

Paper No.
16693



Laboratory Testing of Corrosion Resistant Alloys in Deep Geothermal Well Environment

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ABSTRACT

Harsh geothermal fluid demands corrosion resistant alloys (CRA's) instead of the traditional carbon steel as production casing in a geothermal well. Different CRA's were exposed in a batch autoclave of nickel-based alloy N10276. The different samples and purposes were coupons for weight loss measurements, rod samples for interphase reaction examinations and C-rings for environmentally assisted cracking (EAC). The C-rings simulated the thermal stresses introduced in the casing under thermal contractions that appear when the well is under cooling or during irregularity operation. Going from supercritical conditions into the two-phase region with HCl present, the aqueous phase can become very acidic. After some experience with pure deionized water as fluid, testing of samples in a fluid with low pH are described. The tests were performed at 350 °C, at saturated pressure 165 bars for 300 hours. Corrosion damage of several austenitic alloys including nickel-based alloys N10276 and N06625 in addition to titanium alloys are reported. The samples were visually evaluated, and microstructures and corrosion products were further studied using light microscope, SEM/EDS and XRD. There were low weight loss corrosion rates, but all austenitic alloys showed intergranular corrosion and/or stress corrosion cracking (SCC), while titanium alloys appeared more resistant to EAC.

Key words: Geothermal, environmentally assisted cracking (EAC), corrosion, high temperatures, hydrochloric acid, low pH.

INTRODUCTION

The corrosion aggressiveness of geothermal fluids depends on the chemical composition and physical characteristics of the fluid. When hydrogen chloride (HCl) is present; and condensation and reboiling occurs, localized enrichment of hydrochloric acid can cause severe corrosion of materials. The acidity (pH level) is therefore important, as well as parameters such as temperature, pressure and flow rate. Other well-known corrosive agents in geothermal fluids are the dissolved gases hydrogen sulphide (H_2S), carbon dioxide (CO_2), chloride ions (Cl^-) and others.¹ The source of the chloride ions in geothermal steam can be either salt brine (NaCl) or volatile chloride transported as HCl. Silica (SiO_2) is a common scale that precipitates in geothermal wells but SiO_2 was not included in the test matrix in this work.

One of the major technical challenges in high temperature geothermal wells is to identify suitable materials of construction for the process equipment. Even if the laboratory equipment never can mimic all the field parameters and variations in operation of a well², some of the most important parameters can still be addressed when materials are screened. Important corrosion rate promoters as low pH and temperature $\geq 300^\circ\text{C}$ has been tested in the equipment described here.

Thermodynamic data is the basis for calculating and predicting phase stability and the possibility for corrosion, scale formation, film formation and precipitation. To maximize the output of a geothermal system, one would like to have a fluid with as high enthalpy as possible.³ At higher temperatures, a reservoir with a low pressure will have higher gravimetric enthalpy than a reservoir with a high pressure, see Figure 1. In this respect, an optimal reservoir will be one of low pressure and high temperature. When heating water in a closed system as the batch autoclave in this work, the enthalpy of the two-phase fluid would increase according to the saturation line in Figure 1. The overall fluid density in an autoclave filled with water at ambient conditions will have a constant system density at any temperature.

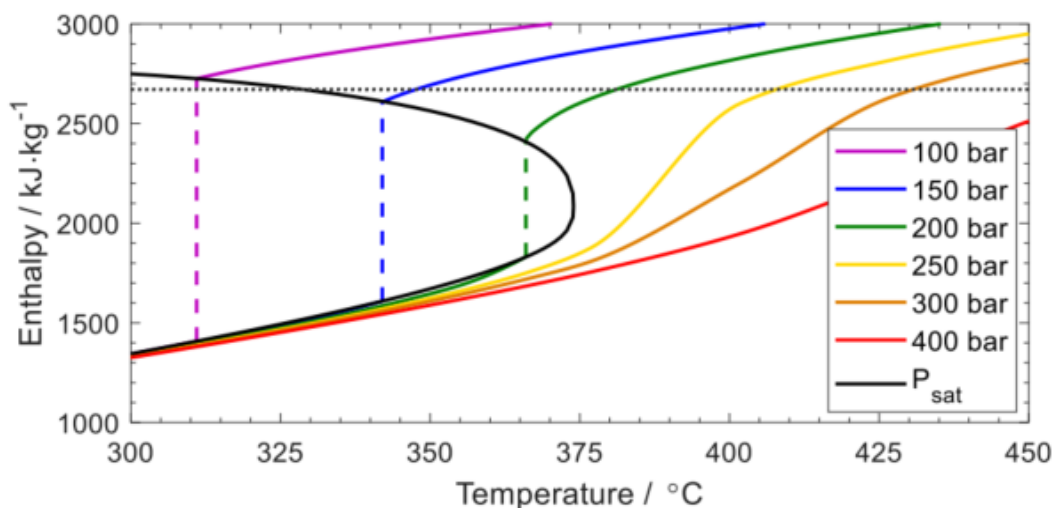


Figure 1: Isobaric enthalpy (H) for water as a function of temperature for selected pressures. Also included is the enthalpy along the saturation line.³

