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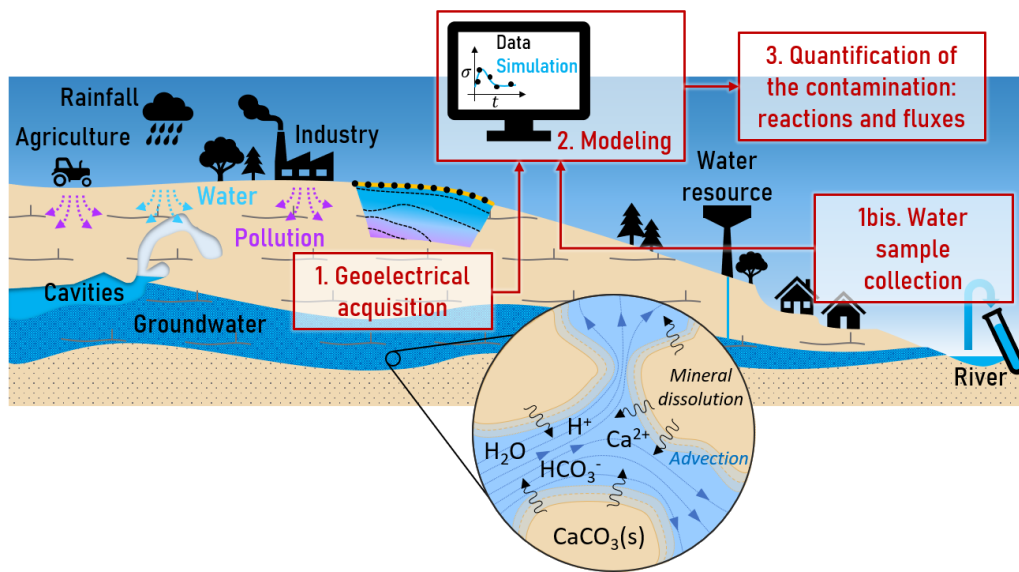
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Graphical Abstract

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Highlights

Investigating solute transport and reaction using a mechanistically coupled geochemical and geophysical modeling approach

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- Geoelectrical methods are used to quantitatively monitor reactive contamination
- Calcite dissolution under different regimes is studied as an example of reactive process
- Reactive transport simulation is coupled with petrophysical modeling
- Self-potential monitoring allows the spatialization of the reactive zone
- Electrical conductivity shows significant variations during intense dissolution regime

Investigating solute transport and reaction using a mechanistically coupled geochemical and geophysical modeling approach

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Abstract

The use of geoelectrical monitoring of groundwater quality and contamination is a growing and promising topic. Nowadays, geoelectrical methods are mostly used as qualitative detection tools. This study aims to better use geoelectrical signals as a complementary tool for the quantitative characterization of chemical species transport and reaction in the porous matrix by developing a coupled mechanistic model. We examine the dissolution of calcite as an effective proof-of-concept. Our investigation focuses on the impact of the reactive zone's position, extent, and intensity of geoelectrical signals under various inlet conditions. We conducted five experiments on flow-through columns equipped with geoelectrical monitoring. This study presents a unique dataset that is analyzed using a workflow that combines reactive transport numerical simulation with numerical modeling of geoelectrical and structural properties. The comparison of the predicted signals with the experimental data clearly shows the characterization of the spatial

and temporal distributions of the reaction rates.

Keywords: Calcite dissolution, Reactive transport modeling, Geophysics, Self-potential, Spectral induced polarization

1 1. Introduction

2 Transport, mixing, and reaction of solutes are ubiquitous issues in char-
3 acterizing the fate of groundwater contaminants (e.g., Dentz et al., 2011).
4 For example, saline intrusion in coastal aquifers and hyporheic zones within
5 river channels are important places of active mixing and reactivity (e.g.,
6 Werner et al., 2013; Boano et al., 2014). In carbonate environments, there
7 is a strong need for monitoring of fluid injection and associated dissolution
8 and precipitation processes dedicated to environmental engineering. These
9 needs for carbonate reservoirs gather applications such as precipitation-based
10 remediation for confinement barriers and soil consolidation, carbon dioxide
11 (CO₂) sequestration, geothermal doublet, artificial recharge, or karst aquifer
12 remediation and phantomization (e.g., Benson et al., 2005; Kaufmann and
13 Deceuster, 2014; Ahmad et al., 2020; Knappett et al., 2020). The common
14 methods to quantify the flow and solute transport are water sampling and
15 conservative tracer tests (e.g., Bufflap and Allen, 1995; Goldscheider et al.,
16 2008). However, these methods rely on a grid of multi-level monitoring wells,
17 from which it is often difficult to determine the flow path and the position,
18 shape, and extent of a tracer plume (e.g., Kemna et al., 2002). In addition
19 to the fact that these methods are intrusive, provide limited and spatially
20 restricted information, and are generally expensive, the use of conservative
21 tracers appears controversial because ionic exchange and rate-limited mass

22 transfer are difficult to capture (e.g., Singha et al., 2011).

23 Environmental geophysics offers the possibility of extended high-
24 resolution monitoring of the heterogeneous and dynamic subsurface with
25 2D and 3D surveys (even 4D considering the time) (e.g., Hermans et al.,
26 2023). Geophysical methods measure the distribution and evolution of phys-
27 ical properties in geological media (e.g., electrical conductivity, magnetic sus-
28 ceptibility, density, seismic wave velocity). Appropriate mechanistic models
29 allow these properties to be expressed in terms of hydrochemical parameters
30 of interest (e.g., porosity, permeability, chemical composition, water con-
31 tent). Some geophysical methods are deployed to address specific hydrogeo-
32 logical problems (e.g., Rubin and Hubbard, 2006; Hubbard and Linde, 2011;
33 Binley et al., 2015). This discipline is called hydrogeophysics and among the
34 existing geophysical techniques, geoelectrical methods show strong capabil-
35 ities for imaging structures and dynamic processes (e.g., Daily et al., 1992;
36 Revil et al., 2012a; Singha et al., 2015; Kaufmann and Romanov, 2016).
37 Enhanced sensitivity of electrical properties (electrical conductivity and di-
38 electric permittivity) to pore water chemistry and dynamics has improved
39 salt tracer monitoring field experiments, imaging plumes non-intrusively with
40 an unprecedented high spatial and temporal resolution compared to tradi-
41 tional sample collection (e.g., Singha and Gorelick, 2005; Cassiani et al.,
42 2006; Jougnot et al., 2015). More recently, saline intrusion has been stud-
43 ied with geoelectrical methods (e.g., MacAllister et al., 2018; Palacios et al.,
44 2020). Some studies also have applied such techniques to better character-
45 ize changes in flow and transport behavior driven by living organisms and
46 contaminants (e.g., Ghosh et al., 2018; Kessouri et al., 2019; Saneiyani et al.,

47 2019; Flores Orozco et al., 2021).

48 To enhance understanding of the role played by reactive transport in
49 groundwater flow, laboratory studies are carried out at various scales (μm to
50 m). Column experiments are traditionally used for percolation studies (e.g.,
51 Wu et al., 2010; Singha et al., 2011; Izumoto et al., 2020; Ben Moshe and
52 Furman, 2022). To explore heterogeneous behavior (e.g., partially satu-
53 rated conditions, local mixing, complex porous rock matrix), core sample
54 experiments with tomographic imaging (e.g., Rembert et al., 2023a) and mi-
55 cro-millifluidic experiments are conducted (e.g., Jougnot et al., 2018; Sun
56 et al., 2021; Izumoto et al., 2022; Fernandez Visentini et al., 2023; Rembert
57 et al., 2023b). However, studies addressing the electrical signature of reac-
58 tive chemical transport (e.g., adsorption, mineral dissolution-precipitation)
59 are scarce (e.g., Ben Moshe et al., 2021; Bate et al., 2021). This knowl-
60 edge gap arises in part from the inherent complexity of reactions between
61 fluids and solids within porous media, which are inherently non-conservative
62 and, thus, distinct from simpler systems such as sodium chloride (NaCl)
63 intrusion (e.g., Maineult et al., 2004, 2006). For example, in the study of
64 carbonate dissolution-precipitation, the literature shows diverging electrical
65 results. Some authors report no or minor complex electrical conductivity
66 variations related to calcite precipitation or dissolution (e.g., Zhang et al.,
67 2012; Halisch et al., 2018), while other studies present results strongly im-
68 pacted (e.g., Saneiyan et al., 2019); highlighting the notable challenges that
69 still exist in modeling electrical signatures of fluid-mineral interactions. In
70 some studies, the electrochemical coupling is oversimplified considering it as
71 an additional empirical constant (e.g., Cherubini et al., 2019), while it can

72 henceforth be addressed when reactivity is treated with a robust method
73 provided by reactive transport simulation (e.g., Rembert et al., 2022).

74 This study aims to focus on the geoelectrical signature of calcite disso-
75 lution as an example of reactive contamination of pore water since it is a
76 ubiquitous, well-studied reaction, and highly representative of fluid-mineral
77 reactivity. We performed five column-experiments of reactive percolation.
78 We evaluated the impact of using weak or strong acids for the injection
79 in promoting calcite dissolution. Two geoelectrical techniques were used to
80 monitor dissolution for comparison. Reactive transport simulations were
81 then performed to determine the spatial and temporal distributions of the
82 ion concentrations, which were then used to inform geoelectrical properties
83 from petrophysical relationships.

84 **2. Material and Method**

85 This section is divided into two parts. First, we introduce the flow-
86 through experimental setup, comprising the presentation of the column de-
87 sign, outlet water monitoring, geoelectrical monitoring, and experimental
88 protocols. Second, we introduce the coupled numerical workflow that com-
89 bines reactive transport simulation and petrophysical modeling.

