USING LOW FREQUENCY ELECTRICAL IMPEDANCE SPECTROSCOPY FOR AN ENHANCED PORE SPACE CHARACTERIZATION AND ASSESSMENT OF CARBONATES

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ABSTRACT
This study investigates the complex electrical conductivity of carbonate samples using low frequency electrical impedance spectroscopy. The analysis is conducted in combination with petrophysical, mineralogical and geochemical measurements. We show that Spectral Induced Polarization (SIP) is a useful tool to obtain detailed information about rock properties and pore space characterization. Rock parameters like permeability, pore-size and specific surface area can be estimated. So far only sandstones or sandy materials were investigated in detail by laboratory SIP measurements. Several robust empirical relationships have been found that combine IP signals and petrophysical parameters, especially hydraulic properties. Nevertheless, only few and incomplete investigations about SIP on carbonates exist in literature.

For our study different types of carbonates were analyzed with laboratory SIP experiments. Rock properties like grain density, porosity, permeability and surface area were determined by routine core analysis. Geochemistry and mineralogy were used to differentiate the carbonate types of carbonates. First results of the SIP-measurements showed polarization effects for all different types. With respect to the frequency dependence, four different types of polarization behavior were observed in the spectra of the imaginary part of conductivity: a constant quadrature conductivity, a constant slope, a combination of both and a maximum type have been identified. Each behavior can be assigned to the specific carbonate type.

A comparison between SIP data and the petrophysical parameter of the sample set showed that it is very challenging to find a clear correlation between polarization effects and any petrophysical parameter for carbonate rocks, in comparison to sandstones. Nevertheless, these data indicates that the surface conductivity controls the conduction and polarization mechanism. The linear gradient of this relation leads to an estimation of the formation factor of carbonates. Furthermore, the investigation of the dissolution
behaviour of carbonate rock will be focused on the estimation of the impact on polarization effects that result from varying pore space.

INTRODUCTION
Impedance spectroscopy (IS) or spectral induced polarization (SIP) is used for a wide range of applications within geophysics. As well as characterization of hydraulic properties of shallow aquifers, IP measurements can improve the reliability of permeability prediction from geoelectric measurements [1, 2, 3]. The method is mainly controlled by the lithological properties of the rock, and the polarization is related to the surface conductivity and the surface area of the interconnected pore network [4, 5, 6]. Laboratory SIP measurements can provide pore radii distribution [7, 8], a simplified description of the pore space geometry and improve the prediction of a formation factor [9].

The electrical conductivity is described as complex quantity. The real part of the complex electrical conductivity ($\sigma^*$) represents the ohmic conduction ($\sigma'$) while the imaginary part represents the polarization phenomena ($\sigma''$).

\[
\sigma^* = \sigma' + i\sigma'', \quad [E1]
\]

with $i = \sqrt{-1}$ being the imaginary unit. Most models of $\sigma^*$ for a porous material at low frequencies assume a parallel circuit consisting of two conduction terms:

\[
\sigma^* = \sigma_{\text{el}} + \sigma_{\text{surf}}^*, \quad [E2]
\]

with $\sigma_{\text{el}}$ representing an electrolyte contribution via conduction and with $\sigma_{\text{surf}}^*$ being a mineral surface contribution through conduction and polarization within the electrical double layer of the pore surface. Polarization is solely associated with the surface conductivity at low frequencies (<1 kHz). For a fully saturated material the complex electrical conductivity can be separated in the following way:

\[
\sigma' = 1/F \ast \sigma_w + \sigma_{\text{surf}}' \quad [E3] \quad \text{and} \quad \sigma'' = \sigma_{\text{surf}}'', \quad [E4]
\]

where $F$ is the electrical formation factor and $\sigma_w$ is the fluid conductivity.

Originally, the formation factor was defined as the ratio between $\sigma_w$ and the electrical conductivity ($\sigma_0$) of a fully-saturated porous rock on the condition that electrical conductivity is purely ionic and only via the pore fluid:

\[
F = \sigma_w/\sigma_0. \quad [E6]
\]

For low salinity measurements an additional conduction mechanism ($\sigma_{\text{surf}}^*$) occurs, which is taken into account using a complex term. SIP can be used to determine this term and correct the formation factor for low salinity measurements.
A preliminary investigation was conducted on clay-rich carbonate samples from the Tushka area in Egypt using SIP [10] and with focus on fractal dimension [8]. The SIP measurements showed polarization effects and a strong relationship between $\sigma_{\text{surf}}$ and $\sigma''$, which is comparable to sandstones. But a correlation between $\sigma''$ and $S_{\text{por}}$ was not observed. Those results were used as the basis for an extended and more systematic study on carbonate rocks. One goal is to improve the SIP data processing for a better correlation and prediction of petrophysical parameters from SIP data. The complex electrical properties were investigated using SIP in combination with petrophysical, mineralogical and geochemical measurements. We want to extend the carbonate data basis and compare these results with existing relationships and the better known polarization behavior of sandstones. Additionally we want to improve the prediction of petrophysical parameters from SIP.

