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Copper in Geothermal Brine: Origin, Reactions, Risks, and Chances

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ABSTRACT

During fluid production at the geothermal research site Groß Schönebeck (Germany) a gradual decline of the production rate and a simultaneous clogging of the bore hole for about 250 m was observed. The fill of the borehole is composed of a mix of mineral precipitates which consist predominantly of native copper (Cu).

In this study, we aimed to characterize the source of the Cu, the relevant reactions responsible for its precipitation and to find out if copper represents a severe problem for plant operation.

Results showed that high amounts of copper can be expected in certain geological formations (such as the Permian Rotliegend sandstone) where highly saline brine circulates through sandstones and underlying volcanic rocks thereby mobilizing heavy metals. Native copper was found to precipitate due to a redox reaction between the iron (Fe) of the carbon steel liner and dissolved Cu.

This reaction was determined, as simulated in lab experiments, to occur quickly at contact between the two elements. Presumably dissolved copper chloride complexes enter the borehole and precipitate immediately at the liner wall. Another lab experiment evidenced that copper also precipitated in the pores of the reservoir rock at the wellbore near area which would have severe impact on the overall well productivity.

In turn, copper precipitation once prevented to happen in the production well by appropriate means and kept as dissolved copper in solution, could be exploited at the surface thus being potentially of economic value.

1. INTRODUCTION

Highly saline and metal-rich formation fluids, also called Mississippi Valley type are a worldwide frequently occurring sediment basin type of fluid (Force et al., 1991). They are generally marked by a complex chemical composition mainly given by high concentrations of sodium (Na), calcium (Ca), chloride (Cl), and many other compounds in various concentrations depending on the particular geological setting of the host rocks (Hanor, 1994). Many of the dissolved species are of major concern for operating geothermal power plants because they are known to be responsible for corrosion (such as chloride) or mineral precipitation (scaling; such as barium (Ba)). In anaerobic, highly saline solutions (> 100 g/L total dissolved solids), as well as in the absence of sulphide, dissolved metals, such as iron (Fe), copper (Cu), or zinc (Zn) occur preferentially as chloride complexes (Hanor, 1994), which explains their high solubility.

Despite their negative effects on plant operation, some of the dissolved components might also be of advantage if they can be effectively separated from the fluid to be used as raw materials. This is discussed so far only for the element lithium which frequently occurs in highly saline geothermal brines and might be of minable value (Kesler, et al., 2012).

The Groß Schönebeck (GrSk) research facility, located in the North German Basin, has been established in 2001 to investigate processes in the geothermal fluid loop and to enhance geothermal technologies. A well doublet has been drilled up to 4.4 km depth into a Permian (Rotliegend) volcanic rock and sandstone formation. These formations have been hydraulically stimulated to increase permeability and thus fluid productivity (Zimmermann et al., 2009; Zimmermann & Reinicke, 2010). At reservoir conditions the fluid temperature is 150°C but due to low pump rates, the surface temperature during circulation tests was 100 °C at maximum. Much information about the fluid composition has been collected over the last decade, due to various sampling campaigns before and after reservoir treatments (drilling, stimulations or production tests) both above ground and at different depths in the two boreholes (Regenspurg et al., 2010). Due to temperature and pressure dependent mineral solubility, however, the fluid composition varies during fluid production (Feldbusch et al., 2013). At periods of continuous fluid production the chemical composition usually stabilized and the concentration of most compounds would be higher, whereas during long production breaks the fluid cools down and many minerals such as barite ($BaSO_4$) would simultaneously precipitate thereby removing components such as barium (Ba^{2+}) and sulfate (SO_4^{2-}) from solution.

In April 2011 the geothermal fluid loop has been established and various production tests have been performed until August 2012. Altogether about 18000 m³ fluids have been produced and re-injected to the underground. Within that time a gradual decline of the production rate and a simultaneous clogging of the bore hole for about 250 m were observed. In January 2014, the fill of the borehole has been removed to a depth of 4346 m by installing a drilling rig and flushing out the fill by reverse circulation. Roughly around 450 l of sediment was removed from the well which is composed of a mix of mineral precipitates consisting predominantly of barite ($BaSO_4$), native copper (Cu), magnetite (Fe_3O_4), lead (as laurionite (PbOHCl) and amorphous phase), as well as occasional calcite ($CaCO_3$) and cuprite (Cu_2O) (Regenspurg et al., 2013; Regenspurg et al, submitted). The large amount of native copper occurs either as fine grains, in tabular shape or as nuggets of maximal 22 mm length. Additionally, a material loss of the casing was observed as determined by measuring the inner diameter of the liner by a multi-finger caliper measurement that indicated 7 to 12 wt. % of material loss within 500 m of the lowest liner segment (Regenspurg et al., 2013).

