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THE LONG RUN***

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Geothermal: Green Energy for the Long Run

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Well Integrity Tech

High-Temperature Corrosion Testing Facility for Coating Materials in Simulated Geothermal Environment

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ABSTRACT

This paper is part of a project entitled “Geo-Coat” aimed at developing new and cost-effective corrosion resistant coatings for geothermal applications. The subject of this study is the design and function of a laboratory facility used for corrosion testing of the developed coating materials in simulated high-temperature geothermal conditions. The coating materials developed within the project for corrosion testing are High Entropy Alloys (HEA), Ceramic-Metal materials (Cermet), and Electroless Nickel Coatings. The performance of these coatings will be compared to material commonly used for geothermal equipment such as carbon steel which can experience corrosion and erosion. Samples coated with such substrates are placed into the flow-through reactor and exposed to prepared geofluid, with acidic pH and elevated H₂S and CO₂ concentration, for several days or weeks. Passing "geothermal" solution is sampled and monitored, and the surface/microstructural inspection with the chemical composition of tested coatings are studied by the scanning electron microscope (SEM/EDS). Best coating candidates can increase the durability of commonly used alloy materials in geothermal applications.

1. Introduction

Geothermal energy is renewable and sustainable compared to conventional fossil-based energy regarding the supply of heat energy and electricity for human needs, and therefore there is a high

demand for renewable energy in the present energy market. However, one of the pitfalls is the aggressive nature of the utilized geothermal fluid and is demanding on the material selection. The materials can and often prematurely fail, and thus increase running cost.

Corrosion is a major issue in all geothermal power facilities. In general, the characteristic of the utilized geothermal fluid is always dependent on the geological situation. This means each geothermal site will have unique conditions (pressure, temperature, one or two-phase fluid, mass flow) and chemical composition. Reservoir fluids have typically mildly acid to neutral pH and Na, Cl, SO₄, and Si as the dominant dissolved solids with CO₂ and H₂S being the major gases (Arnórsson et al., 2006). Dissolved gases present in the fluid such as CO₂, H₂S, NH₃, H₂ and in some cases HCl and HF (as magmatic volatiles) are the main corrosive agents. (Karlsdóttir, 2012; Stefánsson, 2017). As is well-known that carbon steel is a low-cost alloy widely used in geothermal power plants for well production, wellhead equipment, pipelines, valves, and re-injection pumps (Karlsdóttir et al., 2018). However, the properties of carbon steel operating in the geothermal environments are expected to be strictly limited to the corrosion resistance that will reduce because of an effect of aggressive environments, including the high temperature, pressure, flow velocity, H₂S/CO₂ gases, low pH, and high anion concentration (Ghanbari et al., 2018). The carbon steel corrosion resistance reduces with an increase in penetration corrosion rate with being operated in the so-called two-phase system that consists of gas and liquid phases

The integrated effect of the two-phase flow at high temperatures forces the metal degradation mechanism such as scaling and corrosion, thereby the scaling leads to the equipment plugging through deposition on plant-working parts, and the corrosion results in equipment damage owing to the effect of high-temperature corrosion and erosion-corrosion. Taking into account the presence of the liquid phase containing aggressive ions, corrosion in the alloy proceeds as a result of electrochemical reactions with the establishment of anodic and cathodic regions that contributes to the higher corrosion rates. Depending on characteristics of the corrosive environment affecting the alloy, it can lead to form either uniform corrosion or localized corrosion, whereby the latest is accompanied by the formation of pittings and cracks leading to Environmental Assisted Cracking, Stress Corrosion Cracking, Corrosion Fatigue Cracking, Sulfide Stress Cracking, and Hydrogen-Induced Cracking and hence, to the equipment failure (Karlsdóttir, 2012).

In pursuance of the described above, carbon steel is an easily corrodible material in aggressive geothermal environments. However, the corrosion resistance properties of carbon steel can be improved by applying coating materials to the alloy, that will lead to an increase in the service life of plant components. Therefore, carbon steel is used as one of the substrate materials for developing coatings, that are cost-effective and corrosion resistant in geothermal applications. The materials employed as coatings were chosen High Entropy Alloys (HEA), Ceramic-Metal materials (Cermet), and Electroless Nickel Coatings. Based on the stated above, the goal was set to create a laboratory facility for geothermal environment simulation for testing the developed coatings concerning the high-temperature corrosion resistance (Kovalov et al., 2019). Thus, findings after the corrosion testing will allow selecting the best coating candidates and thereby reducing the number of premature equipment failures and, hence, replacement expenses of the plant components. The work were carried out within of the Geo-Coat project (www.geo-coat.eu).