90 *2.1. Flow-through experimental setup*

91 The full setup and the column are presented in Figure 1.

92 *2.1.1. Column design*

93 The column is a Plexiglas cylinder with a length of 31 cm and an inner
94 diameter of 4 cm (Figure 1b). The dimensions of the column and electrode

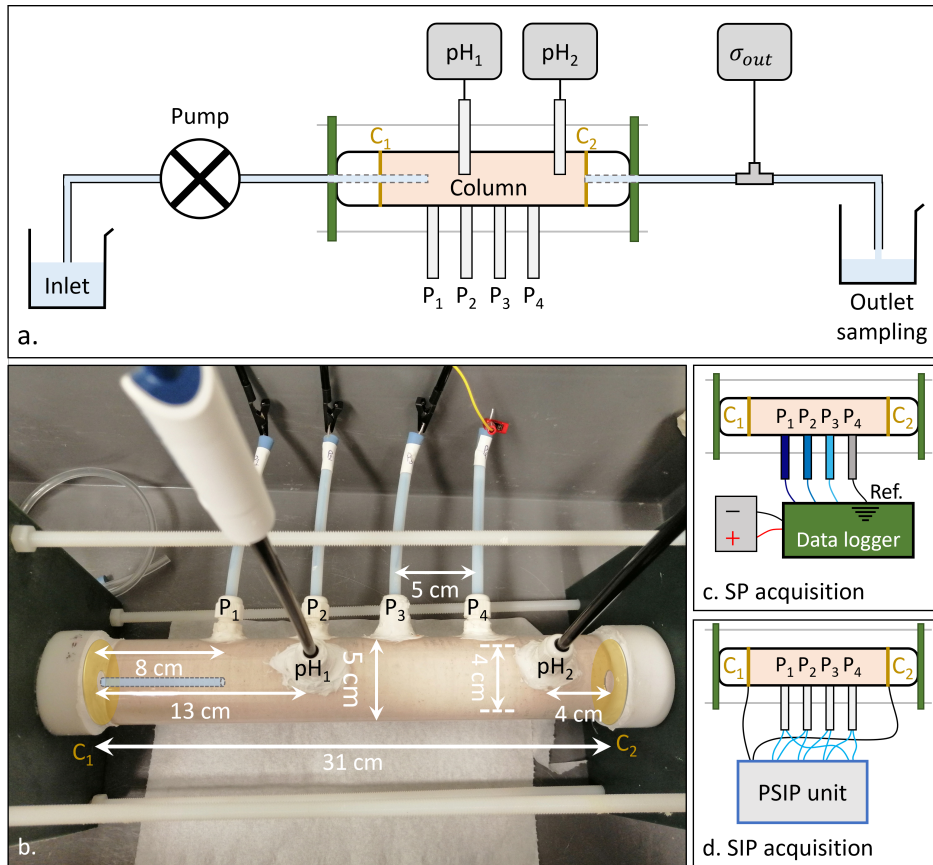


Figure 1: (a) The experimental set-up. (b) The column and its dimensions. Schematic shifted injection and current electrodes are shown in transparency. (c) SP acquisition. (d) SIP acquisition.

95 spacing have been set to respect the geometrical criteria recommended by
 96 Zimmermann et al. (2008) to ensure good quality of electrical acquisition.
 97 The column is sealed at each extremity by two plastic caps maintained with
 98 silicone joints and a tightening structure made of nylon. Plastic materials
 99 are used for this structure, instead of metallic components, because the latter
 100 would cause interference during geoelectrical acquisition. A filter fabric with

101 a mesh of 20 μm is placed between the Plexiglas cylinder and the plastic
102 cap at the column outlet to retain the grains in the column. C_1 and C_2
103 are the electrodes for electric current injection. They are two stainless steel
104 perforated discs placed between the extremities of the Plexiglas cylinder
105 and the sealing plastic caps. For electrical connection, the plastic caps are
106 drilled to thread and glue stainless steel wires. P_1 , P_2 , P_3 , and P_4 are
107 the electrodes for electric potential measurement. They are spaced by 5 cm
108 between them and 8 cm from C_1 and C_2 . At the inlet, the injection tube is
109 inserted in the column 8 cm after the entrance. It corresponds to the location
110 of P_1 . As recommended by Petiau and Dupis (1980), P_1 to P_4 electrodes
111 are silver–silver chloride (Ag–AgCl) electrodes given the low noise and short
112 stabilization time of this electrode type (e.g., Jougnot and Linde, 2013).

113 Pure calcite was used for the porous media in the flow-through columns.
114 Loose calcite grains were obtained from crushed high-purity ($> 99\%$) marble
115 (Durcal 130 from Omya). Since the initially crushed calcite contains a wide
116 variety of grain sizes, it is sieved to extract a range of grain diameters between
117 125 and 250 μm . The initial porosity ϕ_{init} (–) is calculated by weighing
118 the mass of calcite required to fill the entire column volume. The final
119 porosity ϕ_{end} (–) is calculated using the same method from the mass of calcite
120 recovered in the column at the end of the experiment and after being dried in
121 an oven. The porosity increase $\Delta\phi$ (–) is calculated from the initial and final
122 porosity difference. The time variations of the porosity ϕ (–) are retrieved
123 from the mass of dissolved calcite, obtained from the calcium concentration
124 measurements on the collected outlet water samples. Both methods are
125 compared at the end of the experiment.

126 Two pH electrodes (pH Sensor InLab Flex-Micro from Mettler Toledo),
127 labeled pH₁ and pH₂, are inserted in the column at 13 and 27 cm, respec-
128 tively. The pH meters (Lab 845 from SI Analytics) record measurements
129 every 5 min.

130 2.1.2. Outlet pore water monitoring

131 A conductivity meter (Lab 945 from SI Analytics) was connected to con-
132 ductivity flow-through measuring cells (TetraCon DU/T from WTW) to
133 monitor water conductivity at the outlet (σ_{out}) every 5 min. Samples of out-
134 let water were collected, with a sampling rate comprised between 30 min and
135 1 h, to monitor the chemical evolution through time. pH and conductivity
136 are measured immediately after sampling. Then, the samples were filtered
137 ($< 0.2 \mu\text{m}$) and split into two aliquots. The first aliquot was used to measure
138 the total alkalinity through standard acid/base titration and corresponds to
139 the concentration of alkaline species present in the solution, bicarbonate
140 (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide (HO^-) ions. The second aliquot
141 was used to measure concentrations of major ions (calcium Ca^{2+} , chloride
142 Cl^- , sodium Na^+ , potassium K^+ , magnesium Mg^{2+} , and sulfate SO_4^{2-}). An-
143 ions were measured using an ion chromatography system (from Dionex, 10%
144 of global uncertainty), while cations concentrations were generated from in-
145 ductively coupled plasma atomic emission spectroscopy (ICP-OES 5100 from
146 Agilent technologies, 5% of global uncertainty).

147 2.1.3. Geoelectrical monitoring

148 The self-potential (SP) method is based on the passive measurement
149 of the electrical field that results from the electrical current generated by

150 different natural contributions (e.g., Jouniaux et al., 2009; Revil and Jardani,
151 2013). In this study, SP data are recorded with the total field method
152 (Lowrie and Fichtner, 2020). The electrode P_4 is the reference (Figure 1c).
153 The potential difference is measured for the three electrodes P_1 , P_2 , and P_3 .
154 The data logger is a CR1000 from Campbell Scientific. It is programmed to
155 measure the voltage every 1 ms, then to compute and record a mean value
156 every 5 s. Despite the rejection of 50 Hz, the mains frequency, the high level
157 of noise compared to the amplitude of the SP variations requires filtering
158 the data. Thus, the SP signal is filtered using a moving average window of
159 10 min, thus, averaging 120 measurements on each time window.

160 The spectral induced polarization (SIP) method, by injecting an alter-
161 nating current at a low-frequency range (typically from mHz to kHz) (e.g.,
162 Revil et al., 2012a), measures both the sample’s electrical conductivity and
163 the ability of the porous rock to polarize (e.g., Binley and Slater, 2020).
164 An alternating electric current I^* (A) is injected through the current elec-
165 trodes C_1 and C_2 . The resulting voltage V^* (V) is measured simultaneously
166 on four channels between pairs of the Ag-AgCl electrodes P_1 , P_2 , P_3 , and
167 P_4 (Figure 1d). To be able to monitor the SIP signal of different slices of
168 the column, we measure on pairs P_1 – P_2 , P_2 – P_3 , and P_3 – P_4 . We also mea-
169 sure the SIP response on pair P_1 – P_4 to get the overall behavior. The SIP
170 measurements are conducted using a PSIP device from Ontash and Ermacs
171 (www.ontash.com), designed for multi-pair acquisition. The alternating volt-
172 age covers a spectrum from 5 mHz to 10 kHz at 40 frequencies uniformly
173 distributed on a logarithmic scale and with an amplitude of ± 5 V. At each
174 frequency ($f = \omega/2\pi$ in Hz), the device records the complex electrical con-

ductivity $\sigma^* = I^*/(k_G U^*)$, where k_G (m) is the geometrical coefficient determined using numerical simulation accounting for the acquisition geometry and the shape of the electrodes, thus, the electrical conductivity is independent of the electrode configuration. In this study, we use EIDORS (Electrical Impedance and Diffuse Optical tomography Reconstruction Software) for the 3D reconstruction of the electrical impedance tomography based on finite-elements numerical models (Rembert, 2021). We estimate $k_G = 2.5$ cm for the pairs P₁–P₂, P₂–P₃, and P₃–P₄ and $k_G = 0.8$ cm for the pair P₁–P₄.

2.1.4. *Experimental protocols*

Initial conditions and duration for all experiments conducted are listed in Table 1.

For all experiments, the column is filled with packed calcite grains and a saturating solution meant to be at saturation with calcite using the same technique (Rembert, 2021). The initial saturating solution is a mixture of deionized water and calcite grains immersed for several weeks. Despite the long mixing time between the grains and the water before filling the column, we systematically recorded an increase in the outlet water conductivity after a few hours in contact with the grains in the column. Thus, after closing it, the column was flushed for 24 h and the conductivity of the outlet water was recorded to check that it returned to its base value. Only for experiment ④, this procedure was shorter, resulting in some initial fluctuations in the outlet water conductivity presented in the results.

