MEMBRANE POLARIZATION BY CONSTRICTIVITY OF PORES: ITS EFFECTS ON DC AND TEM GEO-ELECTROMAGNETIC MEASUREMENTS

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Introduction. It is well known that the induced polarization (IP) phenomenon is due to at least four known mechanisms, i.e. the so-called electrode polarization, electro-osmosis polarization, Maxwell-Wagner effect, although very weak, and membrane polarization due to presence of clay minerals in rock pores and/or by constrictivity, i.e. the polarization effect is due to change in pore size (Schön, 1996). Of course freshwater saturated pores is essential for the occurrence of the IP phenomena, on the contrary, increased concentration of dissolved salts affects negatively membrane polarization until its complete nullification at elevated concentrations.

In general, traditional practice for IP data collection is done by commercial geo-resistivity meters while acquiring subsurface resistance data, for example by means of the Electrical Resistivity Tomography (ERT: Barker, 1989) technique. In this case, the IP information is measured in Time-domain by observing the IP decay curve over one or several time windows after current switch-off and the measured quantity determines the value of the chargeability (M).

The chargeability M provides additional independent information, which in many circumstances helps to better understand the subsurface. For instance, it is used, since its discovery, for metallic minerals explorations, nowadays, the method is used for solving environmental issues related to the presence of pollutants in the subsurface, both of inorganic (e.g. Abu-Zeid and Santarato, 2004) and of organic origin (see e.g. the review paper by Atekwana and Atekwana, 2010).

Throughout the seventies of the past century, together with the increasing use of the Transient (or Time-Domain) Electro-Magnetic (TEM or TDEM) technique, also, for mineral exploration, geophysicists become aware of the fact that IP may affect the observed decay curve observed after current switch-off of the inducing magnetic field (Sidorov and Yakhin, 1978; Walker and Kawasaki, 1988). Their presence was dealt with by developing specific algorithms being implemented in computer codes to both model this behavior (Ingeman-Nielsen and Baumgartner, 2006) and consequently to remove it (Antonov and Shein, 2008).

Nevertheless, geo-electromagnetic community agrees that the IP phenomenon is “linear”, i.e. not dependent neither on intensity nor on charging time length.

Recently, while conducting intensive resistivity and chargeability measurements on freshwater saturated samples of different rock types, Zadorozhnaya, discovered that both chargeability and resistivity depend on time and intensity of the polarizing direct current (Zadorozhnaya, 2008; Zadorozhnaya and Maré, 2011), although at values that are generally above charging times and current densities which are commonly used in the field. In particular, she observed that chargeability always decreases with increasing current intensity, while resistivity can assume both behaviors. The effect of increasing time of current feeding increased both resistivity and chargeability values. The observed non-linearity of chargeability increase with time is known to be a common occurrence and can be easily understood; however, the remaining non-linear phenomena were quite surprising. That IP could be, under specific conditions, a non-linear phenomenon due to current increase, was a circumstance of which, in early times of the method, scientists were aware of (Bleil, 1953), although the reasons were not investigated further. Few decades later, one of the authors of this paper was involved in laboratory IP measurements on samples of loose sediments (Iliceto *et al.*, 1982), where it was claimed that all the measurements were performed in the range of supplied currents that ensured the linear behavior.

To our knowledge, nobody has published field observations related to the observed remaining non-linear phenomena, in particular, on the dependence of resistivity on charging time and

