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Development and Field Testing of Polymer Heat Exchanger Tube Coatings

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ABSTRACT

The National Renewable Energy Laboratory and Brookhaven National Laboratory have been conducting tests of polymer-based coatings systems to reduce heat exchanger equipment capital and maintenance costs in corrosive and fouling geothermal environments. These coating systems act as barriers to corrosion to protect low-cost carbon steel tubing and are formulated to resist the strong attachment of scale, thus facilitating cleaning. Recently, work has been done in evaluating the long-term durability of polymer coatings with multiple cycles of cleaning and reuse in a field-test apparatus. While a number of the coatings were able to protect the steel tube during the field tests, improvements can be made to the coating surface hardness and to the coating-to-tube adhesion to allow the coatings to withstand repeated hydroblast cleanings.

Introduction

Corrosion, erosion, and fouling by scale deposits are major issues for geothermal fluid-wetted heat exchanger tubes in geothermal power plants at a number of reservoirs. Either expensive, corrosion-resistant alloys are used in shell-and-tube heat exchangers because of the need for corrosion resistance, or frequent heat exchanger retubing is done to repair corroded tube bundles. The capital cost and maintenance costs of geothermal heat exchangers can be reduced considerably if inexpensive carbon steel tubes could be coated with a low-cost thermally conductive coating that provides corrosion resistance equal to high-grade alloy steels. Capital costs of a typical geothermal fluid heat exchanger can be reduced by 67% if polymer-coated carbon steel tubes, tubesheets, and headers are used in place of titanium tubes and titanium clad plates (Scholl, 1997). In addition, polymer coatings can be developed which have anti-fouling properties and can be easily cleaned, thereby improving heat transfer and lowering maintenance costs. Thus, the development of corrosion/erosion/fouling-resistant coatings for carbon steel tubes is the subject of ongoing investigations at Brookhaven

National Laboratory (BNL) and the National Renewable Energy Laboratory (NREL), in cooperation with CalEnergy Operating Company (CEOC).

The coating's surfaces must be resistant to both hydrothermal oxidation and to abrasive wear and tear. Once liners undergo severe oxidation, they allow the corrosive electrolytes to infiltrate through the lining layer. Furthermore, oxidation introduces functional oxygen derivatives, such as hydroxyl, peroxide, carbonyl and carboxylate, on the outermost surface sites of the liners, and the topographical configuration of the lining's surfaces changes from a smooth texture into a rough one. Hydroblasting with pressures of 41 to 83 MPa (6000 to 12000 psi) is a common method to remove scale from tube interiors. Hydroblasting can cause abrasive wear and tear of the lining's surfaces through bombardment by hard mineral particles present in the scales. Thus, it is essential that the lining's surface has a high resistance to this type of damage and a low affinity for bonding to scale.

In our efforts to develop a lining material meeting these requirements, three polymer composite material systems with high-temperature capabilities (silicon carbide (SiC)-filled polyphenylenesulfide (PPS) applied over a zinc phosphate primer, Cr-oxide-filled resol-type phenolic polymer, and TMP-crosslinked styrene/methyl methacrylate (ST-TMP) copolymer containing the antioxidant 1,4-phenylene diamine (PDA)—were evaluated for their usefulness as erosion/corrosion resistant liners of heat exchanger tubes (2.5 cm {1 in} outside diameter, 1.24 mm {0.049 in} wall thickness, and 6.1 m {20 ft} long). The first and third lining systems were designed and made by BNL, and the second one, known by the trade name "Saekaphen Si 14E," was prepared and supplied by Heresite Protective Coatings Co., for field performance tests. In the field tests, the lined tubes were cleaned by hydroblasting regularly every few weeks depending on the amount of online exposure to the geothermal fluid and the tendency of the geothermal fluid to cause scaling, and then were reinstalled in the test skid to continue the field evaluation. Previously, short-duration field tests of phenolic- and PPS-coated tubes showed generally good performance in

protecting the underlying steel (Gawlik et al., 1999). The tubes in those tests were hydroblasted at the end of the period of exposure to the geothermal fluid, whereas in this lengthy test, the tubes were cleaned and put back into service a number of times.