In this study, the dissolution of calcite is induced by the injection of different acid solutions to characterize the impact of strong or weak acids.

Table 1: Experimental conditions of the five experiments.

Experiment	①	②	③	④	⑤
Inlet acid	HCl	CH ₃ CO ₂ H ^a + NaCH ₃ CO ₂	CH ₃ CO ₂ H ^b + NaCH ₃ CO ₂	HCl	CH ₃ CO ₂ H
pH _{inlet}	4.5	4.5	4.5	3	2.5
Duration (h)	25	9	9	50	25
Electrical method	SP	SP	SP	SIP	SIP
Flow rate (mL h ⁻¹)	11	25	11	11	25
ϕ_{init} (%)	43.61	43.99	41.62	43.24	45.70
$\Delta\phi$ (%)	0.04	0.77	0.09	0.04	4.12

$$^a C_{CH_3CO_2H} = 1.74 \text{ mol L}^{-1}$$

$$^b C_{CH_3CO_2H} = 2.5 \times 10^{-3} \text{ mol L}^{-1}$$

199 Strong acids completely dissociate in water. Thus, the pH value is di-
 200 rectly linked to the concentration of acid and induces highly localized dis-
 201 solution (e.g., Garcia-Rios et al., 2014; Rembert et al., 2022). Hydrochloric
 202 acid (HCl) was chosen as our representative strong acid, consistent with prior
 203 studies (① and ④) and the chemistry of the electrodes that can release Cl⁻
 204 ions. The inlet solutions were prepared from the dilution of a commercial
 205 solution with an initial concentration of 36.4%.

206 For experiments ②, ③, and ⑤, solutions of acetic acid (CH₃CO₂H),
 207 buffered or not with sodium acetate (NaCH₃CO₂), representative for weak
 208 acid, are injected. The aim of using such different acid types is to observe the
 209 effect of local versus extended reactive zones in the column on the geoelectri-
 210 cal signal. Buffering the acetic acid with acetate enables further expansion
 211 of the reactive zone (e.g., Garcia-Rios et al., 2014). The inlet solutions were
 212 prepared from Normapur products with guaranteed 99% purity.

213 The experiments were conducted at room temperature. The room tem-
 214 perature was regulated by an air-conditioning system (20 ± 0.9 °C). Inlet
 215 acid injection was ensured through a peristaltic pump. The constant flow
 216 rate was set to 11 or 25 mL h⁻¹. Given the dimensions of the column (ra-
 217 dius $r = 2$ cm) and the initial porosity range, this leads to pore velocities
 218 $V = Q/(\pi r^2 \phi)$ of $V_1 = 2.0$ cm h⁻¹ and $V_2 = 4.4$ cm h⁻¹, respectively. The
 219 microscopic Péclet number is defined as

$$Pe = \frac{V \bar{d}_g}{D}, \quad (1)$$

220 where $\bar{d}_g = 188$ μm is the mean grain diameter and $D = 3.0 \times 10^{-9}$ m² s⁻¹ is
 221 a mean diffusion coefficient. The Péclet numbers calculated from Darcy
 222 velocities U_1 and U_2 correspond to 0.35 and 0.75, respectively. $Pe < 1$ is set
 223 in the experiments, leading to a relatively dominant diffusion regime (Fredd
 224 and Miller, 2000). The Péclet number definition at diffusion scale is used
 225 rather than the dispersion one to investigate the impact of diffusion on the
 226 chemical reaction. In order to grasp the flow regime over the scale of the
 227 column, we calculate the macroscopic Péclet number

$$Pe_{macro} = \frac{U L}{Disp}, \quad (2)$$

228 where $L = 23$ cm is the length of the column from the location of the injec-
 229 tion to the outlet, $U = \phi V$ is the Darcy velocity, and $Disp = \alpha U$ (m² s⁻¹)
 230 is the lateral dispersion coefficient, and α (m) is the dispersivity length
 231 scale, corresponding to the radius of the column, $R_{column} = 2$ cm. Thus,

232 $Pe_{macro} = L/\alpha = 11.5$. This value, suggests that we are in an advective
 233 regime with low velocity differences between the center of the column and
 234 the borders. Therefore, a 1D approximation to model the column is a valid
 235 approach.

236 2.2. Modeling approach

237 Coupled petrophysical, hydrological, and geochemical parameters are
 238 necessary to resolve the petrophysical modeling. Thus, a modeling work-
 239 flow is used to predict the geoelectrical response (Figure 2) based on the
 240 developments from Rembert et al. (2022). The workflow combines reactive
 241 transport simulation with petrophysical modeling to predict the porosity,
 242 electrical conductivity, formation factor, and electro-diffusive contribution.
 243 to relate geoelectrical acquisition both to pore water chemical composition
 244 and porous structure.

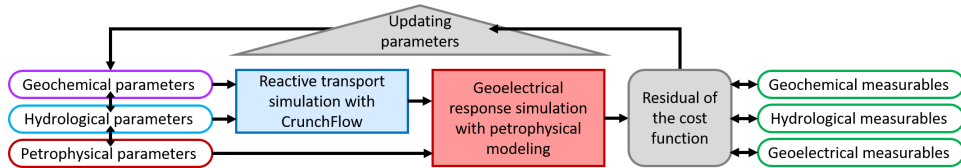


Figure 2: Workflow for the spatial and temporal quantitative characterization of the transport and reaction of solutes from the prediction of geochemical, petrophysical, and geoelectrical properties using reactive transport simulation and petrophysical modeling.

245 2.2.1. Reactive transport simulation

246 Each experiment was simulated using CrunchFlow, a robust multi-
 247 component reactive transport modeling software developed by Carl Steefel
 248 and coworkers (Steefel, 2009). The code is based on a finite volume discretiza-
 249 tion of the governing coupled partial differential equations linking flow, so-

250 lute transport, multi-component equilibrium, and kinetic reactions in porous
 251 media as follows (e.g., Molins et al., 2014; Garcia-Rios et al., 2014),

$$\frac{\partial}{\partial t}(\phi C_i) = \nabla \cdot (\phi \mathbf{D}_i \nabla(C_i) - q \phi C_i) - \sum_{r=1}^{N_r} v_{ir} R_r - \sum_{m=1}^{N_m} v_{im} R_m, \quad (3)$$

252 where C_i (mol kg^{-1}) represents the total concentration for a given primary
 253 species i in the aqueous phase and ϕ is the total porosity of the porous
 254 medium ($\text{m}^3_{\text{void}} \text{m}^{-3}_{\text{porous medium}}$). The mass accumulation rate $\frac{\partial}{\partial t}(\phi C_i)$ is
 255 described by the combined dispersion-diffusion tensor \mathbf{D} ($\text{m}^2 \text{s}^{-1}$), advec-
 256 tion through the Darcy flow velocity vector q (m s^{-1}), and reactivity shown
 257 here as two summations accounting for kinetically controlled homogenous,
 258 aqueous (designated with subscript r) and heterogenous, mineral (designated
 259 with subscript m) reactions.

260 The advection-reaction-diffusion equation (ARDE) is resolved. We use
 261 CrunchFlow to simulate spatial and temporal distributions of aqueous species
 262 during calcite dissolution. The different values are set in the input file and
 263 the input conditions are summarized in Table 2. The porous medium is
 264 set as pure calcite (CaCO_3). For all simulations, the initial pore water is
 265 considered at equilibrium with calcite, and the inlet solution composition is
 266 set to correspond to the injected acid solutions described above. The reaction
 267 considered in the model is the dissolution of calcite and the speciation of
 268 carbonates. The kinetic rate and equilibrium constant come from Palandri
 269 and Kharaka (2004) and Plummer and Busenberg (1982), respectively. A
 270 neutral, linear reaction mechanism (pH 7) was chosen to describe calcite
 271 dissolution rates given the relatively elevated pH and low P_{CO_2} ($\approx 7 \times 10^{-4}$

272 atm) starting conditions for the experiments (Plummer et al., 1978; Chou
 273 et al., 1989; Pokrovsky et al., 2005), which alleviates H^+ dependence (Sjöberg
 274 and Rickard, 1984). Further, sensitivity analyses for calcite dissolution rate
 275 mechanisms show little sensitivity in the reactive transport model to the
 276 choice of rate mechanism under the conditions of the experiments and time
 277 durations (one example is shown in Figure S.1 in Supp. Inf.). The specific
 278 reactive surface area is initially calculated based on the literature which uses
 279 a smooth, spherical grain approximation to determine the effective surface
 280 area (Mito et al., 2013; Beckingham et al., 2016), then it is updated following
 281 a shrinking sphere approximation for dissolution (Lichtner, 1996; Steefel and
 282 Lichtner, 1998),

$$A_m = A_{m,0} \left(\frac{\phi_t}{\phi_0} \right)^{2/3} \left(\frac{\phi_{m,t}}{\phi_{m,0}} \right)^{2/3}, \quad (4)$$

283 where $A_{m,0}$, ϕ_0 , and $\phi_{m,0}$ are the initial surface area ($m^2_{\text{calcite}} m^{-3}_{\text{porous medium}}$),
 284 initial total porosity ($m^3_{\text{void}} m^{-3}_{\text{porous medium}}$), and the initial mineral vol-
 285 ume fraction ($m^3_{\text{calcite}} m^{-3}_{\text{porous medium}}$), respectively. The total porosity
 286 and mineral volume fraction at the current time step are designated as ϕ_t
 287 and $\phi_{m,t}$, respectively, and are individually tracked in the model through
 288 mass-balance (Lichtner, 1996; Steefel and Lichtner, 1998),

$$\phi_{m,t} = \phi_{t-\Delta t} + V_s R_{\text{calcite}} \Delta t \quad (5)$$

289 and

$$\phi_t = 1 - \sum_{m=1}^{N_m} \phi_{m,t}, \quad (6)$$

290 where Δt is the current time step size, $t - \Delta t$ corresponds to the previous
291 time step, V_s the calcite molar volume ($3.69 \times 10^{-5} \text{ m}^3_{\text{calcite}} \text{ mol}^{-1}_{\text{calcite}}$),
292 and R_{calcite} is the calcite reaction rate ($\text{mol}_{\text{calcite}} \text{ m}^{-3}_{\text{porous medium}} \text{ s}^{-1}$).

