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Motivation

Interactions between mineral phases and pore fluids in the subsurface inevitably lead to mineral precipitation reactions and dissolution. One mineral often involved in these naturally occurring processes is calcite due to its strong relationship between the solubility and the pH value. The spectral induced polarization (SIP) method provides the potential not only to localize the precipitate in the subsurface non-invasively, but also to quantify the amount and location within the pore space on a microscopic scale.

However, differentiation between the subprocesses (salinity changes, changes in pH, and changes in the rock texture) occurring during these reactions is a major problem. We conducted a series of dynamic laboratory experiments on sandstones of differing size under controlled chemical conditions, during which we continuously monitored the complex electrical conductivity in the frequency range of 10 mHz to 45 kHz.

We complemented the above-mentioned experiment with isolated measurements on the effects of **NaHCO₃** diffusion to better understand the relationship between the pH value and the relaxation behavior of the rock samples.

Experimental approach

The complex electrical conductivity of a rock, σ^* , can be described by the sum of a real-valued, i.e., pure ohmic, electrolytic conductivity, $\sigma_{el} = \sigma_w/F$, and a complex-valued interface conductivity, σ_s^* , e.g. (Rink and Schopper, 1974) according to:

$$\sigma^* = \frac{\sigma_{\rm W}}{F} + \sigma_{\rm S}^*.$$

With the formation factor F. Therefore, the imaginary component of the complex conductivity, σ'' , contains information on the surface conductivity, and thus pore surface characteristics, alone.

Since mineral precipitation changes the pore surface of a rock, we hypothesize that the precipitation process is reflected in changes of the imaginary conductivity.

- Experiments were performed on Obernkirchen sandstone, a relatively homogeneous quartz-rich sandstone type
- The sample was presaturated with a 0.001 mol/kg **KCl** solution
- Reactants: NaHCO₃, CaCl₂
- Their mixing results in the reaction below:

$2 \text{ NaHCO}_{3(aq)} + \text{CaCl}_{2(aq)} \longrightarrow 2 \text{ NaCl}_{(aq)} + \text{CO}_2 \uparrow + \text{H}_2\text{O} + \text{CaCO}_3 \downarrow$ Samples of two different lengths were measured. The longer sample

has a length of 9 cm, while the shorter sample is 3.1 cm long. For the long sample, the potentials were measured between 4 evenly spaced (2.5 mm distance) ring electrodes, each positioned in a way that should isolate the response of the reactants at early times. For the short samples only the electrodes at end of each tank were used.



Figure 1: Schematic for the experimental setup (long sample configuration). For short samples only one segment (red) and P1 and P4 are in use.

The following aspects were varied during the experiments :

- Number of the non-polarizable ring potential electrodes
- Experimental duration
- Mass and type of reactant solution
- SIP sampling interval (every 12 min for short and every 24 min for long samples)

Spectral comparison of the samples

To isolate the contributions of the reactant solutions present, experiments with samples of differing size were performed:

• Due to the non-linear nature of diffusion, the concentrations of the reactant solutions were increased significantly. Reactant A is a 1 molal **NaHCO₃** solution, reactant B is a 0.5 molal **CaCl₂** solution. For the short sample, the solutions were 0.2 and 0.1 molal respectively.

• The response received in the middle pair (P2 P3) of the long sample seems to represent the signature over the whole sample (P1 P4) quite well.

• We observe very high imaginary conductivities at high frequency in pairs P1 P4 and P2 P3 at later times.

• The data quality on the **NaHCO₃** side is significantly reduced and warrants further investigation especially at later times.

• The **CaCl₂** side experiences significant polarization in the range from 10 mHz to 20 Hz. • Comparison with a **NaCl** tracer test shows significant differences to either reactant side. • Behavior of the short sample shows a significant difference when compared to the response of the longer one.



Figure 2: Development of σ'' for different electrode configurations and sample sizes. Dashed lines show high error due to a leakage

Changes of the CaCl₂ side

• Strong changes in the lower frequency range (10 mHz to 1 Hz).

• Development of a secondary peak at ca. 20-30 Hz.

• Since the diffusion coefficient of NaHCO₃ is higher than the one of CaCl₂, the mixing zone could be shifted toward the **CaCl**₂ side.