The field tests were conducted at CEOC's Hoch power plant in the Salton Sea Geothermal Area, California. Mild carbon steel tubes internally coated with the different liner systems were exposed to flowing hypersaline geothermal fluid for a minimum of 45 days at temperatures up to 110°C (230°F). An extended duration field test ran from February to July 1999 and used tubes coated with ST-TMP/PDA, PPS with and without the addition of silicon carbide (SiC) grit and polytetrafluoroethylene (PTFE; trade name, Teflon), phenolics, and uncoated stainless steel (AL-6XN) as a control. Cleaning by hydroblasting was done at intervals during this test. After cleaning, the tubes were put back into the test apparatus to continue the exposure to the geothermal fluid. This test, the longest ever run during the materials testing program, involved 65 days of online exposure to the geothermal fluid. Another test started in July 1999, but only ran a few weeks before failures occurred with the tubes coated with phenolics. Tubes that were taken from the extended duration test and from the shortened test in the summer of 1999 were analyzed by BNL to determine the mechanism of corrosion.

Analysis of Corrosion

The PPS coating provided more consistent and longer tube protection than the phenolics. The commercial resol-type phenolic (RP) composite liners failed early in a short-term field test started in July 1999. The tubes developed perforations through their walls and leaked geothermal fluid after only two weeks of service that did not include any hydroblast cleanings. However, other phenolic tubes used in the long-duration test lasted for the whole test, and were able to withstand the hydroblast cleanings without apparent damage. In contrast, the tubes using the PPS composite liners had useful lifespans from 45 days to the duration of the test, and their lifespans included at least one hydroblast cleaning.

Work to understand why the liners failed was carried out using scanning electron microscopy (SEM) and energy-dispersive x-ray spectrometry (EDX). Prior to conducting such image and chemical analyses, our focus centered on the locations of corrosion-induced pin holes in one of the PPS-coated tubes. Visual observations revealed that three pin holes appeared in nearly a straight line at a distance of approximately 100, 50, and 20 cm (40, 20, and 8 in) from the edge of the 6.1-m-(20-ft)-long tube. Figure 1 is the SEM micrograph of a cross-sectional profile of a non-corroded area situated at a distance of 100 cm (40 in) from the tube end. The

SEM image showed the presence of three distinctive layers: scale, liner, and underlying steel. Figure 2 is an SEM image, using higher magnification, of a square area marked "A" in Figure 1. As is evident from the EDX spectrum at site "a," the chemical composition of the scale layer in the vicinity of the

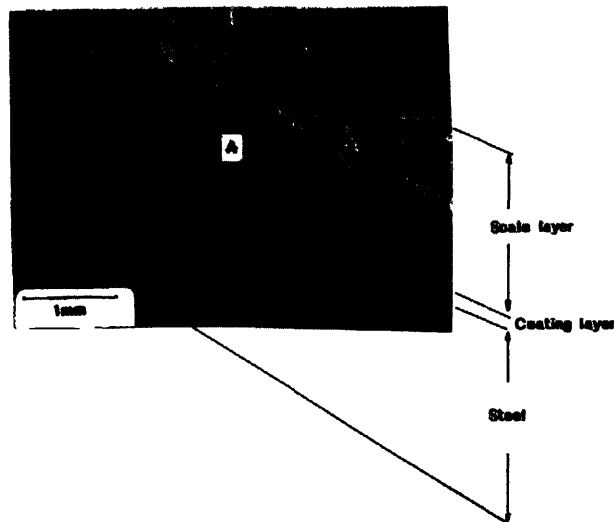


Figure 1. SEM cross-sectional profile of a non-corroded, PPS-coated area.

lining indicated the presence of Ca, Si, and O, reflecting the formation of scale consisting of $\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$, SiO_2 , and $\text{Ca}(\text{OH})_2$ phases. Site "b" is the critical interfacial boundary between the zinc phosphate (ZnPh) and steel. The EDX