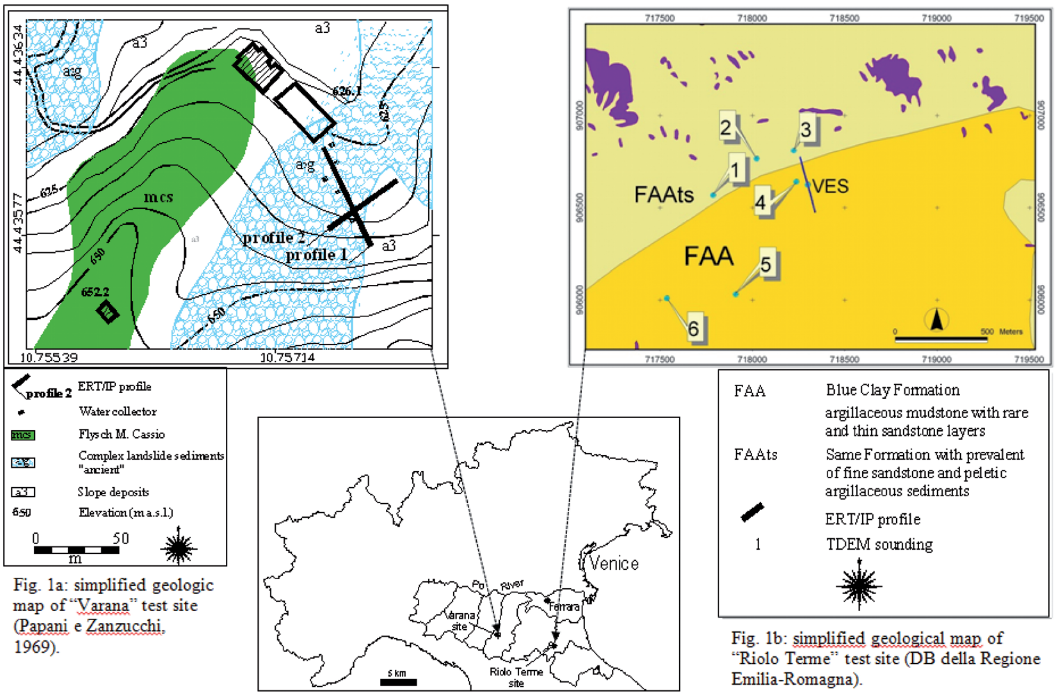

Fig. 1a: simplified geologic map of "Varana" test site (Papani e Zanzucchi, 1969).

Fig. 1b: simplified geological map of "Riolo Terme" test site (DB della Regione Emilia-Romagna).

Fig. 1 – Simplified geological maps of the two test sites tackled in the text.

intensity of the injected current. A reason could be the fact that its specific behavior is observed only in the lab where employed current densities are orders of magnitude greater than those normally available in field measurements, mainly for safety and portability of current sources. In addition, the non-linearity dependence on charging time was observed using longer charging times than those normally used in field resistivity surveys.

In the above-cited papers, Zadorozhnaya published a physical-mathematical model which accounts for the observed non-linear behavior in the tested rock samples. She showed that the non-linearity can be explained by a specific solution of the equations governing the phenomenon of membrane polarization invoking the concept of constrictivity of pores. In her solution, the observed non-linearity depends on the pore-size spectrum, which, if extended successfully to field-scale surveys, shall gain relevance especially for hydrogeological studies (i.e. to be able to indirectly measure porosity from the analysis of the non-linear behavior of specific geoelectric surveys).

In this paper, we show that the non-linearity can be observed in the field too, provided a suitable setup of field measurements. Some hints to the (partly) published model by Zadorozhnaya shall be given in the following.

Direct current experiment. Laboratory studies of Zadorozhnaya were focused on clay-free samples so as to avoid any IP contribution due to the well-known mechanism of membrane polarization. Therefore, our field experiment was carefully planned, firstly by selecting a site where a clay-free, saturated aquifer of very shallow depth (i.e. nearly outcropping), so that measurements certainly involve it and the reduced investigation depth allows that current densities, available from a common, portable geo-resistivity meter, could approach the lab conditions. The test site was found in the northern Apennines, where fresh potable water is exploited from a sandstone aquifer. This site is located in the municipal territory of Serramazzoni (Modena Province, N. Italy, Fig. 1a). The acquiclude layer is represented by fine-grained sediments (clay) underlying the sandstone rocks. The hydrogeological unit belongs to the flysch

