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► **To cite this version:**

Mariangeles Soldi, Flore Rembert, Luis Guarracino, Damien Jougnot. Electrical conductivity model for reactive porous media under partially saturated conditions with hysteresis effects. *Advances in Water Resources*, 2024, pp.104815. 10.1016/j.advwatres.2024.104815 . insu-04701070v2

**HAL Id: insu-04701070**

**<https://insu.hal.science/insu-04701070v2>**

Submitted on 2 Oct 2024

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# Electrical conductivity model for reactive porous media under partially saturated conditions with hysteresis effects

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This paper has been published in *Advances in Water Resources*:  
Soldi, M., Rembert, F., Guarracino, L., Jougnot, D. (2024) Electrical conductivity model for reactive porous media under partially saturated conditions with hysteresis effects. *Advances in Water Resources*. Volume 193, 2024, 104815, ISSN 0309-1708, <https://doi.org/10.1016/j.advwatres.2024.104815>.

## Abstract

The electrical conductivity of a porous medium is strongly controlled by the structure of the medium at the microscale as the pore configuration governs the distribution of the conductive fluid. The pore structure thus plays a key role since different geometries translate in variations of the fluid distribution, causing different behaviours measurable at the macroscale. In this study, we present a new physically-based analytical model derived under the assumption that the pore structure can be represented by a bundle of tortuous capillary tubes with periodic variations of their radius and a fractal distribution of pore sizes. By upscaling the microscale properties of the porous medium, we obtain expressions to estimate the total and relative electrical conductivity. The proposed pore geometry allows us to include the hysteresis phenomenon in the electrical conductivity estimates. The variations on these estimates caused by pore structure changes due to reactive processes are accounted by assuming a uniform dissolution of the pores. Under this hypothesis, we describe the evolution of the electrical conductivity during reactive processes. The expressions of the proposed model have been tested with published data from different soil textures, showing a satisfactory agreement with the experimental data. Hysteretic behavior and mineral dissolution are also successfully addressed. By including hysteresis and mineral dissolution/precipitation in the estimates of the electrical conductivity, this new analytical model presents an improvement as it relates those macroscopic physical phenomena to its origins at the microscale. This opens up exciting possibilities for studies involving electrical conductivity measurements to monitor water movement, and hysteretic and reactive processes in porous media.

## Highlights

- New electrical conductivity model for partially saturated reactive porous media.

- Pore structure composed of capillaries with periodic reductions of their radii.
- Variations in pore structure significantly influence the electrical conductivity.
- Hysteretic behavior is included from geometrical effects, pore radii reductions.
- Geometrical impact on the pores due to mineral dissolution is successfully described.

**Keywords:** Electrical conductivity, Unsaturated flow, Vadose zone, Fractal distribution, Reactive porous media

## 1 Introduction

The water content and dynamics in geological media are largely controlled by their petrophysical properties (such as permeability and porosity) which often exhibit a high degree of spatial variability due to the irregularities of the pore space structure. Knowledge of these properties is important to understand flow and transport processes as they control the movement and storage of fluids. This fact is highlighted for porous media containing carbonates, since dissolution and precipitation processes can drastically change the size and shape of the pore spaces and the degree of their interconnection (e.g., Noiriél et al., 2004; Leger and Luquot, 2021). Therefore, understanding better the effect of pore geometry at the microscale is a key to describe and predict petrophysical and transport properties at the macroscale.

During the last two decades, the use of geophysical methods to non-invasively characterize hydrological processes has been extensively developed (e.g., Binley et al., 2015; Hermans et al., 2023; Loiseau et al., 2023). Among the geophysical methods, the electrical and electromagnetic methods are very useful since they can provide quantitative information on the structure, water content, or fluid composition of the porous media through the measurement of electrical conductivity. Electrical resistivity tomography (ERT), induced polarization (IP), and electromagnetic induction (EMI) are some of the hydrogeophysical methods that have increasingly been used to monitor flow and transport quantitatively (e.g., Revil et al., 2012; Binley and Slater, 2020). Among many other applications of these methods related to groundwater in porous media, it can be mentioned the application of ERT to monitor critical saturated conditions for landslide occurrence (e.g., Olabode et al., 2020; Wicki and Hauck, 2022), the use of IP to describe contaminant plumes and to monitor their remediation (e.g., Deceuster and Kaufmann, 2012; Schwartz and Furman, 2012), or the capability of EMI to detect and monitor groundwater flow (e.g., Wilson et al., 2002; Zhu et al., 2010; Doolittle and Brevik, 2014).

The electrical conductivity  $\sigma$  ( $\text{S m}^{-1}$ ) of the porous medium is one of the petrophysical properties of interest measured with the electrical methods and electromagnetic methods. Many models exist to express the electrical conductivity of a water-saturated porous media (for a review, see Glover (2015) and Schön (2015)). Among the most simple ones, the pore space can be seen as an electrical circuit in parallel, where  $\sigma$  is linked to the electrical currents that arise when charge carriers (i.e., ions) flow through the media and

66 can be expressed as:

$$\sigma = \frac{\sigma_w}{F} + \sigma_s \quad (1)$$

67 where  $\sigma_w$  ( $\text{S m}^{-1}$ ) is the electrical conductivity of the fluid,  $F$  (no units) the forma-  
68 tion factor and  $\sigma_s$  ( $\text{S m}^{-1}$ ) the surface conductivity. This model was first introduced by  
69 Patnode and Wyllie (1950) who discovered that surface conductivity  $\sigma_s$  cannot always  
70 be neglected in reservoir rocks. The first term in Eq. (1) corresponds to the contri-  
71 bution from the electrical conduction in the liquid phase (i.e., electrolyte) whereas the  
72 second term is the contribution due to the electrical conduction in the liquid–solid in-  
73 terface, the so-called electrical double layer (EDL, e.g., Hunter, 1981; Leroy and Revil,  
74 2004). The electrical conductivity of the electrolyte  $\sigma_w$  has a magnitude that depends  
75 on its chemical composition and the ionic concentrations (e.g., Glover, 2015). Experi-  
76 mental and theoretical works, e.g., the three-resistor model (Wyllie and Southwick, 1954;  
77 Lévy et al., 2018), the BHS (Bruggeman-Hanai-Sen) model (Sen et al., 1981), and the  
78 recent models of (Qi and Wu, 2022, 2024), have shown that the surface conductivity  $\sigma_s$   
79 depends on the water and the EDL electrical conductivities. However, when the surface  
80 conductivity  $\sigma_s$  can be neglected, that is when the electrolytic conduction is much larger  
81 than the surface one, the electrical conductivity  $\sigma$  is controlled mainly by the pore space  
82 geometry in which the charge carriers (i.e., usually ions) can move it. That is the porous  
83 medium connectivity and the size and shape of the pores (e.g. Olsen, 2011; Revil, 2013b;  
84 Jougnot et al., 2018). The dependency of the porous medium electrical conductivity to  
85 its microstructure and the electrolyte conductivity is taken into account through the for-  
86 mation factor, a quantitative proxy for the medium geometry. Petrophysical models aim  
87 to establish an expression for the formation factor based on pore structure parameters.  
88 Among the existing approaches, models capturing the true pore space topology play a  
89 major role when considering the partially saturated conditions. To identify physically-  
90 based structural parameters defining the formation factor, several studies have analyzed  
91 the effect of pore structure in electrical properties directly related to the electrical con-  
92 ductivity. Müller-Huber et al. (2015) examined the effect of changes in the pore radius on  
93 the electrical conductivity. They studied a straight pore channel whose radius increases  
94 exponentially between its two extremes showing that pore geometry has a strong effect  
95 on the electrical conductivity. For carbonate rocks, Regnet et al. (2019) analyzed the  
96 influence of microstructural patterns on petrophysical properties (electrical conductivity,  
97 porosity, and permeability). They emphasized the importance of pore space to estimate  
98 these properties through many parameters such as pore size and shape, grain contacts or  
99 cracks, pore network connectivity, and mineralogy. Rembert et al. (2020) derived a model  
100 that estimates the electrical conductivity and the formation factor as a function of both  
101 tortuosity and constrictivity of the pore structure. They observed that the constrictivity  
102 follows a monotonous variation either during dissolution or precipitation processes.

103 Among the models to predict the electrical conductivity of porous media for both  
104 saturated and partially saturated conditions, the most widely used is the one proposed by  
105 Archie (1942). Assuming negligible surface conductivity, this empirical model provides a

106 relationship between the medium and the electrolyte electrical conductivities given by

$$\sigma = \sigma_w S_w^n \phi^m \quad (2)$$

107 where  $S_w$  (no units) is the water saturation and  $\phi$  (no units) the porosity of the medium;  
108 and exponents  $n$  and  $m$  (no units) are the so-called saturation and cementation factors,  
109 respectively. Several authors have found that these empirical factors depend on the ge-  
110 ometry of the pore system or its connectivity (e.g., Knight and Endres, 2005; Glover,  
111 2017; Jougnot et al., 2018). From Archie’s pioneer work to the present, numerous theo-  
112 retical models have been developed within different frameworks such as effective medium,  
113 percolation theory or capillary tube models (e.g., Sen et al., 1981; Herrick and Kennedy,  
114 1994; Wang et al., 2007; Cai et al., 2017). Some models account for the surface electrical  
115 conduction through porous media which occurs in the vicinity of the solid surface of the  
116 pores (e.g. Waxman and Smits, 1968; Bussian, 1983; Thanh et al., 2019, 2020). Based on  
117 Archie’s law and a volume-averaging approach, Linde et al. (2006) proposed a relation-  
118 ship to estimate the electrical conductivity that accounts the surface conductivity under  
119 partially saturated conditions and can be expressed as:

$$\sigma = \phi^m [\sigma_w S_w^n + (\phi^{-m} - 1)\sigma_s]. \quad (3)$$

120 Several phenomena such as hysteresis effects and reactive processes affect the elec-  
121 trical conductivity (e.g. Binley and Kemna, 2005). Hysteresis refers to the non-unique  
122 relationship between electrical conductivity and pressure head or water saturation, which  
123 means that different curves can be obtained during sequences of wetting and drying cycles  
124 of a porous medium. The variations produced in the electrical conductivity are related  
125 to changes in pore fluid distribution caused by changes in the saturation history. The  
126 structure of pore space patterns plays a significant role in understanding the flow dis-  
127 tribution and predicting the electrical conductivity (Sun et al., 2021). Therefore, an  
128 impact at the hysteresis cycle should be observed for porous media under partial satura-  
129 tion as reactive processes produce variations of the pore space geometry. To the best of  
130 our knowledge, studies of hysteresis effects during dissolution or precipitation processes  
131 are lacking in the literature because they focus more on reactive transport description  
132 (e.g. Léger et al., 2022b) rather than water saturation perturbations (e.g. Rembert et al.,  
133 2023b). Nevertheless, various works under partially saturated conditions have observed  
134 the presence of hysteresis in electrical measurements. Longeron et al. (1989) found that  
135 the electrical resistivity of sandstone and limestone samples with a mixture of oil and  
136 brine varied with saturation during imbibition and drainage experiments. Knight (1991)  
137 observed that hysteresis exists in electrical conductivity data at intermediate water satu-  
138 rations and compared the pore fluid distribution at drainage and imbibition to analyze the  
139 phenomenon. Elashahab et al. (1995) studied the effects of hysteresis through saturation  
140 history on electrical conductivity for sandstone rocks of different wetting characteristics.  
141 Verwer et al. (2011) observed that the two-phase flow electrical resistivity curve exhibits  
142 higher values during drainage than imbibition. Mohammadmoradi et al. (2016) developed  
143 a pore morphology approach to predict electrical conductivity in porous media during a

