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FAILURE ANALYSIS REPORT

HEAT EXCHANGER TUBES
GEOTHERMAL BINARY POWER PLANT
MAGMA ELECTRIC COMPANY
EAST MESA, CALIFORNIA

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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION AND BACKGROUND.	1
2.0 FLUID CHEMISTRY.	4
3.0 EXAMINATION PROCEDURE AND RESULTS.	5
4.0 DISCUSSION	17
5.0 CONCLUSIONS.	20
6.0 RECOMMENDATIONS.	22
7.0 REFERENCES	24

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FAILURE ANALYSIS REPORT

HEAT EXCHANGER TUBES GEOTHERMAL BINARY POWER PLANT MAGMA ELECTRIC COMPANY EAST MESA, CALIFORNIA

1.0 INTRODUCTION AND BACKGROUND

Radian received twelve sections of heat exchanger tubing from the Magma Electric Company's 10MW(e) East Mesa binary geothermal power plant. Three tube sections were received from each of four shell and tube heat exchangers (HX1, HX6, HX8, and HX10) of the isobutane vaporizer train. All samples were taken from the upper few rows of tubes. Two months later, four more tube sections were received. These four sections were taken from the lower rows of heat exchangers 1, 6 (two sections), and 10. Radian was requested to investigate the cause of severe pitting failure of these heat exchanger tubes. This report is part of a continuing DOE effort to gain insight into the service life of component materials employed in geothermal energy utilization.

Figure 1 is a flow chart for Magma Electric Company's 10MW(e) geothermal binary power plant at the East Mesa, California, geothermal resource. Geothermal fluid is pumped from five wells approximately 7000 feet deep. In this binary design, isobutane is heated by hot geothermal fluid in ten parallel heat exchangers.

Each heat exchanger contained 109 carbon steel tubes that were 77 feet long and originally had 0.035 inch (nominal) walls. The 1 3/16 inch diameter tubes were bundled and supported in the exchangers by a unique design which incorporated deformed short tubes shaped to fit within each cluster of seven tubes as spacers. These spacers were held in place by the clamping action

FIGURE 1. Flow Chart for Magma Electric's Geothermal Plant.

of a strap around each cluster. The exchanger tube bundle was made up by interlacing the tube clusters along their length as well as laterally across the tube bank.¹

The heat exchangers are indicated as six heaters, two boilers, and two superheaters in the flow chart of Figure 1. The tubes received for analysis are from these heat exchangers. In all heat exchangers, the isobutane is on the tube side, and the geothermal fluid is on the shell side. The geothermal fluid enters heat exchanger 8 at 350°F and exits heat exchanger 1 at 167° to 176°F. The tubes received for analysis were selected from the four heat exchangers with the greatest inlet to outlet temperature differential.

The plant started operation in November 1979, and shut down November 1981. During this period, the plant was operated about 50 percent of the time. During periods of shutdown, the heat exchangers were drained, but geothermal fluid was not completely drained from the bottom of the shells. Additionally, the exchangers were left open to the air for days at a time.² The four tubes from the bottom regions of three exchangers were immersed in geothermal fluid during shutdowns, while the upper regions were exposed to refluxing geothermal vapors.

2.0

FLUID CHEMISTRY

The geothermal fluid supplied to the heat exchangers from the five wells at East Mesa has the chemistry presented in Table I.

TABLE I. ANALYSIS OF GEOTHERMAL FLUID SUPPLIED TO
MAGMA ELECTRIC'S 10MW BINARY PLANT

<u>Key Species</u>	<u>Concentration Range</u>
pH	5.5-5.9
Cl ⁻ ppm	3700-6000
SO ₄ ⁼ ppm	68-84
HCO ₃ ⁻ ppm as HCO ₃ ⁻	400-500
CO ₃ ⁼	Not Reported
Free CO ₂ ppm as CO ₂	1000-1500
Total CO ₂ ^a ppm as CO ₂	1700-2100
H ₂ S ppm	0.7-1.7
NH ₃ ^b ppm	17-23
<u>Other Species</u>	
TDS ppm	7300-10,000
F ⁻ ppm	2.7-3.3
K ⁺ ppm	218-300

Source: Reference 2, except as indicated.

a - Total carbon dioxide species = CO₂ + HCO₃⁻ + CO₃⁼ as CO₂.

b - Reference 3.