The transition area of subcritical two-phase and supercritical water/superheated steam environment is of special interest since the corrosivity is expected to become more severe when liquid phase is present. High temperature production of single-phase superheated steam is expected to keep the corrosion issues at a minimum. Even if superheated steam is produced at steady state operation of a deep geothermal well, water will drop out during start-up, shut-downs and irregular production. When two-phase fluid is present, the H^+ activity is important for the corrosion potential. Thorhallsson et al.⁴ experienced general and localized corrosion on UNS N06625 at 350°C in a flow-through reactor, probably due to liquid droplet transportation and condensation, see the experimental setup details in reference⁵.

Corrosion in aqueous systems up to supercritical temperatures is determined by several solution-dependent and material-dependent factors. Solution-dependent factors are the density, the temperature, the pH value, the oxidizing strength of the species in the solution, and the aggressiveness of the attacking anions, all parameters thoroughly reviewed by Kritzer.⁶ When the degradation of metals (i.e. corrosion) takes place as an electrochemical reaction, the aqueous fluid acts as the electrolyte. At lower pH and at higher content of halides such as chlorides, the increased ion concentration in the fluid will enhance the total corrosion process. The other main deterioration of metals by corrosion in a geothermal system could proceed via gas-metal reaction in the steam phase. At supercritical conditions i.e. above temperature 374 °C and pressure 221 bars, the density becomes one of the most important factors for the corrosivity, where low-density supercritical water (SCW) has a more gas-like behaviour and high-density SCW has a more liquid-like one. At densities below 200-300 kg/m³, general corrosion is assumed low.⁶

The first well IDDP-1 in Iceland deep drilling project ([IDDP](#)) produced superheated steam at 452 °C and 140 bars. The steam was sampled regularly to determine its chemical content.⁷ The HCl and HF gas in the steam made the condensate acidic with a pH range between 2.4 to 3.6.⁷ A new alarming cracking mechanism, High Temperature Hydrogen Attack (HTHA) was detected in the carbon steel production casing.⁸ This substantiated the need for a review of material selection for high temperature geothermal wells in order to find alloys that are much more robust and less prone to hydrogen damage.

Environmental assisted cracking

When a metal exposed to an environment cracks at a stress at which it would not have failed without the special environment, it is called environmentally assisted cracking (EAC). EAC is a term that includes several failure mechanisms like stress corrosion cracking, hydrogen embrittlement, corrosion fatigue and liquid metal embrittlement. Three concurrent factors determine if EAC will occur: metallurgical, environmental and mechanical. The material must be susceptible to the cracking mechanism, the environment must support a cracking mechanism and the component must experience a tensile stress for EAC to occur.

In a geothermal high temperature environment with static loads the EAC mechanisms that are of concern are stress corrosion cracking (SCC) and different hydrogen damage mechanisms. Experimental investigations for EAC are typically done with constant load or constant strain tests using tensile, 4-point bend, U-bend or C-ring specimens. SCC is an anodic process where metal dissolution through a corrosion process accelerates crack growth. Chloride SCC (Cl SCC) would be the primary concern in a geothermal environment. A phenomenon that lies somewhere between regular corrosion and SCC is what is sometimes classified as stress-assisted corrosion (SAC). It can be described as preferential corrosion penetration under stress or strain.⁹ The term SAC is typically used when the attack is blunter than cracks, but a SAC attack may also eventually develop into a crack.^{9,10}

Since cracks in materials due to corrosion in combination with mechanical stress can lead to failure, a study was initiated where EAC and the role of hydrogen were given attention.¹¹ There was shortcoming in literature when it comes to EAC at supercritical conditions, but some relevant testing results at subcritical conditions and low pH was found. SCC has been observed in high temperature water in the presence of either hydrogen or oxygen.¹¹ Low levels (ppm) of hydrogen gas has been detected in produced fluid from geothermal wells, and one source of the hydrogen could be the corrosion reaction of metal alloys. In uncontaminated, high-temperature geothermal fluids, there is no free oxygen. If oxygen gets into wet geothermal steam systems, corrosion is accelerated. Though free oxygen is not present, the conditions can be both oxidizing and reducing. Based on the study the C-ring design was recommended as stressed sample in experimental work.