**SAMPLES & METHODOLOGY**

This systematic study includes the four different carbonate types: Indiana Limestone (ILS), Silurian Dolomite (DOL), Leuders (LK) and Edwards Brown Carbonate (EBK), which were classified as biogenous sediments. Sample sets of each carbonate type show a broad range of petrophysical parameter (Tab. 1). All petrophysical measurements following protocols related to core and scal analysis RP40 [11]. Imaging methods such as scanning electron microscopy (SEM) and x-ray computer tomography (µ-CT) were used to obtain a qualitative image to differentiate the carbonate types and to describe the pore space (Fig. 1).

The LK has a very fine crystalline calcium carbonate matrix with small recrystallization structures. The samples contain also a small amount of iron hydroxide, which can be seen as a white coloured material in Fig. 1 a. The DOL carbonate consists of large crystals with some dissolution structures (Fig. 1 b). The matrix is homogeneous with more than 90% dolomite. The ILS contains almost exclusively calcium carbonate (Fig. 1 c). Aggregates with calcites shells can be seen, which recrystallize towards the pore. The matrix of the EBK is fine-grained and consists of idiomorphic rhombohedral-shaped crystals (Fig. 1 d). Some of them show cavities inside. Cementation can be noticed on the crystal surfaces but does not occur in larger pores. Kaolinite was identified in some samples, but is of minor importance because of its negligible amount. The four samples used are clay-poor carbonates.

SIP measurements were conducted at a constant temperature of 20°C using CaCl$_2$ as fluid with a constant conductivity of 100 mS/m. The used measurement cell is described in [12, this SCA proceedings]. A frequency range of 2 mHz to 100 Hz was used for this analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ILS</th>
<th>DOL</th>
<th>LK</th>
<th>EBK</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$ [%]</td>
<td>17.01</td>
<td>9.76</td>
<td>10.76</td>
<td>18.60</td>
</tr>
<tr>
<td>Min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>19.91</td>
<td>17.62</td>
<td>20.93</td>
<td>41.64</td>
</tr>
<tr>
<td>$K$ [mD]</td>
<td>161.64</td>
<td>4.79</td>
<td>0.08</td>
<td>23.06</td>
</tr>
<tr>
<td>Min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>290.23</td>
<td>260.58</td>
<td>4.41</td>
<td>273.80</td>
</tr>
<tr>
<td>$S_{\text{por}}$ [1/µm]</td>
<td>2.66</td>
<td>0.10</td>
<td>9.67</td>
<td>13.39</td>
</tr>
<tr>
<td>Min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>4.80</td>
<td>24.77</td>
<td>2.93</td>
<td>31.60</td>
</tr>
</tbody>
</table>

Table 1: Range of petrophysical parameter of the carbonate sample sets.
Figure 1:
Left: SEM images.
Right CT images.
a) Leuders
b) Silurian dolomite
c) Indiana Limestone
d) Edwards Brown Carbonate
RESULTS

The real and imaginary part of the conductivity are displayed in Figure 2 using one characteristic curve for each carbonate type. The real part is influenced by the conductivity of the saturating fluid and thus depends on the porosity of the samples. The EBK, with a porosity of 40%, shows the highest value about 11 mS/m, whereas the other three samples with porosities of less than 20% show significantly lower conductivities ranging between 2-6 mS/m. The behavior of the imaginary part of the conductivity is different for all carbonate types exhibiting a constant quadrature conductivity (ILS), a constant slope (DOL), a combination of both (LK), and a maximum type (EBK) with a peak frequency of 0.2 Hz. Each polarization behavior can be assigned to a specific carbonate type and is reproducible for the whole sample set. This observation is in contrast to the Tushka carbonates of the preliminary study, where the specific curve types occur randomly within the sample set and do not correlate with the microfacies association.