144 hysteresis loop. They remarked that neglecting the hysteresis leads to dramatic errors  
145 between the measured and the simulated parameters. Therefore, it is necessary to fully  
146 account for the hysteresis behavior for an accurate flow description and electrical conduc-  
147 tivity prediction when performing a numerical simulation. Furthermore, a considerably  
148 large amount of research studies has been conducted to analyze the different aspects of  
149 reactive behaviors of carbonate rocks at total saturation conditions, such as wormholes  
150 and their complex relationship with transport properties or changes in the dissolution  
151 rate constant (e.g., Alkattan et al., 1998; Liu et al., 2005; Kaufmann and Dreybrodt,  
152 2007; Noiriél et al., 2004; Garing et al., 2015). Among experimental works on the electri-  
153 cal monitoring of dissolution/precipitation processes, Wu et al. (2010) monitored calcite  
154 precipitation on a glass beads column and observed the evolution of this process from  
155 electrical conductivity data. These results have been confirmed by other studies (e.g.,  
156 Saneiyan et al., 2019; Izumoto et al., 2020, 2022). Garing et al. (2014) characterized  
157 natural carbonate samples presenting high heterogeneity resulting from many dissolution  
158 and precipitation processes by measuring the electrical conductivity. However, they did  
159 not monitor electrical conductivity changes caused by these reactive processes. Cheru-  
160 bini et al. (2019) analyzed the increase in the electrical conductivity values due to the  
161 dissolution of calcite in limestones samples. In the numerical field, Niu and Zhang (2019)  
162 simulated the dissolution and precipitation on digital representations of microstructural  
163 images to study the electrical conductivity. Even though they observed changes in this  
164 electrical property values, no significant variations were estimated in other petrophysical  
165 parameters, such as porosity. More recently, Rembert et al. (2023a) studied the impact of  
166 conduits formation in limestone samples on the electrical conductivity measurements due  
167 to calcite dissolution and the relationship between electrical properties and the evolution  
168 of structural parameters over time.

169 The framework of capillary tube models has been useful to provide valuable insights  
170 into different transport phenomena occurring in porous media from the microscopic stand-  
171 point (e.g., Celia et al., 2004; Jackson, 2010; Jougnot et al., 2012; Luo et al., 2023; Thanh  
172 et al., 2023). In addition, petrophysical properties can be directly calculated in these type  
173 of models by simply analyzing the capillary tubes geometry (e.g., Guarracino et al., 2014;  
174 Rembert et al., 2020; Soldi et al., 2017, 2022). Because of these advantages, capillary  
175 tube models have been extensively used considering different pore size distributions to  
176 upscale the petrophysical properties from the contribution of one capillary (e.g., multi-  
177 modal, quasi-fractal, fractal or gaussian, see Jougnot et al. (2019)). Among them, the  
178 fractal distributions have proven to be efficient to represent porous media due to their  
179 simplicity and capacity to describe a wide range of natural geological media (e.g. Guarra-  
180 cino, 2006; Yu, 2008; Guarracino and Quintana, 2009; Ghanbarian-Alavijeh et al., 2011).  
181 Recently, Soldi et al. (2022) derived an analytical model to estimate the hydraulic prop-  
182 erties of porous media under partially saturated conditions. They assumed piecewise  
183 sinusoidal variations of the capillary radii along its length which allowed them a more  
184 realistic description of the porous media. Indeed, the periodic reductions assumed on the  
185 pore structure are defined by two geometrical parameters whose range of values allows  
186 the representation of the hydraulic properties for different soil textures.

187 Electrical properties have been successfully studied within the capillary tube models  
188 and fractal distributions. In the last years, Thanh et al. (2019, 2020) derived electrical  
189 conductivity models for total and partially saturated porous media accounting for surface  
190 conductivity. For both models, they assumed that the bundle of capillaries follows a fractal  
191 pore size distribution and that each capillary is represented by a tortuous cylindrical  
192 tube of constant radius. Chen et al. (2023) derived a theoretical correlation between  
193 the formation factor and tortuous pore structure with a wide distribution of pore sizes.  
194 The authors also consider cylindrical tubes of constant radii, however, they propose that  
195 tortuosity follows a fractal law. Saafan et al. (2023) developed a model to describe the  
196 electrical conductivity for a reservoir porous medium where the fluid phases are water  
197 and oil. They represented the partially saturated pore system using tortuous fractal  
198 capillaries with constant square or triangular cross-sectional areas. Nevertheless, these  
199 models are lacking an important microstructure parameter which significantly controls the  
200 transport and petrophysical properties of porous media, the constrictivity. This parameter  
201 characterizes the so-called bottleneck effect that means that the wide spaces of the pores  
202 or pore bodies are connected through pore throats (i.e. non-constrictive and constrictive  
203 lengths). The previously described models do not account for this type of variations  
204 in the capillary radii along their length which should be considered to provide a more  
205 accurate description of porous media in the framework of capillary bundles. In this work,  
206 we derive an analytical model that considers a realistic pore geometry to estimate the  
207 electrical conductivity under partially saturated conditions. Based on the framework of  
208 capillary tube models and the geometry proposed by Soldi et al. (2022), the pore space is  
209 represented by a bundle of cylindrical capillaries with varying aperture along their pore  
210 length to take into account the structure composed of pore throats and pore bodies. This  
211 geometry has the advantage to represent a wide range of pore geometries due to the  
212 variable lengths of the pore throats and pore bodies. The proposed model is an extension  
213 of the model developed by Rembert et al. (2020) that estimates the electrical conductivity  
214 for total saturated porous media. Their model considers the pores as tortuous cylindrical  
215 tubes with sinusoidal variations of their aperture. Assuming a fractal pore size distribution  
216 that can be either filled by water or by air, we obtain mathematical closed-form expressions  
217 to estimate the saturated and relative electrical conductivity from the upscaling procedure.  
218 The macroscopic expression relies on geometrical parameters defining the pore structure  
219 (e.g., the constrictivity), tortuosity, pore-size distribution, and radii of the pores. The  
220 pore throats and pore bodies present in the proposed geometry allow us to include the  
221 hysteresis phenomenon in the relative electrical conductivity. Considering the structural  
222 variations that reactive processes can cause, we describe the temporal evolution of the  
223 saturated electrical conductivity by assuming a constant dissolution of the pores. The  
224 performance of the model to reproduce experimental data is tested against different sets  
225 of laboratory data of soils with varied textures.

## 2 Electrical conductivity model

The present model is derived based on the pore geometry proposed by Soldi et al. (2022) and follows the work developed by Rembert et al. (2020). Within the framework of capillary tube models, we consider a porous medium represented by an ensemble of tortuous constrictive capillaries in a cylindrical representative elementary volume (REV) of radius  $R_{REV}$  (m) and length  $L$  (m). Since we focus on the porous microstructure, we consider that the surface conductivity is negligible. However, similar developments could be done including the surface conductivity (e.g. Thanh et al., 2020; Luo et al., 2023).

### 2.1 Pore space description

At the microscopic scale, we consider that each pore of the capillary bundle is represented by a tortuous cylindrical tube with varying aperture (see Fig. 1). All the pores are assumed to have the same length  $l$  (m) and tortuosity  $\tau$  ( $\tau = l/L$ , no units). The pore radius varies along all the length of each capillary between its radius value  $R$  (m) and its pore throat radius value  $aR$  (m) where  $a$  (no units) is the radial factor that quantifies the reduction in the pore radius due to the presence of the constrictivity. A sinusoidal piecewise geometry is assumed with a wavelength  $\lambda$  (m) which replicates along the pore length (i.e.  $l \gg \lambda$ ). Thus, the varying radius  $r(x)$  (m) of a capillary can be expressed as (Soldi et al., 2022):

$$r(x) = \begin{cases} (1+a)\frac{R}{2} + (1-a)\frac{R}{2}\sin\left(\frac{\pi x}{\lambda(1-c)}\right) & \text{if } x \in [0, \lambda(1-c)) \\ (1+a)\frac{R}{2} + (1-a)\frac{R}{2}\sin\left(\frac{\pi[x-\lambda(1-c)]}{\lambda c}\right) & \text{if } x \in [\lambda(1-c), \lambda), \end{cases} \quad (4)$$

where  $c$  (no units) is the length factor which represents the constrictive fraction of  $\lambda$  (i.e. the segment of  $\lambda$  where the radius is reduced). The geometrical factors  $a$  and  $c$  vary between 0 and 1. Note that the limit values  $a = 0$  and  $a = 1$  correspond to the cases of periodically closed pores and cylindrical pores of constant radius  $R$ , respectively. Also note that if  $c = 0.5$ , the proposed geometry is consistent with the geometry proposed by Guarracino et al. (2014) and Rembert et al. (2020) that considers equal lengths for the constrictive and non-constrictive fractions of the wavelength.

The porous structure of the medium is assumed to be a bundle of capillary tubes with different sizes of radii varying from a minimum pore radius  $R_{min}$  to a maximum pore radius  $R_{max}$ . Based on the fractal theory for porous media (e.g. Tyler and Wheatcraft, 1990; Yu et al., 2003; Liang et al., 2014), the pore size distribution can be described by the following fractal law:

$$N(R) = \left(\frac{R_{REV}}{R}\right)^D, \quad (5)$$

where  $N(R)$  (no units) is the number of pores whose radii are greater than or equal to  $R$  and  $D$  (no units) is the pore size fractal dimension. Considering the classical fractal object called Sierpinski carpet, Tyler and Wheatcraft (1990) show that this parameter  $D$



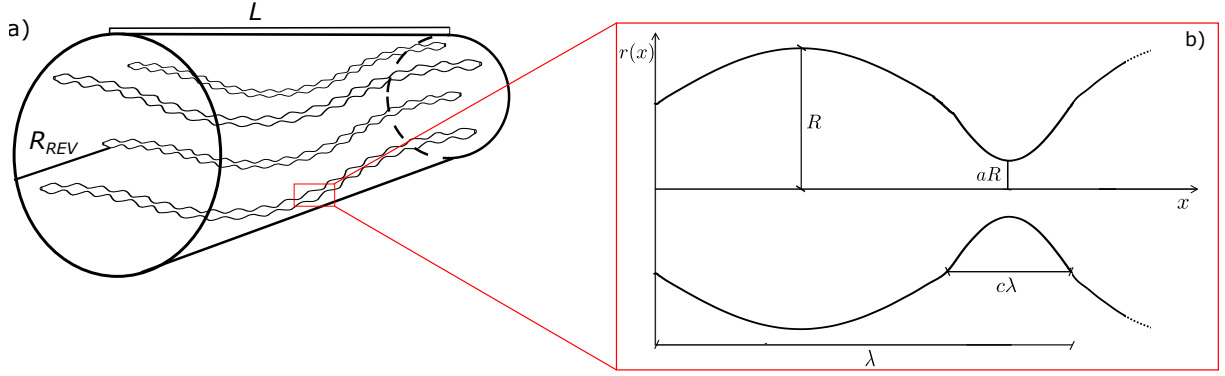


Figure 1: (a) Sketch of the representative elementary volume represented by a bundle of tortuous sinusoidal capillary tubes, and (b) the pore geometry considered for each piecewise sinusoidal capillary.

