In-situ Testing of Corrosion and Corrosion Fatigue Behavior of Stainless Steels in Geothermal Environment

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Abstract. In CCS environment (carbon capture and storage) pipes are loaded statically and/or cyclically and at the same time exposed constantly to the highly corrosive hot thermal water. Experimental procedures such as ambient pressure immersions tests, in-situ corrosion fatigue experiments using a flexibly designed corrosion chamber at ambient pressure and a specially designed corrosion chamber at high pressure. Experimental set-ups for push/pull and rotation bending load are introduced. The corrosion behavior and lifetime reduction of high alloyed steels (X46Cr13, 1.4043), (X5CrNiCuNb16-4, 1.4542) and (X2CrNiMoN22-5-3, 1.4462) is demonstrated (T=60 °C, geothermal brine: Stuttgart Aquifer flow rate: 9 l/h, CO2).

Keywords: Adiabatic calorimeter, thermal energy storage, phase change material, salt eutectics.

1. Introduction

Materials in geothermal power plants are loaded cyclically under pressure and exposed constantly to the highly corrosive hot thermal water (up to ca. 200 °C, ca. 100 bar, ca. 20 % salinity of the geothermal water) where fluid properties may differ strongly [1]. This leads to corrosion fatigue and thus inevitably to the reduction of the lifetime of these components. The influence of frequency, temperature and chloride concentration on the corrosion fatigue behaviour is very well known in literature [2]. In general corrosion processes with or without applied mechanical stress are enhanced, especially in steels with low chromium content [3], with the presence of chloride [4], hydrogen sulfide (H2S) [5] and CO2 [6]. The endurance limit [7] will decrease with increasing temperature, increasing mechanical load and decreasing pH for high alloyed steels. But increasing chromium content of steels as well as internal compressive stress in surface regions will increase the endurance limit [8].

This work was carried out to assess the influence of corrosive media on the cyclically loaded mechanical behaviour of stainless steels in geothermal energy production. Therefore special reaction vessels for ambient and high pressure static corrosion experiments were set up. Furthermore new corrosion chambers for in-situ corrosion fatigue experiments were designed [9] to gain knowledge upon the corrosion behavior of steels in downhole equipment surrounded by geothermal environments.

2. Stainless Steels and Geothermal Water (Saline Aquifer Formations in Germany)

The following steels were investigated (Table 1): X2CrNiMoN 22 5 3 (1.4462) and (Table 2): X20Cr13 (1.4021), X46Cr13 (1.4043), X35CrMo17 (1.4122), X5CrNiCuNb 16-4 (1.4542):

X20Cr13, 1.4034 and X46Cr13, 1.4020 contain 13% chromium but differ in carbon content 1.4034 (0.46 mass% C) 1.4020 (0.2 mass% C). They are used as piping, shafts, or axles in pumps in geothermal energy

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production [10-12]. 1.4542 stainless steel (X5CrNiCuNb16-4) is a precipitation hardening martensitic stainless steel with about 3% copper with small size copper distributed in the matrix ensuring the precipitation hardening mechanism [13]. Martensitic 1.4542 is known to be susceptible to stress corrosion cracking (SCC) and in general less corrosion resistant [14,15]. Duplex steel 1.4462 (X2 CrNiMoN 22 5 3 reveals a much better corrosion resistance Due to its percentage of austenite 1.4462 resulting in a PREN number (35,1) twice as high as 1.4542 [16,17].

| Table 1: Chemical composition of 1.4462 X2CrNiMoN 22 5 3 (UNS S31803) (in mass percent). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| phases                         | C               | Si              | Mn              | Cr              | Mo              | Ni              | N               |
| α & γ**                        | 0.023           | 0.48            | 1.83            | 22.53           | 2.92            | 5.64            | 0.15            |
| α*                            | 0.02            | 0.55            | 1.59            | 24.31           | 3.62            | 3.81            | 0.07            |
| γ*                            | 0.03            | 0.47            | 1.99            | 20.69           | 2.17            | 6.54            | 0.28            |