293 The column is treated as a 1D porous medium. It is discretized with a
294 regular mesh size $\Delta x = 1 \text{ cm}$, except over 3–13 cm range, where the mesh
295 size varies between 0.1 and 1 cm (Figure S.2 in Supp. Inf.). This leads to
296 setting the longitudinal dispersion of 0.09 cm to not exceed the size of the
297 smallest mesh (0.1 cm). Ionic species present in the solution have specific
298 diffusion coefficients (Table S.1 in Supp. Inf.). The Debye-Hückel model
299 for the activity coefficients is used in the model despite the ionic strengths
300 of initial solutions in some experiments being sufficiently high for a Pitzer
301 model treatment. This choice in the specific-ion interaction model can be
302 justified in two ways. First, the Pitzer model is currently not implemented
303 in Crunchflow (Steeffel et al., 2015). Second, the Debye-Hückel model is suffi-
304 cient to characterize ionic interactions for this particular Crunch model and
305 the conditions of this study where aqueous concentrations are dominated
306 by $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{HCO}_{3(\text{aq})}^{-}$ and have low concentrations of $\text{SO}_{4(\text{aq})}^{2-}$ and $\text{Mg}_{(\text{aq})}^{2+}$
307 –both of which are main inhibitors of calcite dissolution (Morse et al., 2007).
308 Additionally, experimental investigations into calcite dissolution rate depen-
309 dence on ionic strength have demonstrated negligible dependence on total
310 dissolved solids (TDS) at pCO_2 values less than or equal to 0.1 bar (Gledhill

311 and Morse, 2006; Finneran and Morse, 2009).

Table 2: Input conditions used in the numerical simulations.

Mineral	Calcite
Reaction stoichiometry	$\text{CaCO}_{3(s)} + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
Equilibrium constant K_{eq} (log10)	1.8487 [†]
Reaction kinetics k (log10, mol m ⁻² s ⁻¹)	-5.81 [‡]
Specific surface area (m ² g ⁻¹)	1.15 [*]
Cementation exponent m	1.78
Longitudinal dispersivity (m)	9×10^{-4}

[†] Plummer and Busenberg (1982)

[‡] Palandri and Kharaka (2004)

^{*} Beckingham et al. (2016)

312 2.2.2. Petrophysical modeling

313 The modeled electrical signals are obtained from CrunchFlow reactive
 314 transport numerical simulation and the petrophysical relationships presented
 315 in this section. Thus, relating the electrical response to the geochemical,
 316 hydrological, and petrophysical parameters.

317 The water conductivity is computed from (e.g., Atkins and de Paula,
 318 2014; Revil and Linde, 2006; Jougnot et al., 2010)

$$\sigma_w = \mathcal{F} \sum_i |z_i| \beta_i \gamma_i C_i, \quad (7)$$

319 where z_i (-), β_i (m² s⁻¹ V⁻¹), γ_i (-), and C_i (mol m⁻³) are the valence,
 320 the mobility, the activity coefficient, and the concentration of each ionic
 321 species i , respectively, and $\mathcal{F} \approx 9.65 \times 10^4$ C mol⁻¹ is the Faraday constant.

322 The ionic concentration value comes from the reactive transport numerical
323 CrunchFlow simulations. Applying Equation 7 to compute the outlet water
324 conductivity enables assessing the quality of the simulations when compared
325 to the measured electrical conductivities.

326 The SP method is simple to set up but complex to interpret as it in-
327 volves the superposition of different possible sources of current (e.g., Hu
328 et al., 2020). Among the contributions, reactive transport can be linked
329 to two potential couplings: electrokinetic and electrochemical. First, the
330 electrokinetic coupling is the generation of a streaming potential from wa-
331 ter flow in the pores. Due to the presence of electric charge at the surface
332 of minerals, the pore water carries an excess charge that generates the so-
333 called streaming current (e.g., Quincke, 1859; Revil and Leroy, 2004; Jougnot
334 et al., 2020; Soldi et al., 2020). Second, the electrochemical coupling called
335 the electro-diffusive potential, is associated with ion concentration gradients
336 that generate separation charge due to the difference of mobilities between
337 migrating dissolved ionic species (e.g., Revil, 1999; Mainault et al., 2004;
338 Revil and Linde, 2006; Mao et al., 2015; Rembert et al., 2022). Therefore,
339 the interest of the SP method is that it allows the study of mixing and re-
340 action zones between fluids as saline intrusions (e.g., Mainault et al., 2005;
341 MacAllister et al., 2018; Graham et al., 2018) or water intrusion into hy-
342 drocarbon reservoir (e.g., Murtaza et al., 2011). We performed several tests
343 on the considered material showing that the electro-diffusive contribution is
344 dominating the SP signal compared to electrokinetic coupling when studying
345 calcite dissolution even when we tested measuring SP variations in advec-
346 tion dominating regime with various fluid velocities, dissolution rates, and

347 electrodes spacing (Rembert et al., 2022). This result comes from the low
 348 surface charge of calcite mineral and the impact of the water electrical con-
 349 ductivity which decreases the thickness of the EDL. The electro-diffusive
 350 contribution to SP voltage for the measuring electrode P_j (with $j = 1-3$)
 351 and the reference electrode P_4 is modeled as

$$\Delta V_{P_j-P_4} = \frac{\mathcal{R}T}{\sigma_w} \sum_i \frac{z_i}{|z_i|} \beta_i \gamma_i (C_{i,P_j} - C_{i,P_4}), \quad (8)$$

352 where $\mathcal{R} \approx 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the molar gas constant and T (K) is the
 353 absolute temperature. Since the water conductivity is not measured in the
 354 column, σ_w is computed from Equation 7.

355 The complex electrical conductivity is expressed as

$$\sigma^* = \sigma' + i\sigma'', \quad (9)$$

356 where σ' is the real part and σ'' is the imaginary part of the complex elec-
 357 trical conductivity. The real conductivity σ' corresponds to the electrical
 358 conduction in the porous medium. This term is related to the lithology, rock
 359 structure, water content, and solute concentrations (e.g., Rembert et al.,
 360 2023a). It is defined as follows

$$\sigma' = \frac{\sigma_w}{F} + \sigma_s, \quad (10)$$

361 where F is the formation factor of the rock sample and σ_s is the surface
 362 conductivity of the minerals. In the case of calcite and considering the
 363 pore water electrical conductivities of this study, σ_s is negligible. Thus, the

364 formation factor F is defined as follows

$$\lim_{\sigma_s \rightarrow 0} F = \frac{\sigma_w}{\sigma'}. \quad (11)$$

365 The equation of Archie (1942) relates the formation factor to the porosity
366 as follows

$$F = \phi^{-m}, \quad (12)$$

367 where m (–) is the cementation exponent. From SIP measurement on the
368 column saturated with the initial solution of known conductivity, we inferred
369 that $m = 1.78$. Using suitable $F - \phi$ relationships is an important topic in
370 petrophysics. The power law described in Archie (1942) is the most famous
371 and widely used relationship. However, its use is inappropriate for a strong
372 dissolution regime (e.g., Niu and Zhang, 2019) but has proven its relevance
373 for a lower one (e.g., Bernard et al., 2007). The imaginary conductivity σ''
374 is associated with polarization phenomena. In the frequency range studied,
375 the polarization results from the transient reorganization of an excess of
376 charges in the so-called electrical double layer (EDL) at the surface of charged
377 minerals. The structure of the EDL comprises the thin Stern layer coated by
378 the wider diffuse layer (e.g., Heberling et al., 2011). The EDL polarization
379 is frequency-dependent and is related to relaxation times, associated with
380 characteristic lengths in the porous medium (e.g., pore length, pore aperture,
381 grain size, roughness Leroy et al., 2008, 2017; Kemna et al., 2012; Revil
382 et al., 2012b). Surface complexation reactions driven by mineral dissolution

383 and precipitation processes can modify the mineral surface state and also
384 influence the imaginary conductivity spectrum (e.g., Wu et al., 2010; Izumoto
385 et al., 2022; Rembert et al., 2023b). This component of the complex electrical
386 conductivity is not modeled with this workflow.

387 **3. Results and Discussion**

388 This section summarizes results for the five calcite dissolution flow-
389 through experiments and associated modeling. It is organized by data type.
390 For all experiments, time zero corresponds to the beginning of the reactive
391 solution injection.

392 *3.1. Outlet water chemistry*

393 Outlet water concentrations as a function of time are presented in Fig-
394 ure 3. Initial values are consistent across all five experiments since the column
395 is initially saturated with the same solution in thermodynamic equilibrium
396 with calcite (mean saturation index $SI = \log_{10}(Q/K) = -0.08$, where Q is
397 the ion activity product). For each experiment, aqueous species show syn-
398 chronous variations between them corresponding to the arrival of the acid
399 front at the outlet of the column. Curves obtained from numerical sim-
400 ulations are also plotted and show good agreement with the experimental
401 data.

