

## The origin of the observed low-frequency electrical polarization in sandstones

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### ABSTRACT

There has been an increasing debate regarding the mechanism controlling the low-frequency polarization (megahertz to kilohertz) in sandstones. The polarization and related electrical relaxation are extremely important because they can be used to provide a significant amount of information on length scales within the sandstone. Complex electrical measurements, in the mHz to kHz range, were made on gel-filled samples. This gel decreases the ionic mobility in the bulk pore fluid while keeping the ionic composition similar to that in a water-saturated sample. The presence of the gel was shown to have little effect on the electrical relaxation. This adds to the argument that the electrical double layer close to the grain surface is where the polarization originates. The correlation between pore-throat size and the relaxation time is consistent with the polarization mechanism of ion diffusion within the electrical double layer. The membrane-type polarization model, used previously to explain the polarization in pore-throat regions, is likely to be incorrect because of the relative thinness of the electrical double layer.

### INTRODUCTION

In 1957, after making induced-polarization measurements on sands and clays for the purpose of groundwater prospecting, Vaquier et al. (1957, p. 660) stated, "Publication at this time is prompted by the promising results obtained in the field and by the realization that a complete explanation of the phenomenon is not likely to be forthcoming in the near future." They had discovered a link between the voltage decay time and the size of the sand grains. While great experimental progress has been made, nearly half a century later this statement could not be truer, with no consensus yet reached by geophysicists on this phenomenon. There has been increasing interest in recent years in low-frequency (mHz to kHz) electrical polarization in sandstones and sediments. Research has focused on a possible

length scale affecting the observed electrical relaxation phenomenon and on the actual polarization mechanism involved (Chelidze and Gueguen, 1999; Lesmes and Morgan, 2001; Titov et al., 2002; Scott and Barker, 2003). This length scale is of great significance because its calculation from the electrical spectra can give information on permeability and mixed-phase fluid flow, including hydrocarbons, contaminants, and water in partially saturated sandstones.

The main theories on the cause of the polarization seem to be divided into two camps. Those in the first camp argue that a charge buildup occurs caused by the excess of ions moving at different speeds in the electrical double layer (EDL) along the surface of the grains (Lesmes and Morgan, 2001; Ulrich and Slater, 2004). Others argue that on meeting a pore constriction, such as a pore throat, ions in the pore fluid encounter varying resistance to their movement, causing charge buildup (Titov et al., 2002). This resistance is caused by the EDL coming together at these constrictions to form an ion-selective membrane. Those following the first theory suggest that this mechanism leads to grain size controlling the electrical relaxation time (related to voltage decay time mentioned above), and those following the second theory suggest that this leads to the pore-throat length controlling the relaxation time. These theories will be examined here along with novel experimental results.

### GEL-FILLED SAMPLES

To determine whether the mobility of the pore fluid has any effect on the polarization, sandstone samples were saturated with an agar gel solution. First the sample was completely dried in an oven for 48 hours at 80°C and then put under a vacuum for 6 hours longer. An agar gel mix of the type used by Taylor and Barker (2002) was allowed into the vacuum chamber, fully covering and saturating the sample. The sample was then allowed to set until the gel was solid.

The gel mix was made by heating a synthetic groundwater solution similar to that used by Scott and Barker (2003) (Table 1) and dissolving the agar in it. The final ionic strength of the agar solution in the pore space cannot be accurately determined. This is partly caused by an increase in concentration as the solution is heated and placed under vacuum, effectively boiling off some of the liquid. Another

Manuscript received by the Editor June 2, 2005; revised manuscript received January 27, 2006; published online August 28, 2006.

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reason for an increase in ionic concentration is that the sample still has some residual salts because it was not washed out with deionized water. This washing out of the sample was not conducted to help preserve the clay structure. What is important is that saturating with an agar solution will effectively prevent the motion of the bulk pore fluid while still allowing electrical current to flow. This enables us to see if there is any variation in the polarization caused by this extreme change in pore filling, while keeping the ionic composition constant.

