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Characterization of the Corrosion Environment of the Desert Near Barstow, California

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D. A. Hughes

Prepared by Sandia National Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550 for the United States Department of Energy under Contract DE-AC04-76DP00789.

Printed September 1981

Sandia Laboratories

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$4.50 ; Microfiche \$3.00

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CHARACTERIZATION OF THE CORROSION ENVIRONMENT
OF THE DESERT NEAR BARSTOW, CALIFORNIA

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ABSTRACT

The corrosion characteristics of the desert atmosphere environment near Barstow, CA have been evaluated for the solar pilot plant receiver panel. Potential degradation mechanisms considered were hot corrosion from molten salts and stress corrosion cracking in aqueous environments. The possibility of degradation from these mechanisms depends on the chemical composition of airborne particulates, aerosols, and gases. These particulates and aerosols were collected near the pilot plant site and analyzed for water and acid soluble Na^+ , Mg^{++} , Li^+ , S^- , SO_4^- , and Cl^- . Comparison and evaluation of the quantities of these ions present with those necessary for corrosion indicate that external corrosion of the receiver due to the desert atmosphere environment is unlikely.

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CHARACTERIZATION OF THE CORROSION ENVIRONMENT OF THE DESERT NEAR BARSTOW, CALIFORNIA

Introduction

A major factor in site selection for solar thermal energy systems is the amount of insolation available per year. The large amount of insolation available in desert regions was a major consideration in siting a 10 MWe solar pilot plant ('Solar One') near Barstow, CA. Although there was no previous negative experience to cause concern, we had very little prior data with which to determine whether the desert atmosphere environment presents a corrosion problem for the solar receiver panel metal tubing. Because of the paucity of data, we felt it prudent to characterize and evaluate the desert environment near Barstow and analyse the results with respect to possible corrosion effects.

Receiver materials compatibility with the desert environment is influenced by both the operating temperature and materials of choice. The maximum design temperature^{1,2} for the pilot plant receiver tubing, 650°C, is achieved by focusing solar energy on the external surfaces of the panel tubing. The hot tubing then acts as a coupled boiler/heat exchanger, creating steam for electric power generation. Material for the receiver, alloy 800, was chosen on the basis of successful experience with heat exchanger designs which employed the same working fluids, water/steam, inside the tubing. This experience, however, does not include the presence of desert air on the outside surface of the tubing. The typical external atmospheres for heat exchangers are neutral (non-oxidizing) flue gases which are less corrosive to some materials than ordinary air. Furthermore, desert atmospheres frequently contain dust which may contain "alkali" (a colloquialism for the salt residue of evaporating natural waters). Seasalt fallout, on the order of 0.337 g/m²/year, may also contribute to the salt content of the desert atmosphere³. A buildup of these natural salts, such as NaCl, CaSO₄, Na₂SO₄, K₂SO₄, in the crevices of the tube panels could lead to hot corrosion from molten salts during the day and/or aqueous corrosion from repeated wetting by heavy nighttime dews.

The probability of corrosion from these mechanisms is dependent on the chemical composition of the airborne particulates and aerosols. Therefore, their collection and analysis is necessary in the determination of the desert environment's potential for damage to the receiver materials. This paper will describe the results of air sampling near Barstow and the subsequent characterization and evaluation of the desert environment's potential for damage to the receiver materials. Judgements concerning the potential for corrosion are presented and discussed. The baseline data generated on the environment is also applicable to heliostat compatibility; however, the scope of this report is restricted to receiver components.

