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Sourcebook for Microbiologically Influenced Corrosion in Nuclear Power Plants

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Technical Report

SOURCEBOOK FOR MICROBIOLOGICALLY INFLUENCED CORROSION IN NUCLEAR POWER PLANTS

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NOTICE

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INTRODUCTION

Microbiologically Influenced Corrosion (MIC) has been identified as a problem in nuclear power plant systems during the past several years. Although recognized over fifty years ago and studied extensively in other industries, the influence of microorganisms, particularly bacteria, on structural materials in nuclear power plants has only recently come to light. The phenomenon has received considerable attention as a result of INPO Significant Event Report SER 73-84 [1] issued in October, 1984, and an NRC Information Notice (IN 85-30) issued in April, 1985 [2]. These reports were prompted by the fact that MIC had been implicated in the degradation of safety related systems in several nuclear power plants. The primary objective of this report is to provide background and methods for the diagnosis, treatment, and prevention of MIC in nuclear power plant components.

Nuclear power plants can exhibit a particular susceptibility to MIC. MIC is most likely under stagnant conditions or operation with low or intermittent flow. The long lead times associated with nuclear plant construction provide for long stagnant periods, often with structural materials in contact with untreated water used for hydrostatic testing; a condition amenable to microbial growth. The large number of stand-by and redundant systems in nuclear plant design also establishes stagnant or intermittent flow conditions, a situation in which a number of systems, some of which are safety-related, will be susceptible to MIC. The use of once-through systems utilizing water from man-made lakes or cooling ponds, water sources rich in organics, may also contribute to the potential difficulty.

This report presents a number of case histories from the power industry illustrating the effects and characteristics of MIC for commonly used materials. Section 3 of the report provides background data from these case histories along with photographic details of the phenomenon. The case histories may be a useful starting point for a brief review of MIC, for comparison to a corrosion problem that may be unexplained, or as a summary of some the effects that manifest microbiologically influenced corrosion. For many readers, Section 3 is a good place to start to get a feel for the type of information that is contained here.

Section 2 provides an introduction to the terminology and basic chemical and physical effects produced by microbial activity and how microbial activity can affect corrosion. Sections 4 and 5 are brief descriptions of how MIC affects commonly used structural materials and nuclear power plant systems. Sections 6, 7, and 8 go into greater detail regarding the diagnosis of suspected MIC, its treatment, and prevention. These sections provide recommendations for design, materials selection, control of fabrication and testing procedures, and operating philosophies to avoid or treat MIC in power plants. For a situation where MIC is suspected, Section 6 provides guidelines for analysis utilizing phenomenological, physical, chemical, metallurgical, and biological determinations to assess whether the observed corrosion is truly a result of microbiological activity. In Section 7, mechanical, chemical, and operational treatments are suggested to eliminate the corrosive condition in the event that MIC is positively diagnosed. Section 8 also offers treatment guidelines but focuses on prevention of MIC in new installations or the mitigation of MIC following treatment and removal of an existing condition.

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BACKGROUND

At first blush MIC seems to be a unique phenomenon that represents a departure from the electrochemical processes that corrosion engineers have investigated and understood for many years. In actuality, MIC does not represent a new form of corrosion; only the influence of living organisms on well characterized electrochemical reactions. In some circumstances, microbial activity does nothing more than set up a localized environment that is conducive to corrosion based solely upon geometric considerations. In this case, the microbes form "living crevices" such that concentration cells are established and accelerated corrosion can result. These conditions may occur simply as the result of biofouling or, more commonly, as the result of absorption of nutrients (e.g., oxygen) creating concentration cells beneath areas of microbial growth. Massive deposits are often produced, as corrosion products (generally but not always from upstream corrosion) are trapped in the sticky exopolymer layer produced by the microbes. In other cases, microbes produce metabolites such as organic or mineral acids, ammonia, or hydrogen sulfide which are corrosive to structural materials. A number of microbes can concentrate halides which result in severe, localized corrosion of ferrous materials. In still other cases, microbial activity interferes with the cathodic half-reaction under oxygen-free conditions resulting in increased anodic dissolution. This is the process by which the sulfate reducing bacteria (SRB) affect corrosion, particularly the corrosion of ferrous materials. The precise influence of associated enzymes, ferrous sulfides, and hydrogen sulfide is subject to dispute, however, the corrosive condition resulting from microbial activity is greater than the effect of H_2S or FeS alone. Other ways that microbes can influence corrosion are oxidation of metal anions to less soluble forms (e.g., Fe^{+2} to Fe^{+3} by iron oxidizing bacteria), destruction of protective coatings, and metabolism of inhibitors (e.g., nitrites and nitrates) [3, 4].

