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Complex electrical resistivity and dielectric permittivity responses to dense non-aqueous phase liquids' imbibition and drainage in porous media: a laboratory study

Mohammad Ali Iravani^{1,2}, Jacques DeParis^{1,*}, Hossein Davarzani¹, Stéfan Colombano¹,
Roger Guérin², Alexis Maineult²

1) BRGM, French Geological Survey, 45060 Orléans, France

2) Sorbonne Université, CNRS, EPHE, UMR 7619 METIS, 75005 Paris, France

Short title: Saturation effects on electrical signatures of DNAPL-saturated media

* Corresponding author. E-mail: j.deparis@brgm.fr

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1 **Abstract**

2 The effective techniques for remediation of sites polluted by dense non-aqueous phase
3 liquids (DNAPLs) remains a challenge. Among the various technical monitoring methods, there
4 is an increasing interest in studying the geophysical characteristics of contaminated soils, as
5 indicators of the progress in clean-up programs. This work sought to investigate the variation
6 of the electrical complex resistivity and the relative permittivity by analyzing the results
7 obtained from spectral induced polarization (SIP) and time domain reflectometry (TDR).
8 Different series of measurements during drainage and imbibition of DNAPLs in porous media
9 were done to validate the clean-up process on sites polluted by DNAPLs. Therefore, a
10 methodology based on laboratory work was designed and carried out to study the electrical
11 complex resistivity (both in magnitude and phase) in the frequency range 0.183 Hz to 20 kHz,
12 and the relative dielectric permittivity at 70 MHz. The experiments were done on small 1D
13 cells. In these cells, glass beads were used as a porous medium. Two different fluid couples,
14 i.e. coal tar (CT)/water and canola oil (CO)/salty ethanol (SE), were used to produce two-phase
15 flow.

16 Our findings highlight that due to the high resistivity of CO and CT, an increase in water
17 saturation led to decrease in amplitude and phase. Saturation change of SE had the same effect
18 on resistivity but no relationship was found for phase and saturation for the mixture CO and
19 SE. It is also showed that the complex resistivity and relative permittivity measurements were
20 compatible with generalized Archie's law and complete complex refractive index method
21 (CRIM) model as two empirical models for defining the correlation between the electrical
22 resistivity, relative permittivity, and saturation of each phase in the multiphase porous medium.

23

24 1 Introduction

25 The remediation of dense non-aqueous phase liquids (DNAPLs) in porous media continues
26 to be one of the most challenging problems facing environmental scientists and engineers.
27 DNAPLs are one of the largest sources of soil pollution in the world (Pankow and Cherry,
28 1996). While it is primarily the responsibility of polluting industries to clean up polluted sites,
29 researchers are left to come up with practical and effective remediation techniques. Among
30 these techniques, various geophysical methods can be used to localize DNAPL plumes and to
31 monitor the effectiveness of remediation processes (Romig, 2000).

32 Optimal usage of geophysical tools and technology based on the economic considerations
33 is a key point for all practical works. To follow field remediation by geophysics, the behavior
34 of geophysical parameters should be understood, and therefore empirical models known to
35 transform geophysical parameters to saturation will be used to obtain the saturation field
36 concerning to magnitude of each parameter. Compared to field works, laboratory measurements
37 have more resolution due to lower electrode spacing and known initial stage. The transposition
38 of these measurements should be validated in the field study. In the field, the saturation of the
39 coal tar (CT) in the contaminated soil was decreased by DNAPL recovery with the method of
40 pump and treat. Validating the clean-up process and calculate residual pollutant saturation is
41 the main responsibility of the geophysics in remediation programs. Quantifying of spatial
42 characteristics of physical properties (e.g electrical resistivity and relative permittivity) of the
43 polluted soil needs precise measurements in both laboratory and field. In this study, the
44 suitability of one electro-geophysical method, spectral induced polarization (SIP), for
45 evaluating the resolution and the accuracy of resistivity data and time domain reflectometry
46 (TDR) for obtaining relative permittivity and their potentials for cleanup monitoring were
47 investigated.

48 SIP might have enough resolution and precision to be suitable for DNAPL detection and

49 validating depollution processes in contaminated soils, but it needs to be proven by further
50 electro-geophysical studies in the laboratory and field. Recently, the induced polarization (IP)
51 method has been used to investigate the geophysical characteristics of soils (e.g., Mashhadi and
52 Ramazi, 2018; Revil *et al.*, 2015; Jang *et al.*, 2014; Slater *et al.*, 2014; Attwa and Gunther,
53 2013; Weller *et al.*, 2010; Candansayar, 2008; Braga *et al.*, 1999). Many laboratory studies have
54 discussed the effects of saturation changes on IP responses (e.g., Maineuil *et al.*, 2018; Schmutz
55 *et al.*, 2012; Breede *et al.*, 2011; Jougnot *et al.*, 2010; Cosenza *et al.*, 2007; Titov *et al.*, 2004),
56 evidencing saturation having a strong influence on complex resistivity spectra.

57 Several studies have documented the potential of using geophysical methods to monitor
58 cleanup at both field and laboratory scales (e.g., Cardarelli and Di Filippo, 2009; Hwang *et al.*,
59 2008; Snieder *et al.*, 2007; Sogade *et al.*, 2006; Brewster and Annan, 1994). Among various
60 geophysical approaches, electrical methods have proven their potential to characterize
61 subsurface changes (e.g., Gharibi and Bentley, 2005; Binley *et al.*, 2005). They have been used
62 to investigate geophysical properties of soils in a wide range of environmental applications
63 (e.g., Grimm and Olhoeft, 2004; Briggs *et al.*, 2004), especially within shallow soils (e.g.,
64 Romig, 2000) and porous rock (e.g., Kaselow and Shapiro, 2004). Some previous studies
65 focused on detecting light non-aqueous phase liquids (LNAPLs) detection (e.g., Atekwana *et*
66 *al.*, 2000). In this study, we focus specifically on DNAPLs. Spherical-glass beads (GB) were
67 used as a porous medium and various conductive fluids - canola oil (CO), salty ethanol (SE),
68 water, and CT - were used as liquid phases.

69 Electrical charge transport and separation in a porous medium are referred to as electrical
70 conduction and polarization, respectively. A saturated porous medium is made of two
71 components, a solid phase (porous matrix) and pores that are filled with fluids. The in-phase
72 electrical conduction of the medium is generally due to the electrical conductivity of the
73 solution inside the pores. Nevertheless, interfacial conduction (in the case of a high specific

74 surface area, for instance when the medium contains clays) on grain surfaces can lead to
 75 polarization phenomena and out-phasing components in the conductivity (Kemna *et al.*, 2000).
 76 In the absence of electrode polarization (Tsonos, 2019), the complex resistivity consists of two
 77 terms, described by $\rho = \rho' + i\rho''$ where $\rho'(f)$ and $\rho''(f)$ are respectively the real and imaginary
 78 parts as a function of frequency f , with $i^2 = -1$. The magnitude $|\rho|$ and the phase φ of the complex
 79 resistivity can be obtained from Eq. (1) and (2):

$$|\rho| = \sqrt{(\rho'^2 + \rho''^2)}, \quad (1)$$

$$\varphi = \tan^{-1}\left(\frac{\rho''}{\rho'}\right). \quad (2)$$

80 The units of phase and magnitude of complex resistivity are radian and $\Omega \cdot m$, respectively.
 81 The phase shift is mainly related to the grain size, to the specific surface area (Börner and
 82 Schön, 1991), and the pore space shape. For instance, the larger the grain size, the smaller the
 83 frequency of the peak of the phase. It means that phase lag in a sandy medium is less than the
 84 lag in silty and loamy media (Kemna *et al.*, 2000).

