Corrosion degradation of pipeline carbon steels subjected to geothermal plant conditions

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Abstract
Purpose – The purpose of this paper is to evaluate the electrochemical behaviour of two carbon steels exposed to acidic geothermal solutions and their resistance to hydrogen induced cracking (HIC), in order to determine the effect of hydrogen damage on the failure process of the steels used for line pipe and casings at a geothermal plant.

Design/methodology/approach – Samples of two different steels: ASTM A-53 Grade B (line pipe) and API L-80 (casing) were immersed for a duration of 96 h in the electrolyte proposed by NACE to evaluate susceptibility to HIC. Samples of the two steels embedded in non-conducting Bakelite were subjected to potentiodynamic polarisation scans at room temperature using as the electrolyte brines obtained from different wells at the Cerro Prieto geothermal plant. Hardness tests were performed on the samples before and after the HIC tests in order to determine hardness changes induced by hydrogen penetration as field results indicated embrittlement of the steels after four months of service.

Findings – The steels, ASTM A-53 Grade B and API L-80 did not exhibit crack sensitivity as no cracks are observed in the tests specimens, though they showed an increase in hardness. The steels exhibited high-corrosion rates in the brine media at room temperature (3.3 mm/yr), which is expected to increase at higher temperatures.

Originality/value – The work revealed that carbon steels used for line pipes and casings at geothermal plants can exhibit high resistance to HIC, however they corrode at high rates and may show embrittlement. It is suggested that due to the high-operation temperature, the damage induced by hydrogen resulted in hardness increase but was not sufficient to develop cracks.

Keywords Corrosion, Pipelines, Acid conditions, Corrosion resistance, Steels

Paper type Research paper

Introduction
The extraction of the high temperature, high-salinity geothermal sources for electric energy production represents a great challenge for materials selection and design because of the corrosive environment. One of the most important issues is the selection of materials for well casings and piping to handle the hot brines, steams and brine/steam mixtures. The chemical composition and characteristics of geothermal fluids have great influence on the degradation process of the materials used. From the corrosion standpoint, the significant characteristics of the well fluids are the salinity (3.8-4.8 M in chloride), temperature (210°C at the wellhead to 260°C at a depth of 550 m), CO2 content (ca. 5,000 ppm), sulfide concentration (ca. 35 ppm), lead concentration (ca. 70 ppm), concentrations of other heavy metal ions (As, Sb and Cu, noble metals–total of 20-50 ppm), and silica concentration (500 ppm). There is no measurable oxygen concentration in these brines in such conditions. The pH of the separated brine (withdrawn at the wellhead and cooled to ambient temperature) is in the range from 5.6 to 6.0. The equivalent room temperature pH of the unseparated fluid (with most of the CO2 retained) is probably around 4.5.

In geothermal plants, carbon steel and martensitic stainless steel normally are used for pipelines and turbine materials. Both materials suffer from corrosion damage in the presence of condensed steam at low-pH values. In the first case, it has been observed general corrosion, whereas pitting phenomena arise in stainless steel (Culivcici et al., 2000). The authors found that the corrosion rate on carbon steel rises with the increasing chloride concentration in the dry superheated steam. Low-corrosion rate was measured with low-chloride concentrations (about 0.2 mm/yr for [Cl–] = 0.5 ppm), while with [Cl–] = 9 ppm the corrosion rate was about 2.8 mm/yr.

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Localized at 30 km southeast from the California US border, Cerro Prieto’s geothermal field has been in operation since 1973 and produces 720 MW net generation. The 32 km² field is associated with the San Andreas fault system, along with Imperial, Cucapah (Cocopah) and Michoaican (Lira, 2005), (Auvinet, 1996). Brine extraction is carried out without pumping because of the high pressure and temperature of the wells. The casing and shore pipes are made of API L-80 and the steam pipelines of ASTM A-53 Grade B steel. There are four power plants named Cerro Prieto One (CPI), Cerro Prieto Two (CPII), Cerro Prieto Three (CPIII) and Cerro Prieto Four (CPIV). Table I presents the amount of generated energy for the plants.

