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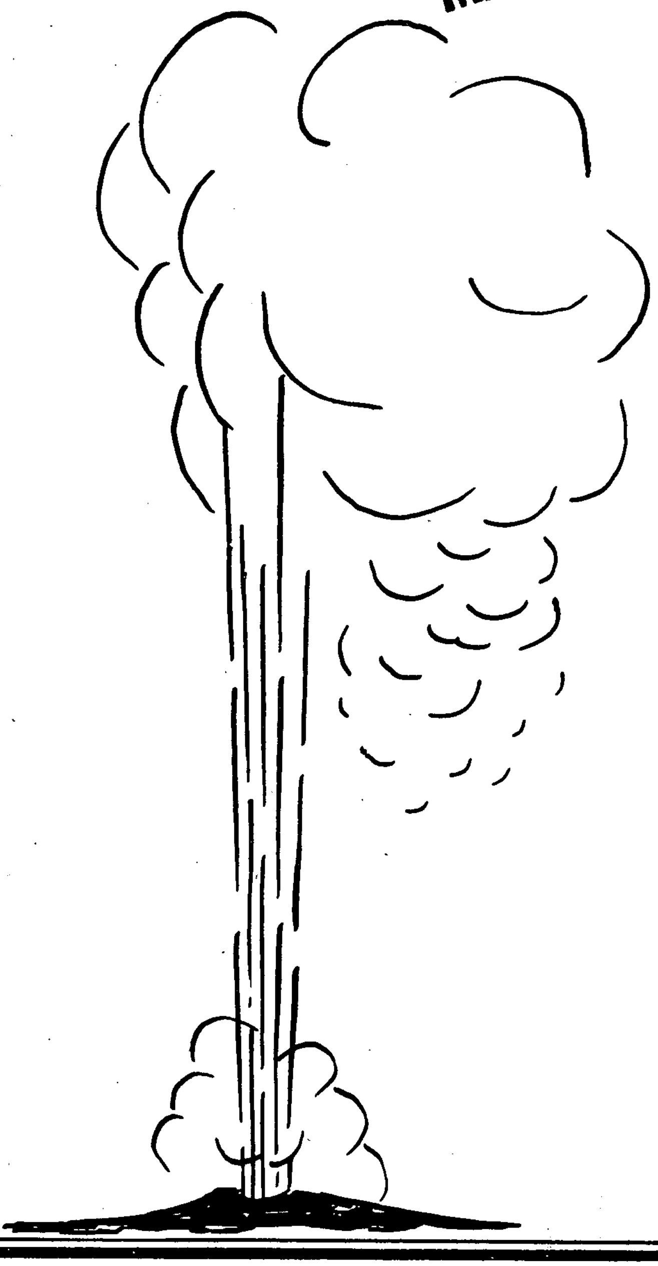

GEOTHERMAL MATERIALS SURVEY: BACA GEOTHERMAL DEMONSTRATION POWER PLANT BACA, NEW MEXICO

By
Peter F. Ellis II

October 7, 1980

Work Performed Under Contract No. AC02-79ET27026

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

This report presents the results of a materials survey for the Baca 50 MW(e) single flash geothermal plant in the Valles Caldera of New Mexico. From the design documents provided both by Union Geothermal Company and by the Public Service Company of New Mexico, materials proposed for use in contact with the plant atmosphere, the two-phase geofluid, the separated steam, and the recirculating condensate cooling water were assessed for suitability. Special emphasis was given to records of performance of the materials in other geothermal plants. Based upon these considerations of chemical reactivity and plant operating experience, a number of recommendations were made. No priority is intended by the order of presentation.

First, the use of condensate traps on the geothermal steam lines or of a demister-separator near the turbine inlet is recommended in order to reduce the amount of liquid water and dissolved solids entering the turbine and the amount of chloride in the cooling water. This will reduce corrosion problems. Failure to remove condensate formed during transmission of steam may also produce turbine inlet steam of quality unacceptable to the turbine manufacturer.

Type 304 stainless steel is not recommended for recirculating cooling water because of the significant risk of pitting and stress corrosion cracking. Type 316 and 317LM or E-Brite 26-1 stainless steel is recommended for condenser and cooler service, providing the temperature does not exceed 108°F and the chloride ion content of the turbine inlet steam does not exceed 22 ppm (for 316) or 29-37 ppm (for 317LM or E-Brite 26-1). The cooling water must be kept clean to prevent fouling of the cooling system, which will result in pitting and possibly in chloride stress corrosion cracking.

A copper-free antimicrobial treatment of wooden cooling tower components should be used in order to prevent contamination of the cooling water with copper ions which may promote pitting in the stainless steel cooling system members; and a PVC lining, coal-tar epoxy coating, or preferably, a polymer concrete coating should be used for the cooling tower basin to resist the concentrations of sulfate ions and acidic pH's in the cooling water. Two inch sacrificial concrete is probably not satisfactory.

Austenitic stainless steels (AISI 300 series) are not recommended for steam valve stems due to the risk of pitting or chloride stress corrosion cracking by aerated condensate at the packings. An alternate material is 17-4PH stainless steel.

Limitations are imposed on the design of 12Cr turbine blades by the severity of corrosion-fatigue in geothermal steam and by the low strength requirements imposed by the presence of hydrogen sulfide in the steam. These limitations may require a blade which is thicker than would be required for boiler quality steam.

Electrical contacts throughout the plant should be plated with chromium, tin, platinum, cadmium, nickel, or gold to avoid problems with hydrogen sulfide which may be present in the atmosphere, and the intakes of air compressors, especially instrument air compressors, should be equipped with filters to remove hydrogen sulfide.

The Larderello Painting Cycle should be used for any metal structures which may be exposed to hydrogen sulfide contaminated air in order to prolong the service life of the metal and reduce maintenance costs. The life of the Larderello Painting Cycle is significantly longer than common painting systems in geothermal environments.