2. Experimental approach

2.1 Simulated geothermal fluid and analysis

The composition of simulated geothermal fluid is based on the fluid chemistry of utilized fluids in real geothermal power plants. Here is formulated acidic geofluid with elevated H₂S and CO₂ concentrations at water saturation pressure at 185°C. The simulated geothermal environment for experimental testing of coupons is first considered with PHREEQC (program version 3.4.0-12927) software for geochemical calculations (Parkhurst et al., 2013). Subsequently, two solutions are prepared separately to maintain their stability. Inlet H₂S-CO₂ solution 1 (Na₂S 10 mmol/kg + NaHCO₃ 46 mmol/kg) is mixed with inlet HCl solution 2 (HCl 66 mmol/kg) and pumped, with 1:1 ratio, into the reactor where sample holder with specimens is located. Inlet solutions are N₂ deoxygenated and prepared with deionized water (Millipore™) and Sigma-Aldrich® reagents. The aggressive geothermal environment is assured with a continuous flow of pumped solution. The pH value of the mixed inlet solution is ~4 at room temperature, dissolved inorganic carbon (DIC = [CO₂] + [HCO₃⁻] + [CO₃²⁻]) is ~23 mmol/kg and ~5 mmol/kg for H₂S, respectively. Samples of inlet and outlet solutions are collected to determine their chemical composition. Samples for major dissolved elements (Si, Ti, Na, K, Mg, Ca, Fe, Al, Cl) are first filtered through 0.2 μm, then acidified to 1% HNO₃ (Suprapur®), and analyzed using ICP-OES. Samples for SO₄ analysis are treated with 2% Zn-acetate and filtered off prior to measuring SO₄ using IC (Ion chromatography). Determination of pH, DIC, and H₂S is conducted on un-treated samples with a combination of a pH electrode and a pH meter, modified alkalinity titration, and precipitation titration using Hg-acetate, respectively (Arnórsson et al., 2006). The outlet DIC samples are collected to NaOH to prevent degassing. The analytical precision at the 95% confidence level based on repeated analysis of an internal standard is ~1–10% for different elements. Based on duplicated determination, the analytical precision of CO₂ and H₂S concentrations is < 3%, and pH is ± 0.05 pH units.

2.2 Corrosion Testing Apparatus

A schematic illustration of the pressurized reactor system is depicted in Figure 1. All wetted parts of the experimental apparatus were made of inert material, including PEEK, titanium, Hastelloy, and Inconel. The CO₂-H₂S solution and HCl solution are mixed and pumped into the working tube/reactor (with 3.34 cm internal diameter and 130 cm total length) using an HPLC pumps (Chromtech®). The pressure is controlled at the end of the system's line with a back-pressure regulator (set to 11-15 bars) and is monitored with pressure gauge inside the experimental line after the solution passes the heated section of the reactor. The photo of the actual laboratory setup of the flow-through reactor is shown in Figure 2.

The reactor was heated to the target temperature of 185°C with the aid of a heating tubular 3-zone oven (Carbolite). The outlet fluid was cooled to room temperature with the help of a cooling loop/jacket placed between the reactor and the back-pressure regulator. Samples of the outlet solutions were collected at the low-pressure end of the back-pressure regulator. Samples of the inlet solutions were collected directly from the inlet solution bottles.

