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Non-invasive monitoring of water content and textural changes in clay-rocks using spectral induced polarization: A laboratory investigation

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ABSTRACT

Seven well-characterized clay-rocks have been taken from three test sites to perform spectral induced polarization (SIP) measurements during desiccation of these samples. These test sites include (1) the Tournemire site (IRSN) located in south of France, (2) The Bure test site (ANDRA) located in west of France, and (3) the Super-Sauze earthflow located in south western of France. We dried the samples at ambient temperature followed by heating between 65 °C and 105 °C. The quadrature conductivity, at very low-frequency, was able to discriminate between the loss of free water from the macropores and the loss of water in the micropores associated with textural changes. The calcite and quartz grain size distributions had a significant effect on the low-frequency spectrum. The inversion of our SIP data demonstrated that the generalized Cole–Cole model is an appropriate empirical and practical model for monitoring changes in water content of clay-rocks.

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1. Introduction

Clay-rocks are presently investigated by several industrial countries regarding their suitability to host radioactive waste disposals (Pusch, 2006). Because of their high-specific surface area, clay-rocks can absorb large amounts of ions (Leroy et al., 2007). In addition, they have low permeabilities, a property that is required to slow down the percolations of fluids around waste disposals. For the long-term safety assessment of radioactive waste disposals a good knowledge of the geology, transport, and sorption processes of water and potential contaminants as well as the thermo-hydro-mechanical behavior of the clay-rock is needed. Among the critical issues related to the long term safety assessment, the study of the so-called Excavation Damaged Zone (EDZ) is of a particular importance. The EDZ is the rock mass immediately surrounding a gallery in an underground facility. In the EDZ, the rock mass is disturbed by desiccation (Matray et al., 2006). Fractures are also associated with the redistribution of in situ stresses during the excavation (Bossart et al., 2002). These hydromechanical disturbances are responsible for a drastic change of permeability (Tsang et al., 2005).

The non-intrusive characterization of the EDZ around a gallery can be performed with geophysical methods like active seismic (Malmgren et al., 2007), passive seismic (Spies and Eisenbläterr, 2001), DCresistivity (Gibert et al., 2006), and spectral induced polarization (SIP) (Kruschwitz and Yaramanci, 2004). Passive seismic shows that the increase of acoustic emission is correlated to the clustering of microcracks in the EDZ. Active seismic methods lead to reliable results but they require the drilling of radial boreholes inducing additional damage to the rock mass. Recently, in situ investigations in the Mont Terri underground laboratory (Kruschwitz and Yaramanci, 2004) showed that the complex resistivity, measured at a frequency of 1 Hz, was able (a) to monitor quantitatively the water content changes in the EDZ and (b) to characterize the EDZ extension as well as the major fractures around the gallery. Despite the fact that spectral induced polarization has a long history (e.g., Ulrich and Slater, 2004; Binley et al., 2005; Seigel et al., 2007), its full potential to characterize clay-rocks is very recent (e.g., Cosenza et al., 2007, 2008). Cosenza et al. (2007) performed experiments on nearly water-saturated argillite samples from the Tournemire test site (South of France). This test site is an underground facility of the French Institute for Radioprotection and Nuclear Safety (IRSN) used to study the potential of clay-rocks for the isolation of nuclear wastes. Their results showed that SIP method is sensitive to both changes in the water content and to textural changes associated with shrinkage of the clay aggregates associated with the

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Fig. 1. (a) Geological cross section of the Tournemire. (b) Locations of the TM90 borehole and TM180 borehole (modified from Cosenza et al., 2007).

formation of microcracks. The classical Cole–Cole model cannot be used to fit the data obtained in the heating phase of desiccation of a clay-rock. A generalized formulation of this model was required.

The investigations reported by Cosenza et al. (2007) concerned only samples from a single test site. They provide also some limited physical insights on the SIP parameters since the mineralogy of the studied samples was not fully characterized. In order to overcome this drawback, the objectives of the present work are threefold. (1) We wish to confirm the experimental results obtained by Cosenza et al. (2007) using the Tournemire clay-rock and two other wellcharacterized clay-rocks. (2) The second goal is to formulate some physical hypotheses concerning the underlying physics associated with the SIP parameters on the basis of these additional measurements. (3) we want to test the ability of the generalized Cole–Cole model and the double Cole–Cole model, to represent the evolution of the SIP parameters during the evolution of the water content during desiccation.