About 1.5 per cent of the extracted steam weight is non-condensable gases, which have the chemical composition: 96 per cent CO₂, 3 per cent H₂S and 1 per cent ammonia, helium, hydrogen, argon, nitrogen and methane. About 75 per cent of the reservoir is saturated brine at 300°C and 900 psi (62 bar), at a depth of 2.5 km.

Soylemezoglu reported the effect of H₂S and oxygen on the corrosion degradation of plain carbon steel in geothermal steam, where at low oxygen levels the corrosion products were iron sulphides (Soylemezoglu and Harper, 1982). It is believed that oxygen acted as a cathodic depolarizer as well as oxidizing the H₂S to sulphur, H₂O, SO₄ and polysulphides. The oxygen present in CO₂, the H₂S and the high temperature would be the factors influencing the corrosion of the carbon steel line pipes used in the geothermal plant at Cerro Prieto. Lichti reported on the corrosion behaviour of carbon steels in New Zealand geothermal brine. He attributed the corrosion-erosion problem in carbon steel pipes to the drag of separated water from the separator to the steam phase (Lichti and Wilson, 1999). This author also mentioned that during pipeline dead times, condensation is produced that forms acid which can attack the pipeline material and corrode the pipeline. Lichti and Bacon (1999).

The beneficial influence of Cu, Cr and Mo additions to carbon steel to improve its corrosion resistance in geothermal service operation conditions at the wet steam lines has been reported and indicates that these are the most beneficial alloy elements (Huijbrgrets and Leferink, 2006).

In the case presented in this work, the API L-80 carbon steel used as casing material suffered dramatic corrosion damage after few months in service at wells 424 and 403 in Cerro Prieto geothermal field, as shown in Figure 1. Pieces of L-80 API carbon steel ejected from well 424 is presented in Table II.

Electrochemical tests
Potentiodynamic polarization tests were carried out to evaluate the electrochemical behaviour of both steels using as electrolyte condensates from wells No. 403 and No. 424 of the zone CPIV. The chemical composition of the condensate is presented in Table III.

A conventional three-electrode electrochemical cell was used to conduct the polarisation tests, with the test material as the working electrode, a saturated calomel electrode as reference electrode and a graphite bar as auxiliary electrode. The electrolyte was condensed brine from the wellhead of wells 403 and 424. The potentiodynamic polarization scan...
was undertaken at room temperature in all cases. The scan rate was 0.166 mV/s and the surface area was 1 cm². The applied cathodic and anodic overpotential was 0.6 V. The tests were carried out using samples with surfaces parallel to the longitudinal and transverse direction of the pipeline steel.

**Hardness tests**

Hardness was measured on samples of both steels before and after the HIC test. The material ejected from the wells also was measured using a Vickers Hardness tester HV 50A.

**Results**

**Microstructure**

The steel A-53 B showed a ferritic microstructure with an average grain size of 30 µm and dispersed small pearlite colonies, as shown in Figure 3. The steel API L-80 presented a martensitic microstructure, as shown in Figure 4. The material ejected from both wells had a martensitic microstructure similar to the L-80, but slightly deformed.

**HIC test**

After 96 h of exposure, as required for the HIC test, the material was removed from the NACE solution and was cut with a diamond slow saw. The cut samples were ground and polished for examination using the metallographic microscope. As the preferential sites for crack growth are the deformation lines of the pipe it was expected that cracks would be found parallel along them, but no significant cracks where visible in the steels, as can be shown in Figures 5 and 6 for steel A53 and API L80, respectively.

**Electrochemical tests**

The potentiodynamic polarization scans were used to determine the electrochemical behaviour of the steels in

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**Table III** Condensate chemical composition from 403 and 424 wells

<table>
<thead>
<tr>
<th>Well number</th>
<th>pH</th>
<th>Conductivity</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Li</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>5.22</td>
<td>16400</td>
<td>2880</td>
<td>630</td>
<td>94</td>
<td>0.05</td>
<td>0.80</td>
<td>6.10</td>
<td>5491</td>
</tr>
<tr>
<td>424</td>
<td>5.22</td>
<td>10700</td>
<td>1880</td>
<td>390</td>
<td>24</td>
<td>0.01</td>
<td>0.68</td>
<td>3.60</td>
<td>3432</td>
</tr>
</tbody>
</table>