85 The relative permittivity (ϵ_r), also named dielectric constant, is a physical parameter that
 86 describes quantitatively the electrostatic characteristics of particles of a medium under
 87 immersed charge (current) and resulting electric field (Archer and Wang, 1990). Relative
 88 permittivity is the ratio of absolute permittivity (ϵ) and permittivity of vacuum (ϵ_0) expressed
 89 by Eq. (3):

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}, \quad (3)$$

90 The relative permittivity is a frequency dependent complex value, $\epsilon(f) = \epsilon'(f) + i\epsilon''(f)$
 91 where $\epsilon'(f)$ is the real part and $\epsilon''(f)$ is the imaginary part. As was illustrated in a previous study
 92 (Iravani *et al.*, 2020), for two-phase fluid saturation in a porous medium made of GB, relative
 93 permittivity is a frequency- and temperature-dependent parameter.

94 In this paper, the effects of two-phase flow (DNAPL saturation change) on complex

95 resistivity and dielectric permittivity are studied. A series of laboratory experiments were
96 performed to characterize the electrical response to saturation changes. Small 1D cells were
97 initially filled with water or SE and GB and were subjected to a vertical CT or CO injection to
98 apply imbibition and drainage tests. The similarity in hydraulic and geophysical properties of
99 CO with CT encouraged us to carry out another experiment with CO in parallel. Before starting
100 experiments, water was used as the reference liquid to evaluate the electrodes, which measured
101 the electrical potential. Originally, the experiments were performed using CT and water. Due
102 to the specific physical and chemical characteristics of CT, it was decided to use a less complex
103 fluid compared to CT with hydraulic and geophysical characteristics close to this DNAPL to
104 perform another set of experiments. CO, which has hydraulic and electrical properties similar
105 to CT, might have been the best option but it is lighter than water. The challenge was finding a
106 fluid lighter than CO but with similar characteristics to water. The optimum option was ethanol,
107 which is considered a non-conductor fluid with null electrical conductivity (Rocha and Simões-
108 Moreira, 2005), but similar to water. As long as there are no ions in a fluid, the current cannot
109 pass through it. Consequently, other chemicals that conduct electricity like salt (NaCl) must be
110 added to ethanol to increase its electrical conductivity. We then applied mixing models to
111 explain the observed responses.

112 2 Experimental setup

113 The laboratory program was designed and carried out in line with methods and procedures
114 defined in previous studies by Colombano *et al.*, (2017, 2020), Philippe *et al.*, (2020) and
115 Iravani *et al.*, (2020) in order to be able to monitor the effects of saturation changes on the
116 electrical complex resistivity and the relative permittivity. To achieve this, two cylindrical cells
117 were used (Fig. 1). Both cells have an internal diameter of 5.8 cm and at a length of 5.56 cm.

118 Cells were manufactured using a thermoplastic non-reactive polymer called polyvinylidene
119 fluoride (PVDF) to prevent potential reactions between strong resistant liquids like CT and the

120 test setup (Schweitzer, 2004). PVDF is a nontoxic material with no impact on liquid or solid
121 phases of the sample. PVDF also has a high temperature refractory (-40 to 120°C). Its low air
122 and gas permeability and high electrical isolation and dielectric constant made this polymer
123 suitable to be used in the setup (Schweitzer, 2004).

124 The cells were filled with a non-consolidated, highly permeable porous medium with 40%
125 porosity, namely 1 mm diameter GBs. There were several reasons behind the application of GB
126 instead of soil samples. The first reason is taking advantage of the transparency of GB to better
127 monitor and report CT and CO levels in the samples to calculate water/SE and CT/CO
128 saturations. The use of GB also prevents the occurrence of unexpected phenomena such as
129 adsorption during the experiment. The relative permittivity of a GB pack is 5.9 (Orlando and
130 Palladini, 2019). The complex resistivity of the medium was measured with SIP using SIP-lab
131 IV manufactured by Radic Research in Germany. The complex resistivity was measured over
132 a broad frequency range (0.183 Hz to, 20 kHz) with an incremental coefficient of 2, according
133 to SIP-lab IV apparatus properties. The relative permittivity was measured with TDR probes
134 (model 5TE, METER Group) with dimensions of 10 cm×3.2 cm (with 2.5 cm space between
135 the first and the third branch, Fig. 1a). The influence of the TDR probe on the experiment is
136 weak because (1) the volume ration between the probe ($3 \times 2.5 \text{ cm}^3$) and cell is around 5%, (2)
137 the flow is in the creeping flow regime (Reynolds number equal to 3.7). In addition, we
138 performed resistivity measurement with and without TDR probe during white test (i.e. column
139 filled with water). The resistivity relative difference is less than 1%, which is negligible
140 compared to the experimental error.

141 TDRs were connected to a Campbell CR-1000 data logger. For these probes, the
142 measurement frequency was 70 MHz. This frequency was chosen to reduce salinity and textural
143 effects of the medium compared to low frequencies (Kizito *et al.*, 2008). For the SE solution,
144 taking into account the solubility of salt in ethanol at 25°C, 0.65 g of NaCl was mixed with 1 kg

145 of ethanol (Burgess, 1978). The resulting conductivity was 0.0251 S m^{-1} at, 20°C which is less
146 than the conductivity of tap water (0.0345 S m^{-1}) at the same temperature but sufficient to be
147 used in the experiments. Liquid (CT/water and CO/SE) saturations were supposed to be variable
148 parameters in our experiments.

149 Each cell and column was equipped with a small tap at the bottom to control the introduction
150 of water/SE to samples by a peristaltic pump (Watson Marlow 530U). Degassed tap water,
151 prepared in an ultrasound tank (VWR Ultrasonic Cleaner - USC500D), was used in this
152 experiment. Degassed water was used to prevent air bubbles forming in samples. There were
153 two holes at the top and the bottom of the main sample for introducing and draining fluids
154 (water/SE and CT/CO). The sample was connected to two graded reservoirs with an internal
155 diameter of 3.5 cm and a height of 36 cm. Two PVDF filters were used at the top and the bottom
156 of each sample to keep the GB (porous media) inside cells/columns. The schemas of a vertical
157 cross-section of a cell and an experimental setup are shown in Fig. 1. In Fig. 1b, the right and
158 the left reservoirs are for water/SE and CT/CO, respectively. Both reservoirs were connected
159 to samples using flexible plastic tubes. The water/SE reservoir was placed and fixed at the top
160 of the sample, while the CT/CO reservoir can move vertically.

161 AC current was injected using two ring metallic electrodes A and B (made of nickel-cobalt
162 alloy (MP35N)), exactly at the top and the bottom of the sample. The voltage response of the
163 medium was measured using non-polarizable potential electrodes, which were inserted in a row
164 with a spacing of 1.85 cm in pre-drilled holes. These hand-made Cu/CuSO_4 potential electrodes
165 (after Mainault *et al.*, 2004) were made of 72.75% milli-Q water (ultrapure water), 26% CuSO_4 ,
166 and 1.25% gelatin. A heating shaker was used to mix the solution at 80°C for approximately
167 one hour. Wenner- α array was chosen with distance $AB=MN=AM=AN$ equal to 1.85 cm.

168 Knowing the conductivity of the tap water at the beginning of each experiment (measured
169 with a portable conductivity meter model pH/Cond 340i (WTW Measurement System Inc.))