2. Geological background and selected samples

Laboratory investigations have been performed with a set of seven samples taken from three different sites.

The Tournemire site is a test site to study the confining properties of argillites to the long-term isolation of nuclear wastes. It is located in southern France, in the western border of the Causses Mesozoic sedimentary basin (Fig. 1). Four samples were taken from the boreholes TM90 and TM180, drilled in 2005, perpendicularly to the wall of a tunnel crossing a Toarcian argillite formation (Fig. 1). Well

Table 1

Mineralogical composition of the clay mineral, CEC, and water content in initial state of the selected samples

		Tournemire samples				Super-Sauze sample	Bure samples	
		TM90-1260	TM90-1280	TM180-1288	TM180-1424		EST05-687	EST12-161
Carbonates (Calcite)		17.0%	17.2%	18.0%	18.0%	26.4%	20.0%	43.7%
Clay mineral fraction		~45%				~37%	~52%	~56%
Clay minerals in % of the clay mineral fraction	Illite/Smectite	36.8%	37.4%	38.1%	37.9%		15.6%	83.4%
	Kaolinite	29.1%	30.9%	24.7%	29.1%		17.2%	
	Illite	18.1%	19.6%	20.2%	16.8%	88.7%		13.1%
	Chlorite	16.0%	12.1%	17.0%	16.2%	11.3%	35.9%	3.5%
	smectite						31.3%	
Water content (wt.%)		3.33	3.42	3.09	3.49	10.97	3.18	6.0
CEC (cmol/kg)		9.62	9.53	10.10	10.60	6.36	18.3	15.40

Note: Carbonate contents and clay mineral fractions are calculated relative to the total mass.

TM90 is subhorizontal and parallel to the bedding in the Toarcian formation while Well TM180 is vertical and normal to the tunnel axis. The dimensions of the samples, TM90-1260, TM90-1280, TM180-1424, and TM180-1288, were 79.5 mm in diameter and 88–205 mm in length. They were located 12 m, in average, from the gallery wall, in a preserved zone outside the EDZ associated with the galleries and outside the influence of the ambient air. Samples were immediately taken after the completion of drilling and put in Al-coated plastic bag under confined N₂ atmosphere.

The mineralogical analyses of this Toarcian clay-rock show that clay minerals (kaolinite, illite, and interstratified illite–smectite) represent in average 40 mass% of the bulk-rock composition (Bonin, 1998). The coarse fraction contains ~20 wt.% silica and carbonates form 15 wt.% of the bulk-rock composition. The cation exchange capacity per unit mass of rock (CEC), the cation exchange capacity per unit pore volume (Q_v), and the mineral composition of the clay minerals obtained by X-ray diffraction of TM90-1260 and TM90-1280 are given in Table 1. The cation exchange capacities were determined by destructive analytical technique of the cobaltihexamine exchange (Ciesielski and Sterckeman, 1997).

The Bure underground research laboratory is located in the Paris Basin in the East of France (Fig. 2). This test site is presently studied by "Agence Nationale de Gestion des Déchets Radioactifs" (ANDRA), in France, to determine the feasibility of a deep repository of radioactive wastes in the Callovo-Oxfordian clay-rock formation at a depth of about 400–500 m. Two samples were taken from two different boreholes EST212 (sample EST12-161, at a depth of 464.19 m) and EST205 (sample EST05-687, at a depth of 489.51 m) (Fig. 2). The samples EST12-161 and EST05-687 measure 100 and 150 mm in length and 60 and 100 mm in diameter, respectively. These samples were immediately taken after the completion of drilling and put in a sealing cell. The EST05-687 sample was stored in a resin after its arrival in the laboratory. The low value of the water content of the EST05-687, in comparison with that of sample EST12-161, suggests that this sample had lost a significant part of its initial pore water (Table 1). The CEC and the mineral composition of these two samples are given in Table 1. The typical distributions of pore-throat diameters of the Bure site clay-rocks is illustrated in Fig. 3.

