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1 Modelling water-rock interactions due to long-term
2 cooled-brine reinjection in the Dogger carbonate
3 aquifer (Paris basin) based on in-situ geothermal
4 well data

5

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15

16 **Abstract**

17 An experimental campaign was conducted using bottom-hole geometry data from a 24-year-
18 old injection well (~1700 m deep) at a geothermal site exploiting the Dogger aquifer (Paris
19 basin). A sonar tool was used to measure the geometry distortion of the open hole due to
20 long-term reinjection of cooled brine. Reactive transport modelling was then performed. The
21 calculated extent of carbonate dissolution at the well outlet was consistent with the sonar
22 observations. The best fit to experimental results was obtained by considering partial CO₂
23 degassing in the reinjected brine, which is consistent with the artesian mode doublet
24 operation.

25

26 **Keywords:** geothermal doublet, porosity, Dogger aquifer, water-rock interaction,
27 geochemical modelling, sonar

29 1. Introduction

30 Located at a depth of 1500–2000 m, the carbonate Dogger reservoir is the main geothermal
31 aquifer exploited in the Paris region of France. This geothermal resource heats
32 approximately 210,000 dwellings in the Ile-de-France region [1] through a significant growth
33 objective defined by the French energy transition law
34 (<http://www.gouvernement.fr/en/energy-transition>). Energy exploitation involves the
35 reinjection of cooled brine into the carbonated reservoir after calorie extraction by heat
36 exchangers [e.g. 1, 2, 3]. The local reinjected fluid temperature depends on the production
37 temperature (55–85 °C), the energy requirements at the surface, and the operating flowrate
38 (100–350 m³ h⁻¹) and typically varies between 40 and 60 °C with a minimum temperature of
39 35 °C. All geothermal operations from the 1970s to 1990s operated according to this
40 principle [2]; however, more recent geothermal operations conducted in the Dogger aquifer
41 employ a heat pump (e.g. Arcueil-Gentilly, Bagneux, Neuilly-sur-Marne, etc.) to optimise the
42 available geothermal resource, resulting in a lower return temperature. This implies that
43 reinjection of cooled brines at the Dogger aquifer occurs at lower temperatures
44 (approximately 25 °C) than previously [4].

45 To date, the majority of studies on the thermal effect on Dogger formation geochemistry have
46 focused on the hydro-geochemical impact of the reinjection of hot fluids into the aquifer from
47 the perspective of heat storage [5, 6]. Only a few studies have quantified the hydro-
48 geochemical impact of cooled-fluid reinjection in a carbonate aquifer [7-9]. Geothermal
49 energy production in the carbonate Dogger formation began in the early 1970s in the Paris
50 basin [2]. The typical lifetime of a geothermal doublet is approximately 30 years (duration of
51 the initial operating permits); therefore, as older wells are shut down, new wells are
52 commissioned. Thus, bottom-hole analysis of former injection wells could allow us to observe
53 and quantify the effects of potential water-rock interactions induced by cooled-brine
54 reinjection, especially in a carbonate aquifer such as the Dogger. Unfortunately, most of
55 these wells were plugged when the abandonment procedure was completed and are thus
56 inaccessible. However, as part of the CO₂-DISSOLVED project and through collaboration
57 with the local geothermal operator (Chelles Chaleur, subsidiary of the Coriance group), the
58 unique opportunity was granted to access the open-hole part of a former injection well in
59 Chelles (Paris basin, France). This injector was utilised for 24 years from 1986 to 2010 but
60 remains accessible as a backup injection well for the current geothermal doublet. An in-situ
61 experimental campaign was conducted in March 2016 to analyse the reservoir geometry at
62 the well outlet using an innovative sonar tool provided and operated by Flodim (Cavity Survey
63 and Well Logging Services Company, <https://www.flodim.fr/>).

64 The results of this study will aid our understanding of water-rock interactions at the well
65 outlet, which is a major concern of the CO₂-DISSOLVED project ([http://co2-
66 dissolved.brgm.fr/](http://co2-dissolved.brgm.fr/)). CO₂-DISSOLVED is an innovative carbon capture and storage (CCS)
67 concept involving the capture, injection, and storage of dissolved CO₂ (rather than
68 supercritical) in a deep saline aquifer coupled with geothermal heat recovery [10-12]. Once
69 out of the injection well, the acidified brine is expected to be chemically reactive with the
70 reservoir porous matrix, particularly in the presence of carbonate minerals [13-15]. In order to
71 quantify these effects, both experimental and numerical modelling studies have been
72 conducted in parallel as part of the CO₂-DISSOLVED project. The most notable results were
73 obtained with the carbonate samples, showing the rapid development of a network of
74 wormholes around the injection pipe outlet [16]. A numerical simulation of this experiment
75 performed with the MARTHE-PHREEQC code [17] reproduced the massive dissolution of
76 calcite near the injection pipe and the formation of wormholes due to the heterogeneous
77 hydraulic conductivity reasonably accurately [18]. As demonstrated in numerous studies, the
78 formation of wormholes depends on several parameters such as the ratios of reaction rate,
79 convection rate and diffusion rate (i.e. Peclet and Damköhler numbers) [15, 18, 19] and
80 material heterogeneities (i.e. permeability and chemical composition) [18, 20]. Regarding the
81 Chelles doublet, no dissolved CO₂ has been added in the injected cooled brine. Contrariwise,
82 the artesian production mode of the doublet led to CO₂ degassing at surface. Near neutral
83 pH of the reinjected brine resulted in a solution close to equilibrium with respect to calcite
84 and therefore, the Damköhler number was low, thus promoting uniform dissolution [15, 18].

85 The aim of this study is to provide reference data for the predicted effects of reactive
86 processes at the well outlet when reinjecting a cooled brine (i.e. a 'standard' cooled
87 geothermal brine). Moreover, it is critical to be able to compare the modelling results to
88 actual bottom-hole measured data in order to evaluate the validity of model predictions. In
89 contrast to other geothermal reservoirs [e.g. 21, 22], such reservoir data are extremely
90 scarce for the Dogger carbonate aquifer and have not previously been made available to the
91 scientific community; therefore, this study provides insights into water-rock interactions in this
92 specific environment. The second objective of this study is to give insights to better interpret
93 predictions of the CO₂-DISSOLVED system related to adding dissolved CO₂ to the reinjected
94 brine. This is because this CCS method has not yet been tested at full scale, so no
95 equivalent in-situ data can be obtained; therefore, modelling remains the only approach to
96 estimate the potential impacts of dissolved CO₂ reinjection on the exploited reservoir. In a
97 such context, the hole stability [23] and permeability increase leading to a risk of thermal
98 breakthrough in the nearby production wells [13, 24] are intensively investigated.

