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25 February 1980

DCN 80-212-003-X

Mr. R. R. Stiger
Manager, Geothermal Technical Development
EG&G, Inc.
P. O. Box 1625
Idaho Falls, Idaho 83415

Dear Mr. Stiger:

We have been funded by DOE/DGE to assist them in the study of geothermal corrosion phenomena, its causes and the selection of appropriate materials and/or processes to mitigate corrosion effects.

In responding to Judd Whitbeck's request, Bob Reeber asked us to visit EG&G to see if we could assist in solving what appears to be a serious pitting hazard in your 5MW power plant's cooling loop. We visited EG&G on February 7 and 8 and spoke with Messrs. Dan Suciu, Dick Miller and Judd Whitbeck.

Attached is our report which documents the results of our preliminary investigation. This report shows that the extremely aggressive, aerated, chloride/sulfate-containing cooling water will probably cause pit penetration of the carbon steel condenser tubing in not more than 11 to 16 weeks if the present chromate treatment is followed. Fortunately, we believe and are recommending that an alternative inhibitor can yield satisfactory pitting protection and may be employable without significant funding or equipment changes.

We also recommend an immediate initiation of a materials test program to prepare for certain component replacements in the event that water treatment does not yield a three year condenser life time.

With the submission of this report we hope that steps can be taken so that we can work together to solve this significant potential pitting problem.

Very truly yours,

Marshall F. Conover
Program Manager

MFC:alc

DCN 80-212-003-07

SERIOUS PITTING HAZARD
IN THE RAFT RIVER 5MW(e)
GEOTHERMAL POWER PLANT
ISOBUTANE COOLING LOOP

Prepared by:

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Contract No. DE-AC02-79ET27026

Prepared for:

US DEPARTMENT OF ENERGY
Chicago Operations and Regional Office
Argonne, Illinois 60439

25 February 1980

CONTENTS

<u>Section</u>		<u>Page</u>
1.0	INTRODUCTION	1
2.0	PROBLEM STATEMENT	4
	2.1 Important Factors	4
3.0	ASSESSMENT OF RISK DUE TO PITTING UNDER INADEQUATE TREATMENT CONDITIONS	7
	3.1 Extreme Value Analysis of Preliminary Pitting Data	8
	3.2 Mitigation of the Pitting Hazard	10
4.0	PRELIMINARY INVESTIGATION OF INHIBITORS CAPABLE OF PREVENTING PITTING IN NEUTRAL AERATED CHLORIDE/SULFATE WATERS	12
	4.1 Mechanism of Pit Nucleation and Propagation	12
	4.2 Inhibitor Action	13
	4.3 Minimum Anodic Inhibitor Requirements (Critical Inhibitor Concentration)	14
	4.4 Estimation of Corrosion Rate of Carbon Steel in Neutral Aerated Chloride and Sulfate Solutions Inhibited by Nitrite	18
5.0	IMPACTS OF CRITICAL INHIBITOR CONCENTRATION REQUIREMENTS FOR THE RAFT RIVER COOLING SYSTEM	21
	5.1 Chromate Inhibitor	22
	5.2 Molybdate Inhibitor	22
	5.3 Nitrite Inhibitor	22
6.0	CONCLUSIONS	27
7.0	RECOMMENDATIONS	29
8.0	REFERENCES	32

1.0 INTRODUCTION

The 5MW(e) Dual Boiling Cycle Geothermal Power Plant, hence referred to as the Raft River plant, is being developed for DOE by EG&G, Inc., Idaho Falls, Idaho. This pilot power plant is of the binary concept and utilizes isobutane as the working second fluid. The plant will demonstrate the feasibility of power generation from an intermediate temperature ($\sim 290^{\circ}\text{F}$) resource. The plant is schematically diagrammed in Figure 1.

During the final design phase and after the major components were specified to be made of carbon steel, and ordered, various conditions forced the power plant design to switch from surface water to geothermal fluid for the condenser cooling loop make-up water. Because the geothermal fluid contains significant concentrations of chlorides and sulfates, about 1000 ppm and 65 ppm respectively, aeration in the cooling tower causes this water to become extremely aggressive, especially in the pitting of carbon steel components.

Although essentially all of the condenser cooling loop materials are carbon steel, the isobutane condenser and turbine lube oil cooler are the most vulnerable. These components are tubed with carbon steel tubes of 0.085 and 0.075 inch wall thickness. These two components are extremely leak critical heat exchangers. For example, even a single pit perforation in the isobutane condenser can cause plant shutdown through loss of isobutane. Such a leak also poses an explosion or fire hazard. As isobutane pressure falls, the incursion of cooling water into the isobutane loop could occur, causing damage to anhydrous service seals.

