

Electrical phenomena during CO₂ sequestration – a pore scale view

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Summary

The electrical rock conductivity is a sensitive indicator for CO₂ migration processes. CO₂ dissolves into the pore water in large amounts and provides additional charge carriers due to the dissociation of carbonic acid.

We present laboratory measurements of the spectral complex electrical conductivity of water-bearing sand samples during exposure to and flow-through by carbon dioxide. Pressures up to 300 bar and temperatures up to 80°C were applied. Steady-state experiments serve for investigating the physicochemical equilibrium of the fluid phases. Dynamic experiments aim at analyzing the impact of partial saturation and chemical interaction on complex conductivity.

The steady-state dissolution experiments show that besides the conductivity-increasing dissociation a second opposing process may be observed which results in a significant reduction of conductivity at high salinities despite the added CO₂. We explain our observations with a semi-analytical formulation for the electrical conductivity taking into account the interactions of ion and neutral species.

A significant reduction of saturation is observed during CO₂ flow and drainage. The spectral complex conductivity maps both changes in saturation and chemical interaction.

1 Introduction

The presence of the reactive gas carbon dioxide (CO₂) in pore space gives rise to a network of physical and chemical processes [Börner et al., 2013], which all act on the complex electrical rock conductivity σ^*

$$\sigma^* = \sigma' + i\sigma'' \quad . \quad (1)$$

We carried out static dissolution experiments to tackle pore water conductivity σ_w and dynamic flow-through experiments with quartz sand to investigate the three-phase system.

We summarize the processes involved from a pore scale perspective. Furthermore, our laboratory observations, data and results regarding the real part of conductivity σ' , the imaginary part of conductivity σ'' and the pore water conductivity σ_w are presented.

2 Effect of CO₂ on rock conductivity

2.1 Partial saturation

CO₂ is forced into the pore space of the storage formation. A connected flowing phase forms due to the pressure gradient. When no pressure gradient is applied, the non-wetting CO₂ forms bubbles in the pore centers. Character and efficiency of the phase replacement depend on pressure, temperature, CO₂ mass flow and pore space characteristics [Sarmadivaleh *et al.*, 2015, Börner *et al.*, 2016].

During flow chemical interaction between gas and pore water take place. Also, water dissolves in the CO₂. This may lead to drying out of connate interface water.

During injection, CO₂ partially replaces the pore water of the storage formation and consequently reduces rock conductivity σ^* according to [Archie, 1942, Vinegar and Waxman, 1984]:

$$\sigma' = S_w^n \Phi^m \sigma_w + S_w^k \sigma'_{if} \quad (2)$$

$$\sigma'' = S_w^k \sigma''_{if} \quad (3)$$

where S_w denotes water saturation, Φ is porosity, m is the cementation exponent, n and k are the real and imaginary part saturation exponent, respectively, and σ'_{if} and σ''_{if} denote the real and imaginary part, respectively, of interface conductivity at full saturation.

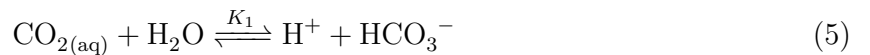
Due to its reactive nature the presence of CO₂ affects not only the saturation S_w but also pore water conductivity, pH and the grain–water interface. The main task of electromagnetic monitoring techniques is to correctly reconstruct $S_{CO_2} = 1 - S_w$ from conductivity measurements.

2.2 Dissolution and dissociation

CO₂ is highly soluble in water. The amount of carbon dioxide, which is dissolved in a pore water with known sodium chloride (NaCl) content at thermodynamic equilibrium (CO_{2(aq)}), is a function of pressure p , temperature T and salinity c_{NaCl} [e.g. Duan *et al.*, 2006]:

$$c_{CO_2} = f(p, T, c_{NaCl}) \quad (4)$$

The dissolved CO₂ forms uncharged aqueous complexes. A small portion of the CO_{2(aq)} forms carbonic acid (H₂CO₃), which is unstable. The carbonic acid dissociates into protons, hydrocarbonate and carbonate ions:



These ions occur in addition to the self dissociation of water and anions and cations of dissociated salts. Consequently, they act on the pore water conductivity σ_w . As a result of the dissociation the pH decreases as well. The formation and dissociation of carbonic acid under pressure results in a significantly reduced pH of the CO₂-rich pore water (computed with PHREEQC: ~3.0).

