# Petrophysical Diagnosis of Shaly Sands by Electrical Impedance Spectroscopy (Spectral Induced Polarization)

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## Abstract

A review of recent publications on the electrical properties of water-saturated sandstones shows no consensus as to exactly how the large low-frequency induced polarization or "IP effect" arises. Nor is it clear whether or not pore size, grain size or permeability can be correlated with time or frequency domain IP parameters. Nevertheless, it is commonly understood that clay content plays a dominant role in the strength of the IP response, while micromorphological parameters such as pore and throat size modulate the frequency range. Most models proposed to explain low frequency polarization are supported by some data and contradicted by other data.

We present some new data on electrical properties of samples of varying clay content and with porosities ranging from 6 to 30% and permeability ranging from a few microdarcies to several hundred millidarcies. We show how features of the polarization spectra acquired in the frequency range $10^{-4}$ to $10^{6}$ Hz shed light on micromorphological features and on the slow reactions between constituent clay minerals and pore fluids.

## Introduction

It has long been known that clay-bearing sandstones show a strong induced-polarization response when subjected to a time-varying electrical field. Since the 1950s attempts have been made to study and analyze this response, with a view to obtain information on clay content, salinity, saturation and permeability. Pioneering works by Klein and Sill (1982) Vinegar and Waxman (1984) have been followed in recent years by a major resurgence in impedance spectroscopy (spectral IP) studies on rocks, which joins an impressive number of studies on analogous colloidal systems.

While early work on induced polarization focused on time domain measurements in a field setting most recent studies on shaly sands have considered frequency-domain measurements of complex impedance using specialized equipment for frequencies between millihertz and megahertz. Today experimental limitations are due to the electrochemical nature of electrodes and their geometrical arrangement. Almost all recent studies of low frequency polarization have used reversible silver-silver chloride electrodes in a four-electrode configuration. These advances give us a common baseline for measurements but it is still not clear exactly which polarization mechanisms operate in sands and sandstones. Moreover it is not clear whether IP responses can be used to make predictions of physical or flow properties that go much beyond empirical correlations. Conclusions reported in a number of recent papers on low frequency electrical properties of sandstones are contradictory. Before presenting our own data we will review some of these recent findings.

## Review of Selected Recent Work Examining Low Frequency Induced Polarization of Sandstones

Garrouch and Sharma (1994), following Vinegar and Waxman (1984) explain the positive correlation between clay content and IP strength as being a consequence of the elevated cation exchange capacity of clay minerals. While the equation of Garrouch and Sharma is empirical it is supported by the theoretical framework of Lima and Sharma (1992), which is a generalized effective medium approach incorporating the clay as a conductive shell around insulating sand grains. Börner et al. (1996) suggest a general inverse relationship between the size of the imaginary conductivity (i.e. strength of polarization) and the permeability, relating this in turn to the clay content.

Lesmes and Morgan (1999) argue for a mechanistic relationship between grain size distribution and relaxation time distribution in water-saturated sandstones. Their argument relates the relaxation time of the polarization of a sand grain to the time needed to restore charge imbalance though diffusion, again based on a modified effective medium theory. Lesmes and Morgan (1999) nevertheless accept that higher and lower frequency components of the relaxation time spectrum are due, respectively, to small scale surface roughness and to ion segregation over length-scales much larger than grains.

Chelidze and Guegen (1999) argue that Maxwell-Wagner type models based on grain scale dipole formation underestimate the total polarization strength. They further point out that the strongest polarization peak is typically associated with a diffusion length scale smaller than the characteristic particle size. Chelidze and Guegen present some convincing arguments supported by limited experimental data.

Chelidze et al. (1999) present some parametric studies where sand was doped with specific ions, which point to the importance of double layer charge as the controlling influence of polarization intensity in sands and sandstones. Similarly Lesmes and Frye (2001) studied the same Berea samples as Lesmes and Morgan (2001), but under a range of salinity and pH. They were able to show that at the point of zero charge (pH 3) both low frequency polarization and surface conductivity were inhibited. These results could be interpreted as "proving" that double layer distortion around grains is responsible for low frequency polarization in rocks. However, Chelidze et al. (1999) do point out that the very same double layers control alternative polarization mechanisms arising from membrane selectivity.