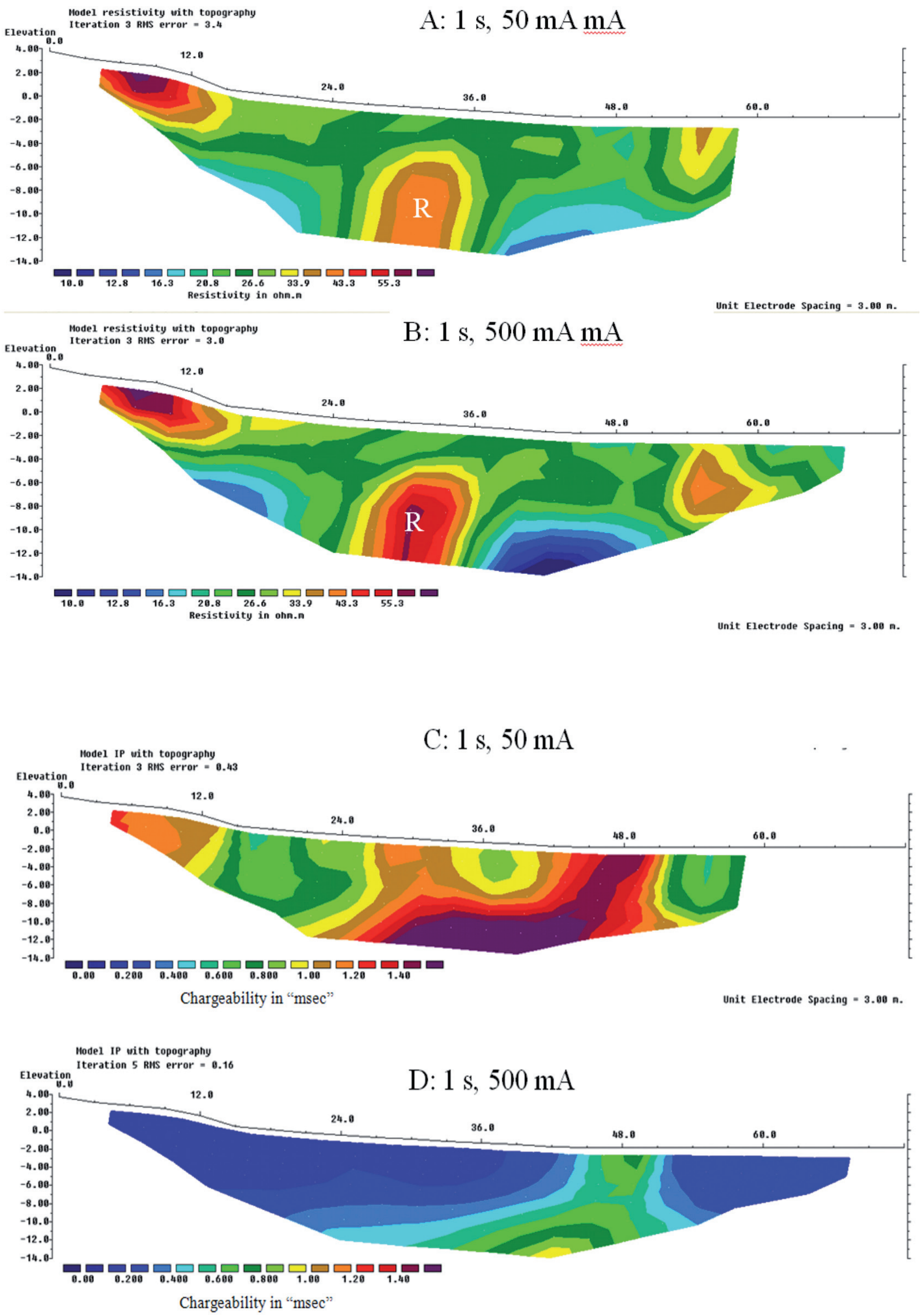

Fig. 2 – 2D inversion resistivity sections obtained using 50 mA (A) and 500 mA of injected current (A,B) and the corresponding chargeability ones obtained using 50 mA (C) and 500 mA (D).

