

Polymer Coatings for Corrosion Protection in Biochemical Treatment of Geothermal Residues

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ABSTRACT

Ceramic-filled epoxy, ethylene methacrylic acid (EMAA) and ethylene tetrafluoroethylene (ETFE) coatings were evaluated for corrosion protection in a biochemical process to treat geothermal residues. The epoxy was brush applied whereas the other coatings were thermal sprayed. Atlas cell and peel strength tests were performed in aggressive environments including hypersaline brine and sulphur oxidizing bacteria (*Thiobacillusferrooxidans*). It was found that the polymers were resistant to chemical attack and biodeterioration at the test temperature of 55°C. Corrosion of mild steel substrates coated with EMAA and ETFE occurred in Atlas cell tests that simulated an uninsulated lined reactor and this resulted in decreased adhesive strength. The ceramic-filled epoxy provided better substrate protection than the EMAA and ETFE. Insulation of the reactors may improve coating performance since this would decrease the thermal gradient which affects permeation. The results of the research are also applicable to low temperature geothermal applications.

Introduction

A biochemical treatment process to detoxify geothermal brines and sludges has been developed at Brookhaven National Laboratory (Premuzic *et al.*, 1995). The process uses sulphur oxidizing bacteria to convert toxic metals, including radionuclides, present in geothermal residues into soluble species. The residues can then be disposed in an economic and environmentally acceptable manner. The process also permits recovery of commercially valuable products such as silica for paint fillers and other applications, technical grade KCl and precious metals. The untreated residues are corrosive towards ferrous metals due to high chloride content and low pH. The biochemical treatment process typically operates at pH values

of 1-2 and temperatures of 50-55°C. Sulphur oxidizing bacteria pose a threat to ferrous metals because they oxidize sulphur or sulphur-bearing compounds to form sulphuric acid. One species of interest for treatment of geothermal residues, *Thiobacillusferrooxidans*, is also capable of oxidizing ferrous compounds. Therefore, the corrosivity of both the biocatalyst and residue must be taken into account when selecting materials for construction of processing equipment.

Stainless steel (316L) vessels were available for use in a pilot scale plant. However, coupons of this material underwent corrosion when exposed to the environments of interest and it was necessary to determine suitable protective coatings (Allan, 1997). In addition, coatings to protect a low cost construction material, such as mild steel, for the planned full scale plant were of interest. The coatings were required to be easily applied as a continuous film to the vessels, resistant to the environments of concern throughout the design life, economic, low VOC, not requiring priming or post curing. Coatings are also of value for protection of ferrous metals in other relatively low temperature geothermal fluids.

This paper covers the results for a brushable ceramic-filled epoxy and thermal sprayed ethylene tetrafluoroethylene (ETFE) and ethylene methacrylic acid copolymer (EMAA) polymers. Coated mild steel specimens were exposed to synthetic hypersaline brine and *Thiobacillusferrooxidans*. The ceramic-filled epoxy was selected on the basis of its predicted chemical and abrasion resistance, in addition to ease of application. Epoxy top coats have been found to provide corrosion protection to low carbon steel in geothermal brines tested up to 60°C (Batis, Kouloumbi and Kotsakou, 1997).

The process used to thermal spray the polymers involves introduction of polymer powder into combustion gases where the polymer melts. The molten particles are then projected

against a preheated substrate where they **solidify** to form a coating. This is a 100% solids method which can be used in the field. Successive passes of the torch permit build up of the coating to the required thickness. Case histories of thermal sprayed EMAA are provided by Loustaunau and Horton (1994) and these include rail cars and wastewater clarifiers. EMAA contains carboxyl groups which enhance adhesion to polar substrates. The adhesion of thermal sprayed EMAA to different substrates has been studied by Brogan *et al.* (1995).

Experimental Procedure

Specimen Preparation

The EMAA copolymer powder was supplied by PFS Thermoplastic Powder Coatings (PF 111). A PFS 124 Powder Pistol with fluidized powder feed was used to apply the EMAA coatings. The propane and compressed air pressures were 41 and 826 kPa, respectively. The standoff distance used for coating test panels was 30-40 cm and the traverse rate was 10 cm/sec. The flow rates of the fluidized bed, combustion air, powder carrier air and propane were 20-25 l/min, 20 l/min, 50 l/min and 8 Vmin, respectively. After blasting with alumina grit the panels were preheated to 82°C and then sprayed.