Figure 3 shows the relationship of the surface area per unit pore volume (Spor) with the imaginary part of conductivity at 1 Hz in comparison with the Tushka carbonates [10] and the relationship to sandstones [6]. The carbonate types with higher polarization effects (EBK, LK) sustain the correlation with sandstones very well, whereas ILS and DOL data with lower polarization effects indicate no clear correlation. ILS show a similar shift towards a higher surface area without being shifted towards higher conductivity values like the Tushka carbonates. No significant change for imaginary conductivity with increasing surface area can be observed for the DOL type.

The relationship between $\sigma''$ and $\sigma'_\text{surf}$ is shown in Figure 4, including the data of the Tushka carbonates and the correlation for these carbonates and the sandstones as well.

Figure 2: Exemplified results of the SIP measurements of the carbonate sample sets. Left: Conductivity spectra. Right: Spectra of the imaginary part of the conductivity.
The ratio of the two surface conductivities corresponds to the linear gradient $l$, which can explain the data

$$l = \frac{\sigma'' \text{surf}}{\sigma' \text{surf}} \quad \text{with} \quad \sigma'' = \sigma'' \text{surf}. \quad [E7]$$

The gradient for sandstones is 0.042 and for the Tushka carbonates 0.019 with a coefficient of determination $R^2$ of 0.911 and 0.853, respectively. In comparison, the carbonate types in this study show a gradient of $l=0.029$ ($R^2=0.98$). The fit of the correlations for all carbonate types (this study and Tushka carbonates) lead to a value of 0.025 ($R^2=0.93$). The two samples sets with higher polarization effects (EBK, LK) follow the trend very well, whereas the DOL and ILS exhibit larger deviations from the given trend. Thus, the observations show clearly that the surface conductivity controls the bulk conductivity and the polarization mechanism.

For experiments with a single salinity of the saturating brine, it is only possible to get an apparent $F$ ($F'$) with equation [E6] due to the complex behavior of the conductivity. Archie’s Law relates $F$ to the interconnected porosity ($\phi$).

$$F = \phi^m, \quad [E8]$$

where $m$ is the cementation coefficient. The cementation coefficient is unknown for the used carbonates types. One possibility to determine $F$ using SIP measurements is to vary the salinity of the pore fluid, but this method is time consuming and impracticable for field measurements. A method which uses only one single salinity measurement can
provide a predicted formation factor. According to [5], the predicted formation factor is determined by

\[
F_p = \sigma_w/(\sigma' - \sigma'_{surf}) = \sigma_w/(\sigma' - \sigma''/l), \quad [E9]
\]

whereas the gradient \( l \) is known from fitting the relationship between \( \sigma'' \) and \( \sigma'_{surf} \).

![Figure 5: Formation factor calculated from [E9] plotted against porosity for the studied carbonates.](image)

![Figure 6: Crossplot of \( F_p \) versus \( F_M \). Average deviation between \( F_p \) and \( F_M \) is 0.096.](image)

Figure 5 shows the results of the calculated \( F_p \) in relation to the porosity \( \phi \). A fit with [E8] provides a cementation exponent of 2.02 for the studied carbonates. The crossplot of \( F_M \) versus \( F_p \) is shown in Figure 6. \( F_M \) is the formation factor determined at very high salinities with a two-electrode measurement and could also be referred to as true formation factor. The comparison of these different determined formation factors offers a good consistency. Considering all samples, the average deviation between \( F_M \) and \( F_p \) reaches \( d=0.096 \).

**CONCLUSIONS & OUTLOOK**

We have investigated four different carbonate sample sets, which showed significant differences in CT and SEM images. Four different types of polarization curves were observed in the spectra of imaginary part of conductivity. Each carbonate type can be attributed to a characteristic curve type. The carbonates with higher polarization effects (\( \sigma'' > 10^{-2} \text{ mS/m} \)) fit the existing relationships for sandstones much better than the types with lower polarization effects. Nevertheless, this data set satisfies a single linear relationship \( \sigma'' = l \times \sigma'_{surf} \) with \( l = 0.029 \). The estimation of the gradient \( l \) is helpful in conjunction with an IP measurement to improve petrophysical interpretation from resistivity and IP measurements. The gradient \( l \) leads to a reliable prediction of formation factors of carbonate rocks. This prediction is useful in well logging and in hydrogeophysics.
To improve the understanding of polarization phenomena of carbonates, we have carried out multi-salinity measurements, determination of cation exchange capacity and 3D imaging. Additionally, the dissolution behavior of carbonates to quantify the influence on the polarization effects resulting from changes of the pore space will be investigated.

REFERENCES