170 made it possible to compute geometric factors for the cells to obtain the resistivity from the
171 measured impedance of the medium when the cell was filled with water. The value of the
172 geometric factor was then used throughout the experiment to transform resistance into
173 resistivity.

174 To examine the stability of the copper sulfate electrodes, the same measurement was carried
175 out at the end of the experiment (i.e. cell fill with tap water). Samples were drained and imbibed
176 by gradually raising or lowering the DNAPL (or CO) reservoir, at the rate of 2 cm per 3 hours
177 to prevent air trapping in the medium, in two series of drainage-imbibition cycles. In a given
178 cell, two cycles per experiment were usually performed in two weeks. We used two cells: one
179 for CT/water and the other for CO/SE. Experiments were performed in an oven at a temperature
180 of, 20°C. The dielectric relative permittivity and the electrical complex resistivity were
181 recorded at a rate of one spectrum every 30 s and 2 hours, respectively. After balancing the
182 level of CT/CO in the left reservoir with the water/SE level in the reservoir at the top of the
183 sample to reach equilibrium and to prevent CT/CO from entering the bottom of the sample,
184 experiments were started. The volume and height of CT/CO and water/SE added to the system
185 were documented precisely. Each time before changing CT/CO reservoir level (2 cm), the
186 water/SE and CT/CO levels were carefully monitored to calculate the drained or injected
187 volume. The volume and the porosity of the samples were determined before starting the
188 experiments. The porosity of the cells was calculated by subtracting the volume of GBs from
189 the total cell volume over the total volume of the cell. Therefore, the saturation could be
190 determined simply by measuring the volume changes. Drainage was finished when the CT/CO
191 was observed in water/SE reservoir and imbibition was finished when water/SE was observed
192 in the linking tube between the sample and CT/CO reservoir.

193 This laboratory setup was designed to assess the effects of saturation changes in saturated
194 multiphase media. Having high reliability for three saturation points is very important for each

195 cycle:

- 196 • The starting point of the experiment, i.e. when the first cycle of drainage and imbibition
197 is going to start. At this point water/SE saturation is 100%;
- 198 • Irreducible saturation (wetting phase) which is the stage after finishing drainage and
199 resistivity and relative permittivity of porous media have become stable at their
200 maximum and minimum values, respectively; and
- 201 • Residual saturation (non-wetting phase) after imbibition and replacement of CT/CO by
202 water in a multiphase porous media, the capillary forces, which act in the opposite
203 direction from buoyancy, and viscous forces might result in some entrapment of fluids
204 with porous media. The residual saturation is the remaining volume of CT/CO, which
205 could not be discharged from samples. In other words, at the residual saturation point,
206 water/SE saturation would be less than 100%.

207 3 Results

208 3.1 Effect of saturation on the complex resistivity

209 The electrical complex resistivity was measured in a wide range of frequencies (0.183 Hz
210 to, 20 kHz) but due to electromagnetic coupling, measurements at frequencies larger than
211 10 kHz were not considered. The results are shown in Fig. 2. As mentioned in the experimental
212 setup description, two cycles of drainage and imbibition were performed. The phase variations
213 during the second drainage-imbibition cycles varied widely for both cells and are difficult to
214 interpret. Consequently, we chose to show only the first cycles. As expected, increased water
215 or SE saturation decreased the amplitude of the resistivity. This occurred because CT and CO
216 are significantly more resistive than water and SE. Resistivity at frequencies between 0.183 to
217 1000 Hz was almost constant and at the higher frequency (more than 187.5 Hz) was increasing.
218 On the other hand, for CO and SE, the resistivity fell at the higher frequencies (more than

219 5.859 Hz). For CT and water, the variation of the phase spectrum at low frequencies was less
220 compared to higher frequencies. In addition, the bell shape part of the phase spectrum was
221 shifted to higher frequencies with increasing water saturation. The changes in amplitude and
222 phase variations are in agreement with the behaviors reported by Mainault *et al.* (2018) from
223 numerical simulation of drainage and imbibition in pore networks.

224 There was no systematic relationship between the error bars measured by SIP for different
225 frequencies, but the measurement errors for the phase were larger for the CO/SE case than for
226 CT/water. In Fig. 2c, for the measurement with SE saturation (S_e) equal to 4.5%, error bars were
227 larger than for other measurements because of the decreasing volume of conductive SE in the
228 cell. In Fig. 2c, error bars significantly decrease at a higher frequency which is a different
229 behavior compared to CT/water column results (Fig. 2a). All resistivity measurements in the
230 frequency domain of CO/SE were selected from the first SE drainage. Except for $S_e=28.6\%$
231 with a different variation trend, all the other measurements have almost the same trend of
232 variations. Time series for the amplitude of the resistivity and the phase at the frequency of
233 1.46 Hz (the frequency close to the field measurements) are shown in Fig. 3. Note that the phase
234 in the second cycle of the CT/water experiment is negative, but we have no explanation.

235 3.2 Effect of saturation on relative permittivity

236 The relative permittivity variations as a function of water and SE saturation are shown in
237 Fig. 4. The variation was measured for five different saturation stages for both experiments.
238 The results showed that an increase in water and SE saturation triggers an increase in the relative
239 permittivity in both cases. According to our last study (Iravani *et al.*, 2020), at higher water
240 saturation, due to higher relative permittivity of water compared to CT, an increase in relative
241 permittivity was expected. Results during imbibition support the idea that increasing water/SE
242 saturation increases measured relative permittivity.

243 4 Discussion

244 4.1 Empirical models for the amplitude of the resistivity

245 Since the electrical conductivity σ ($\rho=1/\sigma$) depends on the geometry and topology of the
246 porous medium, many studies (e.g., Glover, 2010; Glover *et al.*, 2000; Schilling *et al.*, 1997;
247 Guéguen and Palciauskas, 1994; Luo, Wood, and Cathles, 1994; Somerton, 1992; Bussian,
248 1983; Korvin, 1982; Hashin and Shtrikman, 1962; Archie, 1942; Lichtenecker and Rother,
249 1931) have been carried out to investigate the relationship between the bulk electric
250 conductivity of the medium and fluid saturation. Some models work with a maximum of two
251 conductive phases (e.g., Schilling *et al.*, 1997; Waff, 1974; Hashin and Shtrikman, 1962) while
252 some have the option of applying multiple phases (e.g., Parallel model used by Guéguen and
253 Palciauskas, 1994; Luo *et al.*, 1994; Somerton, 1992). The very classical and often used
254 Archie's law (1942) was defined for only one phase. Some proposed models are with (e.g.,
255 generalized Archie's law and Bussian equation) and some without (e.g., Random model by
256 Guéguen and Palciauskas, 1994) variable exponents. For instance, m in generalized Archie's
257 law is the variable exponent that we found for each phase by the least mean square (LMS)
258 method.