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**Figure 2** The arrangement for the HIC test

**Figure 3** Microstructure of steel A53 Grade B

**Figure 4** Microstructure of steel L-80

**Figure 5** Deformation lines in L-80 showing a major crack after the HIC test
contact with the condensed brines from the wells, in addition to their corrosion rates using the Tafel extrapolation method. The polarisation curves for steel A53 immersed in condensate from well 403 with and without oxygen are shown in Figure 7. Figure 8 shows the polarisation curves for samples of steel A-53 immersed in brine from well 424 with and without oxygen. Figures 9 and 10 show the polarisation curves for steel API L-80 in brine condensate with and without oxygen from wells 403 and 424, respectively.

Table IV presents the corrosion rate data obtained for both steels as a function of the electrolyte characteristics. The material collected at the traps on wells 403 and 424 had a Vickers Hardness of 652 and 815, respectively. Hardness measured prior and after HIC experimentation on both steels show a significant hardening, and the results are presented in Table V.

**Discussion**

**Microstructure**

The steel A53-B presented a ferritic microstructure with small colonies of pearlite with an average grain size of 30 µm.
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Table IV Corrosion rate of both steels as a function of electrolyte characteristics (mm/yr)

<table>
<thead>
<tr>
<th>Well number</th>
<th>Bubbled with nitrogen</th>
<th>A-53</th>
<th>L-80</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>No</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>403</td>
<td>Yes</td>
<td>2.8</td>
<td>2.5</td>
</tr>
<tr>
<td>424</td>
<td>No</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>424</td>
<td>Yes</td>
<td>2.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table V Values obtained from Vickers hardness tests

<table>
<thead>
<tr>
<th>Material</th>
<th>Vickers hardness Before HIC</th>
<th>Vickers hardness After HIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-53</td>
<td>248</td>
<td>308</td>
</tr>
<tr>
<td>L-80</td>
<td>254</td>
<td>313</td>
</tr>
</tbody>
</table>

The carbon content of this hypoeutectic steel was associated with the predominant presence of the ferrite phase. The API L-80 carbon steel presented a microstructure consisting of martensite, ferrite and granular bainite. The effect of chemical composition and manufacturing process on the mechanical properties of pipeline carbon steels was reported by Ozekcin et al. (2004) who showed that the combination of grain size, strain and temperature during welding results in a range of microstructures. In the present case, a combination of granular bainite and lath martensite was evident in the L-80 steel microstructure.

The HIC test

The two carbon steels subjected to the NACE test to assess their susceptibility to HIC exhibited high resistance to this kind of damage as no formation, propagation or linking-up of small laminar cracks in a step-like manner was found after the test, as shown in Figures 5 and 6. This result was not expected for API L-80 m carbon steel as it has high yield stress (540 MPa) and it is know that high-strength steels are expected for API L-80 carbon steel as it has high yield stress test, as shown in Figures 5 and 6. This result was not

kind of damage as no formation, propagation or linking-up of their susceptibility to HIC exhibited high resistance to this

The HIC test

of the corrosion of carbon steels as it has high yield stress

steels and high-strength steels are susceptible to HIC. During the exposure period to the NACE solution, a layer of dark corrosion products was observed, which was identified as FeS. The formation of black metallic sulphur deposits is a characteristic of the corrosion of carbon steel in H₂S containing electrolytes (Weiner et al., 2006). In the present case, both steels were resistant to HIC.

Even though the steels presented acceptable resistance to HIC, both exhibited hardening, which can be associated to the uptake of hydrogen into the BCC structure of the steels. This is one of the basic mechanisms of hydrogen embrittlement (hydride-induced embrittlement, hydrogen-enhanced decohesion and/or hydrogen-enhanced localized plasticity).

When atomic hydrogen enters steel and certain other alloys, for example aluminium and titanium alloys, it can cause a loss in ductility and/or load carrying ability, which often is accompanied by cracking (usually as sub-microscopic cracks), or catastrophic brittle failure at applied stresses well below the yield strength or even the normal design strength of the alloys.