1.0 INTRODUCTION

The Public Service Company of New Mexico and the Union Geothermal Company of New Mexico are constructing a 50MW(e) single-flash geothermal plant in the Valles Caldera of New Mexico to utilize the Baca Known Geothermal Resource. This Geothermal Materials Survey is based upon design documents provided by Union Geothermal Company [Union, 1980] and The Public Service Company of New Mexico (PNM) [PNM, 1980], and on presentations made at a detailed design review held in Albuquerque, NM on 24 September. The objective is to review the proposed materials selections in light of other geothermal plant experience.

This work was funded under DOE Contract No. DE-AC02-79ET27026 in a continuing effort to gain insight into the materials problems of geothermal energy utilization.

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

2.0 PLANT DESCRIPTION

The steam gathering system consists of three single flash separation facilities, called satellite stations, each supplied with two-phase geothermal fluid from a number of production wells, two-phase flow lines, steam lines, liquid lines, and reinjection wells.

Two-phase fluid from a number of wells is piped to the satellite facility where it enters two separators connected in series. The estimated droplet carry-over from the second separator is estimated to be 0.5 percent. The saturated steam (337°F) is piped to the plant and the separated liquid is piped to reinjection wells. The total estimated steam production from the three satellite facilities is about 925,000 lb/hr, and the total separated liquid is about 11,040,000 lb/hr [Union, 1980].

At the turbine-generator building about 74,000 lb/hr of saturated steam (about 337°F) is diverted to the gas ejectors while the balance enters the turbine [PNM, 1980]. The steam is condensed in the shell side of a tube-and-shell condenser. This condenser is supplied with 35,100,000 lb/hr of cooling water at a design temperature of 70°F. The condensate from the condenser hot well (120°F) is extracted by pumps and used as make-up water for the cooling system. The cooling tower basin is "blown down" at a rate sufficient to maintain a constant water level.

Noncondensable gases, primarily carbon dioxide and hydrogen sulfide, are removed from the main condenser by a series of steam ejectors. About 25,310 lb/hr carbon dioxide and 183 lb/hr of hydrogen sulfide are routed to the Holmes-Stretford hydrogen sulfide abatement system.

3.0 GEOTHERMAL ENVIRONMENTS

The ability of a material to resist corrosion is controlled by the nature of the environment; including its chemistry, temperature, phase, and velocity, as well as the physical-chemical properties of the material under consideration. An understanding of the chemistries various geothermal environments is essential to the Geothermal Materials Survey. Numerous chemical analyses of separated geothermal fluid, geothermal steam, and condensate have been performed during the development of the Baca geothermal resource [Union, 1980].

Geothermal Steam

The estimated concentrations of the key corrosive species in steam at the turbine inlet are presented in Table 2 [PNM, 1980]. The concentrations of hydrogen sulfide and carbon dioxide depend on the temperature and pressure of separation, while the concentrations of chloride and sulfate depend on the fraction of droplet carry-over from the separators. Based on the chloride concentration (3061 ppm) for separated fluid given in Table 1, the 21 ppm of chloride in the separated steam corresponds to a 0.7 percent droplet carry-over. The droplet carry-over from the second separator is estimated by Union to be 0.5 percent or less so the 21 ppm estimated provides a safety factor of 40 percent.

The proposed Baca plant is similar to the facility at Wairakei, New Zealand, in that separated saturated steam is piped to the power house. Experience at Wairakei has shown that condensate formation on the steam pipe walls causes effective chloride scrubbing: more than 90 percent of the carry-over chloride is scrubbed by the condensate in the first 750 feet of pipeline [McDowell, G.D., 1975]. If this form of scrubbing does occur in the Baca system, and if sufficient suitable condensate traps

TABLE 1. KEY CORROSIVE SPECIES CONCENTRATIONS MEASURED DURING DEVELOPMENT OF THE BACA GEOTHERMAL FIELD

Parameter	Separated fluid ave (samples)	Steam ave (samples)	Condensate ave (samples)
pH	7.2 (26)	N.R.	4.5 (20)
Cl	3061 ppm (43)	N.R.	17 ppm (25)
HCO_3	127 ppm (26)	N.R.	6.6 ppm (20)
CO_3	19 ppm (26)	N.R.	0 (20)
CO_2	N.R.	28254 ppm (wt) (28)	N.R.
SO_4	64 ppm (23)	N.R.	1.8 ppm (17)
H_2S	2 ppm (15)	204 ppm (wt) 31	8.6 ppm (1)
NH_3	N.R.	N.R.	N.R.

N.R. - Not reported

[Union, 1980]

TABLE 2. ESTIMATED CONCENTRATIONS OF KEY CORROSIVE SPECIES IN TURBINE SEPARATED STEAM

Parameter	Concentration (ppm wt)
CO_2	28,250
H_2S	205-300
NH_3	N.R.
Cl	21
SO_4	2
HCO_3	5

N.R. - Not Reported

[PNM, 1980]

or a final separator at the turbine inlet are installed, the concentration of chloride in the steam at the turbine inlet, and hence in the hot well condensate, may be much lower than estimated in the design documents. No such condensate traps or separator are indicated in the design drawings, however, and all condensate formed during transmission, as well as all carry-over water with its dissolved species, is assumed to pass through the turbine and into the hot well.

Condensate

After the steam passes through the turbine, it is condensed in the surface contact condenser. The estimated key corrosive species chemistry of the steam condensate is presented in Table 3. In PNM, 1980, the chloride concentration in the condensate was estimated to be 15.1 ppm, which corresponds to a 0.5 percent droplet carry-over. However, the estimated chloride in the steam was 21 ppm and all of this chloride must appear in the condensate. Therefore, Table 3 gives two values for chloride.

Recirculating Cooling Water

All of the condensate from the hot well is used for cooling water make-up, and therefore the make-up rate is essentially constant during normal plant operation. Blowdown occurs at a rate sufficient to maintain a constant level of the cooling tower basin, and the cycles of concentration of the cooling water is controlled by the rate of evaporation. Table 4, based on data presented in PNM, 1980, gives the estimated concentration of the recirculating condensate corrosive species during the winter and summer, and for periods of maximum cooling tower evaporation.