259 The most investigated simple model to study the relationship between the bulk conductivity,
260 its porosity, and fluid conductivity, when the porous media is nonconductive (Glover, 2010), is
261 the classical Archie's law (1942, Eq. (4)):

$$\sigma = \sigma_{fluid}\varphi^m, \quad (4)$$

262 where σ_{fluid} ($S\ m^{-1}$) is the conductivity of the liquid inside the pores, φ (-) is the porosity, and m
263 is the cementation exponent. One of the advantages of Archie's law compared to many mixing
264 models is that it has a variable component (m) that makes this model applicable in many cases.
265 A more recent model called generalized Archie's law was a derivative of traditional Archie's
266 law (e.g., Glover, 2010). In the last decade, generalized Archie's law has been used in many

267 studies (Glover, 2010; Tiab and Donaldson, 2004; Mendelson and Cohen, 1982; Sen *et al.*,
 268 1981) to investigate the relationship between the bulk conductivity of the porous medium, its
 269 porosity and the conductivity of the liquids in pores. The generalized Archie's law for n phases
 270 is given by Eq. (5) and (6):

$$\sigma = \sum_{i=1}^n \sigma_i \varphi_i^{m_i} \quad , \quad (5)$$

271 where

$$m_j = \frac{\log(1 - \sum \varphi_i^{m_i})}{\log(1 - \sum \varphi_i)} \quad i \neq j . \quad (6)$$

272 In these equations, the summation of all fractions should equal to one (for n phases,
 273 $\sum_{i=1}^n \varphi_i = 1$).

274 In a saturated porous medium $\varphi_1 + \varphi_2 + \dots + \varphi_{n-1} = \varphi^*$ with φ^* the total porosity. In the
 275 interpretation of saturation exponents of generalized Archie's law, water/fluids contents should
 276 be used instead of water/fluids saturations. For instance, if the fluid is water, the relationship
 277 between water content (θ_w) and water saturation (S_w) is $\theta_w = S_w \varphi$.

278 The generalized Archie's law (Eq. (5)) for our experimental setups can be expanded as (Eq.
 279 (7)):

$$\sigma_{mixed} = \sigma_{fluid1} \theta_{fluid1}^{m_1} + \sigma_{fluid2} (\varphi - \theta_{fluid1})^{m_2} + \sigma_{GB} (1 - \varphi)^{m_3} \quad , \quad (7)$$

280 The conductivity values of water, SE, CT, and CO are 0.0345, 0.251, 10^{-9} (reported by
 281 Iravani *et al.*, 2020), and 10^{-11} S m⁻¹ respectively. The electrical conductivity of GB was
 282 determined between 10^{-11} to 10^{-15} S m⁻¹ by Griffiths (1999) and we chose 10^{-14} S m⁻¹. Due to
 283 the low conductivity of CT and GB, the second and third parts of the Eq. (7) are almost
 284 negligible. Coefficients m_1 , m_2 , and m_3 were calculated by the least square method. As
 285 mentioned before, the porosity is 40%, therefore, the solid fraction will be 60%. According to
 286 these characteristics, generalized Archie's law equations for both cells are (Eq. (8) and (9),
 287 respectively):

$$\text{CT+water: } \sigma_{mixed} = 0.0345\theta_w^{1.3} + 10^{-9}(0.4 - \theta_w)^{1.64} + 10^{-14}(0.6)^{2.34} , \quad (8)$$

$$\text{CO+SE: } \sigma_{mixed} = 0.0251\theta_e^{2.01} + 10^{-11}(0.4 - \theta_e)^{0.36} + 10^{-14}(0.6)^{1.23} , \quad (9)$$

288 According to our results, at the frequency of 1.46 Hz (see Fig. 5a,b), generalized Archie's
 289 law fits rather well to experimental data of resistivity in both cells (CT/water with $R^2=0.9845$
 290 and CO/SE with $R^2=0.9996$). After analyzing data, we found that the CT we used for this study
 291 has almost 10-15% of water inside. It became obvious when we left the bottle of pure CT for a
 292 month and surprisingly found that a layer of water appeared at the top of the CT inside the
 293 bottle. The other clue was that the measured resistivity of the medium saturated with 100% CT
 294 was less compared to the true resistivity of CT and GB. Assuming CT conductivity equals 10^{-3}
 295 S m^{-1} , better experimental data fitting (with $R^2=0.9945$) was obtained and the new equation
 296 of generalized Archie's law for CT/water is (Eq. (10)):

$$\sigma_{mixed} = 0.0345\theta_w^{1.8} + 10^{-3}(0.4 - \theta_w)^{5.2} + 10^{-14}(0.6)^{2.34} . \quad (10)$$

297 As shown in Fig. 2, the evolution of phase is regular for CT+water compared to the CO/SE
 298 cell where the phase variation was quite chaotic. This phenomenon can be attributed to the
 299 extremely high CO resistivity. In the CT/water cell, the “-phase” increased after injecting CT.

300 In Fig. 6 for CT/water, a linear fitting equation was suggested for experimental data of -
 301 phase at frequency 1.46 Hz:

$$-Phase \text{ (mrad)} = -0.3811 Sw + 45.21 \quad (11)$$

302 This linear equation gives us a good fitting with the coefficient of determination of $R^2=0.96$.
 303 The phase variation for different CO and SE saturations was not investigated in this work due
 304 to its irregular behavior. For instance, in Fig. 2d, the phase variation as a function of SE
 305 saturation at 1.46 Hz is oscillating and for each saturation, the variation is different. When
 306 $S_e=100\%$, and there is no CO inside the medium, the curve has a trend of variation like any
 307 conductive fluids like water with minimum error and the peak point at 187.5 Hz. In this figure,
 308 the maximum measurement error recorded at the minimum SE saturation ($S_e=4.5\%$) is what we

309 expected: the higher the CO saturation, the higher the measurement error.

310 4.2 Empirical models of relative permittivity

311 Some previous research focused on the mutual effects of fluid saturation and dielectric
312 properties of a mixture (e.g., Carcione *et al.*, 2003) for a saturated soil with non-aqueous phase
313 liquid (NAPL) and Santamarina and Fam (1997) for a contaminated soil with organic
314 contaminations (like benzene, xylene, toluene, tetrachloroethylene, trichloroethylene, and
315 chlorobenzene). Endres and Knight (1991) investigated the influence of fluid distribution on
316 the relative permittivity at the pore-scale, on a semi-saturated medium with a simple mixing
317 model. Endres and Redman (1993) have also presented a mixing model for contaminated soil.
318 They found that geometry and choice of the wetting phase could strongly affect the fluid
319 distribution and its relation to the dielectric properties of the medium. The complex refractive
320 index technique as a volumetric mixing model has also been used to interpret the dielectric
321 characteristics of a medium (Birchak *et al.*, 1974). Persson and Berndtsson (2002) used a
322 method to investigate the relation between the dielectric constant of a medium partially
323 saturated with sunflower seed oil. They carried out their measurement with TDR, which their
324 method can use for a saturated and partially saturated sandy porous medium. They validated a
325 simple model similar to the complete-refractive index method (CRIM) model. Lack of
326 consensus among the scientific communities in this subject led us to perform this study.

327 CRIM, as a simple and common mixing model in the dielectric study of multiphase systems
328 (e.g., Endres and Knight, 1992; Rodriguez and Abreu, 1990; Roth *et al.*, 1990 and Wharton *et*
329 *al.*, 1980), is one of the mixing models that does not have any geometry dependency. CRIM is
330 a simplified form of the Lichtnecker-Rother model (see in Mavko *et al.*, 1998; Guéguen and
331 Palciauskas, 1994) that simply uses one layer at ray limits and complex composites (Ajo-
332 Franklin *et al.*, 2004). The general CRIM equation is given by (Birchak *et al.*, 1974; Roth *et al.*,
333 1990; Endres and Knight, 1992):

$$\varepsilon^* = [\sum_{i=1}^N v_i \varepsilon_i^\alpha]^{1/\alpha}, \quad (12)$$

334 where ε^* is the permittivity of the mixture, ε_i is the permittivity of the i^{th} phase, v_i is the volume
 335 of the i^{th} phase and α is the empirical constant related to the geometry of the grains and their
 336 spatial distribution.

