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DEVELOPMENT AND FIELD TESTING OF POLYMER-BASED HEAT EXCHANGER COATINGS

Keith Gawlik and Stephen Kelley
National Renewable Energy Laboratory   1617 Cole Boulevard, Golden, CO 80401

Toshifumi Sugama, Ronald Webster, and Walter Reams
Brookhaven National Laboratory   DAS, Bldg. 526, Upton, NY 11973

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ABSTRACT

In aggressive geothermal environments, heat exchanger equipment capital and maintenance costs are high due to the expensive, corrosion-resistant materials required and to the maintenance involved in keeping the heat transfer surfaces clean. To reduce these costs, the National Renewable Energy Laboratory and Brookhaven National Laboratory have been conducting tests of polymer-based coatings systems. These coating systems protect low-cost carbon steel tubing from corrosion and are formulated to resist the strong attachment of scale, thus facilitating cleaning. Laboratory and field tests of a variety of polymeric coatings under development show that geothermal deposits bond to the most promising coatings as weakly as they do to expensive stainless steels, and the coated tubes can be easily cleaned using conventional hydroblasting methods without damage to the polymer coating.

1. INTRODUCTION

Corrosion, erosion, and fouling by scale deposits are critical issues for brine-wetted heat exchanger tubes in geothermal power plants at the Salton Sea reservoir. Expensive, high-nickel alloys and stainless steels are commonly used now in shell and tube heat exchangers because of the need for corrosion resistance. The capital cost 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 brine 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).

An ideal polymeric coating that protects steel from corrosion in geothermal environments must act as a barrier against corrosive reactants, such as oxygen, water, electrolyte species (e.g., H^+, Na^+, Cl^-, SO_4^{2-}, NO_2^-), and gases (e.g., O_3, SO_2, CO_2, H_2S) and be stable at elevated temperatures for an extended time. To achieve this goal, three polymeric material systems developed by BNL—TMP-crosslinked styrene/methyl methacrylate (ST-TMP) copolymers containing the antioxidant 1,4-phenylene diamine (PDA), polyphenylenesulfide (PPS), and polytetrafluoroethylene (PTFE)-blended PPS—were evaluated for use as corrosion- and oxidation-resistant coatings. To inhibit the onset of the cathodic reaction, zinc or zinc alloy and zinc phosphate (ZnPh) conversion precoatings are often introduced as intermediate layers to pretreat the steel surfaces (Sard, 1987). BNL demonstrated that the bond structure of PPS/zinc phosphated steel joint systems has both mechanical interlocking and chemical bonds (Sugama and Carciello, 1991) that significantly enhanced ZnPh-to-PPS adhesion.

In addition, a phenolic coating supplied by Heresite Protective Coatings, Inc. was identified by NREL as having good performance characteristics for geothermal service. Phenolics are a candidate because of their inherent chemical stability, good thermal stability and adhesion properties, and low raw materials costs. Phenolic coatings have a long history of commercial service under aggressive conditions, but the challenges posed by geothermal environments are unique. Two coatings from Heresite were exposed to brine in field and laboratory tests in this project.

The coating systems were the subjects of field and laboratory evaluations. The field tests were conducted at CEOC's Hoch power plant in the Salton Sea Geothermal Area. The field tests used mild carbon steel tubes internally coated with the different liner systems and exposed to flowing hypersaline brine for a minimum of 45 days at temperatures up to 110°C (230°F). A number of field tests have been conducted since September 1997 using ST-TMP, PPS, and phenolic-based coatings. Hydroblasting tests were conducted at the conclusion of each of the field tests. Stainless steel tubes (AL-6XN) serve as controls.

The laboratory evaluations consisted of performing accelerated tests on coated steel coupons and analyzing samples of coatings exposed to brine in the field. In addition to coupon tests of ST-TMP- and PPS-based coatings, BNL and NREL performed chemical analyses of the liner and the scale from the tubes from the field tests. To explore the capabilities of phenolics further in an accelerated manner in higher temperature and lower pH conditions than those available at the field test site, a program of testing a variety of phenolic systems and primers on steel coupons was initiated in early 1999 and is ongoing.