Sanada et al.¹² have tested many different metal alloys up to 300 °C, both in a laboratory static autoclave like the one described in this work, and in a flowing two-phase fluid from a geothermal brine at high velocity up to 100 m/s. Most materials had unacceptable high corrosion rates (CR) except from N10276 and titanium alloys, which had low and acceptable corrosion rates respectively, at temperatures up to 300 °C and pH down to 2. These alloys did well both at static and flowing conditions unlike other low and

high alloyed stainless steels and nickel-based alloys. Based on this the authors have given general guidelines for selection of materials in acidic geothermal environments down to very low pH 1, see Figure 3 in reference.¹²

EXPERIMENTAL PROCEDURE

A batch autoclave of nickel-based alloy N10276 was installed and tested with an inner crucible of the same material as the autoclave, see Figure 2. Nickel-based alloys, titanium alloys and some austenitic stainless steels were received from different suppliers and machined into three different shapes. The different sample types and purposes were coupon for weight loss measurement, rod sample for interphase reaction examinations and C-ring for EAC. After samples were added, 20% of the free volume was filled up with fluid. Since there were many parameters in the test matrix of the autoclave screening, the strategy was to select those with the assumed greatest influence first and then introduce them one by one. At first, HCl was added to the water fluid to give a low pH.

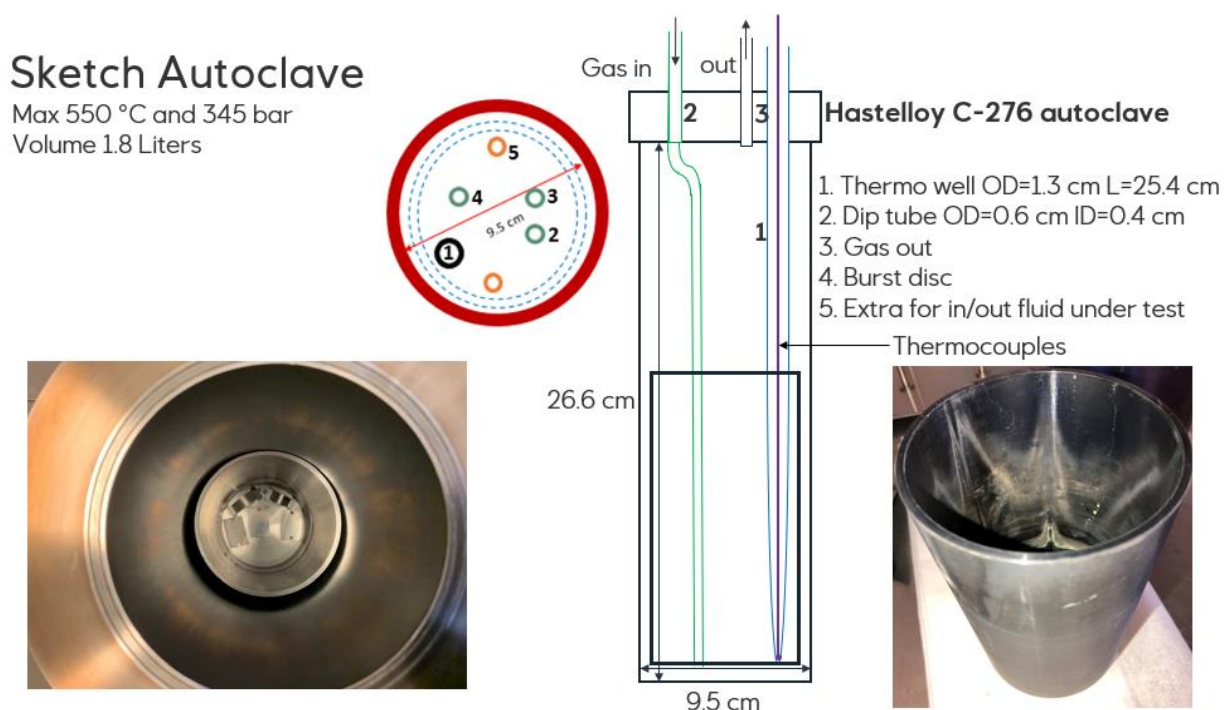


Figure 2: A N10276 batch autoclave with an inner crucible of the same material as the autoclave.

pH variations in a batch autoclave

The transition area of subcritical two-phase and supercritical water/superheated steam environment was of special interest in the experimental work. The corrosivity is expected to become more severe when liquid phase is present.³ The test temperature was in most of this work 350 °C, then the heated fluid consisted of both water and steam (two-phase), right beneath the supercritical point of 374 °C. Both acidity and salinity are known to increase fluid corrosivity. Going from supercritical conditions into the two-phase region with HCl present, the water phase can become very acidic as the dissociation constant is high and increases with decreasing temperature. After some experience with pure deionized water as fluid, testing of samples in a fluid with low pH was the next step.