Under a DOE contract for geothermal failure analysis, Radian Corporation has made a preliminary investigation of the

Isobutane System
 $W_1 = 6.13 \times 10^5$ lbm/hr
 $W_2 = 3.21 \times 10^5$ lbm/hr

Geothermal Water System
 $W_3 = 1.04 \times 10^6$ lbm/hr

Cooling Water System
 $(1)W_4 = 7.53 \times 10^6$ lbm/hr

1 105°F
 2 180°F
 3 240°F
 4 240°F (381.6 psia)
 5 130°F
 6 128°F
 7 101°F (77.5 psia)(2)
 8 180°F
 9 180°F (203.0 psia)
 10 123°F

11 290°F
 12 250°F
 13 222°F
 14 190°F
 15 144°F

16 75°F
 17 95°F

Notes:
 (1) Flowrate is sized for 100% bypass around turbine
 (2) Condenser pressure nominal for 65°F wet bulb temperature

Figure 1. Raft River 5 MW(e) Geothermal Pilot Plant Dual Boiling Cycle.

pitting hazard presented by the aggressive cooling fluid and the corrosion inhibition treatment that has thus far been proposed. This report documents Radian's understanding of the present situation and the results of its investigation on possible mitigation of this hazard.

Finally, various conclusions and recommendations are made that may, if pursued, lead to a satisfactory solution that will avert a certain early prolonged plant shutdown due to failure of the thin walled isobutane and turbine lube oil cooler tubes.

2.0 PROBLEM STATEMENT

Due to a source change from low chloride surface water to high chloride/high sulfate geothermal water for condenser cooling loop makeup, all cooling loop carbon steel components will be subjected to catastrophic pitting rates from the oxygen saturated chloride/sulfate water. Although the conventional water treatments thus far proposed will limit general (uniform) corrosion, they nonetheless will not preclude pitting and are, additionally, not environmentally acceptable.

2.1 Important Factors

2.1.1 The carbon steel heat exchangers are in place and installed in such a manner that tubes can not be replaced.

2.1.2 Well documented research and experience shows that a catastrophic pitting hazard exists in the cooling water loop.

2.1.2.1 Linear extrapolation of recent pitting tests shows that condenser tube penetration will occur in less than 35 weeks. As will be shown in Section 3.1, actual failure may occur much sooner.

2.1.2.2 System Check-out tests (hydrostatic tests of heat exchangers) with inadequately inhibited water will cause pitting damage to such an extent that future inhibition treatments may be ineffective. There is a risk of perforation prior to plant start-up.

- 2.1.2.3 Water treatment proposals thus far have not specifically addressed inhibition of pitting.
- 2.1.2.4 Treatment with chromate even at limits unacceptable from a health and environmental level have been shown to be ineffective in controlling pitting though a satisfactory "uniform" corrosion rate was obtained.
- 2.1.2.5 Rapid permanent damage and/or failures by pitting will occur in the cooling loop unless adequate treatment for corrosion inhibition is applied.
- 2.1.3 Selection of an adequate water treatment program is complicated by several factors.
 - 2.1.3.1 No evidence of the chemistry of all of the Raft River wells can be found. Thus, the chemistry of the cooling fluid is not clearly defined.
 - 2.1.3.2 Little information about the treatment for control of pitting of carbon steel in waters similar to the geothermal derived cooling water is available in the literature.
 - 2.1.3.3 It is essential for satisfactory heat transfer, as well as for corrosion control, that scaling in the cooling loop be completely eliminated. Vendor recommendations for silica removal were ineffective, as shown by jar tests at Raft River. This report does not consider options for scale control, but aggressive investigation for adequate control measures is very important.

- 2.1.4 The possibility of drilling shallow wells to acquire better quality water is under consideration. Such water is expected to contain about 200 ppm chloride, a major aggressive ion, and about 40 ppm silica. Silica removal from this water would be required. This groundwater is also expected to be very corrosive to carbon steel.

- 2.1.5 The replacement of critical components with materials of suitable corrosion resistance, though the best long-term solution to the problem, is not acceptable in the short term because of schedule constraints and because much of the cooling loop plumbing would have to be replaced.

- 2.1.6 Selection of suitable materials for replacement of the present system, or for use in future plants, requires extensive materials tests.
 - 2.1.6.1 No evidence of materials tests relevant to the aggressive cooling loop fluid can be found.