The first twelve tube sections and the second four tube sections received for analysis are shown in Figure 2. All sections were coated on O.D. and I.D. surfaces with a tenacious dark deposit, 3 to 6 mils (0.003-0.006 inch) thick. Covering this deposit was a reddish-brown powdery deposit several mils thick.

A portion of a tube was chemically analyzed and the results are presented in Table II.

TABLE II. CHEMICAL ANALYSIS OF HEAT EXCHANGER TUBE

<u>Element</u>	<u>Weight Percent</u>
Carbon	0.25
Chromium	<0.05
Manganese	0.54
Molybdenum	<0.05
Nickel	<0.05
Phosphorus	0.007
Silicon	<0.05
Sulfur	0.013

Source: Sherry Labs, Muncie, Indiana

An axial cross section was cut from a tube. This section was polished and etched to examine the microstructure. Figure 3 shows the tube microstructure which is characteristic of thin walled carbon steel tubing. The chemical analysis and microstructure verify that the tubes were fabricated from plain carbon steel.

Figure 2. Two groups of tubes received for analysis from the Magma Electric geothermal plant. The upper picture shows the first group of twelve tubes from four heat exchangers. The lower picture shows the four tubes subsequently received from lower portions of three of the same heat exchangers.

Magnification: 100X

Etchant: Nital

Magnification: 400X

Etchant: Nital

Figure 3. Photomicrographs of a tube axial cross section. The microstructure consists of ferrite (light constituent) and pearlite (dark constituent). Elongation grains are evident from the tube drawing process. This microstructure is consistent with plain carbon steel tubing.

The powdery reddish-brown deposit was removed from several tube I.D. and O.D. surfaces. The deposits were analyzed separately by energy dispersive X-ray spectroscopy (EDS) for elemental identification, and by X-ray diffraction (XRD) for compound identification. The results of the scale analyses are presented in Table III.

TABLE III. SCALE ANALYSES OF HEAT EXCHANGER TUBES

<u>Elements Detected by EDS*:</u>	<u>Relative Concentration</u>	
	<u>I.D.</u>	<u>O.D.</u>
Aluminum	Trace	Trace
Calcium	Trace	Trace
Chlorine	Trace	Trace
Iron	Major	Major
Silicon	Trace	Minor
Sulfur	Minor	Minor
<u>Compounds Identified in I.D. and O.D. Scale by XRD:</u>		
Iron Carbonate - FeCO_3 - (Siderite)		
Iron Oxide - Fe_3O_4 - (Magnetite)		
Iron Oxide Hydroxide - $\text{FeO}(\text{OH})$ - (Goethite)		
Iron Sulfide - FeS - (Pyrite)		

*EDS detects trace amounts of those elements of atomic number greater than 10. It therefore does not detect elements hydrogen, carbon, nitrogen, or oxygen.

All the I.D. and O.D. scales analyzed showed essentially the same scale composition. There was no difference between tubes of different heat exchangers nor between I.D. or O.D. surfaces.

Two types of localized corrosion mechanisms were observed on the tube surfaces. Crevice corrosion occurred on several tube O.D. surfaces where tube spacers or bands contacted the tube. One example is shown in Figure 4. The maximum observed depth of localized corrosion on this tube was 4 mils. No areas of tube wall perforation were found at crevice corrosion sites. The second type of localized corrosion was pitting evident on every tube analyzed. Both I.D. and O.D. pits were observed.

