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CORROSION ENGINEERING IN THE UTILIZATION OF THE RAFT RIVER GEOTHERMAL RESOURCE

by

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CORROSION ENGINEERING IN THE UTILIZATION OF THE RAFT RIVER GEOTHERMAL RESOURCE

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ABSTRACT

The economic impact of corrosion and the particular problems of corrosion in the utilization of geothermal energy resources are noted. Corrosion is defined and the parameters that control corrosion in geothermal systems are discussed.

A general background of corrosion is presented in the context of the various forms of corrosion, in relation to the Raft River geothermal system. A basic reference for mechanical design engineers involved in the design of geothermal energy recovery systems is provided.

SUMMARY

Corrosion is one of the primary problems in the utilization of geothermal energy. The proper application of corrosion engineering fundamentals to potential problems will reduce, to a great extent, the effects of the aggressiveness of the geothermal brines.

This report is intended to be a preliminary guide for design engineers supporting the Raft River Geothermal Project. Others who may have a sketchy background in corrosion engineering may also find it to be a useful reference. Data for materials stability in geothermal brines are relatively limited; for this reason the presentation is rather pedagogical. An effort has been made to bring together portions of the available corrosion literature that will apply to corrosion engineering at Raft River. Because the Raft River brines have a somewhat lower dissolved solids content than that of seawater (and may be referred to as hyposaline brines), frequent reference is made to the compatibility of materials in seawater as a first approximation to Raft River conditions. A test program has been initiated to remove the uncertainties associated with materials selection and corrosion control.

Corrosion is, principally, an electrochemical process. Metal surfaces in contact with geothermal brines consist of localized areas that are relatively cathodic (protected) or anodic (corroded). While the site polarities will vary from time to time to yield an essentially uniform corrosion rate, some localized corrosion may occur.

Temperature plays an active role in corrosion processes. As temperature increases, the rate of corrosion is accelerated. The solubility of oxygen in water decreases with increasing temperature over the range of temperatures of interest in the Raft River geothermal resource. Since oxygen is, typically, the most active oxidizing agent in geothermal brine systems, the decrease in oxygen solubility with increasing temperature offsets, to a limited degree, the effect of temperature. Geothermal fluids are largely free of dissolved oxygen as a result of chemical reaction of dissolved meteroic oxygen with underground rocks.

Stresses, whether residual or applied, tend to increase the rate of corrosion by supplying a portion of the energy required to promote a reaction. Crystal lattice disorder introduced by these stresses also contributes to accelerated corrosion.

Many corrosion processes are controlled by diffusion of an oxidizing agent, or perhaps a corrosion inhibitor, through a solution boundary layer. The thickness of the boundary layer is governed by the rate of fluid flow past a metal surface. Thus, velocity is important in determining the rate of corrosion.

Localized corrosion takes on many forms, and is controlled by many variables. In galvanic corrosion, for example, the concentration of electrolyte determines, to some extent, the sharpness of grooves or pits. In crevice and pitting corrosion high chloride concentrations (always present in geothermal brines) are especially bad. The synergistic effects of chlorides and dissolved oxygen in stress corrosion cracking and corrosion fatigue is such that use of stainless steel in many geothermal applications may be precluded. The neutral or slightly basic pH of the Raft River geothermal brines is very favorable with respect to reducing hydrogen damage. The presence of suspended sand or other material in the brine may cause some erosion corrosion problems. Removal of the particulate material prior to the heat exchange cycle should reduce erosion effects in the system. Cavitation in pumps is frequently accompanied by corrosion and will require constant surveillance to avoid unexpected downtime.

A program of testing and evaluation of materials in the Raft River brine prior to construction of the demonstration power plant should provide much of the materials design data required for plant fabrication and operation. Careful materials selection, surveillance during operation, and application of corrosion control measures should reduce the corrosion problem to a manageable level.

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1. INTRODUCTION

The potential for geothermal energy in making a sizable contribution toward supplying the nation's energy needs lies largely in the more abundant medium-temperature reservoirs(1). This document is addressed, primarily, to corrosion of metals in electric power generating plants using medium temperature geothermal heat sources. Other areas of concern in the utilization of medium-temperature geothermal heat are shown in a proposed geothermal energy park, Figure 1.1.1(2). Corrosion and selection of materials for these additional uses are not discussed.

The economic impact of corrosion in the United States is much larger than most people realize, with an estimated loss in the U.S.A. of more than $10,000,000,000 per year. For example, the quantity of iron lost to corrosion is estimated to be one fourth to one third of the annual production(3). Detailed economic analyses of the various corrosion control measures is beyond the scope of this report. Several approaches (models) to economic evaluation of corrosion control practice are available(4,5,6). The NACE (National Association of Corrosion Engineers) (6) approach is the most comprehensive and is recommended when sufficient data are available.

In the perspective of geothermal energy utilization, corrosion is considered to be one of the major factors influencing the expected life of energy conversion systems(7). Much of the data regarding corrosion in geothermal systems was reported by workers in New Zealand. Marshall and Braithwaite(8) have reviewed much of this literature. More recently Banning and Oden(9) have reviewed the literature on corrosion in hot brines, including the geothermal literature. The conclusions of these reviewers will be noted and the relevant data pointed out as various corrosion phenomena are discussed.

The application of the theory and practice of corrosion engineering to potential corrosion problems in the Raft River Geothermal Experiment (RRGE) should result in improved energy utilization, more reliable design criteria, reduced losses of metal and a decrease in unscheduled

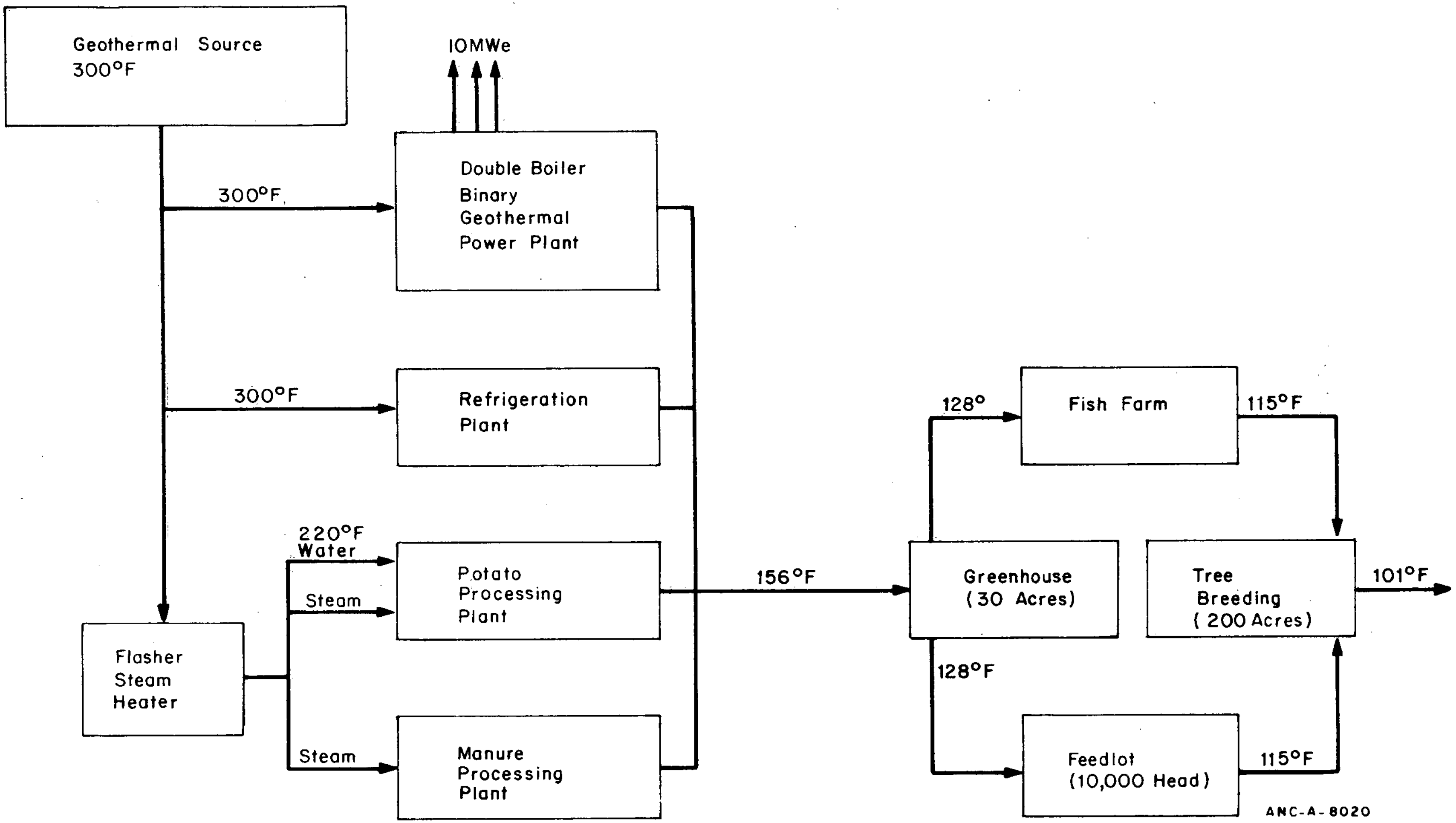

Figure 1.1.1 Geothermal Energy Park Flowsheet with Power Plant(2) and Non-Electric Geothermal Energy Utilization Factors.

shutdown of the facilities. Careful materials testing and plant design should result in safer operation of the facilities, especially in regard to catastrophic failure and release of large amounts of water or isobutane at temperatures up to 300°F.

The primary function of the RRGE is that of an engineering facility. This facility can be used to generate the expertise in materials technology, including corrosion engineering, required to effectively use energy from all geothermal resources. A materials testing station is planned as an important facet of the research and engineering programs at the RRGE facilities.

The purpose of this document is to briefly describe the various forms of corrosion and their relation to recovery and use of geothermal energy and techniques for controlling and/or preventing corrosion. The forms of corrosion exhibited by metals are numerous. Copson(10) has identified about 40 forms while Fontana and Greene(11) have reduced this number to 8 basic forms. For the purposes of the RRGE study the forms of corrosion are ranked into categories of importance.

The most serious forms of corrosion are:

1. Uniform or general corrosion
2. Crevice corrosion
3. Pitting corrosion
4. Stress corrosion cracking
5. Corrosion fatigue

The following four forms of corrosion are less important than those listed above:

1. Galvanic corrosion
2. Selective leaching
3. Erosion corrosion
4. Cavitation damage

Intergranular corrosion, fretting corrosion and hydrogen damage are thought to be of relatively little importance in the RRGE.

Corrosion is essentially an electrochemical process. Some aspects of electrochemistry are discussed under general or uniform corrosion. A detailed account of this important area is beyond the scope of this study; however, in discussion of some particular forms of corrosion additional details will be supplied in order to adequately describe the phenomena.

Corrosion rates are largely determined by several environmental parameters. The following factors are discussed briefly in relation to uniform or general corrosion:

1. Chemistry of the corrosion environment.
2. Temperature and heat transfer.
3. Solution velocity.
4. Residual and applied stresses.
5. The structure and composition of the metal.

The definition of corrosion in regard to geothermal brines is the degradation of properties of a material due to interaction with its environment. Within this definition more specific or detailed definitions are warranted.

Metals:

Corrosion of metals and alloys is the result of an electrochemical process involving the oxidation of the metal.

Concrete and similar composites:

Corrosion of concrete refers to leaching by chemical dissolution of the more active constituents of the cement resulting in loss of mechanical properties.

Plastics and similar organic materials:

Degradation of these materials results from interaction with the water, its dissolved constituents (such as H_2S), or by prolonged exposure to high temperature resulting in increased cross-linking. This may include loss of elasticity or plasticity due to leaching of plasticizers or to increased cross-linking by prolonged exposure to sulfur-containing gases.

Mechanical wear, cavitation and erosion are not corrosion processes unless the rate of property degradation is increased by the environment. If the rate of loss of mechanical property or material is increased by the environment then the process is properly classed as corrosion. A good example of this is erosion corrosion.

This study is addressed primarily to potential corrosion problems between metals (both pure metals and alloys) and the geothermal brine systems likely to be encountered in the RRGE. Plastics and other non-metallics such as wood, brick, concrete and ceramics may also be important in geothermal energy conversion but do not represent the main thrust of this work.

Solids and gases dissolved in water, and the water itself, are the corrosive agents in geothermal systems. The most troublesome species are oxygen, which is very low, about 0.02 ppm (mg of solute/kg of solution), and the chloride ion, which is relatively high, about 800 ppm. Oxygen is a strong oxidizing agent, i.e., it is easily reduced and therefore contributes to the corrosion process. The chloride ions combine with dissolved metal ions to form complex ions that perturb the electrochemical system (12); they also tend to destroy protective films of corrosion products. Other dissolved species also contribute to corrosion; for example, Fe^{+++} and Cu^{++} are easily reduced and tend to promote corrosion of structural materials; hydrogen sulfide, H_2S, tends to cause pitting in carbon steel (13).

The concentrations of dissolved solids in the Raft River geothermal brine are given in Table 1.1. The compositions of several other geothermal brines and seawater are given in this table for comparison with the Raft River brine. Dissolved-gas analyses for the Raft River and Boise, Idaho geothermal brines are given in Table 1.2. As water is produced from the aquifer, changes in the concentrations of the various constituents are likely to occur. Seasonal variations in water chemistry are also likely to occur as fresh water is added to the geothermal aquifer.

TABLE 1.1

APPROXIMATE CONCENTRATION OF DISSOLVED SOLIDS IN RAFT RIVER GEOTHERMAL WATER COMPARED WITH SEAWATER AND OTHER GEOTHERMAL SOURCES

	Seawater	Niland	Holtville	Wairakei	Reykjavik	Norris Basin	Mammoth Basin	Raft River	Boise
						(Yellowstone Nat'l. Park)			
T°C	Variable	232	165 - 180	240	100	81	90	140	80
pH	8.0	6.1	7.6	8.6	9.3	2.0	6.6	7.5	9.0
SiO_2	7.0	400	100	640	162	109	66	100	160
Li	0.1	210	55	14	---	---	2.3	1.3	0.05
Na	10,561	53,800	11,000	1,320	56	2	129	400	90
K	380	16,500	1,430	225	2.5	3	69	26	1.6
Mg	1,272	10	22	0.03	---	---	68	0.8	0.05
Ca	400	28,800	1,370	17	4	2.2	272	57	1.7
Sr	13	440	226	---	---	---	---	2.5	< 0.01
Ba	0.05	250	58	---	---	---	---	---	< 0.02
F	1.4	---	1.5	8.3	1.1	---	2.7	6.3	15
Cl	18,980	155,000	18,000	8,730	30	15	170	700	10
Br	380	---	35	---	---	---	---	< 2.5	---
SO_4	2,650	---	16	36	19	760	500	60	23
HCO_3	140	---	---	19	---	---	667	60	70
CO_3	---	---	---	---	---	---	---	19	4
S	---	30	< 1	---	---	---	2.6	0.1	trace
NH_3	0.05	---	39	0.2	---	30	1.0	7	---
Fe	10^{-9}	2,000	0.18	---	---	---	---	0.09	0.13
Mn	0.01	1,370	0.9	---	---	---	---	0.07	0.01
Ni	---	---	---	---	---	---	---	3.7	---

TABLE 1.2

NOMINAL CONCENTRATIONS OF GASES IN
RAFT RIVER AND BOISE GEOTHERMAL WATERS.
DATA ARE FOR STANDARD TEMPERATURE AND PRESSURE

	Iceland	New Zealand	Raft River	Boise
CO_2	90 ppm	92 ppm	16.4 ppm	0.20 ppm
H_2S	2.6	4.2	--	0.005
H_2	2.0	1.8	0.06	--
CH_4	.03	0.9	0.01	0.065
N_2	--	--	100	18.5
Ar	4.43	0.3	2.6	0.62
O_2	0.0	--	0.02	0.003

2. FORMS OF CORROSION IN METALS

The classification of corrosion by appearance of the attacked metal or by descriptive mechanism permits discussion of phenomena that are common to various materials or environments. This separation, where applicable, permits establishment of testing or simulation procedures.

The forms of corrosion noted in Section 1 are defined and discussed with their relationship to the RRGE system. Some forms of corrosion are more important than others. For example, uniform or general corrosion usually results in the greatest metal weight losses, while pitting and crevice corrosion usually result in the largest amount of system failure or downtime. Stress corrosion cracking and corrosion fatigue frequently cause the most spectacular or catastrophic corrosion-related failures.

The most severe forms of corrosion, relative to the RRGE system, are discussed in Section 2.1. Less important forms of corrosion are discussed in Section 2.2. The forms of corrosion that are thought to be of relatively minor importance in the RRGE system are discussed in Section 2.3.

A detailed discussion of the mechanisms of the various forms of corrosion is beyond the scope of this report. Fontana and Greene(11), Uhlig(14), and Tomashov(15) have elaborated on theories of corrosion processes; those interested in this aspect of corrosion are urged to consult these sources as well as the original literature for more information.

Corrosion prevention or control consists, essentially, of interfering with the mechanism of the corrosion process. Corrosion control is an appropriate subject for this report; the methods are outlined in the discussions of the forms of corrosion that follow. Details of corrosion testing practices are available from American Society for Testing and Materials (ASTM) and NACE. Testing methods are thought to be more appropriate to documents dealing with test plans and test results rather than to this overview of potential corrosion problems in Raft River geothermal system.

2.1 Potentially Severe Forms of Corrosion in the RRGE System

This section addresses forms of corrosion expected to significantly affect the reliability of the Raft River power plant.

