays are a mixture of illite and mixed illite/smectite layers, with minor
225 amounts of chlorite and locally kaolinite. Carbonates are mainly represented by calcite and
226 dolomite. Accessory minerals are represented by quartz, feldspars, pyrite, celestite. To obtain
227 suitable initial conditions, i.e. a stable mineralogical assemblage with nearly equilibrated pore
228 waters at the reference temperature of 75°C , batch numerical calculations have been performed. The
229 mineralogical assemblage used by Marty et al. (2009) has been used as a reference. Sodium and
230 chloride total concentrations and total salinity of the caprock pore waters have been adjusted to the
231 values of the reservoir pore waters to account for equilibration processes likely occurred over
232 geological time at the caprock-reservoir interface. These values are higher than those reported in the
233 literature for the inner, far from reservoir layers of the COx formation. As a first step, no *a-priori*
234 assumptions on the control of f_{CO_2} have been made, but the effects of variable, externally-fixed
235 f_{CO_2} values on the chemical composition of the pore water have been investigated as a part of a
236 sensitivity analysis (see section 4.5). The computed $\log f_{\text{CO}_2}$ values vary between -2.2 to -1.2 bar,
237 depending on small variations in the initial mineralogy used in the calculations. These values reflect

238 the internal buffering exerted by the carbonate and alumino-silicate mineralogical assemblage used
239 in the calculations on the chemistry of the associated aqueous solution. Reference pore water
240 chemical composition and mineralogy used in the 2D simulations are summarized in Tables 2 and
241 3, respectively.

242 An idealized composition for a high alkali (Na_{TOT} and K_{TOT} aqueous concentrations around 3×10^{-2}
243 m), ordinary Portland cement (OPC) has been used in the calculations. From a chemical standpoint,
244 OPC can be considered as a very heterogeneous material with discrete particles typically in the size
245 range of about a few hundred nanometers up to a few hundred micrometers mainly consisting of
246 variable amounts of calcium silicate hydrates, portlandite, calcium aluminates, and minor reactive
247 phases (e.g., hydrotalcite, ettringite, hydrogarnet, ferrite etc.), depending on ambient temperature
248 and initial chemical composition of the cement paste (Paul and Glasser, 2000). A

249 thermodynamically stable mineralogical assemblage that consists of portlandite, tobermorite,
250 katoite-Si, hydrotalcite, ettringite and $\text{C}_3\text{FH}_6(\text{s})$ (Table 3), and the associated pore water chemistry
251 (Table 2) have been reconstructed at 75°C by numerical calculations. This mineralogical
252 assemblage reflects the relative stability of the minerals included in the thermodynamic database
253 and is coherent with some of the few available information on prolonged cement hydration at high
254 ($>50^\circ\text{C}$) temperature reported in the literature (Paul and Glasser, 2000), namely: (i) CSH
255 amorphous phases are metastable with respect to crystalline CSH phases such as tobermorite, and
256 even if they had been found to be only partially crystallized in laboratory experiments and field
257 conditions (Glasser et al., 2005), they are expected to convert to crystalline phases over the
258 reference time frame of our calculations; (ii) the prolonged hydration of cements favors the
259 formation of siliceous hydrogarnets and (iii) hydrotalcite, whereas (iv) monosulphate or ettringite
260 are expected to persist, depending on sulfate and aluminium concentrations in the aqueous phase;
261 (v) katoite-Si and (vi) $\text{C}_3\text{FH}_6(\text{s})$ tend to replace AFm (monocarboaluminate and $\text{C}_4\text{FH}_{13}(\text{s})$) and AFt
262 (ettringite) phases. Based on recent data from Blanc et al. (2010a and 2010b), afwillite emerges as
263 an additional crystalline CSH phase to be considered in the numerical reconstruction of an
264 hypothetical equilibrium OPC mineralogical assemblage at 75°C . However, the limits of the
265 stability field of afwillite are still rather uncertain, as suggested by the discrepancies between the
266 data recently gathered by Blanc et al. (2010a and 2010b) and the thermodynamic properties
267 determined by Dickson et al. (2004) and/or estimated by Babushkin et al. (1985). Moreover,
268 Kusachi et al. (1989) indicated that afwillite is expected to be thermodynamically stable at about
269 100°C , rather than at 75°C . For all these reasons, the association tobermorite + portlandite, whose
270 thermodynamic properties are well defined at 75°C , has been retained in our calculations.

271 Redox conditions are poorly constrained in our system, and for this reason, some redox-sensitive
272 minerals of uncertain occurrence, such as hematite and magnetite, have been excluded from
273 calculations. In contrast, ferrihydrite and goethite have been included because widely reported in
274 the literature as possible secondary phases related to circulation of hyperalkaline fluids in clay-rich
275 formations (e.g. Gaucher and Blanc, 2006). We initially set an uniform Eh value of about -210 mV
276 for all pore waters considered in our model, calculated by batch modeling from data available for
277 CO_x formation (around -175 mV at 25°C; Gaucher et al., 2006). Slightly different values have been
278 then used for cement and reservoir redox conditions in the 2D model (Table 2), after preliminary
279 0D and 1D simulations carried out to achieve nearly equilibrated, steady state geochemical
280 conditions.

281

282 **3.3. Methods for geochemical calculations**

283

284 Aqueous species are assumed in chemical equilibrium throughout the calculations. The detail of
285 primary and secondary species considered in the simulations is given in Table 2. Aqueous activity
286 coefficients are computed using an extended Debye-Hückel equation, according to Helgeson et al.
287 (1981) and Tanger and Helgeson (1988), with minor adaptations (André et al., 2007) to account for
288 the high pressure conditions of the system (around 200 bar). All the dissolution and precipitation
289 reactions involving cement minerals are assumed to proceed at local equilibrium. This approach is
290 justified by the observation made by previous investigators that chemical transformations occurring
291 at the alteration front in cementitious materials are fast if compared with the time frame of hundreds
292 to thousands of years required in the modeling of the deterioration of containment materials of
293 radioactive or non-radioactive waste repositories (e.g. Gaucher et al., 2004b; Burnol et al., 2006;
294 Trotignon et al., 2007), and with the slow rate mass transfer conditions assumed in the model (see
295 sections below). The lack of reliable information on kinetic parameters for these minerals further
296 supports this assumption. The local thermodynamic equilibrium approach has been applied also to
297 simulate the behavior of other fast reacting minerals, such as calcite and anhydrite (Palandri and
298 Kharaka, 2004).

299 Dissolution/precipitation reactions involving the remaining minerals from reservoir and caprock
300 domains are modeled under kinetic constraints. A kinetic formulation derived from transition state
301 theory (Lasaga, 1981, 1984; Aagaard and Helgeson, 1982; Steefel and Van Cappellen, 1990) is
302 applied. Our model takes into account the feedback between transport and chemistry (see section
303 3.5 below) by allowing variations in porosity to be computed from the algebraic sum of mineral
304 volume fractions variations.

305

306 **3.4. Thermodynamic data**

307

308 The primary mineralogy of reservoir, caprock and cement domains is described in terms of 7, 8 and
309 6 minerals (Table 3), respectively, and the complete mineralogical dataset is composed of 56
310 minerals. The choice of this large number of minerals responds to two major needs: accurately
311 describe the geochemical complexity of the three media considered in the simulations and avoid the
312 risk of converging towards an unique, biased numerical solution (e.g. Gaucher and Blanc, 2006;
313 Marty et al., 2009). A complete list of minerals and geochemical reactions included in the
314 simulations is given in Table 1 of the Electronic Annex, thereafter named Table 1_{EA}. The
315 equilibrium constants are taken from the Thermoddem database (February 2008 release), a
316 thermodynamic database compiled at BRGM (<http://thermoddem.brgm.fr/>). Thermoddem uses
317 internally consistent and critically evaluated thermodynamic data derived from a comprehensive
318 review of the published literature. The primary source for equilibrium constants for aqueous species
319 and minerals is the Slop98.dat database (Shock et al., 1998), which is in turn a substantial revision
320 of the SUPCRT92 database (Johnson et al., 1992). A major modification with respect to the original
321 Slop98 data set concerns data for Al aqueous species, which have been taken from the
322 experimentally-derived compilation of Tagirov and Schott (2001). Data for minerals have been
323 thoroughly revised and major changes concern cement minerals (Blanc et al., 2006). Solubility
324 constants for CSH (amorphous and crystalline) phases have been calculated on the basis of
325 thermodynamic data and experimental evidences from Babuskin et al. (1985), Hong and Glasser
326 (2004), Shaw et al. (2000), and Glasser et al. (2005). Thermodynamic properties of minerals
327 belonging to CaO-Al₂O₃-SO₃-H₂O system (ettringite, monosulfate, hydrogarnet) have been
328 extracted from Warren and Reardon (1994), Perkins and Palmer (1999), and Babuskin et al. (1985).
329 Equilibrium constants for portlandite, brucite, magnesite, gibbsite, and Friedel's salt are based on
330 data from Robie and Hemingway (1995), Chase (1998) and Akinfiyev and Zotov (1999), whereas
331 those for Fe-bearing minerals (C₄FH₁₃, C₃FH₆, ettringite-Fe, Monosulfate-Fe, ferrihydrite) have
332 been calculated from Babuskin et al. (1985) and Chivot (2004). Thermodynamic properties of
333 minerals belonging to CaO-Al₂O₃-SiO₂-H₂O system (katoite-high-SiO₂, straetlingite) were
334 calculated on the basis of data from Atkins et al. (1992) and Damidot and Glasser (1995).
335 Amorphous CSH solid solution is discretized into a set of three pure phases with Ca/Si ratios
336 varying between 0.8, 1.2 and 1.6.
337 Several assumptions and simplifications in the primary and secondary mineralogical assemblage
338 have been made to account for the inherent complexity of the investigated system, and the

339 problematic thermodynamic representation of all the phases possibly occurring during the
340 calculations. Major approximations are related to the characterization of highly undifferentiated
341 minerals like clays, zeolites, micas, and amorphous phases. The existence of solid solutions has not
342 been taken into account. The following simplifications hold for these calculations.
343 Calcium carbonates are represented by calcite only. Aragonite and vaterite polymorphs are not
344 taken into account being thermodynamically unstable at the reference temperature of 75°C.
345 Additional carbonates are dolomite, ankerite, magnesite, siderite and dawsonite. The clay fraction
346 of the Callovian-Oxfordian (COx) argillite is dominated by mixed-layer illite/smectite, Mg-illite,
347 and includes minor amounts of Mg-Na-montmorillonite, but several additional types of illites,
348 montmorillonites and saponites have been inserted in the list of potential secondary minerals. The
349 Mg-Na-bearing montmorillonite has been also used as thermodynamic proxy for the mixed-layered
350 fraction of illite-smectite minerals. Quartz is a major phase of the COx formation and has been
351 considered as the primary silica polymorph in the calculations, but chalcedony and amorphous silica
352 are allowed to precipitate as possible secondary phases. Chlorite group minerals are represented by
353 means of two single minerals corresponding to the Mg- and Fe-enriched end-members, clinochlore
354 and daphnite. Sulfur-bearing minerals consist of anhydrite, pyrite and celestine, whereas analcime,
355 and three different phillipsites have been used to represent zeolite group minerals. Non-clay
356 silicates such as muscovite, K-feldspar and low-albite have been considered in the calculations.

