# Organometallic Polymer Coatings for Geothermal-Fluid-Sprayed Air-Cooled Condensers

## Preprint

K. Gawlik National Renewable Energy Laboratory

T. Sugama Brookhaven National Laboratory

D. Jung Two Phase Engineering & Research, Inc.

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National Renewable Energy Laboratory

1617 Cole Boulevard Golden, Colorado 80401-3393

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### Organometallic Polymer Coatings for Geothermal-Fluid-Sprayed Air-Cooled Condensers

Keith Gawlik National Renewable Energy Laboratory

Toshifumi Sugama Brookhaven National Laboratory

Doug Jung Two Phase Engineering & Research, Inc.

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#### Abstract

Researchers at Brookhaven National Laboratory and the National Renewable Energy Laboratory are developing polymer-based coating systems to reduce scaling and corrosion of air-cooled condensers that use a geothermal fluid spray for heat transfer augmentation. These coating systems act as barriers to corrosion to protect aluminum fins and steel tubing; they are formulated to resist the strong attachment of scale. Field tests have been done to determine the corrosion and scaling issues related to brine spraying and a promising organometallic polymer has been evaluated in salt spray tests.

#### Introduction

Interest in using relatively clean brines or treated wastewater for augmentation of air-cooled condensation has increased in the past few years. This augmentation is useful during the summer months when binary plant power outputs drop, which often coincides with the most valuable period to sell electricity. Some plants are experimenting with wetted pads that cool the air approaching the tube bundle. Researchers have explored using spray nozzles well upstream of the condensers to cool the air evaporatively [Jung, 2001].

However, greater increases in heat transfer rate can be obtained by spraying the finned tubes directly with water [Kutscher, 2001]. In Kutscher's study, a hypothetical 1  $MW_{e, net}$  air-cooled binary plant located in Nevada was considered, and the effect of using different enhancement methods on the plant's net monthly energy delivery was determined. Figure 1 shows the results for the scenarios with no enhancement, with Munters packing, and with water sprayed directly onto the finned tubes. The most significant improvement to the plant's performance is obtained by spraying the tubes directly, in which case the plant's output is comparable to that of winter-time conditions.



Figure 1. Increases in monthly energy delivery due to enhancement of air-cooled condensation [from Kutscher, 2002].

Others have found that direct water spray onto the finned tubes offers considerable increases in mean temperature difference and air-side heat-transfer coefficient, and savings in capital cost and plot area, compared to other enhancement methods [Smith, 1972]. But direct water spray can result in significant scaling and corrosion problems. When the finned tube is wet, insoluble salts will precipitate onto the heat exchanger surfaces with strong attachment. When the tube dries out, suspended or dissolved material in the water crystallizes and accumulates on the tube. This material tends to have a weaker bond to the surfaces than the insoluble salts. Pitting corrosion of untreated aluminum is also common. Past work has found that deluge cooling of bare aluminum surfaces is feasible only if (1) the water chemistry is well controlled with regard to pH and level of total dissolved and suspended material, to address the first scaling mechanism, (2) the surfaces are washed with deionized water before dry-out occurs, to prevent the second scaling mechanism, and (3) the aluminum is anodized and sealed [Wheeler et al., 1981]. This approach involves considerable capital expense and operational attention for water treatment and tube preparation.

The objective of this project, which is in the early stages, is to develop a means to use lowquality water, such as relatively clean geothermal fluid or treated wastewater, without any control of its chemistry, for direct spraying onto finned tubes. To address the scaling and corrosion issues, thin polymer coatings for aluminum and carbon steel with corrosion- and fouling-resistant properties are being investigated at Brookhaven National Laboratory (BNL) and the National Renewable Energy Laboratory (NREL), in cooperation with industry partners such as Mammoth Pacific LP. This work builds upon and extends previous research and development of polymer-based heat exchanger coatings, which have now been commercialized [Sugama, 2001, Gawlik et al., 2000, 1999, 1998]. Field tests of uncoated aluminum-finned tubes have been conducted to determine the corrosion and scaling problems caused by geothermal fluid spray. To try to prevent scale deposition on and corrosion of the aluminum fins under these conditions, we have synthesized a new type of water-based organometallic polymer (OMP) coating and developed its application method. Coatings of this type have been substituted for conventional paints and chromium- and lead-based corrosion inhibitors, which are hazardous to the environment. This kind of coating has been used for aluminum substrates in other applications, such as aircraft bodies, but has not previously been developed for geothermal environments. They can have hydrothermal stability up to 300°C [Sugama, 1994]. The new coating developed in this study was tested on aluminum fin samples in a salt spray chamber. Field tests in a geothermal environment will start in the summer of 2002.