 - 2.1.6.2 With few exceptions, sea-water experience and practices should not be applied to geothermal materials selection concerns.

3.0 ASSESSMENT OF RISK DUE TO PITTING UNDER INADEQUATE
TREATMENT CONDITIONS

Since pitting is a localized form of corrosion, conventional corrosion rates based on weight loss cannot be used to indicate the severity of pitting. Furthermore, there is a statistical variation in the depth of pits such that pit depth is usually normally distributed {1}. Average pit depth is a poor measure of pit damage since, especially for a very leak-sensitive component such as the isobutane condenser, the deepest pit causes the leak.

Maximum pit depth is a better measure of pit damage, but maximum pit depths cannot be used to directly predict equipment life for several reasons. First, a wide variation, by a factor of two or more, can be expected in the maximum pit depth observed on replicate specimens {2}.

Second, the probability of finding a deeper pit increases when sample size is increased. For example, if there is a 20 percent chance of finding a pit of a given depth on a sample of unit area, the probability of finding a pit of that depth on a sample four times larger is virtually 100 percent, and there is a 90 percent chance of finding a pit twice as deep as the one sought {1}. Extreme Value Analysis, discussed below, compensates for the effect of increasing area.

Third, propagation rates of individual pits are erratic. Some will speed up, others will slow down. It is rare for pit depths to increase linearly with time and in some cases the rate increases with time.

These factors justify the position that a satisfactory service life for thin wall leak critical components, such as

the lube oil coolers and the isobutane condenser, requires a zero pitting condition.

3.1 Extreme Value Analysis of Preliminary Pitting Data

Extreme Value Analysis (EVA) is a statistical technique used to evaluate pitting damage to high pressure gas lines {2}. EVA allows calculation of the probable maximum pit depth to be found on a large area, based on the maximum pit depth on replicate small area samples. EVA requires that the small samples be from the same population. During the one week tests at Raft River {3}, the coupons were exposed to what at first appears to be a wide range of inhibitor/chloride levels. However, as will be shown in Section 4, the critical factor in such environments is the log ratio of aggressive and inhibitor ions. Since inhibitor level was increased as the chloride level increased, it turns out that little variation in this parameter occurred and these results are tentatively considered to represent a single population suitable for EVA. This analysis will illustrate the severity of the pitting hazard for the existing heat exchangers under inadequate treatment conditions. The method of EVA is outlined below and the Raft River data is analyzed on the worksheet which follows.

The first step in the analysis is to rank the maximum pit depths from smallest to largest, pairing each with a sequential ranking factor (M). The maximum pit depth is the "x-variate" (x). The "reduced y-variate" (y) is given by:

$$y = -\ln \left(-\ln \frac{M}{n+1} \right) \quad (3.1)$$

where: y = reduced y-variate
M = rank value
n = total number of samples
(ln is the natural logarithm)

A plot of maximum pit depth as a function of the reduced y-variate is linear and has the form:

$$x = my + b \quad (3.2)$$

where: x = x-variate (maximum pit depth)
 y = reduced y-variate

The values of m and b are determined by linear regression techniques.

The "return period" is defined as the ratio of the area of the component under analysis and the area of a single sample, or:

$$R = \text{total area/sample area} \quad (3.3)$$

Like the reduced y-variate, R is unitless.

The reduced y-variate corresponding to a given return period (y') is given by:

$$y' = \ln R \quad (3.4)$$

Substitution of y' into equation 3.2 gives the extreme value of pit depth (x') for the entire surface of the component under analysis. There is a 50 percent probability {2} that the maximum pit depth will be greater than x' and the 95 percent probability limits, for values of y' greater than y_n , are given by:

$$95\% \text{ probability limits} = x' \pm 3.067m \quad (3.5)$$

The probability is 95 percent that the maximum pit depth will lie between these limits.

The EVA of the Raft River data, shown on the worksheet which follows, indicates that if the isobutane condenser is exposed to spent geothermal derived cooling water similar to that produced by the present treatment program, after one week the maximum pit depth will be 136 to 196 μm (95 percent probability limits).

Via testing, nothing is known about the effect of time upon the increase in maximum pit depth in the Raft River cooling system. In the absence of more complete test data the penetration rate is taken to be linear. Using the results of the EVA, there is a 95 percent probability that perforation of the 0.085 inch (2159 μm) isobutane tube walls will occur at sometime between 11 and 16 weeks of operation. Actual penetration time can be greater or shorter than this interval.

