455
4/13/81
T.S.

(2)

Dr. 2539

MASTER

DOE/ET/27026-T4

GEOTHERMAL MATERIALS SURVEY
ARKANSAS POWER AND LIGHT DEVELOPMENT
AND DEMONSTRATION PROJECT. 100kW POWER
SYSTEM USING DIRECT CONTACT HEAT
EXCHANGERS, EL DORADO, ARKANSAS

By
Peter F. Ellis II

Dist-382
RT15-22

July 22, 1980

Work Performed Under Contract No. AC02-79ET27026

Radian Corporation
Austin, Texas

U. S. DEPARTMENT OF ENERGY
Geothermal Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

GEOHERMAL MATERIALS SURVEY
ARKANSAS POWER AND LIGHT
DEVELOPMENT AND DEMONSTRATION PROJECT
100kW POWER SYSTEM USING
DIRECT CONTACT HEAT EXCHANGERS
EL DORADO, ARKANSAS

Prepared by:
Peter F. Ellis II

Contract No. DE-AC02-79ET27026

Prepared for:

U.S. Department of Energy
Chicago Operations and Regional Office
Argonne, Illinois 60437

22 July 1980

8501 Mo-Pac Blvd. / P.O. Box 9948 / Austin, Texas 78766

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1.0	INTRODUCTION	1
2.0	DESCRIPTION OF APL 100kW SYSTEM	2
3.0	GEO THERMAL FLUID CHEMISTRY	5
4.0	INVESTIGATIONS	7
	4.1 On-Site	7
	4.2 Laboratory Analysis	10
	4.3 Literature Search	10
	4.4 Simulation of Waste Brine Treatment	10
5.0	DISCUSSION	14
	5.1 Brine pH Instability	14
	5.2 Atmospheric Corrosion	14
	5.3 Materials Alternatives For Future Plants	16
	5.3.1 Brine Handling Equipment	16
	5.3.2 The Isopentane System	17
6.0	CONCLUSIONS	21
7.0	RECOMMENDATIONS	23
8.0	REFERENCES	26
	APPENDIX	A-1

1.0 INTRODUCTION

Arkansas Power and Light, Inc. (APL) is testing a 100kW direct contact boiling/direct contact condensing binary electric generator at Great Lakes Chemical Company's (GLC) geothermal bromine recovery plant near El Dorado, Arkansas. The 100kW system was developed as a joint APL/U.S. Department of Energy project.

The objectives of this report are to: 1) evaluate present pilot plant materials selections, 2) identify potential materials problems, and 3) recommend alternate materials for use in future systems.

This project specific Geothermal Materials Survey is part of a continuing DOE/DGE effort to gain insight into the requirements for materials and components of geothermal systems.

Disclaimer

Mention of a specific product, process, or vendor is not intended to exclude other produces, processes or vendors which may give comparable results or render comparable services.

2.0 DESCRIPTION OF APL 100kW SYSTEM

The 100 kW plant is a direct contact boiling/direct contact condensing binary system using isopentane as the working fluid. Treated waste geothermal brine from the GLC bromine recovery operation is the heat source. Figure 1 illustrates the skid mounted APL plant. Brine is taken from the GLC Treated Brine Line at 205-210°F and supplied to the pilot plant via the APL Brine Inlet Line. The brine enters the direct contact boiler (DCB) and vaporizes isopentane. The cooled brine is discharged into the reinjection pond at 135-155°F. The brine flow rate is 45,655-87,030 lb(m)/hr (pounds mass per hour). The chemistry of the brine is discussed in Section 3.

Isopentane is fed to the DCB at a flowrate of 16,800-23,720 lb(m)/hr. The isopentane vapor exits the DCB at 147-162°F and 42.5-52.5 psia. There is essentially no temperature drop from the boiler to the turbine inlet. In the turbine, the temperature drops to 105-130°F with a corresponding pressure drop to 12.0-20.0 psia.

The isopentane vapor from the turbine exhaust enters the base of the direct contact condenser (DCC) where it is condensed by intimate contact with fresh water from a cooling tower. The condensed isopentane is returned to the DCB.

The rated power output for the unit is 80-88 kW (Herlacher, 1980). The design parameters just discussed are summarized in Table 1.