Potential Corrosion Mechanisms

Before defining the desert environment, potential corrosion mechanisms will be considered in more detail. Two mechanisms, stress corrosion cracking (SCC) and hot corrosion will be discussed for the receiver panel material, alloy 800, which is an autentic iron-nickel-chromium alloy. For the first mechanism, SCC, to occur in the receiver, three elements must all be present: stress, aggressive environment, and a susceptible material. The regions where these elements will most likely exist simultaneously are near the tube-to-header welds on the panel support structure. Stresses in these regions are at or below the yield strength of the alloy. They are comprised of residual stresses from welding and forming operations, plus service loads. These areas also have horizontal surfaces where water from rain or dew, plus airborne particulates and aerosols can collect. Aqueous caustic or chloride solutions may thus be created in these areas. Alloy 800 exhibits SCC in both high concentration chloride and caustic solutions^{4,5,6}. For any aqueous solution present, both temperature and concentration will vary as the receiver heats up diurnally and the water is evaporated. Boiling solutions (100-160°C) could be present for several minutes each day during heatup. In this report the concentrations and exposure life for aqueous external environments of the receiver will be compared with laboratory tests to determine the probability for SCC. Examples of concentrations and exposure times for aqueous environments which have been shown to cause chloride and caustic cracking in alloy 800 are listed in Table 1.

The second potential degradation source, hot corrosion, is an accelerated oxidation and/or sulphidation process⁷⁻¹¹. This process is promoted by molten salts and ions present on the surface of a metal at high temperatures, typically 600-1000°C¹². Many hot corrosion mechanisms are possible depending on the temperature, metal composition, salt composition, and oxygen availability. For example, molten salts¹³ such as Na_2SO_4 and Na_2O , can act as catalysts for oxygen-metal interaction. They can also react with oxide scales and metal substrate, causing alloy depletion and sulfidation. Chloride ions accelerate oxidation by cracking protective oxide scales and baring fresh metal for further oxidation. Molten salt sources include atmospheric SO_3 , NaCl , CaCl_2 and metal ions from the alloy. The amount of salt which is required to cause hot corrosion is estimated to be a replenished steady-state film of 0.01-0.001 mg/mm² of surface^{10,11} and greater than 0.01 ppm NaCl in the atmosphere⁹.

Examples of eutectic sulfate and chloride salt compositions and melting points are presented in Table II¹⁴. Sulfate containing salts which are molten at receiver panel temperatures are likely to cause hot corrosion if present in sufficient quantities. The constituents of these salts are present in the desert environment; however, their quantities were unknown. The next two sections will describe the determination of these quantities and an evaluation of their corrosion significance at the levels present.

Experimental Procedures

To provide information on the desert atmosphere environment, two types of sampling techniques were used: high volume air sampling and flat plate collection. High volume air samplers, which operate similar to a vacuum cleaner, pull air through a paper filter at rates of approximately 35 m³/hr.

Table 1
Stress Corrosion Cracking of Alloy 800

<u>Environment*</u>	<u>Temperature (°C)</u>	<u>Test Type</u>	<u>Life (hours)</u>
10% NaOH ⁶	316	U-bend $\sigma > .2\%$ Yield Strength	1000 (40% Crack Penetration)
875 ppm Cl ⁻⁵	260	U-Bend $\sigma > .2\%$ Yield Strength	840
100 ppm Cl ⁻⁶	350	C-ring $\sigma = 2\%$ Yield Strength	9000
42% MgCl ₂ ^{4,5}	154	U-bend $\sigma > .2\%$ Yield Strength	68

*Tests performed in undeaerated water for Cl⁻ environments and deaerated water for OH⁻.

Table 2
Melting Points of Several Chloride and
Sulfate Eutectic Salts¹⁴

<u>Salt</u>	<u>Eutectic Composition</u>	<u>Melting Point (°C)</u>
MgCl ₂ -MgSO ₄	81-19	657
CaCl ₂ -Na ₂ SO ₄	91.5-8.5	645
CaSO ₄ -KCl-K ₂ SO ₄	13.5-58.1-28.4	644
Al ₂ (SO ₄) ₃ -Na ₂ SO ₄	17.6-82.4	640
CaSO ₄ -NaCl-Na ₂ SO ₄	18.8-46.1-35.1	633
LiSO ₄ -Pb-SO ₄	78-22	632
NaCl-Na ₂ SO ₄	51.8-52.8	628
CaSO ₄ -KCl-NaCl	10.5-42.6-46.9	605
K ₂ SO ₄ -K ₂ S	43-57	587
Li ₂ SO ₄ -Na ₂ SO ₄	63-37	584
Fe ₂ (SO ₄) ₃ -Na ₂ SO ₄	17.5-82.5	562
CaSO ₄ -NaCl-Na ₂ SO ₄	2.7-45.5-51.7	485
LiCl-Li ₂ SO ₄	63.5-36.5	478
Na ₂ SO ₄ -ZnSO ₄	45-55	472
MgCl ₂ -NaCl ₂	40-60	450