402 Experimental data and simulation curves of alkalinity and calcium con-
403 centration show an increase for experiments ②, ③, and ⑤. Calcite dissolution
404 due to acetic acid injection adds calcium ions to the solution. For experi-
405 ments ② and ③, sodium increases due to the presence of sodium acetate

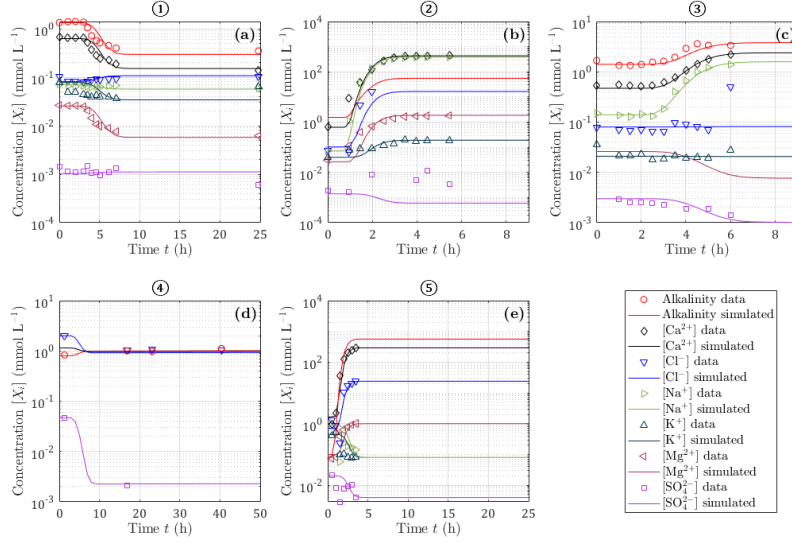


Figure 3: Experimental data and curves from 1D reactive transport numerical simulation of bicarbonate (HCO_3^-), (calcium Ca^{2+} , chloride Cl^- , sodium Na^+ , potassium K^+ , magnesium Mg^{2+} , and sulfate SO_4^{2-}) for (a) experiment ①, (b) experiment ②, (c) experiment ③, (d) experiment ④, and (e) experiment ⑤.

406 in the inlet solution to buffer the acetic acid. Reached values of alkalinity
 407 and calcium concentration are lower for experiment ③, due to lower acid
 408 concentration. Higher calcium concentrations are reached for experiment ②
 409 compared to experiment ⑤ while acid solutions have pH values of 4.5 and
 410 2.5, respectively.

411 For the experiment ①, corresponding to hydrochloric acid injection at
 412 pH 4.5, alkalinity and calcium concentration decrease but do not fall to
 413 zero. The injected acid solution does not contain any calcium or bicarbonate
 414 ions, thus, the reached stable values indicate dissolution. In experiment ④,
 415 corresponding to hydrochloric acid injection at pH 3, alkalinity and calcium
 416 curves show a plateau with higher values compared to experiment ①.

417 3.2. pH monitoring

418 pH values recorded in the column (pH_1 and pH_2) and measured on the
 419 collected samples of outlet pore water ($\text{pH}_{\text{sample}}$) are displayed for all ex-
 420 periments in Figure 4. The experimental data pH_1 , pH_2 , and $\text{pH}_{\text{sample}}$ are
 421 consistent with one another. For each experiment, the variations of pH_1 ,
 422 pH_2 , and $\text{pH}_{\text{sample}}$ follow similar trends with an increasing time delay consis-
 423 tent with the propagation of the acid front through the column. Simulation
 424 curves of pH_1 , pH_2 , and $\text{pH}_{\text{sample}}$ are also displayed and show fairly good
 425 agreement with the experimental data.

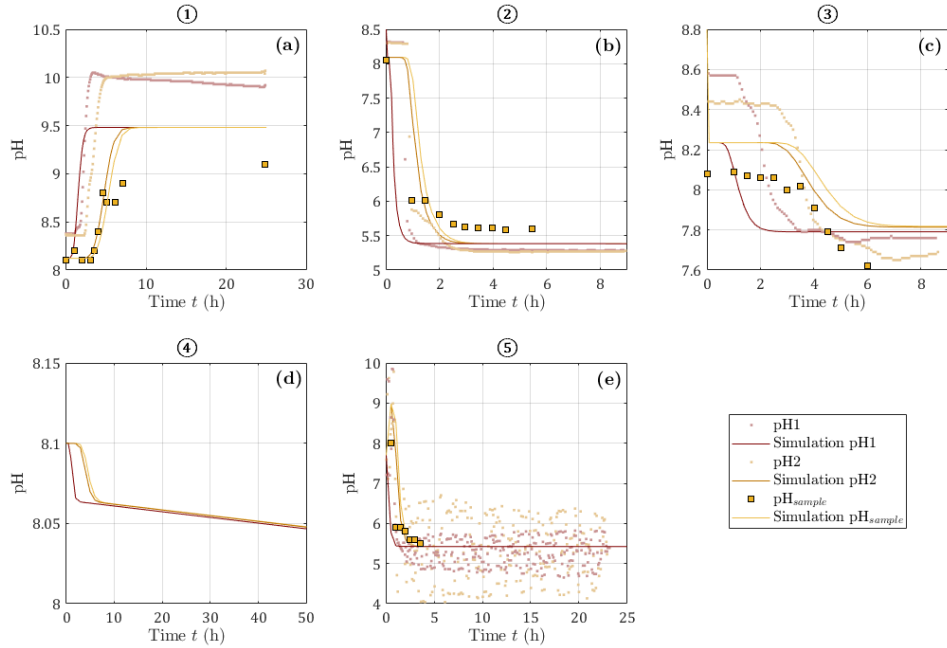


Figure 4: Experimental data and curves from 1D reactive transport numerical simulation of pH for (a) experiment ①, (b) experiment ②, (c) experiment ③, (d) experiment ④, and (e) experiment ⑤. pH_1 and pH_2 correspond to pH at 13 and 27 cm in the column, respectively. $\text{pH}_{\text{sample}}$ comes from the collected samples of outlet pore water. For experiment ④, pH_1 and pH_2 were not measured. For experiment ⑤, pH_1 and pH_2 are noisy because of electric current injection for SIP acquisition, thus, envelopes of the data are displayed for clarity.

426 The smooth variations of pH_1 and pH_2 for experiments ①, ②, and ③ are
427 results of high-precision monitoring. When SIP measurements are performed
428 during experiment ⑤, the injection of electric current generates noise that
429 is higher for pH_2 , located close to the current electrode C_2 . However, the
430 simulated curves are centered with the envelopes of the experimental data,
431 showing the consistency of the numerical simulation.

432 For experiments ① and ③, $\text{pH}_{\text{sample}}$ is shifted in amplitude compared to
433 pH_1 and pH_2 , while it is not visible for the experiments ② and ⑤. During
434 experiments ② and ⑤, a mixture of gas bubbles and pore water was observed
435 at the outlet of the column. The gas bubbles are CO_2 bubbles that form
436 due to the intense dissolution of calcite (e.g., Choi et al., 1998, photos of the
437 columns at the end of each experiment are displayed in Figure S.3 in Supp.
438 Inf.), as observed from the important production of Ca^{2+} ions. Indeed,
439 CO_2 is produced by the high concentration of carbonic acid H_2CO_3 , which
440 is the soluble form of dissociated ions bicarbonate HCO_3^- and carbonate
441 CO_3^{2-} in acid conditions. The experiments are conducted at atmospheric
442 pressure, which induces the release of gaseous CO_2 (e.g., Rembert et al.,
443 2023b). Thus, the amplitude shift of $\text{pH}_{\text{sample}}$ may come from the late
444 degassing of CO_2 after the pore water reaches the outlet of the column in
445 the case of experiments ① and ③.

446 Except for experiment ①, pH values decrease with acid injection. For
447 experiment ①, after pH_2 has risen to the same value as pH_1 , pH_2 remains
448 stable, while pH_1 constantly decreases until the experiment is stopped. For
449 experiment ④, pH_1 and pH_2 were not monitored, and the values from the
450 samples of outlet pore water present a low decrease. For experiment ③,

451 compared to experiments ② and ⑤, the decrease in pH is less important,
452 indicating weaker dissolution, which is consistent with the lower acetic acid
453 concentration in the inlet solution. These results are also consistent with the
454 measurements of the porosity difference (Table 1), showing that more calcite
455 has been dissolved in experiments ② and ⑤ compared to experiment ③.

456 3.3. Outlet water conductivity

457 Outlet water conductivity measured values and simulated curves are plot-
458 ted for all experiments in Figure 5. The outlet conductivity monitored with
459 the in-line conductivity meter is named σ_{out} . The conductivity of the sam-
460 pled outlet pore water σ_{sample} is also displayed except for experiment ④, for
461 which it was not measured. Both measurements are in accordance except
462 for experiments ② and ⑤, for which σ_{out} is unreliable due to CO₂ degassing
463 that creates partial saturation in the tubes and bad detection with the in-
464 line conductivity meter. Therefore, comparing the measured σ_{sample} with
465 the modeled curve is preferred in this case.