Scott and Barker (2003) show a particularly strong correlation between the position of the peak phase angle for low frequency electrical polarization and the pore throat size measured independently by mercury injection porosimetry. Their data, which are for Triassic sandstones show little correlation between clay content, cation exchange capacity and the electrical polarization strength or frequency. Scott and Barker suggest that the inverse relation between the size of the pore throats and the frequency of the phase maximum is a result of membrane polarization across the pore throats. This takes one back to the earlier theories of induced polarization based on ion selective membrane behavior espoused by Marshall and Madden (1959).

Titov et al. (2003) analyzed a Marshall and Madden (1959) type of model for membrane polarization in sands consisting of a serial arrangement of short, narrow pore sections and wider, longer sections. Time-domain data presented on sieved [clean] sands show evidence of a rapid polarization, which is attributable to the Maxwell-Wagner polarization process and a slower processes, which centers on timescales compatible with the membrane polarization process. There is a clear shift towards longer times—and so lower frequencies, as grain diameter is increased from around 0.25 to around 1.2 mm. Unsieved sand containing clay and colloidal iron showed suppressed early-time (high frequency) polarization compared with a clean sand of similar grain size. According to the Titov et al. model, a broad distribution of grain sizes would tend to produce a constant phase angle over a range of low frequencies.

Wong (1999) stresses the importance of surface adsorption/desorption of charges on surfaces as responsible for the large values of dielectric constant measured at low frequencies. In the material science world Jonscher (1990) is the main champion of the theory that surface "reactions" and charge hopping between surface sites control the frequency dependence of polarization in dispersed systems. Jonscher's arguments are quite convincing, and when applied to shaly sands they would predict a positive link between clay content and polarization strength irrespective of micromorphology.

### Inherent Limitations of Experimental Data

Since Vinegar and Waxman (1984) there has been no published study that reports electrical impedance data from a large range of sandstone samples as a function of pore fluid composition. With this in mind, we originally set out to collect data on a range of clean and shaly sands saturated with five fluids ranging in logarithmic increments from very low to high ionic strength.

Previous studies have assumed that only the chemical conditions alter when the solution used to saturate a rock is changed from one composition to another. What we found in practice was that many shaly sands are so incompatible with fluids of weak or very strong ionic strength that key physical properties such as permeability were very strongly modified. We therefore believe that the pore microstructure and even mineralogy can and do change appreciably during the testing cycle.

The impedance curves for a given sample, in function of salinity therefore record the electrical response to both physical and chemical changes in the pores and at surfaces.

### Experimental Methods

We collected electrical impedance spectra over the frequency range 1mHz to 1MHz using a Zahner IM6 electrochemical workstation. The equipment and methods for electrical impedance spectroscopy measurements are similar to those described in Clennell and Lima (2001). We were however able to improve the test cells and calibrations since 2001.

### Measurement resolution and accuracy

We conducted a wide range of measurements with standard resistors and capacitors in order to eliminate and correct for instrumental and test lead effects as far as possible. The IM6 reports phase to 0.01° has a phase accuracy of better than 0.2° up to 30 kHz and better than 1° up to 500 kHz. Accuracy of impedance is better than 1% at low frequency, and about 3% at 1 MHz. When corrected against blanks, and corrected for temperature (24 ±2 °C) the impedance magnitude measurement errors are negligible compared with other uncertainties and the phase errors are less than 0.1° up to 10 kHz.

### Samples

We report data from 10 samples whose properties are listed in Table 1.

Table 1. Properties of Test Samples

| Sample | Description | Porosity | Perm. (mD) |
|---|---|---|---|
| CLA4 | Clashach sandstone (UK) almost pure quartz | 0.067 | 34.0 |
| XA2 | Clean sandstone / feldspar & rock fragments | 0.080 | 0.198 |
| RXP | Shaly, tight sandstone | 0.111 | 0.046 |
| MAST | Clay rich siltstone | 0.112 | 0.038 |
| PUT12 | Sandstone with small amount of clay | 0.118 | 1.30 |
| FQ2 | Sandstone with moderate amount of clay | 0.196 | 2.25 |
| QEXA3 | Sandstone with small amount of clay | 0.197 | 2.55 |
| SWD1 | Shaly sandstone (Sherwood Group UK) | 0.277 | 26.0 |
| ARG1 | Plastic kaolinitic claystone | 0.349 | 0.064 |