Flat plate collectors are passive samplers consisting of double sided sticky tape mounted on a flat vertical surface. Thus, flat plate collectors only gather particulates which impinge on their surface. These two techniques were chosen to complement each other; the high volume air samplers collect particulates and aerosols from a large volume of air and thereby yield a more sensitive air sample, while the flat plate collectors yield a more accurate representation of the quantity of particulates which might accumulate on the receiver panel. Prior to sampling, the air flow rate for the high volume air samplers was calibrated and the surface area of the sticky tape was noted (values in Appendix A). This calibration was necessary for subsequent normalization of particulate quantities to volume or area sampled.

Four samplers of each type were mounted at the top of a 23 meter tall water tower (Figure 1) at the Marine Corp Supply Center (Yermo area) two miles northeast of Daggett. The location of this tower with respect to the pilot plant is shown in Figure 2. It would have been preferable to mount the samplers at an elevation comparable to the elevation of the pilot plant central receiver (85m). However an existing structure of that height was not available for mounting the samplers. The water tower was chosen since it was the tallest structure available; nevertheless it is believed that the particulates sampled at this elevation are reasonably representative of the external environment of the receiver.

When positioning the samplers on the tower (Figure 3), care was taken to place the flat plate collectors into the prevailing wind to maximize particulate collection. The prevailing wind direction was determined by 10 years of climatic data and was consistent with the actual wind patterns during the sampling period, April 8 through May 9, 1980 (Figure 4)¹⁶. During this period the samplers provided continuous collection of particulates; filters and tapes were changed weekly by marine base personnel. Flat plate collection was terminated the week of April 25 because a wind storm blew the small lightweight plate collectors off the tower.

In addition to air samples, soil samples were taken from regions near the tower as located in Figure 5. The soil samples were collected for comparison and possible correlation of the dust particulates in the air and the soil.

At the end of the sampling period all collected samples were analyzed using wet chemistry by Trace Analysis Laboratories in Hayward, CA. This analysis determined the pH and amounts of the following water and acid extracted ions: Na^+ , Mg^{++} , Mn^{++} , Li^+ , Cl^- , SO_4^{--} , and S^- . These ions are considered to be the most important from the standpoint of corrosion. (The analytical procedures are presented in Appendix B). X-ray diffraction was also performed on one filter sample to determine the type of particulates present.

Results and Discussion

The results of chemical analyses of the filter, tape and soil samples are presented in Figures 6 through 11. Each figure is a series of three bar-graphs showing ion concentration normalized to sample weight (sample weights are given in Appendix C) versus location and date for filter and

Figure 1. Water Tower at Yermo Marine Corp Supply Center, Air Samplers were Mounted on Tower Catwalk.

Figure 2. Location of Water Tower with Respect to the Solar Power Plant Site ¹⁵.

Figure 3. Arrangement of air samplers around tower catwalk.

Maximum Wind Direction Frequency Distribution

Figure 4. Wind frequency distribution for April, May and June 1980, April, May and June 1969-1978, and annual average for 1955-1964.¹⁶

Scale 25 mm = 6.4 km

<u>Symbol</u>	<u>Soil Sample</u>	<u>Location</u>
◆	1-3	Pilot plant construction site
▲	4-6	Beneath and near water tower
■	7-8	Yermo supply center
●	9-11	Elephant mountain
●	12	Dry lakebed

Figure 5. Regions Where Soil Samples Were Removed ¹⁷

tape samples or location for soil samples. Water and acid extraction results are placed side by side on each graph. On average the ion concentrations were very small for all samples; sulfate (Figure 6) was the most prevalent ion. Chloride (Figure 7) was not found in any sample by water extraction. However, a few soil and tape samples contained acid extractable chlorides. Since the acid extractable chlorides are tied up in water insoluble minerals they will not be available for aqueous corrosion. Of the metal ions, sodium (Figure 8) was the most common with lesser amounts of magnesium (Figure 9) and manganese (Figure 10) present.