3.2 Mitigation of the Pitting Hazard

The normal method of mitigation of pitting is to select materials which will not pit under expected operating conditions. Because the carbon steel (unacceptable material) heat exchangers are in place, and because of schedule constraints, the treatment of the cooling water to inhibit pitting is required. The possibility of use of anodic inhibitors for this purpose is investigated in the next section.

WORKSHEET
EXTREME VALUE ANALYSIS
RAFT RIVER ISOBUTANE CONDENSER

Rank M	Max. pit depth (μm) X	Reduced y-variate Y
1	22	-0.9962
2	25	-0.7006
3	26	-0.4759
4	27	-0.2790
5	28	-0.0940
6	29	0.0874
7	29	0.2716
8	31	0.4642
9	32	0.6717
10	37	0.9027
11	39	1.1707
12	50	1.4999
13	53	1.9442
14	53	2.6738

$$X = 9.659 y + 29.431$$

$$\text{corr}^* = 0.96$$

Return period (R)

$$\text{coupon area} = 3 \text{ in}^2$$

$$\text{Isobutane condenser area} = 30,000 \text{ ft}^2 = 4.32 \cdot 10^6 \text{ in}^2$$

$$R = 4.32 \cdot 10^6 \text{ in}^2 / 3 \text{ in}^2 = 1.44 \cdot 10^6$$

Extreme value (x')

$$\begin{aligned} x' &= 9.659 \ln 1.44 \cdot 10^6 + 29.431 \\ &= 166 \text{ } \mu\text{m} \end{aligned}$$

95 percent probability limits

$$\text{limits} = 166 \pm 3.067 (9.659)$$

$$\text{lower limit} = 136 \text{ } \mu\text{m}$$

$$\text{upper limit} = 196 \text{ } \mu\text{m}$$

* corr = correlation coefficient. ± 1 signifies a perfect linear correlation. Zero indicates no correlation.

4.0 PRELIMINARY INVESTIGATION OF INHIBITORS CAPABLE OF
PREVENTING PITTING IN NEUTRAL AERATED CHLORIDE/
SULFATE WATERS

This section presents a brief discussion of the mechanism of pit initiation and growth and the action of inhibitors. A basis for estimating the amount of chromate (CrO_4^{-2}), molybdate (MoO_4^{-2}), or nitrite (NO_2^{-}) required to prevent pit initiation of carbon steel in aerated chloride and sulfate waters is presented. A method of calculating the "uniform" corrosion rate of carbon steel in aerated nitrite/chloride and nitrite/sulfate systems is discussed. Equations presented in this section will be applied to the Raft River cooling loop situation in Section 5.

4.1 Mechanism of Pit Nucleation and Propagation

Nucleation of localized corrosion at occluded sites (under deposits and in crevices) is widely accepted to result from differential aeration. In the occluded area, the chloride concentration rises to three to ten times the concentration in the bulk solution and the pH drops to about 2 {4}. The small occluded area serves as a fixed anode, while the large unoccluded area is a cathode where oxygen reduction provides the driving force for the propagation of the localized attack.

Nucleation of pits on clean metal surfaces occurs by a different mechanism. According to current thinking {5-10}, in neutral water free of aggressive ions, especially chloride and sulfate, the surface of steel is protected by a metal oxide film, probably Fe_2O_3 , about 1 nm thick.

Chlorides will adsorb to the metal oxide surface, especially at film defects (high surface energy areas). When the local chloride concentration level exceeds a certain level, the insoluble iron oxide film is converted to soluble iron chlorides, exposing the bare metal surface. This surface is anodic to the metal oxide and because of the large cathode-to-anode ratio, rapid dissolution of the iron (as ferrous ions) will occur. When these ferrous ions reach the bulk solution, they will precipitate, forming a porous deposit or cap over the nucleation site. Thus, an occlusion cell has been formed. Again, the driving force for the propagation of the pit is the reduction of oxygen at the large metal oxide cathode.

The amount of chloride required to nucleate pitting on a clean steel surface in uninhibited aerated water at ambient temperature is not exactly known but is quite low. Kolotyrkin {7} gives the threshold as 13 ppm while Vetter and Strehblow {11} give a value of 18 ppm.

4.2 Inhibitor Action

Uniform corrosion of steel in aerated water can be inhibited if either the metal dissolution reaction (anodic process), or the oxygen reduction reaction (cathodic process) is blocked.

It is very important that the system be kept clean and free of deposits because inhibitors do not work well through deposits. Any water treatment program must completely prevent deposition of scale and must control microorganism growth.

