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## Redox reactions during sandstone flow-through experiments at geothermal conditions

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### Abstract

Copper ions ( $\text{Cu}^+$  or  $\text{Cu}^{2+}$ ) in formation fluids can be reduced by carbon steel of the wells casing at geothermal conditions resulting in native copper ( $\text{Cu}(0)$ ) precipitation, and oxidation and dissolution of iron (Fe). Indeed, high amounts of  $\text{Cu}(0)$  were observed at the bottom of a production well at the geothermal site Groß Schönebeck (Germany). It was expected that this reaction may also reduce the permeability of the reservoir rock close to the well casing. This study aimed to simulate this reaction at laboratorial conditions with special focus on the effect of reaction temperature and kinetics.

A flow-through experiment was designed to simulate the conditions in a geothermal reservoir and well: a saline, and Cu-containing solution flowing through a sandstone media in contact with a steel capillary representing the well casing. Cu and Fe concentration as well as pH-, and redox values were monitored over time. After the experiment, pore spaces were characterized by X-ray computer tomography and by microprobe analysis using EDX on thin sections.

Precipitation of Cu (without Fe) occurred within the sandstone near the wall and bottom of the capillary. The reaction-induced precipitation reduced the flow rate, but did not reach equilibrium after 49 h. While the brine salinity had little impact on the reaction kinetics, an increasing temperature from 25 to 80°C strongly enhanced the overall reaction.

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### 1. Introduction

Water-rock interactions at geothermal conditions are often difficult to predict because access to representative samples at great depth is difficult and even the simulation of those processes at laboratorial conditions is challenging due to elevated temperatures and pressures. However, the geochemical processes assumed to happen at the

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geothermal site in Groß Schönebeck (North German Basin) are of high relevance and therefore a thorough understanding of the processes is important to predict and possibly prevent those reactions.

Briefly, at the geothermal research laboratory Groß Schönebeck a well doublet was drilled into a Permian sandstone and volcanic rock reservoir (1). The fluid at around 4100 m depth is a Ca-Na-Cl brine at a temperature of about 150 °C that contains 265 g/L total dissolved solids<sup>1,2</sup>. During hydraulic tests in 2011 and 2012, a strong decrease in rock permeability was observed over time<sup>3</sup>. Simultaneously, it was found, that the production well was clogged with scaling material that consisted predominantly of native copper, together with barite, laurionite, and magnetite<sup>4</sup>. Based on these observations it was assumed that native copper forms as corrosion product by the reaction of Cu-containing fluid with the carbon steel liner at depth<sup>4</sup>. It was further hypothesized that this reaction also occurs within the reservoir rock on the outer side of the steel tube, where the Cu precipitates would clog the pores<sup>4</sup>. This could be an explanation for the observed reduction in productivity rates<sup>3</sup>. To verify and quantify this, a laboratorial experiment was developed to simulate the reaction in dependence of temperature and salinity.

## 2. Materials and Methods

The set-up of the flow-through laboratorial experiments consists of a steel capillary (representing the well casing) that was first inserted into a pre-drilled rock sample (representing the geothermal reservoir; Fig. 1). The assembly was placed into a 5 l container (“reservoir container”) yielding synthetic brines of various compositions. The capillary was connected to a tube through which the brine was pumped (peristaltic pump) into a second container (“collecting container”). The initial pumping rate was adjusted to 6 rpm (60 ml/h) but needed to be re-adjusted in all experiments over time due to variable flow-through conditions that established during some experiments. Both containers were continuously stirred (magnetic stirrers) and heated to the desired temperature. The brine and the entire system were permanently Ar purged to keep the experiment oxygen-free. Altogether, eight experiments were performed that varied with respect to temperature (25°, 50°, or 80 °C), brine composition (with and without chloride salts), and type of steel (RS carbon steel or stainless steel 1.4307; Table1). For each experiment a “fresh” rock sample (cylindrical sandstone, 50 mm in length, 25 mm in diameter) and steel capillary (30 mm length; 6 mm outer diameter; 3 mm inner diameter) were used. The rock material was a Fontainebleau quartz arenite consisting of 99.98 % of quartz<sup>5,6</sup> with a permeability of ca.  $100 \cdot 10^{-15} \text{ m}^2$ . The synthetic brine always contained 1 mM  $\text{CuCl}_2$  with a background of either deionized water or deionized water with 2 M NaCl and 1.5 M  $\text{CaCl}_2$ . The samples were immediately acidified to  $\text{pH} < 2$  and total Fe and Cu were measured by inductive coupled plasma optical emission spectroscopy (ICP-OES). Before and after each experiment, both the rock samples and the capillary were dried at 105 °C and weighed. After the experiments, the capillaries were separated from the rock and rock samples were transected perpendicularly to the capillary.