466 Comparable initial conditions were set between the experiments with
467 similar initial values comprised between 100 and 150 $\mu\text{S cm}^{-1}$, except for
468 experiment ④, where problems of initial solution injection cause fluctua-
469 tions synchronous with ion concentration data and corresponding to the
470 acid front's arrival at the column outlet. Calcite dissolution is expected to
471 increase the conductivity of the outlet water over time by adding dissolved
472 ionic species (e.g., calcium) to the solution (e.g., Rembert et al., 2023a). This
473 expected behavior is observed for experiments ②, ③, and ⑤, for which acetic
474 acid is injected. On the contrary, for experiments ① and ④, hydrochloric acid

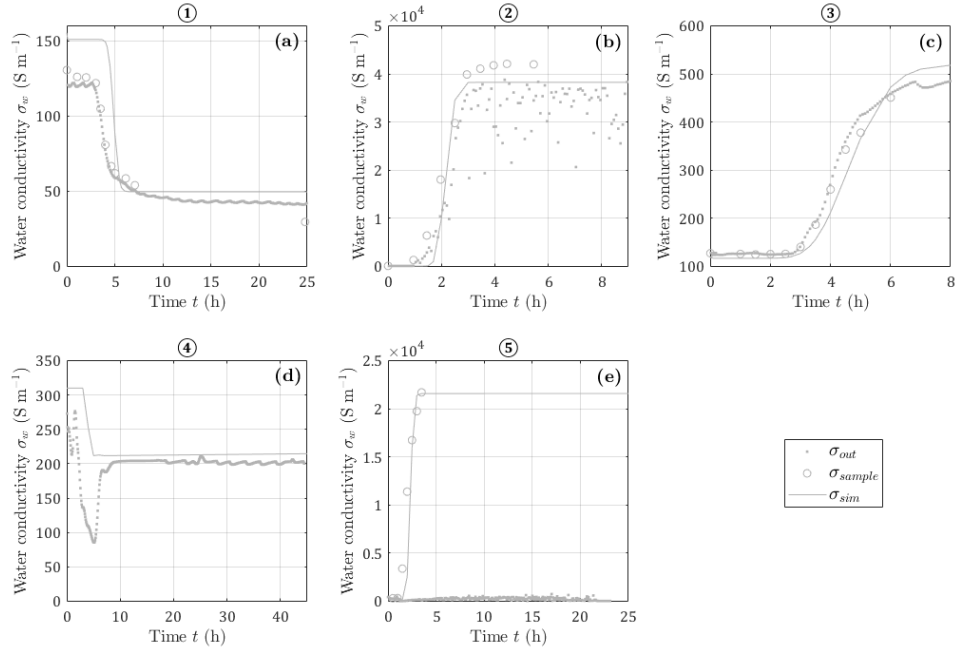


Figure 5: Outlet water conductivity, measured with the in-line conductivity meter (σ_{out}) and from the outlet water samples (σ_{sample}), and modeled with 1D reactive transport numerical simulation (σ_{sim}) for (a) experiment ①, (b) experiment ②, (c) experiment ③, (d) experiment ④, and (e) experiment ⑤.

475 is injected, and σ_{out} decreases. This result is explained by the difference in
 476 ion concentrations and mobilities impacting the solution conductivity (e.g.,
 477 Rembert et al., 2022). Indeed, the consumption of hydrogen ions (H^+) dur-
 478 ing the calcite dissolution decreases the water conductivity because H^+ ions
 479 have a much higher mobility compared to calcium or bicarbonate ions (by
 480 one order of magnitude). Small oscillations and hangings are visible on σ_{out}
 481 experimental data for experiments ①, ③, and ④. They are caused by the
 482 air-conditioning system for room temperature regulation.

483 The curves of the numerical simulations σ_{sim} show good agreement in
 484 dynamics and amplitudes for all of the experiments, while variable inlet

485 acids and broad concentration ranges are used and still with σ_{sample} when
 486 there is CO₂ degassing.

487 *3.4. Porosity, real electrical conductivity, and formation factor*

488 The porosity, the formation factor, and the real electrical conductivity
 489 obtained from experimental data and reactive transport simulation for all of
 490 the experiments are presented in Figure 6.

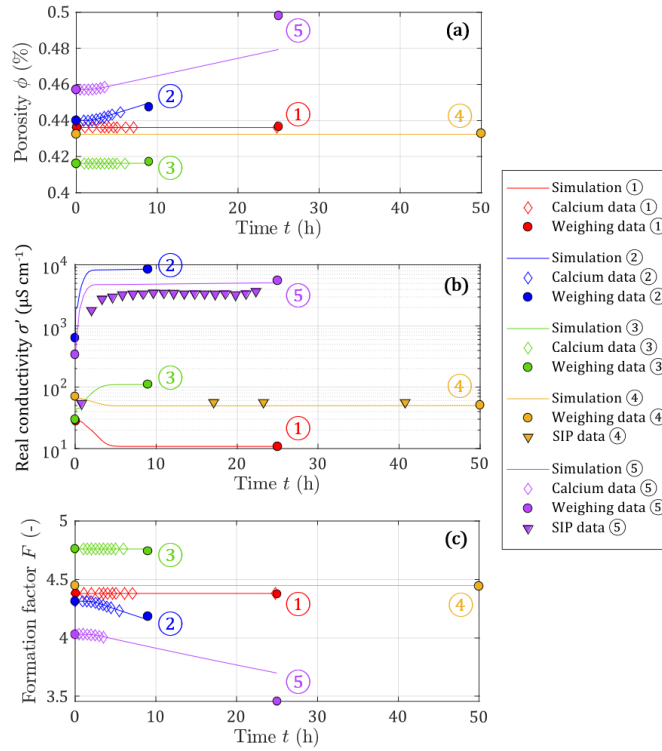


Figure 6: Experimental data and curves from 1D reactive transport numerical simulation of (a) porosity, (b) real electrical conductivity, and (c) formation factor for the five experiments. Porosity values are estimated from calcite grains weighing data (discs), measured calcium concentration (diamonds), and simulated (curves). The real electrical conductivity curves are determined from simulated porosities and simulated water conductivity using the model from Archie (1942). For experiments 4 and 5, the simulated electrical conductivities are confronted with the real electrical conductivity σ' measured with the SIP method.

491 Initial values of porosity estimated by weighing the mass of calcite filling
492 the column are in the close range from 41.62 to 43.99 % (Table 1), showing
493 that comparable initial conditions are set with the column-filling procedure
494 used. For all experiments, the final porosity is higher, with an increase rang-
495 ing from 0.04 to 4.12 %, and more important for experiments ② and ⑤. Time
496 variations of the porosity are estimated from the monitoring (diamonds) and
497 the simulation (curves) of calcium concentration in the samples of outlet
498 pore water (Figure 6a). Porosity values estimated from calcium concentra-
499 tion show excellent correspondence between experimental data and simulated
500 curves. Thus, porosity modeling from the simulated calcium concentration
501 is accurate for most of the experiments. There is also a good agreement
502 with the porosity values estimated from calcite grains weighing data. Even
503 for experiment ⑤ since the difference corresponds to an error of 3.7 % of the
504 final mass of calcite. For experiment ⑤, the porosity reaches a higher value
505 from the weighing data. Nevertheless, the associated percentage of the error
506 in this measurement is of 3.7 % of the final mass of calcite. This low error
507 value can be associated with weighing procedure uncertainty.

508 The real electrical conductivity of the column is experimentally obtained
509 from SIP measurements of $\sigma'_{P_1-P_4}$ (1 Hz) for experiments ④ and ⑤. The
510 real electrical conductivity of the column is also estimated from the porosity,
511 based on the relationship of Archie (1942) for a constant cementation factor
512 (Equations 11 and 12). The literature shows that this assumption is not
513 valid for highly heterogeneous samples (e.g., Garing et al., 2014), and strong
514 dissolution rates in advective regimes (e.g., Noiriél et al., 2004), but it verifies
515 for lower ones (e.g., Niu and Zhang, 2019; Rembert et al., 2023a). In this

516 study, the column is homogeneously filled with calcite grains and the flow
517 regime is diffusion-dominated. For experiment ④, there is a strong agreement
518 between the SIP measurements, the simulated curve, and the initial and final
519 values determined from weighing data. For experiment ⑤, the agreement
520 between the SIP measurements and the real conductivity determined from
521 porosity data and simulations is less accurate, but of the same order of
522 magnitude. These results highlight that Archie’s equation is valid in these
523 conditions of calcite dissolution in a homogeneous sample.

524 All experiments present real electrical conductivity variations consistent
525 with the water conductivity evolution (Figure 4). Acetic acid injection (ex-
526 periments ②, ③, and ⑤) increases the real conductivity, while it decreases
527 for hydrochloric acid injection (experiments ① and ④).

528 The formation factor (Equations 11 and 12) describes the evolution of the
529 pore space structure. As for the real electrical conductivity calculation, the
530 formation factor is determined considering a constant cementation exponent.
531 As previously documented in the literature, calcite dissolution is associated
532 with a reduction in the formation factor (e.g., Rembert et al., 2020, 2023a).
533 The formation factor curves exhibit a reverse relationship with the porosity
534 curves.

535 3.5. *SP and electro-diffusive modeling*

536 SP measurements are presented in Figure 7a–c. They present similar
537 patterns with bell-shaped variations that start first for the pair P₁–P₄, then
538 P₂–P₄, and finally P₃–P₄, but end simultaneously. As documented in the
539 literature (e.g., Mainault et al., 2004; Rembert et al., 2022) such SP signals

540 with bell-shaped variations are generated by concentration gradients. Com-
541 pared to the variations of pH monitored inside the column and the outlet
542 measurement, the bell-shaped variations of SP signals are synchronous with
543 the acid front propagation through the column. Furthermore, following the
544 literature and the configuration of the electrodes, the positive or negative
545 bell-shaped responses are consistent with the increase or decrease of σ_{in} due
546 to the reacting solution injection. At the beginning of the experiment, the
547 SP curves show very similar values for each pair of electrodes, despite their
548 different distances from the reference electrode P₄. This is the opposite of
549 what would be observed in the case of an electrokinetic source. Thus, there
550 is no electrokinetic contribution as observed by Rembert et al. (2022), only
551 the electro-diffusive contribution to SP values is considered.