The ETFE powder was supplied by DuPont. The powder was sprayed using a Eutectic+ Castolin Terodyn 3000 gun with TecFlow 5102 Powder Feeder. An air shroud at 241 kPa was used. Oxygen, acetylene and nitrogen pressures were 207, 103 and 344 kPa, respectively. The standoff distance was 15 cm and the traverse rate was 10 cdsec. The grit blasted substrates were preheated to 162°C before spraying.

The brushable ceramic-filled epoxy was supplied by ITW Devcon (Devcon Brushable Ceramic). Parts A and B were mixed at the recommended proportion and the coating was brush-applied to alumina grit blasted mild steel panels.

Atlas Cell Tests

The chemical resistance and corrosion protective nature of the coatings under simulated service conditions were determined following the test method described in ASTM C 868 (Atlas Cell Test). In this experimental arrangement coated panels were exposed to immersion and vapour zones, in addition to a temperature gradient from the external bare surface to the internal coated surface. This gradient simulated that which an internally heated reactor vessel would generate and is of importance since a temperature differential can accelerate permeation of the coating. This is known as the "cold wall effect".

The test cell basically consisted of a horizontally-oriented, open-ended glass cylinder with a diameter of 152 mm to which the coated panels were clamped on the ends. Neoprene gaskets were placed between the glass and panel to provide a seal. The glass cylinder had ports for a thermometer, immersion heater, air bubbler and reflux condenser. The cylinder was partially filled with 1.2 l of the solution of interest. Partial filling

permitted study of corrosion protection in both the liquid and vapour phases.

The test solutions were synthetic hypersaline geothermal brine and *Thiobacillus ferrooxidans* medium. The synthetic brine consisted of 58,000 ppm NaCl, 25,000 ppm CaCl₂, 15,000 ppm KCl, 1000 ppm FeCl₂, 930 ppm MnCl₂, 430 ppm SrCl₂, 410 ppm LiCl, 370 ppm ZnCl₂, 330 ppm H₃BO₃, and 130 ppm BaCl₂. The pH of the brine was 4.15. The brine was aerated throughout the test.

The nutrient for the *Thiobacillus ferrooxidans* bacteria was prepared from two parts. Part A consisted of 0.4 g (NH₄)₂SO₄, 0.2 g KH₂PO₄, 0.08 g MgSO₄·7H₂O and 400 ml distilled water. Part B consisted of 22.11 g FeSO₄·7H₂O, 1.0 ml 1N H₂SO₄ and 100 ml distilled water. Parts A and B were autoclaved separately and then combined aseptically. This was then inoculated with *Thiobacillus ferrooxidans*. The pH of the *Thiobacillus ferrooxidans* medium at the start of the test was 2.28 and decreased to 1.98 throughout the course of the test. The temperature of the *Thiobacillus ferrooxidans* medium was maintained at 55°C. Air was bubbled into the medium. For all environments the test duration was 12 weeks and the *Thiobacillus ferrooxidans* medium was changed every four weeks.

Mild steel panels, 191 x 191 x 6.3 mm (or 204 x 204 x 6.3 mm), were grit blasted and coated with either Devcon Brushable Ceramic, EMAA or ETFE. The ceramic-filled epoxy coatings had a thickness of 1072 ± 180 pm. The thickness of the EMAA coating exposed to brine was 1782 ± 143 pm. The ETFE coating thickness was 463 ± 61 pm. The thickness of the EMAA coatings for the *Thiobacillus ferrooxidans* test was 768 ± 106 pm. Control tests were also performed in which EMAA coated panels of thickness 912 • 163 µm and 787 ± 106 µm were exposed to distilled water. The test temperature was 55°C and the duration was 18 weeks in all cases. The temperature of the external bare steel surface was 43.3-43.9°C.