NOMINAL DESIGN VALUES

STREAM NUMBER	FLUID OR VAPOR	TEMPERATURE °F	PRESSURE psia	MASS FLOW RATE lb(m)/hr
1	BRINE	205 - 210	NR	45,655 - 87,030
2	BRINE	135 - 155	NR	45,655 - 87,030
3	ISOPENTANE	147 - 162	42.5 - 52.5	16,800 - 23,720
4	ISOPENTANE	105 - 130	12.0 - 20.0	16,800 - 23,720
5	ISOPENTANE	67 - 97	11.0 - 19.0	16,800 - 23,720

10 1822 2

Figure 1. Arkansas Power and Light Geothermal Binary Power Plant

TABLE 1: DESIGN PARAMETERS

Brine

Flowrate (lb(m)/hr)	45,655-87,030
Brine Inlet Temperature (°F)	205-210
Brine Outlet Temperature (°F)	135-155

Isopentane

Flowrate (lb(m)/hr)	16,800-23,720
Boiler Outlet Temperature (°F)	147-162
Boiler Outlet Pressure (psia)	42.5-52.5
Turbine Inlet Temperature (°F)	145-162
Turbine Inlet Pressure (psia)	40.0-50.0
Turbine Outlet Temperature (°F)	105-130
Turbine Outlet Pressure (psia)	12.0-20.0
Condensed Isopentane Temperature (°F)	67-97
Rated Output (kW)	80-88

Herlacher, 1980

3.0 GEOHERMAL FLUID CHEMISTRY

The well fluid produced by GLC is saturated with carbon dioxide at wellhead conditions and contains an unspecified but considerable amount of hydrogen sulfide. The total dissolved solids are on the order of 280,000 ppm and the wellhead temperature is about 210°F. This produced fluid is the feedstock for GLC's bromine recovery process. In this process, the incoming fluid is acidified to $\text{pH} \leq 0$. This results in stripping of all carbonate species and much of the hydrogen sulfide. Chlorine is added to convert bromide to bromine. This also consumes most of the remaining hydrogen sulfide. The fluid is sparged with steam to raise the temperature to 220°F and extract the bromine. The very acid waste water is then treated with lime or caustic and ammonia to raise the pH to more acceptable values. The target pH is 5.5. The treated fluid is retained in earthen holding ponds and eventually reinjected (McAllister, 1980). Considerable difficulty is encountered in attempting to maintain the target pH and rapid fluctuations between zero and five are reported (Herlacher, 1980).

The geothermal water used by APL is taken from the disposal stream after the treatment to raise pH. The nominal chemistry of this fluid is given in Table 2. It should be noted that except in the case of system upsets, the bromine content of the stream is essentially zero, and hydrogen sulfide will also be very low (McAllister, 1980).

TABLE 2. CHEMISTRY OF GEOTHERMAL FLUID ENTERING
THE APL 100kW PLANT

Component		Concentration (ppm except for pH)
Key Species:	pH	0-5
	Cl ⁻	178,000
	HCO ₃ ⁻	0
	CO ₃ ⁻²	0
	CO ₂	0
	SO ₄ ⁻²	200
	H ₂ S	<10
	NH ₄ ⁺	150
Other Species:	TDS	286,000
	Na	67,000
	Ca	38,000
	Cl ₂	0
	Br ₂	<5

McAllister, 1980

4.0 INVESTIGATIONS

4.1 On-Site

On-site investigation occurred on 10 April 1980 and showed that the brine supply piping and much of the plant piping is fiber reinforced polyester resin (FRPR). This piping has been used widely by GLC for a number of years (McAllister, 1980). The DCB is carbon steel lined with Kynar, a fluorinated plastic. The turbine casing, stationary vanes and exhaust inlet are Hastelloy C-276 (Herlacher, 1980). The support members for the turbine exhaust nozzle appear to be a non-stainless grade of steel. The turbine rotor is unalloyed titanium, and the DCC is epoxy lined carbon steel (Herlacher, 1980). It should be noted that the incoming vapor enters the turbine case from above and exits from one end. The vapor exhaust line then turns upward, so that the turbine is in the bottom of a U-bend.

Prior to the site visit the pilot plant has operated intermittently from September through December 1979. All runs were short and there were many upsets during this time. These problems were the result of control system problems according to APL (Herlacher, 1980) and a discussion of these problems is beyond the scope of this report.

After shutdown in December, the turbine and gearbox were opened for inspection. At that time the turbine housing was found to be partially flooded with water that was described as fresh (Herlacher, 1980). No analysis of this water was available. Deposits of minerals were observed in the turbine exhaust inlet. Samples of this scale were obtained during the site visit for analysis.

The titanium turbine rotor had been shipped to Rotoflow, the fabricator, for non-destructive examination (NDE) and was not available for inspection at the time of the site visit. Subsequent contacts with Rotoflow revealed that the NDE showed no significant erosion or corrosion and no cracking of the rotor (Payne, 1980).

The lubricating oil in the gearbox was found to be heavily contaminated with water. Samples of this oil were returned to the manufacturer for analysis. APL determined that the water had entered the gearbox via the turbine shaft seal. This seal is a positive pressure nitrogen seal and leakage was due to insufficient nitrogen pressure, according to APL (Herlacher, 1980).

The aluminum heat barrier, a disk mounted on the turbine shaft on the oil side of the nitrogen seals, was found to be heavily encrusted with deposits. Samples for analysis were obtained during the site visit.

The gearbox casing was found to have several cracks. Radiological examination by APL indicated that the cracks were fabrication defects (Herlacher, 1980).