552 Depending on the experiment, after the bell-shaped variation, some SP
553 pairs return to their base value and remain stable. Thus, these pairs of
554 electrodes are only affected by a transient source of SP current which is the
555 ion concentration gradient caused by the acid front propagation. In con-
556 trast, other pairs reach stable values of different amplitude than initially.
557 These changes in amplitude are related to permanent concentration gradi-
558 ents between the measuring electrode and the reference. For experiment ①
559 (Figure 7a), after the bell-shaped variation, pair P₁-P₄ shows a stable value
560 greater than 1 mV not observed for the other pairs. This is associated with
561 the localization of the reaction zone between the electrodes P₁ and P₂. For
562 experiment ② (Figure 7b), as the three curves show very close final values, it
563 is likely that they all lie within the reactive zone. In addition, there is a no-
564 ticeable pulse at $t = 1$ h and noticeable synchronous oscillations for all pairs

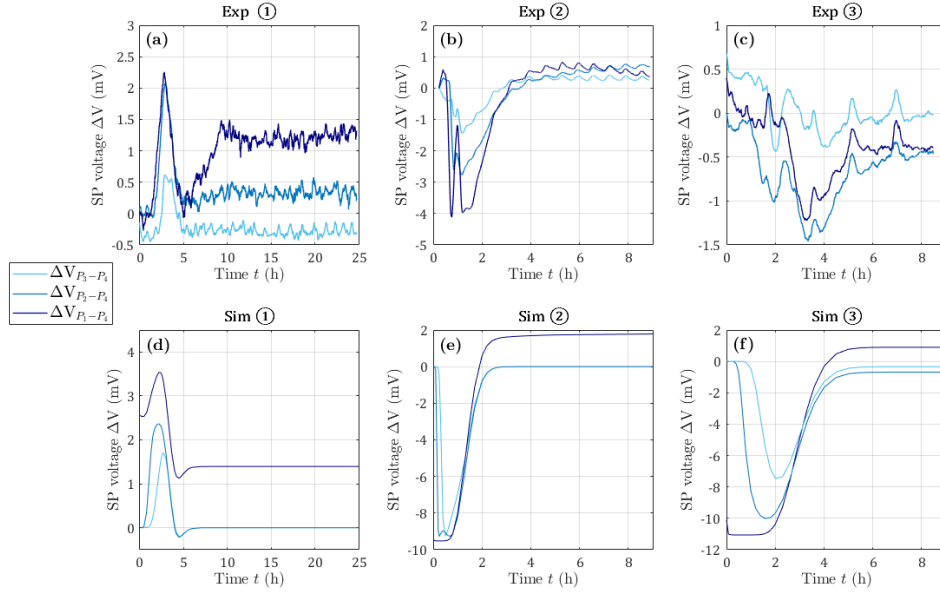


Figure 7: SP monitoring for (a) experiment ①, (b) experiment ②, and (c) experiment ③. The data are filtered with a moving average window of 10 min. Numerical simulations of the electro-diffusive coupling for (d) experiment ①, (e) experiment ②, and (f) experiment ③.

565 of electrodes related to the room temperature control with air conditioning.
 566 For experiment ③ (Figure 7c), the SP curves show negative variations of
 567 lower amplitude compared to the variations of experiment ②. This is consis-
 568 tent with the close conductivity values between the inlet acid and the initial
 569 solution. There are also some pulses due to room temperature regulation.

570 The numerical results are displayed in Figure 7d–f. The curves show
 571 good agreement with the measurements regarding the sign and time evolu-
 572 tion of the bell-shaped variations. The amplitudes are of similar magnitude
 573 for experiment ① with hydrochloric acid injection. On the contrary, SP is
 574 overestimated for acetic acid injection in experiments ② and ③ with an order
 575 of magnitude difference. This difference in magnitude is linked to the acid

576 type. In the case of hydrochloric acid injection, H^+ ions dominate the diffu-
577 sion and are simpler to model. However, when injecting acetic acid multiple
578 species are competing, thus, the concentration gradient is more complex to
579 model. Since the workflow puts modeling results in series, the inaccura-
580 cies accumulate when modeling SP response. In addition, the model is 1D
581 neglecting 3D effects, which are discussed later.

582 Nevertheless, compared to physicochemical monitoring, SP variations
583 during calcite dissolution show that the spatialization of the reactive zone
584 can be revealed with this method. In comparison, pH electrodes inserted in
585 the column do not provide this information, except for experiment ①, for
586 which the slight decrease of pH_1 reveals that the reactive zone reaches this
587 location but does not affect pH_2 similarly.

588 The modeling of the electro-diffusive contribution shows good agreement
589 for the experiment ①, for which strong acid is injected. The results are
590 less accurate for experiments ② and ③ with buffered acetic acid injection.
591 From the outlet water conductivity results, the mobility of H^+ protons plays
592 a major role when injecting hydrochloric acid. On the contrary, for acetic
593 acid injection, other ionic species contribute extensively. This diversity of
594 contributions complicates the modeling, even if it shows that the reactive
595 zone is limited to P_1 – P_2 range for experiment ①, while it is extensive to the
596 outlet for experiments ② and ③.

597 3.6. Imaginary conductivity spectra

598 Figure 8 presents the imaginary conductivity spectra obtained for exper-
599 iments ④ and ⑤ for the three pairs P_1 – P_2 , P_2 – P_3 , and P_3 – P_4 over time.

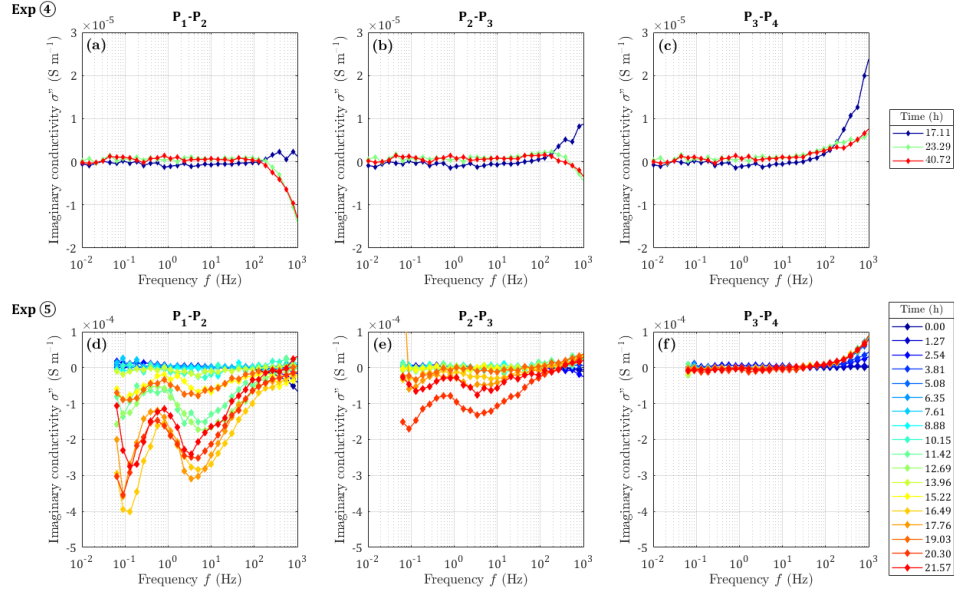


Figure 8: Imaginary conductivity spectra of pairs P_1 – P_2 , P_2 – P_3 , and P_3 – P_4 at different times of (a, b, c) experiment ④ (S4, hydrochloric acid at pH=3) and (d, e, f) experiment ⑤ (acetic acid S5). Injections of S4 and S5 define the time zero of each experiment.

600 For experiment ④ (Figure 8a–c), imaginary conductivity spectra remain
 601 flat for all pairs during the entire experiment for frequencies below 500 Hz.
 602 For frequencies above 500 Hz, the successive pairs present three different
 603 trends. For P_1 – P_2 , imaginary conductivity values are negative, growing in
 604 absolute value, then stabilizing with time. For pair P_2 – P_3 , high-frequency
 605 imaginary conductivities are first positive, then they become negative, with
 606 lower amplitude in absolute value compared to high-frequency imaginary
 607 conductivities of pair P_1 – P_2 for the same time. Imaginary conductivities of
 608 pair P_3 – P_4 are always positive.

609 Experiment ⑤ presents similar patterns for high-frequency imaginary
 610 conductivities (Figure 8d–f), with important negative values for pair P_1 – P_2 ,

611 less negative values for pair P₂–P₃, and positive values for pair P₃–P₄. These
612 negative imaginary conductivity have been seen in reactive media (Izumoto
613 et al., 2022). In addition, there are two bell-shaped negative variations for
614 frequencies below 500 Hz. These bumps are centered on 0.15 and 3.5 Hz.
615 Similar peaks have been observed during calcite dissolution in Rembert et al.
616 (2023b).

617 Imaginary conductivity spectra have contrasted variations between ex-
618 periments ④ and ⑤. Values are close to zero for experiment ④ while there
619 are remarkable variations for experiment ⑤ of acetic acid injection gener-
620 ating strong dissolution regime. In addition, negative values are measured
621 for experiment ⑤. According to the theory, they are associated with a not
622 expected inductive behavior. However, due to the strong dissolution regime,
623 pH is decreased toward acidic conditions, where calcite surface charge may
624 change sign (e.g., Eriksson et al., 2007; Heberling et al., 2021). Sign variation
625 of the imaginary conductivity during precipitation and dissolution processes
626 has already been reported in the literature (Izumoto et al., 2022; Rembert
627 et al., 2023b) but is still difficult to interpret with the existing models. Thus,
628 the results from this method do not show results as clear as SP monitoring
629 and are harder to interpret. Besides, SIP is more difficult to conduct in
630 the field compared to SP setup. Time-domain induced polarization (TDIP)
631 may be another solution to investigate. Thus, for future field studies of re-
632 active contamination, the authors recommend more investigations with the
633 SP method.

634 *3.7. Relationship between acid type and dissolution process*

635 From the description of the results, the impact on calcite dissolution
 636 between chloride (strong) or acetic (weak) acid injections can be clearly dis-
 637 tinguished. There are also contrasted results between buffered with sodium
 638 acetate and not buffered acetic acid solutions, with higher and lower concen-
 639 trations of acetic acid. The numerical simulations can extract the distribu-
 640 tion in space and time of the reaction rate. It is represented at 9 h after the
 641 start of acid injection in each experiment in Figure 9. From the outputs of
 642 the CrunchFlow models we can also get the value of the dissolution rate at
 643 the injection point. The values are summarized in Table 3. They highlight
 644 more dissolution for acetic acid solutions compared to hydrochloric acid so-
 645 lutions for the same pH. In addition, when looking at the spatial variations
 646 of the dissolution rate, we observe that it is more stable for experiments ②
 647 and ③ than for others, coming from the fact that they are buffered with
 648 sodium acetate (rate.out files archived on Zenodo.org).