*PREN α=37.4, γ=32.4 ** P=0.024, S=0.008

| Table 2: Chemical composition of steels tested in geothermal environment (in mass percent). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Elements                        | C               | Si              | Mn              | P               | S               | Cr              | Mo              | Ni              | Co              |
| 1.7225 (42CrMo4)                |                 |                 |                 |                 |                 | 1.05            | 0.22            | 0.04            | <0.01          |
| acc                            | 0.38-           | <0.40           | 0.6-0.9         | <0.035          | <0.035          | 0.90-1.20       | 0.15-0.30       |
| standard a                     | 0.45            |                 |                 |                 |                 |                 |                 |                 |                 |
| analysed b                     | 0.43            | 0.32            | 0.70            | 0.014           | 0.025           | 0.07            | 0.007           | 0.006           |                 |
| 1.4021 (X20Cr13)               |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| acc                            | 0.17-           | <1.00           | ≤ 1.00          | ≤                | ≤ 0.03          | 12.0 – 14.0     |                 |                 |
| standard a                     | 0.25            |                 |                 |                 | 0.045           |                 |                 |                 |                 |
| analysed b                     | 0.22            | 0.39            | 0.32            | 0.007           | 0.006           | 13.3            | -              | 0.123           | -              |
| 1.4043 (X46Cr13)               |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| acc                            | 0.42-           | <1.00           | ≤ 1.00          | ≤                | ≤ 0.03          | 12.5 – 14.5     |                 |                 |
| standard a                     | 0.5             |                 |                 |                 | 0.045           |                 |                 |                 |                 |
| analysed b                     | 0.46            | 0.25            | 0.45            | 0.018           | 0.003           | 13.39           | 0.03           | 0.13            | 0.03           |
| 1.4122 (X35CrMo17)             |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| acc                            | 0.33-           | <1.00           | ≤ 1.00          | ≤                | ≤ 0.03          | 15.5 – 0.8-1.3  | ≤ 1.00          |                 |                 |
| standard a                     | 0.45            |                 |                 |                 | 0.045           | 17.5            |                 |                 |                 |
| 1.4542 (X5CrNiCuNb16-4)        |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| acc standard a                 | ≤ 0.07          | ≤ 0.70          | ≤ 1.50          | ≤ 0.04          | ≤ 0.015         | 15.0- 17.0      | ≤ 0.60          | 3.00 – 5.00     | 3.00 – 5.00     | 0.20 – 0.45     |
| analysed b                     | 0.03            | 0.42            | 0.68            | 0.018           | 0.002           | 15.75           | 0.11            | 4.54            | 3.00            | 0.242           |

a) elements as specified according to DIN EN 10088-3 in %
b) spark emission spectrometry

In-situ tests were performed simulating the geothermal conditions of suitable CCS sites in Germany (Stuttgart Aquifer [18] and Northern German Basin [19,20]) (Table 3).

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Table 3: Chemical composition of the Northern German Basin and Stuttgart Formation electrolyte [18-20].

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>KCl</th>
<th>CaCl₂ x 2H₂O</th>
<th>MgCl₂ x 6H₂O</th>
<th>NH₄Cl</th>
<th>ZnCl₂</th>
<th>SrCl₂⁺ 6H₂O</th>
<th>PbCl₂</th>
<th>Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>According to Northern German Basin [19],[20], pH value: 5.4-6</td>
<td>98.22</td>
<td>5.93</td>
<td>207.24</td>
<td>4.18</td>
<td>0.59</td>
<td>0.33</td>
<td>4.72</td>
<td>0.30</td>
<td>0.07</td>
</tr>
<tr>
<td>According to Stuttgart Formation [18], pH value 8.2-9</td>
<td>224.6</td>
<td>0.39</td>
<td>6.45</td>
<td>10.62</td>
<td>0.321</td>
<td>1.76</td>
<td>0.43</td>
<td>1.27</td>
<td>90.1</td>
</tr>
</tbody>
</table>

3. Ambient and High Pressure Vessels for In-situ Testing – Immersion Tests

Laboratory scale exposure tests in CO₂-saturated aquifer brine and water saturated CO₂ may be carried out using coupons of the steels qualities with 8 mm thickness, 20 mm width, 50 mm length. A hole of 3.9 mm diameter is used for sample positioning. Samples of each base metal are positioned within the vapour phase and within the liquid phase. Flow control (3 NL/h) of the technical CO₂ (purity 99.995 vol.-%) into the brine [10] at ambient pressure was done by a capillary meter GDX600_man by QCAL Messtechnik GmbH, Munich. The exposure of the samples between 700 h to 8000 h was disposed in reaction vessels according to the conditions at the geological site at 60 °C at ambient pressure – each material in a separated reaction vessel [15], [21] and at 100 bar [14], [17] (Fig. 1).

Before corrosion tests the surfaces of the steels are activated by grinding with SiC-Paper down to 120 μm under water. After the corrosion tests, the samples are cut partly for scale analysis with the corrosion layer and prepared partly for kinetic analysis after the scale was etched. Descaling of the samples was performed by exposure to 37% HCl. Then parts of the samples are embedded in a cold resin (Epoxicure, Buehler), cut and polished first with SiC-Paper from 180 μm to 1200 μm under water and then finished with diamond paste 6 μm and 1 μm. Kinetics of the corrosion was determined by the corrosion rates which were calculated via mass change of the samples before and after corrosion testing according to DIN 50 905 part 1-4.