Concentrations of $S^{=}$ and Li^{+} are not shown in the figures because they were below the detection limits of .024 and .002 mg per sample respectively. One soil sample from the dry lakebed, location 12 in Figure 5, is an exception and had a Li^{+} concentration of .02 moles/Kg of sample. Analyses for Ca^{++} and K^{+} concentrations performed on one filter sample (4-25-80-A) yield 0.349 moles/kg of Ca^{++} and 0.054 moles/kg of K^{+} . Ca^{++} is present in a quantity similar to Na^{+} concentrations, while K^{+} is approximately a factor of 10 less.

In general, the filter samples showed the largest concentrations of soluble ions, followed by the tape and then the soil samples. Factors which contribute to this difference are particle size and type of sample collected. The relatively large particulates in the soil samples yield less soluble ions per unit weight; most of the soil samples contained a large proportion of inert minerals. Only the soil sample from the dry lakebed contained significant soluble salts. Filters from the high volume air samplers contain very fine particulates and also tend to pick up aerosols which would be water soluble, thus yielding higher concentrations. (Aerosols and fine particulates are easily trapped in the filter as air is drawn through and are less likely to deposit on the tape). The filters also picked up significantly more SO_4^{--} (Figure 6) than the tapes. The SO_4^{--} concentration is attributed to atmospheric SO_2 and SO_3 concentrations from sources of smog such as vehicle exhaust and oil fired power plants in the area (i.e. Southern California Edison Cool Water Plant and smaller plants on the Marine Base). For SO_4^{--} to form, SO_2 or SO_3 gas must react with moisture forming H_2SO_4 . The hydrophillic paper filters, unlike the tapes, provide an ideal location for this reaction to occur. Comparing the tape and filter samples with the soil samples, it appears that the soil is not the primary source of ions; air pollutants may be a more important source.

Two filter samples were also analyzed using X-ray diffraction to determine what mineral forms were present in the particulates. The results indicate the presence of SiO_2 (alpha quartz), $KAlSi_3O_8$ (orthoclase), $KAl_2Si_3AlO_{10}(OH)_2$ (muscovite), and $Na_2Mg_5Si_{12}O_{30}$ (sodium magnesium silicate).

Relating the quantities of ions found to the probability of corrosion is very difficult because of the many unknowns which cannot be positively determined. Foremost among these are a mechanism(s) for the localized accumulation of contaminants, and unforeseen extraordinary salt loadings. With these caveats in mind, the following discussions will present one way of analyzing the data for the probability of corrosion. The aim of the discussion is to give the reader a feel for the relative quantities of salts found. The necessary assumptions for this analysis are listed below.

1. Samples collected over a one month period are assumed to be typical

Figure 6. Sulfate concentrations for filter, tape, and soil samples.

Figure 7. Chloride concentrations for filter, tape, and soil samples.

Figure 8. Sodium ion concentration for filter, tape, and soil samples.

Figure 9. Magnesium ion concentration for filter, tape and soil samples.

Figure 10. Manganese ion concentration for filter, tape, and soil samples.

Figure 11. pH of the 0.04 m³ water extraction for the filter, tape, and soil sample.

and representative of the whole year and of the average year. Wind directions and speeds are key factors in determining the amount and kind of particulates in the air. Comparisons of the distributions of maximum wind direction for the sample period, ten years of wind data on that period of the year and the whole year are shown in Figure 4; all follow similar trends.