2. PROPERTIES OF COATINGS EXPOSED TO BRINE

BNL determined the degree of hydrothermal oxidation of the surfaces of ST-TMP and PPS coating systems after exposure for 40 days in an autoclave containing a low pH, hypersaline brine (1 wt% H_2SO_4, 13 wt % NaCl, and 86 wt % water) at 200°C (392°F). Figure 1 illustrates the changes in the atomic ratio of oxygen/carbon (O/C) for the coating surfaces before and after exposure. Although all the coating surfaces suffered hydrothermal oxidation to some degree, and the degree of oxidation increased with exposure time, the coating most effective in inhibiting surface oxidation was PPS/PTFE. After exposure for 40 days, the O/C ratio of this coating surface was only 0.22, 77% and 91% lower than that of the PPS and ST-TMP/PDA coating surfaces, respectively.

NREL analyzed the chemical composition of phenolic materials to determine if degradation occurred during exposure to the actual brine at Hoch or to the brine used in accelerated aging tests at BNL. In this evaluation, new Si 14 E and Heresite 4403 coatings were compared to identical coatings that were removed from the test skid in October 1998 and to coated steel coupons tested at BNL. Coating samples were analyzed by pyrolysis mass spectroscopy, which consisted of pyrolyzing the coating at 550°C (1022°F), breaking down the polymer structure and releasing monomeric fragments directly into a molecular beam mass spectrometer (MBMS).

The MBMS results show that there was no degradation of the phenolic coatings during exposure to the Hoch brine, but there was a noticeable change in composition after exposure to the BNL conditions. The molecular fragments of the samples that came from the field test were essentially the same as the new coatings. Thus, exposure of the phenolics to Hoch brine, which is mild relative to the BNL accelerated aging conditions, caused no chemical alteration to the coatings. The coatings that were tested at BNL, however, did show a significant change in their chemical composition. The changes appeared to be related to elimination of the phenolic hydroxyl. Additionally, the coatings did not appear to delaminate during the Hoch field test, but there was delamination during the BNL accelerated test. These results are encouraging for applications similar to the conditions at the field test site, but suggest that further work must be done to make the phenolic coatings more durable and to improve adhesion under conditions similar to BNL's accelerated aging test.

3. FIELD TEST APPARATUS

Tubes coated with different liner systems were put into service at the Heat Exchanger Test Skid, located at CEOC's Hoch plant in the Salton Sea Geothermal Area. The test skid, depicted in Figure 2, consists of two parallel sets of four 6.1 m (20 ft.) long counterflow heat exchangers. Each heat exchanger consists of one lined, 2.54 cm (1 in.) OD tube surrounded by a shell made of 3.81 cm (1.5 in.) schedule 80 pipe. Brine 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 brine 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 1.26 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 brine speed in the tubes is 1.6 m/s (5 ft/s). Total dissolved and suspended solids levels are approximately 250,000 ppm entering the skid. The field tests were at least 45 days in duration, but the tests were often interrupted by plant shutdowns, loss of brine flow, or equipment failures. Thus, a field test could take significantly longer than 45 days to obtain 45 days of online exposure.

A total of eight heat exchanger tubes were fabricated for each field test. The tubes were seamless, mild carbon steel, with 1.24 mm (0.049 in.) thick walls. The ends of the heat exchanger tubes were roller expanded into fittings; this process used the same fabrication techniques used in the construction of a full-size heat exchanger. Two end treatments were used where the tube was roller expanded. One end treatment consisted of welding 7.6 cm (3 in.) long AL-6XN stubs to the ends of a shortened carbon steel tube to provide the "safe end" connections to the tubesheet. The other treatment was to use a carbon steel tube for the entire length and to apply nickel-aluminum to the ends. SW 3670 wires with a nickel/aluminum ratio of 4:1 by weight were used as the starting material for the Ni-Al tube end coatings. This coating was applied using a hand-held wire flame gun (ASB Industries, Inc) to a length of 8 cm (3 in.) from the end of tube.