337 With the hypothesis of α equals 0.5 for a three-phase system (Ajo-Franklin *et al.*, 2004), the
 338 CRIM equation for a mixture of air, water, and solid phase is defined as (Rodriguez and Abreu,
 339 1990):

$$\sqrt{\varepsilon^*} = S_w \varphi \sqrt{\varepsilon_w^*} + (1 - S_w) \varphi \sqrt{\varepsilon_a} + (1 - \varphi) \sqrt{\varepsilon_g}, \quad (13)$$

340 where ε^* , ε_w^* , ε_a , and ε_g are respectively relative permittivity of saturated porous media, water,
 341 air, and solid phase, S_w is the water saturation and φ is the porosity.

342 Eq. (13) is a general form of the CRIM model for a multiphase porous media with two
 343 liquids. This equation for experimental setups of this study can be described by:

$$\varepsilon^* = (\theta_w \sqrt{\varepsilon_w^*} + \theta_{DNAPL} \sqrt{\varepsilon_{DNAPL}} + (1 - \varphi) \sqrt{\varepsilon_{GB}})^2, \quad (14)$$

344 where ε_{DNAPL} is the relative permittivity of DNAPL, ε_{GB} is the relative permittivity of GB, θ_w ,
 345 and θ_{DNAPL} are water and DNAPL contents, respectively. Fig. 4 shows how the relative
 346 permittivity changed as a function of water saturation. The CRIM model has a good fit with
 347 experimental data in both cases but for CO/SE an underestimation of the CRIM model with the
 348 same slope as the experimental setup is observed. Contrary to a previous study (Iravani *et al.*,
 349 2020), experimental data of relative permittivity were not normalized here due to uncertainty
 350 of the normalizing method, especially in higher temperatures. The relative permittivity of water,
 351 SE, and CO were measured in the laboratory (with the error less than $\pm 1\%$) and the relative
 352 permittivity of GB proposed by Louge and Opie (1990) was used to obtain CRIM equations for
 353 each setup.

$$\text{CT+water: } \varepsilon_{mixed} = (\varphi_{water} \sqrt{42.7} + \varphi_{CT} \sqrt{6.73} + (1 - 0.4) \sqrt{5.95})^2, \quad (15)$$

$$\text{CO+SE: } \varepsilon_{mixed} = (\varphi_{ethanol}\sqrt{34.5} + \varphi_{oil}\sqrt{3.1} + (1 - 0.4)\sqrt{5.95})^2 . \quad (16)$$

354 Fig. 4 shows that drainage in both saturated porous media decreased the relative permittivity
 355 because of the decreasing water/SE saturation that is due to greater relative permittivity of
 356 water/SE than CT/CO. During imbibition, because of replacing CO and CT in the porous media,
 357 the relative permittivity values increased.

358 4.3 About the second cycle

359 Laboratory measurements of the complex resistivity show that the first drainage and
 360 imbibition cycle follow some empirical models (see above). Change during the second cycle
 361 was disordered compared to the first cycle for CT+water. Because of hysteresis, since the curves
 362 of the capillary pressure and saturation for each drainage and imbibition for both cycles are
 363 different and our experimental data show different curves for each cycle due to hysteresis
 364 phenomena, that may justify these rather “unexpected” data for the second cycle. The other
 365 hypothesis for this phenomenon is mistakes in the saturation calculation after the first
 366 imbibition. After the first drainage and imbibition cycle, the only indicator for us to stop the
 367 imbibition was observing water/SE in the tube connected to the bottom of the cell. For all
 368 experiments, we considered the volume in the tube, but maybe the mixing of fluids in this tube
 369 or human errors in reporting this volume caused this mismatching. We believe that the precision
 370 and accuracy of our measurements are directly related to the existence of water (as a conductive
 371 fluid) in the porous media. Not all DNAPL can be removed from porous media after the first
 372 imbibition; therefore, that could be the reason for these electro-geophysical data in the second
 373 cycle.

374 In the first cycle, the phase does not show a well-defined variation trend for the CO/SE
 375 experiment, but a linear correlation was observed for phase variation in the CT/water cell. For
 376 CT/water, phase and water saturation had an inverse relationship demonstrating that decreasing
 377 water saturation led to increased phase. At higher frequency, the peak part of the phase spectra

378 moved to a lower frequency due to increased CT saturation.

379 5 Conclusion

380 We studied how complex resistivity and dielectric permittivity varied in two series of
381 experiments in a GB pack saturated with CT/water and CO/ SE. Results showed that SIP and
382 TDRs are practical methods and tools to measure the electrical complex resistivity and relative
383 permittivity of a saturated porous medium contaminated with CT and CO as a function of fluid
384 saturation. The evolution of the magnitude of the complex resistivity with saturation obeys the
385 generalized Archie's law. Observations showed that resistivity increased as water/SE
386 saturations decreased. For the experiment with CT and water, we observed a linear relationship
387 between $-$ phase and water saturation in accordance with the literature. The $-$ phase value
388 decreased when the water saturation increased.

389 Increasing in water and SE saturations caused an increase in the relative permittivity that
390 confirms the direct relationship between water/SE saturation and the relative permittivity of a
391 multiphase porous medium. According to these findings, the relative permittivity decreases and
392 increases during drainage and imbibition in a cycle, respectively. Like what we found for the
393 resistivity, the relative permittivity also obeys the CRIM model. The effects of chemical
394 interaction between contaminants and soil grains cannot be neglected in field conditions. This
395 means that extrapolating results obtained using GBs to the actual site remains an issue.
396 Moreover, the question of the upscaling of laboratory results to field scales is still open (i.e.
397 effect of resolution and detection power).

398 The correlations between saturation and permittivity and electrical complex resistivity
399 could serve as calibration relationship to interpret measurements at the field scale. It is worth
400 mentioning that the application of the laboratory results in the field surveys always has some
401 limitations. In the field experiments with extraneous variables/parameters, it is not easy to avoid
402 any external impact (i.e. temperature effect on resistivity,) on the measurement results. For

403 instance, laboratory measurement highlight that is possible to compute residual saturation from
404 resistivity and permittivity provided that the initial state is known but this is rarely the case in
405 the field.

406

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415

416 We also declare no conflict of interest.

417

418 Data are partly available on demand.

419

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607

608 **Figure captions**

609

610 Figure 1: Scheme of a) a vertical cross section of a cell and b) the experimental setup.

611 Figure 2: SIP response of resistivity and phase spectra of samples with (a and b) CT+water and
612 (c and d) CO+SE as a function of saturation change, for the first drainage.

613 Figure 3: Time series of SIP responses of cells with a and b) for resistivity and phase of
614 CT/water and c) resistivity of CO/SE at $f=1.46$ Hz.

615 Figure 4: Correlation curves of relative permittivity and (a) water saturation and (b) SE
616 saturation fitted by the CRIM model. Yellow point: beginning of the experiment (beginning of
617 the first drainage), red point: residual saturation, and black point: irreducible saturation.

618 Figure 5: Correlation curves of resistivity and (a) water saturation and (b) SE saturation fitted
619 by generalized Archie's law. Yellow point: beginning of the experiment (beginning of the first
620 drainage), red point: residual saturation, and black point: irreducible saturation.

