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Spectral induced polarization in a sandy medium containing semiconductor materials: study of the polarization mechanism

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NTRODUCTION

SUMMARY

Induced polarization (IP) is useful for mineral exploration. In the presence of sulphides (more generally speaking: semi-conductors), the charge carriers inside particles are electrons and electron gaps. The inner diffusivity and the charge concentration are very high with respect to the background solution ones. Mechanisms of induced polarization are still under questioning in those cases.

In order to improve our knowledge about the mechanisms controlling IP in such mediums, we propose new lab experiments on unconsolidated mineralized medium and begin numerical modelling by using the Poisson-Nernst-Planck (PNP) equation set as well. Four different types of semi-conductors (graphite, pyrite, chalcopyrite and galena) are involved in the experiments. The polarization effect of grain size, mineral concentration as well as electrolyte salinity and type are investigated at the lab scale. We find that the total chargeability of the medium is a function of the mineral volume but is independent of the electrolyte salinity and electrolyte type. However, the time constant (τ) is highly dependent on the grain size and the electrolyte salinity, and is slightly dependent on the mineral type. These results appear to be in agreement with the classical Wong's theory, but we assume here that no significant redox phenomenon does happen at the grain surface.

The observed dependence of the chargeability and the time constant on the salinity could be explained by considering the mineral grain as a dipole impacting the potential and consequently charge distribution in its vicinity. This dipole is generated inside the particle to compensate the primary electrical field and the whole particle is –as a first approximation- a spherical boundary (and volume) with a constant potential on (and in) it. The distribution of the charged particles in the area around the dipole electric will respond accordingly to this boundary condition and is driven by the potential. Since the equations are coupled, the potential depends on return on the resulting ions distribution. Although the finiteelement numerical approach used here is still preliminary, it opens wide perspectives in the understanding of IP in more complex media.

Key words: spectral induced polarization, electrolyte effect, mineralized medium.

For a long time, the interpretation of spectral induced polarization has been based on empirical models (Cole and Cole 1941), wherein the physical meanings of the model parameters are difficult to interpret physically. Pioneers like Pelton et al. (1978) showed relationships between chargeability and mineral content in sulphide deposits, but did not provide mechanistic approaches. However several theorists, for instance Schwarz (1962), Wong (1979) and more recently Revil et al. (2015) have proposed mechanistic approaches that light the micro-meso-macro IP in various cases.

One consensus does exist regarding the dependence of the time constant with the grain size and the diffusion coefficient (D in m^2/s) of ions in the pore solution. However it seems not applicable in the case of semi-conductor particles: the diffusion coefficient as numerically derived from the time constant is some orders of magnitude larger than in the case of siliciclastic mediums (Gurin et al. 2015; Revil et al. 2015). In the presence of electronic semi-conductors, Gurin et al. (2015) and Hupfer et al. (2016) prefer to introduce the notion of specific surface area to model the time constant, and D is no more involved in the relationship providing the time constant.

METHOD AND EXPERIMENTAL RESULTS

The complex resistivity of unconsolidated siliciclastic medium containing electron-based semi-conductors minerals were acquired over a frequency range from 91.5 mHz to 20 kHz using SIP Fuchs III electrical impedance spectrometer. We use Fontainebleau sand (consisting of 98 % of pure silica). The particle size lies between (0.1- 0.2 mm). According to our tests, this medium shows a weak polarization, in agreement with all previous works made on such samples. The measurements tank is rectangular with dimensions (28 cm long, 10 cm wide and 10 cm of height). We use a Wenner array with 6.5 cm spacing. Non-polarizable Cu/CuSO₄ electrodes are used to measure the potential difference, whereas the current electrodes are made of stainless steel (Ag 316L) electrodes. The metallic grains are randomly scattered throughout the medium.

We firstly vary the metal content (mass fraction) and the grain size, and secondly the electrolyte type (sodium chloride NaCl, potassium chloride KCl and sodium sulphate Na_2SO_4 separately). Finally the electrolyte concentration is also changed with 0.001, 0.01, 0.1 and 0.5 mol/l respectively.

The chargeability M of the medium is calculated from the amplitude of the complex resistivity at higher and lower frequencies and the time constant τ is derived from the critical frequency (the frequency of the phase peak).

Increasing the mass fraction of metal (galena or chalcopyrite) leads to an increase of M and a decrease of the amplitude of the complex resistivity, while M is independent of the electrolyte type and concentration. The time constant depends on the grain size and electrolyte concentration. The phase peak moves to higher frequencies while the electrolyte concentration increases. Accordingly, the time constant decreases with concentration and from the figure 1 we notice that the shape of the phase spectrum is not influenced by electrolyte concentration. That means that the shape of phase spectra is only controlled (actually: shifted along the frequency axe) by the grain size distribution.