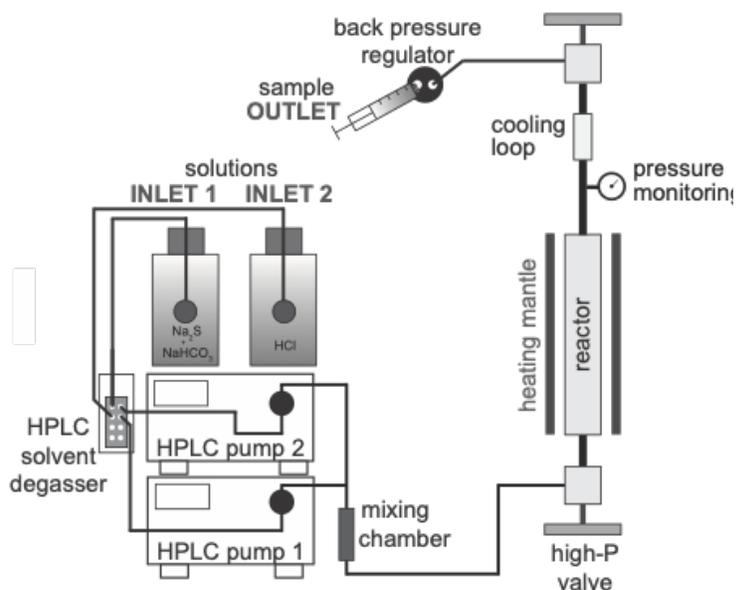


Figure 1: Schematic drawing of the experimental setup.



Figure 2: The laboratory setup of the flow-through reactor.

2.3 Tested materials and analysis

The carbon steel, stainless steels, titanium, and nickel alloy bases were selected as substrates for novel protective coating formulations. As materials for employed coatings were chosen High Entropy Alloys (HEA), Ceramic-Metal materials (Cermet) and Electroless Nickel coatings.

In order to avoid vulnerable regions of metal samples to corrosion effect, the samples were fabricated in a rod form to reduce the area of sharp edges. The dimension of the rod sample was 7 mm-diameter x 80mm-length. The rod samples were custom made from the substrate materials described above. The fabricated metal rods were placed into the high-temperature and aggressive solution resistant custom-made Polyether Ether Ketone (PEEK) TECAPEEK® specimen holder of 15mm-diameter x 28mm-length (see Fig. 3).

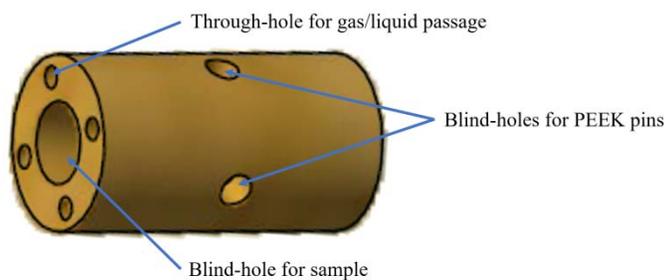


Figure 3: Illustration of the sample holder for the testing reactor.

It is well-known that the geothermal environment consists of two phases, including steam with H₂S/CO₂ gases and liquid phases. The latter (i.e., the liquid phase) in geothermal wells possess electrolyte properties causing corrosion of metals. Taking into consideration that fact that in the pipe of FTR can be placed two different kinds of alloys where one type is working samples, another one is sample holder, the galvanic corrosion will occur between these two different alloys in the solution. The galvanic effect will make an alloy with lower electrochemical potential corrode faster the more noble alloy (i.e., alloy with the higher electrochemical potential) due to a potential drop between the alloys across the electrolyte. This will result in distorting the results for corrosion in the samples after tests. Thus, in order to avoid the galvanic corrosion effect that potentially can exist between samples and sample holders in the electrolyte, the sample holders and their accessories were made from a Polyether ether ketone (PEEK) material. The PEEK material is capable of resisting the influence of the aggressive environment, pressure, and high temperature (up to 300 °C). The demonstration of the PEEK sample holders with carbon steel rod samples are shown in Figure 4.

The designed sample holder allowed several testing configurations, varying the sample location within the reactor and loading up to 12 metallic samples within one experimental run. The scheme depicting the sample holders mounted in the testing reactor is shown in Figure 5. Note, during the experiment, the testing reactor is installed vertically.

For the surface, microstructural and chemical analysis (at low to high magnification) of the carbon rod samples, a scanning electron microscope (SEM/EDS) was used to investigate the corrosion damages. The polished cross-sections of the rod samples were prepared and inspected as well.