100 **2. Materials and methods**

101 **2.1. Chelles geothermal doublet**

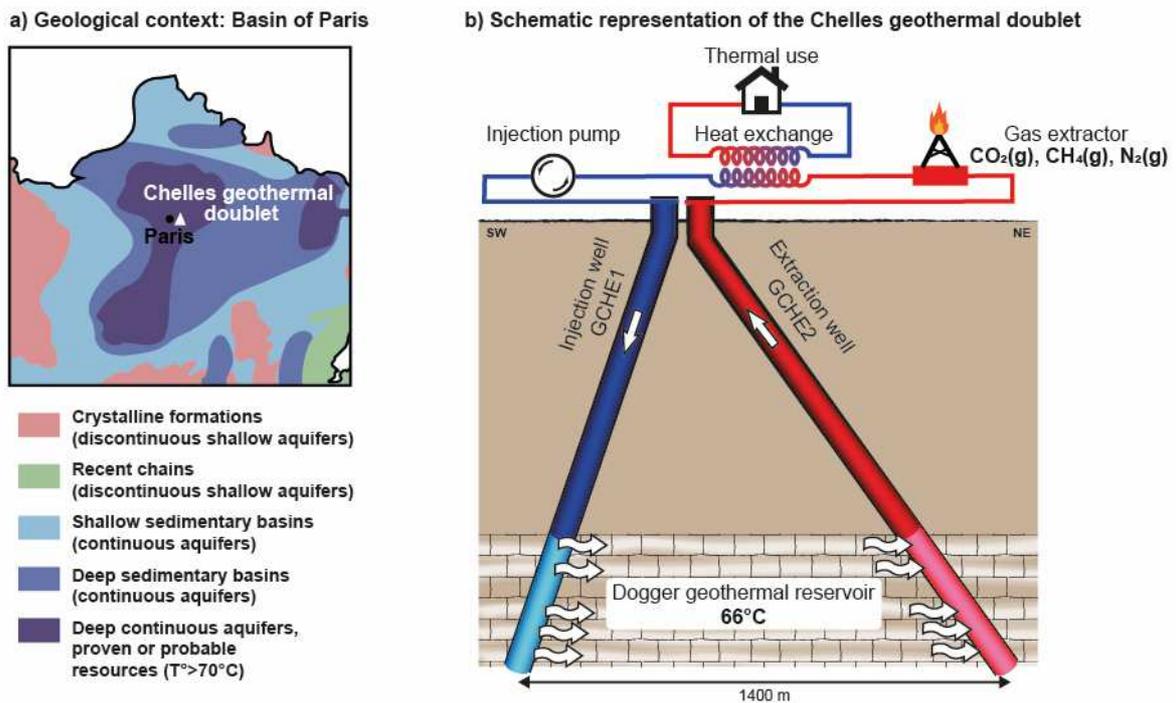
102 The Chelles geothermal district heating doublet was exploited continuously since its
103 commissioning in 1986 until its closure in 2010 in artesian production mode with a maximal
104 flow rate of $250 \text{ m}^3 \text{ h}^{-1}$ (Figure 1). This system operated at high flow rates and a wellhead
105 pressure lower than the bubble point, leading to the partial release of gases initially dissolved
106 in the Dogger pore water and their partial trapping high in the geothermal pipe [25]. The
107 geothermal reservoir has a gas production capacity of approximately 0.125 m^3 per m^3 of
108 Dogger fluid. The gas phase is mainly composed of CH_4 and other alkanes (55%), N_2 (35%),
109 and CO_2 (10%) [25-27]. From 2000–2010, a special degassing device was employed for gas
110 extraction and burning [25]. Unfortunately, gas extraction was not monitored over time;
111 therefore, the partial pressure of CO_2 in equilibrium with the reinjected fluids remains
112 uncertain. In contrast, flow and temperature data of the Chelles doublet GCHE1/GCHE2 are
113 available from the Dogger database (<https://dogger-idf.brgm.fr>); however, data regarding the
114 injection well are very sporadic between 1986 and 2010 (see injection_history file in
115 Electronic Annex). Indeed, only typical injections have been recorded during winters of the
116 first 5 years (one recording per year) and data are not continuous between years 5 to 24
117 years (about one recording per month). Therefore, average flow rates and injection
118 temperatures of the injection well (GCHE1) during summer ($133 \text{ m}^3 \text{ h}^{-1}$ and $52 \text{ }^\circ\text{C}$) and winter
119 ($148 \text{ m}^3 \text{ h}^{-1}$ and $48 \text{ }^\circ\text{C}$) were considered in this study. Such a discretisation in two steps is
120 supported by recorded data from similar doublets in the Paris basin [2]. Conversely, a
121 constant temperature of $66 \text{ }^\circ\text{C}$ was monitored at the production well (GCHE2).

122 The section of the GCHE1 well has been drilled in 1985 with a diameter of $8\frac{1}{2}$ " (Figure S1).
123 However, the exact geometry of the injection chamber has not been determined after the
124 drilling operation (i.e. no caliper measurement). Nonetheless, the numerous drilling
125 operations carried out in the Dogger aquifer do not indicate any enlargement/damage of the
126 borehole. In particular, the GCHE4 well that has been drilled in 2013 at the immediate vicinity
127 of GCHE1, using similar operational conditions in terms of tool (rotary drilling), geometry
128 ($8\frac{1}{2}$ " diameter), and geological formation targeted (Dogger aquifer). Caliper data are
129 available for GCHE4 and they confirm an effective diameter of the open hole consistent with
130 the nominal drilling diameter. As a consequence, we assumed an initial radius of 0.1 m for
131 the open hole of the GCHE1 injection well. Regarding the structure of the geothermal
132 reservoir, the GCHE1 well is characterised by five productive layers of the Dogger aquifer [2,
133 28]: two layers of Comblachian units from -1668 m to -1683 m FOD (French Ordnance
134 Datum), which contribute up to 14.7% of the total flow, and three layers of Oolithic units from

135 -1692 m to -1709 m FOD, contributing 85.3% of the total flow. The porosity, permeability, and
 136 flow contribution of each layer are summarised in Table 1. Measured permeabilities are
 137 greater than the one of the Oolithic limestone studied by Randi et al. [18] (i.e. 88 mD). Such
 138 values may reflect the presence of fractures in the Dogger aquifer. This also raises the
 139 question about the representativeness of the sample studied by the authors.

140

141



142

143 *Figure 1. Location and schematic representation of the Chelles geothermal doublet.*

144

145 *Table 1. Production levels identified by flowmetry analyses conducted in 1985.*

Facies	Layer	Altitude (m FOD*)	Flow contribution (%)	Porosity (%)	Permeability (D)
Comblachian	1	-1667.8 / -1669.8	7.3	12.5	1.03
	2	-1682.4 / -1683.3	7.4	15.8	2.09
	3	-1692.1 / -1698.4	29.4	17.4	1.28
Oolithic	4	-1702.3 / -1703.7	51.0	15.7	9.60
	5	-1707.1 / -1708.6	4.9	14.9	0.92

146 *French Ordnance Datum

147

148 **2.2. Examination of the injection well post-geothermal production**

149 The injection well (GCHE1) integrity was examined in March 2016 by combining ABI
150 technique (Acoustic Borehole Imaging) and a sonar tool developed by Flodim. The technical
151 principle of the sonar probe involves sound propagation (at lower frequency than for ABI) and
152 recording the reflection of the acoustic signal against the cavity wall. The cavity wall is clearly
153 imaged if the density contrast between the fluid and the ground is strong and the wall is
154 regular. The measurement range is several centimetres to hundreds of metres. Currently,
155 sonar does not allow continuous acquisition. The probe performs 360° rotations with a fixed
156 measurement step (5° in this study) at a fixed depth. Once the rotation is complete, the probe
157 moves to another depth to resume measurements.

158

159 **2.3. Numerical tools**

160 MARTHE-PHREEQC reactive transport modelling software is an extension of MARTHE
161 software [<http://marthe.brgm.fr/>, 17], which has been upgraded by coupling with the
162 PHREEQC chemical module [29]. The coupling algorithm is purely sequential; at each time
163 step, MARTHE computes the hydraulic head field and hence the velocity in the entire
164 domain. It then transports all considered dissolved chemical elements and also transports
165 heat to determine the temperature field on which geochemical reactions depend. Then, the
166 geochemistry is computed using the PHREEQC module. The THERMODDEM
167 thermodynamic database [30] (<http://thermoddem.brgm.fr/>) was used in this study. The B-dot
168 model, an extension of the Debye-Hückel activity model, is valid up to salinities of about 1
169 mol L⁻¹ [31, 32].