TABLE 3. ESTIMATED CONCENTRATIONS OF KEY CORROSIVE SPECIES IN STEAM CONDENSATE

Parameter	Concentration
pH	4.8
Cl	15.1^{a} - 21^{b} ppm
SO_4	8.7 ppm
HCO_3	3.3 ppm
CO_3	0
H_2S	0.09-0.41 ppm
NH_4^+	N.R.

N.R. - Not reported

[a] as estimated in [PNM, 1980]

[b] based on estimated steam composition (Table 2)

TABLE 4. ESTIMATED CONCENTRATION OF KEY CORROSIVE SPECIES IN CIRCULATING COOLING WATER

Parameter	CONCENTRATION		
	Winter (ave)	Summer (ave)	Maximum tower evaporation
pH	>4.5	>4.5	>4.5
Cl	33^{a}-46^{b} ppm	109^{a}-149^{b} ppm	147^{a}-204^{b} ppm
HCO_3	7.3 ppm	23.8 ppm	35 ppm
SO_4	19.1 ppm	62.4 ppm	84 ppm
H_2S	<0.9^{b} ppm	<2.9^{b} ppm	6^{a} ppm
NH_3	N.R.	N.R.	N.R.

N.R. - Not reported

[a] as estimated in [PNM, 1980]

[b] based on estimated steam composition (Table 2)

Plant Atmosphere

The Holmes-Stretford hydrogen sulfide abatement system has been shown to be very effective in geothermal applications. However, traces of hydrogen sulfide (less than 10 ppm) can still be expected in the plant atmosphere. Minute quantities of this compound can be very damaging to many painting systems and to silver or copper electrical contacts.

4.0 DISCUSSION

This portion of this report will consider the suitability of some of the proposed materials selections for Baca Unit 1. This survey is based on extensive studies of corrosion problems associated with geothermal applications [DeBerry, et al., 1979; Ellis and Conover, undated]. Four environments will be considered, the plant atmosphere, two-phase fluid, separated steam and the recirculating condensate cooling water.

4.1 Corrosion by Plant Atmosphere

4.1.1 Painted Structures

Within one to two years of application, failure of conventional painting systems has occurred at Otake (Japan), Hatchobaru (Japan), Larderello (Italy), The Geysers, and at other plants. Through research, the Italians have developed a painting cycle which is reported to give at least five years service without maintenance in atmospheres with hydrogen sulfide contamination much more severe than is anticipated at Baca Unit 1 [ENEL, 1979]. The Larderello Painting Cycle is described as follows:

Step 1 Sandblasting to Swedish Standards grade Sa 2½ - 3 (SSPC grade 10 or better).

Step 2 Application of 2.5 - 3 mils (1 mil = 0.001 inch) of flame-sprayed zinc.

Step 3 Application of at least 3 mils of oil based phenolic resin, zinc chromate-rich primer.

Step 4 Application of an intermediate cost of phenolic paint with passivating pigments to a thickness of at least 2.3 mils.

Step 5 Application of a final coat of phenolic/glycerophathalic paint, free of lead or other heavy metals which can react with hydrogen sulfide. Recommended thickness is at least 3.5 mils.

Note: Polyurethane-based paints are not used at Larderello.

In cases where flame galvanizing cannot be used, the Italian practice is to use an epoxy resin paint of high zinc content to a thickness of 2.5 mils in place of zinc galvanizing in Step 2. For surfaces with rust or deteriorated paint, the area is cleaned and the painting cycle is begun at Step 3.

4.1.2 Electrical Equipment and Instrument Air Supply

The plans for Baca Unit 1 call for the use of positive pressure clean rooms (hydrogen sulfide-free) for the protection of electrical equipment, especially copper and silver conductors and/or contacts. This approach has been used at Wairakei, New Zealand, and at The Geysers [DeBerry et al., 1979]. Experience at The Geysers has shown that, in practice, the maintenance of sulfide-free atmospheres is difficult [Friedrich, personal communication]. An alternative is the plating of all electrical connectors with chromium, tin, platinum, cadmium, nickel, or gold.

Particular attention should be given to equipment in the power plant switch yard and to equipment in the steam gathering system. Plating requires more initial effort, and may not be possible for some parts, but requires little maintenance. The use of plated contacts whenever possible, coupled with clean rooms or boxes for unprotected equipment, should give the best long-term results.

Care should also be taken to protect the instrument air supply from contamination with hydrogen sulfide. The air entering the compressor should be filtered to remove any hydrogen sulfide.

4.2 Corrosion in Two-Phase Fluid

In two-phase (or superheated liquid) pipelines droplet velocities of several hundred feet/second may occur, especially in regions of local flashing due to pressure drop from valves, orifices, and similar equipment. The droplet density is often high, and serious impingement or erosion damage may occur.

Like the proposed Baca plant, the Ahuachapan geothermal plant (El Salvador) utilizes bore-flashing wells, and piping between the well, separator, and diffuser (muffler) transports two-phase fluid. At Ahuachapan, the wellhead valve is never cycled unless both the separator and diffuser valves have been closed. Thus, the wellhead valve is protected from erosion. The diffuser and separator valves are carbon steel gate valves. They have a service life, without leaking, of six open-shut cycles. Failure results from erosion of the gate and seat as the valve opens or closes [Ellis and Conover, undated].

Initially at Ahuachapan, two wells were throttled by the separator valves to reduce flow. Failure by erosion of the seats rapidly occurred. These wells are now throttled by austenitic stainless steel orifices which show little erosion

[Ellis and Conover, undated]. This suggests that stainless steel trim may be suitable for two-phase valves. However, at Matsukawa (Japan), erosion tests performed in 280°F steam containing 30 percent droplets at a velocity of 656 feet/second showed Type 304 to have an erosion rate of more than 200 mpy (0.200 inch/year). Stellite No. 6 showed an erosion rate of four mpy [Ellis and Conover, undated].