As discussed in a previous study (Regenspurg et al., 2013; Regenspurg et al. submitted) the native copper at the GrSk site forms as product of a redox reaction between the iron (Fe_0) of the carbon steel of the casing and dissolved copper(II) chloride complexes. As shown in equations 1-3 (Stumm & Morgan, 1996) the standard redox potentials (E_0) of the Cu^{2+} and Cu^+ reduction are clearly higher (more noble) than the oxidation of solid iron (Fe(s)) indicating that these reactions are likely to happen.

- $Cu^{2+} + 2\,e^- = Cu(s)$ $\quad E_{01} = 0.34$ V (1)
- $Cu^+ + e^- = Cu(s)$ $\quad E_{01} = 0.52$ V (2)
- $Fe(s) = Fe^{2+} + 2\,e^-$ $\quad E_{03} = -0.44$ V (3)

The loss of iron from the steel material and the formation of iron oxides (predominantly as magnetite) as part of the sediment fill of the well give further evidence for the likeliness of the reaction.

Measured Cu concentrations in brine sampled both, in the borehole or above ground at the well head were usually very low (0.07 – 7 mg/L). The highest Cu concentration of 7 mg/L was measured in a sample from 2001 after drilling has finished but before borehole operations (stimulation) started in the open hole section of the injection well at 4235 m depth. Even when assuming this concentration to be real, after fluid production of 18000 m³, altogether 126 kg of pure native copper would have been formed in the borehole. However, the 450 l of sediments consist of roughly the double amount of native copper. This leads to the assumption that the Cu concentration of the formation fluid is in fact much larger than the measured Cu concentration collected in samples from the production well. It also cannot be excluded that the real formation fluid Cu concentration is even larger than that, because precipitation might additionally have occurred at the reservoir side of the casing thus clogging the pores of the wellbore near formation rock. This theory would also explain the decreasing productivity of the well by reduced permeability of the reservoir.

From these observations we hypothesize that at the reservoir side of the well a more highly concentrated Cu solution would react immediately at contact with the casing or with conducting materials (like native copper precipitates) being in contact with the casing. Therefore precipitation would occur both, in the reservoir rock around the borehole and within the borehole. The goal of this study is to verify this hypothesis by two lab experiments: The first should prove that copper (Cu^{2+}) reduction in a geothermal fluid takes place quickly when being in contact with low alloyed steel. In the second experiment we aimed at demonstrating that Cu^{2+} reduction might not only take place within the borehole but also in the surrounding reservoir rocks. This could be of major concern for operating a geothermal plant, because the permeability around the borehole would strongly be reduced.

2. EXPERIMENTAL SET-UP

Two experiments have been performed to investigate steel corrosion in the presence of copper ions at reservoir-like conditions (high salinity).

2.1 Reaction of Cu^{2+} solution with two types of steel (autoclave)

Each two coupon samples of either carbon steel St37 (such as typically used as casing material) or highly alloyed duplex steel 1.4472 were exposed for 20 h at 100 °C in a highly saline Ca-Na-Cl solution (5M Cl) to a 2 mM $CuSO_4$ solution over 20h in autoclaves. Each coupon was weighed before and after the experiments (table 1).