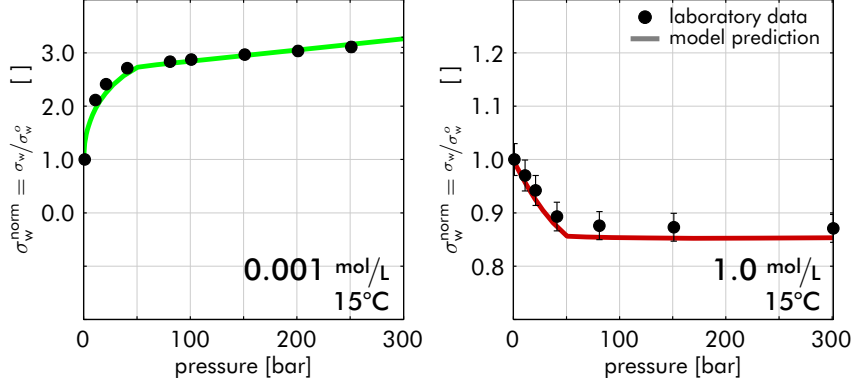


Fig. 1: Change in electrolyte conductivity due to CO₂ dissolution and dissociation at 0.001 M NaCl (left) and 1 M NaCl (right).

2.3 Inner surface area variation

The complex interface conductivity in clean sands is caused by the electrical double layer, which forms at the contact of the quartz grains and the conductive pore water.

Interface conductivity depends on salinity, grain roughness (i.e. inner surface area) and pH. It depends less strongly on water saturation than the electrolytic conductivity. A decrease in pH causes a decrease in σ'' [Skold et al., 2011]. Furthermore, the low-pH environment due to CO₂ dissolution and dissociation may trigger changes of the rock matrix [Wigand et al., 2008], which would result in an increased inner surface area, and consequently affects the imaginary part of conductivity σ'' in multiple ways [Börner et al., 2016].

3 Results

Static dissolution experiments were carried out in order to investigate the impact of CO₂ on pore water conductivity [for experimental details see Börner et al., 2015a]. For salinities below 0.6 g/l we observe an increase in pore water conductivity σ_w with pressure (*low salinity regime*, Fig. 1, left). This is expected, since the additional ions from dissociation contribute to σ_w . For solutions with $c_{\text{NaCl}} \geq 5.8$ g/l we observe an unexpected behavior. No conductivity increase occurs (*high salinity regime*, Fig. 1, right). Instead, σ_w decreases by up to 15% [Börner et al., 2015a]. This behaviour is due to a decrease in ion mobility, which dominates the electrolyte conductivity at high salinities despite the added charge carriers.

The effect of CO₂ dissolution and dissociation on pore water conductivity σ_w may be predicted for all salinities based on physicochemical properties by the following model [Börner et al., 2015a]:

$$\sigma_w^{\text{norm}}(p, T, c_{\text{NaCl}}) = \frac{\sigma_w}{\sigma_w^0} = \frac{1}{\sigma_w^0} \sum_{i=1}^2 [\Lambda_i \gamma_i \alpha_i c_i] \quad . \quad (7)$$

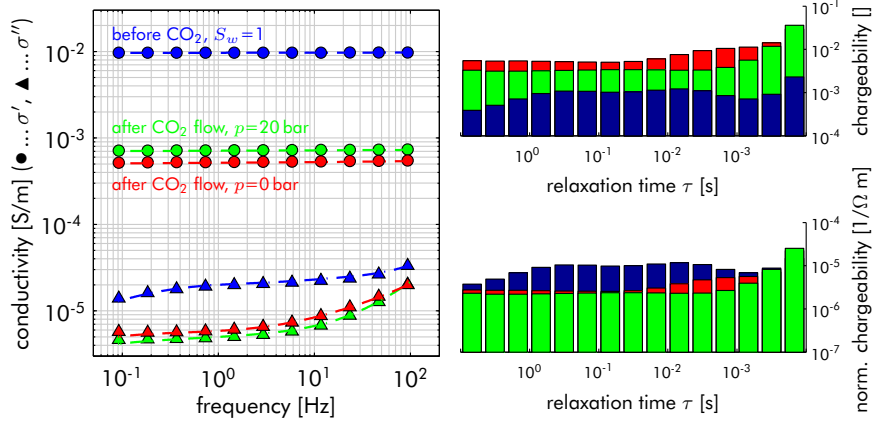


Fig. 2: Conductivity spectra (left) and according Debye decomposition (right) of a flow through experiment with CO₂ at 20 bar and 15°C.