260 varies between 1 and 2 for different textures of porous media where its highest values are  
 261 associated with the finest textured soils.

262 Then, the number of pores whose radii are within the infinitesimal range  $R$  and  $R+dR$   
 263 is obtained from Eq. (5) by differentiating with respect to  $R$ :

$$-dN(R) = DR_{REV}^D R^{-D-1} dR, \quad (6)$$

264 where the minus sign implies that the pore number increases when the pore radius de-  
 265 creases (e.g. Yu et al., 2003; Yu, 2008).

## 266 2.2 Electrical conductivity model

### 267 2.2.1 Electrical model at saturation

268 To derive the expressions of the new electrical conductivity model, we first describe the  
 269 electrical properties of a single capillary. For a water saturated capillary of radius  $R$ , its  
 270 electrical conductance  $\Sigma_p(R)$  (S) can be calculated as:

$$\Sigma_p(R) = \int_0^l \frac{1}{\sigma_w \pi r^2(x)} dx. \quad (7)$$

271 By replacing Eq. (4) in Eq. (7) yields:

$$\Sigma_p(R) = \frac{\sigma_w \pi R^2 f(a, c)}{\tau L}, \quad (8)$$

272

$$f(a, c) = \frac{2a^{3/2}}{1+a} \left\{ 1 + (2c-1) \left[ \frac{4\sqrt{a}(1-a)}{\pi(1+a)^2} + \frac{2}{\pi} \tan^{-1} \left( \frac{1-a}{2\sqrt{a}} \right) \right] \right\}^{-1}. \quad (9)$$

273 The factor  $f(a, c)$  (no units) varies between 0 and 1, and quantifies the reduction in  
 274 the conductance of each pore due to the presence of the pore throats (i.e. the so-called  
 275 constrictivity).

276 The contribution of each single capillary conductivity  $\sigma_p(R)$  ( $\text{S m}^{-1}$ ) to the porous  
 277 medium conductivity is then obtained by multiplying the pore conductance (Eq. (8)) with  
 278 a geometric factor  $f_g = \pi R_{REV}^2/L$  (m) (Hem and Minear, 2012; Rembert et al., 2020):

$$\sigma_p(R) = \frac{\sigma_w R^2 f(a, c)}{\tau R_{REV}^2}. \quad (10)$$

279 According to Ohm's law, the electric current  $i_p(R)$  (A) flowing between the edges of a  
 280 capillary of radius  $R$  is directly proportional to the electrical voltage difference  $\Delta V$  (V)  
 281 across them:

$$i_p(R) = \Sigma_p(R) \Delta V = \frac{\sigma_w \pi R^2 f(a, c)}{\tau L} \Delta V. \quad (11)$$

282 For a fully saturated porous medium, the total electric current  $I^{REV}$  (A) flowing  
 283 through the REV is obtained from Kirchhoff's current law, by summing the electric cur-  
 284 rents contributions of all the capillaries over the entire range of pore sizes:

$$I^{REV} = \int_{R_{min}}^{R_{max}} i_p(R) dN(R). \quad (12)$$

285 Substituting Eqs. (6) and (11) in Eq. (12) and integrating it yields to

$$I^{REV} = -\frac{\sigma_w \pi R_{REV}^D D f(a, c)}{\tau L (2 - D)} (R_{max}^{2-D} - R_{min}^{2-D}) \Delta V. \quad (13)$$

286 On the other hand, based on Ohm's law at the REV scale, the total electric current  $I^{REV}$   
 287 flowing through the porous medium can be expressed as:

$$I^{REV} = -\sigma^{REV} \pi R_{REV}^2 \frac{\Delta V}{L}, \quad (14)$$

288 where  $\sigma^{REV}$  ( $\text{S m}^{-1}$ ) is the electrical conductivity of the porous medium which under total  
 289 saturated conditions is redefined as the saturated electrical conductivity  $\sigma_{sat}^{REV}$ . Combining  
 290 Eqs. (13) and (14), an expression for  $\sigma_{sat}^{REV}$  is obtained:

$$\sigma_{sat}^{REV} = \frac{\sigma_w D f(a, c)}{\tau R_{REV}^{2-D} (2 - D)} (R_{max}^{2-D} - R_{min}^{2-D}). \quad (15)$$

291 The capability to estimate the electrical conductivity  $\sigma_{sat}^{REV}$  of a porous medium as  
 292 a function of the medium's porosity  $\phi$  is significantly valuable in petrophysics. For the  
 293 proposed model, a relationship between these two macroscopic properties can be obtained  
 294 by considering that for this porous medium geometry its porosity  $\phi$  is given by (Soldi et al.,  
 295 2022):

$$\phi = \frac{D \tau f_v(a, c)}{R_{REV}^{2-D} (2 - D)} (R_{max}^{2-D} - R_{min}^{2-D}) \quad (16)$$

296 where  $f_v(a, c) = (1 + a)^2/4 + (1 - a)^2/8 + (1 - a^2)(1 - 2c)/\pi$  is a factor that quantifies  
 297 the reduction in the porosity of the REV due to the presence of the constrictivities (the  
 298 subscript  $v$  stands for volume). Then, combining Eqs. (15) and (16) yields:

$$\sigma_{sat}^{REV} = \frac{\sigma_w f_\sigma(a, c) \phi}{\tau^2} \quad (17)$$

299 where  $f_\sigma$  is a dimensionless factor that varies between 0 and 1, and is defined as the ratio  
 300 between the factor  $f$  and  $f_v$ . The exact expression of  $f$  given in Eq. (9) can be reduced  
 301 similar to Soldi et al. (2022) and  $f_\sigma$  can be expressed as:

$$f_\sigma(a, c) = \frac{16\pi^2 a^{3/2}(1 + a)}{[\pi(1 + a)^2 + 2(2c - 1)(1 - a)(1 + \sqrt{a})^2][2\pi(1 + a)^2 + \pi(1 - a)^2 + 8(1 - a^2)(1 - 2c)]}. \quad (18)$$

302 The variation of the factor  $f_\sigma$  as a function of the radial factor  $a$  is shown in Fig. 2, for  
 303 different values of the length factor  $c$ . Note that the presence of the pore throats affects  
 304 significantly the electrical conductivity of the REV  $\sigma_{sat}^{REV}$  through the  $f_\sigma$  values which  
 305 depends on  $a$ . Also note that if  $a = 0$ ,  $f_\sigma = 0$  and  $\sigma_{sat}^{REV} = 0$ , no electrical conduction  
 306 takes place in the REV as the pores are periodically closed. In that case,  $f_v \neq 0$  which  
 307 means that the REV has a porosity value but the pores are not connected. In order to  
 308 represent this type of porous media using Archie (1942),  $\sigma = 0$  only in the case that  
 309  $\phi = 0$ . Therefore, Archie (1942) cannot represent this media, while the proposed model  
 310 can describe media with a porosity that corresponds to poorly connected pores, and low  
 311 electrical conductivity. The expression of the factor  $f_\sigma$  given by Eq. (18) can be reduced  
 312 while taking into account the main features of the factor's behavior and it yields

$$g_\sigma(a, c) = \frac{8a^{3/2}}{(1 + a)[(1 + a)^2 - (1 - a)^2(1 - 6c + 6c^2)]}. \quad (19)$$

313 This simplified expression is easier to evaluate and, therefore, its implementation in nu-  
 314 merical codes is straightforward.

315 Eqs. (15) and (17) are closed-form expressions that describe the saturated electrical  
 316 conductivity  $\sigma_{sat}^{REV}$  of the medium which depend on the water electrical conductivity,  
 317 porosity and model parameters with physical or geometrical meaning. It is interesting to  
 318 observe that the estimates of  $\sigma_{sat}^{REV}$  are strongly influenced by the parameters  $a$  and  $c$  of  
 319 the pore geometry through the factor  $f_\sigma$ . In the limit case of  $a = 1$  and  $\tau = 1$ , Eq. (17)  
 320 becomes  $\sigma_{sat}^{REV} = \sigma_w \phi$  which is consistent with Archie's law expression for  $m = 1$  where  
 321 the porous medium is composed by a bundle of non-tortuous capillaries of constant radii  
 322 (e.g., Clennell, 1997). For tortuous capillary bundles, the relationship between tortuosity  
 323 and porosity can be expressed by the Bruggeman relation, i.e.,  $\tau^2 = \phi^{-1/2}$  (Holzer et al.,  
 324 2023). Substituting this relation in Eq. (17), we obtain a porosity with an exponent  
 325 equal to 1.5 which is consistent with the  $m$  value observed by Sen et al. (1981) for ideally  
 326 packed spheres. Note also that, if  $c = 0.5$ , the resulting expressions of Eqs. (15) and (17)  
 327 are similar to the ones proposed by the model of Rembert et al. (2020).

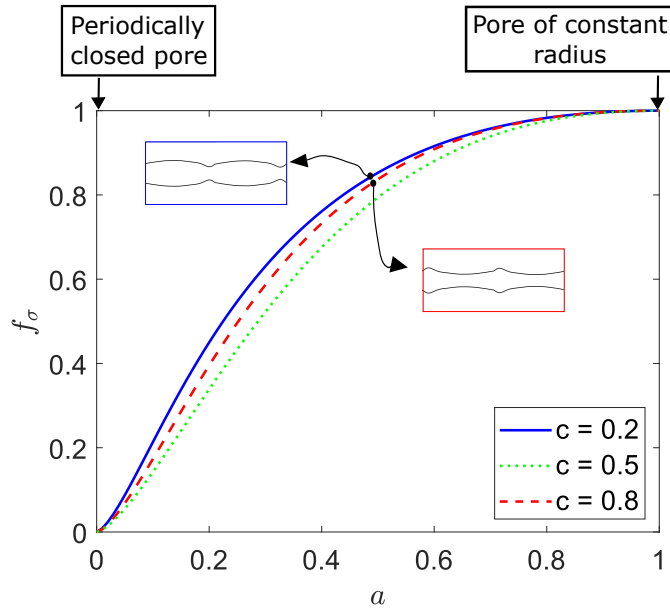


Figure 2: Dimensionless constrictivity factor  $f_\sigma$  (Eq. (18)) as a function of the radial factor  $a$  for different constant values of the length factor  $c$ .