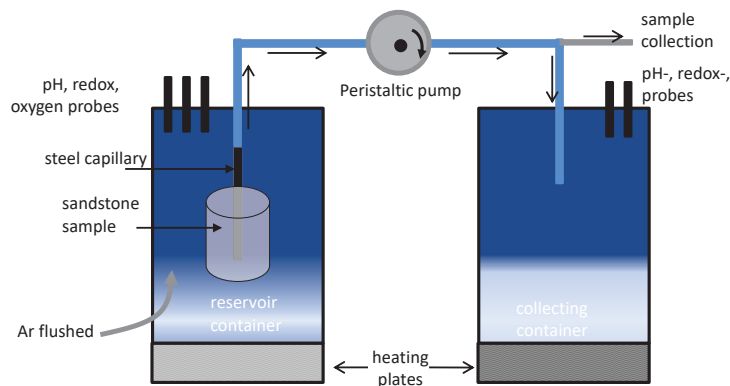


Fig.1. Experimental set-up: the fluid is pumped from the reservoir container (filled with synthetic, Ar-flushed brine) through the rock-steel capillary assembly. Redox-, pH-, and dissolved oxygen are continuously monitored.

Polished thin sections were prepared after embedding the rock samples in epoxy resin. They were analyzed by

electron microprobe (EMP; JEOL JXA-8530F Hyperprobe after Ag<sub>2</sub>O vaporization). Before thin section preparation one selected rock sample (experiment 6) was analyzed by X-ray computer tomography (CT) to obtain 2D and 3D recordings of pore space microstructure. A GE phoenixlx-ray nanotom 180 NF μCT equipped with a 180 kV/15 W X-ray tube and a 5 Mpixel detector was used. During one 360° rotation, recordings were obtained in < 1° steps. By numerical reconstruction these recordings were assembled to a 3D picture with a resolution of 30 μm<sup>7</sup>.

### 3. Results and Discussion

#### 3.1. Fluid analysis

Dissolved O<sub>2</sub> measurements confirmed anoxic conditions (O<sub>2</sub> < 0.2 mg/L) in all experiments. The initial pH-values of the brine in the reservoir were between 4.8 and 4.6 and the redox values between 530 and 460 mV. After reaction with the sample (rock plus capillary) the pH decreased to 2.8 (at 25 °C), 3 (at 50 °C), and 2.5 (at 80 °C), whereas the redox remained relatively constant. In all experiments the decreasing concentration of Cu and increasing amount of Fe over time in the collected samples (Fig. 2) demonstrated an ongoing reaction. Flow rates decreased during all experiments indicating precipitation within the pores of the sandstones thus reducing the rock permeability. As a consequence, the peristaltic pump was re-adjusted during the experiments to allow the continuity of the reaction.

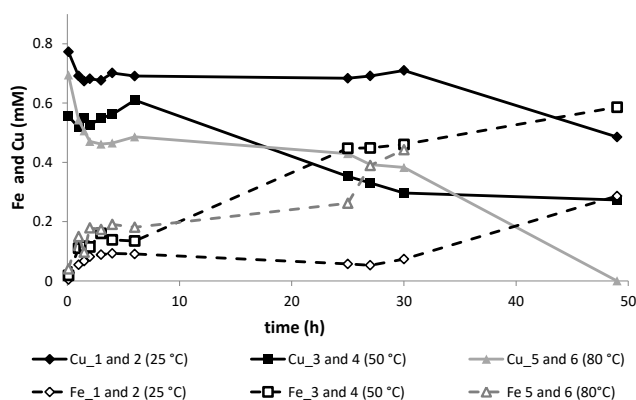


Fig. 2. Cu and Fe concentrations measured from the sampling line over time. Mean values from each 2 measurements.