Electrical measurements of the gel demonstrated that it has no polarization and is completely resistive (as stated by Taylor and Barker, 2002). The gel contains few free conducting ions itself, and conduction is mainly through the ions in the brine solution used to make the gel. However, as previously stated, the concentration of these ions is increased during the saturation process. The change from liquid water to gel should also affect ion mobility because of a significant increase in fluid viscosity by the Stokes-Einstein relationship. Experiments by Al-Baldawi and Abercrombie (1995) show that the mobility of calcium decreases by a factor of two in a 1% agar gel, which is less than one-quarter of the strength of the gel used in this experiment. The electrical spectra for sample Ba31, saturated with a synthetic groundwater, and the same sample filled with gel are given in Figure 1. This sample is a medium-grained, Triassic, red sandstone with a porosity of 30%. It can be seen that although there has been an increase in the conductivity, there has been very little effect on the frequency dependence of the quadrature (imaginary) conductivity, which is a measure of the polarization. The characteristic peak is known as an electrical relaxation. The experiment was repeated on another sample, R5, of similar lithology and a porosity of 25%. This also exhibited no change in the frequency dependence of the spectra but a larger increase in the magnitude of the quadrature conductivity. This increase in the quadrature conductivity magnitude, without changing the character of the spectra or position of relaxation peak, was also demonstrated in experiments with small increases of brine concentration on sample R5. Therefore, the higher quadrature conductivity would also be an expected consequence of the increased ionic concentration in the gel experiment.

This experiment shows conclusively that electrokinetic effects cannot be important for this relaxation, as has been stated generally for induced polarization, but without direct proof, by Marshall and Madden (1959). This follows because the bulk pore fluid cannot flow when in gel form, yet the character of the electrical relaxation remains the same.

The lack of any significant alteration of the relaxation peak also suggests that the mobility of ions in the bulk pore fluid is not important. The reduction of the mobility of the ions in the bulk pore fluid from the gel should cause a significant change in the relaxation if it is caused by a pore-throat membrane-type polarization mechanism.

**Table 1. Ionic composition of synthetic groundwater solution.**

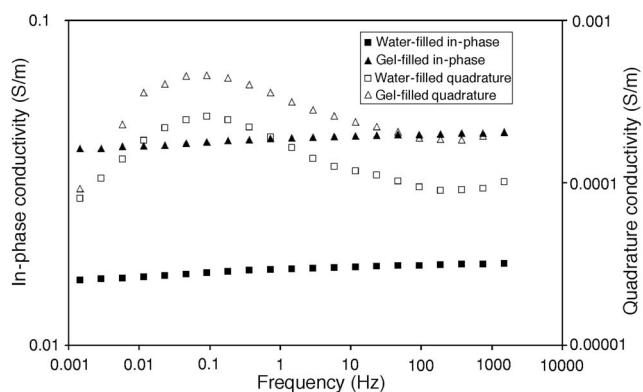
Chemical species	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
Concentration in synthetic groundwater solution (mg/l)	60	30	34	142	120	30

Also, ions in the outer EDL, in the diffuse layer, probably are not the most important ions involved in the relaxation because their mobility would also be reduced by the gel. This is not as conclusive because it is difficult to assess the effects of the gel very close to the pore wall. However, this result adds weight to the argument that ions in the hydrodynamically stagnant zone or Stern layer could be responsible for a major proportion of the polarization. This is also proposed as the most significant zone for carrying the in-phase excess conductivity (Revil and Glover, 1998). It is a logical step to assume that if the excess conductivity is being carried in the Stern layer, there will be an associated polarization resulting from the charge imbalance and different mobility of the ions from those in the bulk pore fluid. Recently published work on surface electrical conduction indicates that the often overlooked importance of the Stern layer is now recognized (Lyklema and Minor, 1998; Löbbus et al., 2000). Lesmes and Morgan (2001) also state that the Stern layer is a significant contributor to the polarization in sandstone.

The gel experiments outlined here are a way of examining the effects of changes in ionic mobility on the electrical relaxation in sandstones without altering the ionic composition. These experiments are as yet inconclusive because of the difficulty in knowing which ions are causing the relaxation and the difficulty in controlling the salinity, which could counter the effect of the gel on the relaxation time. However, more experiments with different gel concentrations could be a useful tool in further investigations, at least for permeable, easily saturated sandstones such as the ones used in this study. This initial experiment demonstrates that the gel does not alter the relaxation phenomena fundamentally. Therefore, in future experiments different gels could be used to alter ionic mobility by varying amounts, following similar work in the field of biochemical research (e.g., Al-Baldawi and Abercrombie, 1995).