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\text{corrosion rate} \left[ \frac{\text{mm}}{\text{year}} \right] = \frac{8760 \left[ \frac{\text{hours}}{\text{year}} \right] \cdot 10 \left[ \frac{\text{mm}}{\text{cm}} \right] \cdot \text{weight loss} \left[ \frac{\text{g}}{\text{cm}^2} \cdot \text{time} \left[ \text{hour} \right] \right]}{\text{area} \left[ \frac{\text{cm}^2}{\text{cm}^2} \cdot \text{density} \left[ \frac{\text{g}}{\text{cm}^3} \right] \right] \cdot \text{time} \left[ \text{hour} \right]} \quad (1)
\]
To characterise the pitting corrosion, 3-D-images were realized by the double optical system Microprof TTV by FRT. Kinetics of the corrosion were determined by the corrosion rates which were calculated via mass change of the samples before and after corrosion testing according to DIN 50 905 part 1-4 and using the semi-automatic analyzing program Analysis Docu ax-4 by Aquinto.

4. Comparison of Surface and Local Corrosion

Comparing the possible injection pipe steels 1.7225-42CrMo4, 1.4021-X20Cr13, 1.4043-X46Cr13, 1.4543-X5CrNiCuNb16-4 and 1.4122-X35CrMo17 the latter shows the best corrosion resistance at ambient pressure in the vapour phase (water-saturated CO2) and 1.4043-X46Cr13 performs best in the liquid phase (CO2-saturated saline aquifer water) (Fig. 2). At 100 bar in the supercritical ((water-saturated supercritical CO2) as well as the liquid phase (Fig. 2) 1.4543-X5CrNiCuNb16-4 and 1.4122-X35CrMo17 show lowest corrosion rates. In general the increased chromium content for 1.4543-X5CrNiCuNb16-4 and 1.4122-X35CrMo17 leads to a passivating layer resulting in lower surface corrosion rates independent of atmosphere (vapour, supercritical, liquid, intermediate) or pressur (ambient pressur 1 bar, high pressur 100 bar). Results have been described in detail by Pfennig et al. [9,11,14-17,21-23].

In general high chromium steels are susceptible to local corrosion showing distinct local corrosion phenomena with high number of pits at high pressure (100 bar) under aquifer water and supercritical CO2 conditions [9,11,14-17,21-23]. Compared to other possible injection pipe steels (X20Cr13, X46Cr13, X5CrNiCuNb16-4) X35CrMo17 is less resistant against pitting at high pressure (100 bar) in the supercritical as well as the liquid phase (Fig. 2). The number of pits per m² counted after 8000 h of exposure is significantly higher even compared to X5CrNiCuNb16-4 known for local corrosion and X20Cr13, X46Cr13.

5. Corrosion Chamber for In-situ Testing of Corrosion Fatigue at Ambient Pressure – Push/pull and Rotation Bending Load

The objective was to simulate in-situ conditions (temperature up to 100 °C, corrosive environment) of a material exposed to dynamic mechanical stress and corrosive gas-saturated saline aquifer environment, such as components in geothermal power plant. This was realized by the design of a flexible corrosion chamber [9,15-17] for a vertical and a horizontal resonant testing machine and its periphery (Fig. 3). Push/pull experimental series were carried out on the horizontal fatigue testing machine Schenk-Eringer Puls PPV.
During mechanical stress-strain tests a magnetically driven gear pump (3) constantly pumps the corrosive media (according to Stuttgart Aquifer, Table 2)) from the reservoir (1) to the corrosion-and temperature-resistant corrosion chamber (bottom) surrounding the test specimen (Fig. 3)). Heating is realized by two independent heating elements (4). The test conditions are controlled via control unit (5). The ratio of sample surface to volume of the corrosive media after DIN 50905 Part 1 (10 ml/cm²) is greater than required. The connecting of the chamber onto the specimen via clamping collar creates a force-fit process ensuring enough force to the corrosion chamber at high frequencies to keep it firmly on the test specimen (Fig. 3). The corrosion chamber is sealed in the area of restraint over 0-rings made of Viton. In order not to impede the change in length occurring during the experiment, the corrosion chamber has a membrane as a motion-compensating element [9,16,17,22]. Electrochemical data is collected during the mechanical tests as well as temperature, pH and electrochemical potential. For measurement of the electrochemical potential a shock resistant silver-silver chloride electrode was fixed in a Teflon channel (Fig. 3) [17].

To simulate non-static operation a resonant testing machine has been used at 30 – 40 Hz where samples of both steels were tested in stress-strain mode under CCS aquifer environment. In addition technical CO₂ was introduced into the closed system at a rate close to 9 L/h to keep stable environmental conditions.