621 Figure 6: Phase as a function of water saturation (with linear fitting) at 1.46 Hz.

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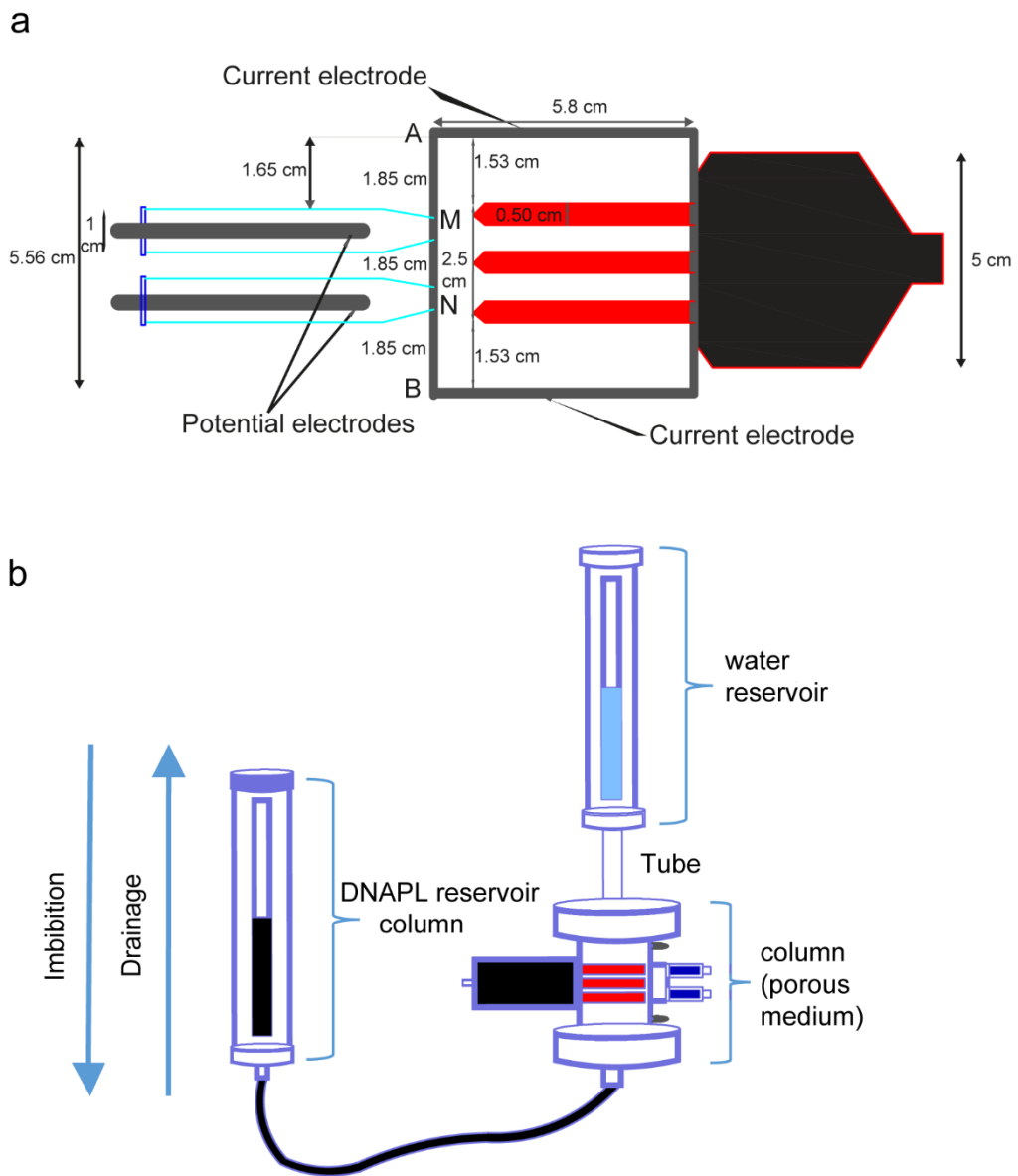
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