2.1.1 Uniform or General Corrosion

Uniform or general corrosion is characterized by a more or less uniform decrease in the weight or thickness of the metal being corroded. Two types of uniform corrosion are common. In one, the corrosion products are soluble in the corrodant or form a non-adhering solid that is washed away. The mass of metal decreases approximately linearly with time as shown in Figure 2.1.1.

The other type of uniform corrosion is represented in Figure 2.1.2 where the corrosion product is shown to form an adherent film on the substrate metal. While the mass of metal decreases with time the mass of the specimen, for example, increases with time. The porosity of the film will markedly influence the rate of corrosion in this case. Metals forming highly porous films may show a linear corrosion rate where the rate of corrosion is proportional to the surface area, and the concentration of corrodant.

Diffusion through a film of corrosion products may be quite slow and decrease with time as the film increases in thickness. The rate of corrosion in this case is frequently described by parabolic or cubic equations. Parabolic corrosion rate processes are controlled by the rate of diffusion through a film of corrosion products that increases in thickness with time. The cubic corrosion rate is usually considered to be a combination of parabolic and logarithmic rate laws. The logarithmic rate law(14) describes a mechanism involving electron transfer through the corrosion film. The details of the corrosion rate laws are beyond the scope of this study.

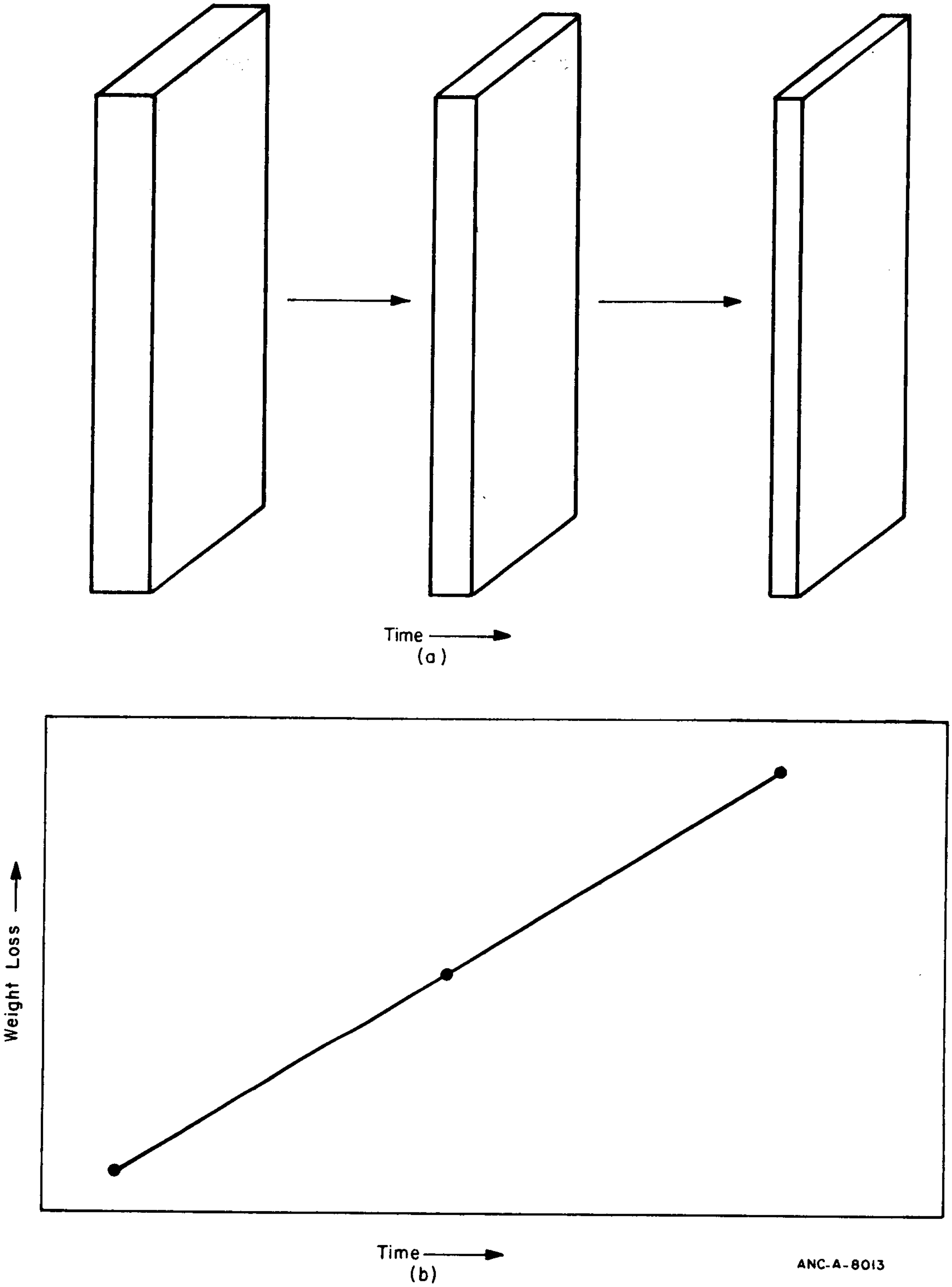

Figure 2.1.1 Schema of (a) uniform corrosion without corrosion product buildup and (b) weight loss (linear) of metal as a function of time.

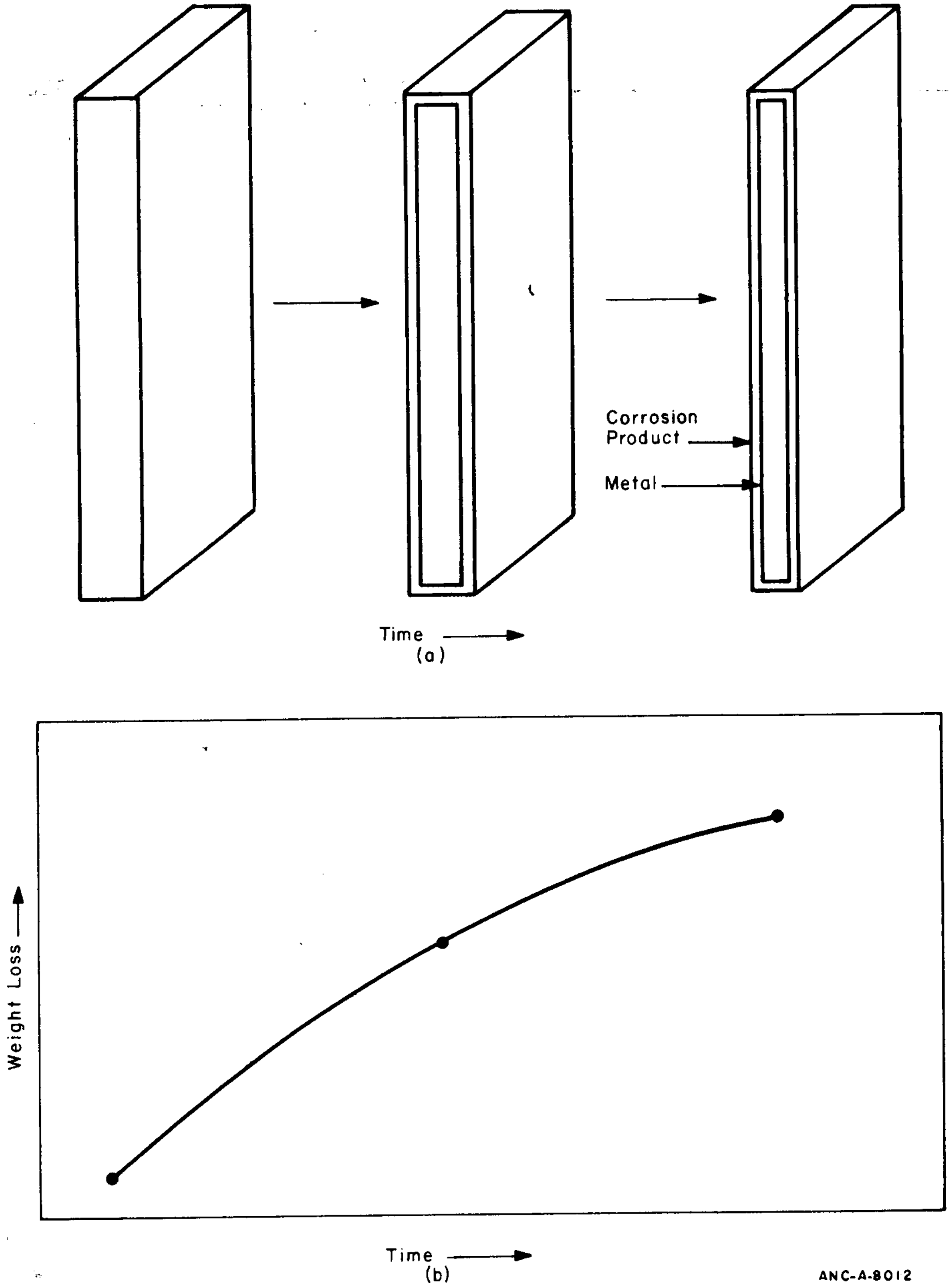

Figure 2.1.2 Schema of (a) uniform corrosion with corrosion product buildup on substrate metal and (b) weight loss (parabolic) of metal as a function of time.

Linear, parabolic and cubic corrosion rates are shown, schematically, in Figure 2.1.3. In the earliest stages of corrosion the differentiation of the three forms of corrosion rates may be difficult. In the later stages of corrosion the separation of parabolic and cubic rates is frequently difficult, owing to the scatter of experimental data.

The formation of corrosion product films is frequently essential for the protection of the substrate metal. If the formation of the film reduces the rate of corrosion, as in the parabolic and cubic cases, the film is said to be passive and the process is usually defined as passivation. On the other hand, if the film is nonprotective, i.e., does not retard the rate of corrosion, it is said to be non-passive.

Chlorides, and to a lesser extent bromides, tend to destroy the passive nature of films(11, 14). The ubiquitous occurrence of chlorides in geothermal brines thus tends to create the worst case, i.e., a linear corrosion rate. Uniform corrosion is expected to result in the greatest loss of metal in the RRGE system. The most frequent corrodant in systems experiencing uniform corrosion is dissolved oxygen. Since the RRGE brine is essentially free of oxygen the parts of the system most likely to experience uniform corrosion are the condenser/cooling-tower circuit, the brine return transmission lines, and the casing of the reinjection well.

Marshall and Braithwaite(8) noted that corrosion in geothermal systems in New Zealand is more pronounced than in the usual steam-boiler power plants but was usually low enough for practical design. Oxygen was noted as being especially aggressive. However, some New Zealand sources are highly acidic with the result that attack by the acid is the main source of corrosion.

Hermannsson(16) noted similar conditions in space heating systems in Iceland in regard to the aggressiveness of oxygen. For example, at a dissolved oxygen concentration less than about 1 ppm, little corrosion was noted on iron and zinc (galvanized iron pipe). At higher oxygen

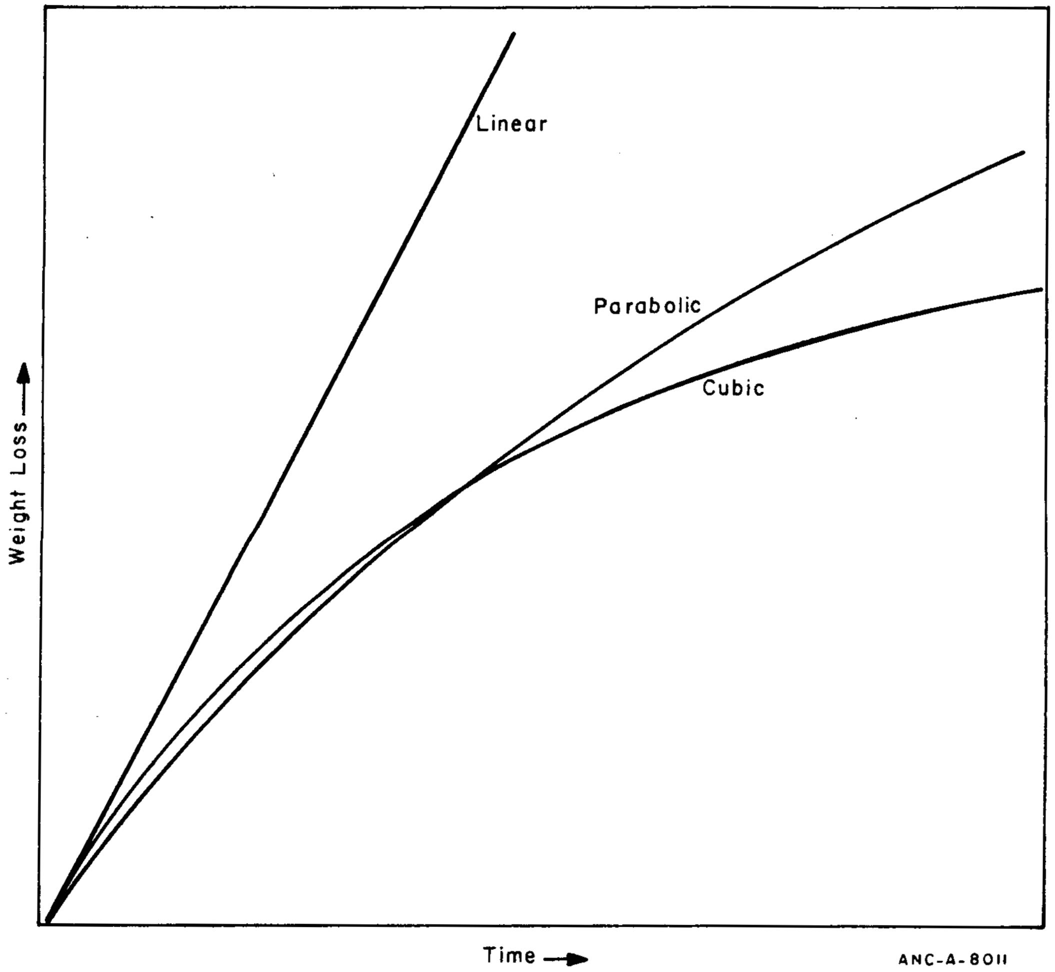

Figure 2.1.3 Comparing linear, parabolic, cubic corrosion rates.

concentrations, e.g., 7.5 ppm, zinc was rapidly "washed away" and brass was severely attacked. Hermannsson noted that sulfite at concentrations of ten times that of the oxygen controlled this form of attack. The mixing of water containing small amounts of sulfides with oxygen-bearing water was also effective in controlling this form of attack. Hermannsson also noted that silica tended to deposit on corrosion scales to a much greater extent than on uncorroded substrates.

Toliva(17) studied corrosion in a number of geothermal systems at Cerro Prieto, Mexico. Much of the corrosion observed in these tests was attributed to sulfides in the brines. Stainless steels in aerated steam showed corrosion rates that were ten times those in air-free steam, once again pointing out the exacerbating effect of oxygen.

Carter and Cramer(18) tested a number of materials in Imperial Valley brines in a study to identify materials that might be useful in geothermal applications. Carbon steel showed a high corrosion rate while copper and copper-based alloys showed slightly better resistance. As might be expected, the Hastelloys*, Inconels and other alloys of high nickel and chromium content showed good resistance. Titanium alloys also had good resistance to corrosion. While these materials were resistant to the Imperial Valley brines they are probably not economically justified in the less-aggressive Raft River waters.

In the Raft River power plant system general corrosion is expected to occur mostly in the cooling towers and on the water side of the isobutane condensers. Chemical treatment of the cooling tower water will be required to keep corrosion rates within acceptable limits. Without treatment the corrosion rate on carbon steel is expected to be about 6 mpy (0.152 mm/year) while effective control will reduce the corrosion rate to 1-2 mpy (0.025-0.051 mm/year). A corrosion rate of 1 mpy (0.025 mm/year) is acceptable while a corrosion rate of 2 mpy (0.051 mm/year) is not.

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* Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Energy Research and Development Administration or the Aerojet Nuclear Company, Inc. to the exclusion of others that may be suitable.

From the corrosion rate data in the above references a preliminary selection of materials can be made. Carbon steel might be acceptable if an effective cooling water treatment can be found and maintained. Monel 400, 70/30 cupronickel, or 90/10 cupronickel would be much better. The 70/30 cupronickel alloy was found to be especially effective in a power plant using seawater as the coolant(19). Corrosion of metals in a seawater environment provides a reasonably good approximation to geothermal systems for preliminary design purposes. Figure 2.1.4 shows general corrosion of a number of materials in quiescent seawater(19) and is useful as a first approximation in designing systems for the Raft River power plant. Of the materials shown in this figure the copper-nickel alloys appear to be among the more effective.

