Thermoelectrical properties of salt solutions and monitoring of mineral precipitation by impedance spectroscopy

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ABSTRACT

Calcite is one of the most abundant scaling minerals in geotechnical installations and the precise knowledge of the hydrochemical solution equilibria is key to predict its precipitation behaviour. In the framework of the EU-funded REFLECT project we perform solubility experiments in the H_2O-NaCl-CO_2 system to broaden the database for temperatures up to 210 °C. Here, we present preliminary results from a series of ongoing solubility measurements as a function of temperature and CO_2 partial pressure (0 – 50 bar) at various salinities ranging between 0 – 20 wt% NaCl. We use electrical conductivity measurements to monitor the progress in dissolution or precipitation from the solutions and to define equilibrium conditions. For this, we have developed a new 4-point electrode system, which was successfully tested at temperatures of up to 213 °C and a maximum system pressure of 70 bar.

1. INTRODUCTION

Scaling is one of the major obstacles for an economically efficient utilization of geothermal energy, as it often causes frequently and costly maintenance of both subsurface and surface installations including production and injection wells, pumps, and heat exchangers (e.g. Wanner et al., 2017, Köhl et al, 2020). Commonly, geothermal fluids contain a multitude of dissolved components such as salts, minerals and gases. However, changes in pressure and temperature during fluid extraction for geothermal energy and power production disturb the hydro-chemical equilibrium and may lead to mineral precipitation due to supersaturation, what in consequence can significantly reduce the flow rates of the geothermal system and rise the economic risk (e.g. Atkinson et al., 1991).

Calcite is one of the most abundant scaling minerals and can be found across a variety of geothermal production sites (Arnórsson, 1981; Haklidir and Balaban, 2019). Calcite is widespread in geothermal reservoir rocks, which is why in-situ formation waters are generally calcite saturated (Arnórsson, 1981). Carbonate scaling is mainly associated with $CO_{2(aq)}$ degassing from the geothermal fluid due to decompression and a subsequent increase in pH, which significantly reduces the solubility of carbonate minerals. Generally, the potential of calcite supersaturation is largely controlled by the initial temperature, the initial CO_2 partial pressure (pH), and salinity of the formation water, and is highest when pH and salinity are highest and temperature is lowest (Arnórsson, 1989). Accordingly, calcite scaling is rampant in low (80 – 120 °C) to medium (130 – 200 °C) temperature sites (Wanner et al., 2017; Quinao et al., 2017), but also causes serious problems in some high-temperature geothermal fields with temperatures of up to 250 °C (Li, 2017). Thus, precise knowledge of hydro-chemical solution equilibria provides an important tool that can be used to prevent unwanted mineral precipitation by adjusting operational production conditions.

Calcite solubilities in water and brines up to 6 M NaCl have been widely studied experimentally at temperatures below 100 °C (Kendall, 1912; Hastings et al., 1927; Miller, 1952; Yanatéva, 1955; Kindyakov et al., 1958; Weyl, 1959, 1966; MacDonald and North, 1974; Plummer et al., 1982, Wolf et al. 1989; Coto et al., 2012 and ref. in it), though a large number of the published data only cover ambient temperature and pressure conditions. Only limited experimental data are available for temperatures up to 300 °C and CO_2 pressures between 1 – 150 bar (Ellis, 1959, 1963; Segnit et al. 1962; Malinin and Kanukov, 1971; Bychkov et al. 2020), and there is a general lack for calcite solubility in high-salinity brines (> 6 wt% NaCl). As a consequence, large uncertainties in current model predictions arise. In order to better predict the scaling behavior of highly saline geothermal fluids in geotechnical installations, new solubility experiments were performed, focusing on fluids with salinities of 35 – 200 g/l NaCl, which are typical for most mid European geothermal sites. Here, we present first preliminary results from a series of ongoing systematic measurements targeting a temperature range of 24 – 210 °C at CO_2 pressures between 1 – 50 bar. We use in-

situ electrical impedance spectroscopy to define equilibrium conditions in the test solutions.

2. EXPERIMENTAL APPROACH

2.1 Development of a high-temperature conductivity probe

The solubility of calcite is highly influenced by the amount of carbonic acid present in the solution and already small fluctuations in pressure and temperature have an immediate effect on its pH. In order to keep system disturbances during the experiments to a minimum, the dissolution/precipitation process was continuously monitored by electrical conductometry. For this, a 4-point electrode system was developed, which had to be capable for electrical conductivity measurements at elevated temperature and pressure. The conductivity probe consists of a rod-like corpus made of PEEK, to which lower end two Ag/AgCl plates (current electrodes) are attached vis-a-vis and supernatant with a defined electrode spacing. Two additionally Ag/AgCl wires, serving as potential electrodes, are sealed into the corpus and placed between the current electrodes. An O-ring sealed adapter was designed for the dimensions of commercial high-pressure screw-in drivers, and is provided for the pressure-tight attachment in the lid of the autoclave. The conductivity probe was used up to 213 °C and a system pressure of 70 bar.