The total amount of Cu removed from the brine increased with temperature increasing, and was little affected by the chloride content as obvious when comparing experiment 7 to experiments 5 and 6 (Table 1). During the reaction with stainless steel little Fe dissolved (< 2.34 mg) as compared to the reaction with carbon steel (20-124 mg) indicating less electrochemical corrosion (Table 1).

Table 1. Mass gain and loss in rocks and capillaries compared to precipitated Cu and dissolved Fe (calculated from concentrations) after 49 h.

experiment	conditions	mass gain rock sample (g)	mass loss steel capillary (g)	amount of Cu precipitated (g)	amount of Fe dissolved (g)
1 + 2	25 °C in 2 M NaCl, 1.5 M CaCl <sub>2</sub> ; carbon steel	+1.593 ±0.059	-0.01 ±0.005	0.0729	0.020
3 + 4	50 °C in 2 M NaCl, 1.5 M CaCl <sub>2</sub> ; carbon steel	+1.582 ±0.004	-0.043 ±0.014	0.122	0.055
5 + 6	80 °C in 2 M NaCl, 1.5 M CaCl <sub>2</sub> ; carbon steel	+1.376 ±0.047	-0.056 ±0.053	0.139	0.124
7	80 °C no Ca and Na salts; carbon steel	+0.061	-0.044	0.145	0.121
10	80 °C in 2 M NaCl, 1.5 M CaCl <sub>2</sub> ; stainless steel	+1.258	-0.008	0.112	0.002

### 3.2. Solid phase analysis

After the experiments the mass gain of the rock samples was between 61 and 1593 mg each and the mass loss of capillaries was between 8 and 56 mg (Table 1). This shows that in all experiments a reaction took place resulting in precipitation in the rock and corrosion of the steel. When comparing the experiments 5 and 6 with experiment 7 (with and without high salinity; Table 1), around 1.2 g of the mass gain derived from chloride salts that most likely precipitated in the rock pores during drying at 105 °C. Since these salts cannot exactly be quantified, a mass balance is difficult: Roughly 1-2  $\mu\text{mol}$  Cu precipitated and 0.5-2  $\mu\text{mol}$  Fe dissolved in each sample.

CT measurements were obtained after experiment 6 (80 °C). The 3D picture shows areas with elevated density (in white; Fig. 3) that are predominantly located at the bottom (capillary inflow) and along the outer capillary wall. Similarly, thin sections analyzed by EMP showed white areas within the pores (black) between the quartz grains (grey; Fig. 3), that were identified by EDX as Cu precipitates.

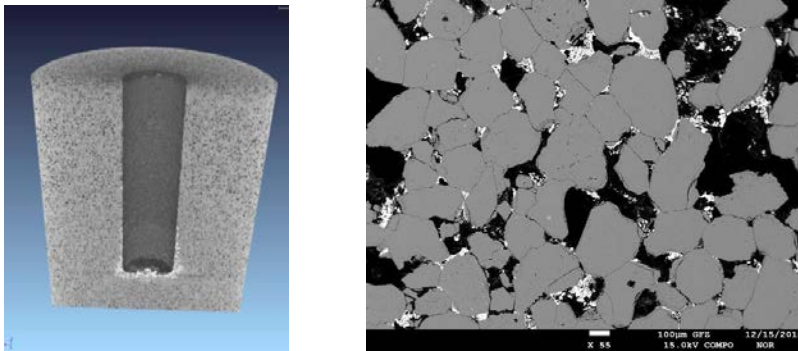


Fig. 3 Rock after flow-through experiment; white areas indicate high density. Left: 3D CT (exp. 6; 80 °C). Right: EMP (exp. 4; 50 °C).

### 4. Conclusions

The experiments evidenced that the proposed redox reaction occurred in all tests with carbon steel resulting in pore space clogging. With temperature increasing the reaction was enhanced. It can be assumed that this reaction also happens in the pore space of a geothermal reservoir formation (e.g. Groß Schönebeck) were it has substantial impact of the overall productivity.

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