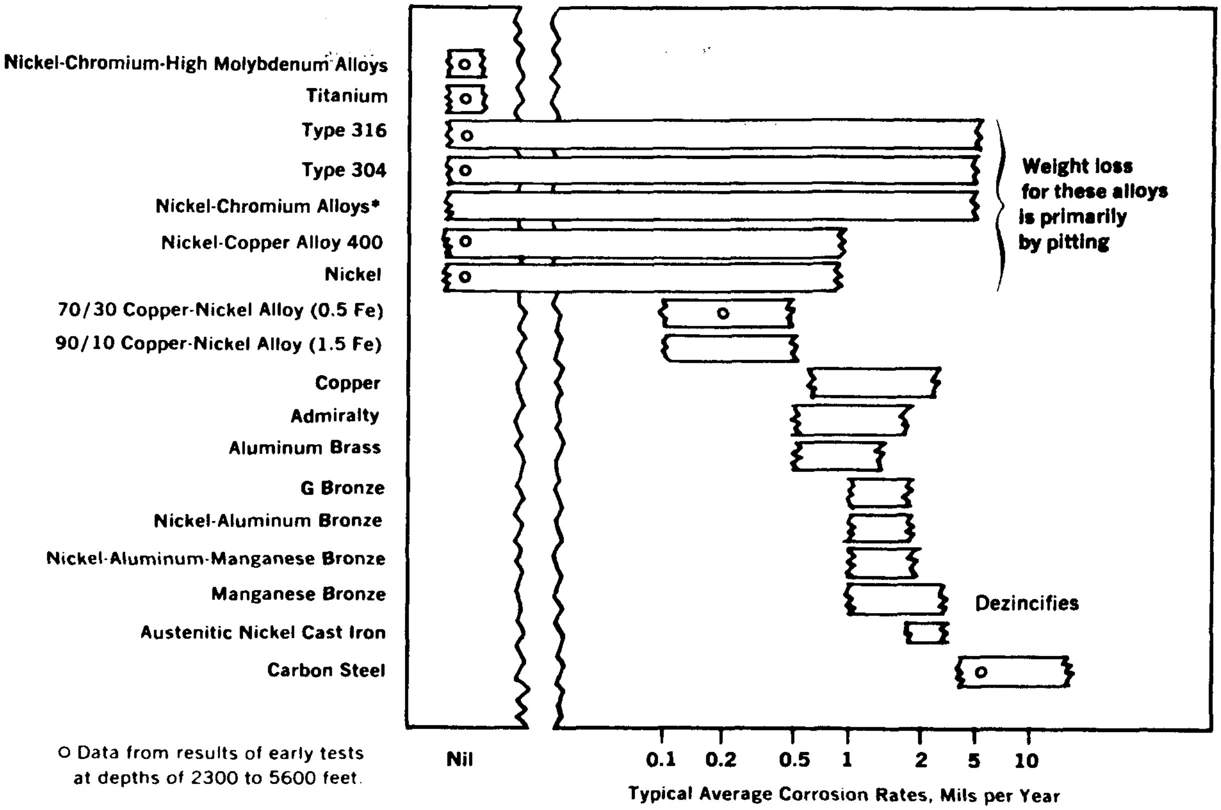
Control and Design Guidelines

Several methods are available for reducing general or uniform corrosion. The following techniques are recommended(11,14):

1. Use high purity metals when their mechanical properties and corrosion resistance are sufficiently good.
2. Select alloys that offer the combination of mechanical properties, corrosion resistance and economy required for the proposed application.
3. Use materials in the proper heat treatment for combined mechanical property and corrosion resistance.
4. Use surface coatings to provide a barrier between the metal and the environment.
5. Use chemical inhibitors to reduce chemical reaction rates.

2.1.2 Crevice Corrosion

The form of localized attack that occurs in regions of severely restricted fluid flow is termed crevice corrosion. The resistance of



○ Data from results of early tests at depths of 2300 to 5600 feet.

* Nickel-chromium alloys designate a family of nickel base alloys with substantial chromium contents with or without other alloying elements all of which, except those with high molybdenum contents, have related seawater corrosion characteristics.

Figure 2.1.4 General corrosion of a number of alloys in quiet seawater (velocity less than 2 feet/second)(17). Reproduced by permission.

material to crevice corrosion is an important consideration in the design and specification of systems involving high concentrations of chlorides. This is especially true in geothermal brine systems such as at Raft River, Idaho.

Crevice corrosion occurs typically at mechanical or welded joints and in association with fouling deposits. Mechanical joints include surfaces where metal-to-metal contact occurs, such as pipe threads, bolt-hole crevices in flanges and bolt-nut threads, between plates in bolted or riveted lap joints, at interfaces between bolt or rivet heads and washers or plates, between mating surfaces in valves, etc. Weldments such as spot-welded lap joints, incomplete fillet welds, and weld beads with porosity are also common sites for crevice corrosion. The interface between gasket material and metal surfaces as found in flanged joints is a common site for crevice corrosion. This form of corrosion is also found in metals that are fouled by debris, corrosion scale, or biological deposits. The sites for crevice corrosion frequently result from design limitations, misapplication of gasket materials, or improper field assembly of structural components. Scratches in paint or other coatings may provide locations for intrusion of corrodant and resulting crevice corrosion. The opening or crevice is usually very small, 0.020 inch (0.5mm) or less. Capillary action and diffusion contribute to movement of the corrodant into the crevice.

Water chemistry changes within the crevice are common. Crevice corrosion is frequently attributed to one, or more, of the following changes within the crevice(11,14,20):

1. Change in pH - The solution usually becomes more acidic.

2. Depletion of dissolved oxygen in the crevice.

3. Buildup of detrimental ion species; for example, Fe^{+++} and Cl- in the crevice.

4. Consumption and non-replenishment of inhibitor in the crevice.

Several types of failure can result from crevice corrosion; for example:

1. Staining of surfaces.
2. Contamination of products.
3. Perforation of component walls.
4. Loss of mechanical strength, leading to failure from overstress due to applied loads or by wedging action of corrosion products.
5. Seizing of operating components.
6. Debonding of protective coatings.
7. Loss of surface integrity resulting in leaks at joints.

The effects of temperature on crevice corrosion have not been thoroughly studied. Brigham(21) investigated the effect of temperature on crevice corrosion for some Cr-Ni-Mo stainless steels and found a correlation between alloy chemistry and the temperature which defines regions of immunity and susceptibility to this form of attack. The crevice corrosion temperature (CCT) is given by the relation:

$$\mathrm{CCT}\ (^\circ\mathrm{C}) = (45 \pm 5) + 11 \times \mathrm{wt\%\ Mo} \qquad (2.1.12)$$

While this correlation is limited to the steels used to develop the relation, it shows the kind of simple model that can be developed for making a first approximation of crevice corrosion failure.

The temperatures and chloride contents of the solutions in the RRGE systems are such that loss of protective oxide films on metal surfaces can become a serious problem. In the event of contamination of the system with air, or other oxidizing agent, the mating faces between gaskets and flanges, or in other occluded locations, could develop crevice corrosion. Air intrusion into the brine should be avoided if at all possible. Corrosion monitoring can help in identifying potential trouble spots.

In the RRGE power plant, crevice corrosion is thought to be most important in the cooling tower, where the highest chloride and oxygen concentrations are likely to be encountered. Other sites likely to develop crevice corrosion are the reinjection and condenser pumps, the hot brine transmission lines (if oxygen in-leakage occurs), the primary heat exchanger systems, and the condenser.

Carter and Cramer(18) noted that most of the alloys they tested experienced crevice corrosion to a measurable extent. Of the readily available materials, Monel 400, Type 316L stainless steel, Carpenter 20, 70/30 cupronickel and 2024-T3 aluminum showed the least resistance to this form of attack and should be tested under conditions simulating the Raft River power plant design before they are selected for applications in critical locations. Copper, titanium alloys, E-Brite 26-1, Inconel 625 and Hastelloy C-276 showed the best resistance to crevice corrosion. In every case the corrosion was more severe in aerated brines than in air-free fluids; noting, once again, the adverse effect of oxygen on corrosion of metals.

Experience with crevice corrosion and pitting-under-fouling in seawater service provides a guide to materials selection for geothermal plant design. Table 2.1.1 indicates that 90/10 cupronickel is very resistant to crevice corrosion(19). Carbon steel is usually severely attacked in seawater.

Control and Design Guidelines

The obvious method for prevention of crevice corrosion is to eliminate all crevices. This will usually be impossible where field fabrication and erection are done. The careful selection of alloys and

Table 2.1.1 Tolerance for Underfouling Pitting and Crevice Corrosion in Seawater(19). Reproduced by permission.

TOLERANCE FOR UNDERFOULING PITTING & CREVICE CORROSION IN SEA WATER

Crevices can normally be tolerated in designs	Group I	Titanium *Hastelloy + C Nickel-chromium alloy 625	These metals foul but rarely pit Titanium will pit at temperatures above 250°F Nickel-chromium alloy 625 after 2-3 years shows signs of incipient pitting in some tests in quiet sea water.
	Group II	90-10 copper-nickel (1.5Fe) Admiralty Brass	Shallow to no pitting 90-10 copper-nickel is standard sea water piping alloy.
	Group III	70-30 copper–nickel Copper Tin and aluminum bronzes Austenitic nickel cast iron	Good resistance to pitting Useful in piping applications.
Useful despite some crevice corrosion	Group IV	Nickel-copper alloy 400	Pits tend to be self limiting in depth at about 1/16" No protection required for heavy sections Cathodic protection from steel or copper base alloys will prevent pitting on O Ring, valve seats, and similar critical surfaces.
		CN7M (Alloy 20) **Carpenter 20 Cb 3 Nickel-chromium alloy 825	Occasional deep pits will develop Protection not normally required for all alloy 20 pumps Cathodic protection from less noble alloys may be necessary for O Ring and similar critical surfaces.
		Type 316 Stainless Steel	Most useful in instrument packages which are removed frequently (less than 30 days) and thoroughly cleaned and maintained.
Crevice corrosion limits usefulness. (Excellent, however, in above the waterline marine applications)	Group V	Type 316 Stainless Steel	Best of this group Deep pits develop Cathodic protection with steel, zinc or aluminum is required.
		Nickel	Many deep pits develop Cathodic protection from less noble alloys required.
		Type 304 Stainless Steel	Many deep pits develop Cathodic protection from steel may not be fully effective.
		Precipitation Hardening Grades of S.S.	Many deep pits develop Cathodic protection with zinc or aluminum may induce cracking from hydrogen.
Crevice corrosion severe. Seldom used.	Group VI	Type 303 Stainless Steel	Severe pitting Cathodic protection may not be effective.
		Series 400 Stainless Steel	Severe pitting Cathodic protection with zinc or aluminum may induce cracking from hydrogen.

gasket materials is important. Some solutions are less prone to promotion of crevice corrosion and some alloys are less susceptible to this form of attack. The actual locations and rates of attack will have to be determined by monitoring and on-site testing. Without these studies one can only guess where crevice corrosion will occur.

Considerations of initial materials cost, availability and ease of fabrication may prevail over "best" corrosion engineering practice. The following recommendations are made to reduce crevice corrosion(11,14,20):

1. Use butt-welded joints in place of riveted or bolted joints.

2. Close lap joints by continuous welding, brazing, soldering or calking.

3. Design tanks and pipe lines for complete drainage.

4. Reduce scale and solids buildup by cleaning systems regularly; design equipment for easy cleaning.

5. Avoid use of fibrous gasket materials, wherever possible.

6. Use solid gasket materials such as PTFE (polytetrafluoroethylene).

7. Design mating surfaces to avoid occlusion; see Figure 2.1.5(22).

8. In heat exchangers and condensers the preferred practice is to weld tubes into the tube sheets rather than using rolled joints.

9. Avoid build-up of solids in tanks and pipelines. Remove solids from the system as soon as possible; continuous removal, using hydrocyclones, is suggested.

10. Keep the external environment as uniform as possible; for example, in backfilling trenches avoid marked changes in soil types.

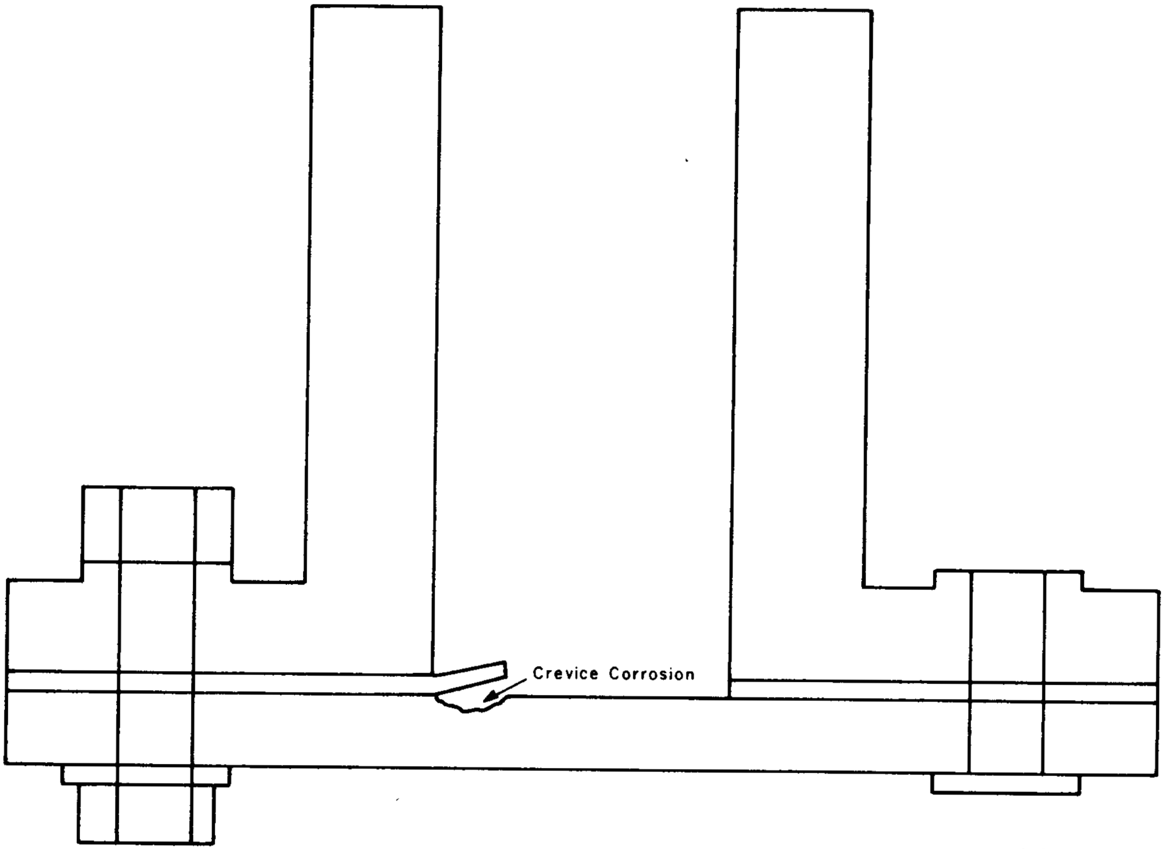


Figure 2.1.5 Gasket-flange configurations showing poor and preferred designs. After Butler and Ison(20).

11. Select materials with high resistance to crevice corrosion. Table 2.1.1 gives the resistance of a number of alloys to crevice corrosion in sea water(19). This table may be used as a guide for materials selection for geothermal brine service.

12. Monitor corrosion rates by coupons and by instrumental methods. This will aid in establishing maintenance schedules and direct attention of the engineering staff to potential trouble.

2.1.3 Pitting Corrosion

The form of localized corrosion that results in small holes or pits in a relatively uncorroded metal is termed pitting corrosion. The pit is typically deeper than the width of its surface opening; however, saucer shaped pits may occur (see Figure 2.1.6). If the pits are small and run together the surface may have a roughened or grooved appearance as shown in Figure 2.1.7. Pitting may be considered as a form of corrosion that is intermediate to immunity and corrosion as shown in Figure 2.1.8(11). Once pits are nucleated, the corrosion process is often self-stimulating. Pits may be initiated by crevice corrosion under particulate matter that settles on the surface of a metal.

As the pits form, the corrosion product may form tubercles which in the case of iron usually consist of a hard outer crust of brown hydrated ferric oxide, with, possibly, some admixture of calcite; and an inner layer of black magnetite. Within the tubercle and the pit the anion concentration is usually higher and, the oxygen concentration and the pH lower, than outside of the pit. Figures 2.1.9 and 2.1.10 show some of the tubercles formed by exposure of metals to geothermal brines.

Water chemistry, fluid flow, and surface finish are important factors in pit nucleation and growth. Slow flow or stagnant conditions promote pitting; slow fluid flow may result in the deposition of particulate matter with the consequent initiation of crevice corrosion which may ultimately appear as pitting corrosion. Even small flow rates tend to make the solutions more uniform and reduce the number and severity of

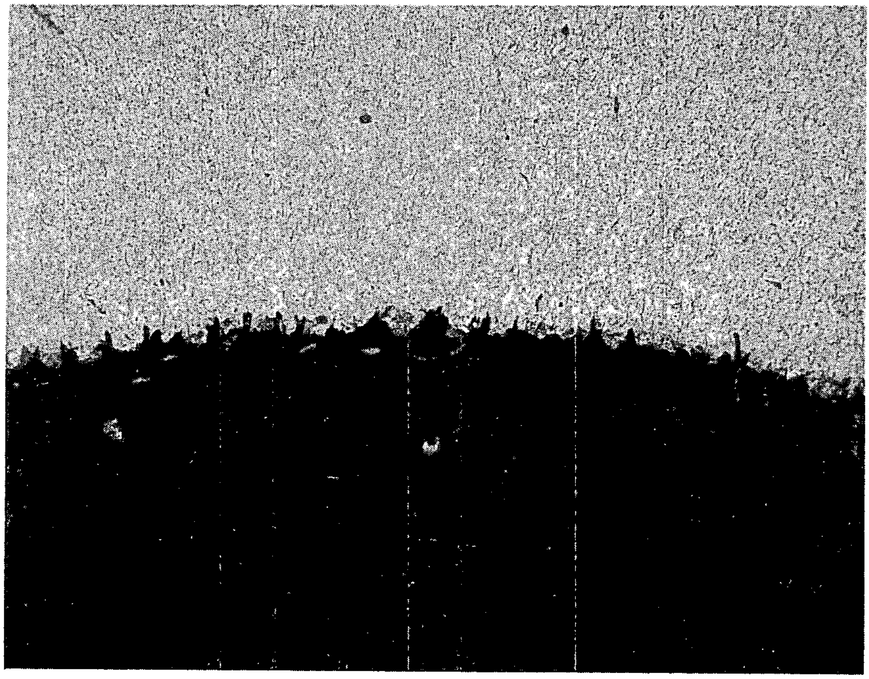


Figure 2.1.6 Corrosion pits in carbon steel tubing used in geothermal water service. Magnification about 400X.