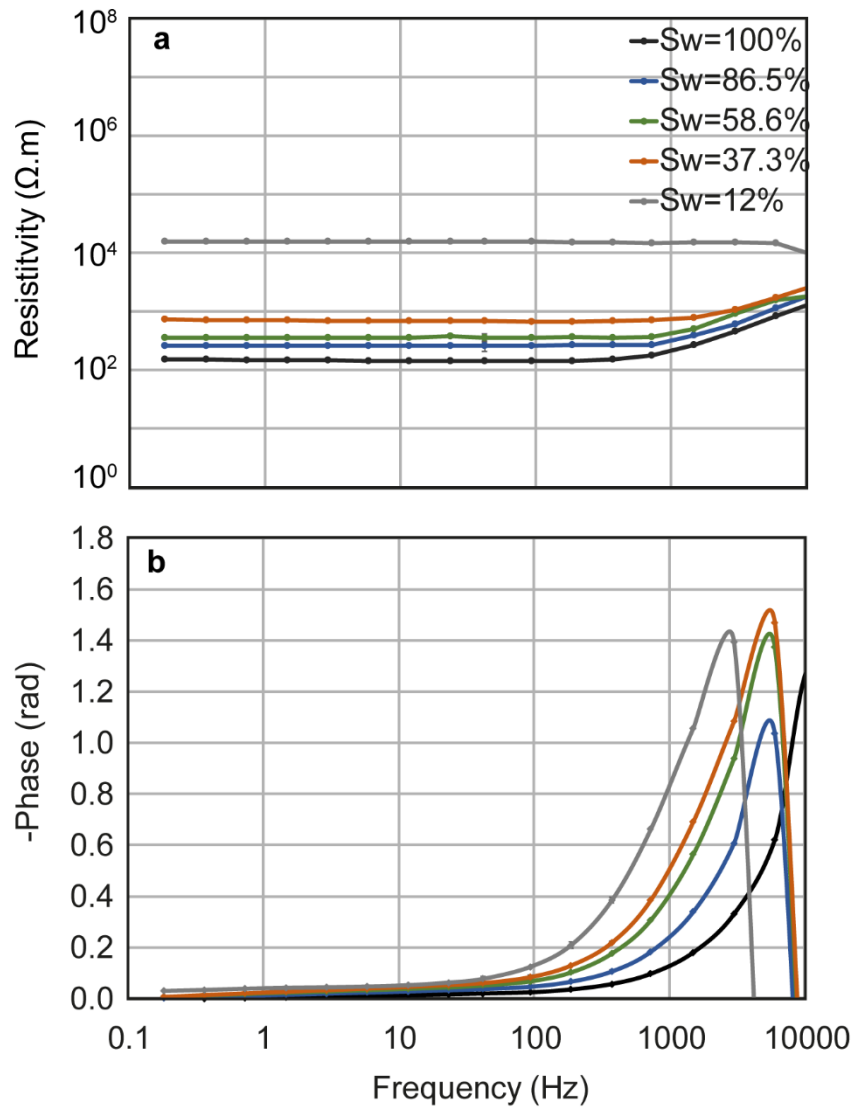
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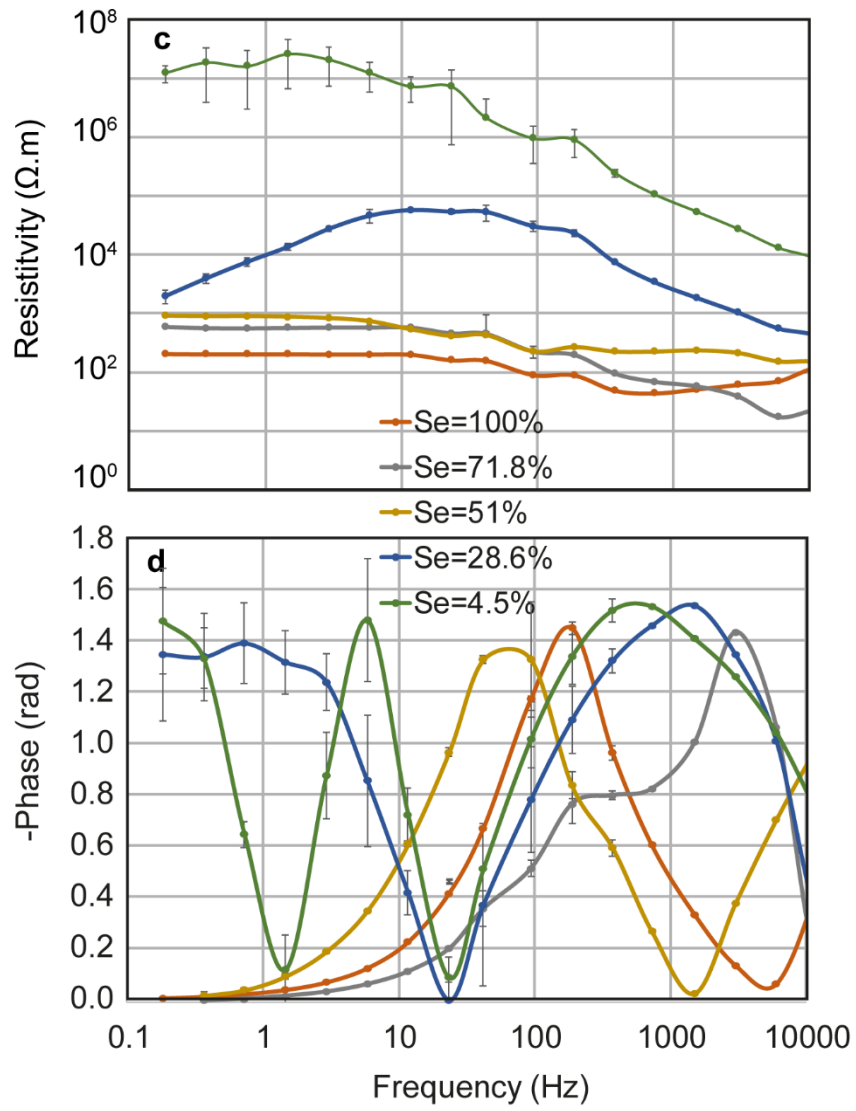
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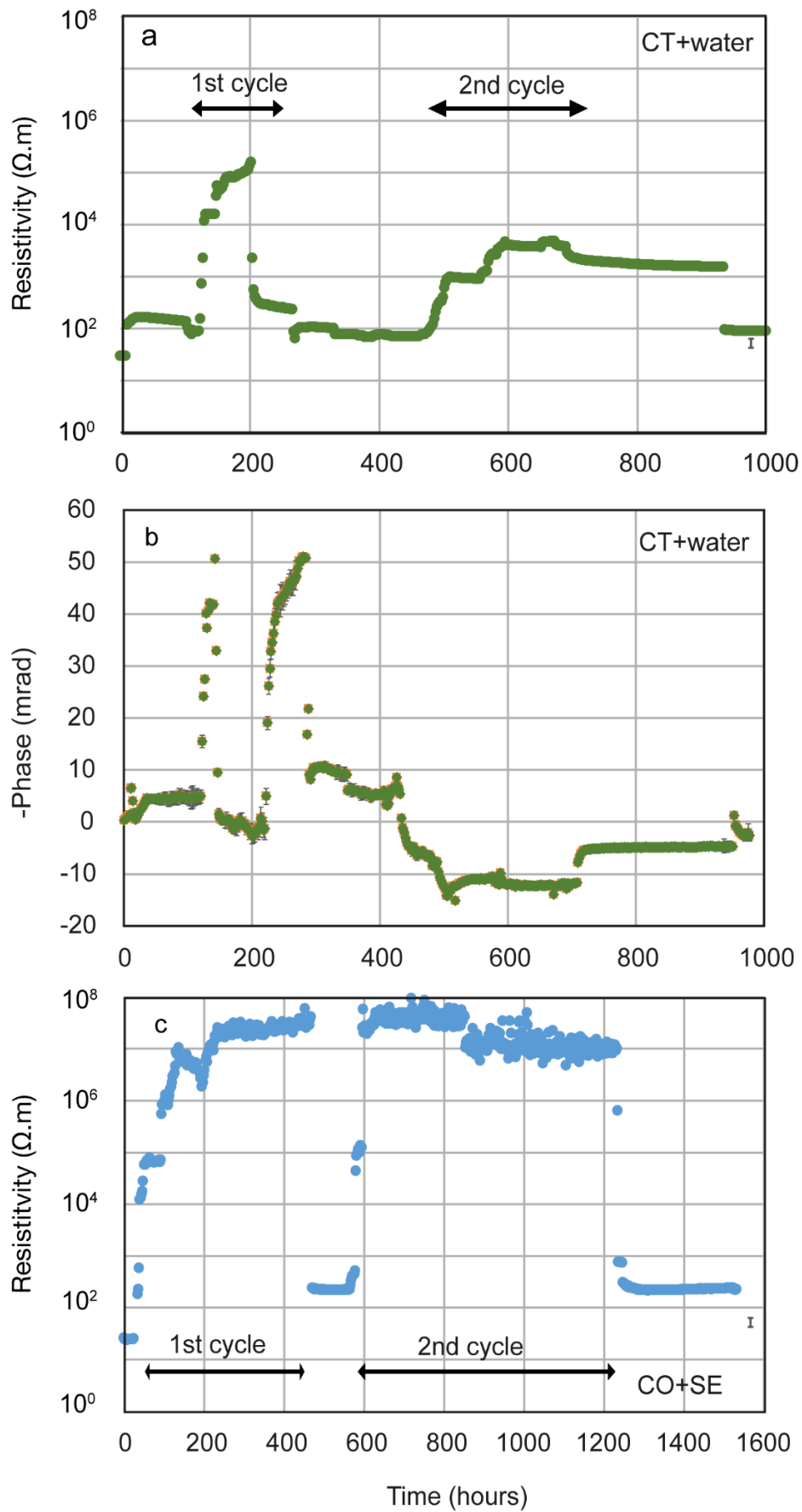