### 328 2.2.2 Effect of partial saturation and hysteresis

329 Under the hypothesis of neglecting surface conduction, the electrical conductivity of the  
 330 REV under partially saturated conditions can be expressed as

$$\sigma^{REV} = \sigma_{sat}^{REV} \sigma_{rel} \quad (20)$$

331 being  $\sigma_{rel}$  (no units) the relative electrical conductivity of the REV. To obtain the expres-  
 332 sion of  $\sigma_{rel}$ , we consider a similar derivation procedure as for the total saturated porous  
 333 medium but with capillaries that can be either fully saturated by water or by air (e.g.,  
 334 Soldi et al., 2017; Thanh et al., 2020). Following the procedure proposed by Guarracino  
 335 et al. (2014), we assume that the REV is fully saturated at its initial state and then is  
 336 drained when subjected to a pressure head  $h$  (m). To determine which pores will be de-  
 337 saturated by the applied pressure head,  $h$ , under a Darcy's flow regime (i.e., low Reynolds  
 338 number), we consider the link between the radius of the water-filled pore  $R_h$  (m) to the  
 339 pressure head  $h$  given by (e.g. Jurin, 1717)

$$h = \frac{2T_s \cos(\gamma)}{\rho_w g R_h}, \quad (21)$$

340 where  $T_s$  ( $\text{N m}^{-1}$ ) is the surface tension of the water,  $\gamma$  ( $^\circ$ ) the contact angle,  $\rho_w$  ( $\text{kg m}^{-3}$ )  
 341 the water density and  $g$  ( $\text{m s}^{-2}$ ) the gravitational acceleration. A capillary tube becomes  
 342 fully desaturated if the radius of its pore throat  $aR$  is greater than the radius  $R_h$  defined  
 343 by Eq. (21). Thus, for the drainage process, it is reasonable to assume that pores with  
 344 radii  $R$  between  $R_{min}$  and  $R_h/a$  will remain fully saturated and contribute to the electric

345 current flowing through the REV. If we now consider an imbibition process where the  
 346 REV is dry at the beginning and flooded by a pressure head  $h$ , the capillary tubes that  
 347 will be fully saturated in this case are those whose radii  $R$  are smaller than  $R_h$ . Then,  
 348 considering the ranges of saturated pores for each process, the electrical current streaming  
 349 through the REV (Eq. (12)) can be expressed as:

$$I^{REV} = \int_{R_{min}}^{R^*} i_p(R) dN(R) \quad (22)$$

350 where  $R^* = R_h/a$  for the drainage and  $R^* = R_h$  for the imbibition. Combining Ohm's law  
 351 at macroscale (Eq. (14)) with Eq. (20), and comparing it with the result of integrating  
 352 Eq. (22), we obtain the expression for the relative electrical conductivity  $\sigma_{rel}$ :

$$\sigma_{rel}(R^*) = \frac{R^{*2-D} - R_{min}^{2-D}}{R_{max}^{2-D} - R_{min}^{2-D}}. \quad (23)$$

353 Substituting Eq. (21) in (23), the relative electrical conductivity can be expressed as  
 354 function of the pressure head for a drainage process as:

$$\sigma_{rel}^d(h) = \frac{(ah)^{D-2} - h_{max}^{D-2}}{h_{min}^{D-2} - h_{max}^{D-2}} \quad (24)$$

355 where  $h$  varies between  $\frac{h_{min}}{a}$  and  $\frac{h_{max}}{a}$ , and for an imbibition process, it yields:

$$\sigma_{rel}^w(h) = \frac{h^{D-2} - h_{max}^{D-2}}{h_{min}^{D-2} - h_{max}^{D-2}} \quad (25)$$

356 where  $h$  varies between  $h_{min}$  and  $h_{max}$ . By inspection of Eq. (24), note that if  $h < \frac{h_{min}}{a}$ ,  
 357  $\sigma_{rel}^d = 1$ , since the REV is fully saturated as the pressure head applied is lower than the  
 358 one necessary to start draining the larger pores, and in the case of  $h > \frac{h_{max}}{a}$ ,  $\sigma_{rel}^d = 0$   
 359 as the pressure head applied is large enough to drain the REV. Similar results can be  
 360 obtained by analyzing Eq. (25) for the imbibition process,  $\sigma_{rel}^d = 1$  and  $\sigma_{rel}^d = 0$ , when  
 361  $h < h_{min}$  and  $h > h_{max}$ , respectively. Note that the  $\sigma_{rel}$  expression differs between the  
 362 drainage and imbibition processes due to the presence of the pore radius reduction defined  
 363 by the radial factor  $a$ . Therefore, these irregularities present in the pore geometry allow to  
 364 introduce the hysteresis phenomenon in the electrical conductivity model. This fact has  
 365 also been remarked by Singha et al. (2007), who explain solute transport hysteresis effects  
 366 in the electrical conductivity through a bicontinuum model composed by mobile (i.e., well-  
 367 connected) and immobile (i.e., poorly-connected) pores. Fig. 3 shows the hysteresis cycle  
 368 on this electrical property for different values of the radial factor  $a$ . For the remaining  
 369 parameters of Eqs. (24) and (25), we considered the following constant values:  $D = 1.5$ ,  
 370  $h_{min} = 0.01$  m and  $h_{max} = 10$  m. It can be seen that the radial factor  $a$  significantly  
 371 affects the main drying curves of the relative electrical conductivity while no variations are  
 372 produced on the main wetting curves of this electrical property since they are independent  
 373 of  $a$ . Indeed, low values of  $a$  produce a shift of the main drying  $\sigma_{rel}$  curves to higher values

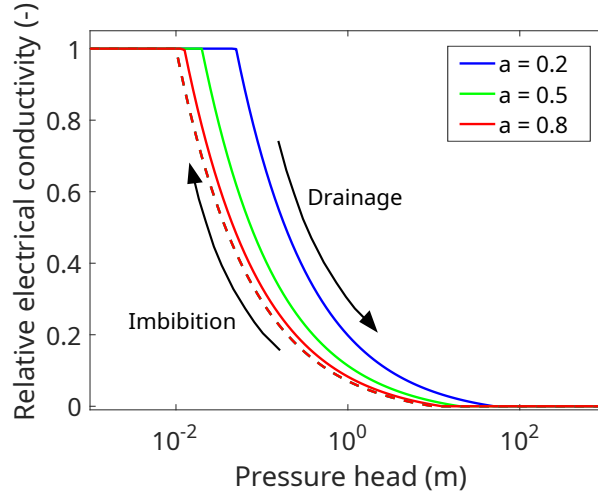


Figure 3: Hysteresis cycle of the relative electrical conductivity as function of pressure head for different values of the radial factor  $a$ . The solid and dashed lines correspond to the main relative electrical conductivity curves for drainage and imbibition experiments (Eqs. (24) and (25)), respectively. Note that all the imbibition curves are superimposed.

374 of the pressure head as higher pressure head values are needed to drain more constrictive  
 375 pores. Also note that, in the limit case of  $a$  approaching 1, the two  $\sigma_{rel}$  curves tend to  
 376 reduce their distance, as it can be expected since this situation represents capillary tubes  
 377 of constant radii and thus no hysteretic phenomenon will be observed.

378 For partially saturated conditions, the behaviour of the relative electrical conductivity  
 379 is often described by its dependence with the water saturation  $S_w$  (no units). Within the  
 380 framework of capillary tube models, the effective saturation  $S_e$  (no units) is the variable  
 381 most used since the tubes are fully saturated or empty, and is related to  $S_w$  through

$$S_w = (1 - S_r)S_e + S_r \quad (26)$$

382 where  $S_r$  (no units) is the residual water saturation. Recently, Soldi et al. (2022) developed  
 383 an analytical model for the hydraulic properties of a porous medium with the geometry  
 384 considered for the proposed electrical model. Note that saturation is obtained from an  
 385 equation which is identical to Eq. (23). Therefore, for the proposed model the relationship  
 386 between  $\sigma_{rel}$  and  $S_e$  yields:

$$\sigma_{rel}(S_e) = S_e. \quad (27)$$

387 From a theoretical point of view, it can be observed that Eq. (27) results in a non-  
 388 hysteretic function, while Eqs. (24) and (25) account for the hysteresis phenomenon.

### 389 2.2.3 Evolution of the model in reactive media

390 The electrical conductivity can be affected by dissolution and precipitation processes par-  
 391 ticularly in porous media composed by carbonate minerals. When a fluid flows through a

392 reactive porous medium produces changes in the structure of the pore space causing varia-  
 393 tions of its volume and surface. In order to estimate the resulting geometrical changes, we  
 394 assume that each capillary tube is dissolved uniformly so that its circular cross-sectional  
 395 shape is retained while only increasing its radius. Then, to evaluate how dissolution  
 396 affects the pore structure, we assume that the volume change of a pore with time  $t$  is  
 397 proportional to the pore surface  $S_p$  that is in contact with the reactive fluid and to the  
 398 dissolution rate  $\alpha$  (Freedman et al., 2004; Guarracino et al., 2014):

$$\frac{dV_p(R)}{dt} = S_p(R)\alpha(R). \quad (28)$$

399 Whereas dissolution will only occur in water-saturated pores, for further developments  
 400 and similar to the film depositional model proposed by Freedman et al. (2004), we assume  
 401 that this reactive process affects all pore radii. Note that in Eq. (28), the dissolution rate  
 402 depends on the pore radius value ( $\alpha(R)$ ) since large pores enlarge faster than small pores  
 403 during dissolution (e.g. Schechter and Gidley, 1969). We assume a linear dependence  
 404 between these variables (i.e.  $\alpha(R) = \tilde{\alpha}R$ ) since a constant rate would reflect an extremely  
 405 slow dissolution independent of the actual occurring dissolution along the flow path. In  
 406 the other extreme, a relationship with a higher exponent would reflect a very aggressive  
 407 dissolution which could lead to wormholes (e.g., Noiriel et al., 2004). Under this linear  
 408 rate hypothesis, the fractal dimension and the radial and length factors can be assumed  
 409 constant during the reactive process. Integrating Eq. (28), we obtain the evolution with  
 410 time of a pore radius (Guarracino et al., 2014):

$$R(t) = R(t_0)e^{\beta(t-t_0)} \quad (29)$$

411 being  $t_0$  (h) the initial time of the dissolution process and factor  $\beta$  ( $\text{h}^{-1}$ ) a function of the  
 412 model parameters  $a$ ,  $c$  and  $\tilde{\alpha}$  ( $\text{h}^{-1}$ ) given by (Soldi et al., 2024):

$$\beta = \frac{\tilde{\alpha}[4\pi(1+a)c + (1-a)(1-2c)]}{2\pi(1+a)^2 + \pi(1-a)^2 + 8(1-a^2)(1-2c)}. \quad (30)$$

413 Note that for a dissolution process both  $\tilde{\alpha}$  and  $\beta$  are positive parameters. Under the same  
 414 hypotheses and considering that parameter  $\tilde{\alpha} < 0$ , we can derive a similar expression to  
 415 Eq. (29) where  $\beta < 0$  (i.e. a decreasing radius with time) which allows us to describe the  
 416 reduction of the pore volume with time that occurs during a precipitation process.