At the Geothermal Loop Experimental Facility (GLEF) at the Salton Sea and at Cerro Prieto failures of carbon steel elbows resulted from impingement by high velocity droplets in fluid lines. This problem was alleviated by installing blind-flanged tees in place of the elbows. A layer of water trapped in the blind leg of the tee prevents impingement of the droplets on the steel [Ellis and Conover, undated].

4.3 Corrosion in Geothermal Steam Pipeline

The anticipated composition of the saturated separated geothermal steam was given in Table 2. This steam will contain droplet carry-over estimated to be not more than 0.5 percent [Union, 1980]. As was mentioned previously, transmission condensate is an efficient scrubber of ionic species in droplet carry-over, and the presence of carbon dioxide and hydrogen sulfide and the absence of ammonia in the steam phase will cause the pH to be acidic, perhaps in the range of 4 to 5. The low pH means that the condensate will be corrosive, but the available data do not justify an estimate of the corrosion rate of steel pipe exposed to this condensate.

Studies at Wairakei showed that the condensate forms a layer of film along the bottom of the pipeline [James, 1980]. Originally, numerous condensate traps were installed near the separators to effectively remove the contaminated condensate. Hydrogen sulfide and carbon dioxide are not scrubbed, however, and it was found that the ultra-pure condensate formed downstream of the condensate traps was far more corrosive, due to dissolved gases, than was condensate contaminated with droplet carry-over. Current practice at Wairakei is to utilize condensate traps in the 200-600 ft. of pipeline closest to the powerhouse in order to minimize the amount of pipe exposed to ultra-pure condensate [James, 1980]. This reference and James, 1975, gives methods for calculating the amount of condensate and number of required traps.

At Larderello, Italy, in cases where steam pipe was in contact with the steel support with no intervening thermal insulation, condensate, which was reported to be quite corrosive, formed at the resulting cold spots [ENEL, 1979]. The steam at Larderello has about 50°F superheat and about 40,000 ppm (wt) carbon dioxide. Whether similar corrosion will occur in Baca steam lines is not known, but the Italian experience suggests the desirability of minimizing cold spots and avoiding the pooling of condensate.

Introduction of air into the steam will cause drastic increases in corrosivity. Experience at Wairakei, New Zealand, confirms this and when pipelines at Wairakei are to be opened for inspection, they are flushed with fresh water [Ellis and Conover, undated; DeBerry _et al_., 1979].

For valves, austenitic (AISI 300 series) stainless steel trim with Stellite hard-facing is probably suitable in both two-phase and steam service because of the lack of oxygen. However, if steam condensate forms on the atmospheric side of valve stem packings, evaporation may lead to high temperature, high chloride concentrations and aerated conditions which make austenitic stainless steel valve stems susceptable to stress corrosion cracking. A common alternative stem material is 17-4 PH. This alloy, with 17 percent chromium and 4 percent nickel, is resistant to stress corrosion cracking (SCC) in boiling magnesium chloride, an extremely severe test [DeBerry, et al., 1979]. Its chromium and nickel content gives considerable resistance to pitting and crevice corrosion. Valves with stainless steel trim, Stellite No. 6 hardfacing and 17-4 PH stems are specified in the Union design document [Union, 1980].

Turbine

Calculations by the method of James [James, 1980], assuming that steam flow is 925,000 lb/hr, that the pipeline is insulated with two inches of rockwool (insulation is not addressed in the design documents), and that droplet carry-over from the separators is 0.5 percent, indicate that about 10,000 lb/hr of liquid water (about 1.08 percent moisture) will enter the turbine. This may be unacceptable to the turbine vendor. The potential problem can be eliminated by installation of a series of condensate traps, or a final separator-demister, in the steam line near the turbine inlet. The separator-demister approach was used at Cerro Prieto (Mexico) and at Ahuachapan, while the condensate trap method is used at Wairakei. Both methods also greatly reduce the quantity of dissolved solids in the turbine inlet stream, and thus in the condensate cooling water.

Steam at Cerro Prieto is supplied to the turbines with about 0.01 percent moisture. During the first five years of operation, nc blade failures were reported. Similar results have been obtained at Wairakei [Ellis and Conover, undated]. Complete drying of the steam may not be desirable, however. Superheated feed steam at The Geysers causes an on-going problem with cracking of the second stage blades, where condensate first forms.

The material specified for the Baca Unit 1 turbine blades is 12Cr stainless steel. This material has been used in a number of geothermal plants including Otake, Wairakei, Cerro Prieto, and The Geysers with satisfactory results. However, satisfactory performance requires the specification of low strength and hardness properties for resistance to sulfide stress cracking (SSC), and because corrosion-fatigue is more severe in geothermal steam than in boiler quality steam, a thicker blade than is typical of turbines operating on boiler steam.

Table 5 shows the results of corrosion-fatigue tests of 12Cr blading alloy and low alloy rotor steel at Otake, Japan, Cerro Prieto, Mexico, Baca, and The Geysers. The reduction in Fatigue Endurance Limit (FEL) relative to a duplicate specimen fatigued in air is presented, as are results for a control specimen exposed to boiler quality steam. It should be noted that in the case of Otake and The Geysers (where the specimens were cyclicly stressed during exposure) there was no inflection or "knee" in the stress-log cycle plot, indicating a continuing reduction in FEL with time.