2. Particulates are assumed to accumulate uniformly during the year and then be washed away each year during the short rainy season. Other methods of ion concentration buildup will be considered later when appropriate.

3. The uniform accumulation is assumed to be equivalent to the concentration gathered on the sample, over the week with maximum concentration of ion, multiplied by the number of weeks per year. The combination of both these assumptions is conservative because all of the particulates which impinge on the sticky tape adhere. Particulates are not subject to the removal actions of wind and rain as they would be on the receiver.

4. The concentration of anions, $\text{SO}_4^{=}$ and Cl^- are assumed to be limiting factors in molten salt formation. Figures 8 through 10 show that there are adequate metal ions to form one or more of the eutectic salts listed in Table 2. Ion combination mechanisms and any difficulties in salt formation will not be considered limiting (very conservative assumption).

5. Water soluble chlorides were not detected; therefore the quantity of Cl^- will be based on the detection limit of 0.4 mg per sample. This is conservative because a second analysis of one filter did not find Cl^- with a detection limit of 0.04 mg per sample.

6. For filter samples and determination of the equivalent concentration of SO_3 in air, we assume that all SO_3 which passed through the filters is converted to $\text{SO}_4^{=}$.

7. The calculated volume of air (Appendix A) passing through the filters is based on the initial calibration of flow rate. A factor of 1/2 is included to account for a decrease in flow rate as the filter becomes loaded with particulates.

Based on these assumptions the amount of chloride which would accumulate on a panel surface is 8×10^{-4} mg/mm²/year. (i.e. 0.4 mg/25800 mm² x 52 weeks per year). To determine whether this amount of chloride would cause SCC, the amount of Cl^- is translated into: 1) a depth of aqueous solution for the concentrations given in Table 2, and 2) an average daily duration of this solution on the receiver during heatup. The approximate duration of the solution is then compared with the lifetimes or necessary exposure times from Table 2. Given the 8×10^{-4} mg/mm²/year Cl^- , one would need a 0.55 μm depth of water to achieve the equivalent of a 42% MgCl_2 solution. (Note 42% MgCl_2 is a saturated solution). Water of this depth would last less than one second each day during heatup, far short of the 1.1 minutes (i.e. 68 hrs. x 60 min/hr/3650 days in 10 years) exposure per day needed to accumulate 68 hours (life in 42% MgCl_2 over a ten year period). The 875 ppm Cl^- solution with an 840 hour life requires a depth of .9 mm of water for 15 minutes a day for ten years to cause failure; 15 minutes is a much longer exposure than possible for the receiver. Consideration of the 100 ppm Cl^- solution yields

similar results; exposure to an 8mm depth of water for 2-1/2 hours per day during heat-up would not occur on the external surfaces of the receiver. Although these three examples do not cover every possibility, they are adequate since they span the range of Cl^- concentrations.

High concentration aqueous caustic solutions would also be improbable, as shown by the nearly neutral pH of the samples in Figure 12. Thus, since only minute amounts of Cl^- and OH^- are present, it is unlikely that external aqueous corrosion or SCC would occur on the receiver panel.

The amount of eutectic salt film possible for hot corrosion is estimated by considering the equivalent amounts of SO_4^{2-} and Cl^- . This yields $0.004 \text{ mg/mm}^2/\text{year}$ accumulation of $\text{Na}_2\text{SO}_4\text{-CaSO}_4$ and $0.0013 \text{ mg/mm}^2/\text{year}$ NaCl . These small values are a factor of ten less than that established in the previous section on hot corrosion in gas turbines. For the receiver, hot corrosion would most likely occur in the top 4 m section of the panel where the temperatures are maximum (the temperature of the panel jumps abruptly from 300°C to 460°C where departure from nucleate boiling occurs, approximately 4 m below the top). If all the salt from the top 4 m of the panel were to collect in a narrow band, this would yield only 14 mg/mm circumference of salt around the panel. Both the uniform film accumulation and vertical accumulation model generate insignificant quantities of salt for hot corrosion. Also the quantities of SO_3 and Cl^- in the air which would contribute to the films are very small: 0.61 ppb SO_3 and 0.088 ppb Cl^- air based on the maximum from the filter samples. Thus, from these considerations, external hot corrosion is also very unlikely.