formation (mcs) of Monte Cassin [Campanian-Maastrichtian epoch of the Upper cretaceous period, Papani and Zanzucchi (1969)]. There, an experiment of electrical resistivity and time-domain IP tomography was conducted, using a commercial geo-resistivity meter capable of transmitting controlled current intensities, in the range of 1 mA to 1 A (ABEM SAS4000/ES464, Sweden). To this end, a profile of 72 m long and 3 m electrode spacing was laid out. Along this profile two data subsequent datasets were acquired using the Wenner-Schlumberger electrode array and two current intensities: 50 mA and 500 mA.

The 2D inversion sections of both resistivity and chargeability distributions were obtained using the commercial software RES2DINV^{tm}, based on the Gauss-Newton inversion method (Loke and Barker, 1996) (Figs. 2a to 2d). While chargeability strongly decreases with increased current intensity, some increase of resistivity is observed in those more resistive volumes (the red color resistivity body indicated with the letter “R” in Figs. 2a and 2b) that, given the local geology and locations of water collectors, certainly correspond to the sandstone aquifer. The authors are glad to provide a copy of this data set to who is interested.

The TEM experiment. In the framework of the EU financed project “Cities on Power” (www.citiesonpower.eu, report 3.4.5) where a number of TEM measurements were performed at and around the RioloTerme town (Province of Ravenna, Northern Italy). The aim of the survey was to aid in the reconstruction of the subsurface conceptual model for hydrogeological assessment of the test site. In this site, a pilot low-enthalpy geothermal plant was planned to be installed in a 100 m deep borehole. The subsurface geology, as given by the simplified geological map and by the visual inspection of the cutting, consists mainly of clayey layers, with some inclusions of sandstone layers and blocks; the local outcropping formations together with the locations of TEM soundings are shown in Fig. 1b. As can be seen, three soundings (1, 2 and 3) were performed over the FAAts geological formation, composed mainly of fine sandstone and pelitic argillaceous sediments, while the remaining 4, 5 and 6 where located on sediments belonging to the FAA formation: a Blue Clay formation composed of gray argillaceous mudstones with rare and thin sandstone layers. The TEM equipment model GDP-3224 by Zonge Ltd was used for data acquisition.

Multi-Function receiver was used to collect the data at the center of a square loop of 50x50 m dimensions. Data were acquired at three different repeating time cycles, at frequencies of respectively 4, 8 and 32 Hz, to get both the maximum resolution in the shallow surface and the maximum investigation depth in accordance with the loop dimensions.

Tab. 1 - 1D petrophysical models of soundings 4, 5 and 6.

Sounding	layer No.	ρ Ohmm	Thickness m	η	τ s
4	1	18	13	2.8°-3	0.0125
	2	3.5	25	-	-
	3	0.75	25	-	-
	4	0.5	45	-	-
5	1	18	13	2.7°-3	0.01
	2	3.5	25	-	-
	3	0.75	25	-	-
	4	0.8	45	-	-
6	1	18	13	2.9°-3	0.02
	2	1.7	22	-	-
	3	0.5	35	-	-
	4	0.7	35	-	-