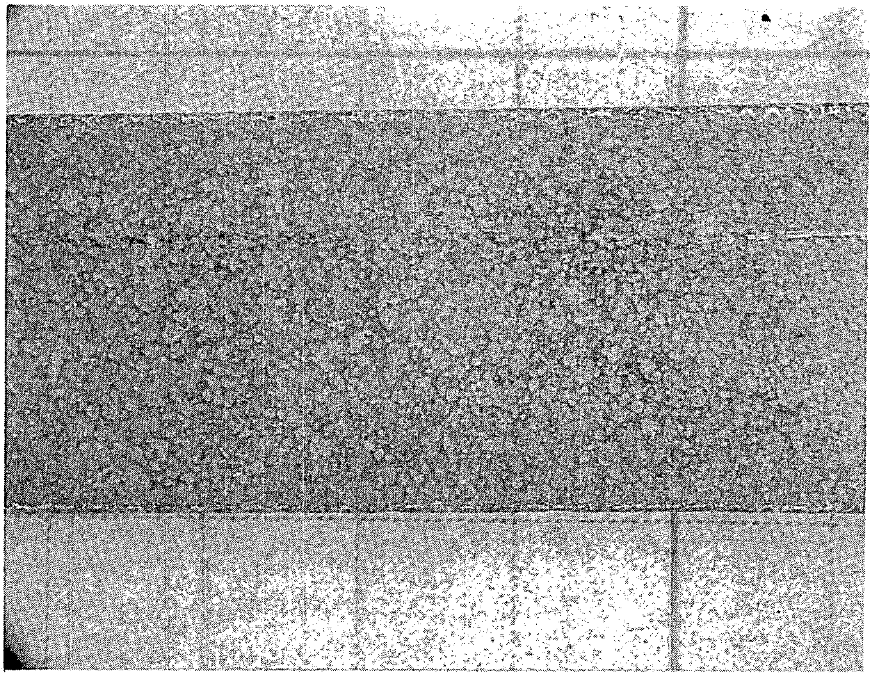


Figure 2.1.7 Pitting in mild steel corrosion coupon subjected to cooling tower water. Magnification about 4X.

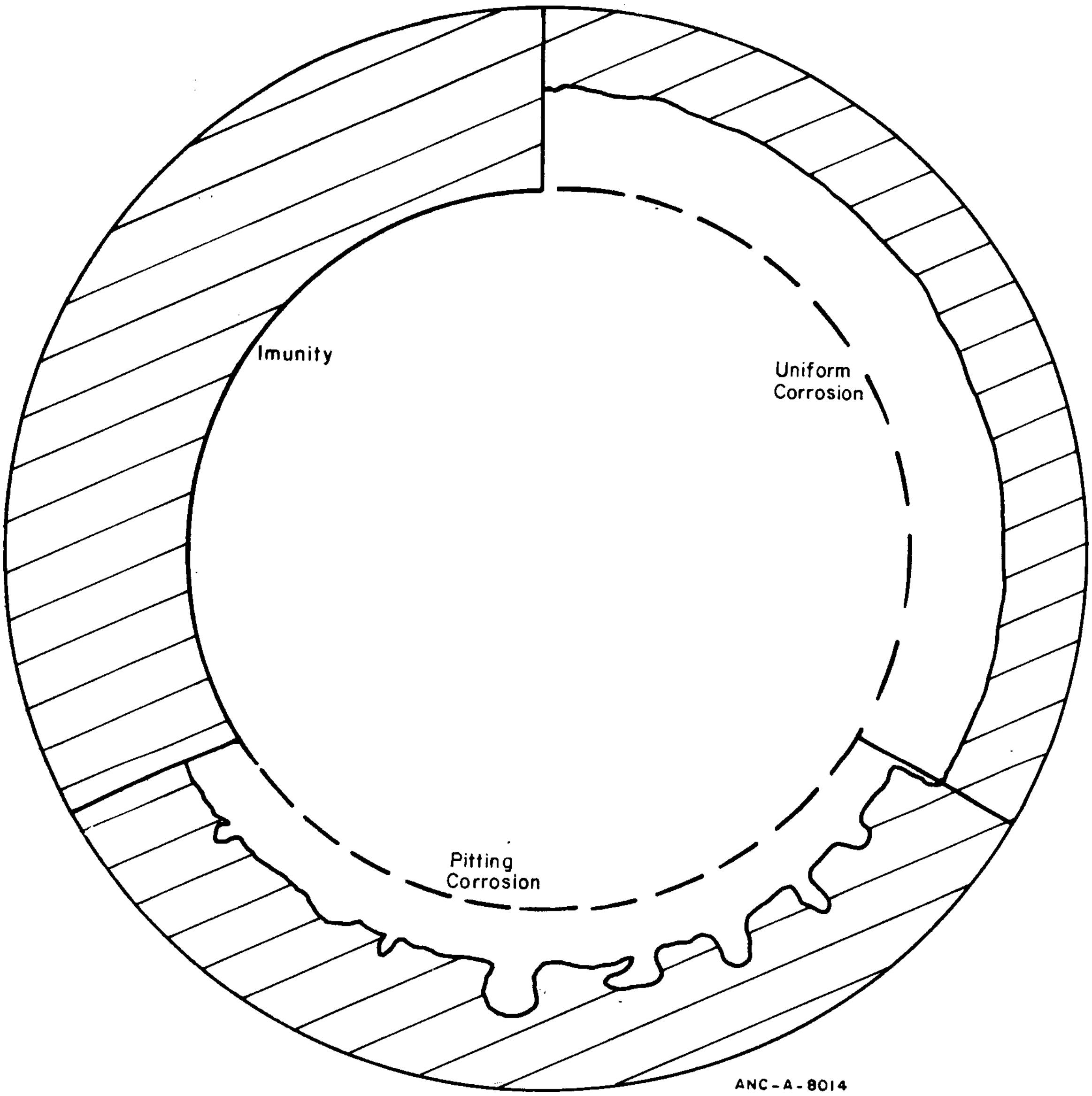


Figure 2.1.8 Pitting may be considered to be intermediate between immunity and uniform corrosion. After Fontana and Greene(11).

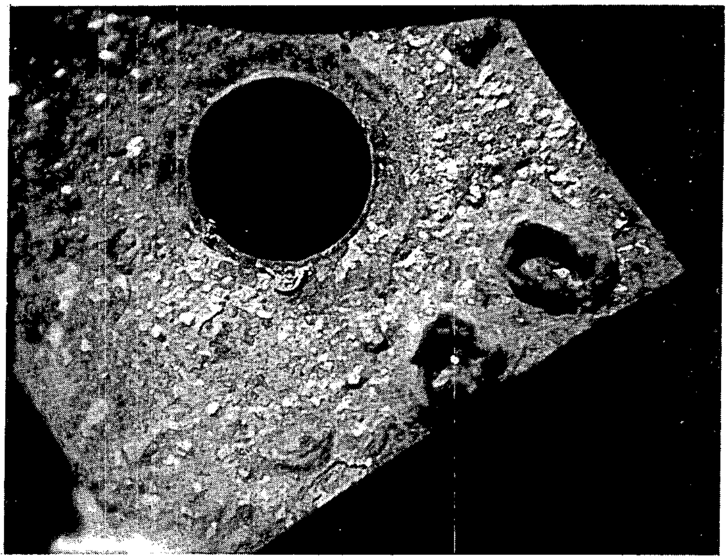


Figure 2.1.9 Tubercles formed on low carbon steel corrosion coupon exposed to aerated geothermal brine for about 7 weeks.

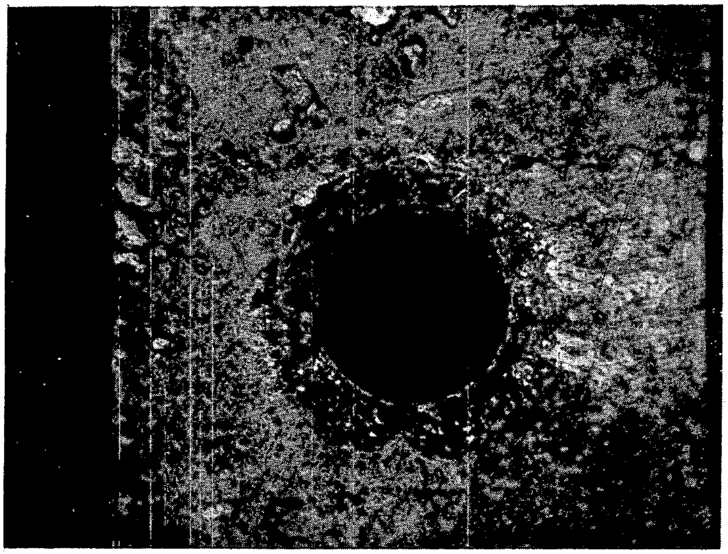


Figure 2.1.10 Tubercles formed on yellow brass corrosion coupon exposed to aerated geothermal brine for 7 weeks. Areas of the coupon also showed dezincification.

pits. Most pits are formed in the direction of gravity; this supports the suggestion that pits may be initiated as crevice corrosion under debris. Further, in stagnant solutions small differences in local solution density may be caused by addition of metal ions to the solution from the corrosion process; this would lead to local increases in density and promote pitting in the direction of gravity. Chloride, bromide, and hypochlorous anions, and iron and copper cations, promote pitting. Chromates and nitrates have an inhibiting effect, while fluorides have little effect on iron and stainless steels. Hydroxides also have an inhibiting effect on pit formation; pit nucleation and growth in iron and stainless steels decreases with increasing pH. Aluminum is pitted by copper in bicarbonate solutions(23).

Geothermal brines usually contain carbonates, bicarbonates and dissolved carbon dioxide; some brines contain copper and iron. For this reason careful consideration must be given to water chemistry in selection of materials for handling geothermal brines. High temperatures promote pitting. For example, aluminum pipes are commonly used for sprinkler irrigation; however, when geothermal brines are used the combination of alkalies leached from the soil and the high surface temperatures of the pipes promotes rapid corrosion from the soil side of the system. Figure 2.1.11 illustrates an example of 4 inch (10cm) aluminum sprinkler pipe used in the Raft River Valley.

In the RRGE system pitting is most likely to occur in the transmission lines and in the heat exchangers. The condenser heat exchangers are those most likely to be attacked by pitting corrosion because of the high oxygen concentration found in that part of the system.

Carter and Cramer(18) noted that pitting occured in titanium when tested in Imperial Valley brines. An autoclave fabricated from Type 316L stainless steel showed severe pitting (0.125 in. or 3.2 mm) after 1500 hr of service in these same fluids. Allegrini and Benvenuti(24) reported that, in Larderello, Italy, Type 316 stainless steel showed pitting to the extent that it could not be used in many applications.

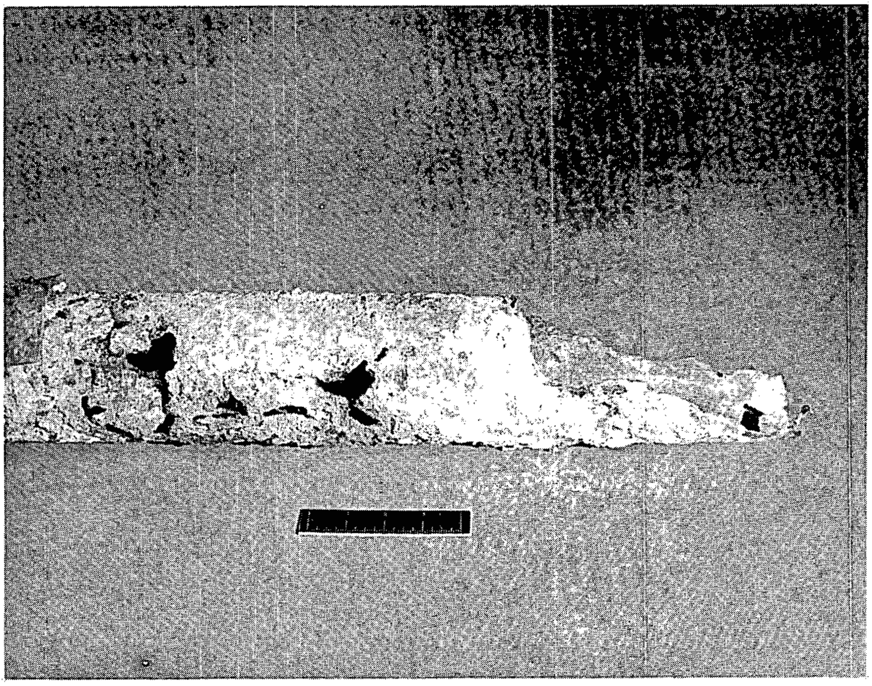


Figure 2.1.11 Pitting and general corrosion on exterior of 4 in. (10 cm) aluminum sprinkler-irrigation pipe used in geothermal brine service in the Raft River Valley, Idaho.

Control and Design Guidelines

Pitting corrosion may be reduced by the following procedures(11,14):

1. Drain brines from pipes and tanks and flush with clean water when facilities are to be shut down for some time.

2. Reduce or eliminate oxygen and other oxidizing agents from the system wherever this is possible.

3. Remove particulate matter from process streams wherever practical.

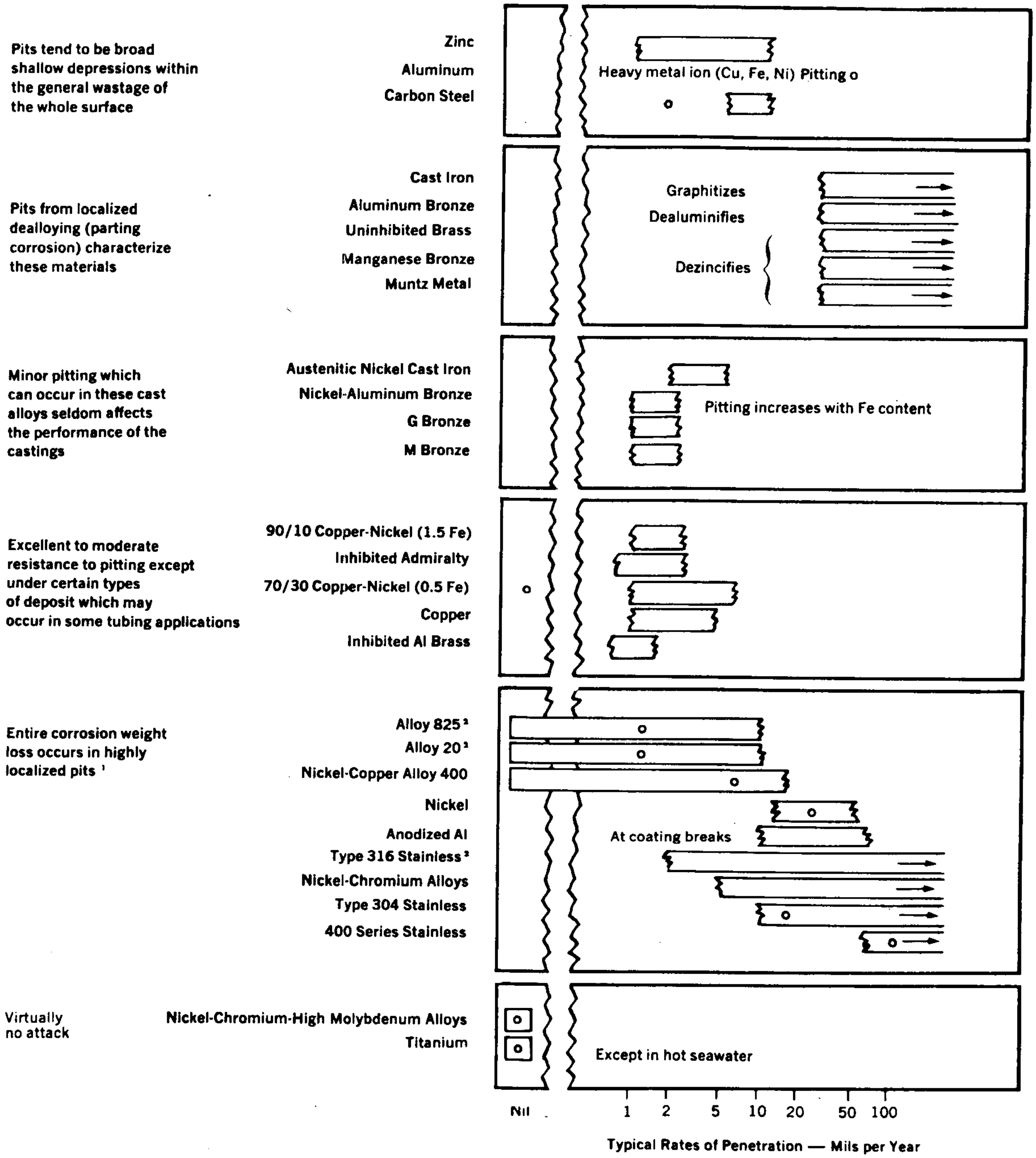
4. Maintain sufficient velocity in the system to keep the solution well mixed. A minimum of 2 ft/sec (0.6 m/sec) should be maintained.

5. Select materials for resistance to pitting. For example, the stainless steels are more susceptible to pitting corrosion than any other class of alloys. Within the stainless steels there are significant differences; Type 316 is much more resistant to pitting than Type 304. Table 2.1.2 lists resistance to pitting of some materials in seawater (19) and provides a general guideline to materials selection for the Raft River power plant.

6. Use inhibitors with caution since, in general, a greater concentration of inhibitor is required to prevent or control pitting than is required for general or uniform corrosion control. Further, localized depletion of inhibitor may result in accelerated corrosion, e.g., pitting.