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641 **Figure 3**

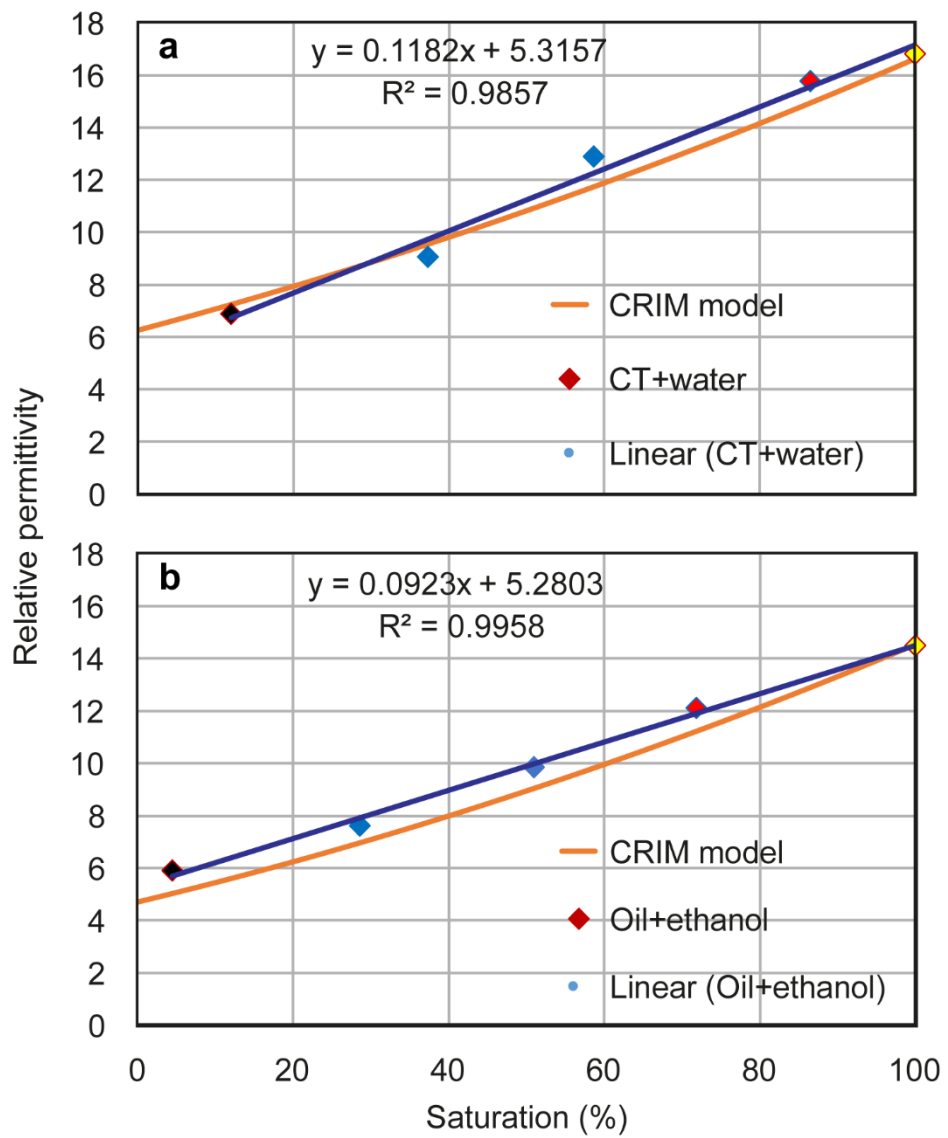


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Time (hours)

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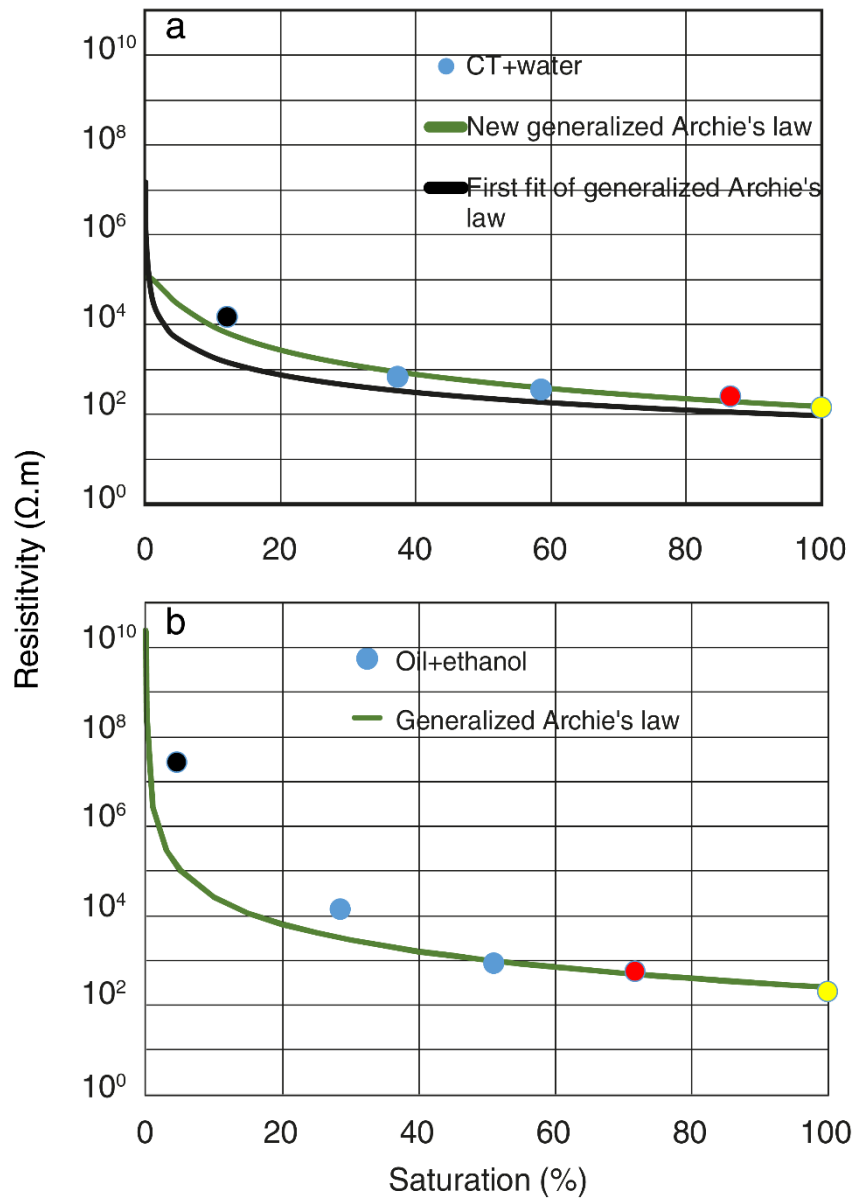
644 **Figure 4**



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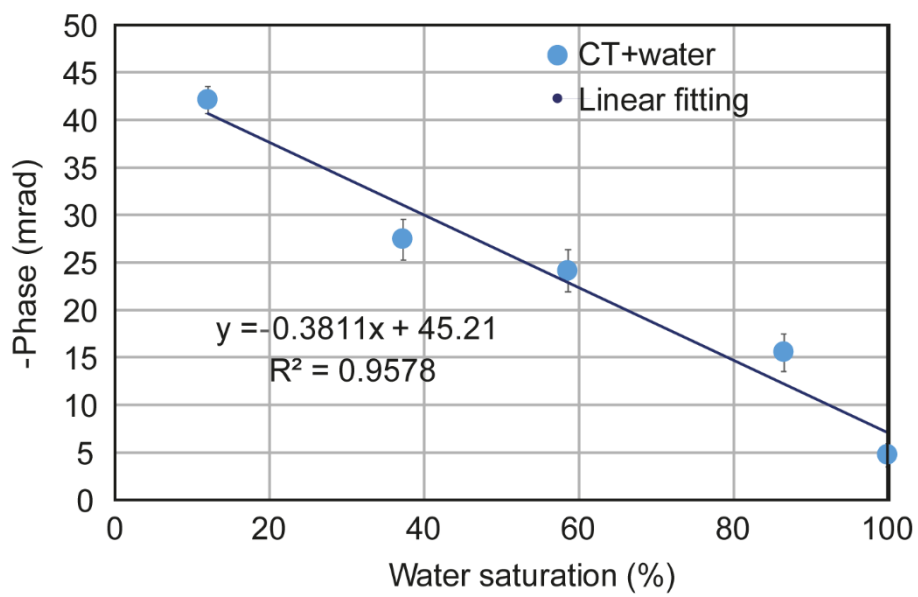
647 **Figure 5**



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650 **Figure 6**



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