The heat exchangers were instrumented to provide data on the temperature change of the brine and cooling water through each heat exchanger, and brine and cooling water flowrates. With this information, one calculates how the resistance to heat flow through the lined tube increases as scale forms in the interior. This additional resistance to heat flow is defined as the fouling coefficient, or

$$R_f = \frac{r_2}{r_4}\left[\frac{1}{U_0} - \frac{1}{h_0} - \frac{r_4}{r_1}\frac{1}{h_i}\right] - \frac{r_2}{k_{steel}}\ln\left(\frac{r_4}{r_3}\right) - \frac{r_2}{k_{liner}}\ln\left(\frac{r_3}{r_2}\right)$$

where r_1 is the inner radius of scale buildup; r_2, the inner radius of the liner; r_3, the inner radius of the tube; r_4, the outer radius of the tube; h_0, tube exterior heat transfer coefficient; h_i, the tube interior heat transfer coefficient; U_0, the overall heat transfer coefficient from brine to water; k_{steel}, the thermal conductivity of the carbon steel tube; and k_{liner}, the thermal conductivity of the liner system. The units for R_f are [Km^2/W]. The geometry is illustrated in Figure 3. The fouling coefficient results are the most important thermal performance results from the field tests.

A combination of techniques was used to apply the various coatings. Common to all applications was careful preparation of the tube interior through degreasing and sandblasting. The zinc phosphate coating is applied using a "fill and drain" technique. The tube is coated by attaching a valve to one end of the tube and then inserting it into a vertically oriented furnace. The coating solution is poured into the tube from the top and then drained from the bottom once the coating process has been completed. The PPS and PPS/SiC coatings are also applied using the "fill and drain" technique. The PPS system consists of two layers of PPS while the PPS/SiC system consists of one layer of PPS and a top layer of SiC-filled PPS. The curing temperature for the PPS coatings was 320°C (608°F). The ST-TMP/SiC and PDA-modified ST-TMP/SiC liners are centrifugally cast inside the tubing and cured at 175°C (347°F). The compositions of these liners are shown in Table 1.

The phenolic liners were applied at Heresite's facilities using a "fill and drain" technique also. 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 coatings tested included one licensed from the supplier, Saekaphen, and designated Si 14 E, and the other was a Heresite formulation, designation 4403. These materials were recommended by Heresite to be the best off-the-shelf coatings for high temperature, acidic geothermal brines.

4. FIELD TEST RESULTS

Thermal results, presented in terms of fouling coefficient, are shown in Figures 4 and 5 for the two sets of four heat exchangers, designated A loop and B loop, for one field test. The materials tried in this test were PPS/PTFE, PPS/PTFE/SiC, PPS/SiC, ST-TMP/PDA, and two phenolic materials, Si 14 E and Heresite formulation 4403. A number of the BNL tube ends were coated with flame-sprayed nickel aluminum. The curves are labelled with the material used to coat each tube, along with their locations in the skid (A1 and B1 encounter the hottest brine, A2 and B2 the next hottest, etc.). The brine temperature successively dropped through each tube in a loop, so the A4 and B4 tubes were exposed to a brine temperature about 17°C (31° F) lower than the A1 and B1 tubes. All fouling coefficient curves show a similar delay period of about 250 hours before fouling begins. Delay periods are a common characteristic of fouling curves (Epstein, 1979) and is the period when sufficient nucleation zones for sustained deposition are established. After the delay period, all tubes experienced sustained fouling at different rates. The tubes exposed to the hottest brines, PPS/PTFE (A1), PPS/PTFE/SiC (A2) and Si 14 E (B1), showed particularly heavy fouling and required mechanical removal of the thickest deposits to maintain brine flow to the other tubes downstream. These partial cleanings appear in the fouling coefficient curves as sudden drops in R_f beyond the 800-hour point. Fouling tended to proceed faster the closer the tube was to the brine flow entering the apparatus. It was observed that fouling was promoted by the presence of seed material, which collected first in the A1 and B1 tubes, and to gradually lesser extents in the tubes downstream.

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 becomes the dominant heat transfer resistance. When clean, a stainless steel tube has an overall heat transfer conductance (UA, including interior and exterior heat transfer coefficients) of 265 W/°C per meter length of tube. The ST-TMP/PDA-lined tube has a UA of 147 W/°C , 55% of the steel tube's value. The PPS/SiC-lined tube's value is 135 W/°C , and for the plain PPS system, 93 W/°C . The phenolic-lined tube has a clean UA of 89 W/°C . While these differences are large when clean, the scale quickly becomes the controlling resistance. An R_f value of only 0.001 °C m^2/W is a conductance of 80 W/°C , 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 . This R_f value is attained shortly after fouling begins following the delay period.