### Results

Figure 1. shows the porosity and permeability of the test samples. The samples are almost all of low permeability, and so extend the range of data presented in other publications by e.g. Vinegar & Waxman (1984). Most samples were tested in moderately fresh mineral water chosen not to interact strongly with the clays. Sample FQ2 was saturated initially with distilled water, and after equilibrium an impedance spectrum was recorded. The salinity was then increased in four increments up to a strong 1.0 NaCl solution. As expected, the increase in pore fluid conductivity suppressed the IP response. In this sample the strongest response was found with the second freshest pore fluid (Fig. 2). The surface conductivity contribution changes with salinity (Fig. 3)
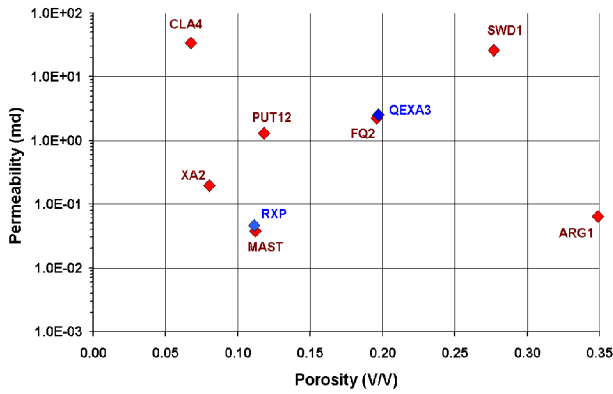
Fig. 1 Porosity and Permeability of the test samples.

Table 3. Water conductivity, 1kHz resistivity and apparent formation factor for each of the rocks tested

| SAMPLE | $S_w$ (S/m) | $R_{1000}$ ($\Omega$m) | Fa |
|---|---|---|---|
| CLA4 | 0.6 | 2065 | 1239 |
| XA2 | 1.027 | 188 | 193.076 |
| RXP | 0.0195 | 360 | 7.02 |
| MAST | 0.126 | 210 | 26.46 |
| PUT12 | 0.062 | 885 | 54.87 |
| FQ2_330 | 0.033 | 405 | 13.365 |
| QEXA3 | 0.0157 | 455 | 7.1435 |
| SWD1 | 0.054 | 44 | 2.376 |
| ARG1 | 0.008 | 28.7 | 0.2296 |

The samples show a remarkable range in apparent Formation Factor ($F_a$) (Table 3), which reflects the differing pore structure and mineralogy of the rocks. Indeed for the claystone sample ARG1, the apparent formation factor is less than one because the water was relatively fresh and surface conductivity dominated. In sample CLA4, the very high formation factor is explained by the low porosity (6%) and near zero surface conductivity. The fact that the permeability of this sample is relatively high (30 md) reflects the fact that pore structure must be relatively efficient for hydraulic flow. On the other hand, sample XA2, which has a similar porosity and much lower permeability, has a formation factor one order of magnitude lower. That is, electrical flow is relatively more efficient and hydraulic flow is very much less efficient. In this rock, the polarization is not completely inhibited even with 1.0 S/m pore fluid (Fig. 4).


Fig. 2 Impedance magnitude and phase angles for sample FQ2 saturated with water of 5 conductivities, ranging from 0.06 to 7.7 S/m. The IP phase peak does not shift much in frequency over this enormous range in salinity and overall impedance.
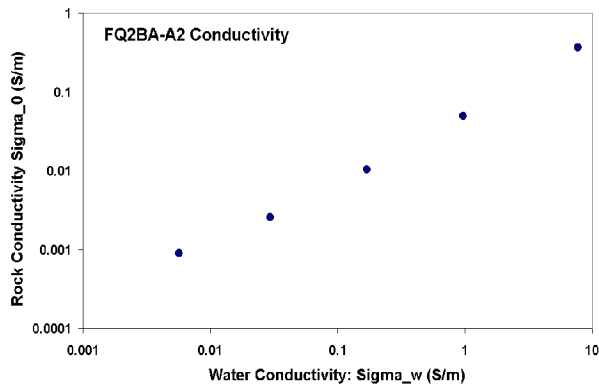

Fig. 3. Water conductivity vs. rock conductivity for FQ2. The curvature is typical of shaly sands, and is due to an increasing importance of surface conductivity. This is reflected in the values for apparent formation factor (Table 2). At 1.0 M NaCl (7.7 S/m) polarization is negligible, the surface conductivity is negligible and $F_a = F_0$ (e.g. Lima et al. 2001).