7. Monitor system behavior and potential problems with both frequent examination and an on-going surveillance program.

Table 2.1.2 Pitting metals immersed in quiet seawater (velocity less than 2 feet/second)(17). Reproduced by permission.



o Data from results of early tests at depths of 2300 to 5600 feet.

(1) As velocity increases above 3 fps pitting decreases. When continuously exposed to 5 ft. per sec. and higher velocities these metals, except Type 400 series, tend to remain passive without any pitting over the full surface in the absence of crevices.

(2) These grades have an advantage over Type 304 stainless steel and related grades in that there is a substantial reduction in the number of pits, i.e., probability of pitting even though the depth of such pits as do occur is not greatly reduced.

2.1.4 Stress Corrosion Cracking

Stress corrosion cracking results from the combined action of stress and attack by a specific corrosive environment. The stress may be either applied or residual (i.e., resulting from fabrication procedures such as welding). The corrosion medium is specific; for example, steel, 18-8 stainless steel, and brass are susceptible to stress corrosion cracking in ammonium nitrate. Of these materials only 18-8 stainless steel is susceptible to stress corrosion cracking in ammonium chloride. Typically, the stress is static; when the stress is varying or cyclic the term corrosion fatigue is usually applied. However, more materials are subject to corrosion fatigue in a given corrodant than to stress corrosion cracking. While virtually all metals are susceptible to this form of corrosion in some environment, most are attacked by relatively few specific environments.

The term "hydrogen embrittlement" is often confused with stress corrosion cracking. The principal reason for this confusion is that hydrogen plays a prominent role in some cases of stress corrosion cracking. The following distinctions are made between stress corrosion cracking and hydrogen embrittlement(14):

1. Cracking due to the introduction of hydrogen but without corrosion of the metal is not stress corrosion cracking.

2. Cracking due to hydrogen which has been produced by a high rate of uniform corrosion, i.e., in the absence of an applied or residual stress, is usually not stress corrosion cracking.

3. When hydrogen is produced, in a stressed metal, by local corrosion in a crack or pit and this results in crack propagation the process is considered to be stress-corrosion cracking.

Crack Morphology

Cracks propagate normal to the applied, or residual, stress. In the initial stages of cracking the opening will not be visible to the unaided eye. At later stages the cracks may become very prominent. Figure 2.1.12 shows large cracks in a stainless steel patch which had been used to repair a geothermal water line in Boise, Idaho. In this instance a combination of chlorides leached from the soil, oxygen from the air and hot geothermal water was probably responsible for the observed failure. Either intergranular or transgranular cracks predominate in stress corrosion cracking, although a combination of the two is frequently observed. Transgranular cracks may follow grain boundaries over short distances; further, intergranular cracks may show some transgranular fracturing.

Intergranular cracking follows the grain boundaries of the metal. This form of cracking is typical of stress corrosion cracking in low-carbon steel, in brasses, and in aluminum alloys. Secondary cracks are frequently found adjacent to the main crack; these are usually smaller than the main crack and are found by metallographic examination.

Transgranular cracking proceeds by fracture through the grains rather than around the grains. This form of stress corrosion cracking morphology is characteristic of the austenitic stainless steels, such as Type 304, in hot chloride solutions.

The environment also has an effect on the type of crack propagation. For example, Type 304 stainless steel shows intergranular cracking in ammonium nitrate, transgranular cracking in magnesium chloride and a combination of intergranular and transgranular cracking in potassium chloride.

Table 2.1.3 lists the types of crack morphology for stress corrosion cracking in steel, 18-8 stainless steel, yellow brass, Monel (66Ni-34Cu), nickel, and titanium, in a number of environments(25). This table also

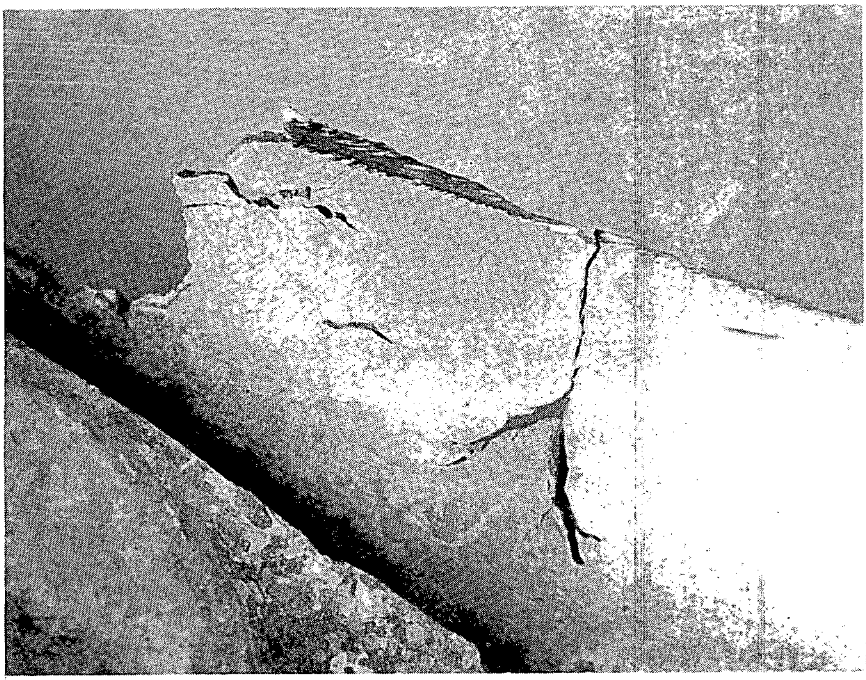


Figure 2.1.12 Stress corrosion cracks in a stainless steel patch used to repair a water main in geothermal brine service.

TABLE 2.1.3

Corrosives That Induce Stress Corrosion Cracking in Metals

	Steel	18-8	Brass	Monel	Nickel
Aluminum chloride	IT				
Aluminum sulfate		IT			
Ammonia (dilute)			IT		
Ammonium chloride		IT			
Ammonium nitrate	I	I	I		
Barium chloride		IT	T		
Calcium chloride		IT			
Calcium nitrate	I				
Chromium chloride		T			
Cobalt chloride		T			
Hydrogen chloride	T	T	T[a]		
Lithium chloride		IT			
Manganese chloride	IT				
Magnesium chloride		T			
Mercuric chloride		IT			
Mercurous nitrate			IT	IT	
Mercury			IT	IT	
Nickel nitrate	I				
Nitric acid + manganese chloride	I				
Potassium chloride		IT			
Potassium hydroxide	I	T			
Potassium permanganate	I				
Sodium aluminate	IT	IT			
Sodium chloride		T			
Sodium hydroxide	I	IT			I
Manganese chloride	I				
Sodium nitrate	I				
Sodium silicate	I				
Manganese sulfate	I				
Sodium sulfate		IT			
Steam			Al bronze Si bronze		
5 ppm NH_3		T	I		
Chlorides (100 ppm)		IT			
Zinc chloride		T			

---

[a] Does not crack unless nitrogen compounds are also present.

I, intergranular cracks; T, transgranular cracks: IT intergranular and/or transgranular cracks.

lists many constituents of geothermal brines, including those at Raft River and Boise, Idaho. Several commonly encountered environments are included for comparison purposes.

The temperature of the Raft River geothermal brines and the chloride concentrations are high enough that particular attention must be given to the exclusion of oxygen from the system to reduce the possibility of stress corrosion cracking. All points where tensile stresses are present are potential sites of stress corrosion cracking. All pumps in contact with geothermal brines have tensile stresses in the impellers and to a lesser extent in the shafts. The heat exchanger tubes in the boilers and preheaters of the high temperature brine circuit and the tubing in the isobutane condenser are potential sites for stress corrosion cracking.

Allegrini and Benvenuti(24) noted stress corrosion cracking in Type 316 stainless steel as well as increased general corrosion when stressed. For example, a carbon steel bellows that had provided 8-9 years of service was replaced with a Type 316 bellows; the latter bellows lasted only 2 to 6 months.

Marshall and Braithwaite(8) reported stress corrosion of stainless steels in New Zealand brines and noted that austenitic stainless steels are not susceptible to this form of attack in air-free conditions. Some non-ferrous alloys also exhibited stress corrosion cracking, for example 70/30 cupronickel and beryllium copper. High-strength steels are susceptible to this form of attack in geothermal brines bearing hydrogen sulfide. Low-strength steels are recommended where they can be used in place of high-strength materials to avoid this form of attack.

Toliva(17) found stress corrosion in two grades of steel in short-term tests at Cerro Prieto, Mexico. In short-term tests in Imperial Valley brines Carter and Cramer(18) did not find stress corrosion cracking in any of the materials tested. Only iron-base alloys suffered stress corrosion cracking in long-term tests.

Stress corrosion cracking in austenitic stainless steels is temperature sensitive. From experiments and plant practice Marshall and Braithwaite(8) concluded that a minimum of 50C (323K) and a minimum of 5 ppm chloride are required in addition to oxygen for stress corrosion cracking in geothermal brines. They reported that there appeared to be no minimum stress for this form of attack. Sulfide stress cracking in high strength steels can apparently occur at temperatures well below 100C (373K) and in geothermal brines up to 190C (463K).

Control and Design Guidelines

The mechanism of stress corrosion is not well enough known to apply theoretical control measures to the reduction or prevention of this form of corrosion. The methods used to control stress corrosion cracking are general and mostly empirical. The following methods are suggested as ways of reducing the problems associated with stress corrosion cracking(11):

1. Reduce stress to less than the threshhold level, if one exists. This may be done by using a thicker section.

2. Modify the environment to remove the aggressive species. For example, the chloride or dissolved oxygen concentration can be reduced to less than the critical values for stress corrosion cracking of austenitic stainless steel; see Figure 2.1.13 for a guide to these values(26).

3. Select a more resistant alloy for critical locations or environments.

4. Apply a cathodic potential to reduce the anodic current levels at the crack tips. The application of this technique is limited by the potential for hydrogen charging of the metal and resultant hydrogen cracking.

5. Use inhibitors in the system if this is feasible. For example, phosphates and other inhibitors have been used to reduce

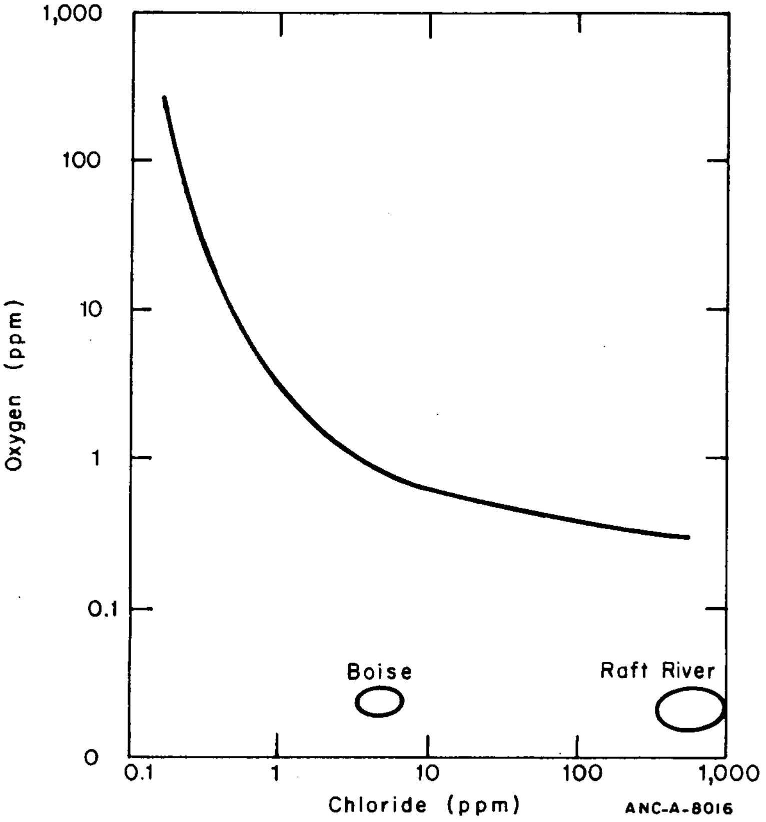


Figure 2.1.13 Proposed relationship between chloride and oxygen content of alkaline-phosphate treated boiler water, and susceptibility to stress corrosion of austenitic stainless steel exposed to the steam phase with intermittent wetting(24).

stress corrosion cracking, generally by pH control or surface passivation.

2.1.5 Corrosion Fatigue

Fracture failure due to cyclic loading is termed fatigue. The cyclic stress may or may not be superimposed on a static load. Generally, the load required to cause fatigue failure is somewhat smaller than the static ultimate strength of the metal. Ferrous alloys usually show a minimum failure stress below which repeated cycling, e.g., 10^6 to 10^7 cycles, does not result in fracture. Copper, aluminum and magnesium alloys do not show such a minimum.

In the presence of a corrodant the number of cycles to failure, at a given stress, is usually significantly reduced. This is corrosion fatigue. More succinctly, corrosion fatigue is defined as the combined action of an aggressive environment and a cyclic stress, leading to a premature failure by fracture(27). The stress-cycles (S-N) curves for corrosion fatigue of iron resemble those of the non-ferrous metals. Figure 2.1.14 shows S-N curves for a low carbon steel.

Corrosion fatigue is often classed as a form of stress corrosion cracking. The environments that cause corrosion fatigue are much more numerous than those for stress corrosion cracking. Under these circumstances the separation of stress corrosion cracking and corrosion fatigue is justified.

Corrodants

Fatigue tests of metals in air generally show an effect due to the presence of oxygen and/or water vapor. For example, the fatigue endurance of 70-30 brass is 26% greater in a vacuum than in air(27). In this case air is a corrodant. However some corrosion is generally required before corrosion fatigue occurs. For example, gold does not corrode in air and has the same fatigue characteristics in air and in vacuum; thus, gold is immune to corrosion fatigue in air.

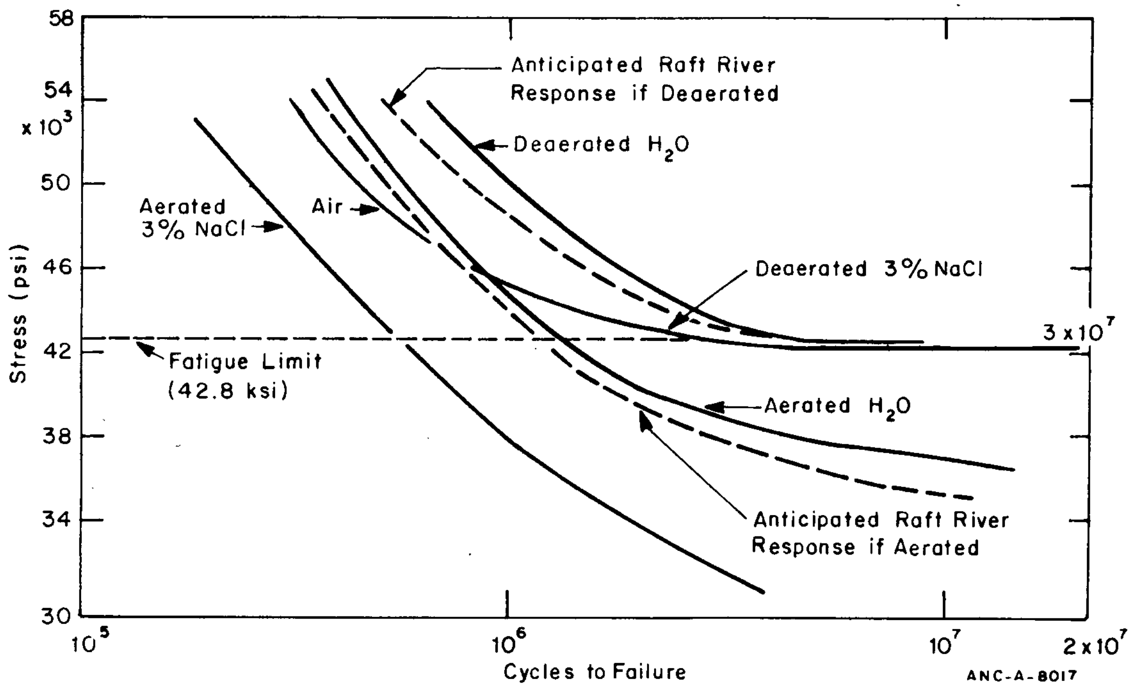


Figure 2.1.14 Effect of dissolved O_2 and chloride ion on the fatigue behavior of low carbon steel in distilled water and 3% NaCl solutions(25).

Moist air is more aggressive than dry air; hydrogen sulfide, sulfur dioxide, and certain other gases in the air can accelerate failure. Pumps and compressors which work in moist air, such as at geothermal facilities, are prone to this form of attack. In addition the steam from geothermal sources usually contains hydrogen sulfide and carbon dioxide which accelerate corrosion fatigue.

Chlorides are generally more aggressive than other anions in solution. In mildly corrosive environments the concentration of the corrodant has a marked effect. At high concentrations, however, the contribution of the corrodant to corrosion fatigue approaches a limit.

Temperature Effect

There is an appreciable temperature effect on the corrosion fatigue process. In artificial sea water, for example, the fatigue life, at 20 ksi, (137.9 MPa) of mild steel was approximately halved when the temperature was raised from 15C (288K) to 45C (318K). Similar effects due to increased temperature would be expected with other materials.

Failure Mode

In fatigue failure there is, typically, a single crack with a reasonably well defined point of origin. In corrosion fatigue, however, there may be numerous cracks, with only one propagating to failure. The point of initiation may be difficult to identify because of either general corrosion or the accumulation of corrosion products in the crack.