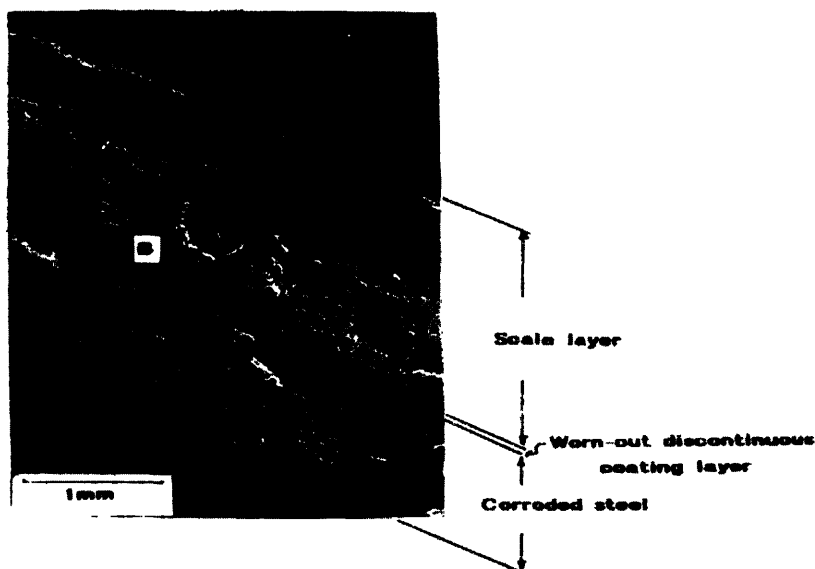
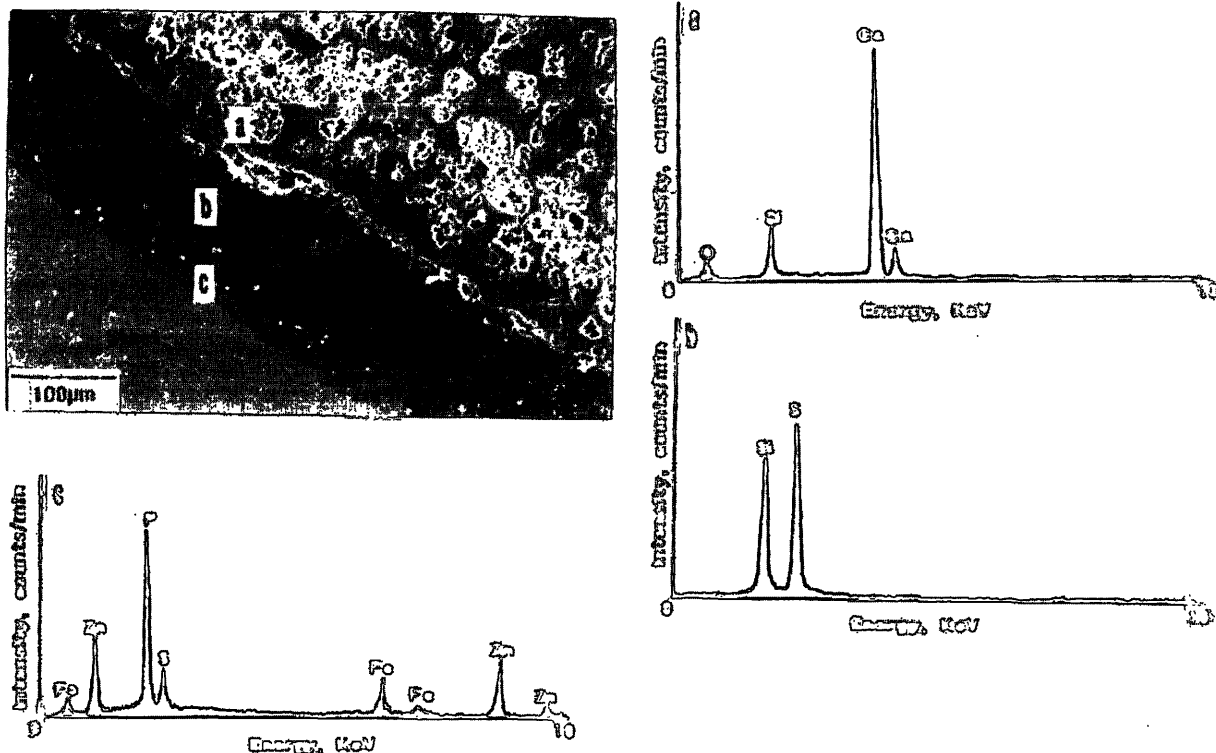