Table 1: autoclave experiments with two types of steel in 2 mM $CuSO_4$ solution at 100 °C.

sample	material	mass before exposure (g)	mass after exposure (g)
1	St 37	19.39	19.29
2	St 37	20.29	20.19
3	Duplex 1.4462	27.24	27.22
4	Duplex 1.4462	27.52	27.51

2.2 Flow through experiment

To simulate the conditions in the borehole a small tube of carbon steel (Ø 6 mm) representing the casing of the well was inserted into a cylindrical, well characterized sandstone-arenite (Fontainebleau, France), consisting predominantly (99 %) of quartz grains (Cooper et al., 2000; Milsch et al., 2008) representing the reservoir rock (Fig. 1). The sample was introduced in a flow-through cell. A Na-Ca-Cl solution (5 M Cl) was mixed with 1 mM $CuCl_2$. Five liters of this artificial brine was first purged by nitrogen to remove dissolved oxygen from a reservoir container. The anoxic brine was pumped at constant flow rate (5 ml/min) first through the rock/carbon steel sample and afterwards it passed a flow-through cell containing probes for measuring oxygen, pH- and redox value (Fig.1). From there it was collected in the outflow collection container where samples could be collected at certain time steps. The whole flow-through set-up was kept anoxic. In the outflow Cu(tot) and Fe(tot) were measured by ICP-OES.

After the experiment the rock sample was split in the middle and visually evaluated.

3. RESULTSAND DISCUSSION

Pictures of the steel coupons after the reaction of carbon St37 or duplex steel with copper (II) chloride solution are shown in Figure 2. After the reaction of carbon steel with the copper solution, a clearly visible layer of native copper had formed on top of the coupons (Fig. 2). Simultaneously a weight loss of about 10 mg was measurable for the carbon steel samples. In contrast, the surface of the duplex steel did not change and no signs of corrosion or precipitation were recognized. The weight of the duplex steel remained constant.

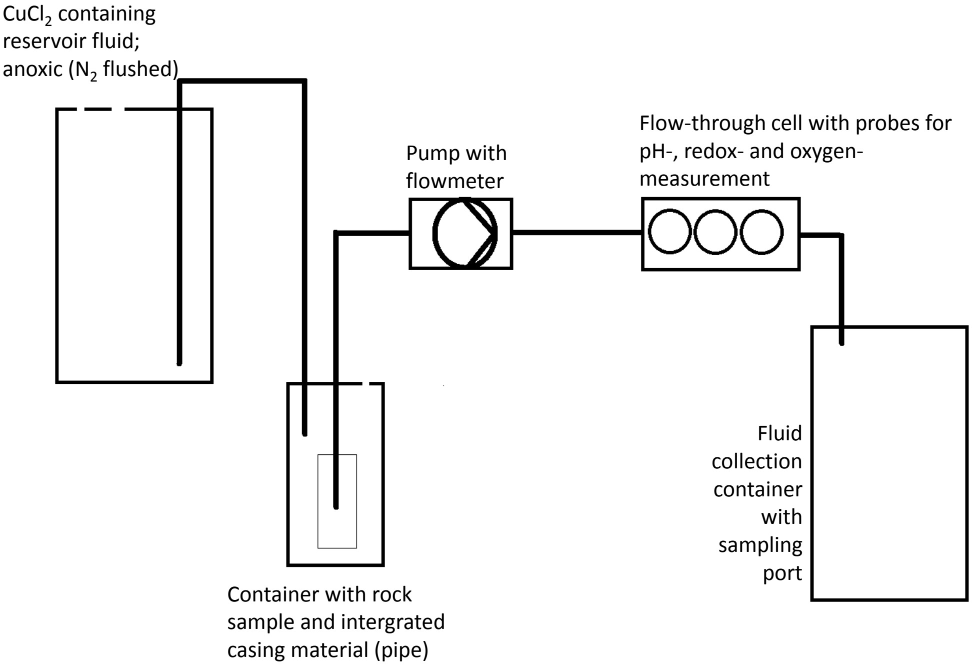

Figure 1: Experimental set up of the flow-through reactor.

Figure 2: Reaction of carbon steel (top) and duplex steel (bottom) with saline copper(II) chloride solution. Native copper precipitation is clearly visible on the carbon steel samples.

This indicates the reaction of iron of the lower alloyed steel with copper solution according to equations 1-3. Higher alloyed steels are in the galvanic series more noble than copper (Atlas Steel, 2010) and a reaction does apparently not take place.

In the flow-through cell, the experiments were finished after 25 h. The pH measured over time in the in-and outflow remained relatively stable between 4.6 and 5.2 (pH-shift corrected according to Feldbusch et al., 2013) over time of the experiment. In contrast, the redox value was at the beginning of the experiment also relatively constant in in- and outflow (497 and 415 mV, respectively) but decreased strongly towards to -200 mV in the outflow at the end of the experiment). This decrease indicates reducing conditions and ongoing redox reactions in the sample.