Table 2. Formation Factors for Test series on sample FQ2

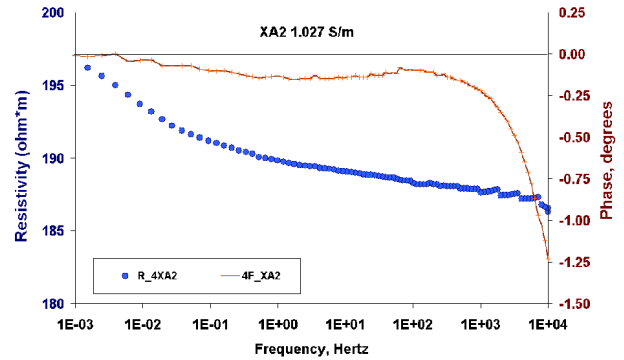| Pore fluid conductivity S/m | Rock resistivity $\Omega$m | Fa: Apparent Formation Factor |
|---|---|---|
| 0.0057 | 1108 | 6.32 |
| 0.0330 | 405 | 13.4 |
| 0.167 | 95.02 | 15.9 |
| 1.00 | 20.47 | 20.5 |
| 7.70 | 2.71 | 20.9 |


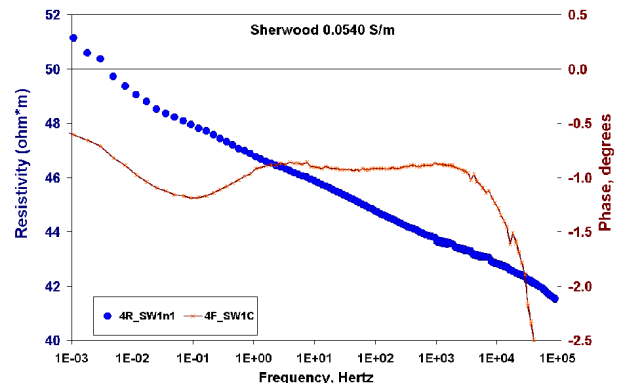Fig. 4. Resistivity and phase spectrum for sample XA2.


Fig. 5. Resistivity and phase spectrum for Sherwood Sandstone sample SWD1 with pore water close to in-situ composition.
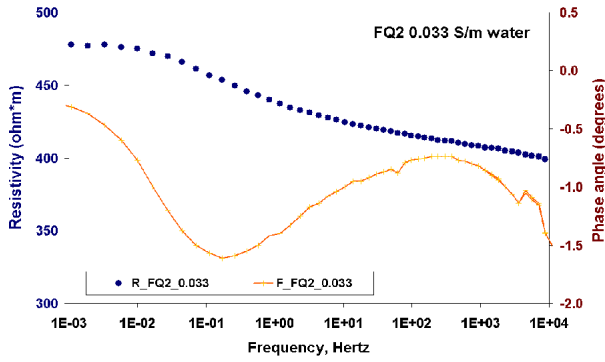
Fig. 6. Resistivity and phase spectrum for sandstone FQ2 with slightly saline pore water.
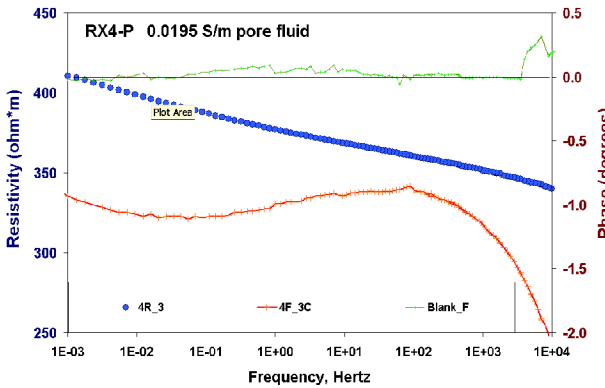