417 The evolution of the electrical conductivity during reactive processes can be obtained  
 418 by considering the changes of the pore radii  $R_{min}$  and  $R_{max}$  with time. Substituting  
 419 Eq. (29) in Eq. (15), the temporal variation of this macroscopic property for saturated  
 420 conditions can be expressed as:

$$\sigma_{sat}^{REV}(t) = \sigma_{sat}^{REV}(t_0)e^{\beta(2-D)(t-t_0)} \quad (31)$$

421 where  $\sigma_{sat}^{REV}(t_0)$  is the electrical conductivity of the REV at the initial time  $t_0$  of the  
 422 dissolution process. For partially saturated conditions, at each time of a dissolution

423 process, the pressure head needed to drain or flood the REV is related to the size of the  
 424 pore throat and pore body radii for the drainage and imbibition processes, respectively.  
 425 Therefore, the relative electrical conductivity (Eqs. (24) and (25)) depends on time and  
 426 for a drainage process it can be expressed as

$$\sigma_{rel}^d(h, t) = \frac{(ah)^{D-2}e^{\beta(D-2)(t-t_0)} - h_{max}^{D-2}(t_0)}{h_{min}^{D-2}(t_0) - h_{max}^{D-2}(t_0)} \quad (32)$$

427 where  $h$  varies between  $h_{min}(t_0)e^{-\beta(t-t_0)}/a$  and  $h_{max}(t_0)e^{-\beta(t-t_0)}/a$ . While for an imbibition  
 428 process, the relative electrical conductivity yields

$$\sigma_{rel}^w(h, t) = \frac{h^{D-2}e^{\beta(D-2)(t-t_0)} - h_{max}^{D-2}(t_0)}{h_{min}^{D-2}(t_0) - h_{max}^{D-2}(t_0)} \quad (33)$$

429 where  $h$  varies between  $h_{min}(t_0)e^{-\beta(t-t_0)}$  and  $h_{max}(t_0)e^{-\beta(t-t_0)}$ . The terms  $h_{min}(t_0)$  and  
 430  $h_{max}(t_0)$  are the minimum and maximum pressure heads at the beginning of the dissolution  
 431 process. Given the exponential nature of Eqs. (29), (31), (32), and (33), we perform a  
 432 parametric analysis of the exponent parameter  $\beta$  (Eq. (30)). Fig. 4 shows the role of the  
 433 model's geometric parameters ( $a$  and  $c$ ) in the estimates of parameter  $\beta$  for a constant  
 434 dissolution rate of  $\tilde{\alpha} = 0.0001 \text{ h}^{-1}$ . Note that for a high value of  $c$  and low values of  
 435  $a$  (i.e., a long pore-throat length and important pore radius reduction), the values of  
 436 parameter  $\beta$  increase significantly as dissolution will produce a significant opening of  
 437 the pore. Therefore, as the flow increases through the capillaries, so does the electrical  
 438 conductivity. It can also be observed that for high values of parameter  $a$  and low values  
 439 of  $c$  (i.e., capillaries with a slight pore throat), parameter  $\beta$  has the lowest value. This  
 440 means that the radius of the pores will increase with the dissolution without significant  
 441 changes occurring in the constrictive geometry as the capillary is almost a cylindrical  
 442 tube. From Eq. (30) it can be seen that the value of  $\beta$  remains constrained in the range  
 443  $0 \leq \beta \leq \frac{4\pi-1}{3\pi-8}\tilde{\alpha} \approx 8.12\tilde{\alpha}$ . Indeed, as the magnitude of the dissolution rates  $\tilde{\alpha}$  are very  
 444 low, parameter  $\beta$  cannot take a significant value. Note also that when the radii of the  
 445 pores increase, the pressure head needed to drain or flood the *REV* decreases, and the  
 446 hysteresis cycle of the final stage of dissolution is shifted to the left of the cycle from the  
 447 beginning of the process.

448 The model proposed in this section is developed within the framework of capillary  
 449 tube models. One of the limitations that affect the models based on this framework is  
 450 that lateral connection between the capillaries is not considered. There are no intersection  
 451 points among the pores and they all have parallel directions. However, many models of  
 452 electrical properties have been developed in this framework and successfully proven to  
 453 provide good estimates of electrical and hydraulic properties (e.g., see comparison be-  
 454 tween 2D pore networks and capillary bundle models in Jougnot et al., 2019). A second  
 455 point of concern in the model regards the relatively high number of model parameters  
 456 compared to previous models such as the empirical model of Archie (1942) which has  
 457 only two parameters (cementation and saturation exponents). Nevertheless, the proposed  
 458 theoretical model can be used for any porous media while Archie (1942) cannot represent



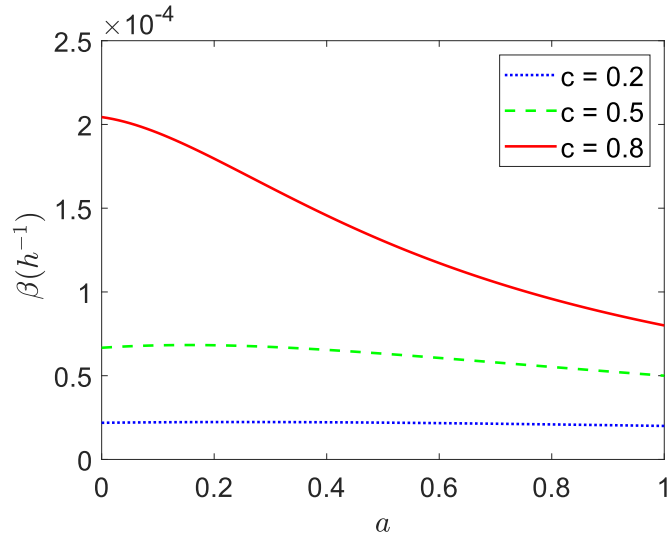


Figure 4: Parametric analysis of the factor  $\beta$  as a function of the radial factor  $a$  for different constant values of the length factor  $c$  and a constant value of the dissolution rate  $\tilde{\alpha} = 0.0001 \text{ h}^{-1}$ .

459 media with high porosity and low electrical conductivity. Beyond that, a step forward  
 460 of the proposed model over the classical is that it accounts for phenomena such as the  
 461 hysteresis effects or dissolution/precipitation. One last point of the proposed petrophysi-  
 462 cal model is that these reactive processes are considered through their effect on the pore  
 463 geometry changes, while chemical variations, such as changes on salinity or pH, are ne-  
 464 glected. These variations were taken into account in the geochemical model proposed by  
 465 Rembert et al. (2022), and in the works of Leroy et al. (2017) and Heberling et al. (2021)  
 466 who developed geochemical models that consider surface alterations. Note that, while  
 467 other electrical models can be used to estimate the electrical conductivity, the proposed  
 468 model can explicitly relate parameters linked to the microstructure to the estimates of  
 469 the property at the macroscale, and with only one set of them is also capable to account  
 470 for hysteresis effects and reactive processes.

### 471 **3 Model comparison with experimental data**

472 The proposed model ability to estimate the electrical conductivity is tested against dif-  
 473 ferent sets of experimental data from the research literature. These data sets consist of  
 474 measured electrical conductivity or relative electrical conductivity values for different soil  
 475 textures.

### 3.1 Electrical conductivity data for different soil textures

In order to test the estimates of the proposed model, we selected experimental data sets from different soil textures: a sandy loam from Amente et al. (2000), a sand from Inoue et al. (2000), a loam from Doussan and Ruy (2009) and a packing of mica particles from Friedman and Robinson (2002). These data series consist of electrical conductivity or relative electrical conductivity values as a function of saturation. As mentioned in Section 2, the proposed model assumes that the surface electrical conduction is negligible and the electrical conductivity is due to the conduction in the porous water. However, the values of surface conductivity for soils can impact the experimentally measured values of soil conductivity. We account for the contribution of the surface conductivity  $\sigma_s$  as a parallel conductivity with an adjustable value, therefore, considering Eqs. (15), (27) and (26), the model expression as function of water saturation becomes:

$$\sigma^{REV}(S_w) = \frac{\sigma_w f_\sigma(a, c) \phi}{\tau^2(1 - S_r)}(S_w - S_r) + \sigma_s. \quad (34)$$

Equation (34) is also compared with the Waxman and Smits (1968) model:

$$\sigma_{WS}(S_w) = \frac{S_w^n}{F} \left( \sigma_w + \frac{\sigma_s^{WS}}{S_w} \right) \quad (35)$$

where the formation factor  $F$  is related to porosity  $\phi$  through  $F = \phi^{-m}$ . The relative electrical conductivity values  $\sigma_{rel}^{REV}(S_w)$  can be estimated, for both models, as the quotient between the electrical conductivity value as function of saturation  $\sigma^{REV}(S_w)$  and its value at total saturation  $\sigma^{REV}(S_w = 1)$ . The proposed model is fitted by an exhaustive search method by minimizing the normalized mean square error ( $NMSE$ ) between the calculated and the experimentally measured values. The comparison between the proposed model and the different experimental data is shown in Figure 5 and the model of Waxman and Smits is also shown. Tables 1 and 2 list the best fitted parameters of the proposed model ( $a$ ,  $c$ ,  $\tau$ ,  $S_r$  and  $\sigma_s$ ) and Waxman and Smits model ( $n$ ,  $m$  and  $\sigma_s^{WS}$ ), respectively. The values of  $\phi$  and  $\sigma_w$  required by the models are listed in Table 1. By comparing the values of parameter  $\sigma_s$  and  $\sigma_s^{WS}$ , it can be observed that the differences between them is lower for the most conductive electrolytes (i.e., high  $\sigma_w$ ) since in those cases the electrical conduction is more significant in the liquid phase than the electrical conduction occurring in the liquid–solid interface. Waxman and Smits (1968) accounted the surface electrical conduction by assuming that this contribution depends inversely with water saturation (Eq. (35)). Therefore, the electrical conduction takes place near the mineral surface for low saturations, while for high saturations the electrical conduction through the electrolyte is the most important contribution. However, the surface conductivity is also dependent on the salinity, the mobility of the ions, and the surface charge density of the EDL (Revil, 2013a). In the proposed model (Eq. (34)),  $\sigma_s$  is treated as a constant for simplicity, not varying with water saturation as assumed by previous works (e.g., Mualem and Friedman, 1991; Friedman, 2005; Laloy et al., 2011; Breede et al., 2011). Even though the differences in the developments of the models, note that the proposed model is able

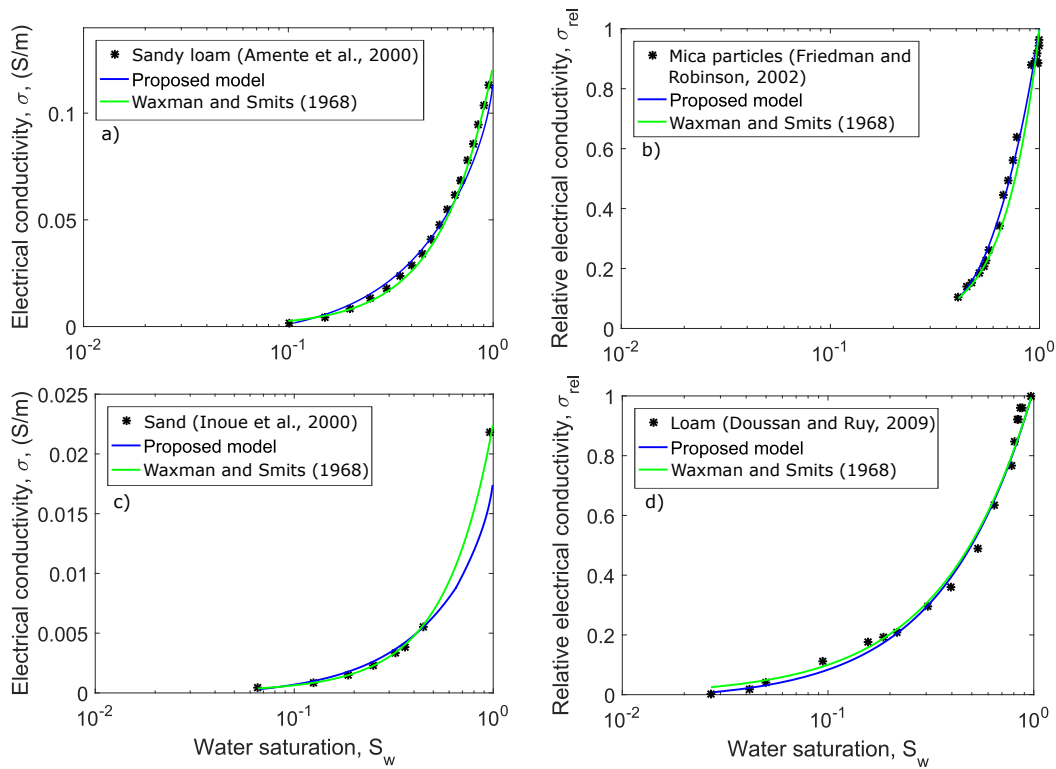


Figure 5: Electrical conductivity as function of water saturation for different data sets: a) a sandy loam from Amente et al. (2000), b) a packing of mica particles from Friedman and Robinson (2002), c) a sand from Inoue et al. (2000) and d) a loam from Doussan and Ruy (2009).