The PPS/PTFE and phenolics coatings performed well in hydroblast tests. For the PPS/PTFE liners, all the scale was removed at the lowest water pressure used (41 MPa, 6000 psi), and about 10% of the liner had its top surface disturbed. At the highest water pressure, all the scale was removed and all of the liner had its top surface removed. These results suggest a lower water pressure would have cleaned the PPS/PTFE liners effectively without any liner surface disturbance. Both of the phenolics showed complete scale removal at all water pressures, and no disturbance of the liner surface occurred at any pressure. The liner surfaces appeared as if they had not been through the test at all, and no liner disbonding was apparent. These results for the phenolics warrant continued work in exploring their application in geothermal service. The ST-TMP/PDA liners, however, did not show any scale removal until the highest water pressures (103 MPa, 15000 psi) were applied, and then the liner often was removed with the scale.

The thicknesses of geothermal brine-induced scales deposited over the coating surfaces and the shear bond strength at the interfaces between the coatings and the scales were measured for the PPS and ST-TMP-based coatings. Thicknesses ranged from ~1.8 mm to ~2.3 mm (0.071 in. to 0.091 in.). The shear bond strength, an average value from six specimens, was used to estimate the adhesive force of the scales to the coating and stainless steel (SS) surfaces. The bond strength of 8.20 MPa (1190 psi) for the scale/SiC-filled ST-TMP/PDA joint specimens was almost seven times greater than that of the scale/SS joints. The weak interfacial boundary for the scale/SS joint made it easy to dislodge and remove the scales from the SS surfaces using hydroblasting, whereas it was very difficult to dislodge the scales in the scale/SiC-filled ST-TMP/PDA joint system. Thus, the PDA antioxidant appears to be ineffective in creating chemically inert coating surfaces. For the SiC-filled PPS/ZnPh coatings, the joint systems had a shear bond strength of 5.82 MPa (844 psi), 71 % lower than that of the scale/SiC-filled ST-TMP/PDA coating joint specimens. This low bond strength is consistent with the ease of removing the scale layers by hydroblasting. A considerably lower bond strength of 1.59 MPa (231 psi) was obtained from the scale/PTFE-blended PPS/ZnPh coating joints. The main reason for such improvement was the phase segregation of PTFE from the PPS, whereby self-segregated PTFE formed at the brine-wetted surface. The susceptibility of PTFE to the hydrothermal reactions with hot brine was considerably lower than that of the PPS, forming surfaces that were chemically inert to the scales. The PTFE surface also has a low surface energy which lowers the adhesion of the scale to the surface.

The Ni-Al-coated heat exchanger tube ends inside and outside of the zone where roller expansion occurred were analyzed by scanning electron microscopy. The coating layer that was not roller expanded had a non-uniform, uneven microstructure, reflecting a wide coating thickness range of ~22.5 µm to ~77.5 µm (8.9×10^{-4} in. to 30.5×10^{-4} in.). The microstructure of the Ni-Al coating layer compacted by roller expansion showed a significant reduction of coating thickness and the formation of discontinuities where corrosive species attacked the underlying steel. Corrosion products such as Fe_2O_3 and Fe_3O_4, appearing to arise from the underlying steel, were present at several different locations in the coating. Accordingly, a thermal-sprayed Ni-Al coating with high plastic deformation and great toughness is needed to ensure that the roller-expanded coatings adequately protect the underlying steel against corrosion. Using an aluminum top coat over the Ni-Al may help seal the Ni-Al and increase uniformity, and this technique will be explored in the future.

5. FUTURE WORK

PPS and phenolics are the most promising coatings so far. They have low bond strengths with the geothermal deposits and can be easily cleaned with little or no damage. Different primer systems and material formulations for the phenolic materials will be evaluated to improve adhesion to the substrate and improve performance in high temperature, low pH brine. Coupon tests of these liner systems will be run in BNL's accelerated test apparatus and the best systems will be used to coat tubes for the field test. The PPS systems will be applied by a commercial coating company to explore the commercialization of these liners.