The final fracture is typically transgranular, with a characteristic fibrous appearance. The last bit of fracture represents brittle, intergranular cracking. Earlier portions of the fracture zone may be smoothed by the mechanical working of the surface as the crack faces contact one another in each cycle. Corrosion may help to remove the microscopic ridges that result from crack advancement during each cycle. If the cycling is interrupted, larger microscopic ridges may develop(27).

The Raft River geothermal brines provide the environment necessary for corrosion fatigue. Several components of the fluid transmission system are either rotating machinery or are subject to vibration. All pumps in the brine system or in the isobutane condenser/cooling tower circuit will be subject to corrosion fatigue. In addition, the tubing in all heat exchangers is subject to vibration and, therefore, to corrosion fatigue.

Marshall and Braithwaite(8) reported fatigue failure of turbine blades in geothermal steam service in New Zealand, and suggested that corrosion fatigue may have been responsible. The failure of metal bellows in geothermal steam service at Larderello, Italy, was attributed to stress corrosion cracking(24); however, the conditions of operating bellows suggest that corrosion fatigue may have contributed to the failure. Steam turbine failures at The Geysers geothermal generating station have been attributed to corrosion fatigue(28).

The mechanisms of corrosion fatigue have been reviewed in depth by Duquette(27).

Control and Design Guidelines

The following methods for reducing or preventing corrosion fatigue are suggested:(11, 14)

1. Reduce tensile stresses in components by redesign.

2. Reduce residual tensile stresses in structures by heat treatment.

3. Place the surface in compressive stress by shot peening or surface rolling.

4. Nitride the surface to increase the strength and fatigue endurance limit.

5. Use inhibitors. (A higher concentration of inhibitor is required than is normally used for prevention of uniform corrosion.)

6. Cathodic protection coatings are sometimes effective. The surface must be unbroken and nonporous.

7. Anodic coatings are usually effective. Electrodeposited coatings are generally more effective than hot dip coatings. Care must be taken to avoid hydrogen embrittlement during coating.

8. Organic coatings serve as a physical barrier between the metal and the environment. They are not effective unless absolutely continuous.

2.2 Less Important Forms of Corrosion

In the RRGE systems the following forms of corrosion are thought to be less important than those discussed in Section 2.1.

2.2.1 Galvanic Corrosion

Galvanic corrosion is the accelerated wastage of metal due to the galvanic action of two dissimilar metals in contact. While both metallic members of the structure may be corroded, the less resistant member shows an increase in corrosion rate while the more resistant corrodes less than if it alone were exposed to the environment. The more resistant member is said to be cathodic and the less resistant member anodic. The parameters that are important in galvanic corrosion are the relative electrochemical activities of the two metals, the temperature, the relative areas of the two metals, and the chemistry of the environment.

The potential differences between various metals in geothermal brines has not been studied. However, the relative ranking of a number of alloys in sea water (Figure 2.2.1) has been made and can serve as a guide in predicting the behavior of these materials in geothermal brines that have been cooled to about 15C (288K) to 25C (298K). Some galvanic potentials have been measured. For example, Brown(29) studied the potentials of a number of aluminum alloys vs. annealed copper, hard drawn copper and brass. While Brown's study was conducted at about 20C (293K) in tap and in distilled water, his results indicate that large electrochemical potentials can occur between the materials he studied.

Temperature effects in galvanic corrosion are not unusual; thus, as the temperature increases the rate of corrosion also increases. However, the rate of change of electrochemical potential with temperature is not the same for all metals. For example, at room temperature zinc is anodic with respect to iron. As the temperature increases the potentials converge and at some elevated temperature the iron may become anodic with respect to zinc(11).

Galvanic corrosion may be combined with other forms of corrosion. For example, if the solution is in the nearly neutral to moderately basic pH range a coating of $Fe(OH)_3$ forms on the iron and pitting crevice corrosion can occur.

Aluminum heat exchanger tubes have been considered for the primary heat transfer system of the RRGE demonstration plant. The possibility that a reaction can take place between the heat exchanger tubes and copper that may occur naturally in the Raft River geothermal brine places a serious limitation on the use of aluminum. The reaction is:

$$2\ \mathrm{Al} + 3\ \mathrm{Cu}^{++} = 2\ \mathrm{Al}^{+++} + 3\ \mathrm{Cu}$$

to give a deposit of metallic copper on the aluminum tubes. These metallic copper deposits would act as galvanic couples and severe pitting of the aluminum would result. The effect of temperature (i.e., the chemical kinetics) on the copper-aluminum reaction has been investigated by MacKinnon and Ingraham(30,31) in Canada and by Malhotra(32) in the U.S. Their work shows that the reaction is controlled by diffusion of copper ion through a boundary layer at the temperatures of interest in the RRGE systems. The effect of bicarbonate ion (present in Raft River geothermal brines) on this reaction has been reported by Becerra and Darby(23).

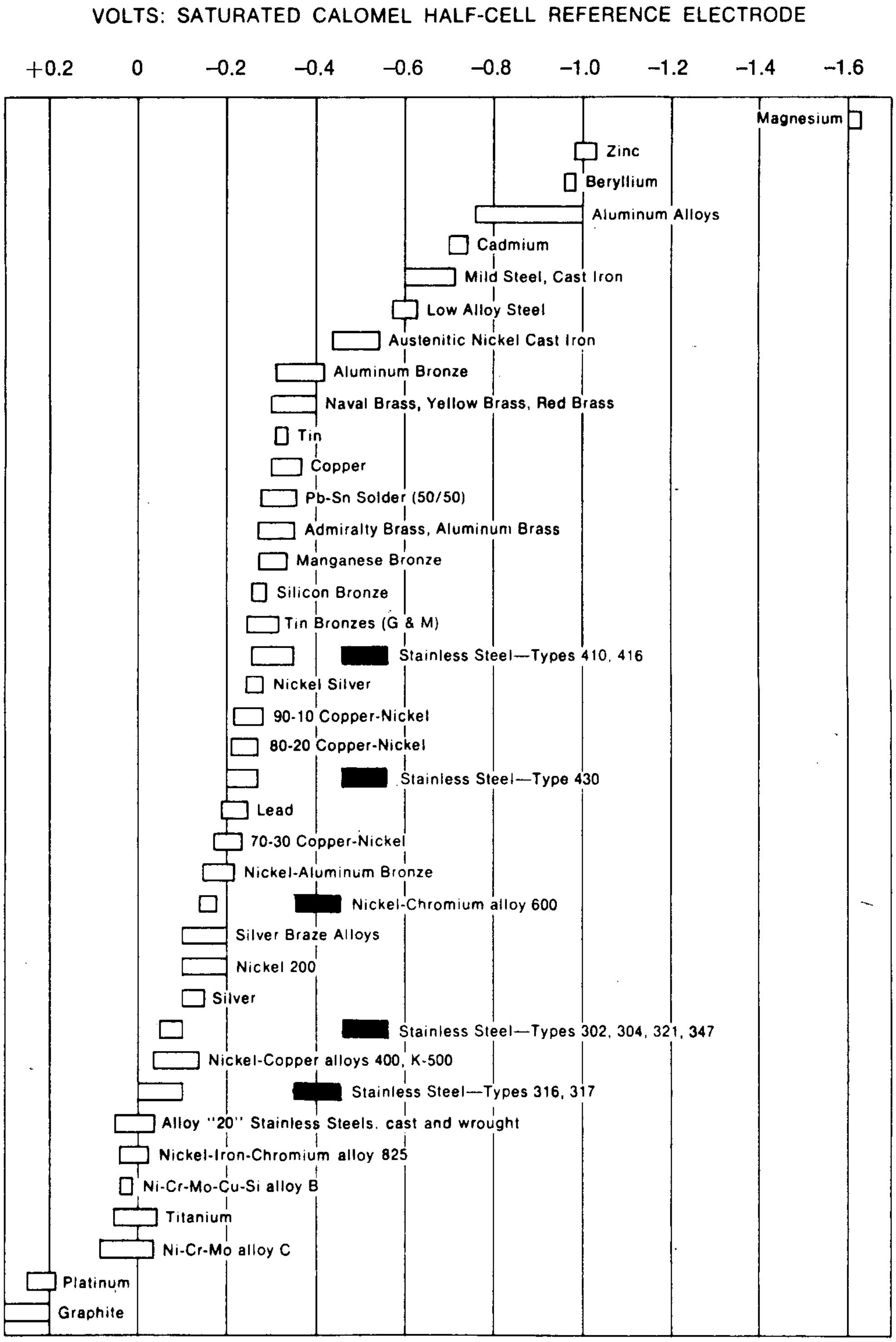
Even when dissimilar metals are in contact, galvanic corrosion may not occur or may be sufficiently slow that serious trouble or short life is not a problem. This can happen because one or both of the metals may be passivated after a short time.

The concentration of dissolved solids and the conductivity of the Raft River geothermal brines are such that they provide a very good electrolyte for galvanic corrosion. The possibility of forming dissimilar metal couples is probably highest in the cooling tower and care must be exercised to prevent accidental coupling. Both the hot and cold brine transmission lines are additional sites for galvanic corrosion and particular attention must be given to materials selection and procurement to insure that galvanic corrosion is prevented or controlled.

Hermannsson(16) noted that zinc on galvanized iron was severely attacked in Icelandic geothermal waters containing more than about 1 ppm dissolved oxygen. This attack is attributed to galvanic corrosion resulting from the depolarization of both iron and zinc surfaces. One must conclude that the propensity for galvanic attack is even greater in the more saline Raft River geothermal brines.

Control and Design Guidelines

A number of practices have been suggested for controlling or preventing galvanic corrosion(19). Sometimes one technique is sufficient to control galvanic corrosion; more frequently a combination of the following techniques is required:



Alloys are listed in the order of the potential they exhibit in flowing seawater. Certain alloys indicated by the symbol: ■ in low-velocity or poorly aerated water, and at shielded areas, may become active and exhibit a potential near −0.5 volts.

Figure 2.2.1 Corrosion potentials in flowing seawater (8 to 13 feet/second) temperature range 50-80°F(17). Reproduced by permission.

1. Eliminate dissimilar metal contacts. If there is no dissimilarity in electrochemical potential then galvanic corrosion is precluded.

2. Insulate dissimilar metals. Where dissimilar metals must be used together, for example, to take advantage of mechanical properties, they should be insulated from one other. To illustrate: The tubes in a heat exchanger may need to be a material that is quite cathodic to the shell of the heat exchanger. In this case the tube sheet should be of a metal similar to the tubes and must be electrically insulated from the exchanger shell.

3. Use inhibitors. These will decrease the overall effect of the environment.

4. Use coatings. When a coating is used, it should be applied to the cathodic portion. This will reduce the effect of the dissimilarity of the areas to a minimum. If the coating were applied instead to the more active member, pin holes in the coating would lead to rapid attack and penetration of the metal.

5. Select materials that are fairly compatible and allow for increased corrosion in the more active metal. Figure 2.2.2 gives a selection of fastener materials for a number of common metals for use in sea water(19). Figure 2.2.3 gives the compatibility of pump and valve trim for seawater(19). The compatible combinations of materials in Figure 2.2.2 and 2.2.3 represent only a guide to materials selection for geothermal use. A testing program will be required to identify compatible metal combinations for use in hot geothermal brines.

2.2.2 Selective Leaching

The removal of one (or more) constituents from a solid alloy by corrosion is termed selective leaching. The selective removal of zinc

BASE METAL	FASTENER							
	Aluminum (1)	Carbon Steel	Silicon Bronze	Nickel	Nickel-Chromium Alloys	Type 304	Nickel-Copper Alloy 400	Type 316
Aluminum	Neutral	Comp. (2)	Unsatis-factory (2)	Comp. (2)	Comp.	Comp.	Comp. (2)	Comp.
Steel and Cast Iron	N.C.	Neutral	Comp.	Comp.	Comp.	Comp.	Comp.	Comp.
Austenitic Nickel Cast Iron	N.C.	N.C.	Comp.	Comp.	Comp.	Comp.	Comp.	Comp.
Copper	N.C.	N.C.	Comp.	Comp.	Comp.	Comp.	Comp.	Comp.
70/30 Copper-Nickel Alloy	N.C.	N.C.	N.C.	Comp.	Comp.	Comp.	Comp.	Comp.
Nickel	N.C.	N.C.	N.C.	Neutral	Comp. (3)	Comp. (3)	Comp.	Comp. (3)
Type 304	N.C.	N.C.	N.C.	N.C.	May Vary (4)	Neutral (3)	Comp.	Comp. (4)
Nickel-Copper Alloy 400	N.C.	N.C.	N.C.	N.C.	May Vary (4)	May Vary (4)	Neutral	May Vary (4)
Type 316	N.C.	N.C.	N.C.	N.C.	May Vary (4)	May Vary (4)	May Vary (4)	Neutral (4)

(1) Anodizing would change ratings as fastener.

(2) Fasteners are compatible and protected but may lead to enlargement of bolt hole in aluminum plate.

(3) Cathodic protection afforded fastener by the base metal may not be enough to prevent crevice corrosion of fastener particularly under head of bolt fasteners.

(4) May suffer crevice corrosion, under head of bolt fasteners.

NOTE: Comp. = Compatible, Protected. N.C. = Not Compatible, Preferentially Corroded.

Figure 2.2.2 Galvanic compatibility of fasteners in seawater(17). Reproduced by permission.

BODY MATERIAL	TRIM		
	Brass or Bronze	Nickel-Copper Alloy 400	Type 316
Cast Iron	Protected	Protected	Protected
Austenitic Nickel Cast Iron	Protected	Protected	Protected
M or G Bronze 70/30 Copper-Nickel Alloy	May Vary (1)	Protected	Protected
Nickel-Copper Alloy 400	Unsatisfactory	Neutral	May Vary (2)
Alloy 20	Unsatisfactory	May Vary	May Vary

(1) Bronze trim commonly used. Trim may become anodic to body if velocity and turbulence keep stable protective film from forming on seat.

(2) Type 316 is so close to nickel-copper alloy 400 in potential that it does not receive enough cathodic protection to protect it from pitting under low velocity and crevice conditions.

Figure 2.2.3 Galvanic compatibility of alloys used for pump and valve trim in seawater service(17). Reproduced by permission.

from brass is probably the most common example of this form of corrosion, and is termed dezincification. However, in other alloy systems the term selective leaching is preferred. Selective leaching is used commercially to remove silver from gold-silver bullion; in this instance the common and preferred term is parting.

Dezincification of brass occurs in two common morphologies. Both layer-type dezincification, and plug-type dezincification have been observed.

Selective leaching occurs frequently in domestic hot water lines and to a lesser extent in cold water systems. Thus, high temperatures accelerate selective leaching. Brass corrosion coupons subjected to geothermal brines exhibited dezincification as shown in Figure 2.2.10. The selective leaching of iron from cast iron is termed graphitization. This has been observed in the hot water distribution lines in the Boise geothermal area. Hermannsson(16) reported that brass exposed to Icelandic geothermal waters containing small amounts of dissolved oxygen, e.g., more than about 1 ppm, was severely attacked. This attack was selective leaching similar to that observed at Raft River.

In reference to the RRGE or other geothermal systems, this form of attack is most likely to occur in alloy heat-exchanger tubing. For example, the leaching of nickel from copper-nickel heat-exchanger tubing would be of some concern. Most other alloys proposed for use in the RRGE should be immune to selective leaching.

The mechanisms of selective leaching of brass have been successfully investigated by Horton(33), Heidersbach and Verink(34-36) and Langenegger and Robinson(37-38). Those interested in this form of attack are directed to these sources for clarification of the processes involved in selective leaching.

Control and Design Guidelines

Several techniques have been proposed for controlling or preventing selective leaching. Some of these are noted below(14). The economics of any control measure must be examined closely. This is especially true in the present case because of the slow rate of corrosion.

1. Oxygen removal will often reduce the aggressiveness of the environment enough to control selective leaching.

2. Application of a cathodic potential will minimize selective leaching.

3. Alloy selection is often the best approach. Single-phase alloys are the most resistant to selective leaching. The addition of 1% arsenic to 70-30 brass effectively controls selective leaching. The use of cupro-nickel alloys in place of brass is suggested in cases of severe selective leaching of brass. However, cupro-nickel alloys are somewhat more expensive than brass due to the relatively high cost of nickel.

2.2.3 Erosion Corrosion

Erosion corrosion is a corrosion process in which the rate of attack is increased by relative motion of the metal and a fluid. This is sometimes termed impingement attack when, for example, a fluid impinges directly on a metal surface. The fluid may or may not contain suspended particles, such as sand particles or gas bubbles entrained in well water.

Erosion tends to remove protective films of oxides or other corrosion products and expose the substrate metal to accelerated attack. Places where the velocity changes are especially susceptible to attack. Typical sites for erosion corrosion are entrance regions of the tubes in a heat exchanger; elbows, bends and tees; valve seats and faces; pump impellers and casings; impingement plates in cyclone classifiers; internals of flow measuring devices such as turbine meters, pitot tubes and drag disks; nozzles and turbine blades. Periodic inspection of sites such as these will be required to prevent or reduce unexpected failures. Virtually all types of equipment involved in handling aggressive fluids are subject to erosion corrosion.

Finnie(39) has noted a number of parameters that appear to be important in defining erosion, and therefore erosion corrosion:

1. Angle of impingement. The rate of erosion is a function of both the ductility of the metal and the angle of impingement. Ductile metals show maximum erosion at small angles while brittle metals show the maximum erosion rate at high angles of impingement.

2. Particle velocity at impingement. From the kinetic energy equation ($U = \frac{1}{2}mv^2$) one would predict an exponential dependence on the velocity of the particle of 2. Ductile materials exhibit a dependence closer to 2.4. One may infer that other factors are contributing to erosion in addition to simple kinetic energy changes on impact.