#### Field tests and analyses of uncoated finned tubing

Samples of steel tubing with helically-wound aluminum fins were exposed to geothermal fluid spray in tests at the Mammoth Lake binary plant and at Soda Lake (conducted by Two Phase Engineering & Research, Inc.). In the Mammoth test, a 2 ft. long section of 1 in. diameter steel tubing with 5/8 in. high embedded aluminum fins was heated internally with geothermal fluid at approximately 160°F. On the exterior, spray nozzles directed geothermal fluid onto the finned tube to wet the surfaces completely. The spray was turned on and off a number of times a day in order to accelerate scaling and corrosion by drying the tube. The test lasted approximately one month. The section was sent to NREL for evaluation of any deterioration of heat transfer capability. Then, it was sent to BNL for detailed analysis of corrosion mechanisms and scale composition.

The tube exposed to Mammoth brine showed no degradation of heat transfer capability, as shown in Figure 2. The tube was tested at NREL's open loop wind tunnel facility and was heated internally by an electric resistance element. Ambient laboratory air was blown over the tube. The tube was placed in the middle of a row of five heated tubes of similar size, fin thickness, and fin spacing. These other tubes were taken from a Balcke-Durr condenser at NREL, which had been exposed only to the outdoor environment in Golden, Colorado. One difference between the tubes is that the Balcke-Durr tubes used tension wound fins, whereas the tube from Mammoth had embedded fins. The tubes were instrumented to determine temperatures at the fin bases. Measurement of the power input to the individual heaters, the tube surface temperatures, and the air upstream and downstream of the tubes allowed calculation of the product of the overall heat transfer coefficient and the bare tube area, UA. The UAs of the tubes per meter tube length (W/°C-m) are shown in the figure as a function of approach air speed. The tube exposed to brine showed a slight increase in UA over the tubes exposed only to atmospheric conditions, but the difference is within experimental uncertainty. The discrepancy in UA may be due to the different fin attachment methods with lower thermal resistance at the fin base presumed for the embedded fin.



Figure 2. Heat transfer results for the tubes exposed to brine and to atmospheric conditions.

A sample of the sprayed tube was then analyzed at BNL with scanning electron microscopy (SEM) and energy-dispersive x-ray spectrometry (EDX). Figure 3 shows that two different areas of the fins, one near the outer edge and the other near the fin base in the vicinity of the steel tube, were analyzed. The SEM microphotograph (top) of the outer edge revealed a very rough surface texture, representing the generation of localized pitting corrosion. Also, the deposition of scales of approximately 2 microns in thickness was observed on the surfaces of the fin in the vicinity of the steel tube (bottom photograph). The EDX quantitative analysis for these scales showed that they were made up of silica-rich compounds containing calcium, magnesium, and iron oxides. It was very difficult to remove these scales from the fin surfaces, reflecting a strong adherence of the scales to the aluminum surfaces. We can predict that the scales would continuously accumulate on the fin surfaces with time. Considerable attention should also be paid to the pitting corrosion, which acts to promote the rate of scale deposition because of the development of numerous oxide layers. If scale deposition and corrosion had been allowed to progress further, the tube may not have maintained its heat transfer performance.



Figure 3. SEM and EDX analyses of fins exposed to Mammoth brine.

Another test of finned tubes downstream of geothermal fluid spray was conducted at Soda Lake [Jung, 2001]. In this test, an apparatus was constructed to evaluate a concept for evaporatively cooling air with geothermal fluid, which is at either injection conditions or has been cooled in a spray pond. The objective was not to flood the tubes with water, as at Mammoth, but to lower the temperature of the air passing over the finned tubes. However, some atomized fluid did reach the finned tubes, the amount of which varied depending on the tube's location in the apparatus. The experiment ran continuously, except for brief periods of maintenance, for three weeks in the summer of 2001. Samples of the tubes were sent to BNL for SEM and EDX analysis. The results for the tube which was exposed to the most fluid impingement will be described in this study. It is not known to what extent the fins were wetted.