357

358 **3.5. Kinetic data**

359

360 The kinetic approach is still inherently problematic in reactive transport modeling because of the
361 partial knowledge of the large complexity of factors on which experimental rates have been proven
362 to depend on. Major flaws of kinetic approach rely on the lack of reliable information on the values
363 of mineral reactive surface areas and their variation with time, of mineral surface roughness, on the
364 variation of rates over large span of Gibbs free energy of reaction, ΔG_r , , speciation conditions of the
365 associated aqueous phase and reaction temperature, and the limited use of laboratory data for
366 predicting the kinetic reactions in natural systems (see, among many others, Yang and Steefel,
367 2008; Hellmann and Tisserand, 2006; Köhler et al., 2005; Zhu, 2005; Lüttge et al, 2003; White and
368 Brantley, 2003; Yokoyama and Banfield, 2002; Gautier et al., 2001; Cama et al., 2000; Cama et al.,
369 1999; White and Brantley, 1995; Ganor et al., 1995; Oelkers et al, 1994; Lasaga et al., 1994; Burch
370 et al., 1993; Casey and Sposito, 1992; Anbeek, 1992; White and Peterson, 1990; Velbel, 1989,
371 1993; and references cited therein). In addition, mineral reactive surface areas cannot be directly
372 measured in nature, but only roughly estimated through laboratory experiments or field evidences.

373 This uncertainty also affects the rates estimated in the laboratory because of the normalization
374 procedures required to allow their extrapolation to natural systems (e.g. Hodson, 2006).

375 Total surface areas, usually estimated in the laboratory by gas adsorption techniques (Brunauer et
376 al., 1938), are often used instead of reactive surface areas in numerical calculations. However, as
377 mineral dissolution commonly occurs at selected sites, they likely overestimate the effective
378 reactive area (Aagaard and Helgeson, 1982). Many authors approximate total surface areas of
379 geologic media using simple geometrical models involving the ordered arrangement of spheres
380 (Bear, 1972; Canals and Meunier, 1995; Kieffer et al., 1999), but this approach require the
381 availability of information, not available in the present study, on the statistical distribution of the
382 equivalent diameters of mineral particles. In addition, the applicability of this approach is
383 questionable in the case of shales or other rocks containing significant clay amounts, where
384 minerals occur in many different habits (platy crystals, interstratified lamellae, etc.) other than
385 spheres.

386 Summing up, despite the large number of investigations already performed, a coherent and
387 complete kinetic database for all pertinent minerals is then still far from being available to date. In
388 addition, a comprehensive sensitivity analysis of all kinetic parameters is not feasible when
389 simulating very complex geochemical systems such as that investigated in the present paper.

390 To circumvent all these limitations, and in consideration of the prototypical nature of our
391 simulations, we used selected kinetic parameters from the literature (Table 4), and performed a
392 sensitivity analysis for the most relevant minerals only (see following sections). The precipitation of
393 secondary minerals is represented using the same kinetic expression and rates as that for
394 dissolution, except for kaolinite (Yang and Steefel, 2008), SiO₂-polymorphs (Rimstidt and Barnes,
395 1980) and dolomite (Arvidson and Mackenzie, 1999). Catalysis by H⁺ or OH⁻ is considered only
396 for mineral dissolution and the related kinetic parameters have been taken from selected literature
397 (see footnote of Table 4).

398 Initial values for reactive surface areas have been set to two single average reference values (RSA₁
399 and RSA₂) taken from the literature (e.g. Köhler et al., 2005; Bickmore et al., 2002; Brantley and
400 Mellott, 2000; Metz et al., 2005; White and Brantley, 1995), in order to account for the larger
401 intrinsic surface areas of phyllosilicates and zeolites (RSA₁=5 m² g⁻¹) with respect to other minerals
402 (RSA₂=10 cm² g⁻¹). The two average values have been selected at the lower end of the range of
403 values reported in the literature to account for the concentrated reactivity along the edges of the
404 phyllosilicates (e.g. Metz et al., 2005; Tournassat et al., 2003; Bickmore et al., 2002, 2001), the
405 ageing effect which allows in situ phases to be progressively less reactive in time due to adsorption

406 of ions, the smoothing of surface defects by recrystallization, and the secondary minerals coating on
 407 primary minerals surface (e.g. Lasaga, 1998).

408 The dissolution and precipitation reactions involving fast reacting minerals, such as calcite,
 409 anhydrite and cement minerals are assumed to proceed at local equilibrium (see chapter 3.3). For
 410 these minerals, no kinetic parameters were provided in Table 4.

411

412 **3.6. Mass transport mechanisms**

413

414 Molecular diffusion in a single aqueous phase has been considered the dominant mass transport
 415 process in our simulations. This corresponds to assuming almost stagnant conditions all over the
 416 modeled system. This assumption could be not strictly valid for the reservoir domain, where, under
 417 field conditions, relatively high porosity and permeability conditions would allow mass transfer to
 418 occur also by advection in response to local hydraulic gradients (e.g. Bear, 1972). The treatment of
 419 the mass transfer process is based on Fick's First Law. The diffusive flux is assumed to be
 420 proportional to the concentration gradient:

$$421 \quad J_i = -d_{eff}^i \cdot \frac{\partial C_i}{\partial x} \quad [eqn.1]$$

422 where C_i is the concentration of the diffusing species in solution and d_{eff}^i is its effective diffusion
 423 coefficient. The latter coefficient can be thought as the product of the diffusion coefficient of the
 424 considered species in an aqueous solution at infinite dilution and a formation factor which accounts
 425 for the spatial variations in porosity and the tortuosity of the paths through the considered media.
 426 Definitions of tortuosity vary in the literature (e.g. Lichtner et al., 1996). In TOUGHREACT
 427 tortuosity is a parameter which allows an effective diffusion coefficient in the porous medium (d_{eff})
 428 to be calculated from the diffusion coefficient in pure water (d_w) according to the following
 429 equation:

$$430 \quad d_{eff} = \phi \cdot \tau \cdot d_w \quad [eqn.2]$$

431 where ϕ is the porosity and τ the tortuosity coefficient. The tortuosity coefficient is always less
 432 than or equal to 1, and may vary in the different rock domains.

433 An alternative formulation for the coefficient for molecular diffusion in porous media is based on
 434 Archie's Law (Bear, 1972). Formation factors generated from Archie's Law have associated large
 435 uncertainties, of at least one order of magnitude, that largely depends on the anisotropic distribution
 436 of the formation factor in geological media and on its sensitivity with respect to different rock
 437 fabrics and grain alignments (Lichtner et al., 1996, and references therein).

438 Due to the lack of specific reliable experimental data and the intrinsic complexity of accurately
 439 describing the influence of the pore structure on macroscopic transport properties of aqueous
 440 solutions migration through natural porous rocks, the relationship between the porosity and the
 441 effective transport properties of geological media still remains difficult to model. Both the
 442 aforementioned approaches can be then equivalently applied to reproduce the behavior of the
 443 natural system. To overcome all these uncertainties in transport parameters, in our model we chose
 444 to explore the sensitivity of numerical outputs with respect to the effective diffusivity, instead of
 445 dwelling into second order refinements such as the testing of different relationships (actually non
 446 supported by any experimental data) between porosity and transport properties. Different tortuosity
 447 coefficients have been then set for the different rock domains and kept constant during the
 448 calculations.

449 Diffusion in the model is expressed with an average diffusion coefficient applied to all dissolved
 450 species. This assumption ignores the different tracer diffusivities of each species and
 451 electrochemical migration effects due to the different charges of various ions (e.g., Boudreau et al.,
 452 2004; Giambalvo et al., 2002).

453 Diffusion coefficients vary by about one order of magnitude among different species at the
 454 temperature of interest of our simulations (75°C). Based on compilations by Oelkers and Helgeson
 455 (1988), and Lasaga (1998), we calculate values ranging between 15 and 20×10^{-9} m²/s, 8.7 and
 456 11.5×10^{-9} m²/s, 1.2 and 1.5×10^{-9} m²/s, 3.1 and 4.2×10^{-9} m²/s, 1.9 and 2.6×10^{-9} m²/s for the
 457 following selected species H⁺, OH⁻, Mg⁺², CO_{2(aq)}, HCO₃⁻, respectively, depending on the value of
 458 the activation energy (between 10 to 15 kJ/mol) used in the Arrhenius-type equation giving the
 459 dependency of the diffusion coefficient on temperature (Lasaga, 1998):

$$460 \quad d_T^i = d_{25^\circ C}^i \cdot \exp\left(-\frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \quad [\text{eqn.3}]$$

461 To obtain values for the effective diffusion coefficient, d_{eff} , reasonably comparable with values
 462 from field and laboratory experiments (De Vera et al., 2007), the largest value of this range,
 463 corresponding to proton bulk diffusion coefficient in water at infinite dilution, $d_T^{H^+}$, has been used,
 464 and a sensitivity analysis on tortuosity coefficient has been performed. In our calculations we
 465 adopted the same value of τ for both caprock and cement domains, with values in the reservoir
 466 larger by one order of magnitude at least, to reflect the different texture and transport properties of
 467 local carbonate formations (see, Descostes et al., 2008; Melkior et al., 2004; Sammartino et al.,
 468 2003, and references cited therein). Reference values for porosity and tortuosity are given in Table
 469 1.

470

471 3.7. Actual limitations of the modeling approach

472

473 Models presented in this work are an idealization of the physical and chemical processes expected
474 to occur in the cement of a hypothetical abandoned well of the Paris Basin, after CO₂ geological
475 disposal in the local Dogger saline aquifer. The accuracy of the numerical predictions should be
476 improved when more detailed site-specific physical and chemical data will be available, particularly
477 on mineralogy and porewater composition of cement materials. The reliability of numerical
478 predictions is also affected by the severe limitations in the current knowledge of kinetic parameters
479 of minerals, especially of both crystalline and amorphous solid constituents of cement. In this study,
480 all uncertainties have been tackled through simplification of conceptual and geometric models, and
481 by carrying out a sensitivity analysis on relevant features. Future work could improve on all
482 simplifications made by (i) considering species-dependent variations in the aqueous phase diffusion
483 coefficients; (ii) considering the presence of amorphous and/or not completely hydrated
484 components in the starting cementitious material and addressing the simulation of their alteration
485 mechanisms by means of a fully kinetic treatment of precipitation/dissolution reactions; (iii)
486 following a different numerical approach, incorporating solid solutions into equations describing
487 reactive transport, to describe the CSH phase evolution, and to reproduce the experimental
488 observations of progressive CSH decalcification with decreasing pH (Carey and Lichtner, 2007);
489 (iv) addressing reactivity at reservoir-caprock-cement interface under two-phase conditions and
490 realistic, site-specific hydraulic conditions, eventually accounting also for the advective transport of
491 chemicals from reservoir; (v) considering the presence of physical discontinuities and the spatial
492 variability of hydraulic parameters, to account for the different geochemical behavior of reactive
493 species expected in fractured and/or heterogeneous rocks from that in homogeneous porous media;
494 (vi) accounting for possible *in-situ* ageing effects induced by the interaction of the cement with host
495 formation porewaters before the beginning of the confinement of CO₂ at depth; (vii) improving the
496 analysis of redox conditions, when more accurate information will be available on thermodynamic
497 data and the occurrence of redox-sensitive, Fe-bearing minerals in the cement, and the reactivity of
498 dispersed organic matter in the caprock; (viii) exploring the effect of different, non-linear porosity-
499 effective diffusion relationships, when experimental data will be available on transport properties of
500 site-specific materials.