3. Particle size. The kinetic energy equation predicts a linear relationship between erosion and particle mass. In practice a minimum or threshold mass must be exceeded before erosion is significant.

4. Particle rotation at impact. A minor contribution to erosion corrosion occurs as a result of rotation of the particle at impact.

5. Particle shape and strength. Cutting rate and hence erosion rate increases with sharpness of the particle, particularly with ductile materials. The effect of the strength of the impacting particles is not well known; some friable soft materials are more damaging than strongly coherent materials, presumably because of fragmentation of the weaker material.

6. Particle flux. The correlation between particle flux and erosion rates is poor.

7. Surface properties of metal. Erosion rates generally decrease as the hardness of the target material increases. However, within a given alloy system there is poor correlation between hardness and erosion. This observation implies that other surface parameters are important; for example, the impingement of particles may result in work hardening of the surface. This parameter is not well understood.

8. Shape of surface. Ripples tend to form in the surface near the angle of maximum attack. The effect of surface curvature is not well known.

9. Stress level in surface. There does not appear to be more than a minor correlation between erosion and surface stresses.

10. Nature and properties of the carrier fluid. Temperature effects are small, with respect to the erosion step of erosion corrosion. However, once a clean surface is exposed to the environment attack can be expected to be rapid.

Hot fluids, such as geothermal brines, that contain significant chloride concentrations are especially aggressive. Water pumped from wells, such as those at Raft River, frequently contains suspended sand or other particulates that could cause severe abrasion and accelerated corrosion.

In the RRGE system the pumps and heat exchangers are those parts of the plant most likely to suffer from erosion corrosion. Erosion in the fluidized bed heat exchangers is expected to be severe.

Marshall and Braithwaite(8) noted that erosion corrosion occurred on turbine blades in geothermal steam service in New Zealand. The rate of attack was reported to be related more closely to static corrosion rates rather than to the hardness of the metal as one might anticipate. Allegrini and Benvenuti(24) found erosion corrosion to be a significant factor in turbine blade performance in the Larderello, Italy, geothermal steam plants. They found that brass and chromium-nickel stainless steels are not suitable for this application. However, martensitic or ferritic chromium steels were successfully used for turbine machines. Toliva(17) conducted erosion-corrosion tests with Cerro Prieto geothermal brines. His results showed that some materials were more rapidly attacked during impingement tests while others were more rapidly attacked by electrochemical mechanisms subsequent to the impingement step. Toliva attributed these differences to variations in chemical and mechanical stability of the materials.

Erosion of metals in seawater service provides a guide to preliminary design for geothermal brine systems. Figure 2.2.4 shows corrosion rates of a number of alloys as a function of seawater velocity(19). Copper-nickel alloys show good overall resistance. Austenitic stainless steels and Monel 400 show a tendency to pit but have good resistance to erosion corrosion.

Control and Design Guidelines

The reduction or prevention of erosion may be accomplished by one or more of the following approaches:

1. Materials selection. The selection of the best alloy will frequently be based on cost-effectiveness factors rather than greatest resistance. Figure 2.2.4 shows the resistance of selected metals and alloys to erosion corrosion in sea-water(19). This provides a guideline for the selection of materials for geothermal piping systems.

2. Design. Several approaches are available. Heat exchangers can be designed with ferrules to protect the entrance region of the tubes from highly turbulent flow, e.g., above about 8 ft/sec (2.5m/sec). Material thickness can be increased to allow for the effects of erosion. Systems can be designed to allow for retrofitting in the event the original (or subsequent) designs prove to be inadequate.

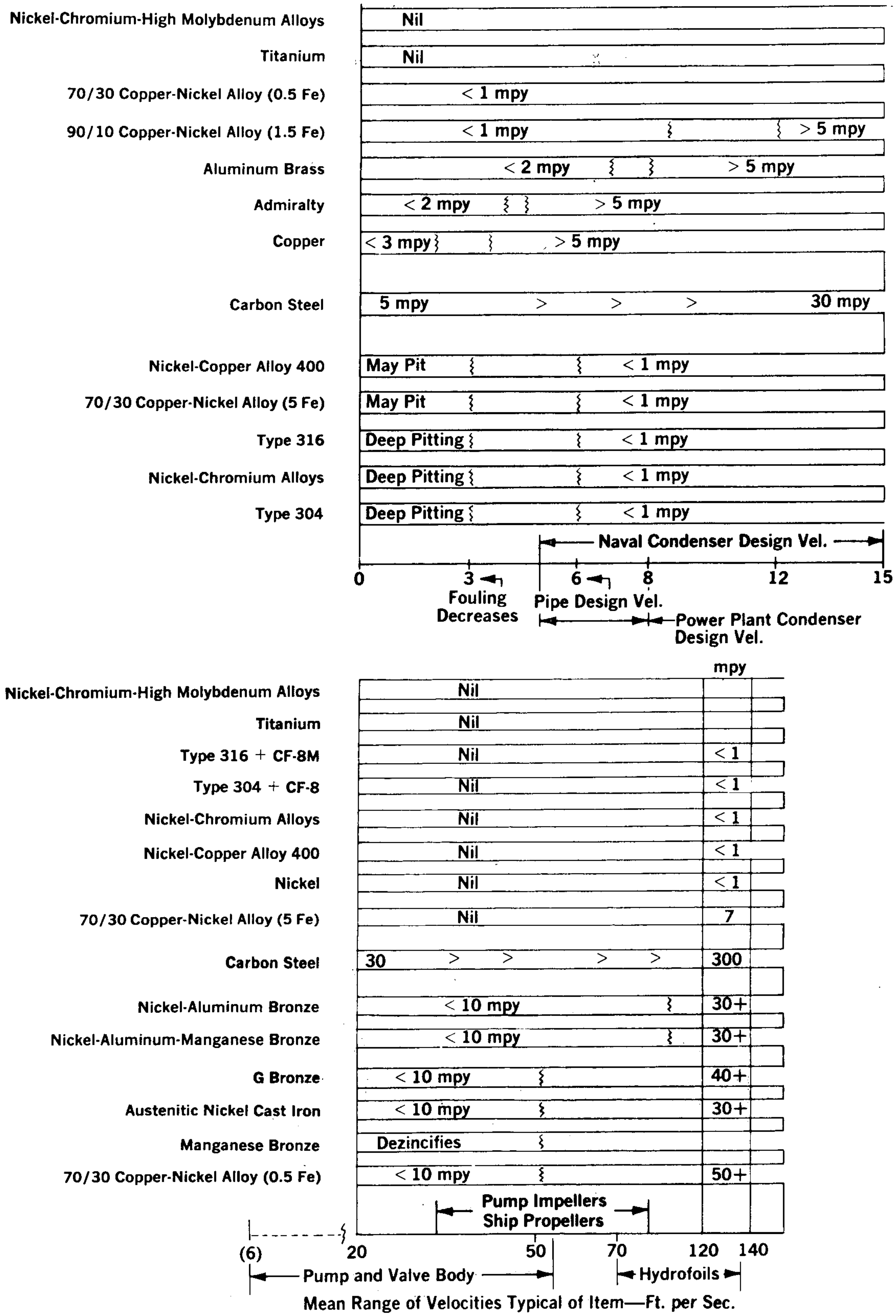


Figure 2.2.4 Effect of velocity on the rate of corrosion of selected alloys in seawater at various velocities(17). Reproduced by permission.

3. Fluid chemistry modification. The use of inhibitors in recirculating systems is frequently helpful. However, in once-through systems, such as for the recovery of heat from geothermal fluids, this would be prohibitive.

4. Separation of solids. The removal of suspended solids by use of cyclones may prevent erosion by this agent.

5. Maintenance of high pressure. A high pressure can maintain gases in solution and thereby prevent impingement of gas bubbles on surfaces.

6. Coatings. The use of hard facing to reduce the effects of impingement is frequently helpful but not always cost-effective. Resilient barriers such as rubber or plastics will reduce corrosion.

7. Cathodic protection. The use of sacrificial anodes, such as zinc, in pumps and heat exchanger heads is sometimes helpful.

2.2.4 Cavitation Corrosion

The form of corrosion attack which results from the formation and collapse of vapor and gas bubbles near the surface of a metal is termed cavitation corrosion. The terms cavitation, cavitation erosion and cavitation damage are sometimes used to describe the phenomena. The differences among these terms are based on mechanical and chemical effects. Cavitation by itself causes the destruction of protective films and can actually remove metal from the surface. If accelerated metal wastage occurs as a result of chemical action, then the term cavitation corrosion is properly applied to the overall process.

Cavitation corrosion frequently occurs in hydraulic turbines, pump impellers, and at other sites where high-velocity liquid flow occurs with large pressure changes. Dissolved gases, such as nitrogen and carbon dioxide, come out of solution during nucleation and growth of bubbles and thereby promote cavitation corrosion.

In geothermal brines, such as those at Raft River, there are, typically, large amounts of dissolved gases which can promote the formation of bubbles. Once released from solution these occluded gases act as a cushion and tend to reduce cavitation damage due to their relatively slow re-solution. However, these gas bubbles tend to increase erosion corrosion damage due to impingement as noted in Section 2.2.3. In the Raft River system all of the pump systems will have a tendency toward cavitation corrosion. In addition, the entrance region of the heat exchanger tubes will be susceptible to erosion corrosion attack.

Control and Design Guidelines

The following methods are suggested as means of controlling or reducing metal wastage from cavitation corrosion.(14)

1. Hydraulic pressure. The mechanism of cavitation corrosion suggests that the operation of pumps and liquid turbines at very high pressure will decrease bubble formation and thereby reduce this form of corrosion.

2. Design. Systems designed to minimize pressure differences will have fewer problems from cavitation and, therefore, from cavitation corrosion.

3. Surface finish. Smooth surfaces are less prone to support bubble nucleation and growth and will therefore reduce cavitation corrosion.

4. Coatings. The use of resilient coatings to absorb the energy from bubble collapse has been used to reduce cavitation corrosion.

5. Materials selection. Alloys vary in their resistance to cavitation corrosion. Table 2.2.1 shows a number of materials with varying resistance to this form of attack in seawater(19).

Table 2.2.1 Order of resistance to cavitation damage in seawater(17). Reproduced by permission.

Resistance to Cavitation Damage Rating	METALS
Group I — Most resistant. Little or no damage. Useful under supercavitating conditions.	Cobalt base hard facing alloy Titanium alloys Austenitic (Series 300) and precipitation hardened stainless steels Nickel-chromium alloys such as alloy 625 and alloy 718 Nickel-molybdenum-chromium alloy C
Group II — These metals are commonly utilized where a high order of resistance to cavitation damage is required but are subject to some metal loss under the most severe conditions of cavitation.	Nickel-copper-aluminum alloy K-500 Nickel-copper alloy 400 Nickel-aluminum bronze Nickel-aluminum-manganese bronze
Group III — These metals have some degree of cavitation resistance but are generally limited to low speed low performance type applications.	70/30 copper-nickel alloy Manganese bronze G Bronze and M Bronze Austenitic nickel cast irons
Group IV — These metals are normally not used in applications where cavitation damage may occur unless heavily protected.	Carbon and low alloy steels Cast irons Aluminum and aluminum alloys

2.3 Relatively Unimportant Forms of Corrosion in the RRGE System

The forms of corrosion discussed in this section are judged to be more of a nuisance than a source of formidable problems in the RRGE systems.

2.3.1 Intergranular Corrosion

Intergranular corrosion is a form of localized corrosion in which a narrow path is preferentially corroded along the grain boundaries of a metal. The mechanical properties are changed as a result of this form of attack. In general the elongation at rupture is decreased significantly while the tensile yield and ultimate strengths are reduced, but to a lesser extent.

The attack is initially on the surface of the structure but penetrates the metal in time. The driving force of the process is the difference in electrochemical potential between the grain boundary and the bulk of the grain, usually as a result of the difference in chemical composition of the two regions.

The grain boundary is a general region of disorder and relatively high free energy. During heating-cooling cycles the disorder may be reduced, for example, by the precipitation of some constituent from a supersaturated alloy system. Age-hardening Al-Cu alloys make use of this behavior to achieve strength. In the Fe-Cr and Fe-Cr-Ni stainless steel systems a carbide forms in the grain boundary regions. The precipitation usually results from welding or improper heat treatment that produces an alloy which is sensitized to intergranular corrosion. The cause of this sensitization is the precipitation of $Cr_{23}C_6$ in the grain boundaries. Stainless steels with less than 0.03% carbon show greatly-reduced susceptibility to intergranular corrosion. These alloys are designated by the letter L following the Type number. For example, Type 304L stainless steel has a carbon content less than 0.03%. Below about 0.009% carbon these steels appear to be immune to intergranular corrosion(15). In some stainless steels an Fe-Cr intermetallic compound can form below 800-850C (1073-1123K). This is the sigma phase(40); its presence renders these steels susceptible to intergranular corrosion in nitric acid solutions. Formation of sigma phase is limited to chromium contents of 20-75%. However, in grain boundaries that are out of the equilibrium with respect to the body of the grain this compound can form at chromium concentrations less than 20%(41).

Stainless steels are not used extensively in geothermal environments because of other corrosion problems. For example, stress corrosion cracking, crevice corrosion and pitting probably place more limits on the use of these alloys in geothermal brines than does intergranular corrosion. However, the use of stainless steels in selected applications or locations may be required in order to take advantage of their unique mechanical properties and general corrosion resistance.

Allegrini and Benvenuti(24) noted that intergranular corrosion was often found in Types 304 and 316 stainless steel pipe weldments in Larderello, Italy, geothermal steam plant systems. These findings reinforce the previously noted precaution of using stainless steels only in selected applications. Because of potential problems from crevice corrosion, welding is preferred to flanged or screwed joints even though the welded joints are susceptible to intergranular corrosion. Such usage should be based on testing.

Control and Design Guidelines

A number of techniques have been used to combat intergranular corrosion. They differ in effectiveness and practicability:

1. Lowering the carbon content of the steel. Since intergranular corrosion is closely associated with carbide precipitation, one of the effective methods of combating this form of corrosion is to use steels with a very low carbon content.

2. Heat treating above 900C (1173K) for austenitic stainless steels or at 650C (923K) for ferritic stainless steels. Under these heat treating conditions the carbon and chromium are more-or-less uniformly distributed throughout the grains. Upon quenching, the carbides are not reprecipitated in the grain boundary regions to such an extent that intergranular corrosion is a problem.

3. Alloying. Titanium, tantalum and columbium are commonly used to combine with carbon in stainless steels. The use of these addition elements is based on the fact that formation and precipitation of carbides of these elements from solid solution takes place at considerably higher temperatures than chromium carbide. Since this is the case, essentially all of the carbon in solid solution will be used up to form carbides of these metals. Thus, formation and precipitation of chromium carbides at lower temperatures can not take place and there can no longer be local chromium impoverishment and the resulting tendency toward intergranular corrosion.

4. Shot-peening the weld area. Intergranular corrosion is effectively reduced if the weld area is subjected to a residual compressive stress; for example, by shot-peening. The grains are broken up near the surface with the formation of numerous slip planes and other lattice defects. During welding, $Cr_{23}C_6$ is precipitated in the grain boundaries and slip planes. However, there is not a continuous path from the surface to the subsurface grain boundaries, and therefore intergranular corrosion cannot proceed in the usual manner. The overall effect is to substantially reduce intergranular corrosion(42).

2.3.2 Fretting Corrosion

When metals in contact undergo slippage, for example, that due to vibration, accelerated metal wastage may occur. This is termed fretting corrosion. The terms false brinelling and friction oxidation have also been used to describe this form of corrosion(15). The corrosion products are typically oxides and the rate of attack may be quite rapid.

Typical sites for fretting corrosion are in ball and roller bearings, pipe hangers and supports in systems with fluctuating flow or water hammer, and in machine mountings. The results of fretting corrosion are removal of metal in the areas of contact, production of an oxide corrosion product, galling, seizing, cracking, fatigue, loss of dimensional tolerance, and loosening of bolted and clamped surfaces. This form of corrosion may lead to others, e.g., crevice corrosion.

In geothermal systems the thermal expansion and contraction due to alternate heating and cooling of the pipes, well casings, machine mountings and heat exchangers may lead to the slippage that results in fretting corrosion. In the RRGE power plant, heating and cooling of transmission lines and tubes in the heat exchangers could result in fretting corrosion. Care will have to be exercised to insure that regular inspections are carried out on systems that may be subject to this form of attack.

The mechanisms of fretting corrosion have been reviewed, in detail, by Waterhouse(43). This reference should be consulted for more information.

Control and Design Guidelines

Fretting corrosion can be minimized by use of the following precautions(11,14):

1. Design the equipment so that slippage between contacting surfaces cannot occur. While this is the ideal situation it may not be feasible in all cases.

2. Increase the hardness of one of the members. The combination of a soft and a hard metal reduces fretting corrosion by excluding corrodants from the faying surfaces. The soft

metals: tin, lead, indium and cadmium are useful in this case though attention must be given to galvanic corrosion. Combinations of stainless steels tend to present the worst situations(20).

3. Increase friction. This reduces slippage between the members. Thin lead coatings have been used to protect bearings during shipping. The lead is quickly worn away during use.

4. Use lubricants (low-viscosity, high tenacity oils and greases) to keep the surfaces protected from the intrusion of the corrodant. Porous surfaces such as those produced by Parkerizing tend to retain the lubricant and thus reduce fretting corrosion.

5. Resilient gaskets can be used to reduce slip between surfaces and exclude corrodants from the interface.

6. Cements (a special form of gasketing material) are available which reduce slippage and access of the corrodant to the surface.

7. Increase load. This reduces the slippage between the surfaces.

8. Decrease load. If the load is small enough, less wear will occur and the amount of fretting corrosion will also be decreased.