At the completion of the tests the coated panels were visually examined for signs of deterioration such as blistering, discolouration and loss of gloss. The residual adhesion was determined for EMAA coatings by measuring the peel strength (ASTM D 3167). The plates were cut into strips 25 mm wide and the orientation was vertical so that the strip traversed the vapour and immersion-exposed zones. The strips cut from the outer edges of the plates were beyond the exposure zone. A schematic diagram of the strips cut from the panels is given in Figure 1. The coatings were peeled back approximately 40 mm using a razor blade to enable the coating to be gripped. An Instron tensile testing machine was used. The crosshead speed was 152 mm/min. It was not possible to measure the peel strength of the ETFE of ceramic-filled epoxy coatings because the materials were brittle.

Results

One of the ETFE coated panels tested in brine exhibited eight blisters 5-10 mm in diameter below the liquid level and three blisters of the same diameter at the liquid/vapour

interface. Where the coating was not exposed (outside the gasket), adhesion was sound. Corrosion had occurred where the coating was blistered. Spotty black corrosion products (probably Fe_3O_4) existed under the coating in the vapour zone. The coating was not blistered in these areas, but adhesion was decreased. The companion **ETFE** exposed to the same solution had one blister 5 mm in diameter below the liquid level and corrosion in the vapour zone. The black corrosion products tended to convert to red (Fe_2O_3) after exposure to air. The ETFE itself did not undergo any degradation.

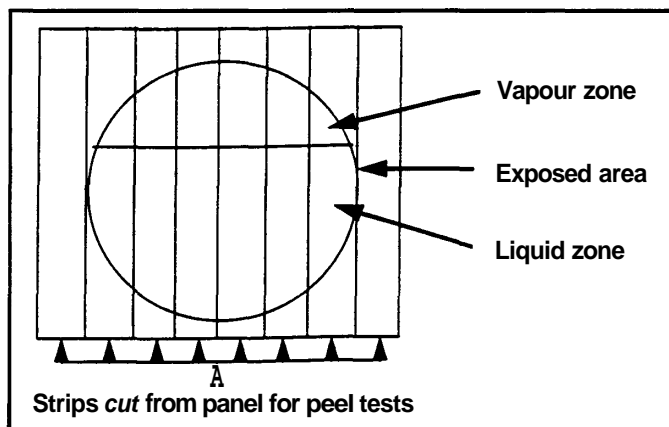


Figure 1. Schematic diagram of peel test specimens cut from Atlas cell panels.

The control panels of EMAA exposed to distilled water showed numerous random small blisters 2 - 5 mm in diameter in the liquid zone. When the coating was peeled, it was found that the blisters corresponded to the presence of black corrosion products. Corrosion was predominant in the liquid zone, although slight corrosion also occurred in the upper vapour zone. A 20 mm wide band above the liquid level was devoid of corrosion. The corrosion in the upper part of the vapour zone corresponded with the presence of condensed water on the coating surface in this area during the test. The failure during the peel tests in the corroded areas was adhesive. The force required to peel the coating varied with the presence of corrosion products, and showed a significant decrease where corrosion was more uniform. In the corroded areas the peel strength was as low as 0.8 N/mm. Where the coating was well bonded the peel strength was typically around 4.92 to 6.89 N/mm. In these areas plastic deformation of the coatings occurred during peeling. The force-displacement curve showed a spike corresponding to the uncorroded area above the liquid level.

The EMAA coated panels exposed to brine did not exhibit any visible signs of blistering or other deterioration. Peel tests revealed black corrosion products beneath the coatings. Energy dispersive X-ray analysis of the corroded substrates did not detect elements contained in the brine. The extent of corrosion was greater than that observed for the panels exposed to distilled water. The failure load and mode were dependent on the presence of corrosion products. Failure was predominantly

adhesive, although localized areas of cohesive failure within the polymer also occurred, particularly where the surface was free from corrosion. Mixed **adhesive/cohesive** failure was observed in a 5-10 mm band above the liquid level where the extent of corrosion was less than for other areas in the vapour zone.

Figure 2 depicts the peel load versus displacement curve for a strip cut from the edge of one of the EMAA panels outside the area exposed to brine. The peel force was relatively constant and the failure mode was adhesive. The average peel strength was 4.33 N/mm. Figure 3 shows the results for a strip cut through an exposed area. The peel force was low in the initial region and this corresponded to the presence of corrosion products at the interface. Peel strength varied from 1.97 to 6.97 N/mm. Figure 4 is another example of low peel forces in the corroded exposed area and increased values before and after this.