GLOSSARY

The following terms are frequently used in descriptions of Microbial Induced (or Microbiologically Influenced) Corrosion.

Terms

Aerobic. Requires oxygen for growth.

Anaerobic. Requires oxygen-free conditions for growth.

Planktonic. Suspended in the fluid stream.

Sessile. Attached to a surface.

Heterotrophic. Utilizes organics as the principal carbon (i.e., nutrient) source.

Autotrophic. Utilizes inorganic carbon sources (e.g., CO_2).

Sporulating. Produces spores as an alternative method of reproduction.

Hydrogenase. An enzyme generally associated with sulfate reducing bacteria. Hydrogenase catalyzes the oxidation of hydrogen. Hydrogenase alone can catalyze the reduction of sulfate and is considered to be the active agent in the cathodic depolarization of iron [5].

Exopolymer. The extracellular material that defines the shape of a particular organism. This material is left behind when the organism dies. It is frequently sticky or slimy and serves to trap debris and other organisms.

Disinfect. A reduction in the number of microbes present or the destruction of certain (unwanted) types. (A relative term).

Sterilize. To kill or remove all forms of life. (An absolute term).

Biocide. A chemical agent (or treatment) that kills bacteria and other simple life forms.

Biostat. A chemical agent (or treatment) that keeps bacteria and other simple life forms from growing.

Tubercle. A localized accumulation on the metal surface containing corrosion product(s), cellular material (e.g., living organisms, exopolymer) and debris. Tubercles may be large discrete entities or may grow together and block pipes.

Modifiers

These terms are used to indicate the degree of a particular characteristic.

Obligately ______________. (Requires small levels of ________________ for growth).

Strictly ________________. (Requires completely _____________ conditions).

Facultatively ________________. (Can grow under ________________ or non-__________________ conditions).

BACTERIA TYPICALLY ASSOCIATED WITH MIC

Microbes which can contribute to corrosion live everywhere—in soil, in water; utilize a variety of nutrient sources; grow over a wide range of temperature and pressure conditions and survive over an even wider range. Many produce spores that can withstand still more adverse environments, then germinate years (possibly even centuries) later under more amenable conditions. Various species are aerobic, others anaerobic with the capability of surviving under a vast range of oxygen pressures. They are capable of rapid reproduction and are highly and rapidly adaptable to environmental changes. They attach themselves to surfaces, sense various chemical compounds and move to them, and develop colonies or consortia such that anaerobes can flourish beneath aerobic organisms. Microbial activity can initiate corrosion with propagation determined by inorganic effects, microbes can cause corrosive conditions to be maintained where they otherwise would not, and microbes can influence corrosion of materials from afar by production of corrosive by-products. The species that can produce corrosive conditions and the basic reactions by which they do so are summarized below.

Sulfate Reducing Bacteria

Desulfovibrio and *Desulfomaculum* are the infamous sulfate reducing bacteria (SRB) and are considered to be the most widely distributed and economically important organism associated with corrosion [6]. They reduce sulfate to sulfide and are strictly anaerobic although they may be found in virtually all soils and are capable of survival in aerated water [7, 8]. A high iron content is generally associated with the cell structure and wastes of the SRB. Their metabolism results in locally alkaline conditions. Their survival depends upon the presence of oxygen scavengers to achieve anaerobic conditions. These rod-shaped bacteria attack cast iron, carbon and low alloy steels, and stainless steels, and contribute to corrosion of high nickel alloys and copper alloys as well [9]. Black FeS films in the center of conical pits generally characterize SRB attack on stainless steels. Bright and shiny surfaces are normally found at the active corrosion front. Rings of different color generally surround the pits. The SRBs can also produce massive deposits on and deep pitting of carbon steels. The bulk of the literature on microbial corrosion is devoted to the SRBs. See for example [3, 4, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21].