Figure 3. SEM cross-sectional profile of corroded, PPS-coated area.



spectrum from this region had strong signals of P and Zn elements and lesser signals of S and Fe. The former two elements appear to be associated with the ZnPh layer, while the S signal is attributable to the PPS penetrated into the ZnPh layer. The iron originated from the steel.

In contrast, a strikingly different morphology can be seen in the SEM image (Figure 3) of a corroded site at the same distance from the end of the tube. The image features a region of

severely corroded underlying steel near a discontinuous layer of PPS liner, with a thickness of less than $\sim 50 \mu\text{m}$ (0.002 in), underneath the layers of accumulated scale. This information strongly suggested that the PPS layer underwent some wear and tear during hydroblasting. The magnified image of site "B," where the PPS liner was damaged, is shown in Figure 4. The image revealed that although the PPS layer was locally removed by hydroblasting, the ZnPh layer adhering to the steel still remains. Nevertheless, when a hostile geothermal fluid came into contact with the tube wall where the PPS liner was missing, its attack not only promoted corrosion, but also caused the erosion of the corrosion products, such as iron oxides, thereby resulting in the generation of a pin hole in the tube.

For the Heresite Saekaphen Si 14E-lined heat exchanger tube, compare the SEM image of the cross-section of the unexposed tube in (Figure 5(a), overleaf) to the image (Figure 5(b)) of the tube which failed shortly after being placed in the test skid and had not been hydroblasted. The image of the failed tube showed that the lining layer is missing, leading to the growth of an iron oxide layer (thickness of $\sim 150 \mu\text{m}$ {0.006 in}) as a corrosion product of the underlying steel. A possible interpretation as to why the Saekaphen liners had failed is that cracking of the coating during processing allowed geothermal fluid to come into contact with the underlying steel as soon as it was put into the apparatus. One problem with phenolics is the large difference in thermal expansion coefficient between phenolic and steel, leading to large stresses in the brittle, thermosetting phenolic that can cause microcracking. Another is that there is no strong adhesion between the phenolic and steel, so that the

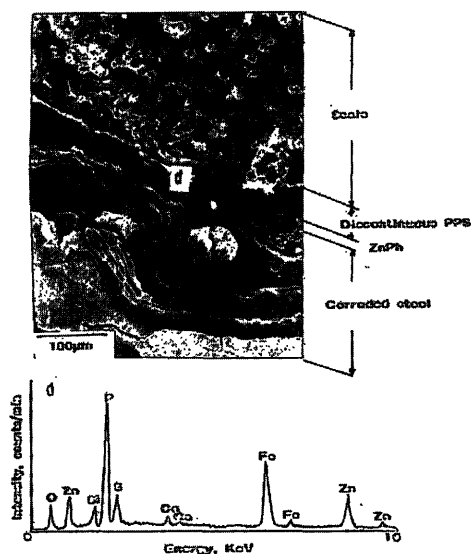


Figure 4. SEM image and EDX analysis of area "B" of Figure 3.