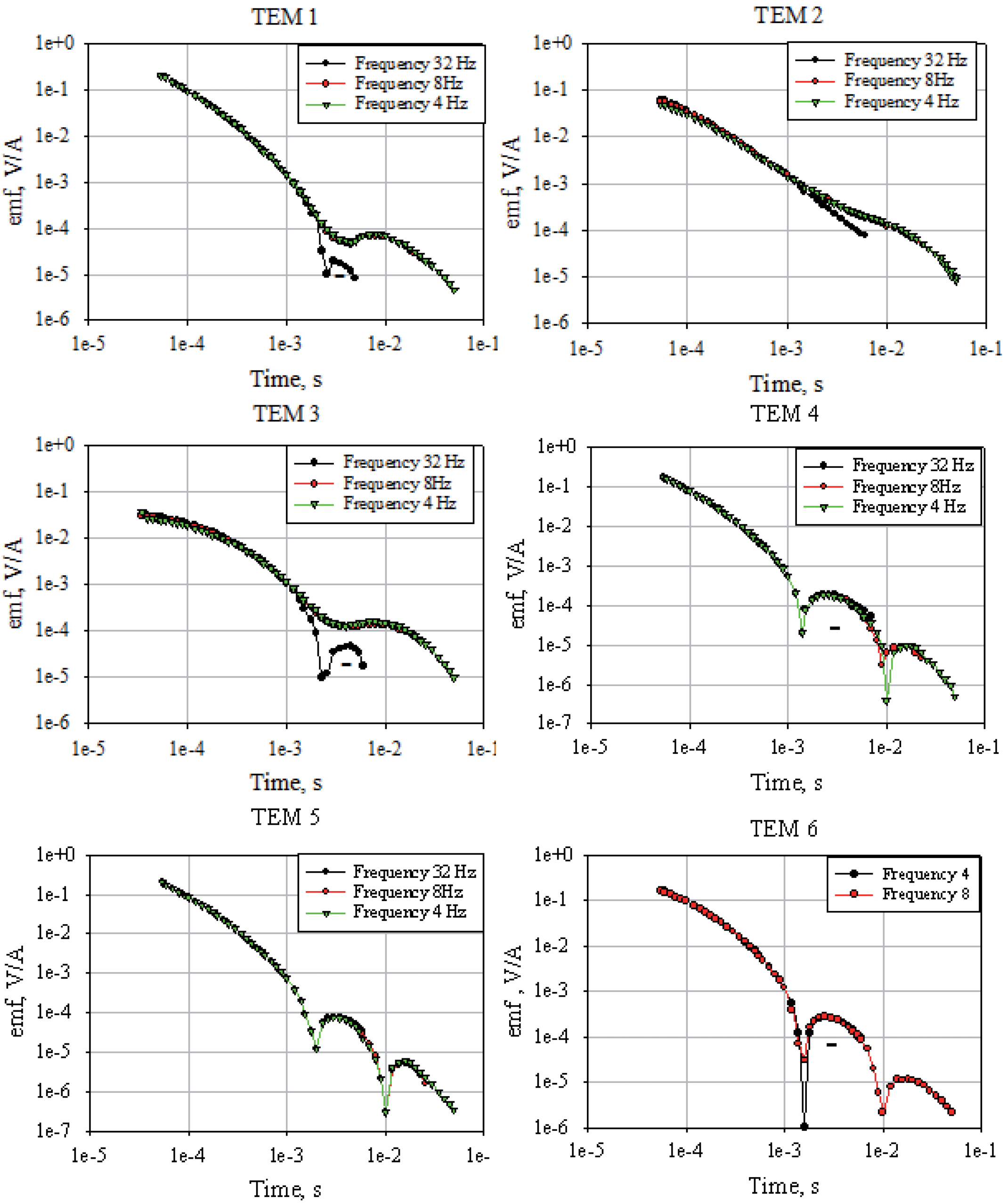

Fig. 3 – Experimental decay curves of the acquired TEM soundings 1 to 6 at the second test site located at RioloTerme town (Ravenna, N. Italy). The curves refer to the used frequencies.