Cathodic inhibitors (such as zinc, polyphosphates and phosphonates) form films, often of visible thickness {12} on the

metal surfaces. These films reduce the rate of oxygen reduction reaction. These inhibitors reduce the rate of uniform corrosion, and, because the driving force of localized corrosion in aerated systems is oxygen reduction, these inhibitors should reduce the rate of pit propagation. These inhibitors do not prevent the nucleation of pits in saline cooling waters {13}. As previously argued, any pitting may represent a large hazard to the isobutane condenser and lube oil coolers.

Anodic inhibitors such as chromate, molybdate and nitrite act by adsorbing to the metal oxide film {5-10}. The adsorbed inhibitor ions strengthen the metal oxide film and occupy adsorption sites that are then not available to aggressive ions such as chloride or sulfate. If the dosage of anodic inhibitor is sufficient, so few sites will be available to the aggressive ion that nucleation of pits will not occur on a clean metal surface. If, however, the dosage rate is insufficient, enhanced pitting will occur {5, 6, 12, 14-16}. It is essential, therefore, that the minimum amount of anodic inhibitor required to prevent pit initiation be determined, and that dosage levels be maintained above this level.

4.3 Minimum Anodic Inhibitor Requirements (Critical Inhibitor Concentration)

Mercer et.al., determined the minimum amount of chromate {14}, nitrate {15} and molybdate {5} required to prevent any localized attack (pitting or crevice corrosion) of carbon steel by chloride or sulfate ions in aerated quiescent water at 77°F. Test duration was 100 days. A linear log-log relationship was found between the concentration of aggressive ion and the concentration of inhibitor required to just prevent localized attack. This is the critical inhibitor concentration. This sort of relationship is to be expected from the competitive adsorption theory of inhibition {5-10}.

Mercer et. al. investigated aggressive ion concentrations of 10^{-4} to 10^{-1} M. Gouda and Sayed {6} extended these tests to 10^{-6} M aggressive ion and discovered a threshold aggressive ion concentration below which the critical inhibitor concentration is constant.

The results of these studies will be summarized in the following sections. In applying these results, several points must be considered. The critical inhibitor concentration is the amount which will just prevent localized attack. Insufficient inhibitor will cause serious pitting. Therefore a suitable safety factor should be applied. Stagnant conditions require more inhibitor than flowing conditions, so the critical concentrations generated may be conservative (high).

No studies could be found which indicate the combined effects of chloride and sulfate. Chloride and sulfate ions compete not only with inhibitor ions for adsorption sites, they also compete with each other. Thus there should be an element of "interference" when both are present in solution. It is therefore assumed, as a first approximation, that the critical inhibitor concentration in a chloride/sulfate/inhibitor system is the sum of the critical inhibitor concentrations due to chloride and sulfate. This estimate is probably high because of the interference mentioned above.

For convenience, in the following sections, molar concentrations have been converted to mass concentrations. All concentrations are ppm. Unless otherwise indicated, threshold values are from Gouda {6} and critical inhibitor concentrations are from Mercer et. al. {5, 14, 15}.

4.3.1 Chromate In Aerated Water

The threshold chloride concentration is 0.4 ppm. Below this level, the critical chromate concentration is 66 ppm. Above 0.4 ppm Cl^- the critical chromate concentration is:

$$\text{critical } \text{CrO}_4^{-2} = 1.25 \cdot 10^2 (\text{Cl}^-)^{0.69} \quad (4.1)$$

The sulfate threshold is 3 ppm and the critical chromate concentration below this level is 53 ppm. Above 3 ppm SO_4^{-2} the critical chromate concentration is:

$$\text{critical } \text{CrO}_4^{-2} = 2.52 \cdot 10^1 (\text{SO}_4^{-2})^{0.67} \quad (4.2)$$

If the chromate dosage is less than the critical chromate concentration, the onset of pitting is rapid, usually on the order of minutes [14], and pitting may be more severe than if no chromate were used.

4.3.2 Molybdate in Aerated Water

No threshold values for chloride or sulfate could be found for molybdate but these values are assumed to be on the order of a few ppm or less. For the molybdate/chloride system, the critical concentration is:

$$\text{critical } \text{MoO}_4^{-2} = 7.88 \cdot 10^2 (\text{Cl}^-)^{0.76} \quad (4.3)$$

while for the molybdate/sulfate system, this concentration is given by:

$$\text{critical } \text{MoO}_4^{-2} = 3.73 \cdot 10^1 (\text{SO}_4^{-2})^{0.83} \quad (4.4)$$