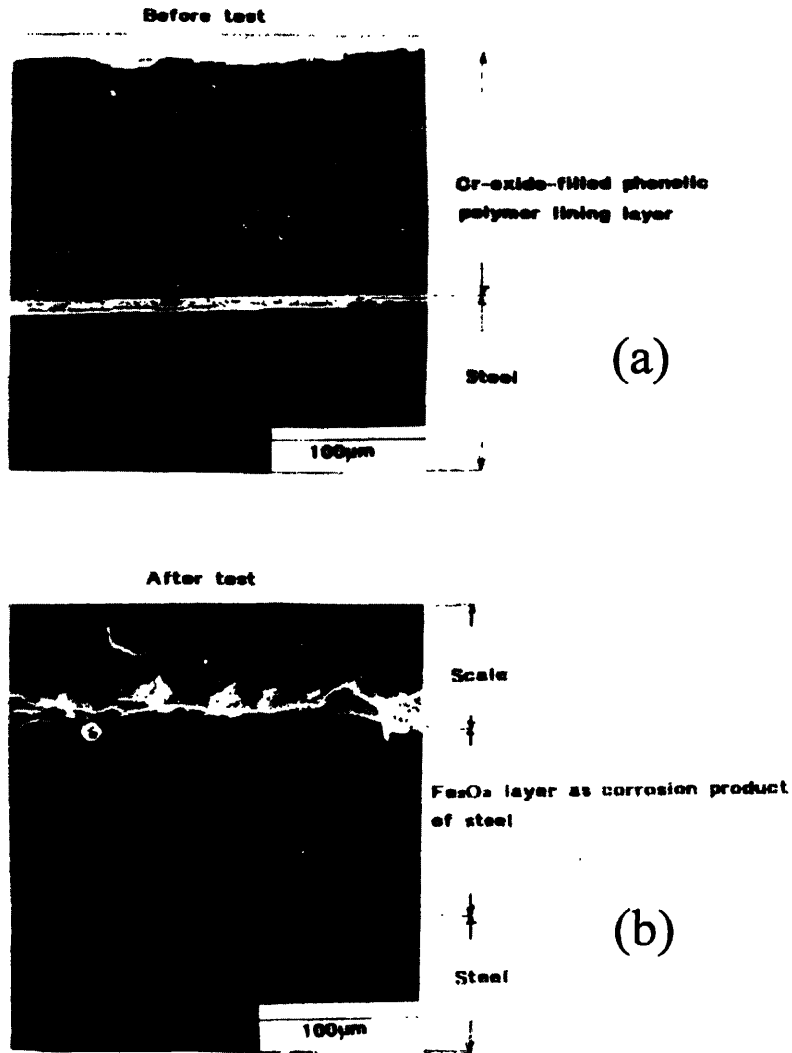


Figure 5. SEM cross-sectional images of Cr-oxide-filled phenolic polymer liners before (a) and after (b) field test.

liner can be lifted from the substrate easily by corrosion products. But the great advantage of phenolics is their high surface hardness, and this characteristic needs to be incorporated in the PPS coating.

Field Test Results

The coated tubes were put into service at the Heat Exchanger Test Skid, located at CEOC's Hoch plant. The test skid consists of two parallel sets of four 6.1 m (20 ft) long counterflow heat exchangers. Each heat exchanger consists of one lined, 2.5 cm (1 in) OD tube surrounded by a shell made of 3.8 cm (1.5 in) Schedule 80 pipe. Geothermal fluid from the secondary clarifier tank flows through the tubes, which are cooled on the shell side by water in a closed loop, air-cooled system. The geother-

mal fluid is supplied from the clarifier tank at 110°C (230°F) and pumped to the test skid with a single pump at a nominal flowrate of 1.3 l/s (20 gpm), which results in 0.63 l/s (10 gpm) through each of the two sets of four heat exchangers. Nominal average geothermal fluid speed in the tubes is 1.6 m/s (5 ft/s). Total dissolved and suspended solids levels are approximately 250,000 ppm in the fluid entering the skid.

A total of eight heat exchanger tubes were fabricated for each field test. The tubes were seamed, mild carbon steel, with 1.24 mm (0.049 in) thick walls. Before coating, the ends of the heat exchanger tubes were roller expanded into fittings and seal welded; this process used the same fabrication techniques as in the construction of a full-size heat exchanger. (The exception is the single ST-TMP/PDA tube, which had 7.6 cm (3 in) long AL-6XN stubs welded to the ends of a shortened carbon steel tube to provide the "safe end" connections to the tubesheet.) Two PPS-coated tubes were reused from a field test that ended in October 1998. At the end of that test they were hydroblasted clean and visually checked for internal corrosion. They appeared to be in good condition, so they were reused.