501 Despite all these approximations, the numerical simulations revealed some general trends that are
502 important for the assessment of long-term integrity of CO₂ storage.

503

504 4. Results and discussion

505

506 Major uncertainties in the calculation of the alteration patterns are related to the effectiveness of
507 diffusive mass transport mechanisms. Uncertainties related to the poor knowledge of kinetic
508 parameters have a negligible impact because of the equilibrium approach used in simulating the
509 behavior of cement minerals. The effective diffusion coefficient is the main parameter governing
510 mass transfer throughout the system. A sensitivity analysis has been performed on its initial value
511 by varying the tortuosity factor (Table 1) for the different rock domains considered in the
512 calculations. Different diffusivity conditions have been explored, and two limiting reference cases
513 have been defined, based on the values of the effective diffusion coefficient, d_{eff} , calculated at
514 reservoir-cement interface. We define a “low-diffusivity” (LD) and a “high-diffusivity” (HD) case
515 simulation, for d_{eff} values equal to 1.65×10^{-11} and $1.79 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. Under these
516 conditions, the effective diffusion coefficient within the cement domain spans the range between
517 3×10^{-13} to $3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. These values roughly encompass the range of effective diffusivity values
518 reported in the literature for cement materials (e.g. Trotignon et al., 2007). Due to the feedback on
519 porosity, mineral dissolution/precipitation reactions affect mass transfer efficiency, and the effects
520 of this feedback on d_{eff} , as calculated at reservoir-cement and reservoir-caprock interfaces, are
521 plotted in Figure 3. In the following sections, the results for both the LD and HD case simulations
522 are presented. Even larger values of d_{eff} (up to about $10^{-10} \text{ m}^2 \text{ s}^{-1}$ within the cement domain) have
523 been explored by increasing tortuosity values. Under these conditions, reactive fronts propagate
524 over wider areas, and then, larger model geometries need to be implemented. The increase in the
525 number of cells of the domain causes the cost of the simulation to increase, and then the
526 computational efficiency to sharply decrease. For this reason, this even higher diffusivity case is not
527 further investigated or presented here.

528

529 **4.1. Propagation of acid and alkaline fluids**

530

531 To facilitate the analysis of the propagation of the acid and alkaline fluids through the system,
532 contour plots of aqueous tracer concentration after 1000 years are displayed in Figure 4. Contour
533 lines for tracers give a general picture of the maximum propagation distances the reactive fronts are
534 expected to cover in our system. Numerical results show that after this simulation time, the
535 influence of reservoir fluids in the overlying layers (marked by the presence of tracer concentrations
536 around 1/10 of the initial value in the reservoir) extend up to less than 2 and more than 8 m from the
537 interface, in the LD and HD case, respectively. Due to the small volume of the cement domain

538 compared to caprock and reservoir, cement pore waters have a reduced capacity to penetrate the
 539 adjacent domains, and a strong dilution effect is observed within the cement domain, with tracer
 540 concentrations lower than 1/10 of the initial values throughout the cement slice in the HD case.
 541 Caprock fluids are predicted to fully penetrate the cement volume in both the LD and HD cases.
 542 Based on these considerations, which reflect the particular geometry and relative volume of
 543 different rock domains in our model (Table 1), it is expected that the alkaline pulse is markedly less
 544 effective than the acid one in controlling the geochemical evolution of the system. The contour plot
 545 of Figure 5, showing the areal variation of pH values after 1000 years, confirm this general picture.
 546 In this figure, a rise of pH values above 7-7.5 in the caprock, due to the migration of the alkaline
 547 pulse from the cements filling, is predicted only in the upper part of the model, near cement-caprock
 548 interface. In contrast, pH sharply decreases both in the lower part of cement and caprock domains,
 549 due to the propagation of the acid fluids coming from the reservoir, and in rightmost slices of
 550 cement domain, due to the ingress of near-neutral fluids coming from the caprock.

551

552 4.2. Mineralogical transformations

553

554 4.2.1 In the cement domain

555 Due to the high buffer capacity of the cement with respect to the acid, C- and Ca-rich fluids
 556 diffusing from reservoir and the local equilibrium approach adopted in describing the behavior of
 557 cement minerals, most of the mineralogical transformations occur at the bottom of the cement slice
 558 and concentrate in the first grid block, near the interface. Mineralogical transformations induced in
 559 the cement by the propagation of acid, C-rich fluids from reservoir are shown in Figures 6A and 6B
 560 with respect to the first block element CEM-01 along the slice #1. Several distinct reactive stages
 561 are recognized in this grid cell. The first stage is characterized by the dissolution of portlandite with
 562 correlated precipitation of calcite, minor precipitation of hydrotalcite, under almost pH-buffered,
 563 alkaline conditions (pH around 11). These processes can be described through the following
 564 reactions ², whose energetic feasibility is verified by inspection of activities of aqueous species
 565 involved:

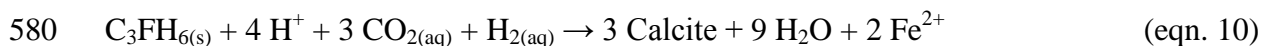
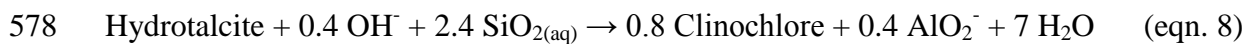
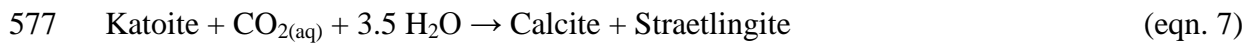
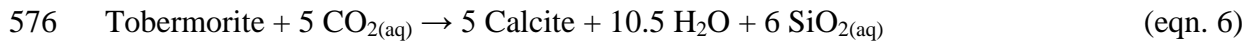


568 and with Al_{TOT} in the aqueous solution supplied by dissolving ettringite.

569 The onset of the second reactive stage, which occurs after about 180 and 20 years in the LD and HD
 570 cases, respectively, is concomitant with the disappearance of portlandite. This stage is characterized

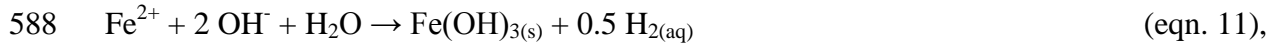
² Reactions are written in terms of predominant species and not basis species, i.e. CO_{2(aq)} and OH⁻ are the predominant C- and H-species in the pH-acid and pH-basic fluids of reservoir and cement domains, respectively

571 by the dissolution of all primary cement minerals (tobermorite, katoite-Si, $C_3FH_{6(s)}$, ettringite,
 572 hydrotalcite), and the precipitation of secondary straetlingite, calcite, and clinochlore. During this
 573 phase, alkaline conditions still persist, but some decrease in pH is observed (pH around 10.2),
 574 because of the partial buffering of H^+ ions coming from the adjacent reservoir. The overall process
 575 can be tentatively represented in terms of the following elementary processes:

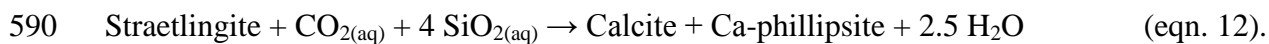


581 The first two stages cover a simulation time of about 250 and 25 years in the LD and HD case,
 582 respectively, and cause porosity to decrease down to 0.12 ± 0.02 (stage 1) and 0.03 ± 0.01 (stage 2),
 583 respectively.

584 A third stage occurs roughly between 210 and 370 years (between more than 25 and 38 years in the
 585 HD case), which is characterized by the dissolution of primary tobermorite and newly formed
 586 straetlingite, and by the precipitation of calcite, Ca-phillipsite, Mg-illite, and $Fe(OH)_3$. The
 587 following equations can be written:



589 characteristic of a very short time domain around 220 years simulation time, and:



591 After about 370 years (about 38 years in the HD case), the code predicts the complete
 592 disappearance of tobermorite, of secondary straetlingite and clinochlore, the precipitation of
 593 magnesite, and a drop of pH to 4.8. The Mg released in aqueous solution by Mg-chlorite
 594 dissolution, is captured by precipitating Mg-illite and magnesite. After the complete alteration of
 595 the cement initial mineralogy, the fluids coming from reservoir exert a total control on the
 596 geochemistry of the medium. This trend is further enhanced in the successive 600 years (LD case),
 597 as shown by the two additional zones predicted by the code. The first is characterized by the
 598 dissolution of Ca-phillipsite and the precipitation of Mg-illite, whereas the second one, roughly
 599 occurring between 600 and 800 years (LD case), is characterized by the precipitation of kaolinite,
 600 dawsonite and quartz. Porosity slightly increases with time up to about 0.10 after 1000 years. The
 601 late precipitation of quartz predicted by the numerical model is qualitatively in agreement with the
 602 end result of the degradation that hardened cement underwent upon carbonic acid exposure in the
 603 laboratory under similar ($50^\circ C$) conditions (Kutchko et al., 2007). The early precipitation of
 604 amorphous silica observed during some laboratory experiments on Portland cement exposed to

605 CO₂-rich fluids for several weeks (up to six months) and at temperatures between 50 to 90°C
 606 (Rimmelé et al., 2008), has not been reproduced in our simulations due to the high thermodynamic
 607 stability of tobermorite (a primary OPC mineral in our calculations) compared to the easily
 608 dissolving amorphous CSH phases considered in the laboratory experiments. Quartz predominates
 609 in our model (amorphous silica and chalcedony precipitate in negligible amounts) as it is the most
 610 stable silica polymorph in our database at the reference temperature of 75°C³.
 611 Additional mineralogical transformations include metastable formation of anhydrite (between 200
 612 and 350 years) and chlorite (between 250 and 400 years), and precipitation of celestite and siderite
 613 (later than 400 years). All these minerals occur in small amounts and do not significantly affect
 614 overall mass transfer in the system.

615 Summarizing, the most important geochemical reactions resulting in porosity changes in the
 616 cement, close to the reservoir interface, are, in a chronological order: i) the early replacement of
 617 portlandite and other dissolving primary OPC minerals with calcite, which leads to a significant
 618 decrease in porosity, down to -15%; ii) the transition katoite → straetlingite, which causes a slight
 619 increase in porosity (up to +2%); iii) the concomitant disappearance of straetlingite and tobermorite
 620 and precipitation of Ca-phillipsite and calcite, which determine a further, slight increase in porosity
 621 (up to 2%); iv) the late disappearance of Ca-phillipsite and the concomitant precipitation of
 622 additional carbonate minerals (magnesite, dawsonite, siderite), which cause, at the end of the
 623 reaction path, an additional porosity increase of up to +4%.

624 Overall, after 1000 years simulation time, cement porosity is lower than in the initial state. This is
 625 due to the early carbonation of portlandite, which causes an average increase of the volume
 626 occupied by solids in the order of 11.5%. In contrast to some laboratory experiments (e.g. Kutchko
 627 et al., 2007; Duguid et al., 2005), the mechanism of late porosity reopening predicted by the code is
 628 not related to the dissolution of calcite. This different behavior mirrors, in part at least, the large

³ Despite a number of field and experimental evidences supporting the low temperature stability of quartz in natural environments (e.g. Rimstidt, 1997; White and Brantley, 1995, and references therein), the predominance of different silica polymorphs in natural and engineered systems appears to be a function of not only the temperature, but also of many additional, often ill-defined factors, such as the chemical composition of circulating fluids, the mineralogical composition of the hosting rocks, fluid flow conditions and reaction times (i.e. amorphous and other unstable silica polymorphs tend to transform into cristobalite, opal, chalcedony or quartz over time).

