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LOCALIZED CORROSION OF STEELS IN GEOTHERMAL STEAM/BRINE MIXTURES

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ABSTRACT

Coupons of eight different carbon and chrome-moly alloy steels were exposed to high temperature, high salinity wellhead brine flow at a geothermal well in the Salton Sea Geothermal Field for periods of up to six months. The corrosion rate and corrosion attack morphology of each coupon was determined. Exposure time was a test variable and ranged from one month to six months. Test results indicate that carbon steels generally suffer high corrosion rates and are susceptible to severe localized attack which shows a mesa-canyon pattern. Chrome-moly alloy steels corrode at much lower rates and show an attack pattern of small shallow pits. With time, these pits grow mostly in the lateral direction. These results suggest that chrome-moly alloy steels offer significant improvement over carbon steels and that the disk-shaped pits are not likely to lead to rapid perforation.

Introduction

The purpose of this work was to determine the time dependent pattern and rate of corrosion of carbon and chrome-moly alloy steels in two-phase geothermal fluid. In earlier work we demonstrated that low to intermediate alloy steels containing molybdenum or chromium and molybdenum (up to 10% total alloy content) exhibited much better performance than carbon steels in the hypersaline brines of the Salton Sea KGRA. We noted that some of the alloy steels showed a mild pitting tendency. The concern was how bad a pitting problem might be encountered with use of alloy steels in geothermal environments. The usual engineering practice is to avoid combinations of materials and environments where pit formation is the form of corrosion. In classical cases of pitting (e.g. Type 304 stainless steel used as a heat exchanger in contact with sea water), the alloy is passive and little generalized corrosion occurs, but pits nucleate and grow at infrequent locations, and the depth of these pits is 4-5 or more times the pit diameter. Accumulation of corrosion products (usually more concentrated in chloride and more acidic than bulk sea water) stimulates propagation of the pit with eventual perforation of the metal tube wall.

Pitting of the alloy steels in geothermal media differs from that in other chloride environments, like sea water, in a number of aspects. First, the pits which we observed were shaped like shallow dishes with pit diameters larger than the pit depth. Second, the alloy steels contain less alloying elements than stainless steels (at least 12% Cr) and do not spontaneously passivate. Third, Salton Sea geothermal environments are anaerobic. Oxygen is necessary for pit nucleation, according to pitting mechanisms. While pitting has been extensively studied in aerated environments, little information is available from the literature concerning localized corrosion of carbon and alloy steels in anaerobic environments.

Experimental Design

We designed an experiment in which coupons of the materials of interest were exposed to full-flow, wellhead conditions of temperature and pressure of the geothermal fluid. Nominal 2-inch x 1-inch flat coupons, approximately 1/8-inch thick, with a 5/16-inch centered hole, were mounted in a 12-inch diameter spool piece. Five identical spool pieces were fabricated and inserted in the 10-inch production line leading from Magmamax I well to the San Diego Gas and Electric (SDG&E), U. S. Bureau of Mines (USBM), and Lawrence Livermore Laboratory (LLL) test facilities near Niland, California. The five spool pieces are shown emplaced in the production line in Figure 1. Flow was directed through the spools by opening the large WKM valves.

We selected eight different commercially-available carbon and low-to-intermediate alloy steels. The alloy steels contained from 1/2% Mo to 9% Cr plus 1% Mo. The steels were used in the as-fabricated condition and metallographic sectioning and polishing indicated that these steels were moderately to heavily cold-worked.

The steels which were used for the experimental program are listed:

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* Private Consultant
AISI 1009: a low-carbon steel (0.10% max. C)
ASTM A106B*: a standard pipe steel, intermediate carbon content (0.30% C)
ASTM A204B*: a carbon-molybdenum steel, nominal 0.50% Mo, 0.20% C
ASTM A387-12*: a chromium-molybdenum steel, nominal composition of 1% Cr and 1/2% Mo. Maximum carbon content 0.17%
ASTM A387-22*: 2-1/4% Cr, 1% Mo. Maximum carbon: 0.15%
ASTM A387-5*: 5% Cr, 1/2% Mo. Maximum carbon: 0.15%
ASTM A387-9*: 9% Cr, 1 Mo, Max. carbon: 0.15%
500 90: A modified AISI 9130 steel with 0.95% Cr, 0.30% Mo, 0.32% C, 0.27% Si, 0.75% Mn.

* Details of the composition and mechanical requirements for ASTM Steels are listed in volume 4 of the ASTM Book of Standards.

Coupons were mounted in the 12 o'clock, 2 o'clock, 4 o'clock, and 6 o'clock positions in each spool piece. The five identical spool pieces were installed at the same time. After one month of brine flow, one spool piece of coupons was removed from the line and its place taken by a blank spool piece. Subsequent spool removals occurred after 2 months, 3 months, 4 months, and 6 months of exposure.

The wellhead temperature and pressure were measured at least once a day during the exposure period. During periods of flow the temperature ranged between 210 and 2250 C and the pressure between 310 and 360 psi. The flow rate was 450-500 gallons/minute during the first two months of exposure and dropped to 80-150 gallons/minute during the last four months of exposure because of shut-down of some of the downstream test facilities.

The experiment began operation in June 1979 and was completed in January 1980. The exposure time reported here is the accumulated time with flow. During shut-down periods of more than a day, the spool pieces were drained and high purity N2 was bled into the line of spools to prevent leakage of air.