2.3.3 Hydrogen Damage

Hydrogen damage is the general term which refers to the mechanical changes in a metal caused by the presence of hydrogen or the interaction of dissolved hydrogen with the metal. Atomic hydrogen is the only hydrogen species that can dissolve in a metal. Molecular hydrogen, (H_2) does not dissolve in or diffuse into metals. Hydrogen damage takes several forms, viz.,(11).

1. Hydrogen blistering
2. Hydrogen embrittlement
3. Decarburization
4. Hydrogen attack

Hydrogen blistering results from the diffusion of atomic hydrogen in a metal, the formation of molecular hydrogen in voids, and the formation of blisters due to buildup of molecular hydrogen pressure in the voids, and delamination of the metal.

Hydrogen embrittlement also results from the diffusion of atomic hydrogen into a metal. The hydrogen atom is small enough that it can occupy interstitial sites in the crystal lattice or form metal hydrides. The presence of these impurities reduces the tensile strength and ductility of the metal.

Decarburization results from the reaction of dissolved carbon with hydrogen at the surface of the metal. Methane (CH_4) is formed and the carbon at the surface depleted. The tensile strength of the alloy is reduced by the decarburization process.

Hydrogen attack is limited to oxygen-containing copper and results in the loss of oxygen from the copper with a concurrent degradation of the properties of the alloy.

Decarburization and hydrogen attack are both high temperature processes and are of limited interest in the utilization of geothermal energy.

The Raft River geothermal brines are slightly basic. For this reason little hydrogen will be reduced on the surfaces of the metals in contact with the hot brines and hydrogen damage is not likely to occur in this system. The use of sulfuric acid for control of scaling in the cooling tower may result in some hydrogen damage. Normal surveillance of the system should detect this form of damage.

Foster, et al.(44) noted that hydrogen blistering in geothermal fluid service in New Zealand was generally associated with severely laminated steel. Blistering was thought to be more closely associated with poor materials than with a general tendency of the brines to promote this form of damage. Hydrogen embrittlement was not detected in geothermal steam service and could be produced only in cold geothermal steam condensate that was saturated with H_2 and CO_2. Hydrogen-induced delayed fracture was observed in some low strength steels used for well casing when exposed to geothermal steam condensate. The samples tested were severely notched. Foster, et al., concluded that such stress raisers should be avoided where practical. Hydrogen damage appears to be a minor consideration at the Raft River power plant or in non-electric applications.

Prevention of Hydrogen Blistering

The proper application of one or more of the following techniques should result in reduction of this form of attack(14).

1. Select the proper grade of steel. Rimmed steels contain numerous bubbles or voids that result from the deoxidation practice and appear during ingot casting(45). Fully killed steels have very few bubbles(45). The rimmed steels are much more subject to hydrogen blistering than are the killed grades of steel. The killed grades should be selected where hydrogen blistering is expected to be a problem.

2. Use coatings. Some coatings act as barriers to diffusion of hydrogen by preventing the adsorption of hydrogen at the surface of the metal or promoting the formation of molecular hydrogen. Rubber, plastic and ceramic coatings are frequently used as barriers to reduce hydrogen blistering. Nickel and austenitic stainless steel cladding are also effective in

preventing blistering. Care should be used in selecting the method of cladding application since electroplating frequently results in hydrogen blistering.

3. Use inhibitors. The reduction of hydrogen ion formation by the use of inhibitors is effective in the reduction of blistering.

4. Remove those compounds (sulfides, cyanides, arsenic compounds and phosphorus-containing ions) which promote hydrogen embrittlement by preventing molecular hydrogen formation. Sulfides and phosphates are usually found in geothermal brines and their presence should be considered when selecting materials.

5. Select proper materials. Nickel-based alloys and nickel-containing steels are resistant to hydrogen blistering.

Prevention of Hydrogen Embrittlement

The mechanisms of hydrogen blistering and hydrogen embrittlement suggest that different techniques would be effective in prevention of these two forms of hydrogen damage. The following techniques are of help in preventing hydrogen embrittlement(14):

1. Reduction of overall corrosion. Since hydrogen is frequently produced in electrochemical processes, the reduction of overall corrosion will lead to a reduction in hydrogen embrittlement.

2. Changing electroplating procedures. Hydrogen charging during electroplating is a frequent source of hydrogen for hydrogen embrittlement. Minimizing the production of hydrogen during plating will aid in reducing hydrogen embrittlement.

3. Baking. The baking of steels, at 100C (373K) or above, that have been hydrogen-charged reduces the amount of hydrogen in metallic solution and returns the structure to about the same mechanical condition as before charging.

4. Materials selection. The high strength steels are most susceptible to hydrogen embrittlement. Susceptibility to hydrogen embrittlement is reduced by alloying with nickel or molybdenum.

5. Proper welding procedures. Water and water vapor present during welding contribute to hydrogen embrittlement. The use of low-hydrogen welding rods is suggested as a means of reducing hydrogen embrittlement when this is a problem.

3. Nonmetallic Materials for RRGE Construction

3.1 Concrete

Corrosion of concrete by Raft River geothermal brines is a potential problem in utilization of this resource. Corrosion of concrete in the vapor region results from gases discharged from the brine. In the water region corrosion results from dissolution by water-borne lixiviants. Corrosion in the vapor region is frequently more severe than in the water region. The vapor-water interface region usually represents the worst location for attack by geothermal brines. The only data available are those reported by Allegrini and Benvenuti(24) at Larderello, Italy. They reported extensive damage in the vapor-water splash zone.

In the vapor region etching occurs by acid attack, for example, by sulfuric acid produced by oxidation of sulfides. Dissolution of calcium compounds occurs by reaction with CO_2 in the vapor. Calcium in free lime is attacked first. The calcium combined in silicates is probably the last to be attacked.

Exposure of reinforcement bars or mesh results in corrosion of these materials. The corrosion products are voluminous and may exert a wedging action which accelerates deterioration of the concrete. The concrete is cathodic with respect to the metal(46) and this will tend to accelerate corrosion of the reinforcement by galvanic processes.

In the liquid region the corrosion is generally less than in the vapor region. The constituent causing most of the damage is thought to be CO_2. Additional damage by boric acid and sulfates contributes to the deterioration of the concrete. Carbon dioxide combines with the lime to form relatively-soluble bicarbonates. Deposition of elemental sulfur, produced by oxidation of sulfides, on the structures tends to decrease the rate of attack.

Polymer concrete and polymer-impregnated concrete (PIC) have been suggested as alternatives to regular concrete for geothermal environments(47). These materials are undergoing testing at a number of sites in the U.S. The resistances of PIC and regular concrete to attack by hydrochloric acid are compared in Figure 2.3.1.

Cement-asbestos is corroded by CO_2 contained in the brine(24). Corrosion occurs by dissolution of the lime in the binder. Preliminary examination of cement asbestos pipe used in geothermal service at Boise, Idaho, has not shown evidence of attack.

3.2 Plastics

Polymers offer potential advantages in terms of strength-to-weight ratios as well as corrosion resistance. There are many kinds of polymers; however, only a few types have demonstrated chemical stability in high temperature brines. Some types of polymers flow at too low a temperature to be useful.

The glass transition temperature is a measure of the freedom of molecular motion within the polymer and therefore, a measure of the tendency of the material to flow under stress(48). The long chain molecules in amorphous polymers are usually coiled and randomly intertwined. At temperatures below the glass transition temperature there is essentially no molecular motion and the polymers are hard and glassy and frequently brittle. Above this transition temperature the polymer molecules tend to untangle and can rotate about their carbon chains. Under stress the molecules can slip past each other and be permanently deformed. The coefficient of thermal expansion usually shows a marked increase as the temperature is raised into the plastic region.

In geothermal applications only those polymers with high glass transition temperatures should be considered. For example, polyethylene has a glass transition temperature of -125C (148K); polytetrafluoroethylene (PTFE), on the other hand, has a transition temperature of +125C (398K). PTFE is useful in geothermal applications while polyethylene is not.

From the chemical point of view there are two general classes of polymers, those produced by addition polymerization and those produced

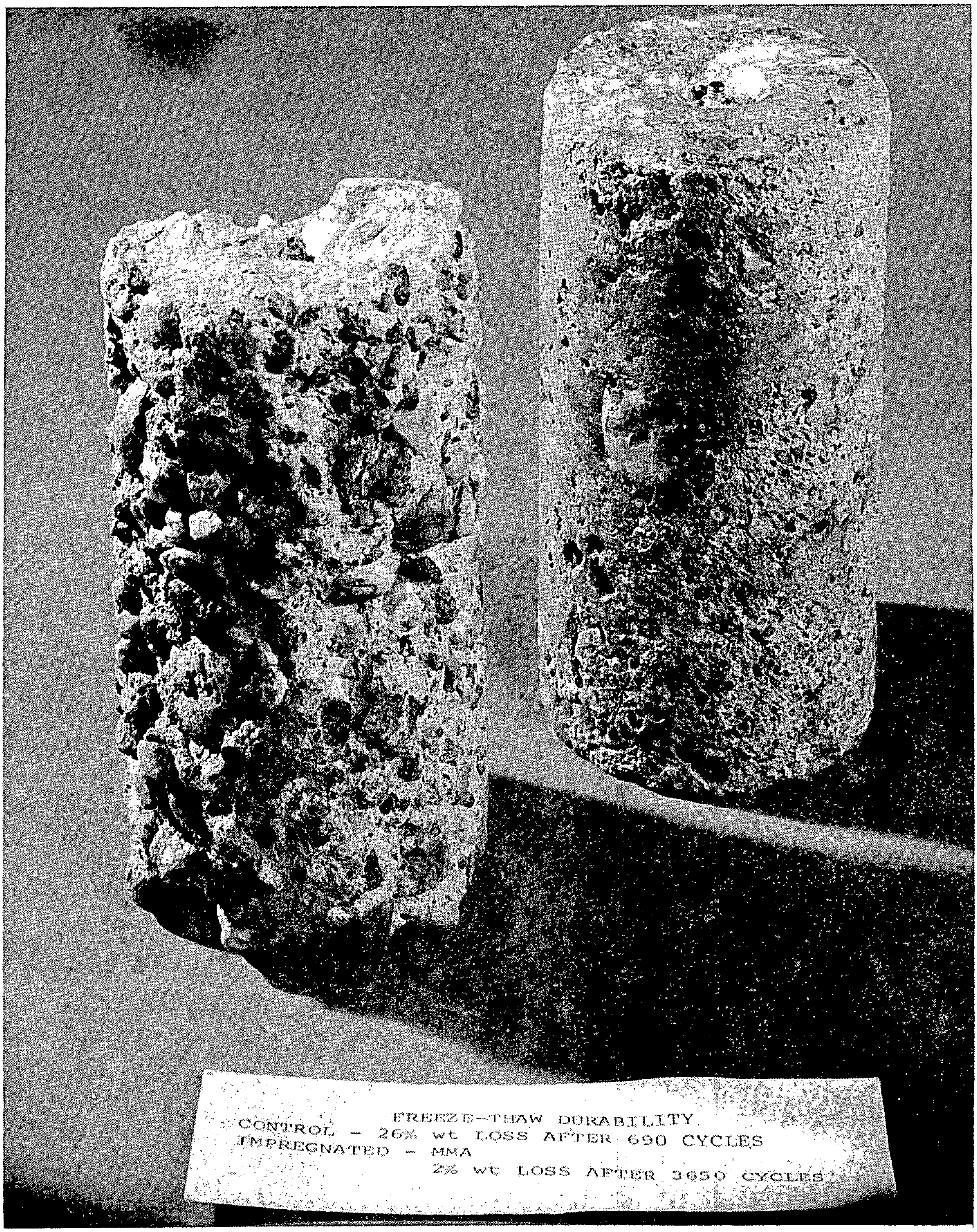


Figure 2.3.1 Comparison of degradation of ordinary concrete and plastic impregnated concrete subjected to 15% hydrochloric acid corrosion (47).

by condensation reactions. Of the addition polymers those produced from vinyl-like compounds are most familiar.

Condensation polymers result from the reaction of two compounds to produce a polymer and a byproduct molecule, such as water. For example the reaction of adipic acid and 1,6-diaminohexane produces Nylon 6/6 (an amide polymer) and water. Polyesters result from reaction of organic acids and alcohols.

In testing a number of polymeric materials in natural and synthetic brines Lorensen, et al.(49) found that those polymers having one or more of the following chemical characteristics were substantially resistant to corrosion:

1. Substantial aromaticity
2. Fluorine content
3. Carbonized structure
4. Cross linked aliphatic unsaturation (e.g., divinyl benzene)

Those polymers containing water-sensitive groups, i.e., hydrolyzable linkages, were unstable in the brine even though the polymer exhibited high temperature stability when subjected to "dry" thermogravimetric analysis. Amides, imides and esters are typical water-sensitive groups.

Of the materials tested by Lorensen, et al., the following proved to be the most stable.

1. Carbon-graphite cloth (heat-shield type) composite
2. Polytetrafluoroethylene (DuPont Teflon TFE)
3. Fluorinate (perfluoroalkoxy) copolymer (DuPont Teflon PFA)

4. Polyaromatic (Hercules H104 and H124)

5. Polybenzimidazole (Whittaker Imidite 2803)

6. Polyphenylquinoxaline/carbon fiber

7. Phenolic/glassfiber (Ferro Corp.)

Several of the materials listed above are composites. Such blending of polymer and a reinforcing material usually adds substantially to the strength of the material but at a sacrifice in ductility.

The conditions used by Lorensen, et al. in their work are substantially more severe than those expected at Raft River. Some polymer systems rejected by these workers may be useful in our applications. The investigation of polymers in the Raft River brine will be a part of our testing program.

4. CONCLUSIONS

The selection of materials for new geothermal installations is a formidable task. Not only are there significant differences in the water chemistry and temperature from one field to another but there may be variations from one well to another within a field. Materials selection should be based on plant experience and field testing until a broader base of corrosion test data is available. Prior to the availability of sufficient design data much of our design activity will have to be based on seawater experience.

The presence of oxygen, or other reducible species, in the brine is the main contributor to corrosion. The ubiquitous occurrence of chlorides in geothermal brines adds significantly to the potential corrosion problems. The exclusion of air from the transmission lines between the producing wells and the power plant should be an achievable goal. In-leakage of air to the system appears to be most likely at pumps, valves, flanged pipe joints, etc,. Rejection of cooled brine to a holding pond prior to reinjection of the water into the geological formation could result in excessive corrosion of the reinjection pumps and well casing.

The greatest corrosion problems are likely to occur in working fluid condensers and cooling towers using aerated waters with a high dissolved solids content. The selection task will be further exacerbated if geothermal brine is used for cooling tower make-up. This system will require the greatest care in final materials selection. The 90/10 cupronickel alloy is recommended for the condenser tubes. Cast iron or cast steel pumps and valves with bronze, Monel 400 or Type 316 stainless steel trim should provide adequate service in this environment. However, Banning and Oden(9) noted that cast iron may corrode at 8 mpy (0.2 mm/year) in some geothermal systems; carbon steel also corrodes at excessively high rates in some systems. These results suggest that those materials be tested before they are selected for use in critical locations in the Raft River power plant.

A number of materials may be selected for cooling tower structural members. Steel and cast iron are probably the most economical. Carbon steel fasteners would be acceptable with these materials; however, Types 304 and 316 stainless steels or Monel 400 would provide more reliable service. The stainless steel would corrode at about 0.1 mpy (0.025 mm/year)(9). A corrosion allowance of about 0.5 mpy (0.13 mm/year) should be made in designing the cooling tower where this material is used. Monel may corrode at a rate as high as 5 mpy (0.13 mm/year) and would be less acceptable than the stainless steel(9).

Carbon steel and cast iron should be suitable for the isobutane preheaters and boilers if tube-and-shell heat exchangers are used for this system. If fluidized-bed heat exchangers are selected for these applications a more abrasion-resistant material may be required. The selection of carbon steel is based on the premise that oxygen in-leakage will not occur or will be negligible. A corrosion allowance of 1.25 mpy (0.032 mm/y) should be adequate for the heat exchanger tubes. Pitting should not be a major problem in these structures in the absence of air.

Transmission lines between the producing wells and the power plant may be cement-asbestos or carbon steel. Since the concentration of oxygen in the water carried by these lines should be very low, corrosion should not be a problem. Transmission lines from the plant to the reinjection wells should be corrosion resistant if the brine has been aerated; for example, if the water has been rejected to a holding pond its oxygen content may be high. In this application cement-asbestos should be suitable. A corrosion allowance of 5-10 mpy (0.13-0.25 mm/year) is recommended for carbon steel lines because of possible air intrusion(9). API-5L pipe has been recommended for this purpose(50); similar grades of ASTM or ASME pipe would be equally acceptable. Concrete pipe should also be suitable for this purpose but would not be recommended for hot brine service. Since reinjection wells may be used as producing wells and, conversely, producing wells may be used for reinjection, the use of either cement-asbestos or carbon steel is recommended.

K55 steel pipe has been used for casing RRGE wells 1 and 2. No change in this material is suggested(50). A corrosion rate of 5-10 mpy (0.13-0.25 mm/year) may be expected here due to air contamination of the water(9).

Concrete structures subjected to prolonged contact with geothermal brine should be overcoated with coal tar pitch or similar material to reduce attack by the carbon dioxide in the water. The use of concrete pipe for transmission lines is not recommended.

Filament-reinforced polymers may be cost-effective materials in moderate- and low-temperature applications. Although these materials have a history of use in the chemical process industries, the high temperatures of geothermal brines suggest that testing be carried out to determine the resistance of these materials to degradation by water absorption and wicking action along exposed filaments as well as to chemical action.

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