The heat exchangers were instrumented to provide data on the temperature change of the geothermal fluid and cooling water through each heat exchanger, as well as geothermal fluid and cooling water flowrates. With this information, the resistance to heat flow through the lined tube can be calculated as deposits accumulate on the interior of the tubes. This additional resistance to heat flow is defined as the fouling coefficient, and has the units of [°C-m²/W] ([°F-ft²-hr/BTU]). Details of the calculation of the fouling coefficient are given in Gawlik et al. (1998). The fouling coefficient results are the most important thermal performance results from the field tests.

The coatings were applied by flooding or casting, and then cured. The phenolic liners were applied at Heresite's facilities using a fill-and-drain technique. The tubes were flooded internally with coating, allowed to drain, dried at low temperature and then recoated. This process was repeated 6 to 8 times to build up the coating to the desired thickness. The coatings were fully cured at 200°C (392°F). The techniques used for the PPS-based coatings were similar, but fewer coats were needed and the curing temperature was 320°C (608°F). The ST-TMP coating was spun-cast and cured at 175°C (347°F). The details of the PPS, ST-TMP, and zinc phosphate application processes are contained in an earlier report (Gawlik et al., 1998).

The fouling coefficient results of the long duration field test are shown in Figures 6 and 7 for the two sets of four heat exchangers. The curves are labelled with the material used to

coat each tube, along with their locations in the skid. One set is designated A1 through A4, and the other as B1 through B4. The A1 and B1 tubes first encounter the geothermal fluid, which is cooled as it goes through the heat exchangers. The geothermal fluid exits the last tube approximately 20°C (36°F) to 30°C (54°F) cooler than its inlet temperature. All tubes experienced sustained fouling at different rates. The tubes exposed to the hottest geothermal fluids showed particularly heavy fouling, suggesting a reverse solubility of dissolved material and also the tendency of the upstream tubes to catch and hold large chunks of solid material that act as seeds for further, rapid scaling. The effects of hydroblast cleanings appear in the fouling coefficient curves as sudden drops in R_f . Due to corrosion and perforation

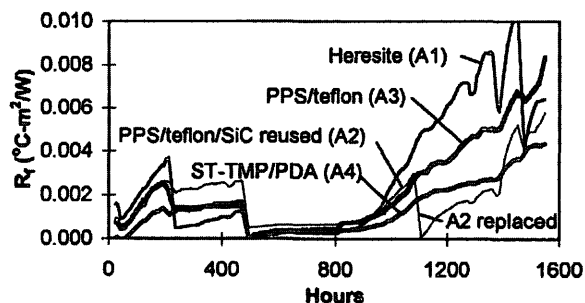


Figure 6. Fouling coefficient results for the A-series of tubes.

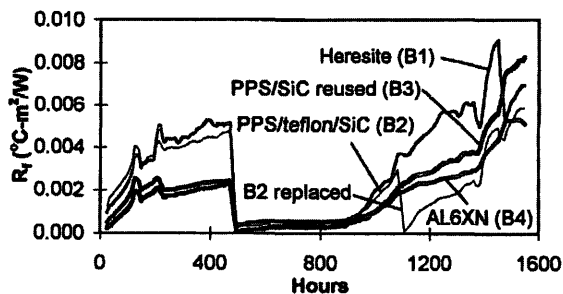


Figure 7. Fouling coefficient results for the B-series of tubes.

of the tube walls, the A2 and B2 tubes had to be removed and replaced by stainless steel tubes to continue the test.