The pH in the water phase at room temperature would be lower than the resulting pH at top temperature 350 °C. The proton activity from H₂O alone increases with increasing temperature, while the activity of protons from dissociated HCl decreases with increasing temperature.¹³ HCl – which is commonly known as a strong acid – behaves as a weak acid at high temperature.^{3,6} The chloride concentration at 350°C will be low, at pH 2 and pH 3 it has been calculated to a molar fraction in the water phase of $9.6 \cdot 10^{-4}$ and $1.6 \cdot 10^{-4}$ mol Cl⁻/mol H₂O_{liq} (53.3 and 8.9 mmol Cl⁻/kg H₂O_{liq}) respectively.¹³

Coupons for corrosion measurement

Two types of metal coupons were exposed in the test. The rectangular coupons had the following dimensions: 20 mm wide by 30 mm long with square corners. The thickness somewhat varied for the materials tested; UNS N10276, N06625 and R56404 samples were 4.7, 4.8 and 2.9 mm thick respectively. The samples were placed on the bottom of a crucible made of N10276 with alumina isolators in between and were completely submerged in water through the whole test. The other type of sample was rods of the same materials as the rectangular coupons. Dimension of the rod was 5 mm wide by 3 mm thick and the length was 255 mm. The length was chosen to ensure exposure to both phases along the whole length of the autoclave. The rods had a machined hole in one end which made it possible to hang them under the lid by use of Pt wires isolated with alumina tubes. The samples were ground to FEPA 1200-grit SiC and stored in a desiccator before and after the test and during characterization steps. Weight loss procedure was performed according to ASTM G01:03 2017 and the coupons were inspected visually and in microscope for localized corrosion. Since it was challenging to remove the corrosion layer from titanium alloys, the surfaces were not cleaned in order to give corrosion rates.

C-rings for environmental assisted cracking tests

From the literature review of Kongstein et al.⁹, it was recommended to use C-rings as stressed samples with constant strain loading. The selected design is described in ASTM test procedure G38-01,¹⁴ see Figure 3.

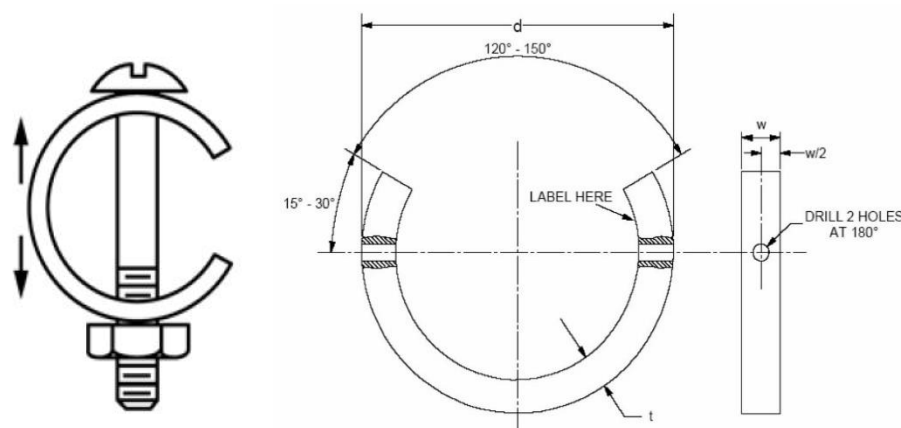


Figure 3: C-ring with constant strain design. All parts were of the same material to avoid galvanic corrosion.^{9,14}

In a geothermal well it is the thermal expansion/contractions that are the main source for the loading, and such loads are strain controlled and not stress controlled by nature. In a rigid casing concept where the casing is not moving, the casing will be loaded in a constant strain, like the suggested C-ring set-up in Figure 3. One difference is that tensile stresses in the casing will appear first when the well is cooled down. It is difficult to design the test like the loading in a casing of a well. The C-ring test will, however, say something about the sensitivity to stress corrosion cracking. If it fails, it signalizes that the material is sensitive to this failure mechanism.

C-rings of four different alloys, and one U-bend Ti-475 sample, were included in the tests in accordance with standard practice ASTM G38 or G30.¹⁴ The samples were tested with a fixed deflection, i.e., in constant strain. The C-ring samples were cut from hollow tubes using the outer diameters and wall thicknesses as the C-ring dimensions, see Table 1. To avoid the galvanic effect, screws and nuts of materials with the same or a similar chemical composition were used to compress the C-rings. The C-ring sample surfaces were, except in the first run, ground with FEPA 1200-grit SiC abrasive paper prior to the test. This was done to ensure that the underlying base metal was tested without possible surface artifacts from manufacturing. The surface of the Ti-475 U-bend was not ground before testing but left as-