In order to circumvent any possible uncertainty about the predominance of different silica polymorphs at 75°C, in our simulations we then considered the possibility that chalcedony, a silica microcrystalline mineral that can be considered a particular habit of quartz rather than a different phase, could be the only secondary silica polymorph allowed to precipitate over the time frame of interest of our model. Numerical results indicate that under these conditions, no appreciable variations are observed in the mineralogical patterns compared to the reference case simulations (with quartz allowed to precipitate) discussed in this paper.

629 differences in the initial geochemical conditions (i.e. porewater chemistry and initial mineralogy),
630 and both time and spatial observation scales (months and millimeters vs. hundreds of years and
631 centimeters to meters), between laboratory experiments and our numerical exercise. Laboratory
632 experiments set a severe, upper bound on the degradation rate of cement materials (pH values of the
633 reacting brines as low as 2 to 4; e.g. Duguid and Scherer, 2010), whereas our numerical simulations
634 realistically accounts for the capacity of reservoir rocks to buffer the pH of CO₂-rich reservoir
635 porewaters to values around 5.

636 Inspection of the mineral reactivity in the second grid block CEM-02, reveals that minor
637 transformations of the primary mineralogical assemblage are predicted moving away from reservoir
638 interface. In this grid cell, the main processes controlling the geochemical evolution of the medium
639 are still represented by the dissolution of portlandite, the precipitation of calcite and the decrease in
640 pH values, but the computed variations (about -1300 mol m⁻³; +1000 mol m⁻³; -0.5 pH units,
641 respectively) are now lower than in the first grid block (CEM-01). In addition, tobermorite,
642 C₃FH_{6(s)}, hydrotalcite and ettringite tend to precipitate instead of dissolving. No additional
643 secondary minerals are predicted to precipitate over 1000 years. In the HD case, the thickness of the
644 heavily altered zone (along the vertical slice #1) extends up to 0.175 m from reservoir interface
645 after 1000 years.

646

647 **4.2.2 In the reservoir domain**

648 The mutual interaction between cement and reservoir fluids induces very minor variations in the
649 reservoir mineralogical assemblage. The largest variations are observed in the grid cells adjacent to
650 cement interface. Here numerical outputs indicate that the disappearance of accessory magnesite
651 and Mg-illite, and a small increase in calcite, kaolinite and quartz abundances are possible.

652 Associated to these variations, a minor reduction in porosity, in the order of 1%, is also predicted.

653 The effects of the alkaline pulse migration from cement into reservoir domain are also revealed by
654 the spatial and temporal variations in chemical composition of reservoir porewaters. However, due
655 to the relatively large volume of reservoir elements compared to cement (Table 1), alkaline fluids
656 are diluted at very early times, and their maximum impact on reservoir geochemistry occurs in the
657 first 100 years simulation (LD case). During this stage, pH rises up to about 5.15, CO_{2(aq)}
658 concentration decreases to 0.2 mol kg_{H₂O}⁻¹, and aqueous cement tracer rises up to about the 30% of
659 its initial value in the cement, in the RES-01 element, near cement interface. A quite complex
660 behavior is shown by Ca²⁺ concentration profile, which reflects the interplay between diffusive
661 migration patterns in the aqueous phase and capture/release effects associated to
662 dissolution/precipitation mechanisms involving Ca-bearing minerals (mainly portlandite and

663 calcite) near the interface. Under HD conditions, the migration of acid fluids from reservoir into
664 cement is maximized, and accordingly, the impact of cement alkaline fluids on reservoir
665 geochemistry further reduced.

666

667 **4.2.3 At the cement-caprock interface**

668 Water-rock interactions occurring at the interface between caprock and cement, far from reservoir
669 interface, cause porosity to slightly increase in the cement and to decrease (up to -2%) in the
670 caprock. The diffusion of H⁺ component from caprock to cement allows pH to decrease in the
671 cement (buffered at about 10.8 after few tens of years), and to progressively increase in the caprock
672 (up to about 9.4 after 1000 years). Apart from significant portlandite dissolution, minor
673 mineralogical transformations are predicted in the cement. Ettringite, tobermorite, hydrotalcite and
674 calcite precipitate, and katoite dissolve in very low amounts (delta values up to a few moles m⁻³-
675 MEDIUM). Apart from calcite, no secondary minerals form in the cement.

676 The mineralogical transformations observed in the caprock, far from reservoir interface (CAP-03
677 grid block in our monitoring system; Fig. 2), are coherent with the alteration patterns already
678 described in the literature in association with high-alkaline fluids circulating through argillaceous
679 matrix (Gaucher and Blanc, 2006; and references cited therein). The most relevant processes
680 predicted in this part of the system are the dissolution of montmorillonite, quartz and dolomite, and
681 the precipitation of Ca-zeolites (Ca-phillipsite), illite, chlorite and calcite. The occurrence of
682 zeolites at the cement/clay interface is well documented over a large temperature range, up to about
683 150°C. Precipitation of phillipsite and analcime is documented by Bauer and Berger (1998),
684 Chermak (1993), de la Villa et al. (2001), Mosser-Ruck and Cathelineau, (2004), Ramirez et al.
685 (2002, 2005), Sanchez et al. (2006). Chabazite has been observed by Ramirez et al. (2005) during
686 alkaline alteration of CO_x. Field data and experimental evidences then suggest that zeolites could
687 be thermodynamically stable at the temperature of interest of our simulations (i.e. 75°C), and that
688 their precipitation may exert some control on aqueous Ca concentration of caprock and cement
689 porewaters. No CSH (amorphous and crystalline) phase precipitation is predicted, because of the
690 limited increase of Ca/Si ratio in aqueous solution which does not allow these minerals to reach the
691 saturation state over the time frame of 1000 years. Montmorillonite dissolution is the most
692 significant mineralogical transformation predicted in the caprock, close to cement interface. Similar
693 to many other clays, montmorillonite swells with the addition of water, acting as a natural plug
694 against fluid leakage. Its decrease in concentration may then negatively affect the sealing integrity
695 of the repository all along the annulus between the cement and the caprock. In the next forthcoming
696 years, the advancement of focused fundamental research and the development of fully coupled

697 geomechanical-reactive transport codes will likely help better clarify on this issue currently not
698 addressed by conventional reactive transport codes. Additional mineralogical transformations
699 include the transitory precipitation in traces of saponites and phillipsites (in the first 600 years), and
700 minor dissolution of celestite and pyrite.

701

702 **4.3 Porosity variability**

703

704 The potential impact to the integrity of wellbore cement as a result of exposure to CO₂-charged
705 natural brines is a primary concern with respect to long-term effectiveness of geological storage of
706 CO₂. Whereas CO₂ migration in defect-free cement is expected to occur over geological timescales
707 and does not present a major risk, the possibility that some leakage will occur along fractures of the
708 cement plugs should be taken into consideration and carefully analyzed (e.g. Wigand et al., 2009;
709 Carey et al., 2007; Kutchko et al., 2007). Porosity variations predicted by reactive transport codes
710 can be used to evaluate if the geochemical processes expected in the simulated systems may affect
711 isolation properties of cement, providing high permeability rising pathways for CO₂. The basic
712 assumption is that any computed decrease in porosity can be thought to be beneficial in terms of
713 containment capacity of the storage reservoir, whereas any increase in porosity can be considered of
714 some concern with respect to the long-term potential for undesired fluids leakage. This simplified
715 approach presents a major drawback in that it does not account for the changes in petrophysical and
716 geomechanical properties of rocks and cement, likely associated with the largest mineralogical
717 transformations predicted by the reactive transport code. Field and laboratory evidences, and
718 modeling results (e.g. Taylor, 1990; Barlet-Gouéadard et al., 2007; Carey et al., 2007; Duguid,
719 2008; Rimmelé et al., 2008; Fabbri et al., 2009; Wigand et al., 2009; among several others) indicate
720 in fact that, whereas moderate carbonation can be beneficial to cement strength, the formation of
721 cracks is usually recognized in association with extensive carbonation processes. For instance,
722 Barlet-Gouéadard et al. (2007) reported a strength loss of up to 65% for heavily carbonated Portland
723 cements exposed to CO₂-saturated fluids for six weeks, and the occurrence of cracks in the
724 carbonation layer during compressive strength measurements. Fabbri et al. (2009) observed a
725 significant degradation of mechanical properties of carbonated cement under wet supercritical CO₂
726 conditions at 90°C, associated with the presence of micro-cracks in the carbonated layers of the
727 Portland cement. Although the deposition of calcium carbonate in the pores may locally allow the
728 porosity to decrease, massive carbonation episodes within the OPC should be then considered not
729 only as mechanisms of possible further sealing of the cement, but also as possible sources of late
730 mechanical degradation of the material. Stresses and potential differential pressures likely occurring

731 during the injection of supercritical CO₂, and later on, during the in-situ ageing of materials, may in
732 fact develop fractures and preferential rising pathways for reservoir fluids. As of today, the lack of
733 fully coupled geomechanical-reactive transport codes, prevents any quantitative assessment of these
734 contrasting effects. Two possible scenarios can be then envisaged: i) in the best possible conditions,
735 massive cement carbonation can be considered as a beneficial effect of water-rock interactions,
736 which ensures site containment capability; ii) in a less favorable scenario, massive cement
737 carbonation leads to a degradation of the desirable properties of cement plugs. Reactive transport
738 modeling can be used to recognize as zones of potential concern all the portions of the modeled
739 system where large variations in mineralogical composition and/or porosity are predicted.

740 In our model, the largest mineralogical transformations occur at the caprock-cement interface, in
741 close proximity to the reservoir, where the interaction between the three chemical systems is
742 maximum. For instance, portlandite preferentially dissolves along the vertical slice #4, showing an
743 appreciable decrease in the volume fraction over a distance of about 0.5 m from reservoir interface
744 after 1000 years (LD case; Fig. 7). In the HD case, a complete dissolution of portlandite is predicted
745 all over the lower portion of the cement domain, up to a distance of about 0.175 m from reservoir
746 interface, together with a decrease in volume fraction from 0.328 to about 0.24 in the upper part of
747 the vertical slice #4, up to the top of the modeled system. Carbonation is also predicted already after
748 a few years of cement exposure to external fluids in this part of the system.

749 Under the diffusion-controlled conditions of these calculations, the thickness of the calcium
750 carbonate layer formed in the cement at reservoir interface increases progressively from the vertical
751 slice #1 (between less than 0.1 to about 0.25 m after 1000 years in the LD and HD case,
752 respectively), towards the vertical slice #4 (up to more than 1 m in the HD case; Fig.8).

753 Abundant crystallization of carbonate minerals is also predicted in the caprock, at the cement
754 interface, along the vertical slice #5, as a result of the coupling between the three different zones.