Table 3: Dissolution rates at the injection point from CrunchFlow modeling at the first time step.

Experiment	①	②	③	④	⑤
Dissolution rate at the injection point ($\text{mol m}^{-3} \text{s}^{-1}$) at 0.1 min after starting the injection.	$8.89 \cdot 10^{-4}$	2.08	$1.46 \cdot 10^{-2}$	$5.97 \cdot 10^{-2}$	2.05

649 The impact of acid type can be seen in the extent of the reactive zone in
 650 the column. The expansion of the reactive zone is minimal for experiments
 651 with hydrochloric acid injection (① and ④), and broader for experiments
 652 with acetic acid injection (②, ③, and ⑤). Despite a low concentration of
 653 acetic acid for the experiment ③, the reactive zone is extended from P_1 to

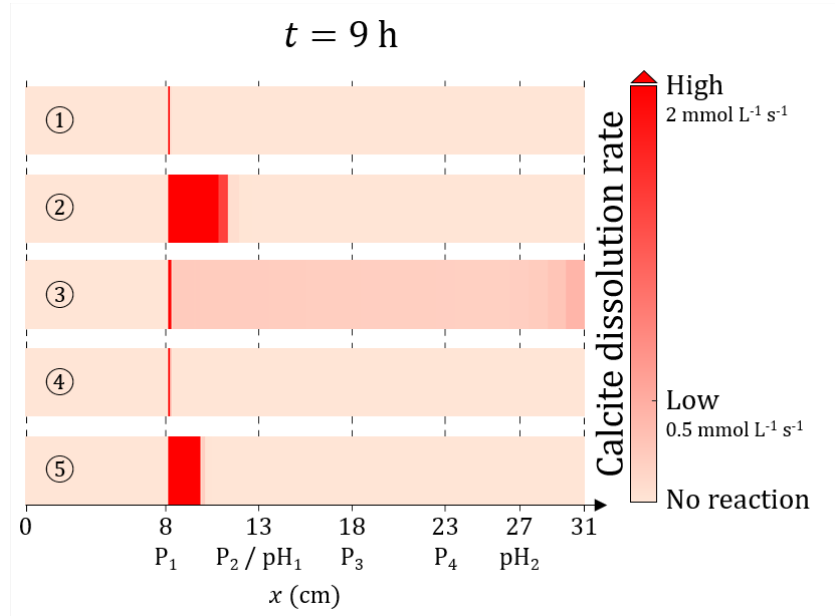


Figure 9: Reactive zone location for the different experiments of calcite dissolution from the dissolution rate extracted from the numerical simulations at 9 h after the start of acid injection for the five experiments. The same color scale is used for all of the experiments. The maximum value is set to $2 \text{ mmol L}^{-1} \text{ s}^{-1}$, but the red color indicates values that can be higher.

654 the outlet of the column, opposite to the experiments with the hydrochloric
 655 acid injection of the same or lower pH. This spreading of the reactive zone
 656 when injecting acetic acid compared to hydrochloric acid is in agreement
 657 with the results of the literature (e.g., Garcia-Rios et al., 2014).

658 From experiments ② and ⑤, the reactive zone is more extended for exper-
 659 iment ②, while the inlet acid has a higher pH value (pH=4.5) compared to
 660 the injected acid in experiment ⑤ (pH=2.5). The inlet acid is a buffered solu-
 661 tion of acetic acid with sodium acetate for experiment ②. From the porosity
 662 increase simulated after 9 h of acid injection, porosity has increased by a
 663 third more for experiment ② compared to experiment ⑤, showing that dis-

664 solution is more intense for experiment ②. Buffering the inlet acid increases
665 the dissolution power.

666 3.8. *Specific discussion about the reactive transport simulation*

667 The experimental results presented in this study reveal that calcite dis-
668 solution does not exhibit a unique geoelectrical response, but rather distinct
669 signatures that can be opposite, depending on the porous medium, inlet
670 chemistry, and flow regime. Thus, addressing the reactivity using a sophisti-
671 cated, robust treatment of reactivity through a reactive transport framework
672 improves interpretations for geoelectrical signals compared to the use of em-
673 pirical constants (Cherubini et al., 2019).

674 The strongest hypothesis in the model is to consider the column as a
675 1D system. This assumption is valid considering the small diameter of the
676 base, although it is worth 13% of the column length. Furthermore, the col-
677 umn is filled with well-sorted sieved grains of calcite, to ensure maximum
678 homogeneity opposite to using consolidated limestone samples as in Rembert
679 et al. (2023a), for which preferential dissolution pathways formed due to ini-
680 tial heterogeneity (Leger et al., 2022). The porous medium is considered an
681 effective medium, where the formation of a preferential path is neglected.
682 However, local heterogeneity of the flow through granular media is not a
683 detail (e.g., Stevenson, 1997). Some additional 3D effects may arise from the
684 column horizontal orientation and density difference between the injected
685 acid and the initial saturating solution, especially for experiments ② and ⑤.
686 For these two experiments, there is a density contrast $\Delta d > 0.02$ between the
687 initial pore water and the injected acid solutions. It is known from the study

688 of saline intrusions in coastal aquifers, that for such a density contrast, salt
689 wedges form under the freshwater (e.g., Rattray and Mitsuda, 1974). This
690 leads the injected acid solutions to flow preferentially in the lower half of
691 the column before replacing the initial pore water. The good agreement be-
692 tween the sampled and the modeled outlet water conductivity is in favor of
693 the replacement of the less dense water. This stratification induces calcite
694 dissolution preferentially on the lower side of the column (Figure S.3 in Supp.
695 Inf.). In addition, the production of CO₂ bubbles that accumulate in bigger
696 pores and on the upper side of the column also influences the flow path.
697 However, geoelectrical methods are integrative measurements, and sensitiv-
698 ity analysis of the electrodes reveals that they integrate the signal over the
699 entire volume comprised between the measurement electrodes. The column
700 geometry gathers the offset of acid injection via a tube inserted at the level
701 of the first electrode P1. At this injection point, the acid concentration is
702 heterogeneous, resulting in a cone effect to disperse across the entire cross-
703 section of the column. In relation to the total length to be covered, this cone
704 effect should only be present over a thin section of a few centimetres. This
705 cone effect could therefore pose a problem for the resolution of the P1-P4
706 channel compared with the P2-P4 and P3-P4 channels. However, we did
707 not observe any significant difference in the accuracy of the modeling results
708 between the measurement channels. On the other hand, the macroscopic
709 advective dissolution regime certainly involves some complex channelization
710 effects. However, as the electrical measurement is integrative over the entire
711 volume between the electrodes, the measurement is still sensitive to disso-
712 lution, but only reflects actual behavior, which can be modeled with a 1D

713 approximation under the imposed experimental conditions.

714 Therefore, the framework linking reactive transport simulation to petro-
715 physical modeling from combined physicochemical and geoelectrical mon-
716 itoring is of high interest to address multi-species reactive transport and
717 mixing (e.g., Ghosh et al., 2018; Oliveira et al., 2020). This makes the novel
718 approach presented in this study a relevant method for the characterization
719 of reactive fronts across scales and systems, from the laboratory bench to
720 groundwater contaminant plumes in regional aquifers.

721 In order to take complex channeling effects into account, as well as any
722 gravitational flows, it would be interesting to model the reactive transport
723 occurring within the column with a 3D model and a spatial resolution of a
724 few microns. However, CrunchFlow only offers an axisymmetric model and
725 resolution by homogenizing the concentration field over the voxel distribu-
726 tion. Such a 3D geometry would not suit the complexity of the problem and
727 would require implementing a sophisticated, hybrid approach combining our
728 reactive transport model (RTM) with a computational flow dynamics (CFD)
729 model. Such RTM-CFD coupling frameworks have only recently been ap-
730 plied for 3D problems (Bao et al., 2018) and are currently under development
731 for CrunchFlow (Li et al., 2022). While it would be interesting to explore
732 such alternative strategies, these tasks go beyond the objectives set by this
733 study.

734 **4. Conclusions**

735 This study addresses the enhancement of reactive percolation
736 monitoring in a flow-through column through the combined use of tradi-

737 tional physicochemical measurements on collected water samples and geo-
738 electrical acquisition on multiple channels along the column. The innovative
739 aspects of the study encompass the rare level of entanglement of the geo-
740 physics and geochemistry to address the complex processes and the use of
741 different types of acids to induce local versus extended reactive zones. Two
742 geoelectrical methods are tested: SP and SIP. Characterization of the re-
743 action zone spatialization, reaction rate, and porous structure changes can
744 be achieved through the use of a workflow that couples reactive transport
745 numerical modeling with petrophysical laws. The key findings of this study
746 are:

- 747 • SP monitoring highlights reactive solution front propagation through
748 the porous medium. Even a low reaction rate is detected, while the
749 outlet pore water samples present results contrary to expectations.
- 750 • SIP imaginary conductivity enables the characterization of strong dis-
751 solution regimes. However, it is less sensitive to low reaction rates.
- 752 • The reactive transport simulations well-reproduce the outlet pore wa-
753 ter concentrations and pH. Water electrical conductivity, porosity, and
754 the real electrical conductivity of the sample are retrieved from petro-
755 physical computation. Experimental data and simulation results are
756 in accordance, whatever the reaction rate and the reactive zone extent.
757 SP monitoring enables the characterization of concentration gradients
758 and the extent of dissolution.

759 This novel study in which geophysical and geochemical methods are intrinsi-
760 cally intertwined paves the way to broader and more interdisciplinary studies

761 of solute transport and reactivity in porous media. In a more general per-
762 spective, the presented methodology applies to contaminant transport.

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770 **Research Data**

771 The experimental data, reactive transport simulation outputs, and videos
772 of the dynamic calcite dissolution rate are available online at [https://doi.](https://doi.org/10.5281/zenodo.10018406)
773 [org/10.5281/zenodo.10018406](https://doi.org/10.5281/zenodo.10018406).

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