Summary

Airborne particulates and aerosols were sampled in the desert near the solar pilot plant site. The collected samples were analyzed for the concentrations of water and acid soluble Na^+ , Mg^{++} , Mn^{++} , Li^+ , Cl^- , SO_4^{2-} and $\text{S}^{=}$. Screening for these ions was done to determine if the desert environment would present a corrosion problem for the solar receiver panel. The concentrations of ions present in the samples were compared to data on hot corrosion and SCC. Based on these comparisons and the small amounts of these ions present, it is unlikely that either hot corrosion or SCC caused by the external desert environment will occur on the receiver panel.

Acknowledgement

I am grateful to T. Devlin and L. Brewer for discussions on air sampling techniques, C. L. Mason and coworkers at the Marine-Corp. Supply Center, Yermo area for their cooperation and assistance in monitoring the samplers, H. C. Feemster for chemical analysis, C. A. Scott for compilation of climatic data, D. R. Boehme for X-ray analysis and to C. F. Casey for typing the manuscript. I acknowledge the chemical analysis of S. Furman.

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Appendix A
Net Weights for Samples Collected and Analyzed

<u>Sample</u>	<u>Weight (mg)</u>
Filters	
4-8-80A	50.7
4-15-80-A	94.6
4-25-80-A	57.2
5-2-80-A	92.1
4-8-80-B	49.6
4-15-80-B	40.3
4-25-80-B	65.5
5-2-80-B	71.1
4-8-80-C	46.9
4-15-80-C	80.6
4-25-80-C	51.8
5-2-80-C	63.5
4-8-80-D	72.0
4-15-80-D	90.8
4-25-80-D	14.6
5-2-80-D	74.8
Tapes	
4-8-80-A	54.7
4-15-80-A	219.2
4-8-80-B	34.6
4-15-80-B	98.0
4-8-80-C	32.0
4-15-80-C	288.5
4-8-80-D	49.5
4-15-80-D	293.0
Soil	
all samples	1000

Appendix B

Procedures for Chemical Analysis

Prior Preparation

Tapes were ashed in a furnace at 500°C for 2 hours to remove organic material from the tape.

Filters were cut in 1/2" x 1" strips to maximize extraction efficiency.

Extraction Methods

Water: Samples were extracted with 0.02m³ ASTM Reagent Grade water at 95°C for 2 hours. Sample centrifuged and supernatant diluted to 0.04m³ for pH and other measurements.

Acid: Centrifuged residues from the water extraction were extracted with 0.02m³ reagent grade concentrated nitric acid at 86°C for 2 hours. Samples centrifuged and supernatant removed for analysis.

Analysis Methods

Metal ions: atomic absorption spectrophotometry. Cl⁻: colorimetric, S⁼: titration, SO₄⁼: turbimetric

Appendix C

Initial Calibration of High Volume Air Samplers

<u>Sampler</u>	<u>Flow Rate (m³/hr)</u>
A	36.5
B	37.4
C	24.6
D	36.5

Volume of Air Sampled for High Volume Filters

$$\text{Volume} = \frac{\text{Initial Flow Rate}}{2} \times \text{hours sampled}$$

<u>Sample</u>	<u>Volume of Air (m³)</u>
4-8-80A	2.97×10^3
4-15-80-A	4.45×10^3
4-25-80-A	3.07×10^3
5-2-80-A	4.82×10^3
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4-15-80-B	4.55×10^3
4-25-80-B	3.14×10^3
5-2-80-B	4.94×10^3
4-8-80-C	2.00×10^3
4-15-80-C	3.00×10^3
4-25-80-C	2.07×10^3
5-2-80-C	3.25×10^3
4-8-80-D	2.97×10^3
4-15-80-D	4.44×10^3
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