Fig. 7. Resistivity and phase spectrum for sandstone RXP equilibrated with fresh water. The green curve is the blank phase curve for the test cell used for correcting the data.
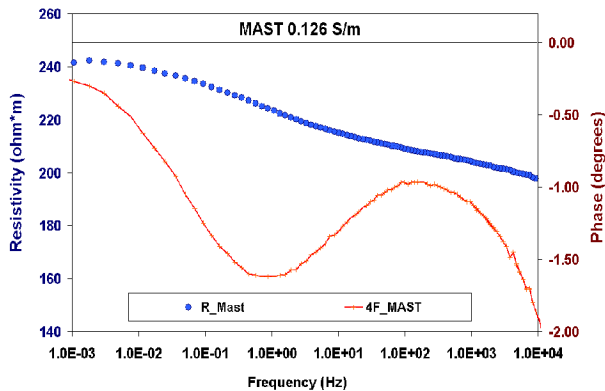


Fig. 8. Resistivity and phase spectrum for siltstone MAST.

Figures 5-8 show results for shaly sandstones with widely varying porosity and permeability. Phase angle curves for all samples are presented in Fig.12. There is no simple relationship between the resistivity dispersion with frequency, the size and shape of the phase angle curve, and the flow properties or grain size. However in general there is a stronger IP response (larger phase angle at frequencies =< 1KHz) for samples with more clay. Curves for FQ2 (Fig. 6) and MAST (Fig.8) are quite similar, even through FQ2 is only moderately shaly, and has 80 times greater permeability than the shaly siltstone sample MAST. Pore and particle sizes must be much smaller in MAST than in FQ2. The resistivities and apparent

Formation Factors of these two samples are on the same order as a third sample, RX4 (Fig.7). RX4 is a very low permeability and low porosity shaly sand. The phase peak is notably much broader in this sample than in either MAST or FQ2. This could be an indication of imperfect equilibration of the pore fluid in sample RXP.
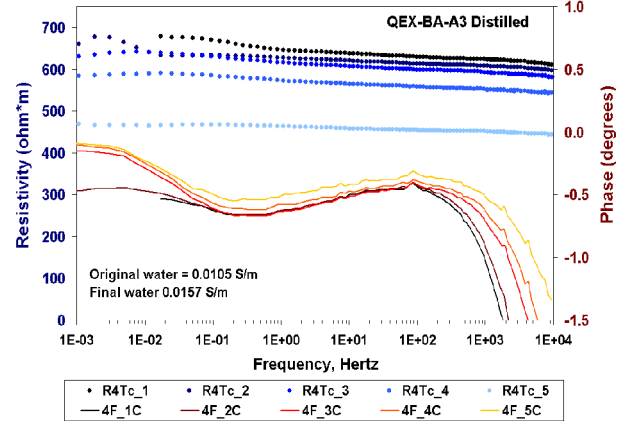


Fig. 9. Resistivity and phase spectra for sandstone QEX saturated originally with distilled water. Over time the water composition changed as ions leached into the pore fluid. Total resistivity decreased by about 30% over 4 weeks. The 0.1 Hz phase peak is little changed, but the roll-over frequency increases in accordance with the decreased bulk resistance.
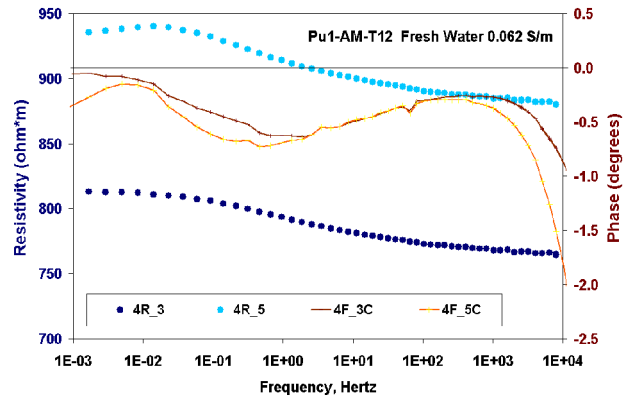