Here, σ_w denotes the electrolyte conductivity with CO₂, σ_w^o is the initial electrolyte conductivity. Λ denotes molar conductivity, γ is the activity coefficient, α is the degree of dissociation and c is concentration. The activity coefficients γ_i of NaCl and dissociated CO₂ are described by:

$$\ln(\gamma_{\text{NaCl}}) = \ln(\gamma_{\text{NaCl}}^o) - g_{12}c_{\text{CO}_2} - h_{12}c_{\text{CO}_2}^2 \quad (8)$$

$$\ln(\gamma_{\text{CO}_2}) = \ln(\gamma_{\text{CO}_2}^o) - g_{21}c_{\text{NaCl}} - h_{21}c_{\text{NaCl}}^2 \quad (9)$$

The parameters g_{ij} , h_{ij} and Λ_{CO_2} are determined by a least squares inversion. A purely empirical formulation is also available (with empirical parameters q_i ; for parameter values and details see Börner et al. [2015a]):

$$\sigma_w^{\text{norm}}(p, T, c_{\text{NaCl}}) = 1 + \frac{q_1 + q_2T + q_3p}{c_{\text{NaCl}}} \left(1 - e^{-(q_4+q_5T)p}\right) - (q_6 + q_7T) \left(1 - e^{-q_8p}\right) \quad (10)$$

When interpreting measurements of complex rock conductivity σ^* in terms of saturation the reactive nature of CO₂ has to be considered. CO₂ flow, the resulting partial saturation, dissolution/dissociation and pH act on the spectral complex conductivity of a sand sample. σ' and σ'' react differently (Fig. 2, left; 20 bar, 15°C, 0.2 g/l NaCl).

The impact of chemical interaction on the three-phase system of CO₂–electrolyte–sand may be deduced from the flow experiments (for experimental details see Börner et al. [2016]). As expected, the surfaces of the quartz sand used for our experiments are not affected by the CO₂ or the low pH of the pore water under pressure (see secondary electron micrographs in Fig. 3). Changes in the imaginary part of conductivity σ'' may be related to chemical effects, therefore. This does not hold for reactive rock matrices.

Chemical interaction may be quantified by comparing the complex conductivity under pressure to the complex conductivity after depressurization at the end of the flow experiments. During pressure release saturation remains the same and CO₂ degasses. Nevertheless, σ' and σ'' change [Börner et al., 2016]. For all pressures and temperatures, σ' reflects the salinity regime predicted by our model (Eqs 7 – 10). At the same time σ'' increases stably due to the change in pH from acidic back to near neutral during degassing. It is known that a lowering of the pH-value causes a reduction of the imaginary part of conductivity σ'' . This effect is also

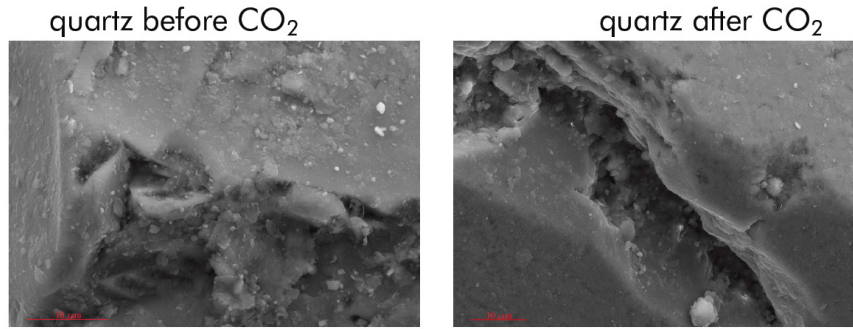


Fig. 3: Secondary electron micrographs of the sample material before (left) and after (right) exposure to CO₂ (courtesy of Dr. Franziska Wilke, GFZ Potsdam).

detectable for the CO₂–electrolyte–sand system. Taking into account the chemical interaction allows for reliably reconstruction the sample saturation from electrical measurements. A Debye decomposition approach might help to separate physical and chemical effects (Fig. 2, right).

4 Conclusions

The electrical rock conductivity is a sensitive indicator for CO₂ migration processes and interactions between the phases of the system CO₂ - pore water - sand. Our experimental results reveal the complicated network of processes, which occur simultaneously, and influence the electrical rock conductivity in multiple ways.

The dominating effect is the reduction of pore water saturation due to the injection of CO₂. This is the basis for electromagnetic monitoring techniques [Börner et al., 2015b]. For the correct calculation of pore contents the chemical interaction between the reactive CO₂ and the pore water have to be taken into account.

The dissociation of carbonic acid adds charge carriers to the pore water. Depending on salinity either the additional conductivity contribution causes an increased pore water conductivity or the mutual impeding of all species results in a decrease in pore water conductivity. We provide a model to predict these effects.

In our study the imaginary part of conductivity is dominated by the chemical interaction processes. It reflects the change in pH caused by the formation of carbonic acid. Measuring the SIP response bears the potential to better differentiate between saturation and chemical effects. This may improve the saturation reconstruction.

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