Figure 3: Daily sampled development of σ'' between P3 and P4 over 22 days.

The influence NaHCO₃ diffusion

The ionized forms of water are the most mobile ionic species. From multiple experiments, it became clear that we have a strong correlation between the polarization behavior of the sandstone sample and the pH value. By introducing NaHCO₃ into the rock sample, both the pH value of the pore fluid and σ'' increase. This can be expected due to the fact that in most mineral-water interfaces **H⁺** has a strong tendency to be adsorbed onto the surface in the stern layer, effectively reducing the surface charge. These adsorbed ions compensate the surface charge of the mineral interface, reducing the polarizability significantly even in low concentrations. By increasing the pH more less mobile **Na⁺** adhere to the surface, effectively reducing the charge mobility of the averaged bound surface ions. Therefore we observe changes not only in polarizability as the larger ions can compensate less charge per volume, but also a shift in the peak time constant we receive in response to an external Figure 4: Temporal evolution of au_{peak} received from Debye decomposition vs the electrical field (as seen in Figure 3). To characterize these changes in relaxation be- modeled pH value in the pore space. havior we performed a Debye decomposition (DD) after Nordsiek and Weller (2008) of a **NaHCO₃** diffusion experiment and calculated the predicted change in pH per timestep with *Phreeqc*. Figure 4 highlights the relationship between the peak characteristic time and the pH, it is to note that since pH is a logarithmic property, the time constant and the pH follow a linear relationship in the logspace.

 $log_{10}(\tau_{peak}) = bpH + a$ with a = 0.222, b = -1.501

Since ions in the EDL are stronger bound and at higher concentration due to the surface-charges attraction, the average diffusion coefficient gets reduced to $D_+(I) =$ $D_w m$, where m is the reduction in ionic mobility in the stern layer. However, both D_w and m are dependent on the ionic strength of the solution I. We can correct D_w for the activities of each species, but *m* is a surface-specific property. Lykelma et al. (1983) proposed an additional Term M, which describes the decrease in relaxation time due to the presence of the Diffusive layer:

$au_{peak} = d^2/(8D_+M)$

However, this parameter needs precise information on the surface composition to be estimated accurately. We introduce a simplified reduction function K = $\kappa^{-1}(I)/\kappa_0^{-1}$, which represents the reduction in the Debye length κ^{-1} with I and κ_0^{-1} being the Debye length at the beginning of the experiment. We can then receive an estimate for the product of both M and m via $R = m_0 K$ without direct assumptions on the zeta-potential. Here m_0 is a dimensionless fit parameter capturing both $M \ge 1$ and $0 < m \le 1$, while K captures the slope given by M. Note: For systems in equilibrium R should be smaller than 1. With that, we can determine the characteristic time constant for a grain with a diameter d via:

$au_{peak} = d^2/(8D_wR)$

With $m_0 =$ 1.872 and d = 69.5 μm (average grain diameter received by SEM imaging of a similar sample) Figure 6: Temporal evolution of σ'' for the short NaHCO₃ sample. The lines are fitted spectra through DD, dots represent the data.

Summary and outlook

The precipitation of calcite results in significant changes in SIP response sulting in two features:

- . One low-frequency phenomenon associated with the pH value chan • Analysis of this peak relaxation time received from **NaHCO**₃ diffusi suggests a linear relationship between relaxation time and pH-va in the logspace.
- The change in the relaxation time can be connected to a reduction mobility due to the shrinking of the diffusive layer with increasing concentrations.
- 2. One higher-frequency one that can be connected to $CaCO_3$ growth a suggested by (Wu et al. 2010; Leroy et al., 2017; Izumoto et al., 2020)
- Here it is not yet clear, which effect **CaCl**₂ infiltration has on the compound signature needs to be investigated further.
- However due to the appearance of the peak in the late stages of a experiment, one can assume that the second peak is not caused pure **CaCl**₂ diffusion







Figure 5: τ_{peak} data (blue dots) and fitted τ_{peak} (orange line) vs the averaged (over mass fractions) diffusion coefficient of cations in water corrected for the decreasing activity with ion concentration.



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