Test Results and Discussion

Figure 3 shows corrosion coupons exposed for three months. The scale which formed on the coupons was primarily PbS with smaller amounts of iron sulfide, calcium carbonate, and amorphous silica present. The principal corrosion product was magnetite, Fe3O4. The thickness of scale and corrosion product accumulated on the coupon as a function of time and position is given in Table 1. From the appearance and
Figure 3. Corrosion Coupons after 3 Months of Exposure to Two-Phase Wellhead Geothermal Fluid.

The thickness of the scale, it appears that stratified flow prevails in the pipe. Evidence of a meniscus between brine and brine mist/vapor phases was noted at the 4 o'clock position. The quality of the steam is about 10%.

Table 1. Thickness of Scale Accumulated on Coupons Exposed to Magmamax Brine as a Function of Time and Position.

<table>
<thead>
<tr>
<th>Scale Thickness</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>Mo.</td>
<td>Mo.</td>
<td>Mo.</td>
<td>Mo.</td>
<td>Mo.</td>
</tr>
<tr>
<td>12 o'clock</td>
<td>8</td>
<td>37</td>
<td>65</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>2 o'clock</td>
<td>27</td>
<td>75</td>
<td>100</td>
<td>110</td>
<td>115</td>
</tr>
<tr>
<td>4 o'clock</td>
<td>45</td>
<td>110</td>
<td>125</td>
<td>135</td>
<td>135</td>
</tr>
<tr>
<td>6 o'clock</td>
<td>45</td>
<td>110</td>
<td>132</td>
<td>160</td>
<td>160</td>
</tr>
</tbody>
</table>

After removal of scale and insoluble corrosion products by grit blasting, each coupon was weighed and the overall corrosion rate calculated from the weight loss during the appropriate exposure time. The cleaned specimens were further examined for the pattern of corrosion attack. The general corrosion penetration rates (exposed in mils/year) are given in Table 2 for coupons mounted in the 6 o'clock position and Table 3 for the 6 month exposure time for all clock positions.

Table 2. General Corrosion Rates (in mils/year) as a Function of Exposure Time. Six O'clock Position.

<table>
<thead>
<tr>
<th>Steel</th>
<th>1 Mo.</th>
<th>2 Mo.</th>
<th>3 Mo.</th>
<th>4 Mo.</th>
<th>6 Mo.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 1009</td>
<td>95</td>
<td>73</td>
<td>82</td>
<td>57</td>
<td>65</td>
</tr>
<tr>
<td>ASTM A106B</td>
<td>85</td>
<td>56</td>
<td>67</td>
<td>72</td>
<td>53</td>
</tr>
<tr>
<td>ASTM A2048</td>
<td>1.4</td>
<td>4.2</td>
<td>0.7</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>S00 90</td>
<td>1.8</td>
<td>2.0</td>
<td>1.1</td>
<td>1.4</td>
<td>0.4</td>
</tr>
<tr>
<td>ASTM A387-12</td>
<td>1.5</td>
<td>1.9</td>
<td>0.8</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>ASTM A387-22</td>
<td>1.2</td>
<td>2.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>ASTM A387-5</td>
<td>1.3</td>
<td>1.3</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>ASTM A387-9</td>
<td>1.5</td>
<td>1.9</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The data in Table 2 indicate that the corrosion rate generally decreases with time, but that the decrease is not striking. This observation suggests that accumulation of scale and insoluble corrosion products is not completely protective. This statement is further supported by comparison of data in Tables 1 and 3. The thickest scale and corrosion product accumulation occurred in the 6 o'clock position; the corrosion rate was generally highest in this position. The scale/corrosion product constituents PbS, FeS, Fe_3O_4 are semiconductors or electronic conductors. The product layer is porous, cracked, and often non-adhering so that the metal surface is accessible to the fluid. The results corroborate those from the USBM for carbon steel.

Observations on localized corrosion tendency indicated severe mesa-canyon attack of the carbon steels which was heaviest in the 6 o'clock position. The alloy steels suffered only slight pitting attack of about 3 mil depth with a greater pit density in the 12 o'clock position than in the 6 o'clock. The environment is likely more acid in the 12 o'clock position because of separation of CO_2 from the brine.

The pattern of attack observed for the carbon steels in which "canyons" of heavily corroded metal alternate with "mesas" of nearly
unaffected metal has been previously described and is characteristic of corroding systems where CO₂ is the principal corrodent. CO₂ hydrolyzes to form carbonic acid; evolution of hydrogen gas from the acid environment is the cathodic reaction. This reaction is structure dependent and occurs on sites where electron transfer has less activation energy associated with it. Thus, rather small compositional and microstructural changes in the steel can create large changes in the cathodic reaction rate. While investigation of the mechanism of the corrosion reaction is beyond the scope of the present work, the improvement in corrosion performance of steel containing small amounts of Cr and Mo is dramatic and possibly unique to anaerobic geothermal environments.

Conclusions

The chrome-moly alloy steels were found to have more than an order of magnitude improved resistance to general corrosion than carbon steels. Additions of chromium beyond 1% or molybdenum beyond 0.5% do not markedly reduce the corrosion rate. Further, the alloy steels show only a very moderate amount of localized attack. The extent of this kind of attack could be incorporated in the design corrosion allowance of the pipe or vessel wall. The results of these six month tests indicate that, unlike rapid pit perforation of stainless steel in sea water, the low alloy steels are not likely to fail by rapid perforation. Further testing of actual pipe spools is needed to confirm this conclusion. As the cost of chrome-moly alloy steels is roughly two to three times that of carbon steel, the substantial reduction in corrosion suggests that the chrome-moly alloy steels are cost-effective, viable, alternative materials for geothermal installations. Care must be taken, however, to properly qualify welding and heat treatment procedures to avoid possible sudden catastrophic failures due to stress corrosion or hydrogen-induced cracking.

References