The stationary vanes (Hastelloy C-276) were examined non-destructively by APL and were found to be free of damage.

Figure 2 shows the exhaust end of the turbine housing with stationary vanes removed. As mentioned earlier, the exhaust support studs appear to be a non-stainless grade of steel. They appear to have been welded with a stainless rod. These studs, exposed to inlet vapor, were covered with a brown deposit. No exfoliation was noted.

Figure 3. Exhaust End of 100kW Isopentane Turbine

- a = casing
- b = turbine exhaust pipe
- c = turbine exhaust nozzle
- d = support stud
- e = isopentane inlet manifold

The exhaust pipe was also coated with a thin brown film. A waterline was observed at about the four and eight o'clock positions in the turbine exhaust pipe.

During the site visit, serious corrosion of the copper connectors and terminals in the control closet was observed. This was characterized by blackening of the wires. Failure of paint in some locations on the piping was also noted.

4.2 Laboratory Analysis

The two deposit samples obtained during the site visit were examined by Energy Dispersive Spectroscopy (EDS). This analytical method gives elemental results and does not detect elements with atomic numbers lower than sodium. The results of these analyses are presented in Table 3. X-ray Diffraction Analysis (XDA) indicates that the deposits are amorphous (non-crystalline). For this reason, no compound identification is possible.

4.3 Literature Search

An extensive automated literature search was performed to gain a better understanding of 1) the transport of water in an isopentane vapor system, 2) the fate of water entering such a system, and 3) the potential corrosion problems resulting from such water. The search was essentially unrevealing, indicating a lack of published data relating to these points.

4.4 Simulation of Waste Brine Treatment

Because pH is critical to materials selection, the pH control instability of the input brine was investigated by use of Radian's Aqueous Equilibrium Program to simulate the titration from pH 0-9 of the water leaving the bromine extraction stage.

TABLE 3. ANALYSES OF DEPOSITS

Deposit from Heat Barrier

EDS (Elemental* Analysis)

Aluminum	major
Silicon	trace
Sulfur	trace
Chlorine	trace
Calcium	trace
Chromium	trace
Iron	trace
Nickel	trace

XDA (Compound analysis)

Sample amorphous, no compounds identified.

Deposit from Turbine Exhaust Inlet

EDS (Elemental Analysis)

Aluminum	major
Sulfur	trace
Chlorine	trace
Calcium	trace
Chromium	trace
Iron	trace
Nickel	trace

XDA (Compound Analysis)

Sample amorphous, no compounds identified

* analytical method does not detect elements with atomic number less than 11 (sodium)

The bases (titrants) used were lime $[\text{CaO}]$, hydrated lime $[\text{Ca}(\text{OH})_2]$, and caustic $[\text{NaOH}]$.

The input fluid chemistry was given in Table 2. For the purposes of this simulation, the input pH was set at zero. The reaction temperature was set at 205°F. Figure 3 presents the results of this simulation in terms of pH as a function of parts base per million parts of pH = 0 feed brine. The simulation results also indicate that no species will be precipitated at any pH considered.

026314-1

Figure 3. Computer Generated Titration Curves for GLC Brine at 205°F.

Note: The endpoint of this brine at 205°F is pH 5.8

5.0 DISCUSSION

5.1 Brine pH Instability

The pH of incoming brine will have a major impact on materials performance. Virtually all corrosion phenomena will be far more severe in very acidic brines. Large fluctuations in pH will probably be even more damaging than continuous very acidic conditions.

Consideration of the brine chemistry (Table 2) and the simulated titration curves (Figure 3) indicate that the brine is totally unbuffered. The endpoint (where $[H^+] = [OH^-]$) of unbuffered water at 205°F is ~5.8 at the ionic strength of the input brine according to the Aqueous Equilibrium Program. This is essentially the target pH of the treatment process. Control of pH in the region of the endpoint is fundamentally not possible because minute variations in feedrate of base will cause large fluctuations of pH. Figure 3 shows that at a target pH = 5.5, a one percent base underfeed will lower the pH to ~2, while a similar overfeed will result in a pH of ~8. Figure 3 indicates that pH can be reliably maintained at values less than two or greater than 8.5.

5.2 Atmospheric Corrosion

Corrosion of copper and silver electrical contacts by atmospheric hydrogen sulfide is known to be a major problem at The Geysers, CA, Wairakei, New Zealand, Cerro Prieto, Mexico (DeBerry et.al. 1978) and at Larderello, Italy (ENEL, 1980).

Only two effective solutions have been applied to this problem. At The Geysers, in California, and Wairakei, New Zealand, electrical equipment is kept in positive pressure clean air rooms. Air entering these rooms is filtered through activated

charcoal, or some other sorbant, to remove hydrogen sulfide. In practice, it is difficult to maintain a sulfide-free environment in the clean air rooms.

The other protective measure is the plating of all electrical connectors and contacts with chromium, tin, platinum, cadmium, nickel, or gold. This method requires more initial work, but little later maintenance.