Figure 4 presents the SEM-EDX data for the scales deposited on the surfaces of the aluminum fin. The distinctive features of two different scales can be seen in the SEM images; namely, one was the crystalline cubic salt scale (top left), and the other the calcium silicate scale (bottom left), which had a flake-like microstructure. The EDX spectrum (top right) accompanying the SEM image for the cubic crystal scales included a pronounced chlorine signal, and less intense signals of sodium, potassium, and calcium. Undoubtedly, these crystalline scales were due to the formation of NaCl, CaCl<sub>2</sub>, and KCl salts, which are presumably soluble in water. In contrast, three prominent signals for silicon, chlorine, and calcium were detected from the flake-like scale spectrum (bottom right). Although some chlorine elements belong to the CaCl<sub>2</sub> salt, the calcium silicate compounds related to the calcium and silicon elements appeared to be deposited as water-insoluble scales. No sodium signal was detected in this scale. Also, SEM imaging (Figure

5) revealed the complete coverage of this silicate scale, rather than the salt scale, over the entire surface of the fin, inferring that the silicate scale preferentially deposited on the aluminum surfaces.



Figure 4. Two different scale compounds collected from the fin surface in the Soda Lake test.





In the induction period of the deposition of calcium silicate, the oxide layers existing on the surface of the aluminum fin may act to promote the deposition rate because of a high reactivity of calcium silicate with the metal oxides. Thus, the silicate compounds may preferentially react with the oxide layers, unlike the chloride-based salt scales. This reaction may be detrimental to retaining the function and efficacy of the finned tube because of the development of a strong bond at the critical interfacial zones between scale and metal. In addition, the combined scale formation of silicate and salts seems to promote the rate of pitting corrosion of the aluminum fin.

#### Test of new OMP coating for aluminum in geothermal environments

BNL-developed organometallic polymer coatings of ~10 micron thickness are candidates for a coating to prevent corrosion and the adhesion of scale to the fin surfaces. A new type of OMP precursor for use as a water-based coating and its coating technology were developed. This new precursor consisted of aminopropylsilanetrial (APST) as a network-forming organometallic monomer, HCl as the acid mineral catalyst, and water. Its pH was ~ 9.0. Samples of aluminum fin were coated with the OMP in the following sequence. First, to remove surface contaminants, the samples were immersed for 10 min. at 70°C in an alkaline solution consisting of 0.4 wt% NaOH, 2.8 wt% tetrasodium pyrophosphate, 2.8 wt% sodium bicarbonate, and 94.0 wt% water. The alkali-cleaned samples were washed with deionized water at 25°C for 5 min., and dried for 30 min. at 100°C. Then the samples were dipped into a soaking bath of precursor solution at room temperature and withdrawn slowly. The wetted pieces were preheated in an oven for 30 min. at 70°C to yield a xerogel (xero means dry) coating film, which was subsequently heated for 2 hours at temperature of 175°C to make the polymerized coating film.

OMP-coated and uncoated samples were placed in a salt spray chamber and underwent 5 wt% salt spray testing in accordance with ASTM B 117. Figure 6 shows the state of the coated and non-coated aluminum fin samples after salt spray tests for 30 days. As seen in the figure (right), the uncoated fin was corroded after exposure to the salt fog. In contrast, a very promising result was obtained from the OMP-coated fin; namely, there is no sign of any corrosion of the aluminum substrate.



Figure 6. Coated aluminum fin (left) and non-coated aluminum fin (right) after one month test in salt-spray chamber at 35°C.

### Conclusions

Evaluations of aluminum-finned tubing wetted by geothermal fluid have shown that scaling and corrosion are promoted, which will lead to increased maintenance costs and decreased condenser life if this strategy is used to increase the heat transfer rate of binary plant condensers. Flooding the surface of finned tubing with geothermal fluid will provide a large amount of heat transfer enhancement, but using this technique requires the application of a corrosion- and scale-resistant coating. A proposed organometallic polymer coating was developed and tested in a salt spray chamber. It successfully protected the aluminum substrate completely. An OMP coating will next be developed for the steel tube to provide complete protection for the finned tube assembly, and field tests at a geothermal power plant are planned.

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