512 to fairly reproduce the behaviour of the data for the different soil textures and is in good  
513 agreement with the previous model of Waxman and Smits.

514 The experimental samples from Weerts et al. (1999) correspond to four undisturbed  
515 soil cores of a loamy sand (named PS9, PS10, PS11 and PS13) where the electrical  
516 conductivity was measured as function of water saturation. Figure 6 illustrates the fit  
517 of the proposed model (Eqs. (17) and (27)) for the four samples and the best-fitted  
518 parameters are listed in Table 3 which were found using the same method as for the  
519 previous experimental data sets. It can be observed that the proposed model produces  
520 a fairly good agreement with the data sets for all the samples. From the comparison of  
521 the fitted model parameter values, note that even though their values differ between the  
522 different samples, they vary between close values which can be expected as the samples  
523 are from a same soil type. The pore geometry described by these parameters presents  
524 smooth changes between the throat and wide pore body. Indeed, the high values of  $c$  and  $a$   
525 represent that the pore radius varies moderately. We can compare our model performance  
526 to the previously published model of Thanh et al. (2020) to fit these experimental data.  
527 They derived a model based on a capillary bundle of constant radii pores and proposed a  
528 similar number of fitting parameters. Note that our new model performs better than the

529 one from Thanh et al. (2020), which shows nearly 15% error when it is around 2-3% for  
530 our model.

531 The data from Tartrat et al. (2019) consist on electrical conductivity-water saturation  
532 values measured in five core samples. These samples were made of mixes of a background  
533 illitic clay material and pyrite grains. The electrical measurements were performed on each  
534 sample during their desiccation. This process causes a variation on the water electrical  
535 conductivity that cannot be neglected as salinity increases during the decrease of the  
536 saturation due to evaporation. To account this phenomenon on the estimates of the  
537 electrical conductivity model (Eq. (34)), we assume that the water electrical conductivity  
538 increases inversely with saturation during the desiccation process,  $\sigma_w(S_w) = \sigma_w(S_w =$   
539  $1)/S_w$  where the water electrical conductivity at saturation is  $\sigma_w(S_w = 1) = 0.115 \text{ S m}^{-1}$   
540 (Tartrat et al., 2019). The performance of the proposed model for the different samples is  
541 shown in Figure 7 and Table 4 lists the best fitted parameter values. The porosity value  
542 needed to estimate  $\sigma_{sat}^{REV}$  was taken from Tartrat et al. (2019) being its value  $\phi = 0.65$ .  
543 The proposed model is able to fairly well reproduce the behaviour of all the experimental  
544 data sets. The values obtained for the geometrical parameters  $a$  and  $c$  that define the  
545 constrictivities of the pores vary between the different samples. However, they remain  
546 in a narrow range of values, from 0.40 to 0.63 for  $a$ , and from 0.36 to 0.49 for  $c$ . These  
547 ranges of  $a$  and  $c$  values represent pores with a fairly significant constrictivity (i.e. a large  
548 fraction of the pore with reduced radius) which can be expected since clays present these  
549 reductions in the pore structure due to the packing of its fined grains.

550 Saafan et al. (2023) measured electrical conductivity variations with water saturation  
551 in low-permeability sandstone samples, called S6, S9, S13, S14, S16 and S18. The test of  
552 the proposed model relies on fitting the electrical conductivity data sets with Eq. (34).  
553 As sandstones usually present very low surface conductivities, we considered negligible  
554 its contribution to the electrical conductivity. Using an exhaustive search method as  
555 previously, we found the best-fitted parameters which are listed in Table 5. To fit these  
556 parameters we considered the value of the water electrical conductivity  $\sigma_w = 5.38 \text{ S m}^{-1}$   
557 which was taken from Saafan et al. (2023). Figure 8 shows predicted and measured data  
558 where it can be observed that the proposed model produces a fairly good agreement  
559 for all the samples. The low values of parameter  $a$  and high values of  $c$  fitted for the  
560 proposed model represent pore geometries with a strong reduction of the pore radii along a  
561 significant length of the capillary. This pore geometry can be expected since the enclosure  
562 of the pore radii hinders the water flow which translates in low permeability samples.

### 563 **3.2 Electrical conductivity during dissolution**

564 The performance of the model to describe the dissolution phenomenon on the electrical  
565 conductivity is tested with experimental data obtained by Rembert et al. (2023a). They  
566 measured the evolution of the electrical conductivity  $\sigma_{sat}^{REV}$  with time on two limestone  
567 samples, named E04 and E05, during dissolution. Moreover, they also measured the  
568 variations of porosity  $\phi$  and permeability  $k$  of the sample due to this process. Based on  
569 the expressions of  $\phi$  and  $k$  developed by Soldi et al. (2022) and considering the changes

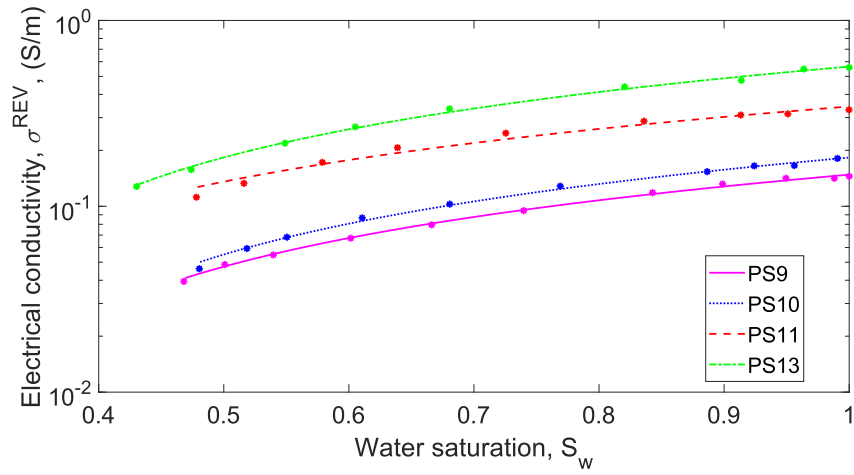


Figure 6: Comparison between the electrical conductivity proposed model (solid lines) and experimental data sets (points) from a loamy sand (Weerts et al., 1999).

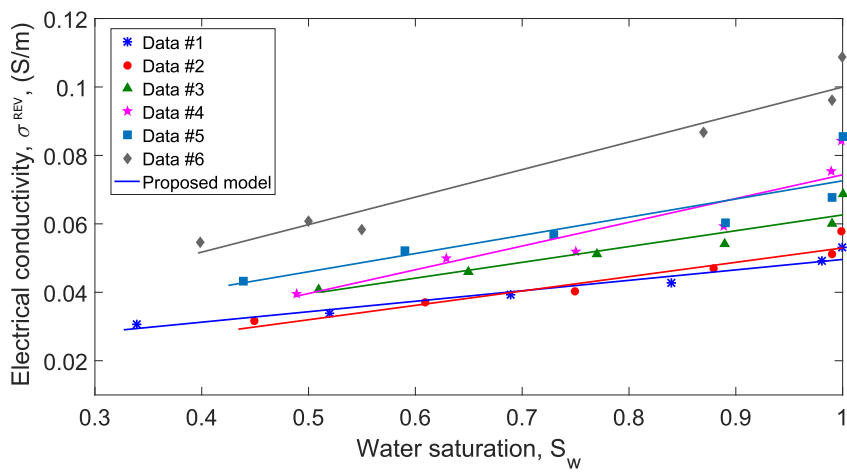


Figure 7: Comparison between the electrical conductivity proposed model (solid lines) and experimental data sets (points) measured in a illitic clay material with pyrite grains from Tartrat et al. (2019).

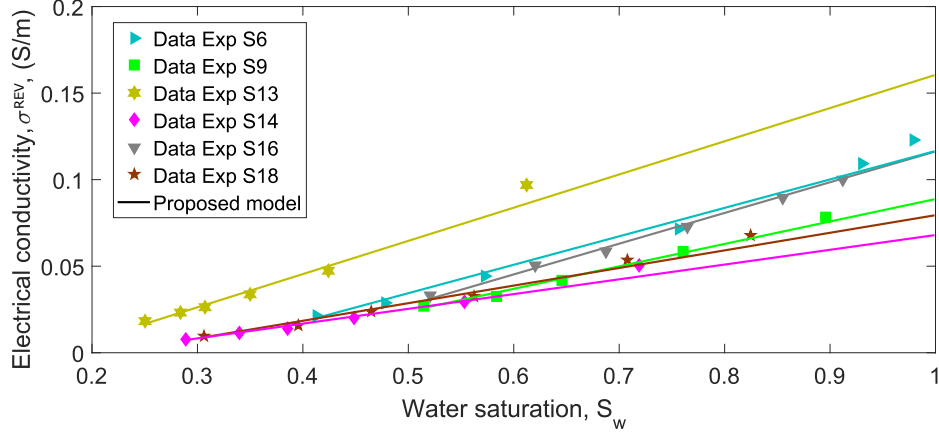


Figure 8: Comparison between the electrical conductivity proposed model (solid lines) and experimental data sets (points) from a low-permeability sandstone from Saafan et al. (2023).

Table 1: Values of the parameters used to estimate the electrical conductivity for experimental data from Amente et al. (2000), Inoue et al. (2000), Friedman and Robinson (2002) and Doussan and Ruy (2009). The porosity  $\phi$  and water electrical conductivity  $\sigma_w$  values were taken from their works.

Sample	$\phi$ (-)	$\sigma_w$ (S m <sup>-1</sup> )	Proposed model parameters					<i>NMSE</i>
			$a$ (-)	$c$ (-)	$\tau$ (-)	$S_r$ (-)	$\sigma_s$ (S m <sup>-1</sup> )	
Sandy loam	0.40	0.565	0.59	0.84	1.40	0.100	$10.0 \times 10^{-4}$	0.0167
Sand	0.45	0.058	0.66	0.71	1.36	0.056	$2.00 \times 10^{-4}$	0.0280
Mica particles	0.77	0.510	0.78	0.87	1.12	0.387	$1.80 \times 10^{-4}$	0.3430
Loam	0.44	0.072	0.55	0.65	1.54	0.028	$0.45 \times 10^{-4}$	0.3127

Table 2: Fitted Waxman and Smits parameter values to estimate the electrical conductivity for experimental data. The porosity  $\phi$  and water electrical conductivity  $\sigma_w$  values are the values listed in Table 1.