For conductivity measurements, an impedance spectrometer (Zahner-Zennium electrochemical work-station) was used to apply an AC voltage of 50 mV to the current electrodes. The conductance bridge provides the impedance, Z, and phase angle, φ, at distinct frequencies. The conductivity of the test solution, σ_{fl}, is given by

$$\sigma_{fl} = c/R, \qquad [1]$$

with R is the sample resistance, derived from

$$R = \cos\varphi \cdot Z, \qquad [2]$$

and c is the cell constant, which considers the geometry of the electrode layout. The cell constant of the conductivity probe was experimentally determined using distilled water, tap water, as well as 0.01 M and 0.1 M NaCl solutions at ambient conditions. Variations in the electrode spacing due to thermal expansion is regarded to be < 1 % at 200 °C, leading to an overall underestimation of σ_{fl} by 3% at maximum temperature.

2.2 Experimental equipment and procedure for the measurement of calcite solubilities

Solubility experiments at elevated temperature and pressure were conducted in two stainless steel batch reactors with a total capacity of 800 ml, which are lined with beakers made of Teflon or silica glass, respectively, to avoid corrosion. The test solutions were made of 670 g of solvent (degassed bi-distilled water or NaCl solutions at known concentrations) to which a sufficient excess of pure commercial calcite powder of
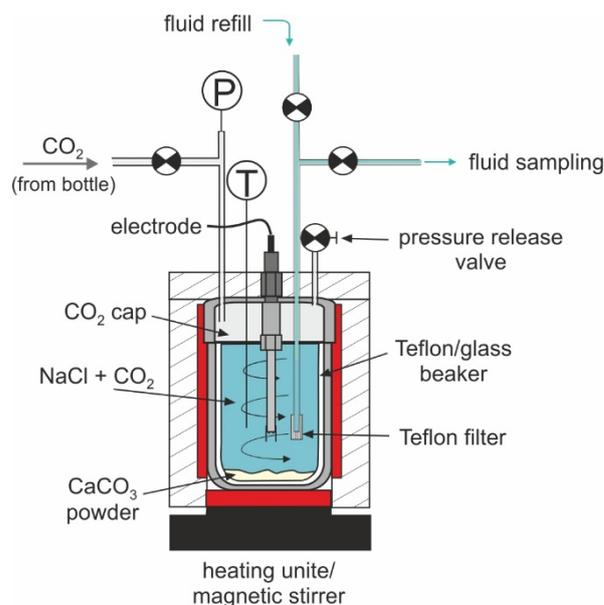

Figure 1: Schematic overview of the batch reactors.

20 g was added, thus a constant particle surface can be assumed over the entire course of the experiments. During the experiment, the solution was stirred by a magnetic stirrer at a continuous rate of 300 rpm.Experiments were performed between 24 – 210 °C and 1 – 50 bar pCO_2. A schematic overview of the set-up is shown in Figure 1.

For pressurization, both autoclaves were connected to a CO_2 bottle, whereby the system pressure was regulated via a pressure reducing valve at the bottle and metering valves at the autoclaves. Autoclave pressures were monitored by high- precision, dead-weight calibrated sensors with an accuracy of ± 0.2 bar. Before the experiment, CO_2 was flushed for approximately 15 - 20 min through the gas cap volume of the autoclaves to remove air from the vessels via open pressure release valves, which were closed afterwards to apply the desired pressure. For temperature control, the autoclaves were placed on heating plates /magnetic stirrers and jacketed with thermally-insulated heating sleeves, so that essentially the whole vessel including the gas cap was at constant temperature. The heating-sleeves were connected to controllers to keep the temperature constant ± 0.1 °C. The fluid temperatures were monitored by K-type thermocouples, placed in dead-ended and Teflon coated Hastelloy capillaries, which again were immersed directly in the tested solutions.

The achievement of equilibration between solution and calcite powder at the desired pressure and temperature conditions was determined via continuous electrical conductivity measurements. When changes in the electrical conductivity were less than 0.5 % for 12 hours, solubility equilibrium was assumed and fluid samples were extracted at system pressure and temperature through a PEEK capillary with attached 2 µm Teflon filter. To avoid contamination, the sampling capillary was flushed with about 10 ml of the produced fluid, which was poured away, before the proper sample was taken. Samples, taken at

temperatures below 150 °C, were discharged directly into a tube, containing a weighted amount of bi-distilled water to avoid precipitation, when the pressure was released to atmospheric conditions. In total, a maximum sample volume of ca. 280 cm^3 could be extracted from the vessel, before the electrodes became partially exposed. Several fluid samples could therefore be taken from the test solutions at different temperature and pressure levels, before the vessel had to be recharged.