4.4 Corrosion in the Recirculating Condensate Cooling Water System

4.4.1 Use of Stainless Steel

The cooling water system design contains large amounts of Type 304 and Type 304L stainless steel. Both grades have equivalent resistance to localized corrosion. The main steam condenser, inter and after condensers of the gas extractor system, and the hydrogen and lubricating oil coolers are all tubed with

TABLE 5. CORROSION-FATIGUE IN GEOTHERMAL STEAM ENVIRONMENTS

Site	Environment	Method	Material	Reduction in FEL Relative to Air
Otake[1]	CO_2 = 4950 ppm (wt) H_2S = 51 ppm (wt) T = 212°F P = atm	Cyclic stresses applied during exposure to environment.	2.5Ni-Cr-Mo-V	26% at 10^6 cycles 43% at 10^7 cycles 50% at 10^8 cycles
			13Cr	22% at 10^6 cycles 32% at 10^7 cycles 38% at 10^8 cycles
The Geysers[1]	CO_2 = 2200 ppm (wt) H_2S = 220 ppm (wt) NH_3 = 400 ppm (wt) T = 338°F P = 100 psig	Cyclic stresses applied during exposure to environment.	Type 403 (12Cr)	13-24% at 10^7 cycles
Cerro Prieto[2]	CO_2 = 19500 ppm (wt) H_2S = 2000 ppm (wt) T = 297°F P = 61 psig	Exposed to environment with out stress, then fatigued in air.	3.5Ni-Cr-Mo-V	39% after 180 days exposure
			12Cr	18% after 180 days exposure
Baca[2]	CO_2 = 33700-47390 ppm (wt) H_2S = 290-570 ppm (wt) T = 340°F P = 110 psig	Exposed to environment without stress, then fatigued in air.	Type 403 and Type 616 (12Cr and 12Cr-1Mo-.25V)	16-24% after 34 days exposure 36-52% after 160 days exposure
Control[1]	Boiler quality steam T = 212°F P = atm	Cyclic stresses applied during exposure to environment	2.5Ni-Cr-Mo-V	12% at 10^6 cycles 17% at 10^7 cycles 17% at 10^8 cycles
			13Cr	11% at 10^6 cycles 13% at 10^7 cycles 13% at 10^8 cycles

[1] [Ellis and Conover, undated]

[2] [DeBerry et al., 1978]

[3] FEL = Fatigue Endurance Limit

Type 304 stainless steel. Condensate and circulating water pumps are Type 316 or its cast equivalent.

The onset of pitting and crevice corrosion of stainless steels in aerated waters is a function of the chromium and molybdenum content of the alloy and the chloride content and temperature of the water. Increases of chromium and molybdenum increase the threshold temperature above that at which pitting or crevice corrosion occurs. Increasing chloride content lowers the threshold temperature. In the range 4 to 8, pH probably has little effect on the threshold temperature, although an acidic pH favors more numerous pits with more rapid penetration rates. Pit penetration rates are extremely difficult to predict, and corrosion allowances can not be defined. Especially for thin walled components, a go/no-go pitting criteria should be used for material selection.

Once pitting conditions have been obtained, initiation typically occurs within hours. Once this has occurred, an autocalytic process (pitting) is established and in many cases will be self-sustaining even when process conditions moderate. For this reason, the upper limits of temperature and chloride, to which a component will be exposed, are of particular interest.

As was discussed in Section 3 and Table 4, the estimated range of chloride concentration in the recirculating condensate is 33-147 ppm [PNM, 1980], while, based on the estimated steam composition [PNM, 1980], the chloride concentration will be 46-204 ppm. Both of these estimates neglect removal of chloride enriched condensate upstream of the turbine inlet.

The design temperature for the cooling water is 70°F inlet (cooling tower basin) and 96°F return. However, the surfaces of the condenser tubing will be hotter than the bulk cooling water and it is the temperature of the tube wall which will determine whether or not pitting will occur at a given chloride concentration. The design condensate temperature is 120°F, and as a first approximation, it is assumed that the maximum tube wall temperature will be mid-way between the condensate temperature and maximum cooling water temperature, or about 108°F.

The threshold temperature for localized corrosion of Type 304 and Type 316 as a function of chloride concentration was explored by Efird and Moller [Efird and Moller, 1978]. Figure 1 shows the results of their work. The shaded rectangle superimposed on the figure shows the estimated range of temperature and chloride ion concentration expected in the Baca Unit 1 cooling loop. The more darkly shaded rectangle assumes 99.5 percent steam quality at the separator outlet, while the lighter rectangle assumes 99.3 percent separation. Table 6 summarizes the operating experience with Type 304 and Type 316 in recirculating condensate at three other geothermal plants. That experience is in reasonable agreement with Figure 1.

Figure 1 shows that at even a 99.5 percent separator efficiency, the nominal operating conditions intrude into the region where pitting and/or crevice corrosion of Type 304 (or Type 304L) may occur. At a separator efficiency of 99.3 percent, Type 316 (or Type 316L) is marginal.

Studies of the threshold pitting temperature for a number of stainless steels in 10 percent ferric chloride solution have been conducted and an expression for the threshold pitting temperature in ferric chloride as a function of chromium and molybdenum content has been derived. Nickel was shown to have negligible effects on threshold pitting temperature [Brigham and Tozer, 1976].