170 **3. Experimental results**

171 The cavity extension was measured by the sonar tool at depths of approximately every 0.5
172 m. Investigations were focused on the exploited part of the geothermal reservoir (from -1650
173 to -1710 m FOD), where the well is characterised by the absence of open-hole casing.
174 Maximum and minimum extensions are reported in Figure 2. The shape and volume of the
175 cavity were irregular in both horizontal and vertical orientations. Nonetheless, regardless of
176 the amount of dissolved rock, preferential alteration leading to cavity formation was clearly
177 identified in the SW direction. This observation fully agrees with the tilt of the GCHE1 well
178 (Figure 1); i.e., the direction of injected flow strongly influences the shape of the formed
179 cavity. Note that ABI data (GCHE1_ABI file in Electronic Annex) of the well section located
180 below the productive layers do not indicate any enlargement/damage of the bore hole due to
181 drilling operations, thus supporting an initial open hole diameter of 0.1 m.

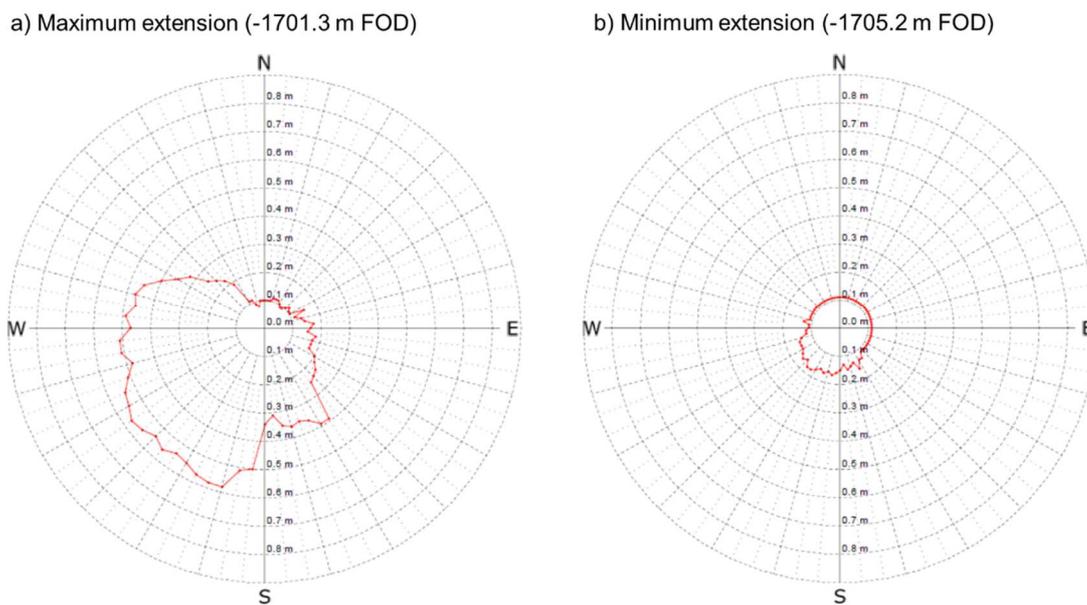
182 Surfaces and thus volumes of irregular polygons have been directly calculated by the tool
 183 software knowing the coordinates of the vertices and the thickness of the investigated area
 184 (Figure 3a). Despite the observed slight shift of data with depth, the productive layers
 185 identified in 1985 (Table 1) were in reasonable agreement with the maximum altered
 186 volumes of rock. These volumes were converted to equivalent radii, assuming a cylindrical
 187 geometry for the cavity (Figure 3b) following:

188
$$r_{eq} = \sqrt{\frac{V}{h \cdot \pi}} \quad (\text{Eq. 1})$$

189 where r_{eq} is the equivalent radius (m), V the volume given by the sonar tool (m^3) and h the
 190 thickness of the area investigated (m).

191 The average calculated radius was 0.21 m. Considering an initial well radius of 0.1 m,
 192 approximately 6 m^3 of the Dogger formation was dissolved during the operating period of the
 193 injection well (1986–2010). The average radius was compared with numerical results in order
 194 to evaluate the effect of various modelling assumptions (i.e. the geometry considered and the
 195 chemistry of the injection solution).

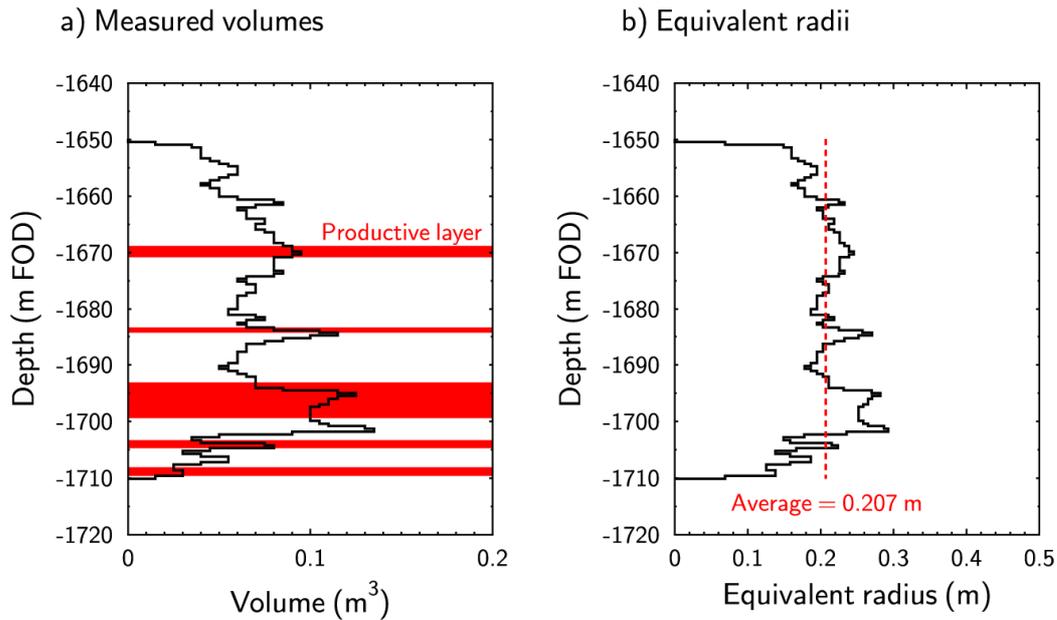
196



197

198 *Figure 2. a) Maximum extension of the cavity observed at -1701.3 m FOD and b) minimum extension*
 199 *of the cavity observed at -1705.2 m FOD. Experimental data were measured by the sonar tool every*
 200 *~0.5 m.*

201



202

203 *Figure 3. a) Volumes measured by the sonar tool every 0.5 m and b) calculated equivalent radii*
 204 *assuming a cylindrical cavity.*

205

206 4. Modelling strategy

207 4.1. Dogger formation parameters

208 The mineralogical composition of the Dogger formation (Table 2) was established from the
 209 volume percentages given in [33] and [6]. The Dogger assemblage consists essentially of
 210 calcite and dolomite. Siderite, illite, albite, and K-feldspars are present as accessory
 211 minerals. The chemical composition of the Dogger brine was calculated for a temperature of 66
 212 °C according to the value recorded at the production well. The simulation assumed a
 213 thermodynamic equilibrium between the Dogger pore water [13, 34] and the mineralogical
 214 assemblage reported in Table 2. Note that the formation of albite and K-feldspars is unlikely at
 215 66 °C and only dissolution reactions occurred during equilibration. In addition, a CO₂ partial
 216 pressure of 100 mbar (log pCO₂ = -1.0 atm) was assumed for the Dogger formation. Such a
 217 partial pressure is in the lower range of values reported for this aquifer [35]. Constraints
 218 assumed for the fluid composition calculation are reported in Table 3. The fluid is in equilibrium
 219 with carbonates (calcite, dolomite, and siderite), illite, and quartz (Table 4). It is also close to
 220 equilibrium with sulphate bearing minerals such as barite (BaSO₄) and celestine (SrSO₄).