The I.D. pits were barely visible to the unaided eye, but were clearly visible at 20X magnification. The O.D. pits were profuse and readily visible to the eye. These pits were approximately hemispherical in cross section, and a number of them had perforated the tube wall.

Acid cleaning of the areas around the visible perforations removed the adherent iron oxide/sulfide scale and revealed three or four additional perforations for each readily apparent hole. Figure 5 shows a typical area of perforated pits as they appeared after cleaning with inhibited hydrochloric acid. Only the largest pit was visible prior to cleaning. All of these pits are larger on the O.D. than the I.D., indicating that they initiated on the shell (brine) side.

Eight obvious holes were found in the 63 feet of uncleaned tubing examined. Assuming that acid cleaning would have revealed three or four additional perforations for each observed hole, it is estimated that there is about one perforated pit per two linear feet of tubing, though the perforations may not be uniformly distributed.

Figure 4. Tube section 12N from heat exchanger 10 showing crevice corrosion (at arrows) where tube spacers contacted the O.D. surface.

Magnification: 1.5X

HX1 6N

Figure 5. O.D. surface of tube 6N from heat exchanger 1 after acid cleaning to remove scale. Hemispherical pits initiated on the O.D. surface and penetrated through the tube wall. Only the largest pit was visible prior to cleaning.

Samples from several tubes were cleaned ultrasonically in a laboratory detergent, followed by increasing concentrations of hydrochloric acid with inhibitor. After all cleaning attempts, some tenacious scale still adhered to tube surfaces. Cleaned O.D. and I.D. tube surfaces were imaged with scanning electron microscopy. Figures 6 through 9 show typical views of these surfaces. Pits were more common on both surfaces of the bottom tubes than on the tubes from upper portions of heat exchangers. Where pitting did occur, it was generally more advanced on the O.D. surfaces than on the I.D. surfaces.

A statistical evaluation of the average remaining wall thickness of the tube sections was undertaken to assess "uniform" corrosion of the tubes. Numerous ring and axial cross sections were cut at random from the tube sections, cleaned, and polished. The wall thickness at several points on each section was measured to the nearest 0.2 mil (0.0002 inch) with an optical metallograph. The points of measurement were selected to show typical wall thickness, and obvious pits were avoided. A total of 143 thickness measurements were made on samples from the 12 upper row tube segments, while 96 measurements were made on the four bottom row tube segments.

Figure 10 is a histogram showing the distribution of measured thicknesses from the upper level tubes, while Figure 11 presents the same data from the lower level tubes. The average measured wall thickness of the upper level tubes is 31.3 ± 0.8 mpy (95 percent confidence limits), while average tube wall thickness of the lower level tubes is 28.7 ± 0.5 mpy. Tests showed that the difference between the two sets of data is statistically significant (at the 95 percent confidence level).

Magnification: 300X

Figure 6. Scanning electron micrograph of the I.D. surface of tube 10N from heat exchanger 8 showing no discrete pitting.

Magnification: 300X

Figure 7. Scanning electron micrograph of the I.D. surface of the bottom tube from heat exchanger 6. Some indication of pitting is evident.

Magnification: 100X

Figure 8. Scanning electron micrograph of the O.D. surface of tube 10N from heat exchanger 8 showing no microscopic pitting.

Magnification: 100X

Figure 9. Scanning electron micrograph of the O.D. surface of the bottom tube from heat exchanger 6. Several pits are evident.

Figure 10. Thickness measurements of remaining wall of upper level heat exchanger tubes. (Cells without indicated cell counts contain single counts.)

Figure 11. Thickness measurements of remaining wall of lower level heat exchanger tubes.