In 1934 von Wolzogen Kuhr and van der Vlugt [22] theorized that corrosion of iron buried in an anaerobic soil was due to the activity of these anaerobic, sulfate reducing bacteria. The half-cell reactions involved, as offered by von Wolzogen Kuhr and van der Vlugt, are:

$$4Fe \rightarrow 4Fe^{+2} + 8e^- \qquad (1)$$

anodic reaction

$$8H_2O \rightarrow 8H^+ + 8OH^- \qquad (2)$$

electrolytic dissociation of water

$$8H^+ + 8e^- \rightarrow 8H \qquad (3)$$

cathodic reaction

$$SO_4^= + 8H \rightarrow S^= + 4H_2O \tag{4}$$

cathodic depolarization (by SRB)

$$Fe^{+2} + S^= \rightarrow FeS \tag{5}$$

corrosion product

$$3Fe^{+2} + 6OH^- \rightarrow 3Fe(OH)_2 \tag{6}$$

corrosion product

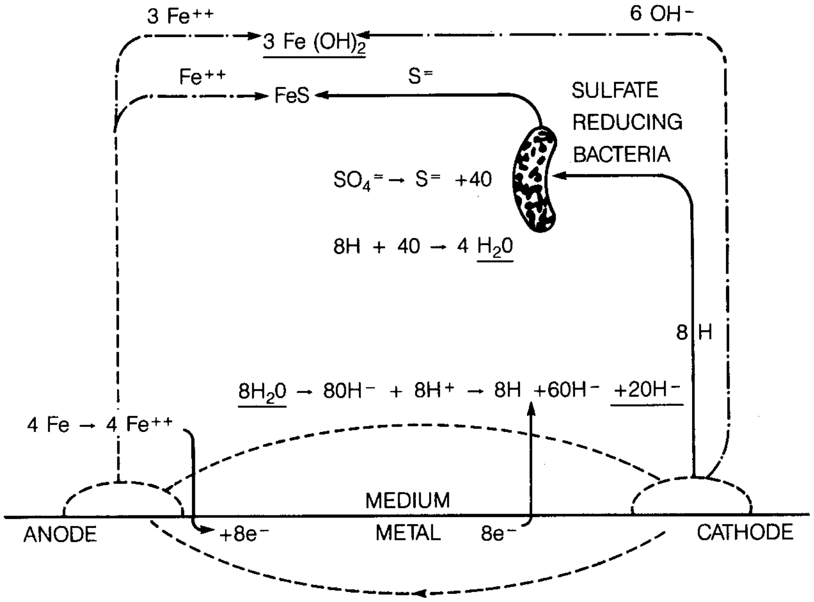
$$4Fe + SO_4^= + 4H_2O \rightarrow 3Fe(OH)_2 + FeS + 2OH^- \tag{7}$$

overall reaction

This process is presented graphically in Figure 2-1.

Equation 4 has been the subject of considerable controversy in attempts to describe the role of the bacteria in the overall corrosion reaction. Various theories have been offered as to the importance/necessity of the enzyme hydrogenase to the process, the depolarizing influence of iron sulfide, interaction between iron sulfide and hydrogenase, the effect of hydrogen sulfide (alone), and the "corrosive metabolite" theory offered by Iverson [3] that requires formation of a phosphorus-containing metabolic by-product which enhances general corrosion. The various theories have been reviewed and compared extensively elsewhere [3, 6, 8, 10, 11, 12, 15, 17, 18, 19, 23, 24, 25].

FIGURE 2-1
Influence of Sulfate Reducing Bacteria on Corrosion of Iron (after Sharpley [5])



The thoughts offered by Bibb and Hartman [15] and Pope, et. al. [17] appear to be the most useful for utilizing the accumulated knowledge on SRBs. In summary:

1. The evidence for cathodic polarization (whatever the exact mechanism) is quite convincing.
2. The precise roles of hydrogenase, ferrous ion, iron sulfide, and hydrogen sulfide have not been positively determined but are probably all interdependent upon the local environmental and ecological conditions.
3. The corrosive metabolite theory is interesting but not well established. A correlation between MIC and increased pollution of surface waters with phosphate, nitrate, and sulfate over the past fifteen years is circumstantial evidence for such a theory.

The processes noted above apply to ferrous materials, particularly, the steels and cast irons. Sulfate reducing bacteria also contribute to the corrosion of stainless steels which rely upon the formation of a passive film high in Cr_2O_3 for protection. They also attack high nickel alloys and copper alloys albeit by other means. Random pitting of carbon steels under nodules or tubercles (where anaerobic conditions are achieved), generally in the presence of black FeS, indicates the influence of SRB. In the case of stainless steel, involvement of SRBs results in open pits filled with black iron sulfide. Pitting in high nickel and copper based alloys appears to be the result of sulfide attack (i.e., a corrosive metabolite). Obviously, the black, smelly iron sulfide that typically characterizes SRB invovlement on steels is absent but the result is the same—hemispherical pits that can penetrate the wall. In these cases, the effects of the microbes are not so mysterious and can be readily reproduced in low oxygen sterile water with H_2S additions. For example, pitting of condenser tube alloys is significantly increased in the presence of as little as 0.2 ppm sulfide [26].