Italian experience at Larderello (ENEL, 1980) has lead to development of the following painting process for structures in environments contaminated with hydrogen sulfide:

- 1) Sandblasting to Swedish Standards grade Sa 2½ - 3 (SSPC grade 10 or better).
- 2) Applications of 2.5 - 3 mils (1 mil = 0.001 inch) of flame sprayed zinc.
- 3) Application of at least 3 mils of oil based, phenolic resin, zinc chromate rich primer.
- 4) Application of an intermediate coat of phenolic paint with passivating pigments to a thickness of at least 2.5 mils.
- 5) Application of a final coat of phenolic/glycerophthalic paint, free of lead or other heavy metals which can react with hydrogen sulfide. Recommended thickness is at least 3.5 mils.

In cases where flame galvanizing cannot be used, the Italian

practice is to begin the cycle with an epoxy resin paint of high zinc content to a thickness of 2.5 mils. Polyurethane paints are not allowed in the Italian painting process.

For surfaces with rust or deteriorated paint, the area is cleaned and the painting cycle is begun at step three.

5.3 Materials Alternatives For Future Plants

With the exception of the unprotected copper electrical equipment discussed previously, most of the materials selections for the pilot plant appear conservative and suitable. One possible exception is the epoxy coating lining the DCC. In other geothermal condensate systems, the life of epoxy on steel has been only a couple of years (DeBerry, et al., 1978). The objective of this section is to consider some alternate materials for future generating plants at this location. If suitable, some of these alloys are less costly than the materials selected for the pilot plant.

5.3.1 Brine Handling Equipment

The brine supplied to APL is very corrosive because of its temperature (205-210°F), high chloride concentration (~178,000 ppm) and because it is aerated. The very acidic pH's which may occur (see Section 5.1) severely increase the corrosivity of the brine. Maintenance of the input brine at $\text{pH} > 8$ would ease materials problems in all parts of the process.

Fiber Reinforced Polyester Resin (FRPR) piping appears to be suitable for piping, based on the experience of GLC (McAllister, 1980). For metallic parts, other geothermal experience in hypersaline brine (DeBerry, et al., 1978) indicates that the following alloys have a high probability of satisfactory

performance in the input brine: E-Brite 26-1, Allegheny-Ludlum 29-4, Allegheny-Ludlum 29-4-2, Sea Cure 26-3, Hastelloy C-276, Inconel 625, titanium, Ti-1.7W, Ti-1.5Ni, and Ti-10V.

Austenitic stainless steels containing more than four percent molybdenum have an intermediate chance of success. Such grades are T317LM and Allegheny-Ludlum 6X. Grades containing less than the above molybdenum content will have a high risk of stress corrosion cracking, pitting, and crevice corrosion. Such grades are T304, T316, T321, T347 and Carpenter 20Cb3.

The following alloys have a higher risk of failure by crevice corrosion and/or pitting: Inconel X-750, Incoloy 825, Hastelloy C and Hastelloy G.

Monel 400 and copper, or aluminum- based alloys represent extremely high risk materials in the input brine environment.

5.3.2 The Isopentane System

The presence of calcium, sulfur and chloride in the deposits taken from the turbine casing and gearbox indicate that some geothermal brine makes its way into the turbine. Thus it is apparent that the direct contact isopentane boiler produces a working fluid with a composition more complex than pure isopentane.

Research on direct contact heat exchangers at the U.S. DOE Oak Ridge National Laboratory (ORNL) (Urbanek, 1979) shows that under non-upset conditions water enters the isopentane loop in two forms; as water vapor and as droplet carryover. Consideration of these two mechanisms will give some insight into the corrosive nature of the isopentane loop.

The amount of water vapor, not to be confused with droplet carry-over, entering the isopentane loop via the boiler can be calculated on the basis of the partial pressures of isopentane and water at the DCB outlet conditions and the mass flow rate of isopentane. Using the conditions described in Table 1 with water vapor pressure adjusted for twenty percent salinity, calculations (see Appendix A) indicate that, depending on operating conditions, between 333 and 563 lb(m)/hr of water vapor will be transported as vapor from the DCB. Of this water vapor, about 225-310 lb(m)/hr will be condensed at turbine outlet conditions.

The pilot boiler is not equipped with a demister, so a considerable amount of carry-over may occur. However, it should be noted that the steam separators of conventional geothermal plants, analogous to the DCB, are equipped with demisters. These separators typically allow 0.01 to 0.1 percent droplet carry-over. Assuming similar separation efficiencies for DCB demisters, brine droplet entrance into the isopentane stream is estimated to be in the range of 1.7-24 lb(m)/hr. These droplets will carry 0.3-4.3 lb(m)/hr of chloride ion. This chloride input, combined with the aqueous condensate from water vapor in the isopentane leaving the DCB, will result in an aqueous phase at turbine outlet conditions containing about 1330 to 13500 ppm chloride.