Extended field tests will be run to determine the long-term durability of liners with repeated cleanings and exposures to brine.

6. CONCLUSIONS

Field and laboratory tests of PPS-, and phenolic-based coatings show that coatings have been developed that provide corrosion protection to low-cost carbon steel tubes, are easily cleaned using conventional methods, and resist disbonding. Phenolics and PPS have especially good abilities to be cleaned without damage. These results suggest that reductions in capital and maintenance costs for heat exchangers in geothermal service are possible by using coated carbon steel tubes in place of expensive, corrosion-resistant materials currently in use. Further work will develop better adhesion between phenolics and the substrate, and commercial application of the PPS coatings will be explored.

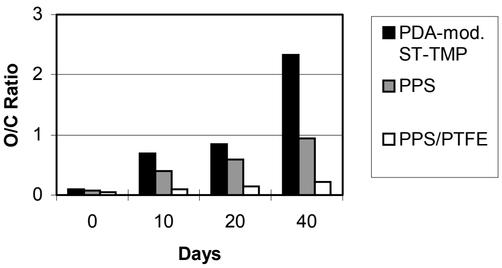

Figure2. Changes in O/C ratio for PDA-modified ST-TMP, PPS, and PPS/PTFE coatings during exposure to low pH, hypersaline brine at 200°C.

REFERENCES

Epstein, N., "Fouling in Heat Exchangers," *Heat Transfer 1978*, Proceedings of the Sixth International Heat Transfer Conference, vol. 6, Hemisphere Publishing Corporation, New York, 1979.

Gawlik, K., Sugama, T., Webster, R., and Reams, W., "Field Testing of Heat Exchanger Tube Coatings," Geothermal Resources Council *Transactions*, vol. 22, p. 385-391, September 22-23, 1998.

Sard, R., "Advances in functional zince and zinc alloy coatings," *Plating and Surface Finishing*, 74, p. 30-34, 1987.

Scholl, K., "Report on Liner Application/Heat Exchanger Construction Techniques," NREL Milestone Report 2.2.3, July 1, 1997.

Sugama, T., and Carciello, N.R., "Corrosion protection of steel and bond durability at polyphenylenesulfide-to-anhydrous zinc phosphate interfaces," *J. Appl. Polym. Sci.*, 45, 1291-1301, 1992.