4.3.3 Nitrite In Aerated Water

The threshold concentration of chloride in this system is 10 ppm. At less than 10 ppm Cl^- , the critical nitrite concentration is 6.5 ppm while above 10 ppm Cl^- the critical concentration is given by:

$$\text{critical NO}_2^- = 6.50 \cdot 10^{-1} (\text{Cl}^-)^{1.0} \quad (4.5)$$

Nitrite is much more susceptible to sulfate than chloride. The sulfate threshold is 1 ppm and below this level the critical nitrite concentration is 17 ppm. Above 1 ppm SO_4^- the critical concentration is:

$$\text{critical NO}_2^- = 1.66 \cdot 10^1 (\text{SO}_4^{-2})^{0.62} \quad (4.6)$$

At inhibitor levels less than the critical nitrite concentration, pit induction times may be several days or even weeks {15}. The length of the induction period of pitting indicate that tests should be run for seventy days to assure detection of pitting {15},

Studies of up to 150 days {16} in nitrite/chloride solutions in which the nitrite was just less than the critical concentration show that maximum pit depths are proportional to the square root of the exposure period, or:

$$d = at^{0.5} \quad (4.7)$$

where: d = maximum pit depth
 t = exposure time
 a = empirical constant

Kononova and Yudina {8} investigated critical nitrite concentration as a function of chloride concentration in aerated water at 122°F. Flow conditions are not stated, but the methods used suggest quiescence. They found the following relationship:

$$\text{critical NO}_2^- = 1.12 \cdot 10^{-1} (\text{Cl}^-)^{1.1} \quad (4.8)$$

Comparison of the pre-exponential terms in equations 4.1 and 4.2 with equations 4.5 and 4.6 show that in aerated, neutral solutions nitrite is more effective than chromate for inhibition of pit nucleation. Comparison of equations 4.5 and 4.8 indicate that the critical nitrite concentration decreases with temperature in the range of 77-122°F.

4.4 Estimation of Corrosion Rate of Carbon Steel in Neutral Aerated Chloride and Sulfate Solutions Inhibited by Nitrite

This section develops a method for calculating the "uniform" corrosion rate in nitrite/chloride and nitrite/sulfate systems. This method will be applied in Section 5.

Legault et al. {10} used linear polarization methods to measure the corrosion rate of carbon steel in aerated nitrite and chromate solutions at 77°F containing chloride or sulfate from 1 to 10,000 ppm. They found that in aerated solutions, nitrite is more effective than chromate in reducing uniform corrosion rate. This is contrary to the prevailing assumption, based on treatment of closed loop systems.

Legault found that

$$R = A + B \log \frac{[\text{agressor ion}]}{[\text{inhibitor ion}]^n} \quad (4.9)$$

where R is reciprocal slope of the linear polarization curve and has units of $\mu\text{A cm}^{-2}\text{V}^{-1}$. A and B are empirically derived constants. The relationship expressed by equation 4.9 is consistent with the competitive adsorption mechanism of inhibition.

The corrosion current density, which is proportional to corrosion rate is given by:

$$i_{\text{corr}} = R K \propto \text{mpy} \quad (4.10)$$

where: R = reciprocal linear
polarization slope
K = emprical constant

Kononova and Yudina {8} have shown that for the nitrite/chloride system, $K = 0.016\text{V}$.

Using this value, the corrosion rate in mils/yr (mpy) can be calculated for the chloride/nitrite system. Thus, for the nitrite/chloride system using values of A, B and n published by Legault {10}.

$$\text{corr} = 50.5 + 46.0 \log \frac{[\text{CL}^-]}{[\text{NO}_2^-]^2} \quad (4.11)$$

where corr is the uniform corrosion rate in mpy and concentrations are molar.

Assuming that Kononova's value of K is valid for the nitrite/sulfate system,

$$\text{corr} \approx 47.2 + 50.0 \log \frac{[\text{SO}_4^{-2}]}{[\text{NO}_2^-]} \quad (4.12)$$

where the units are as previously defined.

No studies of the aerated nitrite/chloride/sulfate system were found. As in the case of critical inhibitor concentration, as a first approximation, it is suggested that the corrosion rate due to chloride and the corrosion rate due to sulfate can be added. This process does not account for "interference" between chloride and sulfate, so the resulting estimate is probably conservative (high).

5.0 IMPACTS OF CRITICAL INHIBITOR CONCENTRATION
REQUIREMENTS FOR THE RAFT RIVER COOLING SYSTEM

This section presents estimates of the amount of chromate, molybdate and nitrite required to prevent initiation of pitting of carbon steel in the cooling loop at Raft River. Use of these inhibitors at concentrations less than the critical inhibitor concentration, the amount that will inhibit pitting, may lead to enhanced pit growth.