Iron and Manganese Bacteria

Pseudomonas are aerobic slime formers. They are generally found in corrosion deposits as relatively thin, uniform films. Their main involvement in corrosion processes is to scavenge oxygen and harbor other species such as the sulfate reducing bacteria [7]. They reduce Fe^{+3} to Fe^{+2} and in doing so may expose active metal and thereby increase corrosion [17].

Gallionella are obligately aerobic iron bacteria that exude hydrated metal oxide. Their wastes are high in iron and manganese and they can concentrate chloride. MIC associated with Gallionella is typically manifested by pitting of carbon and stainless steels. Pits in stainless steel generally exhibit very small entry and exit holes that open to a cavernous corroded area [3,4,7,9,13,27]. Corrosion deposits are hemispherical on carbon steels and low conical shapes on horizontally oriented stainless steel; rusty streaks on vertical surfaces. Deposits can be massive—they can choke carbon steel pipes. The bacterium itself is kidney shaped although the hydrated metal oxide appears in the form of twisted ribbons or twisted filament pairs [7].

Crenothrix, Leptothrix, Clonothrix, and *Sphaerotilus* are aerobic, filamentous bacteria that can corrode carbon steel and stainless steels. Their main metabolic effect is to oxidize soluble Fe to the insoluble $Fe(OH)_3$. They may also concentrate and oxidize manganese [7]. Crenothrix are more often found in the United States while Leptothrix are more common in the United Kingdom [11]. Sphaerotilus are particularly abundant in heavily polluted waters [28]. White [28] and others [29,30] have suggested that these genera might actually be different forms of the same organism. These bacteria generally form low, hemispherical tubercles on carbon steels with oxygen depleted conditions beneath the tubercle. Deposits are typically brown or reddish brown.

Iron oxidizing bacteria such as Gallionella, Sphaerotilus, Leptothrix, and Crenothrix oxidize the soluble ferrous ion to the less soluble ferric state as their primary energy source leading to deposition of ferric hydrate and creation of creviced geometries under tubercles comprised of the metal hydrate and the bacterial exopolymer. Many of these species also tend to concentrate chloride and manganese as well leading to high local concentrations of chloride in oxygen deficient areas—prime contributors to pitting and general corrosion on carbon steels with potentially devastating pitting on stainless steels [3, 7, 9, 11, 13, 17, 18, 28, 31]. A simplified illustration of an oxygen concentration cell that can form under a tubercle is shown in Figure 2-2. As Figure 2-3 shows, pits can grow as ferrous ions are produced at the base of the pit. To maintain electrical neutrality, chlorides are concentrated inside the pit and the pit grows. This pit growth sequence is exactly the same as that encountered in oxygenated chloride solutions without any microbial influence. The influence of the iron oxidizing bacteria can be two-fold. First, the aerobic bacteria form a colony and the oxygen concentration is depleted such that a differential aeration cell is produced. Localized corrosion may then proceed at the locally anodic region (as depicted in Figure 2-2). Second, as Fe^{+2} is oxidized to the less soluble Fe^{+3}, the electrochemical potential at the surface is shifted in the noble direction such that the pitting potential is exceeded and pits initiate. The iron oxidizing bacteria may further assist in the autocatalytic process by oxidizing ferrous ions to the ferric state, thus keeping the potential in the pitting regime. The pits induced on stainless steel as influenced by Gallionella frequently take precisely the shape shown in Figure 2-3 with very small entry and exit holes with massive subsurface cavities. [25]. This shape is to be differentiated from the more rounded and shallow pits noted in the presence of SRBs.