The last site is the Super-Sauze site. This site corresponds to an earthflow developed in the Callovo-Oxfordian Black Marls in the Barcelonnette Basin (Alpes-de-Haute-Provence, Southern France) (Schmutz, 2000). The coarse fraction contains quartz (about 30 wt.%) and carbonates (about 30 wt.%) (see the mineral composition in Table 1). The porosity is in the range of 17 to 26%. Percussion drillings in dry condition have been carried out from the surface in order to take a representative sample of this material. The extracted core sample measures 600 mm in length and 50 mm in diameter. This sample was carefully closed in a tight tube sampler. In the laboratory, a sample of 160 mm in length was prepared by cutting slowly and directly the tight tube sampler in order to perform the low-frequency electrical measurements immediately afterwards.

3. Experimental procedure

Following the experimental procedure described by Cosenza et al. (2007), the samples were first dried at ambient air (relative humidity



Fig. 2. Location of boreholes drilled by ANDRA (modified from Trouiller, 2006).



Fig. 3. Typical distributions of pore-throat diameters (Borehole EST205) (modified from Yven et al., 2007).

and temperature equal to 40% and 25 °C in average, respectively) until the mass remained constant (desaturation phase). In the second step (called the heating phase below) the same samples were heated successively at 70 °C, 80 °C, 90 °C, and 105 °C. Sample EST05-687 was heated to 75 °C, 85 °C, 95 °C, and 105 °C. Temperature was maintained constant during 24 h (48 h for sample EST05-687). The heating phase was started immediately after the desaturation phase. The mass of the samples at 105 °C allowed the determination of the water content during desaturation. Before and after each temperature change, the loss of mass and the complex resistivity spectrum were measured. The complex resistivity measurements were taken at least 5 h after removing the sample from the oven in order to reach thermal equilibrium.

SIP measurements were performed with the FUCHS-II apparatus starting at 12 kHz. *N* other decreasing frequencies were investigated from 12 kHz/2^N. Optical fibers were used to minimize electromagnetic cross-couplings between transmitter and receiver. The measured data were transferred to the base unit, where the apparent resistivity and the phase shift were determined. To reduce the signal-to-noise ratio, each spectra were repeated and added together 32 times in the frequency range [1.46–1500 Hz] and 24 times in the frequency range [0.18–0.73 Hz] and averaged. At each water content, at least two runs were performed.

To minimize electrode polarization (Vanhala and Soininen, 1995), measurements were performed with a four-electrode device using medical electrodes. The potential (or measuring) electrodes and the current (or source) electrodes are electrocardiogram (ECG) Ag/AgCl electrodes (Asept Co.) and thin carbon films (Valutrode[®] electrodes from Axelgaard Manufacturing Co.). Silver–silver chloride (Ag/AgCl) electrodes are widely used in SIP measurements (Vanhala and Soininen, 1995). The ECG Ag/AgCl electrodes consists of a small metallic round piece (10 mm in diameter) galvanized by silver and covered with a soft sponge imbibed by an AgCl gel. The circular carbon films (50 mm diameter, 1 mm thick) used in electrotherapy were covered with a conductive adhesive gel. It provides a good electrical contact with the sample (care was taken to avoid the entrapment of air bubbles between the electrodes and the rock samples).

The accuracy of the four-electrode device was validated using porous and non-polarizable rocks. Limestone samples, free of clay minerals and saturated with a highly-conductive brine (0.1 Ω m), were chosen for that purpose. No polarization was observed between 0.18 Hz and 12 kHz except for the highest frequency value of 12 kHz for which a small but significant phase shift was observed likely associated with an electromagnetic coupling/noise effect. The existence of this phase shift implies a small error of 1 mrad on the measurements for frequencies higher than 6 kHz. To estimate the phase error associated with the instrument, the phase was measured on pure resistors ranging from 1 Ω to 100 k Ω . We used the measured phase values, i.e., the respective deviation from zero, to calculate the



Fig. 4. Water content of the clay-rocks as a function of time. (a) Mass loss of the Tournemire samples, the Super-Sauze sample and the Bure sample EST12-161 as a function of time. (b) Mass loss of the Bure sample EST05-687 as a function of time.