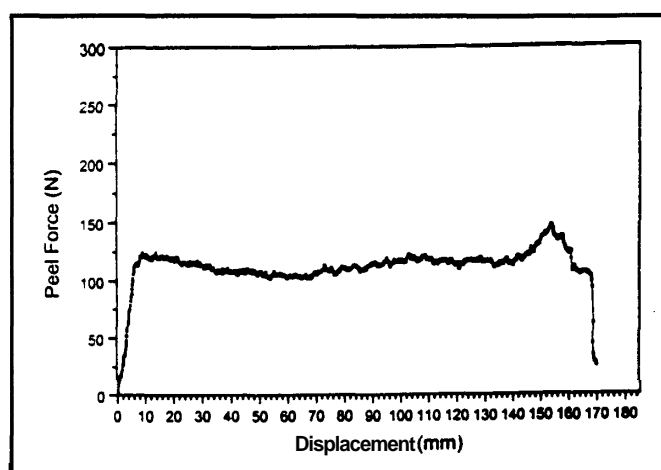


Figure 2. Peel force-displacement curve for EMAA outside brine-exposed area.

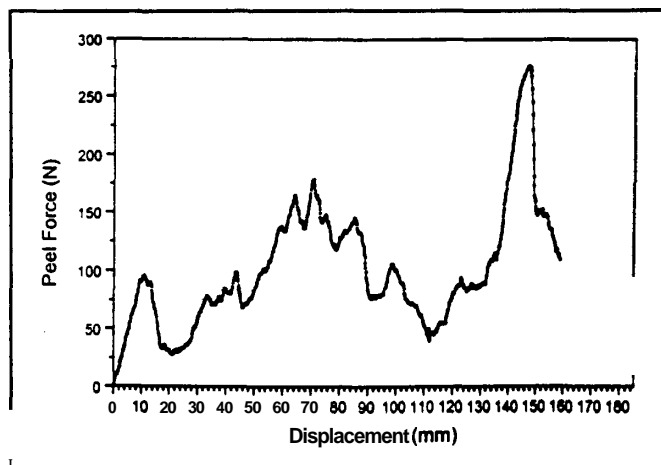


Figure 3. Peel force-displacement curve for EMAA exposed to brine.

The **ETFE** coatings exposed to *Thiobacillus ferrooxidans* exhibited biofouling in the liquid zone and surface staining from iron salts above the liquid level. The coating material itself was not degraded by the bacteria. One of the panels

displayed a blister 10 mm in diameter in the liquid zone. The coatings were removed with a razor blade to examine the steel condition. It was found that spots of black corrosion products had formed at the interface between the steel and coating in both the liquid and vapour zones. Corrosion was more extensive in the upper half of the liquid zone than the lower.

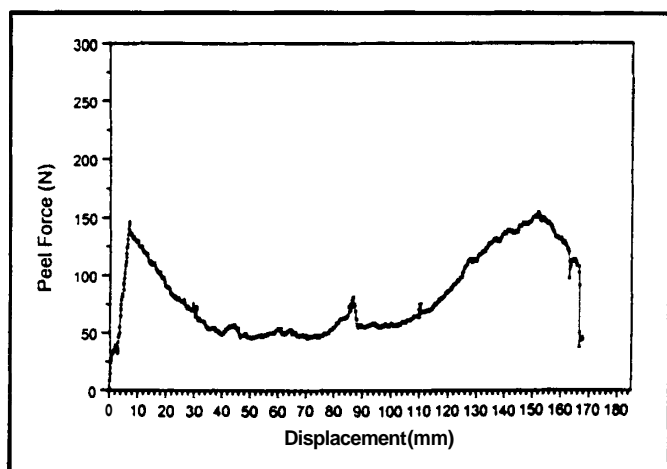


Figure 4. Peel force-displacement curve for EMAA exposed to brine.