After the experiment, the rock sample was split into two parts. Visually a dark red radial reaction front of about 4 mm has formed radially around the steel pipe within the white quartzite sandstone (Fig. 3).

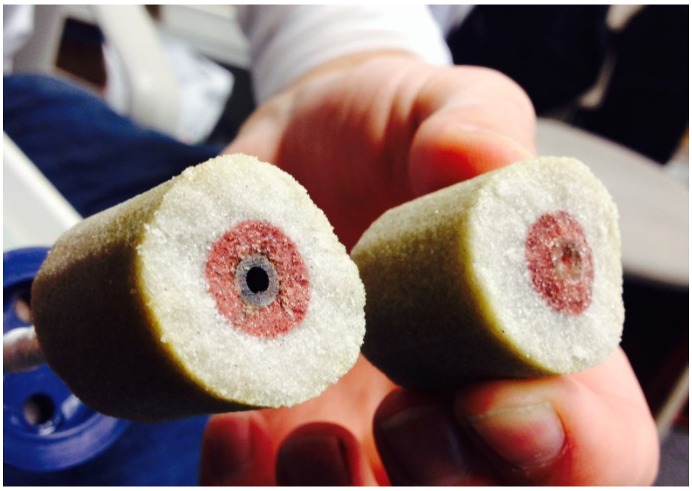

Figure 3: Rock sample with integrated carbon steel pipe after the flow-through of a $CuCl_2$ solution. The red precipitation is assumed to be cuprite (Cu_2O).

Due to its dark red color it can be assumed that the red phase is composed of the copper(I)oxide cuprite (Cu_2O) as well as possibly additional hematite (Fe_2O_3). This indicates an incomplete reduction of the Cu(II) solution. A similar reaction can be expected to occur in the reservoir when the Cu(II) chloride-rich fluid arrives at casing wall. Most probably, a complete reduction to Cu(0) is possible only when the copper comes in direct contact with the Fe(0), whereas in some distance from the steel, an incomplete reduction would take place.

4. CONCLUSIONS

Although so far never really evidenced, the occurrence of Cu-rich brine in Rotliegend sandstones of the North German, Thuringian, or Polish Basin has already been assumed in several studies (Blundell et al., 2003; Hitzman et al., 2010). Measuring the Cu concentration of these Rotliegend fluids is almost impossible since dissolved copper probably immediately precipitates as native copper on any kind of carbon steel device thus being removed from solution.

The present study confirms these assumptions because (i) high copper content was found to be the main component in massive scale formation in the Groß Schönebeck well and (ii) experiments indicated a fast copper precipitation with carbon steel.

Our experiments further indicated that the reaction not only takes place at the surface of carbon steel but also might happen in some distance from the well within the pores of the reservoir rock forming either native copper or the copper(I) oxide cuprite.

This has several implications for operating a geothermal plant in this or similar metal-rich geothermal systems: (1) lab experiments indicate that severe reservoir damage can be expected to occur around the casing on the reservoir side. However, this can only be evidenced by obtaining drill cores form an area close to the wellbore. (2) Corrosion of the casing and material loss of the pipes can be assumed as evidenced by multi-finger caliper measurements performed in December 2012 in Groß Schönebeck. (3) The application of a different casing material is recommended for future geothermal wells in this formation. This could be either more noble steel (such as duplex steel, stainless steel, and austenitic steel) or coated, galvanized, or glass fiber reinforced plastics. However, for all these materials, their resistivity in high temperature, high pressure and high salinity solutions has to be considered for application at the respective geothermal conditions.

Apart from the negative effect that the copper-steel reaction might have for the casing of the well and for the reservoir, the high copper concentration in Rotliegend fluid could also represent a unique chance for further development of geothermal energy. We assume that if native copper can be prevented to precipitate in the well and kept in solution instead until the fluid is transported to the surface, another method could be developed to remove the copper above ground. This would not only prevent copper precipitation in the injection well, where the same reaction is expected to happen, but also the recuperated copper could be further used as raw material. Thus the exploitation of geothermal energy would not only produce hot water but also metal of economic value.

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