Fig. 5. Real (a) and imaginary (b) part of the complex conductivity. Error bars are calculated from the amplitude and phase errors that are obtained by the SIP-FUCHS II instrument.

errors of the real and imaginary parts of conductivity. The maximum phase error measured for 100 k Ω at 1500 Hz was 5 mrads. This error decreased drastically and non-linearly with the frequency down to 1 mrad at 0.18 Hz. The instrumental errors were larger at 10–1500 Hz and much lower at 0.18–10 Hz.

The major effects of the heating phase are (1) to remove a significant part of the bound water in the microporosity and (2) to generate textural changes associated with the shrinkage of the clay aggregates inducing microcracking in the samples (see Fig. 1 of Gasc-Barbier and Tessier, 2007). Microcracks are created in response to two processes. Heating induces local thermal stresses in the different minerals and the interstitial liquid because of the different thermal expansion coefficients. In turn, these thermal stresses induce local thermal strain incompatibilities and hence microcracks. In addition, cooling of the samples after removal from the oven generates a high tensile stress, which may exceed the low tensile strength of the argillaceous rock (Bérest and Weber, 1988). The average uniaxial tensile strength of Callovo-Oxfordian argillites is 2.6 MPa (Ghoreychi, 1999). Contrary to the heating phase, the desaturation phase involves mainly the water removal from the macropores and hence induces only moderate textural changes. Fig. 4a and b show the water content during desaturation and heating. At the end of the desaturation phase, the samples contained 2 mass% of water (relative humidity about 40%).

4. SIP measurements near saturation

The low-frequency resistivity can be expressed in terms of a complex conductivity σ^* . Polarization is primarily included in the imaginary part σ'' whereas conduction is related to the real part σ' (Ulrich and Slater, 2004). The measured complex resistivity ($\rho^*=1/\sigma^*$) and the measured phase ϕ , are not direct measurements of the polarization of the material. Fig. 5a and b show the real and imaginary parts of the complex conductivity in the initial state prior to desaturation. In Fig. 5a, spectra of σ' are nearly frequency independent. The higher conductivity (~0.08 S/m) is observed for the most porous clay-rock, the Super-Sauze sample. The smallest conductivity (~0.005 S/m) for the Tournemire sample TM180-1288. The lowest value of 0.005 S/m is associated with the anisotropy of the Tournemire clay-rock (Cosenza et al., 2007) perpendicularly to the bedding.

The spectra of the imaginary part of the complex conductivity of the Tournemire TM180-1288-Sample and the Super-Sauze samples are nearly linear in a log–log plot. Those of the Bure samples and Tournemire sample TM180-1424 show a flat maximum between 10^{-1} and 10^{2} Hz corresponding to relaxation times τ from 0.002 s to 2 s. The $\sigma^{"}$ spectra do not show significant correlation with the CEC values (Table 1).



Fig. 6. Microscopy electronic photo of EST05-687 perpendicular to the stratification surface (Jorand, 2006).



Fig. 7. The relaxation frequency estimated from the Schwartz's model as a function of the grain size. $D = to 8.10^{-11} \text{ m}^2/\text{s}$ (Boisson et al., 2001). A change between 5 and 10 μ m can change the maximum phase shift from critical frequency from 1 Hz to 0.3 Hz.



Fig. 8. (a) Real and (b) imaginary parts of conductivity at 1.5 kHz as a function of water content. Error bars are calculated from the amplitude and phase measurements obtained on pure resistors corresponding to the sample resistances.