Sample	$n$ (-)	$m$ (-)	$\sigma_s^{WS}$ (S m <sup>-1</sup> )	<i>NMSE</i>	Source
Sandy loam	1.70	1.66	$32.0 \times 10^{-4}$	0.0147	Amente et al. (2000)
Sand	2.00	1.53	$16.5 \times 10^{-3}$	0.0034	Inoue et al. (2000)
Mica particles	2.60	2.73	$97.0 \times 10^{-4}$	0.3050	Friedman and Robinson (2002)
Loam	1.60	2.62	$77.4 \times 10^{-3}$	0.3144	Doussan and Ruy (2009)

Table 3: Values of the parameters used to estimate the electrical conductivity for the experimental data from Weerts et al. (1999). The porosity  $\phi$  and water electrical conductivity  $\sigma_w$  values were taken from their work.

Sample	$\phi$	$\sigma_w$	Proposed model parameters				$NMSE$
	(-)	(S m <sup>-1</sup> )	$a$ (-)	$c$ (-)	$\tau$ (-)	$S_r$ (-)	
PS9	0.41	0.48	0.72	0.62	1.23	0.17	$1.16 \times 10^{-2}$
PS10	0.37	0.90	0.73	0.67	1.21	0.26	$1.07 \times 10^{-2}$
PS11	0.41	1.34	0.69	0.65	1.27	0.28	$2.90 \times 10^{-2}$
PS13	0.40	2.25	0.74	0.58	1.28	0.27	$2.50 \times 10^{-2}$

Table 4: Values of the parameters used to estimate the electrical conductivity for the experimental data from Tartrat et al. (2019).

Sample	Proposed model parameters					$NMSE$
	$a$ (-)	$c$ (-)	$\tau$ (-)	$S_r$ (-)	$\sigma_s$ (S m <sup>-1</sup> )	
1	0.53	0.46	1.55	0.34	0.026	$4.40 \times 10^{-2}$
2	0.47	0.49	1.51	0.44	0.028	$4.00 \times 10^{-2}$
3	0.62	0.36	1.67	0.50	0.036	$3.30 \times 10^{-2}$
4	0.58	0.40	1.50	0.47	0.039	$5.50 \times 10^{-2}$
5	0.40	0.59	1.37	0.42	0.042	$5.10 \times 10^{-2}$
6	0.63	0.42	1.28	0.39	0.050	$5.30 \times 10^{-2}$

Table 5: Values of the parameters used to estimate the electrical conductivity for the experimental data from Saafan et al. (2023).

Sample	$\phi$	Proposed model parameters				$NMSE$
	(-)	$a$ (-)	$c$ (-)	$\tau$ (-)	$S_r$ (-)	
S6	0.084	0.14	0.79	1.67	0.35	$3.12 \times 10^{-2}$
S9	0.076	0.13	0.71	1.42	0.31	$2.06 \times 10^{-2}$
S13	0.102	0.20	0.54	1.47	0.21	$3.55 \times 10^{-2}$
S14	0.074	0.17	0.65	1.62	0.26	$4.05 \times 10^{-2}$
S16	0.068	0.16	0.75	1.22	0.04	$1.60 \times 10^{-2}$
S18	0.078	0.15	0.60	1.28	0.27	$4.23 \times 10^{-2}$

570 of the pore radii with time (Eq. (29)), these two properties can be estimated during  
 571 dissolution by (Soldi et al., 2024):

$$\phi(t) = \phi(t_0)e^{\beta(2-D)(t-t_0)} \quad (36)$$

572

$$k(t) = k(t_0)e^{\beta(4-D)(t-t_0)} \quad (37)$$

573 where  $\phi(t_0)$  and  $k(t_0)$  are the porosity and permeability of the REV at the initial time  $t_0$   
 574 of the dissolution process.

575 The time series that we selected to fit the model correspond to a stage of the ex-  
 576 periment when the dissolution has been already occurring since the data at the initial  
 577 and final stages are out of the hypotheses of the model. The data from the beginning  
 578 of the process is disregarded due to the strong dissolution, and the data from the final  
 579 stages were measured after the complete percolation and the sample which then cannot  
 580 be considered as a REV. Eqs. (31), (36) and (37) are fitted using an exhaustive search  
 581 method by minimizing the weighted normalized error between the calculated and mea-  
 582 sured values of  $\sigma_{sat}^{REV}$ ,  $\phi$  and  $k$  simultaneously. Figure 9 shows the fit of the proposed  
 583 model to these petrophysical properties and the values of the fitted parameters are listed  
 584 in Table 6. To estimate  $\phi(t_0)$ ,  $k(t_0)$  and  $\sigma_{sat}^{REV}(t_0)$  in Eqs. (36), (37), and (31), the  
 585 model also requires a  $R_{REV}$  and  $\sigma_w$  values for which we consider the values from Rembert  
 586 et al. (2023a),  $R_{REV} = 9$  mm,  $\sigma_w = 1200 \mu\text{S cm}^{-1}$  for E04 and  $\sigma_w = 1000 \mu\text{S cm}^{-1}$   
 587 for E05. Note that the evolution over time of  $\phi$ ,  $k$ , and  $\sigma_{sat}^{REV}$  of the experimental data  
 588 can be satisfactorily reproduced by the proposed model, as shown in Fig. 9(a-b), (d-c)  
 589 and (e-f) respectively. It can be observed from the values of the best fitted parameters  
 590 (Table 6) that they do not change significantly between the two samples. Moreover, the  
 591 fitted minimum and maximum radii are consistent with the values obtained from statis-  
 592 tical computations on tomographic images of the samples (Rembert et al., 2023a) while  
 593 the fitted dissolution rate may be slightly higher than the one calculated in Léger et al.  
 594 (2022a). It is important to notice that we analyse the evolution of these macroscopic  
 595 properties due to the changes in the pore geometry caused by the dissolution. Therefore,  
 596 variations of other parameters during the process, such as ionic concentration of the pore  
 597 water, are neglected. The experimental data used in this section from Rembert et al.  
 598 (2023a) account for water electrical conductivity measured at the outlet. They observed  
 599 that the electrical conductivity of carbonate samples presents a significant increase at the  
 600 beginning of the dissolution followed by a gentle slope that decreases its magnitude. This  
 601 fact can be related to an initial strong dissolution regime that diminishes with time since  
 602 water electrical conductivity is stable over this period.

603 To highlight the link between the evolution of hydraulic and electrical properties dur-  
 604 ing the dissolution, the permeability and electrical conductivity are plotted as functions of  
 605 the porosity. Fig. 10 shows the relationship between these properties for the data sets and  
 606 the proposed model. We use the fitted parameters of the proposed model from Table 6.  
 607 In addition, we compare them with the most classical equation to represent permeability-  
 608 porosity and electrical conductivity-porosity data, the Kozeny-Carman equation (Kozeny,  
 609 1927; Carman, 1937) and Archie (1942). Following the Kozeny-Carman equation, perme-



610 ability can be expressed in terms of porosity as:

$$k = p \frac{\phi^3}{(1 - \phi)^2}, \quad (38)$$

611 where  $p$  is a fitting parameter that depends on the specific internal surface area, an  
 612 empirical geometrical parameter, and the tortuosity. The best agreement between the data  
 613 and the Kozeny-Carman equation is obtained for  $p = 1.732 \times 10^{-12}$  ( $NMSE = 6.514 \times$   
 614  $10^{-3}$ ) and  $p = 2.7949 \times 10^{-12}$  ( $NMSE = 7.161 \times 10^{-2}$ ), for E04 and E05, respectively.  
 615 It can be observed that the proposed model provides better results than the Kozeny-  
 616 Carman equation for both samples (see Figs. 10a and b). In fact, the  $NMSE$  values for  
 617 the proposed model are  $NMSE = 1.595 \times 10^{-5}$  for E04 and  $NMSE = 3.401 \times 10^{-3}$  for  
 618 E05 which are significantly smaller than for the Kozeny-Carman equation.

619 The relationship between the electrical conductivity and porosity given by Archie  
 620 (1942) in Eq. (2), which under fully water-saturated conditions yields:

$$\sigma = \sigma_w \phi^m, \quad (39)$$

621 where  $m$  is the cementation exponent. For the  $\sigma_w$  value, we considered the values from  
 622 Rembert et al. (2023a), previously mentioned for the fitting of the proposed model. The  
 623 value of this fitted parameter is  $m = 2.679$  ( $NMSE = 1.490 \times 10^{-2}$ ) and  $m = 2.712$   
 624 ( $NMSE = 2.390 \times 10^{-2}$ ), for E04 and E05, respectively. Figs. 10c and d show the  
 625 comparison between the data, the proposed model, and Archie (1942). It can be seen that  
 626 the model from Archie (1942) has a poor performance in reproducing the data behavior  
 627 while the proposed model predicts closer values. The  $NMSE$  values for the proposed  
 628 model are  $NMSE = 7.378 \times 10^{-5}$  for E04 and  $NMSE = 1.276 \times 10^{-4}$  for E05. Note that  
 629 the  $NMSE$  values between the Archie (1942) and the proposed model differs between 2  
 630 and 3 orders of magnitude.

631 From a geometrical approach, the proposed model can represent the changes of the  
 632 pore structure which results in a larger porosity, permeability, and electrical conductivity  
 633 of the porous medium. The comparison with classical models shows that they cannot  
 634 reproduce the variations that affect these properties of the porous media under dissolu-  
 635 tion. Therefore, the proposed analytical model represents a step forward to estimate the  
 636 petrophysical properties during reactive processes.

## 637 4 Discussion and conclusions

638 Based on the framework of capillary tubes approach, we present an analytical model  
 639 to determine the electrical conductivity of a porous medium represented by tortuous  
 640 capillaries with varying aperture. The periodic fluctuations of the capillary radii follow  
 641 a sinusoidal piecewise behaviour along the pore length. This pore geometry determines  
 642 periodical fractions of the capillaries with pore throats and pore bodies defined by two  
 643 geometrical parameters, the radial  $a$  and length  $c$  factors, which allow us to represent  
 644 a wide range of pore geometries. The model has analytical closed-form expressions that

Table 6: Values of the parameters used to estimate the electrical conductivity for the experimental data from Rembert et al. (2023a).