221

222 *Table 2. Mineralogical assemblage of the Dogger formation (data extracted from André, Audigane,*
 223 *Azaroual and Menjoz [33] and Gille [6]).*

Mineral	Mineral name in THERMODDEM	Volume fraction
Calcite	Calcite	0.7
Dolomite-des	Dolomite(disordered)	0.1
Siderite	Siderite	0.05
Illite	Illite(IMt2)	0.05
Albite	Albite(low)	0.05
K-Feldspaths	Microcline	0.05

224

225 *Table 3. Chemistry of the Dogger pore water at 66 °C.*

Element	Concentration (mol L⁻¹)	Constraint
Al	1.67 10 ⁻⁰⁷	Gibbsite
Ba	1.09 10 ⁻⁰⁶	Barite
C(4)	5.24 10 ⁻⁰³	P _{CO2}
Ca	1.12 10 ⁻⁰²	Calcite
Cl	3.14 10 ⁻⁰¹	
Fe	8.39 10 ⁻⁰⁵	Siderite
K	9.38 10 ⁻⁰³	Illite(IMt2)
Mg	1.63 10 ⁻⁰²	Dolomite-des
Na	2.70 10 ⁻⁰¹	
S(6)	9.01 10 ⁻⁰³	
Si	5.06 10 ⁻⁰⁴	Quartz
Sr	5.23 10 ⁻⁰⁴	
pH	6.48	
pe	-3.51	
log P _{CO2} (atm)	-1.0	

226

227 Table 4. Saturation indices of the Dogger pore water at 66 °C ($SI = \log IAP/K$, where IAP is the ionic
 228 activity product and K the thermodynamic constant).

Phases	Saturation indices (SI)
Calcite	0
Dolomite(disordered)	0
Siderite	0
Gibbsite	0
Illite(IMt2)	0
Albite(low)	0.48
Microcline	1.09
Quartz(alpha)	0
Celestite	-0.19
Barite	0

229

230 **4.2. Chemistry of injected fluids**

231 The numerical simulations considered fluid reinjection at different temperatures according to
 232 different periods (heat extraction being more important in cold periods). In the heat exchanger,
 233 calculations did not consider the mineralogical assemblage of the Dogger because no mineral
 234 phase was theoretically present. However, potential secondary phases such as calcite, and
 235 barite were implemented. If oversaturated, their precipitation should occur primarily in the heat
 236 exchanger and in the downstream pipe portion (i.e. in the coldest zone).

237 As a first approximation, CO₂ degassing was not considered and the fluid chemistry at 48 °C
 238 and 52 °C was calculated from simple cooling of the Dogger pore water (“No degassing” case,
 239 Table 5). As expected, the temperature decrease destabilises the carbonate minerals, which
 240 are then undersaturated (Table 6). However, between 1986 and 2010, the Chelles geothermal
 241 doublet operated in artesian mode, resulting in degassing at the wellhead that favoured
 242 carbonate precipitation instead. A second model (“Partial degassing” case, Table 5) was then
 243 established assuming partial degassing of CO₂ until a calcite saturation index of -0.01 (i.e.
 244 almost in equilibrium with this carbonate). This value was adjusted to reasonably match with
 245 the observed calcite dissolution using a single-layer geometry. Finally, a third solution
 246 chemistry was calculated considering the CO₂ atmospheric partial pressure (i.e. $\log P_{CO_2} = -3.45$
 247 (atm)) related to calcite precipitation (“Total degassing” case, Table 5). Regardless of the fluid
 248 chemistry (i.e. CO₂ degassing), the cooling of brines leads to barite and quartz precipitation
 249 (Table 6). Nonetheless, silica precipitation is known to be a slow process at considered
 250 temperatures [e.g. 37] and Si concentrations reported in Table 5 are probably under estimated.
 251 Note that numerous studies have reported quartz, barite, and calcite scaling in geothermal wells

252 [e.g. 38, 39, 40]; however, this study was not focused on such surface and subsurface
 253 processes.

254

255 *Table 5. Injected brine compositions as a function of temperature and CO₂ partial pressure.*

Element	Concentrations (mol L ⁻¹)					
	No degassing		Partial degassing		Total degassing	
	48 °C	52 °C	48 °C	52 °C	48 °C	52 °C
Al	4.15 10 ⁻⁰⁸	5.67 10 ⁻⁰⁸	6.02 10 ⁻⁰⁸	7.59 10 ⁻⁰⁸	1.67 10 ⁻⁰⁷	1.67 10 ⁻⁰⁷
Ba	7.12 10 ⁻⁰⁷	7.89 10 ⁻⁰⁷	7.12 10 ⁻⁰⁷	7.90 10 ⁻⁰⁷	6.94 10 ⁻⁰⁷	7.68 10 ⁻⁰⁷
C(4)	5.24 10 ⁻⁰³	5.24 10 ⁻⁰³	4.71 10 ⁻⁰³	4.80 10 ⁻⁰³	4.01 10 ⁻⁰⁴	3.70 10 ⁻⁰⁴
Ca	1.12 10 ⁻⁰²	1.12 10 ⁻⁰²	1.12 10 ⁻⁰²	1.12 10 ⁻⁰²	9.64 10 ⁻⁰³	9.63 10 ⁻⁰³
Cl	3.14 10 ⁻⁰¹	3.14 10 ⁻⁰¹	3.14 10 ⁻⁰¹	3.14 10 ⁻⁰¹	3.14 10 ⁻⁰¹	3.14 10 ⁻⁰¹
Fe	8.39 10 ⁻⁰⁵	8.39 10 ⁻⁰⁴	8.39 10 ⁻⁰⁵	8.39 10 ⁻⁰⁵	1.61 10 ⁻⁰⁶	1.25 10 ⁻⁰⁶
K	9.38 10 ⁻⁰³	9.38 10 ⁻⁰³	9.38 10 ⁻⁰³	9.38 10 ⁻⁰³	9.38 10 ⁻⁰³	9.38 10 ⁻⁰³
Mg	1.63 10 ⁻⁰²	1.63 10 ⁻⁰²	1.63 10 ⁻⁰²	1.63 10 ⁻⁰²	1.63 10 ⁻⁰²	1.63 10 ⁻⁰²
Na	2.70 10 ⁻⁰¹	2.70 10 ⁻⁰¹	2.70 10 ⁻⁰¹	2.70 10 ⁻⁰¹	2.70 10 ⁻⁰¹	2.70 10 ⁻⁰¹
S(6)	9.01 10 ⁻⁰³	9.01 10 ⁻⁰³	9.01 10 ⁻⁰³	9.01 10 ⁻⁰³	9.01 10 ⁻⁰³	9.01 10 ⁻⁰³
Si	3.30 10 ⁻⁰⁴	3.64 10 ⁻⁰⁴	3.30 10 ⁻⁰⁴	3.65 10 ⁻⁰⁴	3.40 10 ⁻⁰⁴	3.76 10 ⁻⁰⁴
Sr	5.23 10 ⁻⁰⁴	5.23 10 ⁻⁰⁴	5.23 10 ⁻⁰⁴	5.23 10 ⁻⁰⁴	5.23 10 ⁻⁰⁴	5.23 10 ⁻⁰⁴
pH	6.50	6.49	6.70	6.64	7.78	7.77
pe	-3.24	-3.31	-3.50	-3.49	-4.77	-4.82
log P _{CO2} (atm)	-1.14	-1.11	-1.34	-1.26	-3.45	-3.45