All TEM soundings were perturbed by IP, but, surprisingly, in a quite different way: as shown in Fig. 3. This IP perturbation was found to depend on the repeating frequency in soundings 1, 2 and 3, while it was identical at all frequencies in the remaining 4, 5 and 6. It is worthwhile to specify that this behavior has never been reported before in the literature, at least to the knowledge of the authors.

Of course we can try to invert these data by merging the IP effect into the constitutive TEM equations. We can use the well-known Cole-Cole model (Pelton *et al.*, 1978), as expressed in eq. 81):

$$\rho(\omega) = \rho_0\left\{1-\eta\left[1-\frac{1}{1+(i\omega\tau)^c}\right]\right\}, \qquad (1)$$

(Where, ϱ: is the frequency-dependent resistivity, ϱ_0: the resistivity at zero frequency, ω: the angular frequency, η: the chargeability at 0 time after current switch-off, τ: the relaxation time and $0< c <= 1$ a suitable exponent) and implement its Fourier transform in the time-domain into a suitable computer program. If c=1 in this equation, in time domain the function can be expressed as in eq. 2):

$$\sigma(t) = \frac{\sigma_0}{1+\eta}\left[1-\eta\cdot exp\left(-\frac{1-\eta}{\tau}\,t\right)\right], \qquad (2)$$

where σ: indicates the electrical conductivity $\sigma=1/\varrho$. Using a proprietary Matlab code, written by Zadorozhnaya and described by Zadorozhnaya and Lepyoshkin (1998), we obtain reasonable model parameters (i.e. solution) when we invert soundings 4, 5 and 6 (Tab. 1), while we obtain a similar solution for soundings 1, 2 and 3 only if we invert the data pertaining to the repeating frequency of 32 Hz (Tab. 2, model on left). If we try to invert, with the same algorithm, data pertaining to the repeating frequency of 4 Hz, we obtain nonrealistic low resistivity at depth. As an example we show, in Tab. 2, both models obtained for TEM-3.

Tab. 2 - Model parameters obtained.

1D petrophysical model parameters of sounding 3 using the Cole-Cole formula at 32 Hz repetition rate

1D petrophysical model parameters of sounding 3 using the Cole-Cole formula at 4 Hz repetition rate

Layer No.	ρ Ohmm	Thickness m	η	τ s	Layer No.	ρ Ohmm	Thickness m	η	τ s
1	90	15	-	-	1	30	30	-	-
2	12	25	-	-	2	8	45	-	-
3	2.3	19	-	-	3	0.92	45	0.25	3°-3
4	0.5	20	0.25	3.5°-3	4	0.05	45	0.99	3.5°-3
5	0.5	25	0.25	3°-3	5	0.05	45	0.99	3°-3
6	0.6	24	0.25	3°-3	6	0.05	45	0.99	3°-3

How to explain both the time-dependent behavior and the obtained very low resistivity values? If we are successful to explain and model it, we should obtain coherent TEM inverted models throughout. Perhaps we could be so lucky to find second order parameters linked to hydrogeology. Moreover, is this time-dependent behavior correlated with observed time- and current-dependence of resistivity in the (more usual) geo-electrical method? In both reported cases geology suggests the presence of membrane polarization linked to saturated sandstone, which is more abundant in the FAA formation, i.e. below soundings 1, 2 and 3. We remember that sandstone is the same rock type where these phenomena were clearly observed in the lab.

Non linearity of DC and TEM data: preliminary common model. The foundation of membrane polarization caused by constrictivity of pores is as follows: when the electrical current flows through a porous channel with pores of different radii (transfer numbers), an excess/loss of ions accumulates at the boundaries (Marshall and Madden, 1959). Obviously captions have higher mobility (transfer more electrical charges) when in a large capillary because in narrow capillaries some of the anions are absorbed by the double electric layers (DEL) hence they become immobile. When a steady state current is applied, concentration of ions at one side of a

Tab. 3 - 1D models of sounding 3 using the Cole-Cole formula and eq. (4) at 4 Hz repetition rate.

