



Inhibitor influence on corrosion of carbon steel with respect to the Upper Rhine Graben geothermal brines

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ABSTRACT

Corrosion of construction materials in geothermal brine environments is of great concern in the long-term operation of geothermal power plants. In case of geothermal energy production there are many site-specific factors influencing corrosion processes e.g. high salinity, pH, high temperature, presence of non-condensable gases, fluid velocity, corrosion products, geometry of the power plant, acid treatment and acid cleaning procedures (Guerra & Jacobo 2012). To prolongate the lifetime and thus decrease downtime periods and economic losses, a careful material selection at acceptable costs is essential (Carter & Cramer 1992). Nogara & Zarrouk (2018b) summarized the results of 172 tested metals and alloys for the use in geothermal environment. Among low cost carbon steels, stainless steels, alloys and titanium are employed for functional parts as turbine blade or heat exchanger material respectively (e.g. Ravier et al. 2016). In geothermal power plants up to 12 types of corrosion may occur depending on the corrosiveness of the produced brine (e.g. Nogara & Zarrouk 2018a).

Deep geothermal fluids of the URG have salinities up to 200 g/L and a high CO₂ content (e. g. Sanjuan et al. 2016) resulting in corrosion of the construction materials. For example the produced Na-Ca-Cl brine at the geothermal power plant in Soultz-sous-Forêts (Alsace, France) exhibit high salinity with 100 g/L total dissolved solids, a temperature of 160 °C and a gas:liquid volume ration of nearly 1 (mainly CO₂) (Sanjuan et al. 2010). Several corrosion studies (e.g. Mundhenk et al. 2014) have been performed in the last years. For the geothermal power plant in Rittershofen material evaluation tests were performed on heat exchanger materials (Ravier et al. 2016).

Corrosion and/or scaling control can help to extend the lifetime of geothermal power plant facilities from downhole to surface like casing, tubings, pumps or heat exchangers. The use of corrosion and/or scale inhibitors is a common method for material protection and one of the most useful in industry due to low cost and good handling (e.g. Finsgar & Jackson, 2014). Inhibitors are mostly organic substances interfering with the anodic or cathodic corrosion reaction, forming a protective barrier on the metal surface. The efficiency of an inhibitor depends on flow patterns, solution chemistry, temperature, pressure, the mode of interaction with the metal surface, specific inhibitor concentration and on the inhibitor properties (Wang et al. 2001). Main aspects influencing inhibitor performance in geothermal environment are: a) the compatibility of the inhibitor in high saline brine (avoiding precipitation, clogging), b) competition of dissolved ions and inhibitor molecules for sorption sites on the metal surface and c) existing scales may have a synergistic or antagonistic effect. However, incorrect choice or use of organic inhibitors can lead to corrosion stimulation. Organic inhibitors have a threshold concentration value, below which no corrosion inhibition occurs (Schweitzer 2010).

The aim of this work is to evaluate the corrosion processes of different steel materials and the performance of several corrosion inhibitors in the geothermal environment of the Upper Rhine Graben. Corrosion behavior of carbon steel in CO₂ saturated artificial geothermal brine, was tested in absence and presence of an amine based inhibitor by weight loss tests and electrochemical measurements. Experimental conditions were adapted to the conditions existing at the re-injection side of geothermal power plants located in the Upper Rhine Graben. Experiments were performed with carbon steel in CO₂-saturated artificial NaCl- and Na-Ca-Cl brine (pH ≈ 5, 80 °C). The influence of Ca²⁺-ions on the corrosion behavior due to scale formation and its impact on inhibitor performance was investigated. The inhibitor performance was tested by weight loss tests and the use of electrochemical measurements as potentiodynamic polarization (PP) and impedance spectroscopy (EIS), depending on inhibitor concentration and time. The impact of corrosion scale on inhibitor performance was tested on pre-corroded steel surface as well as the corrosion behavior of blank material in geothermal environment. All experimental tests (weight loss, PP and EIS) showed a decrease in corrosion rate (CR) with increasing exposure time in artificial geothermal brine (Na-Ca-Cl brine, 80 °C, CO₂, pH ≈ 5). The formation of a (Fe,Ca)CO₃ layer restricts the mass transfer process at the interface metal surface

– scale – bulk solution, resulting in lower CR. In the presence of Ca²⁺-ions the CR decreases compared to pure NaCl-brine at the same chloride content. Both steel qualities exhibit a similar corrosion behavior at same experimental conditions. The experimental tests (weight loss, PP and EIS) showed that the inhibitor performance depends on inhibitor concentration. There is an area of concentration where the inhibitor perform most. Too low and too high inhibitor concentrations were not sufficient. The Presence of Ca²⁺-ions resulted in the interplay between the formation of carbonate deposits and adsorption of inhibitor molecules on the metal surface resulting in lower inhibitor efficiency at scaling conditions. Accepted CR of carbon steels in geothermal environment < 0.3 mm/a were achieved by inhibitor addition of 200 ppm (Figure 1). Inhibitor performance decreased significantly on pre-corroded metal surface compared to fresh samples at same experimental conditions.

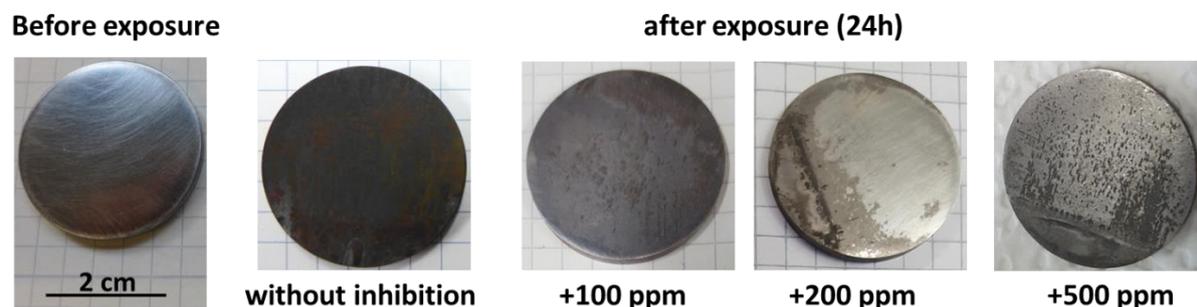


Figure 1: Steel coupons before and after exposure with different kind of inhibitor concentrations.

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