256

257 *Table 6. Saturation indices of injected brines as a function of temperature and CO₂ degassing (SI =*
 258 *log IAP/K, where IAP is the ionic activity product and K the thermodynamic constant).*

Phases	Saturation indices (SI)					
	No degassing		Partial degassing		Total degassing	
	48 °C	52 °C	48 °C	52 °C	48 °C	52 °C
Calcite	-0.20	-0.16	-0.01	-0.01	0	0
Dolomite (disordered)	-0.59	-0.46	-0.21	-0.16	-0.12	-0.08
Siderite	-0.21	-0.17	-0.03	-0.03	-1.69	-1.79
Illite (IMt2)	-0.77	-0.59	-0.38	-0.30	-0.07	-0.23
Albite (low)	0.11	0.19	0.30	0.34	0.81	0.74
Microcline	0.96	0.99	1.16	1.14	1.66	1.54
Quartz (alpha)	0	0	0	0	0	0
Celestite	-0.24	-0.23	-0.24	-0.23	-0.23	-0.21
Barite	0	0	0	0	0	0
Goethite	-0.59	-0.48	-0.25	-0.22	0	0

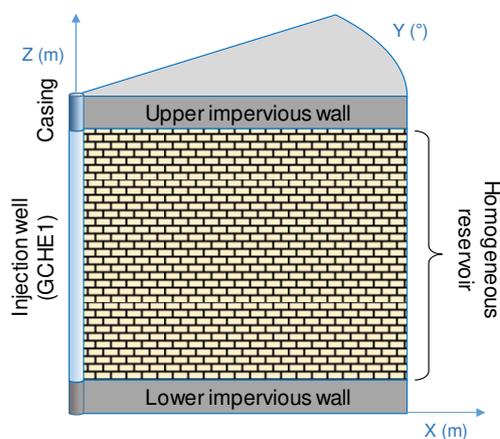
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260 **4.3. Geometries and key modelling assumptions**

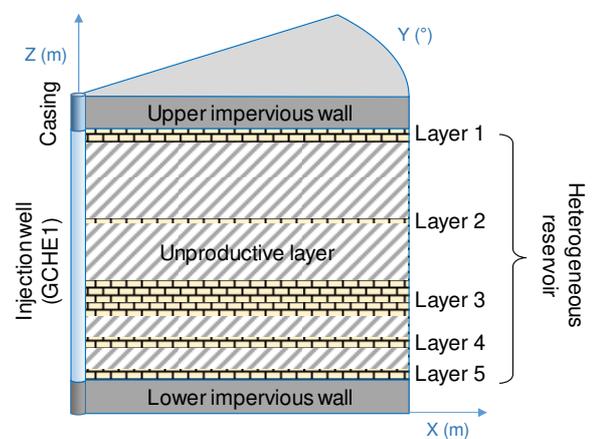
261 Two distinct but simplified geometries were considered: homogeneous and heterogeneous
 262 (Figure 4). A single-layer homogeneous model was first applied to simulate the geothermal
 263 reservoir. The mesh was radial type with X, Y, and Z coordinates coinciding with the radius,
 264 angle, and layer of the model, respectively. A homogeneous porosity of 15% was assumed in
 265 the geological formation [i.e. average porosity, 2]. The model assumed upper and lower
 266 impervious walls following the approximate analytical solution of Vinsome and Westerveld
 267 [41] (thermal conduction perpendicular to the aquifer) implemented in MARTHE. This
 268 analytical solution avoiding the vertical discretization of the clay layers so considerably
 269 reduced the number of meshes in the model, thereby decreased the computation time. Note
 270 that a single-layer geometry leads to an over estimation of the cooling down of the reservoir
 271 [42], however, such an assumption is widely used when the knowledge of the geothermal
 272 reservoir is low (e.g. in the case of predictive modelling). Moreover, even if several
 273 productive layers have been identified (Table 1), the open hole extension shown on Figure
 274 3b appears to be relatively homogeneous and thus a single layer geometry could be a
 275 correct assumption for assessing mineralogical transformations. A second, heterogeneous
 276 model was proposed using the Chelles injection well data (e.g. the productive layers
 277 identified by flowmeter, Table 1). The Dogger reservoir was discretised into five layers with
 278 specific properties. The mesh was also radial type and assumed upper and lower impervious
 279 walls using an analytic solution for the heat diffusion. Injected flows were distributed
 280 according to the contribution of the productive layers (Table 1). In contrast, according to
 281 flowmeter data, unproductive layers were considered as impervious layers only contributing
 282 to heat diffusion. The general parameters used for the simulations were defined using data from
 283 previous literature and are summarised in Table 7. A radial extension of 1000 m was assumed
 284 whatever the geometry considered.

285

a) Single-layer geometry



b) Multi-layer geometry



286

287 *Figure 4. Schematic representations of the two model geometries: a) single-layer geometry and b)*
288 *multi-layer geometry using flowmeter data from 1985.*

289

290

Table 7. General parameters used for the simulations.

Simulation parameters	Values
Initial temperature (°C)	66
Volumetric heat capacity of the mineral ($\text{J m}^{-3} \text{ } ^\circ\text{C}^{-1}$)	$2 \cdot 10^6$
Heat capacity of the water ($\text{J kg}^{-1} \text{ } ^\circ\text{C}^{-1}$)	4185
Thermal conductivities of the mineral ($\text{W m}^{-1} \text{ } ^\circ\text{C}^{-1}$)	2.5
Thermal conductivities of the water ($\text{W m}^{-1} \text{ } ^\circ\text{C}^{-1}$)	0.6
Molecular diffusion ($\text{m}^2 \text{ s}^{-1}$)	$1.5 \cdot 10^{-10}$
Mesh refinement (m)	0.025-20
Time step (month)	1
Division of the time step	33000

291

292 **5. Numerical results and discussion**

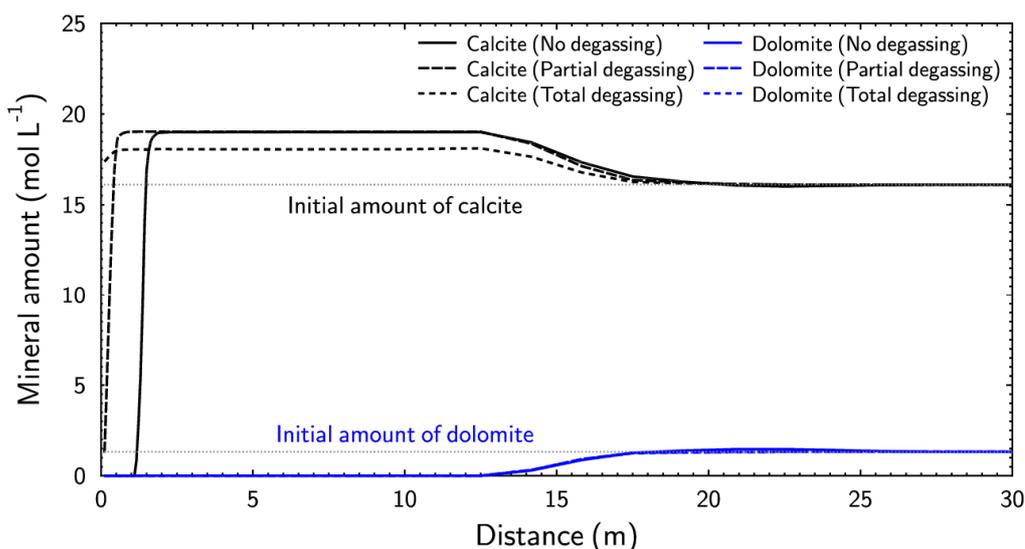
293 The numerical results for the single-layer model are predominantly focused on the
294 mineralogical evolution whereas those for the multi-layer model mainly deal with porosity
295 modifications and temperature profiles. According to the work of Castillo and co-workers [13],
296 gibbsite, quartz, goethite, barite, anhydrite, hydromagnesite, and celestine were selected
297 here as potential secondary minerals. Note that the hydromagnesite phase was considered
298 instead of magnesite (another Mg-carbonate) because the latter forms at temperatures
299 above 60–80 °C [43]. Similarly, precipitation of anhydrite rather than gypsum was assumed
300 because the predicted temperatures were over 40 °C [44].