FIGURE 2-2
Oxygen Concentration Under Tubercle [18]

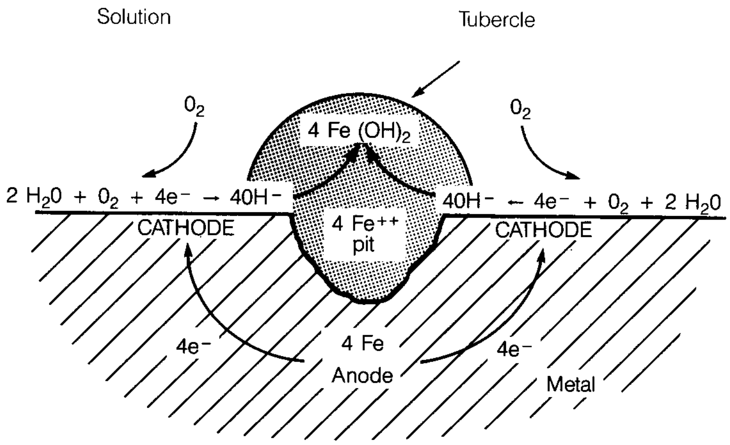
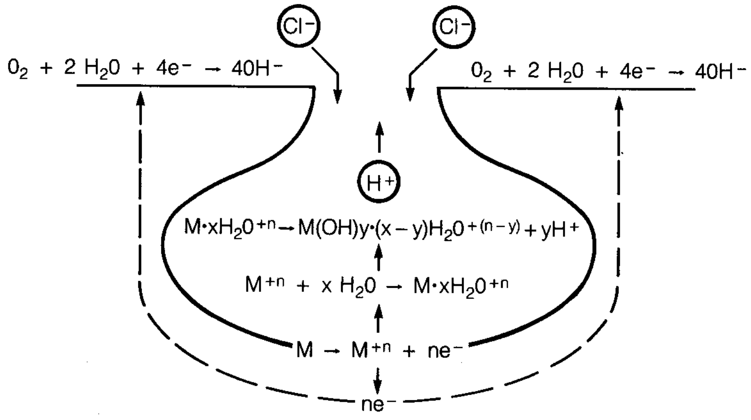


FIGURE 2-3
Schematic Diagram of a Growing Pit (after Duquette & Ricker [25])



Whether iron bacteria contribute to corrosion by concentration of aggressive ions, deposit iron from solution, or even assist in dissolution by reducing ferric ions to the ferrous state (e.g., Pseudomonas) they can always contribute to corrosion, whether on ferrous or nonferrous materials, by

1. creating differential aeration cells under deposits or slime masses, and
2. harboring sulfate reducing bacteria, both by production of anaerobic conditions necessary for the SRBs and by providing physical protection from fluid forces and biocides.

Sulfur Oxidizing Bacteria

Thiobacillus and *Ferrobacillus* [32] are strictly aerobic and obligately autotrophic. Thiobacillus oxidize sulfide to sulfate and form H_2SO_4; some species can generate $pH < 1$ [23]. They also oxidize ferrous ions to the ferric state [7]. They often coexist with the sulfate reducing bacteria [23]. Brown deposits of ferric sulphate are often noted in waters containing these organisms [32]. They do not appear to be a major contributor to the corrosion of metals although they are responsible for rapid deterioration of concrete structures [8, 11, 18].

Thiothrix and *Beggiatoa* are rod-shaped, aerobic bacteria that oxidize H_2S to elemental sulfur. The result of their involvement in a corrosion reaction is often characterized by a yellow sulfur deposit. Their major contribution to corrosion processes, however, is to form a slime in which SRB may thrive [7].

Microbes such as Thiobacillus, Ferrobacillus, Thiothrix, and Beggiatoa oxidize sulfur and sulfur compounds under aerobic conditions. Sulfuric acid produced in their metabolic process is a potential source of metallic corrosion although one that is infrequently reported [7, 11, 23]. These organisms do, however, frequently contribute to the failure of concrete, whether in structures, large pipes, or linings for steel pipes. Cemented joints can be particularly susceptible [6, 8, 18].