## PORE SURFACE AREA

Previous results at low frequencies (mHz to kHz) have shown a link between the pore surface area and the magnitude of the polarization (Börner and Schön, 1991; Börner et al., 1996). A relationship has also been shown at higher frequencies between the pore surface area and the dielectric permittivity (Knight and Nur, 1987). However, the results of Scott and Barker (2005) indicate that at low frequencies (mHz to kHz) this relationship is very weak. Sandstones split



**Figure 1.** Comparison between the electrical spectra of Permo-Triassic sandstone sample Ba31 saturated with a synthetic groundwater solution and the same sample filled with an agar gel.

into two groups, or clusters: those with very low polarization and low pore surface areas and those with higher polarization and higher pore surface areas (Scott and Barker, 2005). Interestingly, the recent results of Binley et al. (2005) show an inverse relationship between the pore surface area per unit volume and the relaxation time for sandstones (taken from a Cole-Cole model fit to their experimental measurements). These results suggest that pore surface area can be linked to polarization strength and relaxation time.

The sandstones used in the study by Scott and Barker (2005) were measured for pore surface area using a five point BET nitrogen adsorption method similar to that used by Binley et al. (2005). Surface area per unit pore volume  $S_{\text{por}}$  was calculated in the same way. Figure 2 shows the relationship between peak relaxation time  $\tau_{\text{peak}}$  (Scott and Barker, 2005) and  $S_{\text{por}}$ . Figure 2 demonstrates that for this group of sandstones, taken from across the U. K., there is no correlation between pore surface area and peak relaxation time  $\tau_{\text{peak}}$ . The results presented in Figure 2 do not vary significantly if the relaxation parameter  $\tau$  from a Cole-Cole or generalized Cole-Cole model (Binley et al., 2005; Scott and Barker, 2005) is used instead of the peak relaxation time.

Pore surface area in a clean quartz sandstone will depend strongly on pore size. Sandstones with small pores and pore throats will generally have a higher surface area to unit pore volume than those with larger pore spaces. However, it is well known that pore surface area measured by a BET method will be dominated by the quantity and type of pore linings, including clays and oxygen hydroxides, in other types of sandstone. It is possible that the relationship seen by Binley et al. (2005) could be a result of using a very similar set of sandstones, where clay type and quantity and pore shape variations were low. This also allowed the size of the pore space (or length scale) that controls the relaxation time to be the main control on the surface area. Sandstones used by Scott and Barker (2005) were from more diverse locations with a greater variety of pore surface linings. This is demonstrated by the greater range of cation exchange capacities (CECs) measured (Table 2) and from the lithological studies carried out (Scott and Barker, 2005).

## LENGTH SCALE AND RELAXATION

Whatever the relaxation mechanisms at higher frequencies, it is becoming apparent that there is a length scale of around the size of the pore, grain, or pore throat that often controls the relaxation times for both sandstones and unconsolidated sands at frequencies below 100 Hz (Vaquier et al., 1957; Klein and Sill, 1982; Lesmes and Morgan, 2001; Titov et al., 2002; Scott and Barker, 2003, 2005). The results from Scott and Barker (2003, 2005), using mercury injection and optical microscopy, show that, for Permo-Triassic sandstones from the U. K., the length scale controlling the relaxation is likely to be associated with the pore-throat region. On real sandstone samples this relaxation length scale correlation between pore-throat size and relaxation time is the only one that has so far been verified experimentally. The recent work of Binley et al. (2005) also demonstrates this correlation. It is difficult to verify the exact length scale because of the many other variables involved, including clay coatings and complex variations in the internal geometry of real sandstones. Extensive laboratory investigations are still needed. However, the major theoretical problem is if the pore throat is the dominant length scale, how can it be a controlling factor in the relaxation when the polarization is dominated by EDL ion diffusion (possibly in the

Stern layer) and not by a more classic pore-throat membrane-type model (Titov et al., 2002).

## THEORY

The correlation of pore-throat size to relaxation time shown by Scott and Barker (2003, 2005) has been taken by some (Ulrich and Slater, 2004) to imply an ion-selective membrane model. Ions in the free pore fluid encounter a membrane, which is created when the EDL comes together in the pore-throat regions (Titov et al., 2002). It is a common assumption that the membrane model originally suggested by Marshall and Madden (1959) implies that these membranes are the whole pore-throat regions, but Marshall and Madden (1959) never actually referred to the location of these membranes. In fact, the EDL is on the order of 1 to 100 nm (Reppert and Morgan, 2001), too narrow to block ion motion through pore throats of around 10 to 50  $\mu\text{m}$ . The theory suggested by Scott and Barker (2003), but not expanded upon, is that the pore surface polarization contribution from the EDL, which exists in the main pores and the pore throats, is greater in the pore-throat regions simply because of the relative size of these regions. Mercury injection measurements demonstrated that the pore-throat diameters were around 20 times smaller than the main pore diameters.