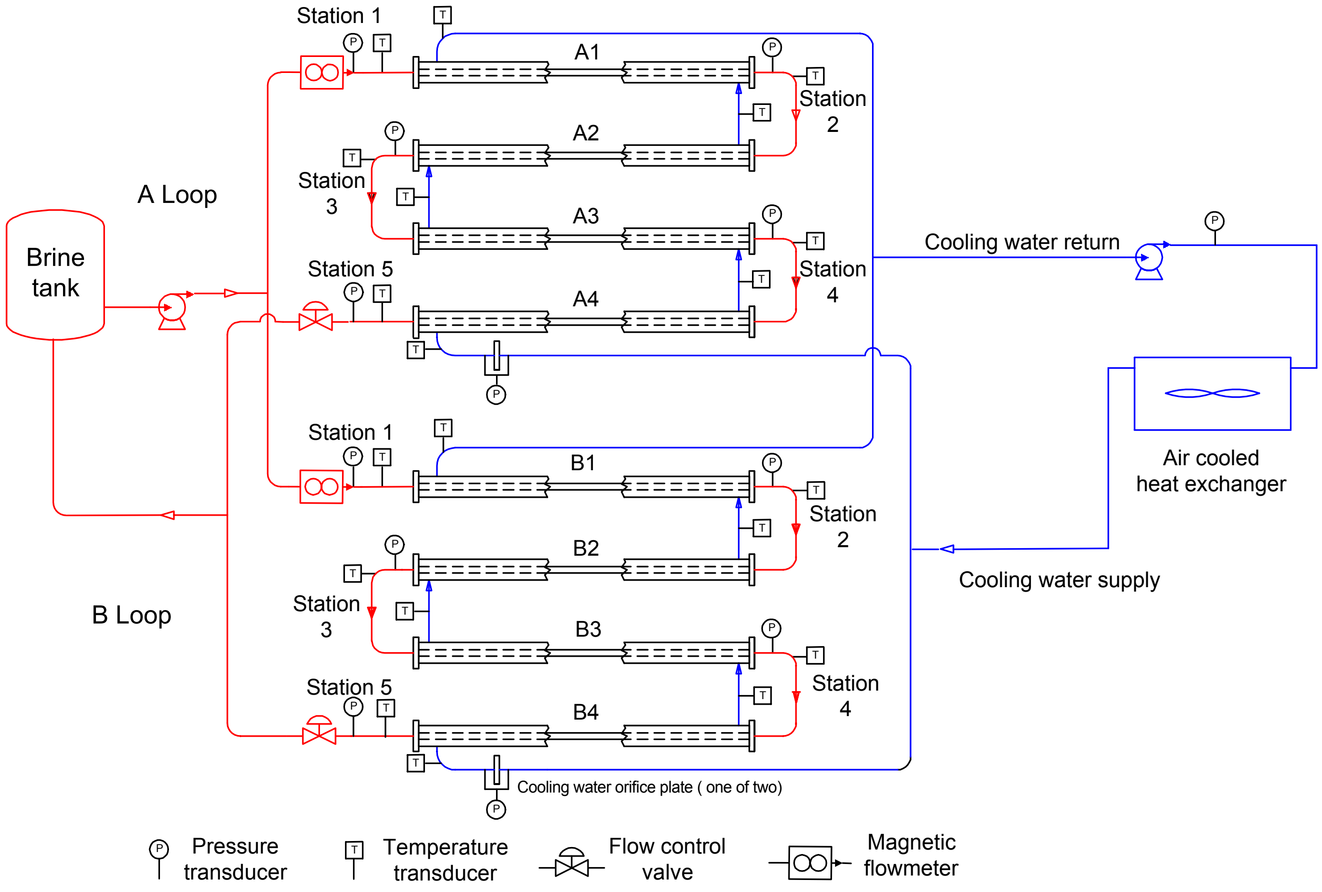

Figure1. Schematic of the Heat Exchanger Test Skid.

Table 1. *Compositions of PPS/SiC and ST-TMP.*

Composition of the PPS/SiC slurry
45 wt% isopropyl alcohol
36 wt% PPS
18 wt% SiC
1 wt% surfactant
Composition of the ST-TMP monomer system
53 wt% styrene-polystyrene mixture
35.4 wt% TMP
4.8 wt% poly(methyl methacrylate)
4.8 wt% ambient and high temperature initiators
1 wt% silane coupling agent
1 wt% promoter

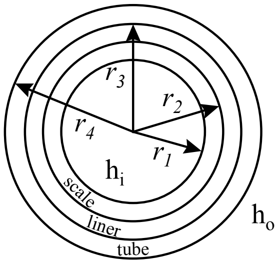

Figure 3. Definition of system used in R_f eqn.

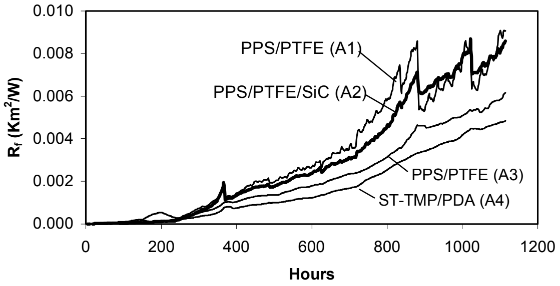

Figure 4. Fouling coefficient results for the A side of the test skid.

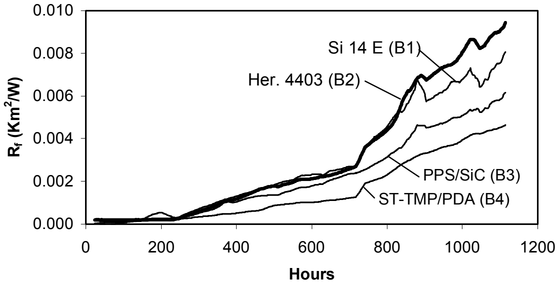

Figure 5. Fouling coefficient results from the B side of the test skid.