# of layer	ρ Ohmm	h m	η_1	τ_1 s	η_2	τ_2 s	α_2
1	50	28	4.0e-3	0.032	2.0e-2	0.5	0.17
2	1.5	25	-	-	-	-	-
3	1.1	25	-	-	-	-	-
4	2.0	29	-	-	-	-	-

capillary increases while at the opposite side it decreases. Decreasing of concentration cannot continue infinitely: it will reach zero causing a rupture of the electrical circuit. No electrical current flows through the capillaries any more, since the current pass is blocked.

Calling t_0 the time of blockage, i.e. the time when rupture of the electrical circuit occurred, it has been shown (for more details we address the reader to the above-cited papers by Zadorozhnaya) that, for cations and anions respectively the following equation apply:

$$t_0 = -\frac{u_{0k} FzDS_1S_3\sigma_k}{I^2 M_k (n_{1k} - n_{3k})}, \quad -\frac{u_{0a} FzDS_1S_3\sigma_a}{I^2 M_a (n_{1a} - n_{3a})}: \tag{3}$$

t_0 is controlled by current I and it depends on transfer numbers n_a and n_k, i.e. on pore radii of the connected pores and on the conductivity of pore fluid σ_k and σ_a. In Eq. (3) S_1: is the surface area of the central pore, S_2: and S_3: are surface areas of left and right pores/channels respectively, F: the Faraday number, z: valence, u_0: ion's salinity of free solution. Subscripts k and a indicate captions and anions, respectively. The amplitude of the potential difference (voltage) also depends on the mobility's of both anions M_a and cationes M_k and on the diffusion coefficient D too. The process of polarization continues up to time t_0, after which the rupture of the electrical circuit occurs and the potential difference between the ends of the pore becomes constant. During the polarization process all contacts between pores of different transfer numbers will be blocked and the electrical current will flow through the remaining pore channels.

This brings us to define the phenomenon of membrane polarization as the successive blockage of inter-pore connections due to the excess/loss distribution of ions during current flow. Under these premises, it can be shown that both resistivity and chargeability of a model built by many capillaries of different diameters depend on current intensity, which means that the electrical behavior is not linear.

Moreover, since the response of the model depends on the pore-size parameterization, i.e. the amount of non-linearity can be predicted, the inverse path is also possible, i.e. it becomes possible to estimate the pore-size distribution using measurements made in the non-linear range of the supplied electrical current.

Another consequence of the mechanism, which produces the excess of ions concentration at the boundary between pores, is that it depends on time of the applied current: if the pulse length is short, then the excess of the ions is small and time of levelling (discharging) is also short. However, increasing current pulse length the membrane effect increases. The direction of accumulation of ions along the boundaries is the same as the current flow; therefore the direction of discharge is also the same as the direction of transient emf. That is why the resistivity of bodies, where this membrane IP effect occurs, can considerably decrease.

To account for the time-dependence of the phenomenon, the solution of the constitutive diffusion equation:

$$\frac{\partial u}{\partial t} = -D\frac{\partial^2 u}{\partial x^2}, \tag{4}$$

which led to Eq. (3), consists of numerous exponentials. For a preliminary interpretation we assumed that the membrane IP effect could be modelled using Cole-Cole model [Eq. (2)] with opposite sign and we added a new function, which takes into account also of the amplitude of the above-described membrane effect as expressed in Eq. (5):

$$p_{ME} = \alpha \frac{\eta_2}{\tau_2} exp\left(-\frac{1-\eta_2}{\tau_2}t\right). \tag{5}$$

where η_2: is Chargeability and τ_2: is relaxation time for membrane polarization, α: is a coefficient referred to attenuation. In this way, re-interpreting the low-frequency curves of TEM 3, resulted in a 1D model that is consistent with the "normal" soundings, as is shown in Tab. 3. Obviously, TEM1 and 2 show coherent 1D models with TEM3.

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