301 **5.1. Single-layer geometry**

302 Calcite alteration was observed in the near field of the injection well (from 0 to <1.5 m, Figure
303 5). The numerical results were affected by the modelling assumptions; calcite alteration
304 decreased from “No degassing” to “Partial degassing” to “Total degassing” cases.
305 Regardless of the injected fluids (Table 5), the model indicated dolomite dissolution up to
306 about 15 m from the injection well occurring concomitantly to a calcite precipitation (from
307 >1.5 to 15 m, Figure 5). Dolomite/ankerite conversion (approximately equivalent to
308 dolomite/calcite conversion) has been observed in several experiments [45, 46]; thus, even if
309 such reaction is probably overestimated (i.e. minerals processed at local equilibrium), a
310 similar process is expected in the Dogger formation. Note that the amount of precipitated
311 calcite was also promoted by the Ca concentrations in the injected fluids (Table 5) and the
312 amount of mineral is lower for the “Total degassing” case. Regarding other mineralogical
313 transformations, the amounts of microcline and albite remained constant. Considering the

314 low amounts of accessory minerals (illite and siderite) as well as precipitated secondary
315 minerals (gibbsite, quartz, goethite, and barite), their impacts on porosity evolution were very
316 limited; these numerical results are reported in the Supplementary Data. The formation of
317 anhydrite, hydromagnesite, and celestine was not observed in any simulation case.

318



319

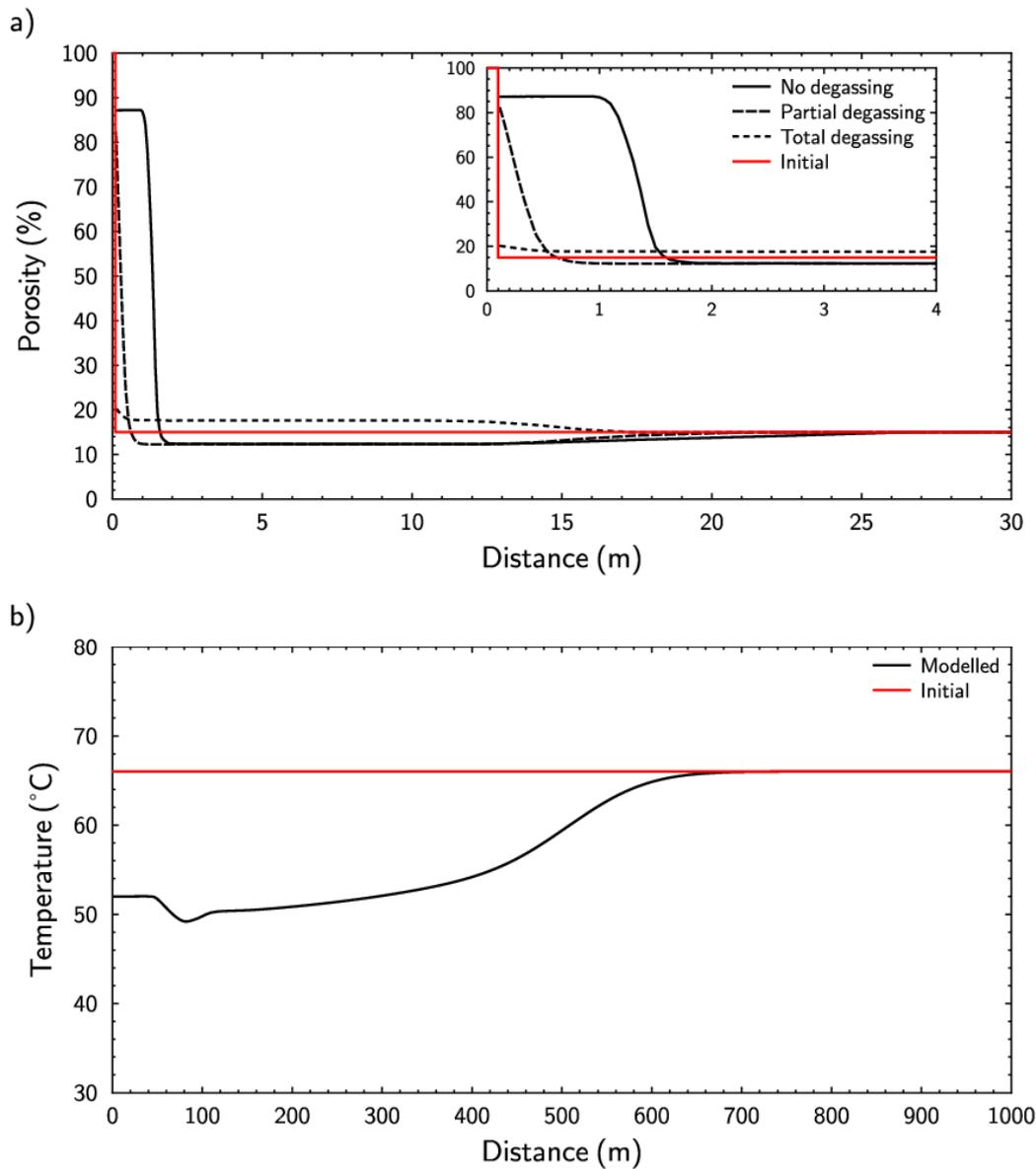
320 *Figure 5. Calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) profiles calculated with the single-layer model*
321 *after 24 years of cooled brine injection. No degassing, partial degassing, and total degassing*
322 *correspond to the different modelling cases based on injected fluid chemistry (see section 4.2).*

323

324 As calcite and dolomite constitute 80% of the initial mineralogical assemblage of the Dogger
325 formation (Table 2), modelling assumptions affected the resulting porosity (Figure 6a) while
326 temperature profiles remained identical whatever the injected fluid chemistry (Figure 6b). The
327 experimental results indicated an average radius of 0.21 m for the open hole. The modelling
328 case omitting gas extraction (“No degassing” model) showed total dissolution of carbonate
329 minerals up to 1 m around the injection well; the formation of an open hole around the
330 injection well was clearly an overestimate. In contrast, the numerical modelling indicated that
331 total degassing of the cooled injected fluid was unlikely as its effect on porosity was very
332 limited (i.e. no significant variation around the injection well). Additionally, the low Ca
333 concentration of the injected fluid (Table 5) limited the calcite precipitation promoted by the
334 dolomite/calcite conversion and a slight porosity increase was predicted despite the molar
335 volumes of minerals (i.e. $36.9 \text{ cm}^3 \text{ mol}^{-1}$ for CaCO_3 and $64.4 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{CaMg}(\text{CO}_3)_2$).
336 Finally, only partial CO_2 degassing of the injected fluid could explain the field observations.