As was discussed in Section 2, spent geothermal fluid will be used as cooling water make-up. Table 1 gives the nominal composition of the raw fluid, and its composition after warm lime-magnesium chloride treatment to reduce carbonate and silica. The treated water has pH approximately 8 with approximately 1500 ppm Cl^- and 65 ppm SO_4^{2-} . Cycles of concentration are limited to fifteen by the solubility of gypsum. This water is referred to as Case I in the following discussion.

An alternative to Case I is the drilling of a number of shallow wells which will produce low silica, low chloride water. This water has been estimated to contain about 200 ppm Cl^- . No information on sulfate levels, or restrictions on cycles of concentration by gypsum solubility, are available. This water is defined as Case II.

Inhibitor requirements were calculated for Case I assuming that requirements due to individual aggressive ions are additive as discussed in Section 4.3. Requirements for Case II are based on chloride only and will change drastically if this water has a high sulfate level.

It will be shown in Sections 5.1 and 5.2 that the amounts of chromate and molybdate required to prevent pit initiation are extremely large. The amount of nitrite required, as shown in 5.3.1, is probably acceptable. Several important questions, discussed in Section 5.3.2, remain in connection with the possible use of this inhibitor.

5.1 Chromate Inhibitor

Based on equations 6.1 and 6.2, the critical chromate concentrations for Case I are 20,000 ppm (2.0 percent) at one cycle of concentration and 82,000 ppm (8.2 percent) at eight cycles of concentration.

Assuming that 200 ppm hexavalent chromium is the maximum allowable for occupational health and environmental reasons, chloride cannot exceed approximately 7 ppm without pitting of the steel at this hexavalent chromium level.

5.2 Molybdate Inhibitor

The critical molybdate concentration at one cycle of concentration of Case I feedwater is 200,000 ppm (20 percent).

The critical molybdate concentration for Case II water is 44000 ppm (4.4 percent) at one cycle of concentration and 200,000 ppm (20 percent) at eight cycles of concentration.

5.3 Nitrite Inhibitor

5.3.1 Critical Nitrite Concentration

The critical nitrite concentrations in Case I water at 77°F are 120 ppm (0.12 percent) at one cycle of concentration,

TABLE 1. RAFT RIVER COOLING WATER CHEMISTRY {17}

Parameter	Untreated Makeup ¹	Treated Makeup ²
T°F	140	NR
pH	8.2	~8
	<u>ppm</u>	<u>ppm</u>
Silica	200	10-15
SO ₄	65	65
Cl	1000	1200-1500
Na	650	780
F	9	9
Total Alkalinity ³	40	NR
Total Hardness ³	140	100
H ₂ S	0.5	NR
NH ₃	0.03	NR
O ₂	None	NR

¹Raft River geothermal fluid

²Warm lime softening (MgCl₂-lime-soda ash)

³As CaCO₃

NR - Not reported

8600 ppm (0.86 percent) at eight cycles of concentration and 16,000 ppm (1.6 percent) at fifteen cycles of concentration.

In Class II water the critical nitrite concentrations at one, eight and fifteen cycles of concentration are 130 ppm (0.013 percent), 1000 ppm (0.10 percent) and 1500 ppm (0.15 percent). Figure 2 shows the critical nitrite concentration (solid lines) and dose rate assuming an arbitrary safety factor of 1.5 (broken lines) for Case I and Case II waters.

It should also be noted that equation 4.8 shows that the requirement of nitrite is lower at 122°F than at 77°F. This indicates that dosages based on 77°F requirements may be adequate for the temperature range expected in the cooling loop.

Using only equation 4.11, the estimated uniform corrosion rates for steel in Case I and Case II aerated water at 77°F, treated with the critical nitrite concentration, are less than 2 mpy at all cycles of concentration considered. Provided that the nitrite level is maintained above the critical concentration, no pit nucleation should occur.

5.3.2 Unresolved Points About Use of Nitrite

Nitrite is used in closed loop systems {12} and its use in once-through systems has been reported {8}, but during this preliminary effort, no discussion of its use in recirculating cooling tower systems was found. Several important questions require answers before use of nitrite can be recommended.

5.3.2.1 Consumption Rate In Cooling Tower

In the work by Mercer et. al. {5, 15}, solutions of nitrite were aerated by exposure to atmosphere for 100 days. Gouda and

Sayed {6} used similar methods for 45 day exposures. In the work by Legault et al {10}, air was bubbled through the nitrite solutions for 72 hours. In none of these reports was any mention made of oxidation of nitrite to nitrate, and no provision for refreshing the test solutions was reported. However, nitrite is oxidizable, and its rapid destruction in the cooling tower is a possibility. This would preclude its use because very large feed rates would be required.