Ca^{2+} concentration were determined via EDTA titration with the titration end point being color-indicated by Eriochrome Black T, whereby the determined $CaCO_3$ concentrations are based on the mean values of 5 individual titrations. Usually, the analytical uncertainty in the titration was less than 1 %.
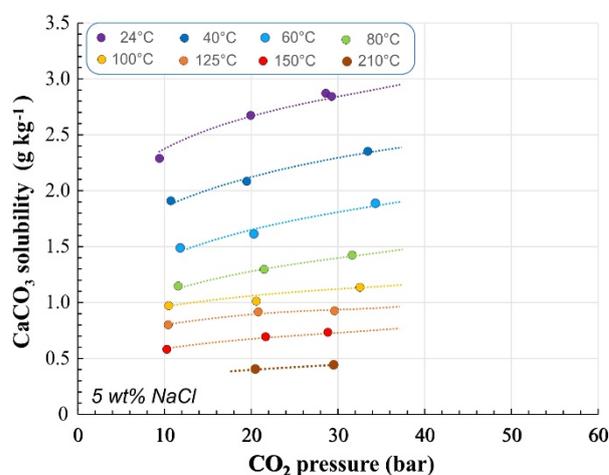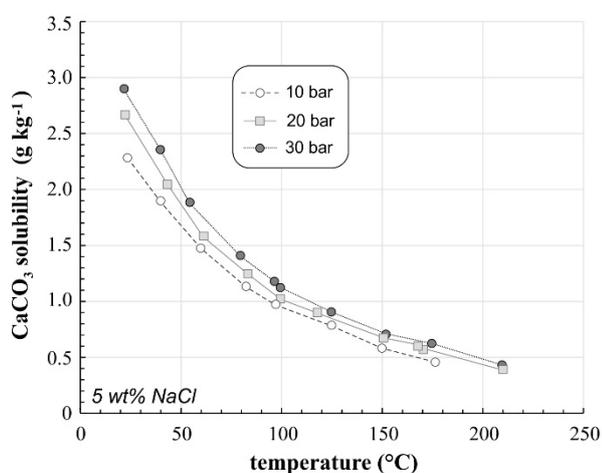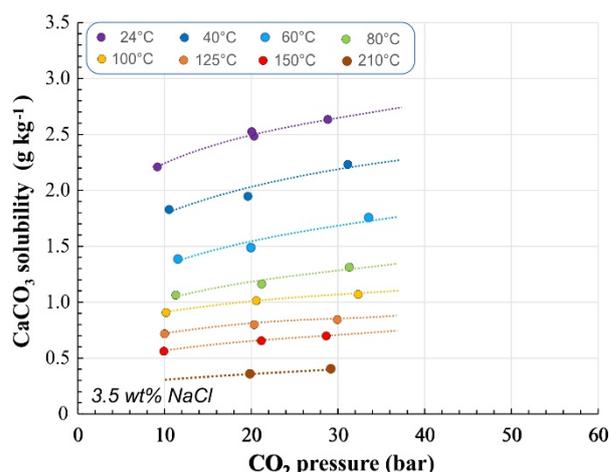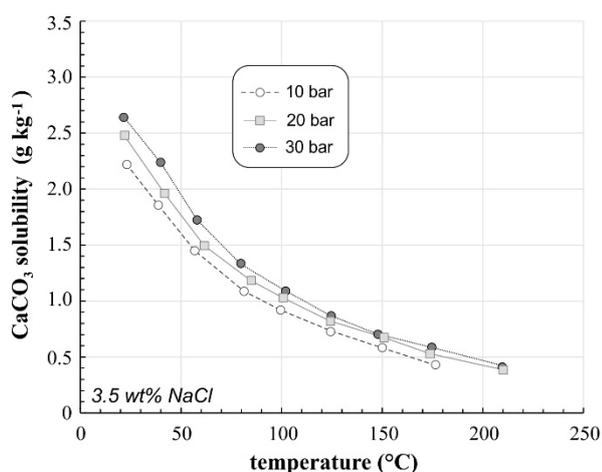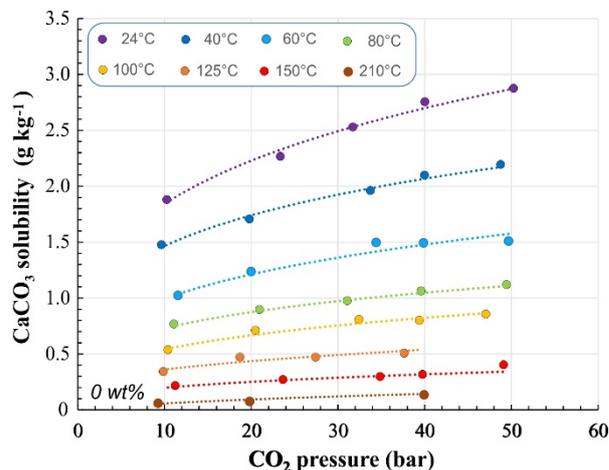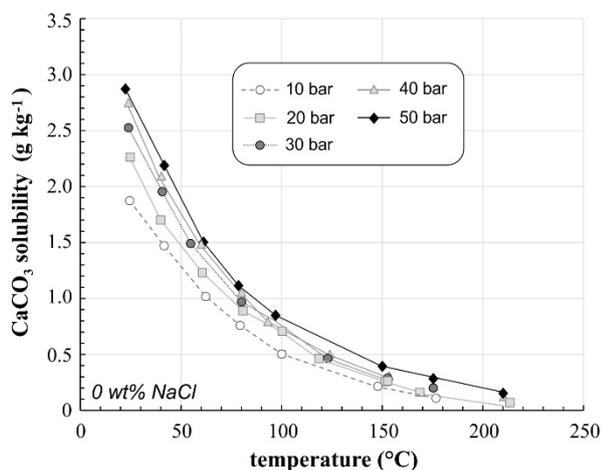