When clean, the tubes have different overall heat transfer coefficients, but within 1 to 2 days after fouling begins the difference is no longer important as the scale offers the dominant heat transfer resistance. Clean stainless steel tubes have an overall heat transfer conductance (UA, including interior and exterior heat transfer coefficients) of 265 W/°C (502 BTU/hr°F) per meter length of tube. An ST-TMP/PDA-lined tube has a UA of 147 W/°C (279 BTU/hr°F), 55% of the steel tube's value. A PPS/SiC-lined tube's value is 135 W/°C (256 BTU/hr°F), and for the plain PPS system, 93 W/°C (176 BTU/hr°F). A clean phenolic-lined tube has a UA of 89 W/°C (169 BTU/hr°F). While these differences are large when clean, the scale quickly becomes the controlling resistance element. An R_f value of only

0.001 °C-m²/W (0.006 °F-ft²-hr/BTU) corresponds to a conductance of 80 W/°C (152 BTU/hr°F), which is lower than any of the clean tube UAs, and would lower the overall conductance of the stainless steel tube to 61 W/°C (116 BTU/hr°F). This R_f value is attained shortly after fouling begins following the delay period.

The thermal resistance of a 76 μ m (0.003 in) thick PPS coating, which would be suitable for locations where scaling is not heavy and only corrosion resistance is desired, is 0.0015 °C-m²/W (0.0085 °F-ft²-hr/BTU). A typical fouling coefficient assumed for carbon steel exposed to mildly corrosive fluid, which would promote the development of an oxide layer on the steel, is 0.001 to 0.002 °C-m²/W (0.006 to 0.011 °F-ft²-hr/BTU). The PPS coating would therefore have the same thermal resistance as a layer of corrosion products. However, the PPS-coated tube would have corrosion resistance while the uncoated steel would continue to corrode until failure occurs. For applications where regular hydroblasting is not required because of the low scaling tendency of the geothermal fluid, the currently available PPS coating system would be suitable. For applications where hydroblasting is often used, a harder surface for the PPS must be developed.

Future Work

A new field test apparatus is planned to be installed at the Mammoth Lakes Binary Plant in California and put into operation late in the summer of 2000. This apparatus will have access to production geothermal fluid at 166°C (330°F) and to cool geothermal fluid that enters the last set of heat exchangers. The tests at Mammoth will evaluate two things: the high-temperature capabilities of the PPS coatings and their ability to prevent pitting corrosion. The production geothermal fluid at Mammoth is much hotter than the geothermal fluid accessible at Hoch, and represents a typical production geothermal fluid used in a binary plant. The plant operators have observed pitting corrosion of carbon-steel heat exchanger tubes at the low-temperature end of the series of geothermal fluid heat exchangers. The apparatus will also have access to the low-temperature geothermal fluid and evaluations will be made to determine the ability of the coating to prevent this type of corrosion.

In addition, harder surface finishes for the PPS coatings and better bonding between phenolics and steel will be investigated. PPS already has high bond strength to the underlying steel through the zinc phosphate primer, but has experienced erosion after repeated hydroblast cleanings. A harder surface finish would enable the PPS to last longer under conditions where heavy scaling is experienced, requiring frequent cleanings. The use of a zinc phosphate primer may strengthen the bond between phenolics and steel, and this will be investigated.

Conclusions

In the longest field test ever run, the long-term durability of PPS and phenolic coatings was evaluated with repeated hydroblast cleanings and re-exposure to geothermal fluids. A

test was also performed that was of short duration due to unusually quick tube failure. A number of the coated tubes in both field tests were able to reach the end of the tests without failure, but approximately one-half did experience corrosion to varying degrees.

Although the PPS composite liner displayed far better performance than the commercial phenolic composite liner in mitigating corrosion of carbon steel, the surface hardness and anti-adhesive properties of the PPS liner must be enhanced to alleviate the wear and tear of hydroblasting. The adherence of the phenolic composite liner to the steel substrate was found to be very poor. Such a weak bond was detrimental to its durability. Means to improve the surface hardness of PPS and the

adhesion of phenolics to steel will be explored in future tests, which will occur at a new site where a higher temperature geothermal fluid will be available to the test skid.

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