The difference between the above mean wall thicknesses and the 35 mils nominal tube wall specification is in qualitative agreement with the 2-5 mpy corrosion rates for carbon steel measured by Battelle Pacific Northwest Laboratories at Magma. However, this difference cannot be reliably used to calculate the corrosion rate because of the uncertainty of the actual, as opposed to nominal, initial thickness of the tube walls. Figure 10 shows that between two and eight percent of the measured wall thicknesses in the upper level tubes were greater than the nominal 35 mils tube wall.

These carbon steel heat exchanger tubes have suffered from three corrosion mechanisms: "uniform" corrosion, crevice corrosion, and pitting. The available data do not allow a quantitative measure of the uniform corrosion rate, but do tend to support the 2-5 mpy rates measured by Battelle Pacific Northwest Laboratories in corrosion tests at the plant. In view of the severe pitting, any estimates of "uniform" corrosion are of only academic concern.

Crevice corrosion appeared at tube surfaces where spacers and bands contacted tubes. The crevice corrosion was mild in comparison with pitting, and was not the cause of any tube perforations. However, the presence of even mild crevice corrosion may indicate a need for re-evaluation of the unique tube bundling method used in these heat exchangers.

Pitting corrosion was the most severe form of corrosion observed on these tubes and caused the failure of the heat exchangers. The pitting was much more advanced on the O.D. (brine side) surfaces than on the I.D. (hydrocarbon side) surfaces, and pits perforated tubes from the O.D. rather than from the I.D. This observation indicates that I.D. pitting likely occurred from geothermal fluid which had entered the tubes via O.D. pitting perforations and contaminated the otherwise uncorrosive isobutate. The finding of identical corrosion product deposits on O.D. and I.D. surfaces supports this hypothesis. No difference in pitting could be discerned between inlet/outlet regions or as a result of temperature differentials. Pitting was more abundant on tubes from the bottom regions of heat exchangers. These bottom tubes were exposed to aerated geothermal fluid during downtimes while the upper tubes were exposed to

geothermal vapors. This probably accounts for the more severe attack on the lower tubes.

Oxygen allowed to enter during downtimes, sulfides, and carbon dioxide species, all contributed to pitting corrosion in this system. Each of these species produced corrosion products detected in the deposits of these tubes (i.e., iron oxides, iron sulfides, and iron carbonates). Of these three species, oxygen was probably the most detrimental to the tubes, and much of the damage likely occurred during shutdown periods. It has long been recognized that aeration of geothermal fluids causes drastic increases in carbon steel corrosion rate. For example, researchers at Wairakei, New Zealand, reported such findings in 1964⁴, and numerous similar reports have occurred since.⁵

It is also possible that some of the pitting damage resulted from attack by dissolved carbon dioxide during normal operations. Short-term (560-hour) heat exchanger tests using pumped geofluid at Heber--similar chemistry and temperature--showed pits 3 mils deep, for a linear annualized pitting rate of 46 mpy.⁶ Other tests at Heber--using brine from which the free carbon dioxide had been vented--did not show pitting.⁷ Comparison of these results substantiates the hypothesis that free carbon dioxide in the Magma fluid may have caused some of the pitting damage. Generally, however, carbon dioxide attack has the appearance of sizable patches of unattacked metal interspersed with areas of broad shallow attack--mesa and canyon attack. The observed discrete hemispherical pits on these tubes tend to support the oxygen attack mechanism as the major cause of the damage.

The short-term tests with pressurized (carbon dioxide laden) geofluid discussed in the previous paragraph raise

serious questions as to whether carbon steel can be successfully used for binary geothermal power plant heat exchanger tubes even under the most carefully controlled operating conditions. If carbon steel tubing is used, it is absolutely imperative that atmospheric oxygen be rigidly excluded at all times, but especially during shutdown.