The figure 2 exhibits the dependence of the relaxation time with the solution conductivity. If we remove the distilled water point (which in reality may be acidified by carbonic acid), the relationship seems extremely linear with a slope of -0.85 s.m/mS.



Figure 1: experimental phase with graphite (1% volume) for several electrolyte (KCl) concentrations.



Figure 2: experimental relaxation time versus solution conductivity. Excluding the distilled water point, the slope is very close to -0.85 s.m/mS.

FINITE ELEMENT METHOD MODELLING

The Poisson-Nernst-Planck (PNP) equation set is a theory (or model) which includes the two major determinisms involved in electrolytic solutions. Precisely, it takes into account the dispersion caused by the Brownian motion (as set by Einstein

for each ion type as:
$$D = \frac{\mu k_B I}{q}$$
, where D is the diffusivity,

 μ the mobility, $\mathbf{k}_{\rm B}$ the Boltzmann constant, T the temperature, and q the electrical charge of the ion) coupled with the Poisson equation. In the presence of several kinds of ions numbered (i), the system is written:

$$\begin{cases} \frac{\partial \mathbf{c}_{i}}{\partial t} = \nabla \left(\mathbf{D}_{i} \nabla \mathbf{c}_{i} + \frac{\mathbf{z}_{i} \mathbf{e}}{\mathbf{k}_{B} T} \mathbf{c}_{i} \nabla \boldsymbol{\phi} \right); & i = 1, \dots, N \\ \nabla \left(\epsilon \nabla \boldsymbol{\phi} \right) + \sum_{i} \mathbf{z}_{i} \mathbf{e} \mathbf{c}_{i} = \mathbf{0} \end{cases}$$

where \mathbf{c}_{i} is the concentration of ions (i), \mathbf{z}_{i} valence of ion (i), e the elementary charge, $\boldsymbol{\phi}$ the potential, and N the number of involved ion species.

The coupling of the concentrations \mathbf{c}_i with the potential $\boldsymbol{\phi}$ leads the system to be nonlinear.

We undertake computation by using the Finite Element Method as proposed by the free but powerful and convivial software named "freefem++" (see Hecht, 2012 and <u>http://www.freefem.org/</u>). Our modelling is preliminary 2-D. The figure 3 shows a typical mesh within a box of 2X2 mm² including a 40 μ m diameter particle, supposed to be very conductive. It assumes that the phenomenon inside the particle is rapid and anticipates the major phenomenon occurring outside the particle (later on we shall take into account the diffusion of charges inside the particle).



Figure 3: the mesh used to study the concentration and potential evolution in the vicinity of a conductive particle.

Only two kinds of ions (one cation and one anion) of equal diffusivity are involved in this preliminary modelling.

At the beginning of the experiment, the potential is null everywhere and the ion concentration is homogeneous. Then we set potentials on the two opposite faces as depicted on figure 3 and run the software using finite differences in the time domain.

The diffusivities D_1 and D_2 are close to 2.10-9 m²/s (K⁺ and Cl⁻ standard value). As expected, the resulting concentrations are just opposite through the experiment.

On figure 4 we show the potential and cation concentration for two initial concentrations and after 1 s and 100 s. The potential evolution with time or concentration is so weakly perceptible, that we only show the potential one time. The concentration varies in the vicinity of the particle: the polarization phenomenon is mainly driven by the particle dipole at a distance of a few radiuses. The Gouy-Chapmann layer role is not taken into account here; actually we expect that its contribution is negligible when considering such conductive particles.

CONCLUSIONS

The chargeability of the medium is a linear function of the concentration of the metallic particle (in volume), and it has a small and negligible dependence on the mineral type and solution conductivity. The phase of the complex resistivity is a direct indicator of the mineral content. The chargeability of the medium is slightly depending on the grain size and on the water conductivity. The relaxation time is depending on the grain size and electrolyte concentration: we find a clear logarithmic correlation between relaxation time and electrolyte conductivity. The polarization is at least partially controlled by the solution ions.

The correlation between relaxation time and the resistivity of the medium is still one of the obstacles to use SIP in minerals discriminations. We expect that a good use of the numerical modelling by using the Poisson-Nernst-Planck model will improve our common understanding of IP in the future.

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Potential (hardly changes with concentration and time)



Cation concentration after 1 s



Figure 4: potential and cation concentration: (a) potential; (b) cation concentration after 1 s with 0.001 mol/l; (c) after 1 s with 0.1 mol/l and (d) after 100 s with 0.1 mol/l. The potential modification is hardly perceptible, while the ion concentration varies in the vicinity of the particle.