Figure 2: CaCO₃ solubilities in dependence of temperature and CO₂ pressure for solutions with different NaCl concentrations.

3. RESULTS AND CONCLUSION

So far, the solubility of calcite has been tested in pure water and NaCl solutions with concentrations of 3.5 wt% and 5 wt%. The measurements were conducted in a temperature range of 24 – 210 °C and covering pressures of 1 – 50 bar. Experiments with 10 wt% and 20 wt% NaCl solutions are ongoing.The preliminary results are plotted in Figure 2 as function of temperature and pCO$_2$, defined as the difference of the absolute pressure in the autoclave and the vapour pressure of water at the particular temperature. It can be seen that the solubility of calcite in all tested solvents decreases exponentially with increasing temperature and constant pressure, while the solubility increases with increasing pCO$_2$ at isothermal conditions. Where available, this is in agreement with data from previous studies (Miller, 1952; Ellis, 1959, 1963; Segnit, 1962; Bychkov et al., 2020). Figure 3 depicts the variation of calcite solubility in dependence of NaCl concentration for two temperatures. For comparison, data measured at 10 bar in this study were checked against data from Ellis (1963), which were determined at comparable pressure and temperature conditions. The agreement between the two datasets is reasonably satisfactory. Over the range of measured salinities, the solubility increases with the NaCl concentration in the solution.
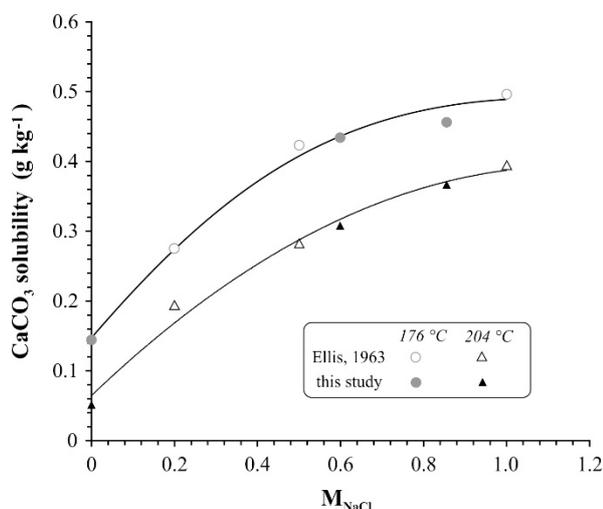

Figure 3: CaCO$_3$ solubility as function of the NaCl concentration at 176 °C, 204 °C and an approximate pressure of 10 bar. Open symbols are for literature data from Ellis, 1963. Solid symbols represent this study.

Precise knowledge of hydrochemical solution equilibria provides a tool that can be used to prevent unwanted mineral precipitation by adjusting operational production conditions. Thus, the new measurements carried out in this study contribute to a broadening of the existing experimental database with the final aim of calculating the solubility product and stability constants of aqueous calcium carbonate and bicarbonate complexes.

From the development of the specific conductivity over time and the titrated Ca^{2+} concentration, the course of the calcium concentration can be deduced, which shows a linear relationship and so that the measured conductivity can be used as a measure for the Ca^{2+} concentration (Baumann et al., 1985, Dreybrodt et al., 1996, Vosbeck, 2004)

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