The corrosion fatigue strength of stainless steels with 13% and 16% chromium (X46Cr13, 1.4043 and X5CrNiCuNb16-4, 1.4542, hardened and tempered with martensitic microstructure) was examined in dynamic stress-strain tests in CO₂-saturated aquifer (Stuttgart Aquifer [18]) at 60 °C via resonant testing machine (sinusoidal dynamic test loads, R=-1; resonant frequency ~ 30 Hz). In addition technical CO2 was introduced into the closed corrosion chamber system at a rate close to 9 L/h to keep stable environmental conditions. In each test series 30 specimens were tested. The steels were tested between 150 MPa and 500 MPa. Due to the rather heterogeneous fine machined surfaces (surface roughness Rz=4) the specimens are comparable with prefabricated parts. Without corrosive environment the fatigue strength of the material (theoretically an infinite number of load cycles without failure) has a relatively smooth slope (Fig. 3).

Because in corrosion fatigue the load type is known to significantly influence the fatigue life and endurance limit a test set up for rotation bending load was accomplished and a specific corrosion chamber was designed (Fig. 4). Taking into account the rotation of the specimen, a modified Open Circuit Potential OCP measuring setup was applied. Additionally to the Ag/AgCl wire electrode a brush was installed to establish direct contact with the shouldered section of the specimen. The installation of sensors and additional components in immediate proximity to the critical cross-section of a specimen was also
advantageous as for push/pull load before. The additional insulating components manufactured of glass-reinforced epoxy and PVC allowed insulation of the subsystem specimen/corrosion chamber from the rest of horizontal fatigue testing machine. The shape and dimensions of hourglass specimens were selected in accordance to the standard DIN EN ISO 117821 and to the recommendations of the FKM Research Issue 217 [25]. The critical cross-section is 12.5 mm in diameter; the total contact surface area did not undergo 25 cm² in order to minimize the influence of irregularities [9].

The volumetric constant flow of the corrosion medium (Northern German Basin, Table 1), which was provided by the internally developed gear type pump, accounted to \( \dot{v} = 2.5 \times 10^{-6} \text{ m}^3/\text{s} \). The theoretical flow velocity of the electrolyte at specimen’s critical cross-section was therefore \( \omega_0 = 1.7 \times 10^{-3} \text{ m/s} \). The electrolyte underwent preheating within the main electrolyte reservoir and was held at a constant temperature of 369 K via control unit and additional heater, which was installed directly prior to the corrosion chamber entry. The resulting temperature fluctuation did not exceed \( \pm 0.3 \text{ K} \). The mean frequency of cyclic load applied accounted to 30 33 Hz. The open-circuit potential of the specimen was recorded by the shock proof Ag/AgCl wire electrode.

Duplex stainless steel X2 CrNiMoN 22 5 3 showed no corrosion phenomena in static immersion experiments and an endurance limit of 485 MPa in air considering \( 10^7 \) cycles as threshold reference in corrosion fatigue tests. The experimental data and corresponding 50% probability S-N curves are demonstrated for both load types in Fig. 4, right.

6. Conclusion

Experimental test set-ups for immersion tests at high temperature (up to 200-400 °C) and ambient pressure as well as high pressure (up to 200 bar) were introduced, to predict the corrosion behaviour in highly corrosive geothermal aquifer water with addition of flowing corrosive gasses, such as CO₂. Generally, higher chromium content results in lower surface corrosion rates and therefore better corrosion resistance. Although X35CrMo17-1 and X5CrNiCuNb16-4 show low surface corrosion rates, their resistance against local corrosion in CCS environment is not significantly better compared to the much less costly steels X20Cr13 and X46Cr13.

A highly flexible corrosion chamber allowing for electrochemical testing, O₂-partial pressure or gas partial pressure measurement was designed to support stress-strain loaded corrosion fatigue experiments by enabling an in-situ corrosive environment which may be used up to 100 °C at ambient pressure. The corrosion fatigue behaviour of X46Cr13, 1.4043 and X5CrNiCuNb16-4, 1.4542 may be described by statistical crack initiation but characteristic crack propagation and fracture surfaces for one stress amplitude.
A typical fatigue strength of the S-N-curve does not exist under CCS corrosive conditions. In general duplex stainless steel X2 CrNiMoN 22 5 3 shows the best corrosion resistance in CCS environment as tested in this study.

Comparing load types showed a significant dependence of the corrosion fatigue life of potential CCS steels, such as duplex stainless steel X2 CrNiMoN 22 5 on the type of cyclic load. Life expectancy of specimen exposed to rotation bending load is higher. However, the fatigue life decreased with increasing experimental duration due to the corrosive degradation of the alloy.

7. Acknowledgements

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8. References

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