5.3.2.2 Consumption By Metal Surfaces

Some consumption of inhibitor by the metal being treated occurs. The consumption rate for nitrite in the Raft River system is not known.

5.3.2.3 Microbiological Factor

Nitrite is a nutrient to both nitrate-forming and ammonia-forming bacteria. If nitrite is acceptable from a cooling tower oxidation standpoint, its use could pose prohibitive microbiocidal requirements.

5.3.2.4 Compatability With Other Treatment Agents

A viable treatment plan will include dispersants and antifoulants to prevent disposition, as well as cathodic inhibitors (such as zinc, polyphosphate, or phosphonates) to retard penetration of initiated pits and to reduce crevice corrosion. Compatability of nitrite with these agents is not known.

Figure 2: Nitrite Dosage Requirements for Pitting Inhibition of Carbon Steel in the Raft River Cooling Loop.

6.0 CONCLUSIONS

6.1 Operation of the cooling loop without adequate inhibitor may result in isobutane condenser failure in less than 16 weeks. Charging with water for check-out tests, without adequate inhibition, will result in either tube failure prior to start-up, or damage to such an extent that future treatment efforts will be jeopardized.

6.2 An acceptable treatment program for this aggressive cooling water should:

- completely inhibit pitting
- contain sufficient cathodic inhibitors to mitigate crevice corrosion
- completely prevent scaling
- contain sufficient antimicrobial agents to prevent slime fouling.

6.3 It is doubtful that cathodic inhibitors (such as zinc, polyphosphates, and phosphonates) alone can prevent pitting in this environment, but they may retard penetration rates enough to provide a satisfactory service life. This is the approach taken in some saline water systems [13].

6.4 Chromate or molybdate-based systems are not acceptable because of the extremely large dose rates required. In the case of chromate, these dosages pose extreme health and environmental hazards.

6.5

Sodium nitrite appears to offer a good chance of inhibition of pitting at acceptable concentrations in aerated geothermal derived cooling water. A number of important questions, such as consumption rate in the cooling tower, effect on microbiological (slime) control, and compatability with other agents must be answered before this agent can be recommended.

7.0 RECOMMENDATIONS

To develop a satisfactory and timely solution to the Raft River cooling water problems, the following parallel paths are recommended.

- 7.1 Immediate effort to develop a scale deposition and microorganism control system (treatment program). Complete prevention of scaling and slime (microorganism) fouling is required regardless of what other options are selected.
- 7.2 Immediate testing of the best available conventional corrosion treatment system of the type used to treat brackish or salt water cooling tower systems. Such a system is discussed in Reference 13. These systems, based on cathodic inhibitors (such as zinc, phosphonates and polyphosphates) will not stop pitting, but may greatly reduce the penetration rate. This test should be designed to provide data for Extreme Value Analysis (EVA) at several points in time in order to provide a reliable basis for predicting component life. Such a test requires:
- Exposure of identical coupon sets for various time periods. EVA's (data points) for at least four exposure periods are required.
 - Exposure of a minimum of ten replicate coupons of the largest practical area for each EVA. The large number of coupons is inherent in the EVA method.

- Testing of "hot finger" heat transfer surfaces to evaluate the effect of heat transfer, which may significantly alter corrosion behavior.

Work in this recommendation should begin immediately, but actual exposure of coupons is meaningless until recommendation 7.1 is complete.

7.3 Investigation to determine the feasibility of using nitrite to inhibit pitting of existing heat exchange surfaces. Immediate questions to be answered are:

- Will oxidation to nitrate in the cooling tower be excessive?
- Will nitrite cause unacceptable microbiological control problems?
- Is nitrite compatible with agents required in 7.1?

7.4 If necessary, delay charging of the cooling loop until a satisfactory treatment has been demonstrated. Charge-up without adequate treatment will seriously damage the isobutane condenser and lube oil cooler and could cause failure prior to the plant start-up.

7.5 Immediate start of materials tests to select alternative pit resistant materials for replacement components in the event that adequate corrosion inhibition of carbon steel is not obtained. This effort would also support any future power plant development at this or similar geothermal resources.

- 7.6 Immediate characterization of the fluids from all wells at Raft River. This effort supports all the preceding recommendations. The necessary analyses can be performed by DOE/PNL at no cost to EG&G, Inc.
- 7.7 Reroute feedwater make-up to top of cooling tower to avoid a thermodynamic penalty.

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