755 Porosity variations reflect all the mineralogical transformations described above. Again, patterns
756 differ significantly along the three vertical slices used as reference. Along the slice #1, the buffer
757 capacity of cement minerals prevents the alteration front from propagating more than a few
758 centimeters from reservoir interface, resulting in a very steep pattern of porosity decrease (up to -8
759 to -14% in the LD and HD case, respectively), whereas a more effective decrease in porosity over
760 wider portions of the system is predicted along the slices #4 and #5. Overall, the greatest effects of
761 the geochemical perturbation are predicted along the slice #4 (Fig. 9), where, under HD conditions,
762 an increase in porosity (up to +8%) is observed far from reservoir interface, next to the portion of
763 the cement domain characterized by the largest porosity decrease (up to -16% in the HD case). The
764 decrease in porosity in the lower part of the slice #4 could be put in relation with the migration of

765 acid fluids from reservoir, whereas the increase in porosity along the upper part of the same slice
766 reflects the penetration of fluids from the adjacent caprock and the concomitant leaching of species
767 from cement into caprock. The alteration of the cement with the surrounding host shale formation is
768 relevant for the assessment of the sealing integrity of the repository, because it might lead to the
769 formation of a vertical preferential ascent route towards the surface, and allow reservoir fluids to
770 leak over larger simulation times than considered here. Of course, this pessimistic scenario is
771 strictly related to the possibility that the enhanced carbonation of OPC predicted at the bottom of
772 the cement domain, may develop a set of interconnected fractures connecting the reservoir with the
773 zone of enhanced porosity along the cement-caprock interface.

774 In the lowermost part of the caprock domain, near the reservoir interface (distance < 1m), minor
775 variations in porosity are predicted, but significant mineralogical transformations are still expected,
776 consisting of calcite, illite and siderite precipitation, and chlorite dissolution.

777 A sensitivity analysis on calcite dissolution/precipitation behavior indicates that the numerical
778 model is quite robust (Fig. 10). Calcite was selected because carbonation is the most relevant
779 process predicted at cement edges, which controls the spatial and temporal evolution of water-rock
780 geochemistry and porosity. Again, porosity may be used as a master variable to trace the overall
781 geochemical effects induced under equilibrium and kinetically controlled conditions. As shown in
782 Figure 10, almost negligible differences can be recognized in terms of porosity variation when
783 switching from kinetic to equilibrium dissolution/precipitation conditions for calcite, compared with
784 variations related to low- (LD) and high-diffusivity (HD) end-member conditions.

785

786 **4.4 Additional sensitivity analysis**

787

788 **4.4.1 On caprock porewater composition**

789 The direct measurements of f_{CO_2} on core samples in the COx caprock have given a range of
790 $\log f_{CO_2}$ roughly between -3 to -2 at 25°C (Girard et al., 2005; Gaucher et al., 2006). These values
791 correspond to a range of $\log f_{CO_2}$ roughly between -1.8 to -0.8 at 75°C. Following the model of
792 Coudrain-Ribstein et al. (1998), Gaucher et al. (2006, 2009) consider that a mineralogical buffering
793 of f_{CO_2} is possible in this formation. However, as different mineralogical assemblages (with
794 different thermodynamic values) are possible for this buffering (Gaucher et al, 2009), it is difficult
795 to reduce the range of uncertainties for this parameter under a log unit. Moreover, we can recall the
796 $\log f_{CO_2}$ values obtained for the underlying Dogger aquifer ($\log f_{CO_2}$ roughly between -1.5 to -0.4,
797 Michard and Bastide, 1988; Coudrain-Ribstein and Gouze, 1993) for a temperature close to our

798 simulation temperature. Consequently, the chemical composition of a second, relatively “high-
 799 P_{CO_2} ” COx pore water (“Caprock #2” water of Table 5), compatible with the mineralogical
 800 assemblage shown in Table 3, has been then computed using batch numerical modeling, and used in
 801 2-D simulations for sensitivity analysis. A reference $\log f_{CO_2}$ value of -0.98 has been obtained.

802 Despite the lower initial pH value (6.33), and the higher C_{TOT} contents of this water (3×10^{-3} mol
 803 $kg_{H_2O}^{-1}$), very minor differences in the mineralogical assemblage alteration have been predicted by
 804 the code with respect to the reference case already discussed. In particular, minor porosity changes
 805 at the caprock-cement interface are computed after 1000 years (up to -0.4% and -1.2% in the
 806 cement and caprock, respectively), which are prevalently driven by calcite precipitation in the
 807 caprock (up to 318 mol m^{-3} -medium at the interface) and portlandite dissolution in the cement (up
 808 to -310 mol m^{-3} -medium). Near the caprock interface, cement primary mineralogy is also affected
 809 by katoite dissolution (up to -15 mol m^{-3} -medium) and precipitation of traces of ettringite,
 810 tobermorite, hydrotalcite and C_3FH_6 (always lower than $+10 \text{ mol m}^{-3}$ -medium), whereas the most
 811 significant modifications in argillite mineralogy are Mg-illite and quartz precipitation (up to $+25$
 812 mol m^{-3} -medium), and Mg-montmorillonite-Na dissolution (up to -35 mol m^{-3} -medium).

813

814 **4.4.2 On cement mineralogy and porewater composition**

815 The effects of different portlandite and tobermorite relative amounts in the initial idealized
 816 Portland-type cement have been tested by introducing into the calculations the mineralogical
 817 composition and associated pore water chemical composition (“Cement #2”) listed in Table 5. The
 818 new configuration of the system (Caprock #2 + Cement #2 initial conditions) leads to more
 819 conservative results compared to the scenarios already discussed. The most remarkable differences
 820 concern the alteration products predicted in the element CEM-01 of the cement, near the reservoir
 821 interface. Here, larger amounts of precipitated silica minerals (i.e. quartz in the reference case
 822 simulation, chalcedony when quartz is not allowed to precipitate), and almost no precipitation of
 823 Mg-illite are now computed, together with slightly lower amounts of precipitated magnesite and
 824 dawsonite. MonoSA-Fe and anhydrite appears among the secondary alteration products during a
 825 transient phase comprised between about 200 and 280 years and between about 280 and 780 years,
 826 respectively, in the low diffusivity case. Relevant amounts (up to about 1075 mol m^{-3} -medium) of
 827 newly precipitated kaolinite are also predicted after about 800 years simulation time. Again,
 828 porosity variations are used to trace the overall effect of all the occurring mineralogical
 829 transformations: the larger variations are predicted to occur along the slice #4, near caprock
 830 interface, with values between -11.5 to -4.5%, after about 200 and 1000 years simulation time,
 831 respectively (Figure 11_{EA}).

832

833 **5. Conclusion**

834

835 A complex 2D diffusive transport numerical model has been developed to assess the geochemical
836 integrity of a well cement filling connected to two separate mineralogical assemblages
837 representative of both reservoir and caprock porous rock. Cement alterations of abandoned wells
838 may play an important role in guideline definition and selection criteria of carbon dioxide geological
839 storage sites. The consideration of three different mineralogical domains induces a very complex
840 fluid rock geochemical interaction system which summarizes as the following major conclusions.

841 (a) Numerical simulations predict a two-stage evolution of the cement porous matrix, after
842 interaction with acid fluids from reservoir: (i) a first, “clogging” stage, characterized by a decrease
843 in porosity after precipitation of calcium carbonate (calcite in our model), and (ii) a second stage of
844 pore volume reopening, related to a decrease in calcite precipitation, the complete disappearance of
845 primary cement phases and the re-dissolution of large-molar volume secondary minerals, such as
846 Ca-zeolites. The penetration of these alteration fronts is limited to the first few to few tens of
847 centimeters from reservoir interface (up to a maximum of about 25 cm after 1000 yrs), depending
848 on the efficiency of mass transfer mechanisms, i.e. on variations of aqueous diffusion coefficient,
849 porosity and tortuosity.

850 (b) This mechanism of porosity reopening differs from experimental observations made by Kutchko
851 et al. (2007) and Duguid et al. (2005), who related the porosity reopening to calcite dissolution. In
852 this work, calcite is not predicted to dissolve because the numerical model realistically accounts for
853 the capacity of reservoir rocks to buffer the pH of CO₂-rich reservoir porewaters to values around 5.
854 In order to reproduce the short-term re-dissolution of calcite observed during laboratory
855 experiments, less realistic geochemical boundary conditions, i.e. lower pH fluids with time-
856 invariant chemical composition in the reservoir, should be adopted. This has already been shown for
857 a Class G high Sulfate Resistant commercial oilwell cement exposed to CO₂-rich aqueous solutions
858 over a period of 100 years and at a constant temperature of 45°C (Biagi and Gherardi, 2010). Initial
859 and boundary conditions of these calculations set an upper limit to the degradation rate of cement
860 materials, and closer represent laboratory experiments already published in the literature (e.g.
861 Duguid and Scherer, 2010).

862 (c) Geochemical interactions at the top of the reservoir generally induce some pore clogging in the
863 lowermost part of both cement and caprock domains, primarily due to enhanced precipitation of
864 secondary calcite. In contrast, porosity is predicted to increase in the cement, in the upper part of the
865 system, along the caprock interface. Close to the reservoir, along the cement-caprock interface,

866 porosity initially decreases down to about 3% (after 200 years), and then increases up to about 10%
867 (after 750 years). Overall, the mineralogical transformations predicted at the bottom of the system,
868 after the penetration of acid fluids from reservoir, and above, the increase in porosity caused by
869 caprock-cement interactions, might lead to the formation of a vertical preferential ascent route,
870 along the external edge of the cement filling, for reservoir fluids. This scenario is related to the
871 possibility that a set of interconnected fractures may develop in the cement, as a consequence of the
872 enhanced carbonation of the OPC plug near the reservoir interface.