337 According to the work of Deng and co-workers [47], dissolution of 35% is a reasonable
338 threshold for a fast-reacting mineral (i.e. calcite), above which erosion of the altered layer
339 occurs. Following the removal of the altered layer, the open-hole aperture increases.
340 Assuming an initial porosity of 15% in the current model, a porosity increase of more than
341 50% would lead to disaggregation of the remaining matrix. The remaining minerals (e.g.
342 albite and microcline) are expected to fall to the bottom of the injection well or be further
343 transported. The “Partial degassing” model led to a porosity increase of up to 50% at 0.25 m
344 (Figure 6a). An open-hole aperture of 0.25 m was then estimated, which is in reasonable
345 agreement with the experimental data. Note that more recent doublets use two pumps to
346 keep fluids under pressure and avoid the bubble point [48]. Therefore, the porosity profile
347 obtained without degassing corresponds to the open-hole expected under such conditions.

348



350

351 *Figure 6. a) Porosity profile calculated with the single-layer model after 24 years of cooled brine*
 352 *injection. No degassing, partial degassing, and total degassing correspond to the different modelling*
 353 *cases based on injected fluid chemistry (see section 4.2). b) Temperature profile calculated with the*
 354 *single-layer model after 24 years of cooled brine; results are identical for all the injected fluid*
 355 *chemistries considered.*

356

357 **5.2. Multi-layer geometry**

358 Mineralogical transformations calculated using the multi-layer model were similar to those
 359 already described with the single-layer model; the open-hole formation resulted in carbonate
 360 dissolution. Therefore, only the porosity profiles after 24 years of geothermal production are
 361 reported in Figure 7 whereas open-hole extensions are given in Table 7. As already
 362 observed with the previous model, the absence of fluid degassing led to an overestimation of
 363 open-hole formation (up to 6.2 m for layer 4). In contrast, the porosity change that was
 364 modelled assuming that total degassing was negligible. The best fit to the experimental data
 365 was obtained considering partial degassing of injected fluids. Assuming a threshold of 35%
 366 for carbonate alteration [47] and specific initial porosities for each layer (Table 1), the
 367 numerical results indicated an open-hole radius ranging from 0.37 m (layer 1) to 1.18 m
 368 (layer 4). Nonetheless, the reactivity of unproductive layers may buffer the alteration of
 369 productive layers, which is therefore likely to be overestimated if those unproductive layers
 370 are assumed to be impermeable. Such a reactivity is supported by experimental results
 371 effectively showing an alteration of layers identified as unproductive from flowmeter
 372 measurements (Figure 3). This explains why the use of a single-layer geometry allowed a
 373 better approximation of the alteration front progression in the Dogger aquifer.

374 *Table 7. Open-hole extension modelled for the multi-layer geometry. No degassing, partial degassing*
 375 *and total degassing correspond to modelling assumptions made on fluid chemistries (see section 4.2)*

Productive layer	Observed radius (m)		Modelled radius (m)		
	min-max	average	No degassing	Partial degassing	Total degassing
1	0.23-0.25	0.24 ±0.01	2.03	0.37	0.1*
2	0.21-0.28	0.24 ±0.02	2.96	0.56	0.1*
3	0.21-0.29	0.25 ±0.02	2.23	0.45	0.1*
4	0.14-0.25	0.19 ±0.05	6.16	1.18	0.1*
5	0.11-0.14	0.13 ±0.01	1.89	0.38	0.1*

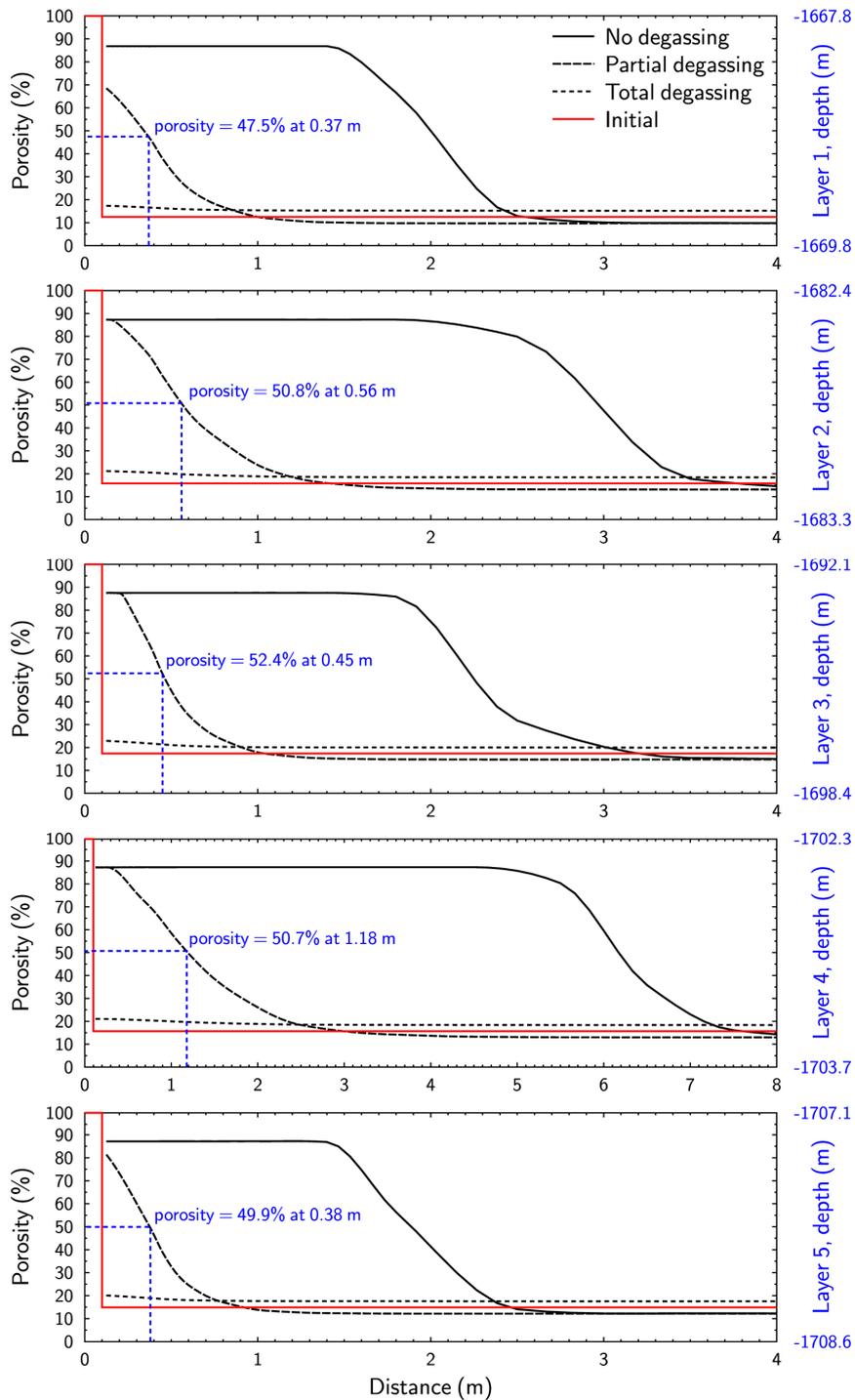
376 * no extension, 0.1 m being the initial radius of the borehole

377 The geothermal doublet induces the formation of a “cold bubble” in the reservoir around the
 378 injector [1, 3]. The migration of the “cold bubble” was similar regardless of fluid chemistry
 379 assumptions and therefore, only one temperature profile is reported on Figure 8. After 24
 380 years of geothermal production, the cold injection front progressed up to 700 m, which
 381 corresponds to half the distance between the injection and the production wells. The
 382 numerical results indicated that a decrease in temperature at the production well was unlikely
 383 and was in accordance with recorded data (i.e. no thermal breakthrough). Nonetheless,
 384 numerous studies have shown a dissymmetry of the temperature profile resulting from the
 385 shape of the velocity profile induced by fluid extraction at the production well [e.g. 13]; the
 386 production well has been neglected here as the modelling of the exact progression of the
 387 “cold bubble” was not an objective of this study. The consideration of two injection periods

388 (48 °C in winter and 52 °C in summer) led to an inhomogeneous temperature profile in the
 389 near field of the injection well. Consistent with the temperature dependence of the mineral
 390 solubility [30], both the temperature decrease and the mass transport led to a calcite
 391 alteration that was attenuated when enabling CO₂ degassing.