Biofouling and surface stains were also observed for the EMAA coatings exposed to *Thiobacillus ferrooxidans* and the polymer was not visibly attacked. Peel tests revealed that the extent of corrosion on the mild steel substrate was greater than that for the brine tests and was evident in both the liquid and vapour zones. However, the EMAA coatings used in the *Thiobacillus ferrooxidans* tests were thinner, hence the results are not directly comparable. Directly above the liquid level was a band approximately 10 mm wide that was completely devoid of visible corrosion. This observation is similar to the panels exposed to distilled water and brine and corresponds to where the surface is free from condensed liquid.

Failure during the peel tests on EMAA panels exposed to *Thiobacillus ferrooxidans* was totally adhesive. The peel load versus displacement curves showed similar form to those obtained from the panels exposed to brine and distilled water. The strips cut from outside the test cell had relatively constant load required to peel the coating. The average peel strength in such regions was 6.64 N/mm. Load versus displacement curves obtained from area of exposed coating had a bathtub shape with higher loads being measured outside the test cell.

The panels coated with the ceramic-filled epoxy showed no visible signs of deterioration other than surface staining at the conclusion of the Atlas cell tests. The coatings were mechanically removed and the mild steel substrate inspected for corrosion. Slight corrosion occurred in the upper half of the liquid zone for the panels exposed to *Thiobacillus ferrooxidans*. No corrosion was observed in the vapour zone or the lower half of the liquid zone. The coated panels exposed to hypersaline brine underwent very slight corrosion in the liquid zone and were uncorroded in the vapour zone.

Discussion

The low residual adhesion of ETFE after exposure suggests that this coating will have insufficient long-term durability for protection of mild steel. Performance of the ETFE coatings was better in the *Thiobacillus ferrooxidans* environment. However, eventual substrate corrosion tends to preclude the mild steel-ETFE system from the application of interest.

Corrosion observed on the EMAA-coated panels exposed to distilled water in the Atlas cell tests was attributed to permeation of water and oxygen. Carboxylic acid groups, which are partially responsible for good adhesion of the coatings, also attract water. Corrosion protection afforded by the EMAA coating is primarily by high resistance rather than complete exclusion of water and oxygen. Corrosion resulted in a decrease in residual adhesion, particularly in the liquid zone.

Blistering, such as that for the EMAA panels exposed to distilled water, was not observed for the thicker coatings exposed to brine. The lack of penetration by ionic species in the brine as revealed from energy dispersive X-ray studies on the substrate together with the findings from the panels exposed to distilled water suggest that corrosion is primarily associated with permeation of water and oxygen. In addition, the presence of salts in the brine will affect the osmotic pressure. Substrate corrosion of the EMAA-coated panels exposed to *Thiobacillus ferrooxidans* suggests that this system lacks long term durability at the temperature of interest.

It is predicted that longevity of 316L stainless steel exposed to brine and bacteria will be extended by EMAA coatings, although further testing is required to confirm this. In particular, the coatings need to be tested under a thermal gradient as this influences permeation. Although corrosion of mild steel occurred with both the ETFE and EMAA coatings, it should not be neglected that the brine and bacteria test environments were severe and that corrosion would have been rapid in the absence of the coatings. One potential means of improving the performance of the coatings on mild steel is to insulate the reactors. This will reduce the temperature differential and the propensity for blistering induced by the cold wall effect.

The ceramic-filled epoxy coatings showed good corrosion protective properties and appear suitable for the application of interest. This coating may have other potential applications in low temperature geothermal environments. Further tests under pilot-scale plant operating conditions are recommended to determine the effects of other parameters such as thermal cycling and fluid velocity on the ability of the coating to provide long-term corrosion protection.

Conclusions

Coatings were investigated for protection of mild steel substrates in reactors used for biochemical treatment of geothermal residues at 55°C. Long term tests under a thermal gradient revealed that corrosion of mild steel substrates coated with EMAA or ETFE eventually occurs when exposed to

hypersaline brine or *Thiobacillus ferrooxidans*. Coating effectiveness may be improved if the reactors are insulated to reduce the temperature differential across the coating and further tests are planned to evaluate this strategy. A more expensive alternative would be to use stainless steel reactors in conjunction with a suitable coating. Brushable ceramic-filled epoxy coatings performed well in the tests and are suitable for more extensive evaluation.

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