873

874

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FIGURES

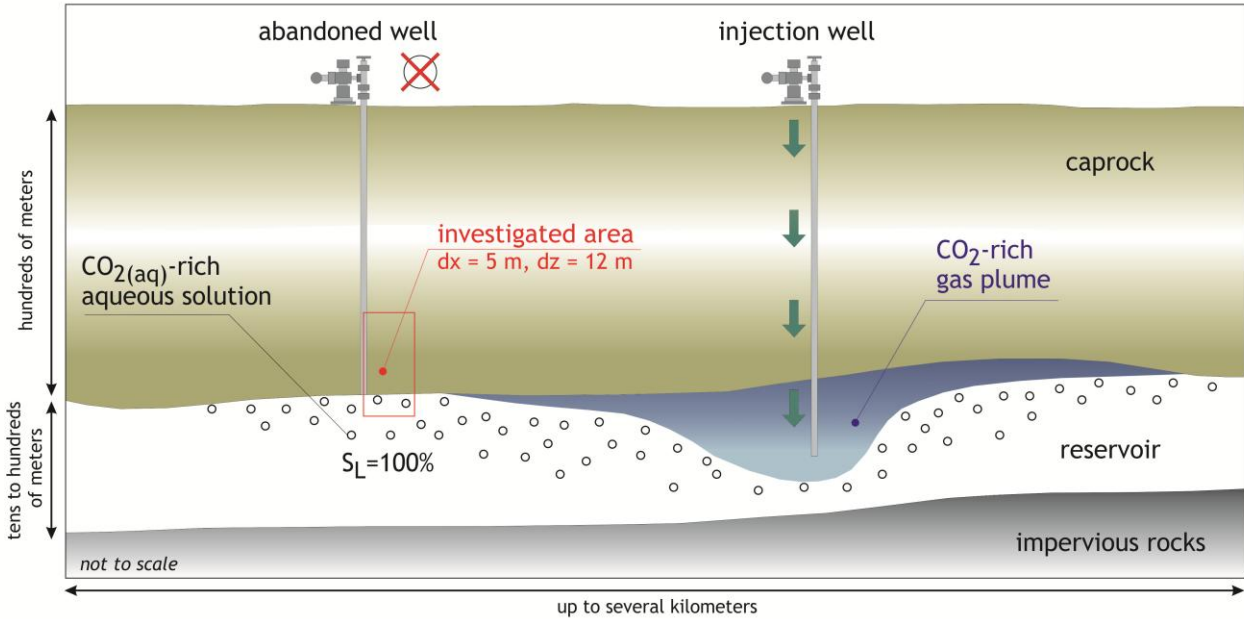


FIGURE 1

FIGURES

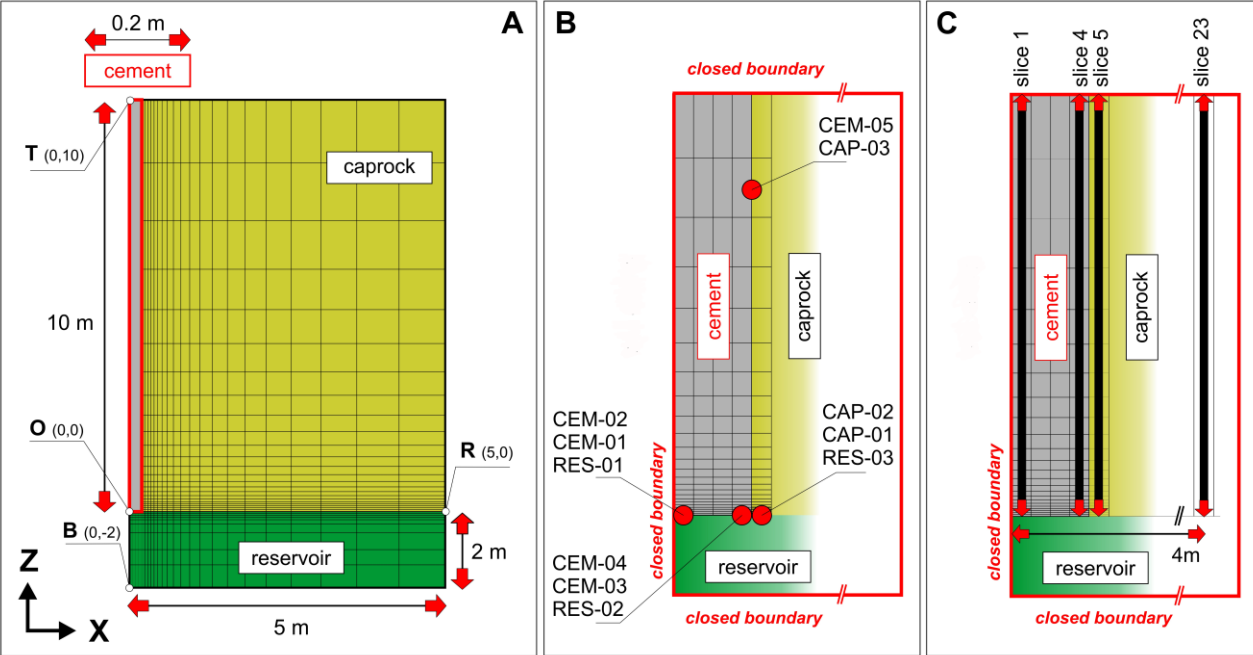


FIGURE 2

FIGURES

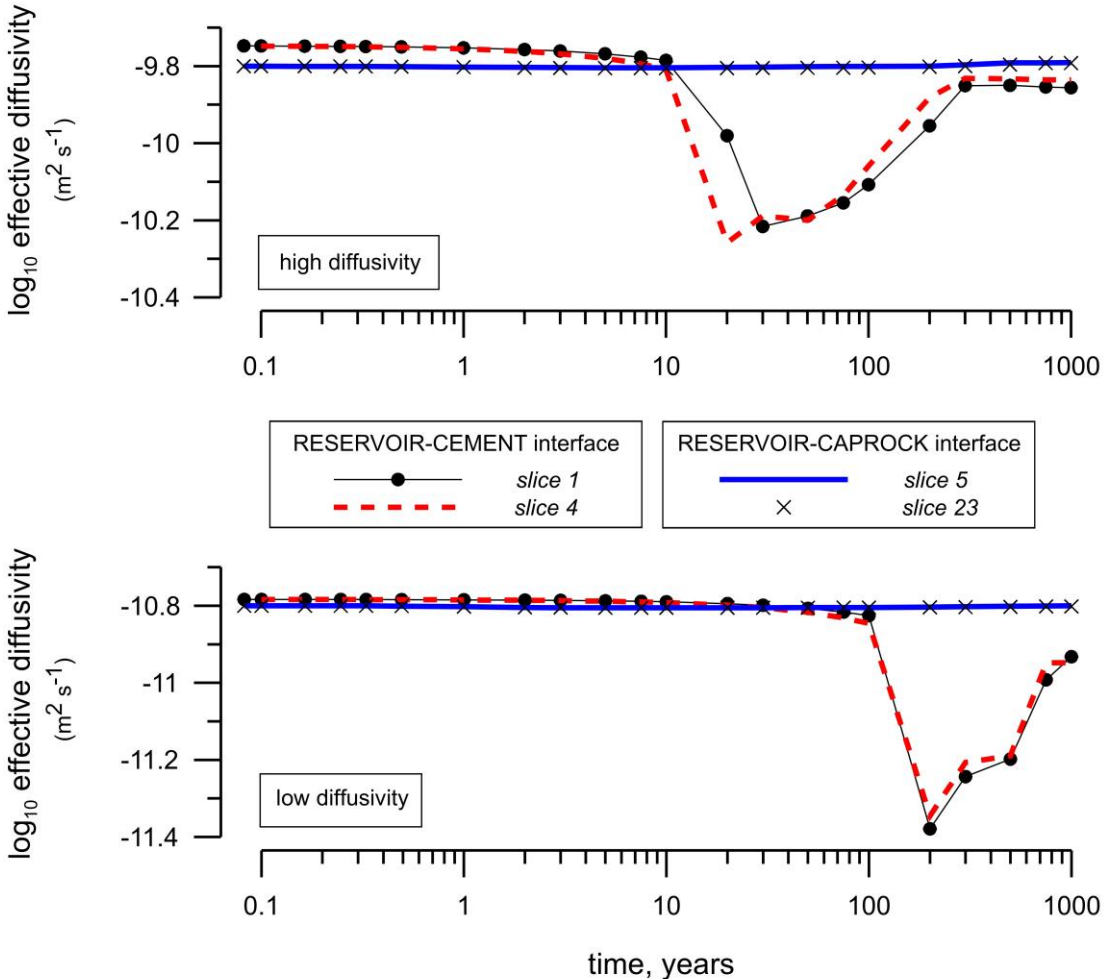


FIGURE 3

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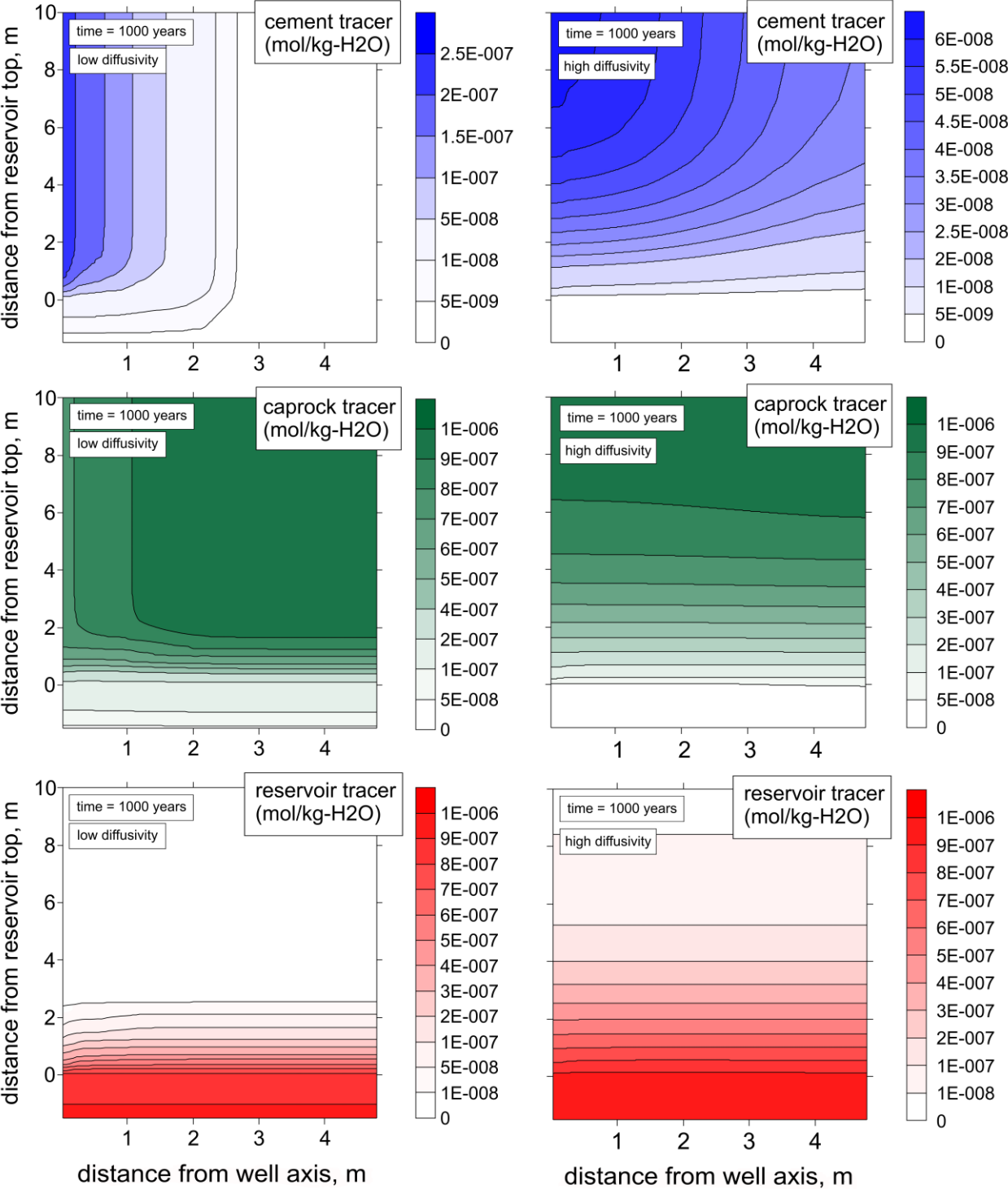