The distribution of this aqueous phase in the isopentane stream is not known. Given that the stream leaving the boiler is saturated with water vapor and carrying water droplets, it is conjectured that the aqueous phase consists of a mist of droplets and as a film wetting the various parts of the isopentane piping and turbine.

The isopentane will also be contaminated with hydrogen sulfide if any is present in the input brine and the isopentane entering the boiler from the condenser will probably be saturated with oxygen. Both of these gases will be carried into the vapor stream and can dissolve in the aqueous phase.

Thus, under normal operating conditions, and optimistically assuming that droplet carry-over is only 0.01 percent, the environment in the isopentane loop is surmised to consist of a fog or mist of water droplets and a moisture film covering most if not all surfaces. The film is estimated to contain at least 1300 ppm chloride ion as well as dissolved oxygen and possibly hydrogen sulfide.

Other geothermal experience (DeBerry et. al, 1978) indicates that the corrosiveness of moisture films formed from carried-over droplets is similar to the corrosiveness of the bulk solution. Materials selections for the isopentane loop must consider the corrosive nature of the possible moisture films.

The following alloys may have a high probability of success in the isopentane stream at turbine inlet conditions: E-Brite 26-1, Allegheny-Ludlum 29-4, Allegheny-Ludlum 29-4-2, Sea-Cure 26-3, Hastelloy C-276, Inconel 625, titanium and many titanium alloys.

The temperatures involved (145-210°F) are sufficiently high to cause chloride stress cracking of many AISI 300 series stainless steels. As discussed previously, grades containing more than four percent molybdenum may be satisfactory.

As in the case of the brine system, Inconel X-750, Incoloy 825, Carpenter 20Cb3, Hastelloy C and Hastelloy G represent a higher risk because of pitting and crevice corrosion.

The lower temperature (105-130°F) of the stream exiting the turbine makes this environment less severe from a corrosion standpoint. The alloys listed in the previous paragraph may be suitable in this environment. T316L stainless steel may be suitable for nonstressed parts provided that it is not sensitized and is fully annealed after forming.

The performance of carbon and low alloy steels in the isopentane stream will depend largely on the aqueous film pH and oxygen content. There is no basis in the literature for estimating the performance of these materials in the isopentane loop.

Electrochemical tests (DeBerry et. al, 1978) in air-free hypersaline brine (155,000 ppm chloride) at pH 2.0-4.5 and 187-208°F show that corrosion rate of carbon steel was 0.100 inch/year. The following low alloy steels had corrosion rates less than one-fifth as great as carbon steel in this test: ASTM A-204, Grade B, ASTM A-387, Grade 12, and H-43. If these or similar low alloy steels have sufficient resistance to pitting and crevice corrosion, they may be useful for thick walled applications where maintenance of tolerances is not critical.

Aluminum alloys, Monel 400, and most copper alloys probably represent high risk materials in all parts of the isopentane loop.

The selection of a suitable titanium alloy for the rotor is very important. Titanium alloys are not normally considered to be susceptible to stress corrosion cracking. However, chloride ions will accelerate propagation of pre-existing cracks in some titanium alloys. This could represent a significant hazard in the case of turbine rotors which are subjected to cyclic stresses.

Titanium alloys containing aluminum, tin, manganese, cobalt, and/or oxygen (greater than 0.317 percent) are susceptible to this effect. (DeBerry, et al, 1978). Table 4 gives lists of titanium alloys that are resistant and sensitive to precracked conditions.

6.0 CONCLUSIONS

- Rapid large fluctuations in the pH of brine entering the APL plant will greatly increase the corrosiveness of the brine. Such fluctuations may be even more damaging than continuous low pH's. Rapid fluctuations in pH can be expected if an attempt is made to control the pH in the range of 3 to 7. This instability is inherent in the chemistry of the water. Stable pH can be obtained at values less than two or greater than eight. From a corrosion standpoint, a target pH = 8.5, which would require about a four percent increase in chemical feed, is very desirable because it may allow use of less expensive alloys.
- The titanium rotor should be satisfactory provided that the alloy has an oxygen content less than 0.3 percent. At higher levels chloride enhanced propagation of preformed cracks may occur.
- Though not observed during the site visit, probably due to the short operating time, serious problems with corrosion of gauges by geothermal fluid, or by moisture and gases from geothermal fluid, can be expected.
- With the exception of bare copper electrical connections, and possibly of the epoxy lining of the DCC, materials choices for the pilot plant