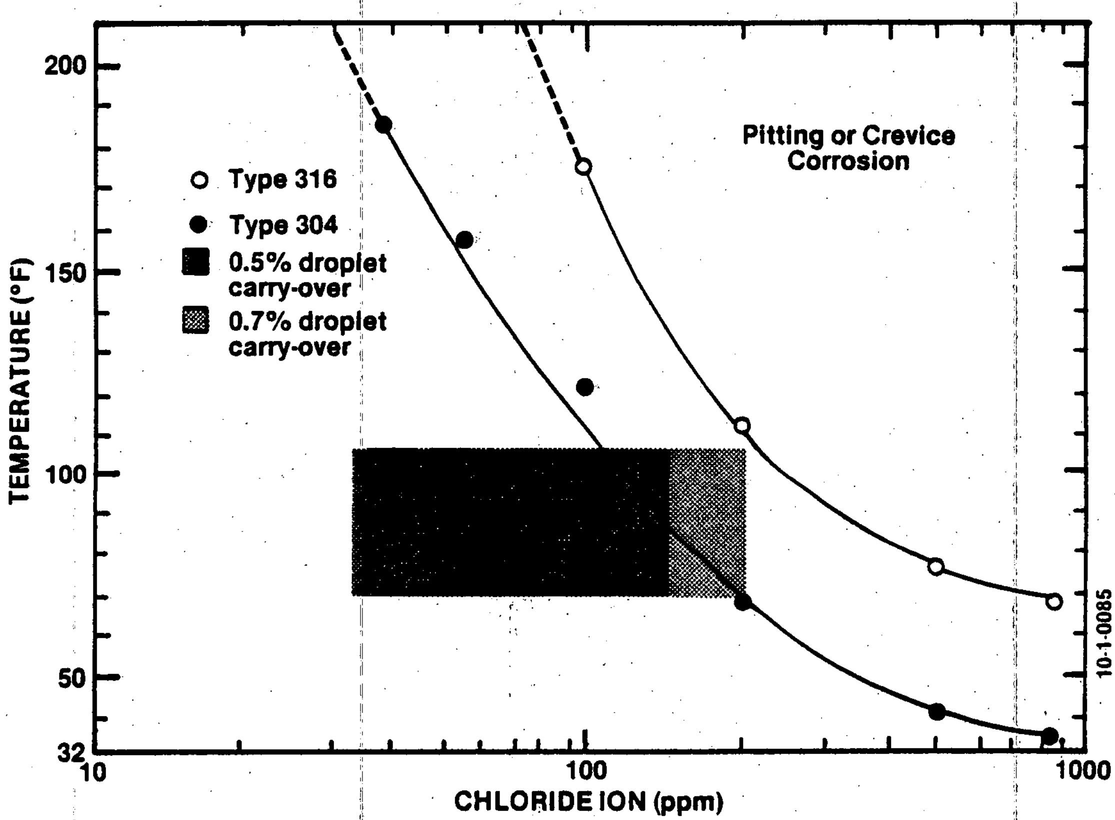

Figure 1: Critical Temperature for Localized Corrosion of Type 304 and Type 316 Stainless Steel as a Function of Chloride [Efird and Moller, 1978]

Pitting or crevice corrosion may occur to the right of the curves. Shaded area indicates Baca Geothermal Station cooling loop conditions.

TABLE 6. GEOTHERMAL PLANT EXPERIENCE WITH TYPE 304 AND TYPE 316 IN RECIRCULATING CONDENSATE COOLING WATER

Geothermal Plant	Conditions	Materials Test Results	Material Operating Experience
Wairakei, N.Z.	• Cl = unknown • T = 140°F	• Pitting of austenitic grade equivalent to Type 304[a]. • No pitting of austenitic grade equivalent to Type 316[a].	
Cerro Prieto, Mexico	• Cl ≈ 50-60 ppm • T = 104-113°F	• No pitting of Type 304 coupons after 180 days[a].	
	Cl = unknown T = 114-145°F		• Type 304 oil cooler tubes perforated after several months. Hydrogen cooler tubes not failed because of greater wall thickness. Occlusion cell corrosion a factor in failure.[b] • Original barometric condensers Type 304 clad. All future units to be Type 316L clad.[b]
The Geysers, CA	• Cl = 1-10 ppm[c] • T = 81-134°F before ferric sulfate additions	• Significant pitting of Type 304 in both solution annealed and heat sensitized conditions. Severity of attack increased with time.[a] • No pitting of Type 316 observed.[a]	• Original Type 304 piping has been replaced with Type 316 on an as needed basis[d]. • Occasional minor pitting of Type 316 pipe observed.[a] • Addition of ferric sulfate for hydrogen sulfide abatement caused serious corrosion problems.[a]

a [DeBerry et al., 1979]

b [Ellis and Conover, undated]

c [McAlpin and Ellis, 1980]

d [Friedrich, personal communication]

The ferric chloride test is an accelerated test and the actual threshold pitting temperatures indicated probably are not applicable to low chloride solutions, but the ferric chloride test can be used to rank the relative threshold pitting temperatures of different stainless steels.

E-Brite 26-1 (ASTM XM27) is an ultra-low interstitial ferritic stainless steel tubing alloy containing 26 percent chromium and one percent molybdenum. Its relative threshold pitting temperature (in terms of absolute temperature) is 1.105 with respect to Type 304 and 1.043 with respect to Type 316. Assuming that this relative resistance is applicable to low chloride solutions, the threshold pitting temperature for E-Brite 26-1 is estimated to be 123-137°F at 200 ppm chloride. At 108°F, the allowable chloride concentration in the cooling water would be 280-360 ppm, corresponding to droplet carry-over of 0.95-1.2 percent.

It is worth noting that threshold pitting temperatures calculated for Type 316, using the relative threshold pitting temperature for Type 316 and Type 304 in ferric chloride and the threshold pitting temperature for Type 304 in Figure 1, are 17 to 28 percent lower than the threshold pitting temperatures shown for Type 316. This indicates that the performance of E-Brite 26-1 may also be better than was estimated in the previous paragraph.

Another alternative alloy, comparable to E-Brite 26-1 in the ferric chloride test, is Type 317LM. The LM grade must be specified to obtain the desired 4.25 percent molybdenum content.

A potential concern with austenitic (AISI 300 series) stainless steels is chloride stress corrosion cracking (chloride-SCC). The phenomenon is a function of pH, chloride concentration, oxygen concentration, and temperature. Figure 2 shows the threshold temperature for chloride-SCC of Type 304L stressed near the yield point as a function of chloride concentration in air saturated sodium chloride brine, and indicates that the threshold temperature for chloride-SCC of Type 304L at yield stress is greater than 140°F. However, tests at Wairakei [DeBerry et al., 1979] set the threshold for Type 304 under plastic stress at 121°F. Type 316 with its increased molybdenum content will have a higher chloride-SCC threshold temperature than Type 304, while Type 317M is resistant to chloride-SCC in the wick test, a relatively severe test [DeBerry et al., 1979]. E-Brite 26-1, with its ferritic microstructure is essentially immune to chloride-SCC.