Fig. 10. Resistivity and phase spectrum for sandstone PUT12 saturated with fresh water, 0.0053 S/m. The initial peak in the phase spectrum 3C, and also the rollover frequency, shift slightly as the fluid equilibrates with the rock (final 5C).
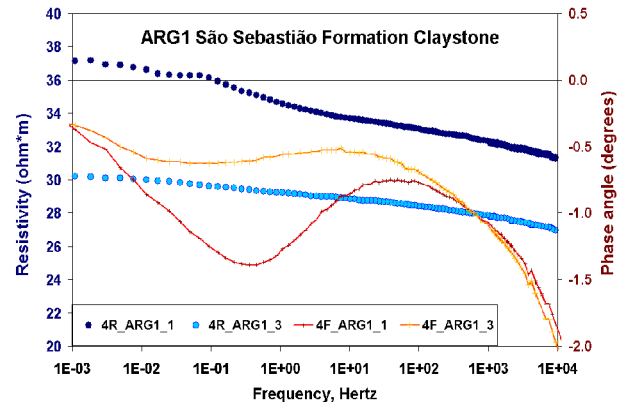
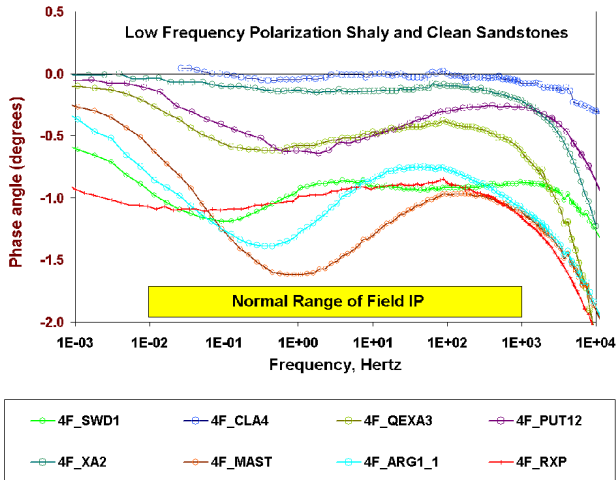Fig. 11. Resistivity and phase spectrum for claystone ARG1.



Fig. 12. Compilation of phase curves for all the samples.

## Water-Rock Interactions

Figures 9-11 show low frequency electrical spectra from samples undergoing chemical equilibration with originally fresh pore fluids. Over time there is usually some leaching of ions from the sample into the pore fluids, leading to a decrease in bulk resistivity. The lower bulk resistivity inevitably leads to an increase the rollover frequency, which is the frequency at which a transition occurs between dominant resistance at low frequency (conduction currents) and dominantly capacitance (displacement currents) at high frequency. This tendency is seen as a shift in the frequency at which the phase curve moves to high values (about 10 kHz in the case of SWD1, Fig.5). Other electrical effects of water-rock interactions are more subtle, and vary from sample to sample. In sandstone QEX (Fig. 9) the low frequency phase peak stays in the same position, but the very low frequency phase plateau disappears over time. On the other hand, in the outwardly similar sample PUT12, the phase peak at around 1 Hz broadens and moves slightly to lower frequencies, while the lowest frequency component increases. Most marked is the effect seen in the claystone sample ARG1. Over time the resistivity decreases by 20% and the distinct phase peak centered on 0.5 Hz is suppressed and shifted to lower frequencies. This must be a reflection of ion redistributions between surfaces and pore fluids within the sample.

## Discussion of Results

There is a clear trend for larger phase angles in the more clay-rich samples (Fig. 12), but aside from this we have not been able to identify clear trends with porosity, permeability, formation factor or particle size. Note that the two "pairs" of samples on the porosity-permeability plot have rather different electrical behaviour. The simple idea of polarization time scale depending on the diffusion distance across pores or on grain surfaces is not borne out by data presented in this study. Data of Klein and Sill (1982) shows a decrease in the characteristic frequency with clay content in sand/clay mixtures, and again this is not consistent with a simple dependence of relaxation time on mean pore or grain size.