TABLE 4. SENSITIVITY OF TITANIUM ALLOYS TO CRACK PROPAGATION BY CHLORIDE

Titanium Alloys Which Undergo Accelerated Crack Propagation in Ambient 3 wt. % NaCl	Titanium Alloys Which Do Not Undergo Accelerated Crack Propagation in Ambient 3 wt. % NaCl
Unalloyed Ti (with high oxygen content, i.e., 0.317 percent)	
Ti-8Mn	Ti-2Al-4Mo-4Zr
Ti-2.25Al-1Mo-11Sn-5Zr-0.2Si (IMI-679)	Ti-4Al-3Mo-1V
Ti-3Al-11Cr-13V	Ti-5Al-2Sn-2Mo-2V
Ti-4Al-4Mn	Ti-6Al-2Mo
Ti-5Al-2.5Sn	Ti-6Al-2Sn-1Mo-1V
Ti-6Al-2.5Sn	Ti-6Al-2Sn-1Mo-3V
Ti-6Al-4V	Ti-6Al-2Cb-1Ta-0.8Mo
Ti-6Al-3Cb-2Sn	Ti-6.5Al-5Zr-1V
Ti-6Al-4V-1Sn	Ti-7Al-2.5Mo (as received and beta annealed + WQ + 1100 F, aged for 2 hr)
Ti-6Al-4V-2Co	
Ti-6Al-6V-2.5Sn	
Ti-7Al-2Cb-1Ta	
Ti-7Al-3Cb (as received and beta annealed)	
Ti-7Al-3Mo	
Ti-7Al-3Cb-2Sn	
Ti-8Al-1Mo-1V	
Ti-8Al-3Cb-2Sn	

DeBerry et al., 1978

appear conservative. Such conservative choices are prudent for experimental pilot plants. However, other less expensive materials may be available which would be attractive in future plants. Selection of such candidate materials is addressed in the recommendations.

- Under normal operating conditions, with a demister efficiency of 99.9-99.99 percent, the vapor stream exiting the DCB will contain 1.7-24 lb(m)/hr water droplets. These droplets will transport 0.3-4.3 lb(m)/hr of chloride. The vapor stream will also contain 330-560 lb(m)/hr water vapor, of which 224-312 lb(m)/hr will condense in the turbine. All parts of the isopentane loop are postulated to be exposed to a film of water containing at least 1300 ppm chloride. This will have a strong impact on the selection of materials for the isopentane portion of future plants.

7.0

RECOMMENDATIONS

- The pH of the input brine should be stabilized in the region of 8.5 to mitigate corrosiveness of droplet carryover. This would require about a four percent increase in base feed rate.
- Demisting equipment should be installed in the DCB's of any future units to minimize droplet carry-over, reducing materials selection problems in the isopentane loop.

- Exhaust plumbing from the turbine of future units should run downhill to the condenser to avoid possible pooling of corrosive aqueous condensate.
- Electrical connectors should be protected with platings of chromium, tin, platinum, cadmium, nickel, or gold. An alternative is the use of positive pressure rooms supplied with sulfide-free air.
- To reduce maintenance costs external surfaces should be better protected using such practices as the Italian Painting Cycle described in Section 5.2.
- The following alloys, or alloys of comparable composition, should be considered for testing and possible use in the brine system of future plants. If these materials have sufficient corrosion resistance, they may be less expensive than the currently used materials.

E-Brite 26-1
Allegheny-Ludlum 29-4
Allegheny-Ludlum 29-4-2
Sea Cure 26-3
Inconel 625
Allegheny-Ludlum 6X
Carpenter 20Cb3
T 317LM
T 317L
T 316L

- The following alloys should be considered for testing and possible use in the isopentane loop of future plants. If they have sufficient corrosion resistance, these materials may be less expensive than Hastelloy C-276.

E-Brite 26-1
Allegheny-Ludlum 18-2
Allegheny-Ludlum 29-4-2
Allegheny-Ludlum 6X
Sea Cure 26-3
Inconel 625
T317LM
T-317L
T-316L
Inconel X-750
Incoloy 825
Carpenter 20Cb3
Hastelloy C
Hastelloy G
ASTM A-204 Grade B
ASTM A-387 Grade 12
H-43

- Testing of the above potentially less expensive materials should be done by the exposure of coupons to measure uniform, pitting and crevice corrosion, and U-bends to detect stress corrosion cracking. ASTM Practice G-1 (ASTM, 1978) discusses the methods of cleaning, preparing and evaluating coupons. Practice G-46 discusses in detail the evaluation of pitting. Practice G-30 discusses the preparation and evaluation of U-bends. Practice G-4 describes

a number of mounting devices for use in the plant environment. It is recommended that the coupons be mounted parallel to the direction of flow in the brine inlet line, in the isopentane upstream of the turbine, in the isopentane line downstream of the turbine, and in the brine discharge line.

- A number of vendors supply a polyethylene bellows protector for gauges in corrosive service. It is recommended that such devices be used, as opposed to specifying corrosion resistant valves.

8.0

REFERENCES

ASTM (1978), 1978 Annual Book of ASTM Standards, Part 10, Metals-Mechanical, Fracture, and Corrosion Testing, Fatigue, Erosion, Effect of Temperature, American Society for Testing and Materials, Philadelphia, PA.