All of the proceeding performance estimates are predicated on clean (unfouled) tubing. If the tubing becomes fouled, the wall temperature will rise due to the insulating effect of the deposit. An occlusion cell will form under the deposit and that area will become enriched with chloride ion and depleted of dissolved oxygen. These two effects will lead to pitting. The elevated temperatures may also result in chloride-SCC of austenitic stainless steels. For this reason, cleanliness of the cooling water system is essential.

The preceeding discussion can be summarized as follows:

- Type 304 piping in recirculating condensate service was unsatisfactory at The Geysers because of pitting. Type 304 oil cooler tubes at Cerro Prieto were perforated by pits in only a few months.

- The threshold chloride-SCC temperature for Type 304 under plastic stress, as measured at Wairakei, is 121°F, while for similar steel

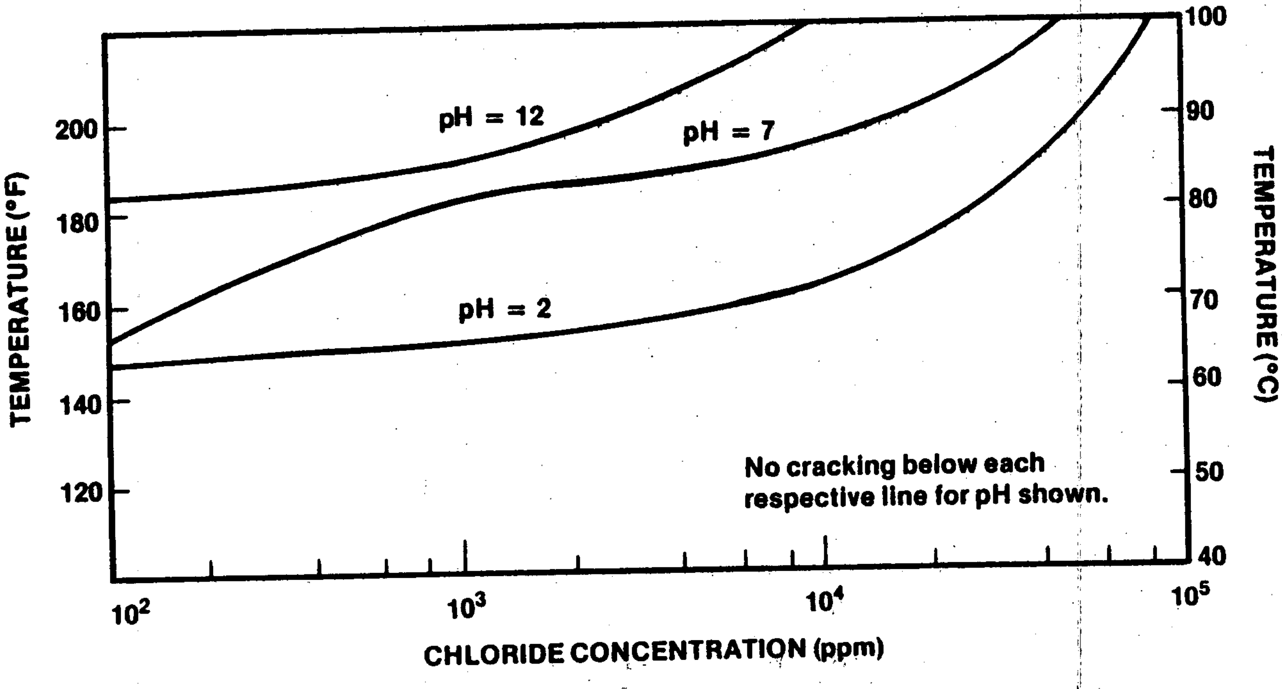

Figure 2. Effect of pH, Chloride, and Temperature on Stress Corrosion Cracking of Type 304L Stainless Steel Under Residual Weld Stresses [DeBerry et al., 1979).

Welded tube specimens in sodium chloride solution under air. Exposure period up to 8000 hours.

at near yield stresses, the threshold chloride-SCC temperature is between 140°F and 150°F.

- On the basis of Figure 1, Type 316 piping will be subject to pitting if the chloride level in the recirculating cooling water exceeds 850 ppm at 70°F and 250 ppm at 96°F (cooling water inlet and outlet design conditions).
  Type 316 heat exchanger tubing will be subject to pitting at cooling water chloride levels in excess of 210 ppm.

- Type 316 is subject to chloride-SCC but the threshold temperature is somewhat higher than that of Type 304.

- E-Brite 26-1 and Type 317LM are predicted to have similar pitting and crevice corrosion resistance. These alloys should tolerate at least 280 ppm chloride in heat transfer service at Baca Unit 1.

- E-Brite 26-1 is essentially immune to chloride-SCC because of its microstructure. Type 317M is resistant to chloride-SCC in the wick test and in the boiling saturated acidic sodium chloride test, and should therefore not be at the risk of chloride-SCC in the Baca cooling system.

- Fouling of the cooling water system would probably result in pitting of any of the alloys under consideration and would also increase significantly the risk of chloride-SCC of Type 304 and Type 316.

The selection of alternate materials for condenser and cooling service is a technical and economic decision, and although an economic analysis is beyond the scope of this report, two points should be considered. First, on the basis of prices of large orders of 0.25 inch plate, as of July 1980 the costs of E-Brite 26-1, Type 317 and Type 317LM relative to Type 304L, are 0.83, 1.46 and 2.36, respectively. Thus, E-Brite 26-1 may be comparable in cost to Type 316 and may even be competitive with Type 304.

Another factor to consider is the containment sensitivty (impact of minor leakage on performance) and replacement and contingent costs of failure. Components which will be "failed" by minor leakages, and which have long lead times, merit more conservative material selections because of the risk of prolonged forced outage of the plant.