There is a widespread view expressed that membrane polarization, or at least diffusion currents arising from differential ionic mobility play a significant role in very low frequency polarization (<10 Hz), while Maxwell Wagner processes, originating from space charge accumulations at the grain-solution interface contribute to low-frequency polarizations in the range 10 Hz to 10 MHz. The Maxwell-Wagner component can be treated in terms of simple inclusions (e.g. Maxwell, Wagner, Fricke, Bruggeman, Hanai...), inclusions with a simple surface conductivity dominated by the immobile Stern layer (O'Konsky), inclusions with a clay shell (Lima and Sharma 1992), or inclusions with an open double layer surrounding them (the preferred model of Chelidze and Guegen 1999, who review the above works in detail).

In Chelize and Guegen's (1999) model, the polarization mechanism attributable to the segregation of the double-layer ions essentially becomes a membrane-type polarization once the grains come close together. It is interesting therefore that Shilov et al. (2001) presented an analytical model for low frequency electrical polarization of macroscopic dispersions and porous media that explicitly includes the differential ionic mobility in the pores as the low frequency mechanism and a gradual transition into double layer Maxwell-Wagner polarization at the higher frequencies. Both mechanisms are of course space-charge polarization processes.

Clays seem to contribute a chemical capacitance over and above the capacitance attributable to membrane and Maxwell-Wagner polarizations. This capacitance depends on the amount of clay surface and is a "scalar" contribution that has nothing to do with the vectorial fields of **P** and **D** that appear in the constitutive equations of electrostatics. Rather it is a result of electrochemical, not electrostatic energy storage due to reversible "reactions" on surfaces. Jonscher (1990) and others would suggest that this "battery storage" process is dominant in low frequency polarization, but we believe that the weight of evidence points to space charge polarizations arising from different mobilities of cations and anions being the main source of the IP effect in shaly sands.

These space charge polarizations have long been associated with diffusional relaxation processes (since at least Mashall and Madden (1959); see Baretto and Dias (1999). Over time this has come to mean "membrane polarization". Attempts by Dias (1972) to include the diffusional component explicitly in the constitutive equations of dielectric behaviour were unfortunately ignored in favor of formulations that lump out-of-phase diffusion currents, electrical displacement due to the vacuum ($\varepsilon_0\mathbf{E}$), and electrical polarization due to paired charges (i.e. **P**) all together. We are working on a formulation that will include these effects separately, and also account for scalar, time dependent ion adsorption/desorption at surfaces that contribute to energy storage over the charge-discharge cycle.

## Conclusions from the Experimental Study

Electrical impedance spectroscopy is a useful tool for characterizing shaly sandstones. At low salinity appreciable polarization is detectable even in clean sandstones, whereas at high salinity,IP is suppressed. The degree of shaliness is still apparent in the level of conductivity its frequency dependence, and apparent formation factor trends.

Claystone and compacted clayey siltstone show similar polarization strength to shaly sandstones. The shapes of the curves do not reflect the enormous difference in average pore and grain size, permeability and surface area between these rocks and clay-bearing sands.

There is some evidence that EIS spectra of genetically related sets of sandstones correlate with pore size or throat size and thereby give more or less strong indicators of permeability. However, the varied electrochemical and micromorphological nature of shaly sands (Fertl 1987) suggest that these relationships cannot be universal. With a limited number of samples we found rocks that can fit into some proposed theories, and other rocks which "disprove" these same models.

Study of shaly sandstones in the laboratory is complicated by disequilibrium chemical processes. On the other hand, EIS can be used to monitor and quantify these same fluid-rock interactions during such processes as cation exchange, which may lead to clay swelling and formation damage.

### The way forward for understanding shaly sands?

Chelidze et al. (1999) conclude their review of IP mechanisms with a call for more parametric studies on the physical (microstructural, environmental) and chemical controls on rock electrical properties. They call for the use of independent methods (electron microscopy, NMR and electrokinetic studies) to determine key variables. We endorse this philosophy, which is compatible with the significant attempt of Revil (1999) to produce a unified model of electrochemical behaviour which can explain conduction, diffusion and membrane potentials. Lima et al. (2001) have reviewed the DC conduction behavior of freshwater shaly sands. In a future paper we will present the results of electrokinetic measurements on several samples described here. We propose in future to use low field NMR spectroscopy together with high frequency dielectric spectroscopy to better understand shaly sand properties.