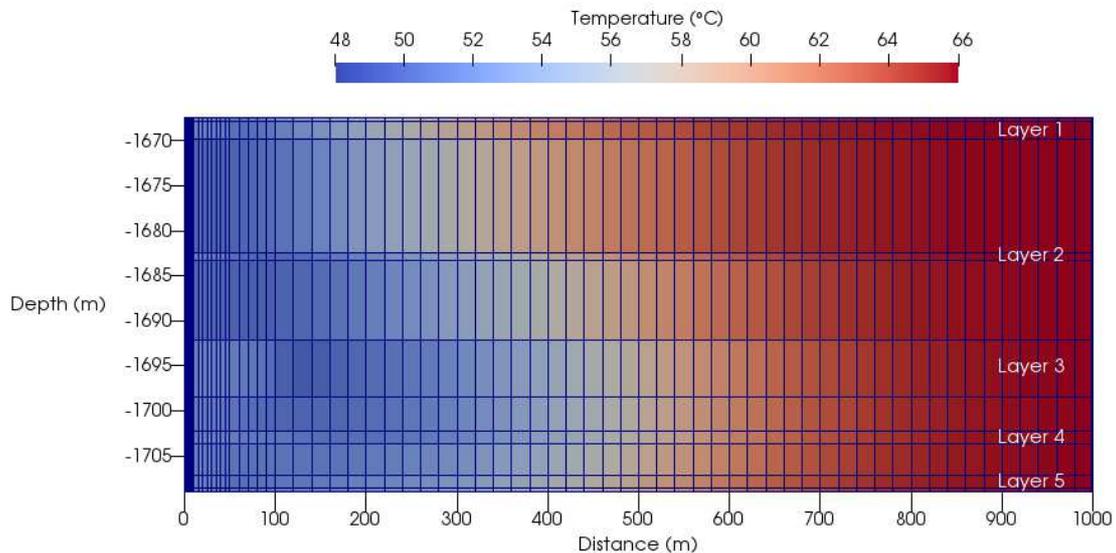
392

393



394

395 *Figure 7. Porosity profile calculated with the multi-layer model after 24 years of cooled brine injection.*
396 *No degassing, partial degassing and total degassing correspond to modelling assumptions made on*
397 *fluid chemistries (see section 4.2).*
398



399
400 *Figure 8. Temperature profile calculated with the multi-layer model after 24 years of cooled brine*
401 *injection. Note that results were identical whatever modelling assumptions made on fluid chemistries*
402 *(see section 4.2).*
403

404 **5.3. Model limitations**

405 The modelling results of open-hole extension remain uncertain because several processes
406 can affect its progression. The effects of porosity changes on the resulting permeability were
407 neglected in this study. Following the Kozeny-Carman relationship, a porosity increase would
408 lead to a permeability increase favouring mass transport and rock alteration. In contrast, the
409 particles released by cement alteration could be mobilised and transported further, where
410 particle re-deposition could cause clogging in the productive layer and a reduction of
411 permeability [47, 49]. Unfortunately, the balance between higher porosity leading to higher
412 permeability and porosity clogging by particles leading to a decrease of mass transport
413 properties is difficult to determine. Therefore, our models assumed constant permeability and
414 imposed average flow rates monitored at GCHE1. Moreover, the reinjection of cooled brine
415 in the GCHE1 borehole could have a thermomechanical impact on the integrity of the
416 reservoir rock that cannot be considered by MARTHE-PHREEQC. The current sonar
417 technique is limited to the identification of open-hole walls and cannot detect porosity
418 increases inside the rock matrix and/or the possible formation of wormholes in carbonated
419 rock [18, 50]. However, despite these uncertainties, the model and field results were in

420 reasonable agreement, even if a simplified geometry was considered. Nevertheless, the non-
421 iterative sequential coupling algorithm of the MARTHE-PHREEQC code implies using a
422 relatively small time step fulfilling the Neumann criterion, thus leading to a high number of
423 iterations and then a high computation time (i.e. several days). The time step used for this
424 study (80 s, Table 7) is the best compromise between calculation efficiency and numerical
425 dispersion possibly observed when the Neumann criterion is not strictly respected, which is
426 the case for the smallest cells at the immediate vicinity of the well. However, keeping in mind
427 that for all these cells, water-rock interactions rapidly became negligible as calcite was
428 entirely dissolved, time step could be relaxed without negative consequence on calculation
429 accuracy.

430

431 **6. Conclusions**

432 Field investigations of the Chelles former injection well after 24 years of continuous
433 geothermal operation offered a novel opportunity to evaluate reservoir mineralogical
434 transformations at the well outlet induced by cooled-brine reinjection during a typical
435 geothermal exploitation period. Sonar data acquired on the open-hole part of this well
436 showed significant and uneven distortion of the initial cylindrical geometry. The investigation
437 technique, used for the first time in the Paris basin, is a promising tool for borehole
438 examinations, especially when a camera is not practical due to groundwater turbidity as in
439 the Dogger aquifer.

440 Using parameters as close as possible to actual well operation data as well as simplified
441 geometries that are widely used in predictive modelling, this study attempted to quantify the
442 water-rock interaction processes in the near-well area of the exploited reservoir. Because of
443 the partial monitoring of production data and more specifically a lack of data on the chemistry
444 of the injected fluids (e.g. rate of CO₂ degassing) as well as drawbacks of current reactive
445 transport software (e.g. transport of eroded particles is not accounted for), the accuracy of
446 the numerical results had some limitations. Nonetheless, the simulation results confirmed
447 significant carbonate alterations in the near-well part of the reservoir on the same orders of
448 magnitude as the average measured open-hole aperture (0.21 m). This gave us more
449 confidence in our modelling approach and suggested that the observed geometry alteration
450 could mainly have a geochemical origin. Best-fit results were obtained for partial CO₂
451 degassing in the reinjected brine, which is also consistent as the geothermal doublet was
452 operated in artesian mode.

453 Although previous studies on the CO₂-DISSOLVED concept involving cooled CO₂-rich brine
454 reinjection in a geothermal well (i.e. CO₂ concentration less than 1 mol L⁻¹ under field

455 conditions, so that CO₂ remains entirely dissolved in brine) used a similar modelling
456 approach, they lacked reference field data for evaluating the predictive capability of the
457 models. Therefore, the results of this study, based on unique bottom-hole data showing the
458 geochemical impact of brine reinjection in a “standard” geothermal doublet, constitute a
459 valuable baseline for future calibration of reactive transport models. These reactive transport
460 models could then be more confidently used to perform the pre-dimensioning calculations of
461 dissolved CO₂ injection in a doublet, which forms the first operational test-phase of the CO₂-
462 DISSOLVED system.

463

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474

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