FIGURE 4

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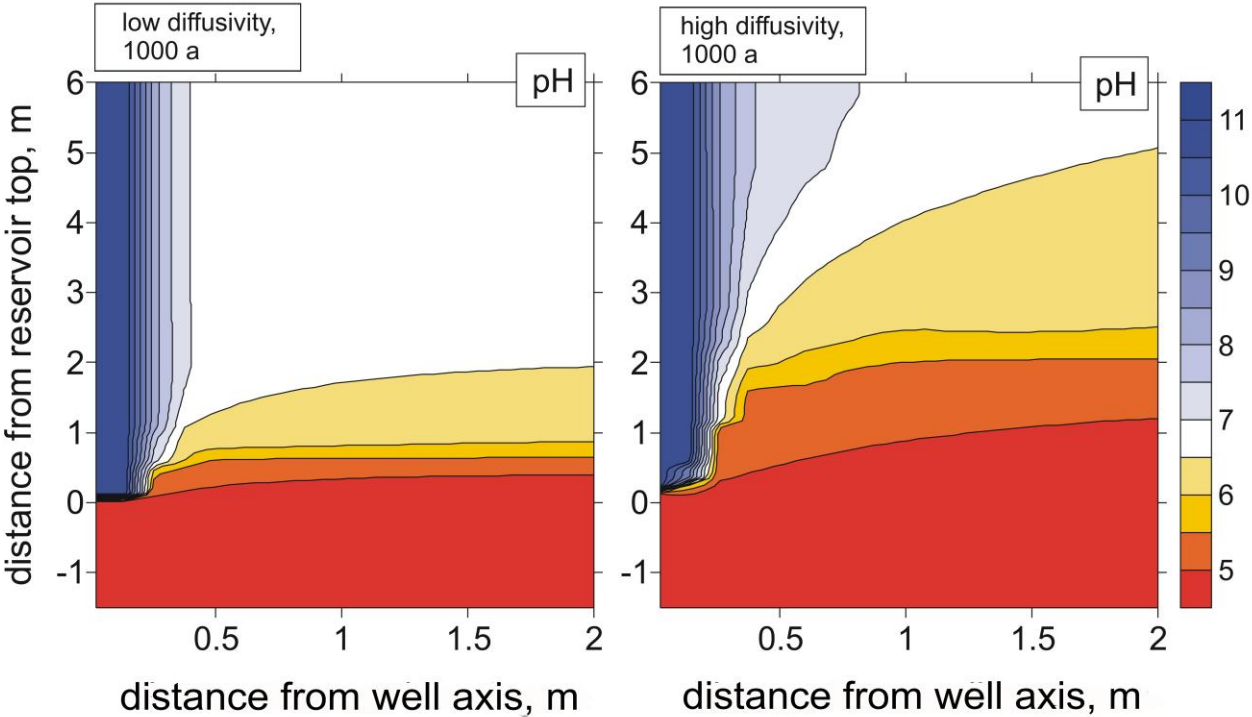


FIGURE 5

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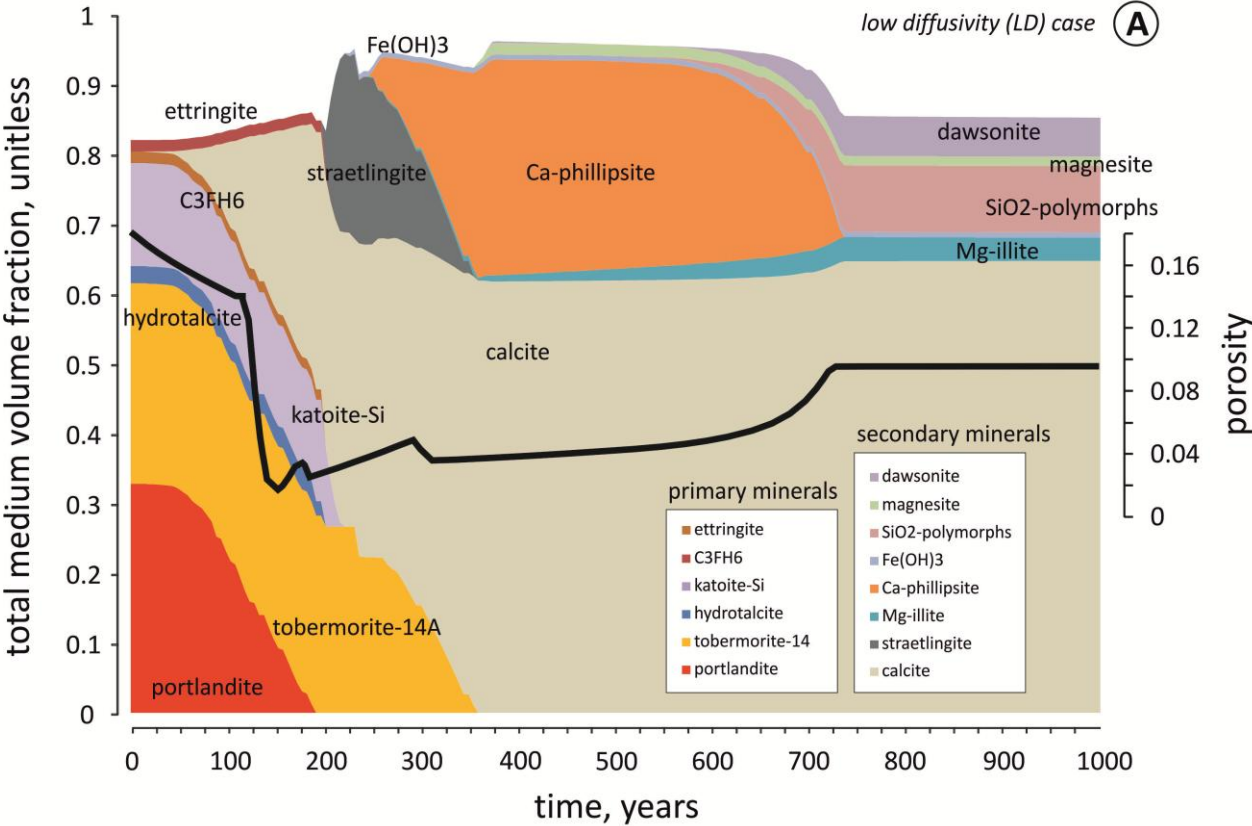