Given the problems of chemical incompatibility exhibited by shaly sands we propose to develop electrochemical assays that start from equilibrium pore fluid composition (i.e. matched to the *in situ* formation water) and probe the sensitivity of the rock to perturbations in ionic composition, pH, temperature and other independently controllable system variables. In this way we obtain a good baseline response, and can begin to disentangle the parameters of interest such as surface charge density, ionic mobility and surface area.

### References

**Barreto, A.N. & Dias, C.A.** 1999. Uma análise do modelo de Madden & Marshall para descrever a polarização eletrica observada em rochas contendo argila disseminada. VI SBGf. Rio de Janeiro.

**Chelidze, T.L., Guegen, Y. 1999.** Electrical spectroscopy of porous rocks: a review. I. Theoretical methods. Geophys. J. Intl. Vol. 137, p1-15.

**Chelidze, T.L., Guegen, Y. & Ruffet, C.** 1999. Electrical spectroscopy of porous rocks: a review. II. Results and interpretation. Geophys. J. Intl. Vol. 137, p16-34.

**Clennell, M**.B. & Lima, O.A.L. 2001. Laboratory methods for relating electrical and hydraulic properties of shaly sandstones. VII SBGf, Salvador.

**Dias, C.A.** 1972. Analytical model for a polarizable medium at radio and lower frequencies. J. Geophys. Res. Vol. 77, p4945-4956.

**Fertl, W.H.** 1987. Log-derived evaluation of shaly clastic reservoirs. J. Petroleum Technology, Feb 87; SPE paper number 14061.

**Garrouch, A.A. & Sharma, M.M.** 1994. The influence of clay content, salinity, stress and wettablility on the dielectric properties of brine-saturated rocks: 10Hz to 10 MHz. Geophysics, Vol. 59, p909-917.

**Klein, J.D. & Sill, W.R. 1982.** Electrical properties of artifical clay-bearing sandstone. Geophysics Vol. 47, p1593-1605.

**Jonscher, A.K.** 1990. Admittance spectroscopy of systems showing low-frequency dispersion. Electrochim. Acta Vol. 35, 1595-1600.

**Lesmes, D.P. & Frye, K.M.** 2001. Influence of pore fluid chemistry on the complex conductivity and induced polarization responses of Berea sandstone. J. Geophys. Res. Vol. B106, p4079-4090.

**Lesmes, D. & Morgan, F.D.** 2001. Dielectric spectroscopy of sedimentary rocks. J. Geophys. Res. Vol. B106, p13329-13346.

**Lima, O.A.L., Clennell, M.B. & Niwas, S**. 2001. Theoretical model for the geo-electrical response of fresh water shaly sandstones. VII SBGf, Salvador.

**Lima, O.A.L. & Sharma, M.M.,** 1992, A generalized Maxwell-Wagner theory for membrane polarization in shaly sands. Geophysics, Vol. 57, p431-440.

**Marshall D.J. & Madden T.R.** 1959. Induced polarization, a study of its causes, Geophysics Vol. 24, p790-816.

**Revil, A.,** 1999. Ionic diffusivity, electrical conductivity, membrane and thermoelectric potentials in colloids and granular porous media: a unified model. J. Coll. & Interf. Science Vol. 212, p503-522.

**Scott, J.B.T. & Barker, R.D.** 2003. Determing throat size in Permo-Triassic sandstones from low frequency electrical spectroscopy. Geophys. Res. Lett. Vol. 30 GL016951.

**Shilov, V.N., Delgado, A.V., Gonzalez-Cabellero, F. & Grosse, C.** 2001. Thin double layer theory of wide-frequency range dielectric dispersion. Colloids & Surfaces Vol. A192, 253-265.

**Titov, K., Komarov, V., Tarasov, V. & Levitski, A.** 2002. Theoretical and experimental study of time-domain induced polarization in water-saturated sands. J. Appl. Geophys. Vol. 50, p417-433.

**Vinegar, H.J. & Waxman, M.H.** 1984. Induced polarization of shaly sands. Geophysics Vol. 49, p1267-1287.

**Wong, P-z. (ed.)** 1999. Methods in the Physics of Porous Media. *Academic Press*.

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