A maximum of σ'' is usually associated with a characteristic grain size (Klein and Sill, 1982) or pore size (Scott and Barker, 2003). Leroy et al. (2008) measured the low-frequency conductivity response of water-saturated packs of glass beads. At low-frequencies the electrochemical polarization is determined from the grain size distribution of the porous material. Leroy et al. (2008) observed two peaks corresponding to the grain size and to the roughness of the grains. In our case, the flat maxima of the Bure samples are probably related to the size of the non-clayey grains. Indeed, the microscopic observation indicated that grains of quartz and calcite of about 20 µm (Fig. 6). These coarse grains are surrounded by clay mineral particles. A rough estimation of the main relaxation times au was obtained from the equation: $\tau = R^2/2D$ (Schwarz, 1962; Leroy et al., 2008) where *R* mean radius of the grains, and D the diffusion coefficient of ions in the interstitial water. If $R = 10 \,\mu\text{m}$ and $D = 8 \times 10^{-11} \,\text{m}^2/\text{s}$ (see Boisson et al., 2001), τ =0.625 s. The corresponding relaxation frequency is about 0.3 Hz. Since the relaxation frequency is very sensitive to small changes of the grain size (Fig. 7), this order of magnitude is consistent with the values of the flat maxima in Fig. 5b.

5. Effect of drying on SIP measurements

The low-frequency conductivity increased with the water content (Figs. 8a and 9a). The salt concentration of the remaining pore water during desaturation has a low impact on the conductivity response. Anisotropy influences significantly the electrical properties. The samples obtained in the horizontal boreholes (TM90-1260 and TM90-1280) show higher conductivity in comparison to those extracted from the vertical boreholes (TM180-1424, TM180-1288, EST05-687, EST12-161). The conductivity measured parallel and normal to the stratification differed by one order of magnitude.

Considering the desaturation phase, the real conductivity of samples of the horizontal boreholes (TM90 samples) was 3 to 5 times larger than those of the vertical boreholes (TM180 and EST samples). Among the samples from the vertical boreholes, EST05-687 and EST12-161 show the highest real conductivities due to the higher water content and their higher CEC (Table 1). During desaturation, small differences were noticed between the conductivity at 0.18 and 1.5 kHz. The real conductivity spectrum is nearly flat for this frequency



Fig. 9. (a) Real and (b) imaginary parts of conductivity at 0.18 Hz as a function of water content. Error bars as in Fig. 8.



Fig. 10. Experimental and modelled resistivity spectra obtained during (a) desaturation (modelled by the double Cole–Cole model), (b) heating (modelled by the generalized Cole–Cole model) in an Argand diagram. The real and imaginary parts in heating phase are normalized by the greatest value taken in each spectrum.

range. Thus, removal of the free water from the macropores does not significantly influence the real conductivity spectrum at low frequencies. When a saturated rock sample is dried at ambient temperature conditions, it will release water from the largest pores (following the Jurin's law, e.g., Baver et al., 1972). The process continues until equilibrium is reached: the capillary forces existing at the air–water–solid interface are balanced by the gravity forces. During heating, the real conductivity decreases by more than two orders of magnitude. The spectrum between 0.18 and 1.5 kHz was strongly distorted because of the desorption of a significant part of bound water in the micropores and textural changes associated with the shrinkage of the clay particles.

Textural changes of the clay minerals due at high suction pressure and temperature have been investigated on clay minerals rock samples in three experimental studies. Gasc-Barbier and Tessier (2007) performed wetting-drying tests on small samples from the Bure site at the relative humidities of (RH) range of 20–100%. Using mercury intrusion porosimetry on wet samples, they showed that strong drying caused microcracks generated by the shrinkage of the clay minerals. Confocal microcopy observations has confirmed that these microcracks were mainly localized at the boundary between the silica or calcite grains and the clay minerals (Fig. 1 of Gasc-Barbier and Tessier, 2007). Montes et al. (2004) obtained similar results using ESEM: the hydration and/or dehydration (until RH=2.5%) of swelling clay minerals in Bure argillite sample lead to strong structural changes including formation of cracks at the surface of the sample, aggregation/disaggregation of the particles, and opening/closing of pores and/ or cracks. Bounenni (2002) dehydrated three argillites samples from the Bure Site in a microwave oven which led to temperatures up to 134 °C and also induced microcracks.

The quadrature conductivity σ'' versus the water content (Figs. 8b and 9b) revealed that the real and imaginary conductivity decreased continuously with the water content. Figs. 8b and 9b showed similar trends between the quadrature conductivity and the in-phase conductivity except for the quadrature conductivity at low-frequency (0.18 Hz). During desaturation σ'' did not change too much as the water content decreased. As the heating begins, σ'' decreased strongly. Consequently, σ'' seems to be a good indicator at very low-frequency



Fig. 11. Amplitude (a) and phase (b) spectra obtained during the desaturation phase (modelled by the double Cole-Cole model) for the Bure site samples.