ENEL (1979), Survey of Corrosion Data and Average Analyses of The Geothermal Fluids of Larderello, Travale, and Monte Amiata, Ente Nazionale per l'Energia Elettrica (ENEL) Internal Report No. 19723, translated by Radian Corporation, Austin, TX.

DeBerry, D.W., Ellis, P.F., and Thomas, C.C. (1978) Materials Selection Guidelines for Geothermal Power Systems, First Edition, DOE Contract No. EG-77-04-3904, NTIS Pub. Code ALO-3904-1, Radian Corporation, Austin, TX.

Herlacher, T (1980), Plant Manager, Arkansas Power and Light, personnel communication.

McAllister, D. (1980), Chemist, Great Lakes Chemical Co., personal communication.

Payne, D. (1980), Rotoflow, Inc., personal communication.

Urbanek, M.W. (1979) Experimental Testing of a Direct Contact Heat Exchanger For Geothermal Brine, ORNL/Sub-79/13564/1 and ORNL/Sub-79/4573611, DSS Engineers, Ft. Lauderdale, FA.

APPENDIX A
DERIVATION OF EQUATIONS
AND
SAMPLE CALCULATIONS

A.1 INTRODUCTION

This appendix gives formulas and sample calculations for estimating the amount of water vapor transported from a Direct Contact Boiler (DCB) and the amount of liquid water formed at turbine outlet conditions. Methods of estimating chloride carry-over are presented. The sample calculations consider the range of operating conditions for the APL 100kW pilot plant.

A.2 THEORETICAL BASISA.2.1 Water Vapor in Isopentane Stream At Boiler Outlet

In the temperature/pressure region in which the turbine operates, both isopentane vapor and water vapor behave as ideal gases and the ideal gas law (eq. 1) applies

$$PV = nRT \qquad \text{Eq. 1}$$

where P = pressure
 V = volume
 n = moles of gas
 R = Thermodynamic gas constant
 T = absolute temperature

For a mixture of two ideal gases, 1 and 2, at constant temperature and volume:

$$\frac{P_1 V}{P_2 V} = \frac{n_1 RT}{n_2 RT} \qquad \text{Eq. 2}$$

$$\text{or } \frac{P_1}{P_2} = \frac{n_1}{n_2} \qquad \text{Eq. 3}$$

Equation 3 states that the mole ratio of gas 1 to gas 2 is equal to the ratio of their partial pressures. Multiplying by the ratio of formula weights gives the mass ratio (R_m)

$$R_m = \frac{\text{lb}(m)_1}{\text{lb}(m)_2} = \frac{P_1}{P_2} \left| \frac{FW_1}{FW_2} \right| = \frac{n_1}{n_2} \left| \frac{FW_1}{FW_2} \right| \quad \text{Eq. 4}$$

In the case of water vapor and isopentane (I-C5) vapor, equation 4 becomes:

$$R_m = \frac{\text{lb}(m)_{H_2O}}{\text{lb}(m)_{I-C5}} = \frac{P_{H_2O}}{P_{I-C5}} \left| \frac{18.016}{72.15} \right| \quad \text{Eq. 5}$$

The transport rate of water vapor (W_v) is given by:

$$W_v = \frac{P_{H_2O}}{P_{I-C5}} \left| \frac{18.016}{72.15} \right| \text{ I-C5 flow rate} \quad \text{Eq. 6}$$

A.2.2 Water Vapor Condensed At Turbine Outlet Conditions

The fraction of water condensed at turbine outlet conditions is given by:

$$F_c = \frac{P_{H_2O_i} - P_{H_2O_f}}{P_{H_2O_i}} \quad \text{Eq. 7}$$

where: $P_{H_2O_i}$ = partial pressure of water at boiler inlet temperature

$P_{H_2O_f}$ = partial pressure of water at turbine outlet temperature

The amount of water vapor condensed is given by:

$$W_c = \frac{(P_{H_2O_i} - P_{H_2O_f})}{P_{H_2O_i}} \left| \frac{W_v}{1} \right| \quad \text{Eq. 8}$$

where

W_ℓ = amount of water condensed

W_v = amount of water vapor transported from boiler (Equation 6)

A.2.3 Carry-over Calculations

The mass flow of droplet carry-over is given by the following equation:

$$M_D = (1-E)(M_v) \quad \text{Eq. 9}$$

where

M_D = mass rate of droplet carry-over

E = separator efficiency as a decimal.

M_v = mass flow rate of the vapor stream

In the case of the water/isopentane system M_v is the sum of the isopentane flow rate and the water vapor transport rate, so:

$$M_D = (1-E) (\text{I-C5 flow rate} + W_v) \quad \text{Eq. 10}$$

The transport rate of the i th dissolved species via droplet carry-over (M_i) is given by:

$$M_i = (X_i)M_D \quad \text{Eq. 11}$$

where

X_i = wt. concentration of i th species in feed water

The transport rate of water via droplet carry-over (M_w) is given by

$$M_W = (1 - X_T) M_D \quad \text{Eq. 12}$$

where

X_T = total dissolved solids in feed water

A.2.4 Concentration of Dissolved Solids in Condensate

It should be recognized that dissolved ionic species will not be soluble in the organic working fluid even if this fluid is present in liquid phase. Therefore, the organic fluid can be disregarded in this calculation. Also, the only source of dissolved solids is taken to be droplet carry-over. The concentration of a dissolved species (C_i) in the condensate is given by

$$C_i = \frac{10^6 M_i}{W_L + M_W} \quad \text{Eq. 13}$$

where all terms have been previously defined.