A basic circuit model for electrical conduction through sandstone is given in Figure 3. The conduction through the main pore space is in phase, with a surface conduction along the EDL that has both in-phase and quadrature components in parallel with this. There also exists a similar circuit for the pore-throat region, and this is placed in series with the main pore region. The quadrature component of the conduction from the pore-throat region dominates the overall quadrature conduction for the combined circuit because it is not bypassed by a large in-phase component as in the main pore space. This is only a first-order approximation, but following this argument the pore throats are the dominant regions controlling the polarization. The electrical conduction path through sandstone must be considered in this way. It is not possible to regard the conduction in sandstone as conduction in a colloidal suspension, where there is a free path around the colloidal particles, allowing their size to control the

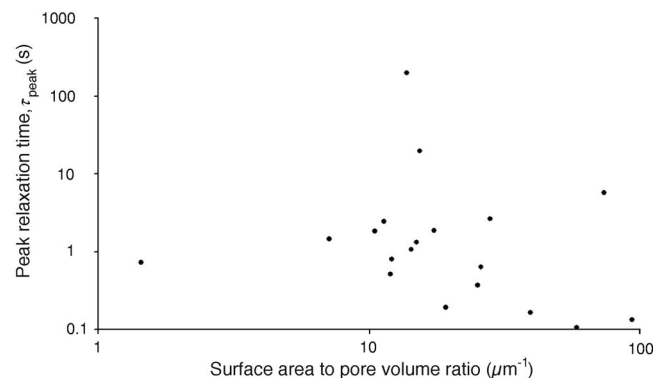


Figure 2. The relationship between peak relaxation time  $\tau_{\text{peak}}$  and pore surface area to unit pore volume  $S_{\text{por}}$ . Data are taken from Permo-Triassic sandstones used by Scott and Barker (2005). Electrical measurements were made on samples saturated with a synthetic groundwater solution.

**Table 2. Range of CEC values measured.**

CEC (meq 100 g <sup>-1</sup> )	Number of samples	Average	Standard deviation	Minimum	Maximum
Sandstones measured by Binley et al. (2005)	22	6.22 (median)	—	4.15	8.30
Sandstones used by Scott and Barker (2005)	22	6.65 (mean)	5.29	0.16	19.21

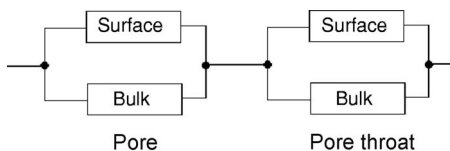


Figure 3. A circuit-type analogy for conduction through a pore and a pore throat in series. With in-phase conduction in the bulk pore fluid and complex conduction in parallel along the pore surface.

relaxation time. Although, this approach can give a useful empirical model for calculations, theories used previously to demonstrate the grain size relationship with electrical relaxation can actually point to the pore-throat regions being more important for low frequency (< 100 Hz) electrical polarization and relaxation.

### SATURATION

The recent results of Binley et al. (2005) show that the saturation also affects the relaxation, with a noticeable reduction in relaxation time as sandstones reach 50% or less saturation. This result could be suggested to be contrary to the proposed theory in this paper because larger pores dewater, cutting the bypass to the surface polarization. Inspection of the results of Binley et al. (2005) shows that there may be another, previously absent, relaxation mechanism that becomes present as the saturation decreases. There are several new complications arising from the multiphase pore contents. An electrical double layer will form at the fluid-air boundary, and relaxation lengths could also be dictated by fluid pathways (width and length). If it is not a new relaxation mechanism, another explanation for the reduction in relaxation time is that water would drain from the larger pore throats and from the pore areas in the sandstone connected by these larger pathways first. Hence, this process would leave areas joined by smaller connecting pathways (pore throats) to carry the current. This is also suggested by Binley et al. (2005) and would give rise to a shorter relaxation time.

### CONCLUSIONS

The low-frequency polarization in sandstone originates through ion diffusion in the electrical double layer, with the Stern layer probably being of greater importance than the diffuse layer. The experi-

ments on gel-filled samples, outlined above, and the relatively small extent of the EDL indicate that the membrane mechanism is not causing the observed polarization. The in-phase, excess conductivity originates from the EDL, and this must also produce an associated polarization effect resulting from an imbalance in ionic charges. This EDL polarization is the origin of the observed quadrature conductivity in sandstones. The polarization contribution from the pore-throat regions can dominate that from the main pore space even when using diffusion in the EDL-type polarization models.

### ACKNOWLEDGMENTS

I would like to thank Lee Slater, Andreas Weller, and an anonymous reviewer for their helpful comments that have improved this paper. I would also like to thank Ron Barker for his help throughout this work.

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