For at least three reasons, an alternative material, rather than carbon steel, should be used in future heat exchangers. First, there is the real risk that dissolved carbon dioxide in the pumped Magma brine is an active pitting agent for carbon steel. Second, the requirement for fail-safe oxygen exclusion to protect the carbon steel tubes will vastly complicate plant operations. Third, it has been shown that highly corrosion resistant alloys suffer far less fouling in geothermal heat exchange service than does carbon steel.⁶

The selected tubing alloy should be resistant to pitting, crevice corrosion, and stress corrosion cracking, both under normal operating conditions, and when exposed to aerated geothermal fluid or vapors. It should have a low enough uniform corrosion rate to have a reasonable probability of providing twenty or more years of service. A number of highly alloyed ferritic stainless steels, as well as some nickel- and titanium-based alloys, satisfy these requirements under Magma hydrocarbon vaporizer conditions.

CONCLUSIONS

- The heat exchanger tubes failed by pits which penetrated the tube wall from the O.D. (brine) surface.
- Pitting on the I.D. (hydrocarbon) side of the tube wall was minor. From the identification of identical corrosion product deposits on both the O.D. and the I.D., it is concluded that this pitting resulted from geothermal brine contamination of the otherwise noncorrosive isobutane. No evidence for initiation of failure from the hydrocarbon side was discovered in this failure analysis.
- The observed pitting failure is typical of oxygen damage to carbon steel and the most probable cause of failure of these carbon steel tubes was oxygen ingress during shutdown periods when the heat exchangers were partially drained and left open to the atmosphere.
- Crevice corrosion to a depth of four mils was observed where the tube bundle spacers and straps contacted the tube wall.
- The average wall thickness in unpitted areas was 31.3 ± 0.8 mils on the upper tubes and 28.7 ± 0.5 mils on the lower tubes, indicating more severe corrosion of the lower tubes. The difference between these thicknesses and the 35 mil (nominal) initial thickness cannot be used to calculate a corrosion rate because the actual--as opposed to

nominal--initial wall thickness is unknown. However, these data show qualitative agreement with results of corrosion tests previously done at the Magma plant.

- Continuous fail-safe oxygen exclusion would be required with carbon steel tubes to prevent the kind of rapid, oxygen-induced pitting which lead to the current failure.
- The small amount of data available indicates that carbon steel heat exchanger tubing may also suffer premature failure by pitting attack from carbon dioxide in pumped (unflushed) brine at East Mesa and similar resources, even if oxygen is excluded. The attack would likely be slower than occurred in this failure.
- The vast complication of plant operations required for protection of the carbon steel tubes from oxygen-induced pitting, plus the risk that dissolved carbon dioxide would also lead to premature failure, makes carbon steel a poor choice for hydrocarbon vaporizer tubes at the Magma, or similar plants.

RECOMMENDATIONS

- Materials other than carbon steel should be selected for replacement heat exchanger tubes, as well as for tubes of any future heat exchangers at Magma or similar power plants. It is recommended that the selected alloy be resistant to pitting, crevice corrosion, and stress corrosion cracking both under normal operating conditions and when exposed to aerated geothermal fluid or vapor. It should also have a low enough uniform corrosion rate to have a reasonable probability of providing twenty or more years of service.
- The following highly alloyed ferritic stainless steels--costing two to three times as much as carbon steel--are recommended for heat exchanger tubing at the Magma binary power plant:
 - Allegheny-Ludlum 29-4
 - Allegheny-Ludlum 29-4C
 - Allegheny-Ludlum 29-4-2
 - Monit (25Cr-4Ni-4Mo)
- The titanium alloy TiCode 12, and nickel-based Inconel 625 would also be excellent from a corrosion standpoint but at much higher cost. The titanium alloy would fail catastrophically however, if hydrofluoric acid were used to remove silica scale. All the other alloys discussed should resist this solvent.

- Austenitic stainless steels, such as Type 304 and Type 316, are strongly contraindicated because they are subject to stress corrosion cracking under normal operating conditions.
- Cupronickels and Monels are also strongly contraindicated because they are subject to accelerated corrosion by part-per-billion levels of hydrogen sulfide, as shown in other geothermal experience.

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