A.3 SAMPLE CALCULATIONS

The sample calculations illustrated will use the Case I values given in Table A-1. The result for Case II will also be given.

Water Transported from Boiler as Vapor (W_v)

$W_{(v)}$	= I-C5 flow rate	P_{H_2O}	18.016	(re: Eq. 6)
		P_{I-C5}	72.15	

TABLE A-1. GIVEN DATA FOR CALCULATIONS

	<u>CASE I</u>	<u>CASE II</u>
Boiler outlet temperature (°F)	147	162
Isopentane Partial pressure at boiler outlet temperature (psia)	42.5	52.5
Isopentane mass flow rate (lb)(m)/hr	16,800	23,720
Partial pressure of water vapor over 20% salinity water at boiler outlet temperature (psia)	3.37	4.99
Turbine exhaust temperature (°F)	105	130
Partial pressure of water at turbine exhaust temperature (psia)	1.10	2.22
Demister efficiency (%)	99.99	99.9
Chloride concentration in feed brine (ppm)	178,000	
Total dissolved solids in feed brine (ppm)	286,000	
Formula weight of water	18.016	
Formula weight of isopentane	72.15	

Case I:

$$W_{(v)} = \frac{16,800 \text{ lb(m)} \text{ I-C5}}{\text{hr}} \left| \frac{3.37 \text{ psia}}{42.5 \text{ psia}} \right| \frac{18.016}{72.15}$$

$$= 333 \text{ lb(m)}/\text{hr}$$

Case II:

$$W_{(v)} = 563 \text{ lb(m)}/\text{hr}$$

Water Condensed at Turbine Outlet Conditions (W_i)

$$W_l = \frac{(P_{H_2O_i} - P_{H_2O_f})}{P_{H_2O_i}} \left| W_v \right| \quad (\text{Re: Eq. 8})$$

Case I

$$W_l = \frac{(3.37 \text{ psia} - 1.10 \text{ psia})}{3.37 \text{ psia}} \left| 333 \text{ lb(m)}/\text{hr} \right|$$

$$= 224 \text{ lb(m)}/\text{hr}$$

Case II

$$W_l = 312 \text{ lb(m)}/\text{hr}$$

Rate of Droplet Carry-over

$$M_D = (1-E)(\text{I-C5 flow rate} + W_v) \quad (\text{Re: Eq. 10})$$

Case I:

$$M_D = \frac{(1-0.9999)}{\text{hr}} \left| 16800 \text{ lb(m)} + 333 \text{ lb(m)} \right|$$

$$= 1.71 \text{ lb(m)}/\text{hr}$$

Case II

$$M_D = 24.28 \text{ lb(m)/hr}$$

Rate of Chloride Transport from DCB

$$M_i = (X_i)(M_D) \quad (\text{Re. Eq. 11})$$

Case I

$$\begin{aligned} M_i &= \left(\frac{1.78 \cdot 10^5 \text{ lb(m) Cl}}{10^6 \text{ lb(m) H}_2\text{O}} \right) \left(\frac{1.71 \text{ lb(m) H}_2\text{O}}{\text{hr}} \right) \\ &= 0.30 \text{ lb(m)/hr} \end{aligned}$$

Case II

$$M_i = 4.32 \text{ lb(m)/hr}$$

Transport Rate of Water Via Droplet Carry-Over

$$M_W = (1 - X_T) M_D \quad (\text{Re. Eq 12})$$

Case I

$$\begin{aligned} M_W &= \left(1 - \frac{2.86 \cdot 10^5 \text{ lb(m)}}{10^6 \text{ lb(m)}} \right) \left(\frac{1.71 \text{ lb(m)}}{\text{hr}} \right) \\ &= 1.22 \text{ lb(m)/hr} \end{aligned}$$

$$M_W = 6.94 \text{ lb(m)/hr}$$

Chloride Concentration in Combined Condensate

$$C_i = \frac{10^6 M_i}{W_\ell + M_W} \quad (\text{Re. Eq. 13})$$

Case I

$$C_i = \frac{(10^6)(0.30 \text{ lb(m) Cl/hr})}{\frac{224 \text{ lb(m) H}_2\text{O}}{\text{hr}}} + \frac{1.22 \text{ lb(m) H}_2\text{O}}{\text{hr}}$$
$$= 1330 \text{ ppm Cl}$$

Case II

$$C_i = 13500 \text{ ppm Cl}$$