FIGURE 6A

FIGURES

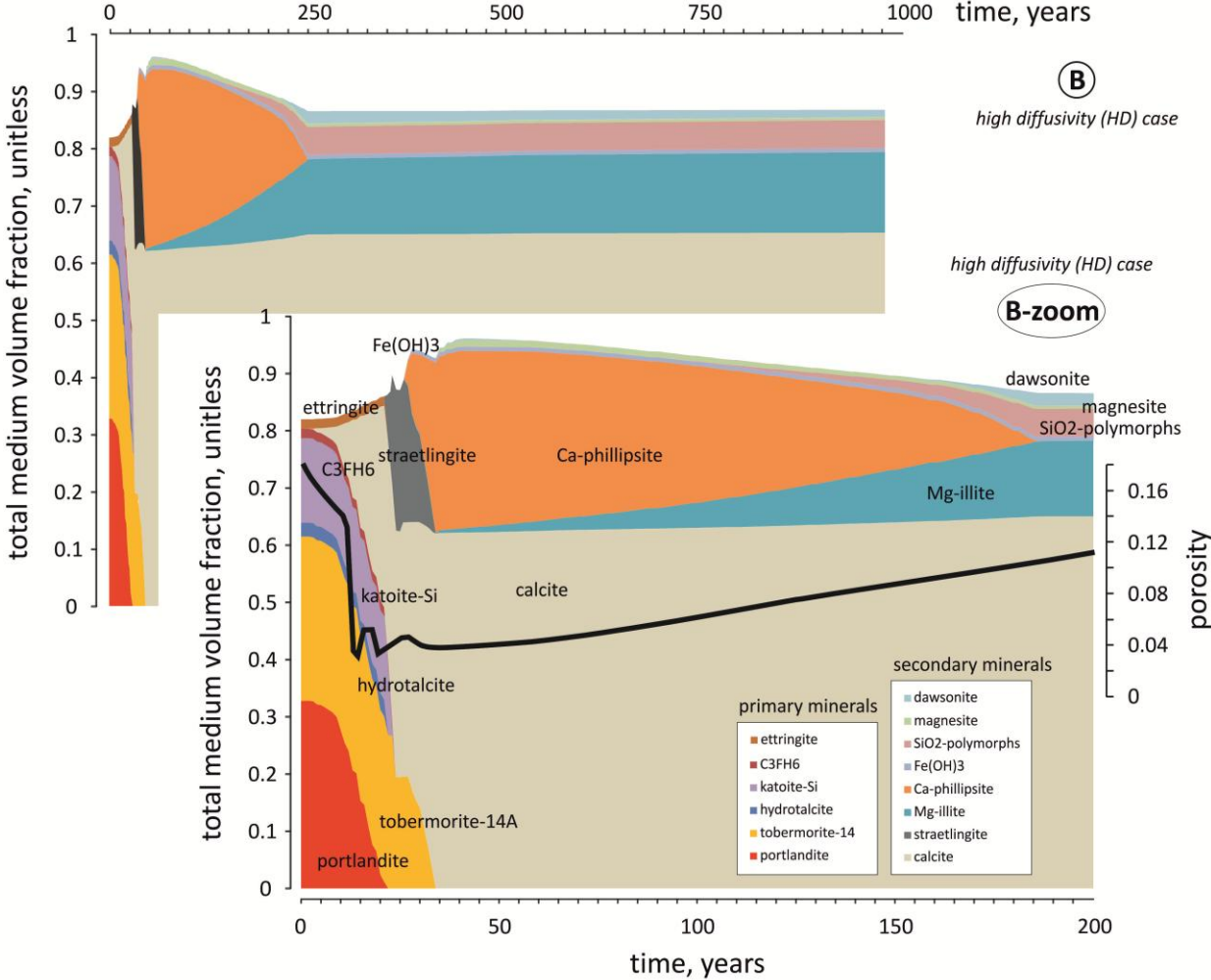


FIGURE 6B

FIGURES

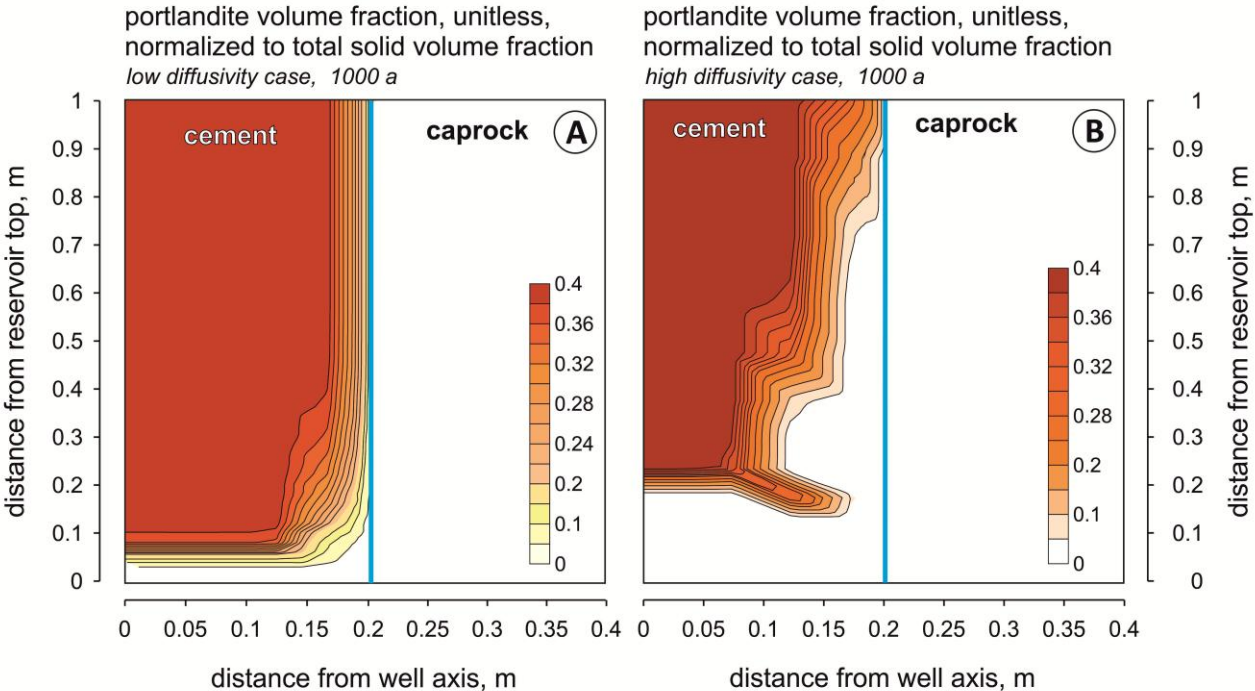


FIGURE 7

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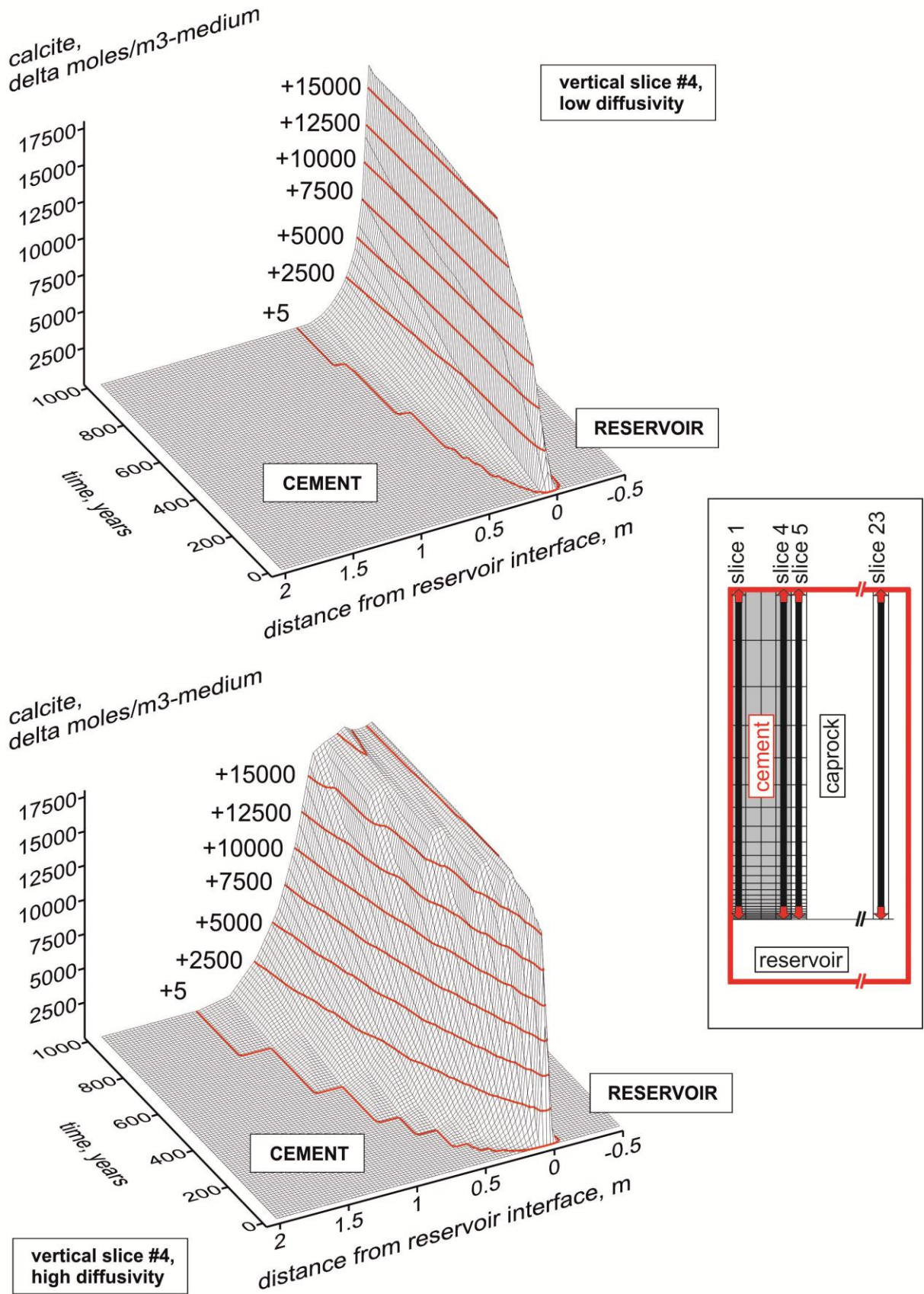


FIGURE 8

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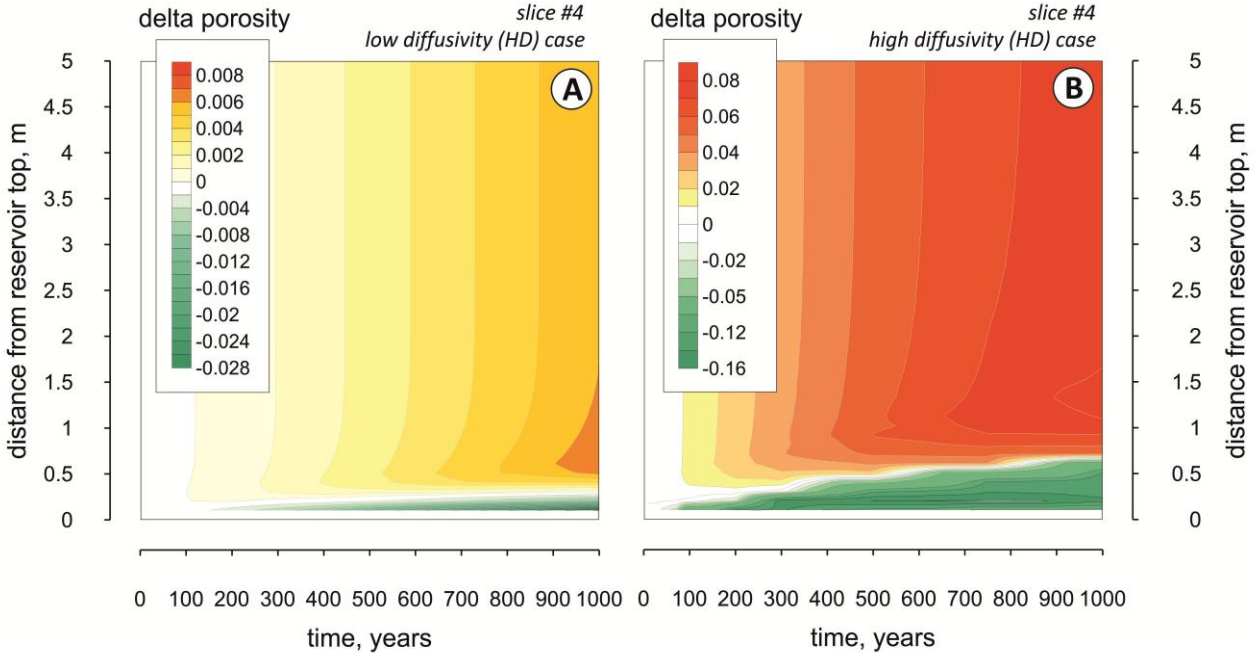


FIGURE 9

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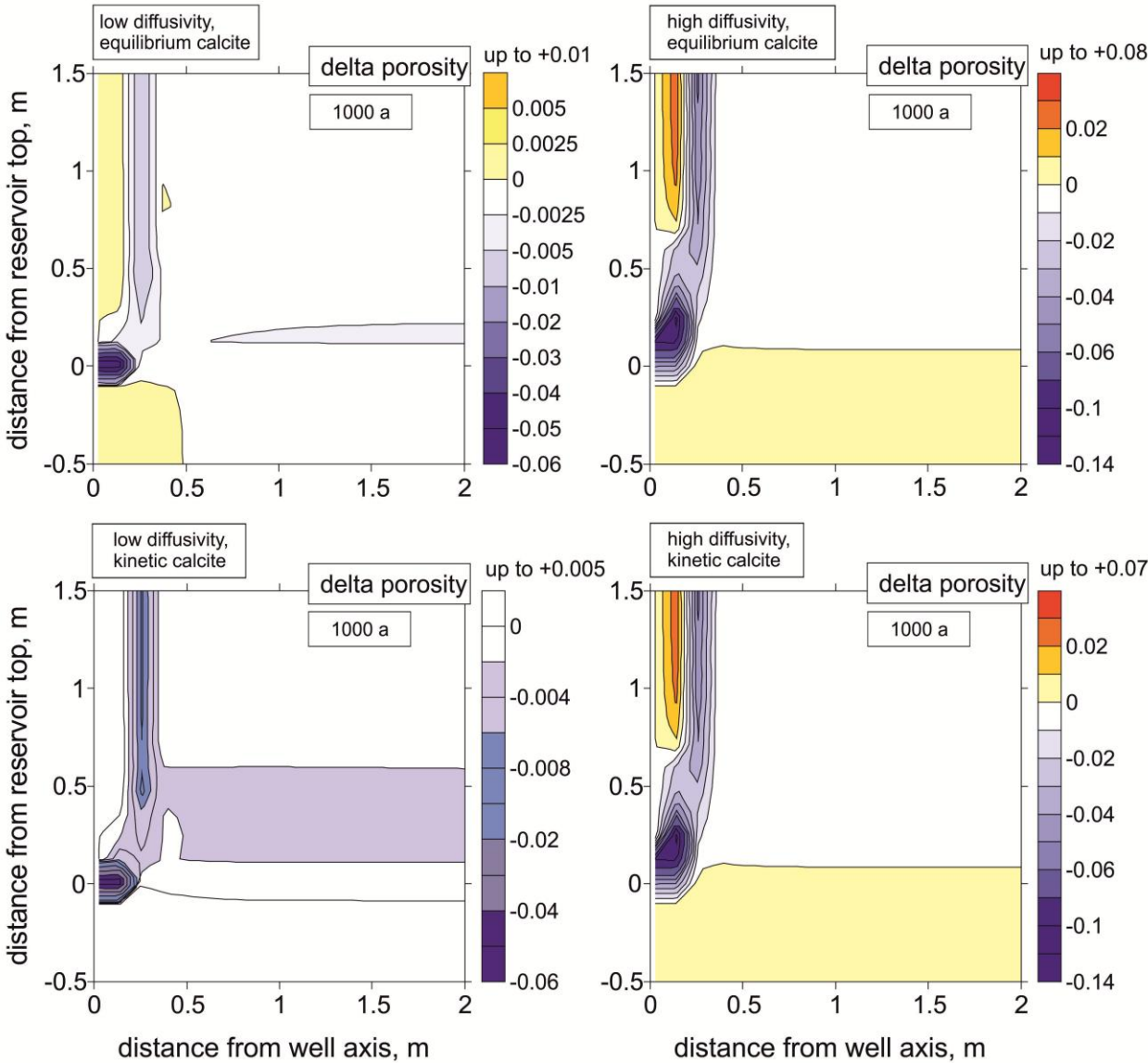


FIGURE 10