Here we report on the developed laboratory for the higher temperature corrosion tests with being carbon steel substrate selected for the preliminary testing that was performed to verify that the simulated geothermal environment was achieved in the testing environment. This was conducted by measuring the corrosion rate of the samples aligned along the reactor length. Also, the investigation of the corrosion damage of the samples was carried out, and the corrosion mechanism occurred was described and compared to known corrosion forms occurring for the material in a real geothermal environment.



Figure 4: Actual components of the PEEK sample holders assembled with carbon steel rod samples for demonstration purpose.

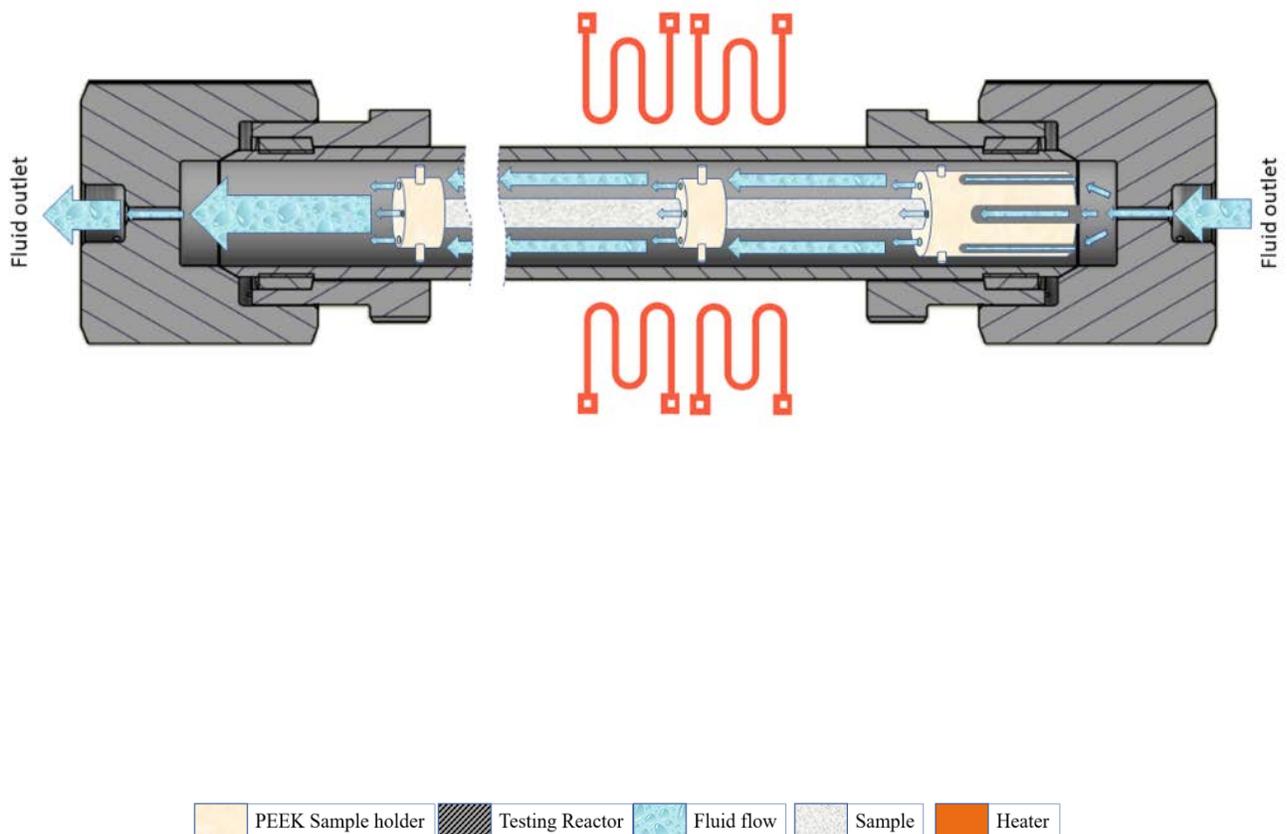


Figure 5: Schematic drawing of the sample holders in the testing reactor.

Conclusion

In this work, we presented the developed laboratory facility that is capable of testing various materials, particularly the metallic substrates and coating materials, to corrosion resistance at different simulated high-temperature geothermal conditions.

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