This phenomenon often occurs in alloys that show no significant loss in ductility when measured by conventional tensile strengths, and is frequently referred to as hydrogen induced delayed brittle failure, hydrogen stress cracking, or hydrogen embrittlement.

Hydrogen is the smallest atom possible and is the most abundant element in the universe. Two hydrogen atoms combine to form a molecule H₂, which is a stable state. For hydrogen to do damage to steel, it must be present initially in the atomic form, and usually recently produced, called nascent hydrogen. As the atom is so small, it can enter the structure of steel. Hydrogen can be introduced during heat treatments, such as carbonizing, cleaning, pickling, phosphating, electro-plating, autocatalytic processes and in the service environments as a result of cathodic protection.

Under the service conditions at Cerro Prieto, the two carbon steels are exposed to H₂S containing electrolytes and high temperature, which facilitates the absorption of hydrogen that results from the corrosion reaction in absence of oxygen.

Potentiodynamic polarization

At room temperature, the electrochemical behaviour of the steel A53-B in condensate from well 403 with and without dissolved oxygen was very similar, with anodic and cathodic reactions under activation control. The principal difference was the corrosion potential, which was more positive in the case of condensed brine that contained oxygen.

The potentiodynamic polarization of this steel in condensed fluid from well 424 showed that the anodic behaviour is almost the same, i.e. activation controlled, with or without the presence of oxygen in the electrolyte. The corrosion potential was less negative when the polarization was conducted using aerated electrolyte. The cathodic reaction tended to be mass transfer controlled in a potential range from ~800 to ~1,000 mV for the test in aerated electrolyte. At potentials more negative than ~1,000 mV the kinetics were again under activation control, showing an increase of about five times with respect to the reaction in oxygen-free electrolyte. The highest corrosion rate was always when oxygen entered into the electrolyte, a condition that takes place when the temperature decreases and condensation of some of the gases creates a vacuum in the pipes that promotes the entry of air to the system and, in consequence, the dissolution of oxygen in the condensed liquid phase.

The electrochemical behaviour of Steel API L80 in electrolyte from well 403 showed that the presence of oxygen changed the corrosion potential from ~820 to ~610 mV vs Ag/AgCl and induced a tendency for mass transfer control of the cathodic reaction. The anodic behaviour was almost identical in both conditions, with and without oxygen.

In the case of polarization in condensate from well 424, the corrosion potential changed just 30 mV with the presence of oxygen in the electrolyte. The kinetics of the anodic and cathodic reactions were the same for both conditions.

As is evident from Table IV, the corrosion rate values were very similar in both cases. The values were obtained using the Tafel extrapolation method, taking the anodic branch of the polarisation curves.

Conclusions

The results obtained showed that the steels A53-B and API L80 suffer a hardening tendency as well as weight loss when in contact with brines from wells 403 and 424 of the Cerro Prieto geothermal field.
The corrosion rate was determined for these steels at room temperature. The corrosion rates were very high (2.6 mm/yr) and were similar for both conditions: oxygen containing geothermal wells and electrolytes free from oxygen.

The pipes showed an incremental increase in hardness after the 96 h of exposure to the NACE solution, but the entry of atomic hydrogen to the steels structure was not sufficient to induce HIC.

Based in these results it can be concluded that the geothermal field at Cerro Prieto has wells with aggressive condensed brines that induce severe corrosion degradation on the pipeline carbon steels. It is possible that because the real operation conditions do not allow oxygen to be present, the carbon steel is subjected to hydrogen embrittlement as a consequence of the $\text{H}^+$ reduction during the corrosion process in $\text{H}_2\text{S}$-containing brines.

Owing to the very high-degradation rate exhibited by both carbon steels under service conditions, it can be suggested that a combined mechanism of erosion-corrosion and high-temperature electrochemical corrosion is the responsible for the rapid failure of the pipelines.

The formation of FeS on the surfaces of the steels when they are in contact with oxygen-free brines may induce the formation of a pseudo-passive films, which promote the high-dissolution rates obtained during the polarization tests.

References


Further reading


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