Sample	Proposed model parameters							$NMSE$
	$a$ (-)	$c$ (-)	$D$ (-)	$\tau$ (-)	$R_{max}$ (mm)	$R_{min}$ (mm)	$\tilde{\alpha}$ (h <sup>-1</sup> )	
E04	0.20	0.87	1.31	1.36	0.45	$1.26 \times 10^{-4}$	0.0046	$1.814 \times 10^{-3}$
E05	0.28	0.82	1.29	1.25	0.86	$5.50 \times 10^{-4}$	0.0055	$3.521 \times 10^{-3}$

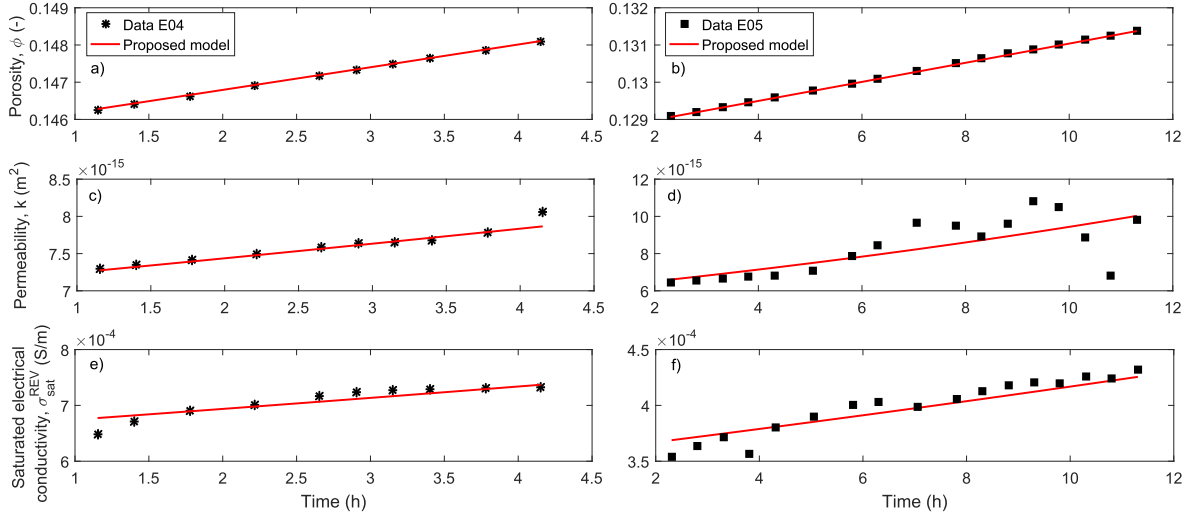


Figure 9: Model fit to the time evolution of: a-b) porosity, c-d) permeability and e-f) electrical conductivity data for samples E04 and E05 from Rembert et al. (2023a).

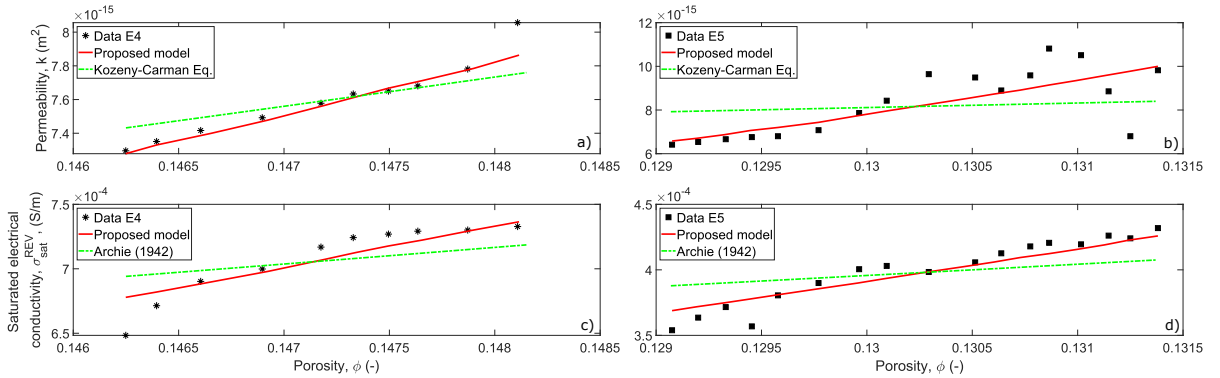


Figure 10: Comparison among the estimates of: a) and b) permeability-porosity for the proposed model and the Kozeny-Carman Equation, c) and d) electrical conductivity-porosity for the proposed model and Archie's law or samples E04 and E05 from Rembert et al. (2023a).

645 depend on parameters which all have a physical or geometrical meaning. In the particular  
646 case of  $c = 0.5$ , the proposed model is consistent with the model developed by Rembert  
647 et al. (2020) for a porous medium under water saturated conditions. In addition, the  
648 proposed model addresses partially saturated conditions and more complex processes.

649 The periodic throats of the pore structure allow us to introduce the hysteresis phe-  
650 nomenon in the relative electrical conductivity when expressed as a function of the pres-  
651 sure head. The resulting expressions for drainage and imbibition experiments also depend  
652 on only four independent model parameters (the fractal dimension  $D$ , the radial factor  
653  $a$ , the minimum  $R_{min}$  and maximum  $R_{max}$  radii). Hysteretic behaviour of the electrical  
654 conductivity has been observed in experimental and numerical studies as function of sat-  
655 uration (e.g. Knight, 1991; Zhang et al., 2017; Mainault et al., 2018). However, from our  
656 theoretical results, hysteresis phenomena are not visible when expressed as a function of  
657 the saturation. Phenomena observed by other studies may be related to different effects,  
658 such as contact angle hysteresis, disconnection of the fluid phase (i.e., snap off), or film  
659 flow (e.g. Jury et al., 1991; Blunt et al., 2002; Spiteri et al., 2008).

660 In our model, the reactivity of the porous medium is introduced by considering the  
661 variations in the structure of the capillaries. Therefore, it should be noted that the  
662 model focuses only on the geometrical changes that these processes produce on the porous  
663 medium. The proposed model is compared against experimental data of electrical con-  
664 ductivity, porosity, and permeability during dissolution. This comparison shows that  
665 the model is satisfactorily able to reproduce the evolution of these three petrophysical  
666 properties with time simultaneously.

667 The performance of our model to estimate electrical conductivity is tested against  
668 different sets of experimental data. The proposed relationship between the relative elec-  
669 trical conductivity and effective saturation can fairly reproduce the data from different  
670 soil textures and a packing of mica particles. Moreover, when estimating the electrical  
671 conductivity for several samples of a same type of soil, the fitting parameter values vary  
672 in a narrow range for each soil. For the loamy sand case, the high values of the radial  
673 factor  $a$  and length factor  $c$  represent pores whose radii vary slightly between their con-  
674 strictive and non-constrictive fractions which results in less tortuous paths due a higher  
675 connection between the fractions (e.g. Xing et al., 2021). For the illitic clay samples, the  
676 values of  $a$  are low while the tortuosity values are higher than the ones for the loamy  
677 sand. This result is consistent with this type of soil that may present more constrictive  
678 pores and complex flow paths (i.e. more tortuous) due to the packaging of its finer grains.  
679 While in the case of the sandstone samples, the significant low values of  $a$  and high values  
680 of  $c$  represent strong constrictivities of the pores (i.e. high pore radii reductions over a  
681 large length of the pores) causing that the water flow hinders and a high decrease of the  
682 permeability.

683 The model developed in this study represents an improvement over available models  
684 within the framework of capillary tube models by its capability to describe a wide variety  
685 of porous space geometries. In fact, it could be used to represent micropores which  
686 may have long and narrow necks (i.e. high  $c$  value and low  $a$  value) connected to larger  
687 and short pore bodies (e.g. Sun and Torres-Verdín, 2022). When compared to most

688 widely used models, the proposed model is consistent with the empirical model of Archie  
689 (1942) for the cases of non-constrictive capillaries, and is in good agreement with the  
690 model of Waxman and Smits (1968) for simple rock characterization. Even though the  
691 expression of these classical models to describe the electrical conductivity might be less  
692 complex, they cannot account for hysteresis effects which are of significant importance for  
693 unsaturated flow, nor for reactive phenomena that can predominate in carbonate media.  
694 On the contrary, the proposed model can represent both of these phenomena and with  
695 one set of the model parameters. This new analytical model to estimate the electrical  
696 conductivity is developed under the same framework and assumptions used previously  
697 to derive hydraulic properties (permeability, porosity). From a geometrical approach,  
698 we are capable of describing petrophysical and flow properties while accounting for their  
699 characteristic physical phenomena such as hysteresis and reactive processes. Thus, this  
700 work represents a significant step toward a unified model for many important petrophysical  
701 properties, and therefore, a way to characterize hydraulic properties of porous media from  
702 electrical measurements.

## 703 5 Notation List

Symbol	Description	Units
REV	Representative elementary volume	-
$\sigma$	Electrical conductivity	S m <sup>-1</sup>
$\sigma_w$	Electrical conductivity of the electrolyte	S m <sup>-1</sup>
$F$	Formation factor	-
$\sigma_s$	Surface electrical conductivity	S m <sup>-1</sup>
$\phi$	Porosity	-
$S_w$	Water saturation	-
$n, m$	Archie's saturation and cementation factors, respectively	-
$R$	Radius of a circular tube	m
$l$	Pore length	m
$\tau$	Tortuosity	-
$a$	Radial factor of the constrictivity	-
$c$	Length factor of the constrictivity	-
$\lambda$	Wavelength	m
$r(x)$	Pore radius variation along the longitudinal variable $x$	m
$R_{REV}$	REV radius	m
$R_{min}, R_{max}$	Minimum and maximum pore radii, respectively	m
$N(R)$	Number of pores of radius equal or larger than $R$	-
$D$	Fractal dimension	-
$L$	REV length	m
$\Sigma_p$	Electrical conductance of a pore	S

(It continues in the following page).

Symbol	Description	Units
$f$	Reduction factor in a pore conductance due to the presence of constrictivities	-
$\sigma_p$	Electrical conductivity of a pore	$\text{S m}^{-1}$
$i_p$	Electric current in a pore	A
$\Delta V$	Electrical voltage difference	V
$I^{REV}$	Electric current in the REV	A
$\sigma^{REV}$	Electrical conductivity of the REV	$\text{S m}^{-1}$
$\sigma_{sat}^{REV}$	Electrical conductivity of the total saturated REV	$\text{S m}^{-1}$
$f_v$	Reduction factor in the porosity due to the presence of constrictivities	-
$f_\sigma$	Reduction factor in $\sigma^{REV}$ due to the presence of constrictivities	-
$h$	Pressure head	m
$T_s$	Surface tension	$\text{N m}^{-1}$
$\gamma$	Contact angle	degrees
$\rho_w$	Water density	$\text{kg m}^{-3}$
$g$	Gravitational acceleration	$\text{m s}^{-2}$
$R_h$	Pore radius related to pressure head $h$	m
$R^*$	Integration variable	m
$\sigma_{rel}$	Relative electrical conductivity of the REV	-
$\sigma_{rel}^d, \sigma_{rel}^w$	Main drying and wetting relative electrical conductivity, respectively	-
$h_{min}, h_{max}$	Minimum and maximum pressure heads, respectively	m
$S_e, S_r$	Effective and residual water saturations, respectively	-
$V_p$	Pore volume	$\text{m}^3$
$t$	Time	h
$S_p$	Pore surface	$\text{m}^2$
$\alpha$	Dissolution rate	$\text{m}^3 \text{h}^{-1}$
$\tilde{\alpha}$	Dissolution rate	$\text{h}^{-1}$
$\beta$	Dissolution factor	$\text{h}^{-1}$
$\sigma_{WS}$	Electrical conductivity from Waxman and Smits (1968)	$\text{S m}^{-1}$
$k$	Permeability	$\text{m}^2$

## Acknowledgements

704

705 This research was carried out as part of M. Soldi's postdoctoral fellowship funded by  
706 the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentine). The authors  
707 strongly thank the Editor Graham Sander, and the reviews of Youzheng Qi and two  
708 anonymous reviewers for their careful assessment of our work and their valuable comments  
709 and suggestions which helped to improve the manuscript.

## 710 **CRedit authorship contribution statement**

711 Mariangeles Soldi: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing. Flore Rembert: Investigation, Formal  
712 analysis, Methodology, Writing - review & editing. Luis Guarracino: Conceptualization,  
713 Methodology, Writing - review & editing, Investigation, Supervision. Damien Jougnot:  
714 Conceptualization, Methodology, Writing - review & editing, Investigation, Supervision.  
715

## 716 **Data availability**

717 No original data, everything has been published before.

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