Fig. 12. Amplitude (a) and phase (b) spectra obtained during the heating phase (modelled by the generalized Cole–Cole model) for the Bure site samples.

(0.18 Hz) to discriminate the loss of free water from the macropores and the loss of water from the micropores associated with textural changes.

6. Modeling

The generalized form of the Cole-Cole model (Vanhala, 1997) is:

$$\rho^*(\omega) = \rho_0 \left\{ 1 - m \left[1 - \frac{1}{\left(1 + (i\omega\tau)^c \right)^a} \right] \right\},\tag{1}$$

where ρ_0 is the direct-current (DC) resistivity (Ω m), *m* is the chargeability (dimensionless), *c* and *a* are two Cole–Cole exponents, τ is a relaxation time (s); ω is the angular frequency, and $i^2 = -1$. With *a*=1, Eq. (1) reduces to the classical Cole–Cole model. The Cole–Cole phase spectrum is symmetrical and *c* gives the slope of the phase spectrum in a double logarithmic plot (Major and Silic, 1981). Eq. (1) with *c*=1 defines the Cole–Davidson model characterized by an

asymmetrical circular arc in an Argand diagram (Davidson and Cole, 1950). Pelton et al. (1978) defined the double Cole–Cole model by:

$$\rho^{*}(\omega) = \rho_{0} \left\{ 1 - m_{1} \left[1 - \frac{1}{1 + (i\omega\tau_{1})^{c_{1}}} \right] \right\} \left\{ 1 - m_{2} \left[1 - \frac{1}{1 + (i\omega\tau_{2})^{c_{2}}} \right] \right\},$$
(2)

where ρ_0 is the DC resistivity (in Ω m), m_1 and m_2 are chargeabilities, c_1 and c_2 are Cole–Cole exponents (dimensionless), τ_1 and τ_2 are time constants (in s), and ω is the angular frequency. The index 1 and 2 refer to lower and higher frequency dispersions, respectively. The first Cole–Cole model was traditionally used to represent the low-frequency dispersion and the other to represent electromagnetic (EM) coupling. However, the formulation can also be used to model the influence of the superposition of different grain or pore size distributions.

The SIP spectra were inverted using the non-linear iterative leastsquare method proposed by Tarantola and Valette (1982) using the generalized Cole–Cole and the double Cole–Cole models given above. In the inversion process, the modified Cole–Cole parameters, $Log\rho_0$ and $Log \tau$ were considered. The input data used in the inversion



Fig. 13. Time constants of the Cole–Cole model obtained by inversion of experimental data as a function of the water content. (a) Inverted time constant, τ_1 , obtained from the double Cole–Cole model for desaturation. τ_1 refers to the lower frequency part of the spectrum. (b) Time constants, τ_2 , for desaturation obtained from the same the double Cole–Cole inversion but for the induced polarization diffusion in the higher part of the spectrum. Generalized Cole–Cole time constants are obtained from heating phase data.



Fig. 14. Chargeability (a) and normalized chargeability (b) of Cole–Cole model obtained by inversion of experimental data as a function of water content. Inverted chargeabilities, *m*₂, are obtained from the double Cole–Cole model for desaturation phase and from generalized Cole–Cole model for heating phase. *m*₂ refers to the frequencies of higher part of the double Cole–Cole model phase spectrum.

process were the real and imaginary parts of complex resistivity ρ^* , calculated from the amplitude and phase values measured at different frequencies. We used the following Root Mean Square (RMS) error as the criterion to quantify the quality of the fit:

RMS =
$$\sqrt{\frac{\sum_{i=1}^{N} (\rho'_{ci} - \rho'_{di})^2 + \sum_{i=1}^{N} (\rho''_{ci} - \rho''_{di})^2}{N}},$$
 (3)

where ρ'_{ci} and ρ''_{ci} are the real and imaginary parts of the complex resistivity ρ^* from the model and ρ'_{di} and ρ''_{di} are the real and imaginary parts of the measured complex resistivity, and *N* is the number of frequencies used to obtain a complex resistivity spectrum.