The main condenser is the largest component, and probably has the highest replacement cost. Because the plant could operate with a few percent crossleakage, via pits, between the steam and recirculating water, this component is not particularly containment sensitive.

On the other hand, because of the low viscosity of hydrogen, even a few small perforations of the hydrogen cooler could result in a large loss of hydrogen and risk of explosion. This component is very containment sensitive. If the lead time on a replacement hydrogen cooler is long, an extended forced outage could result from failure. The containment sensitivities of the lubricating oil coolers and hydraulic power unit cooler are probably intermediate to the hydrogen cooler and main condenser.

4.4.2 Cooling Tower

The structural support of the cooling tower is chemically treated wood, but the treatment (for inhibition of microbiological degradation) is not specified [PNM, 1980]. Treatment with copper compounds is a common practice but will cause contamination of the cooling water with copper ions which can promote pitting of stainless steel. For this reason, unless a copper inhibitor is used in the cooling loop, a copper-free wood treatment should be specified.

4.4.3 Cooling Tower Basin

The cooling tower basin water is expected to have a temperature of about 70°F and to contain sulfate ($SO_4^{=}$) concentrations of about 19-84 ppm. The pH may be as low as 4.5. Consultation with the DOE Brookhaven National Laboratory [Kukacka, personal communication] indicates the proposed two-inch sacrificial concrete layer will not survive the life of the plant due to attack by acid and sulfate. Furthermore, wastage will not be uniform and cleanup of the basin concrete for resurfacing will be very difficult.

Use of Type 5 cement (which is sulfate resistant) would reduce the severity of attack, but the cement would still be degraded by acidic conditions. Availability of Type 5 cement may also be a problem.

Brookhaven recommends lining the basin with polymer concrete about 0.375 inch thick and estimates that under the anticipated operating conditions this coating should last more than twenty years. Application of this polymer concrete layer does not require erection of forms and can be done despite the many irregularities in the basin geometry.

The suggested monomer is:

55 wt% styrene
36 wt% acrylonitrile
9 wt% trimethylolpropane trimethacetylate (TMPTMA)

The liquid monomer mixture would be applied to the concrete surfaces to be protected. Before it cures to a polymer, sand would be spread and pressed into the monomer mixture with a roller. The resultant layer would be about 0.125 inch thick. Three applications would give the desired thickness.

Other basin coating alternatives to sacrificial concrete include the use of coal-tar epoxy coatings or PVC liners as has been done at other geothermal power plants. At Cerro Prieto and Larderello, the coal-tar epoxy coating require replacement after a few years [Ellis and Conover, undated].

5.0 RECOMMENDATIONS

The recommendations below are not listed in any order of priority.

- The use of condensate traps on the geothermal steam lines or of a demister-separator near the turbine inlet is recommended in order to reduce the amount of liquid water and dissolved solids entering the turbine and the amount of chloride in the cooling water. Failure to remove condensate formed during steam transmission may result in turbine inlet steam of insufficiently quality to meet the turbine manufacturer's specifications.

- On the basis of experience at flashed steam geothermal plants at The Geysers, Wairakei (New Zealand), and Cerro Prieto (Mexico), Type 304 stainless steel is not recommended for recirculating cooling water service because of the risk of pitting.

- Type 316 should be suitable for condenser and cooler service provided that the tube wall temperature does not exceed 108°F and the chloride content of the turbine inlet steam does not exceed 22 ppm. A prudent safety factor should be applied to the chloride limit.

- Consideration of E-Brite 26-1 and Type 317LM is recommended. These alloys should be suitable for condenser and cooler service provided the tube wall temperature does not exceed 108°F and the turbine inlet steam chloride content does not exceed 29-37 ppm. Again, a prudent safety factor should be applied by the plant designer.

- Fouling of the cooling water system will cause pitting of all of the alloys under consideration and may cause chloride stress corrosion cracking of Type 304 and Type 316. Great care in maintenance of system cleanliness is recommended, and a vigorous antimicrobiological treatment program will be required.

- In the event that it is not feasible to specify alternate materials for all condensers and coolers, it is recommended that priority should be given to those components in which minor cross-leakage would result in a prolonged forced outage due to a long lead-time for replacement parts. The hydrogen cooler should probably have first priority.

- Austenitic stainless steels (AISI 300 series) are not recommended for steam valve stems due to a risk of pitting or chloride stress corrosion cracking by aerated condensate at the packings. An alternative material is 17-4PH.

- Limitations are imposed on the design of 12Cr turbine blades by the severity of corrosion-fatigue in geothermal steam and by the low strength requirements imposed by the presence of hydrogen sulfide in the stream. These limitations may require a blade which is thicker than would be required for boiler quality steam.

- The antimicrobial treatment of wooden cooling tower components should be specified to be copper-free in order to prevent contamination of the cooling water with copper ions which may have a deterimental effect on the pitting resistance of stainless steel.

- It is recommended that a polymer concrete coating, PVC lining, or coal-tar epoxy coating of the cooling tower basin should be considered as an alternative to the proposed 2-inch sacrifical concrete layer because the sacrificial layer would probably require replacement during the plant life. This would represent a difficult (and costly) maintenance task. Of the above options, the polymer concrete coating may be the best option because it is estimated to have a life of more than twenty years. It does not require the erection of forms.

- Because of practical difficulties in maintaining hydrogen-sulfide-free rooms, it is recommended that whenever possible electrical contacts and connectors should be plated with chromium, tin, platinum, cadmium, nickel, or gold. Copper or silver contacts will fail rapidly if exposed to air contaminated with traces of hydrogen sulfide.

- It is recommended that the intakes of air compressors, especially instrument air compressors, be filtered to remove hydrogen sulfide.

- Use of the Larderello Painting Cycle is recommended for metal structures which may be exposed to hydrogen sulfide contaminated air in order to significantly prolong the protection of metal and reduce O&M activities.

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