In the desaturation phase, the inversion of EST05-687 and EST12-161 data shows two distinct dispersions (Fig. 10a). In an Argand diagram, the first dispersion is in the frequency range from 0.18 to 94 Hz (takes the form of a semicircle) and the second dispersion between 94 Hz and 1.5 kHz. The double Cole-Cole formulation provides a better fit of the data by comparison with the generalized Cole-Cole model. Fig. 10b illustrates the Argand diagram of the data inversions corresponding to the heating phase. Among the two considered models, the better agreement with the SIP spectra is obtained with the generalized Cole-Cole model. This model reproduces very well the specific asymmetrical arcs observed in the Argand diagram of the complex resistivity. In the heating phase (water content <0.33 in Fig. 10b), one dispersion was observed in the whole frequency range. When the major part of bound water around the quartz and calcite grains was eliminated, the dispersion at lower frequencies (observed in desaturation phase) also disappeared.

Figs. 11 and 12 show the amplitude and the phase spectra during the desaturation and heating phases for the two Bure site samples. Contrary to desaturation phase, the amplitude during the heating phase (Fig. 11a) is strongly dependent on the frequency. A maximum resistivity of 300 k Ω is reached in the low part of the EST12-161 spectrum. The models fit well the observed amplitudes. The agreement between the models and the phase data is still good (Figs. 11b and 12b), but the phase exhibits a more complex behaviour that is difficult to quantify with the conventional empirical models described above.

Figs. 13 and 14 show the relaxation times τ_1 and τ_2 and the chargeabilities as a function of the water content. The double Cole–Cole model was used to model the desaturation phase (see parameters τ_1 and τ_2 in Fig. 13a and b, respectively) and the generalized Cole–Cole

model to model the heating phase (Fig. 13b). The inverted two relaxation times have distinct relationship to the water content: τ_1 was nearly constant during desaturation (Fig. 13a) while the second relaxation time (Fig. 13b) was very sensitive to changes of the water content. Although two different models (the double Cole–Cole model and the generalized Cole–Cole model) were used, the changes of τ_2 during drying (desaturation and heating) showed a remarkable continuity (Fig. 13b). Since τ_2 increases strongly (by three orders of magnitude) during heating, the physical processes involved may be related to textural changes (i.e., microcracks) or/and polarization process associated with the bound water in the micropores.

Fig. 14a shows the inverted chargeabilities during desaturation and heating. The chargeabilities m_1 and m_2 refer to the lower and higher part of the spectra, respectively. The chargeability plotted for the heating phase (Fig. 14a) is obtained from the generalized Cole-Cole model. During the inversion, m_2 of Tournemire site samples (samples TM90-1280 and TM90-1260) were close to 1. Consequently, in the following and only for the Tournemire site samples, m_2 was taken as a constant equal to 1 during desaturation. Considering the samples from Bures (samples EST05-687 and EST05-161), the inverted chargeabilities do not show any significant change during the desiccation and heating. The normalized chargeability is obtained by dividing the chargeability by the DC resistivity $m_N = m/\rho_0$ (Fig. 14b). It is used to separate the effects of ohmic conduction from polarization (Lesmes and Frye, 2001; Slater and Lesmes, 2002). The normalized chargeability increases with the water content (like the imaginary part of the complex conductivity, see also Ulrich and Slater, 2004, for sands).

7. Conclusions

SIP measurements were conducted on different types of wellcharacterized clay-rocks from Tournemire and Bure test sites and from the Super-Sauze earthflow. The SIP spectra were recorded during desaturation at ambient air followed by heating to 105 °C. The quadrature conductivity σ'' is a good indicator, at very low-frequency (0.18 Hz), of the loss of free water from the macropores and the micropores. The loss of water in the micropores was associated with textural changes. The amplitude of the polarization processes at very low-frequencies was controlled mainly by the clay minerals and not by the macropores. The non-clayey grains (calcite and quartz) had a significant effect on the low-frequency spectrum. The generalized Cole–Cole model is the most appropriate phenomenological model to monitor changes in the water content of clay-rocks at low saturation.

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