OTHER EFFECTS

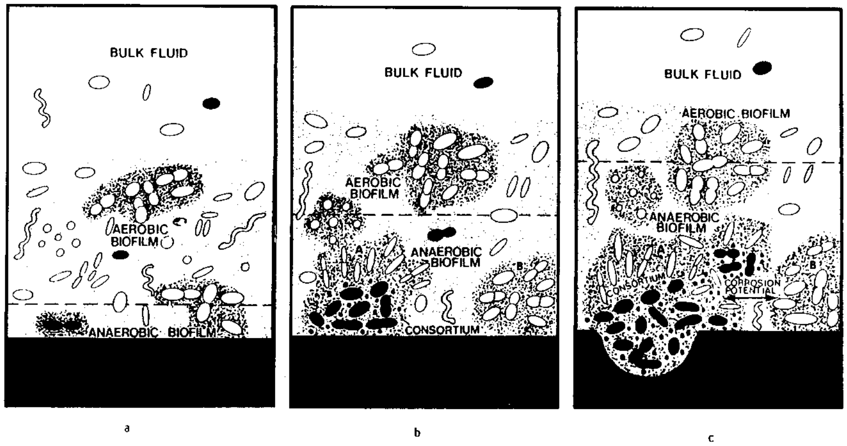
Many other microorganisms have been identified as potential contributors to MIC in various laboratory studies, corrosion investigations in other industries, and water analyses [e.g., 6, 12, 13, 18, 23]. Foremost among them are

Cladosporium resinae, the so-called "kerosene fungus." It is an imperfect fungus that excretes acetic acid. It has received considerable attention relative to the attack of aluminum tanks used for storage of aircraft fuel.

Nitrosomonas and *Nitrobacter* metabolize chemical species that form a part of the nitrogen cycle. This effect may be important since nitrites (and to a lesser extent, nitrates) may be used as corrosion inhibitors.

Acid forming microbes of different types can result in localized attack of a wide variety of materials including coatings. Some microbes may attack specific constituents of organic coatings such as pigments or corrosion inhibitors. The synergism among different genera of microbes is another area of considerable importance. For example, aerated environments do not preclude attack by anaerobic organisms. Colonies such as that illustrated in Figure 2-4 from Costerton [21] are commonplace and demonstrate the coexistence of aerobic and anaerobic organisms. In such consortia the underlying microbes are also well protected from biocides by the various layers above. The importance of mechanical removal of tubercles and other deposits that can harbor damaging organisms as well as the necessity of dispersing organic and inorganic materials cannot be overemphasized.

FIGURE 2-4
Development of a Microbial Consortium (from Costerton & Geesey [21])



3

CASE HISTORIES

Individual histories of cases in which MIC has caused problems in water lines with details of material, operating condition, description of problem, method of discovery, analysis of the environment and corrosion site, treatments (and their success), plus color photos are presented in the following pages.

CASE HISTORY 1: Carbon Steel

COMPONENT/SYSTEM Emergency Equipment + Cooling Water (+ Other Service Water Systems)

MATERIAL Carbon steel pipe to 24 in. diameter and larger. Vertical & Horizontal runs.

OPERATING HISTORY
Eight years' service. Aerated river water: stagnant/near stagnant conditions. Results correlated with experience with pipes up to 35 years' service in river water.

METHOD OF DISCOVERY
Inadequate cooling water flow to heat exchangers. Problem found to be ΔP from (massive) deposits in Nuclear & Fossil water lines to 35 years' operation.

DIAGNOSTICS
WATER:

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:
Extent ~Everywhere
Size Clog pipe ID ($\Delta d/D$ max ≅ 60%)
Color Rust
Location Throughout pipe ID
Density <½ density of parent metal
Moisture Content
Texture/Friability
Other
Analysis:

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other
									Organic	Inorganic	

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species		
Count		

METALLURGICAL ANALYSIS:
Location of Attack
Nature of Attack

TREATMENT
Mechanical
Chemical (1) Zinc polyphosphate (2) Chlorination
Compound
Concentration
Method of Addition
Effectiveness Some effect No effect
Additional Mitigation Measures
Outside: Large pipe changed to cement lined carbon steel.
Small pipe replaced with 316L SS.
In Building: All replaced with 316.

CASE HISTORY 2: Carbon Steel

COMPONENT/SYSTEM Residual Heat Removal

MATERIAL Carbon steel (.24C, 0.5Cu, .05Cr, .65Mn, 0.5Ni, .012P, .23Si, .21S) 2″ SCH40

OPERATING HISTORY
~10 years' service

METHOD OF DISCOVERY
Pipe removed

DIAGNOSTICS
WATER: River Water

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:
Extent 44% occluded
Size Indeterminate
Shape Indeterminate
Color Brown/Reddish Brown
Location Everywhere
Density Much less than that of parent metal
Moisture Content N/A
Texture/Friability Hard (dried out on sampling)
Other Wall thickness reduced from .154″ to .073″ (min.). H_2S noted in deposit.
Analysis: (by EDAX) %

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Chlorine	Carbon		Ca	K	Si
									Organic	Inorganic			
46.2	.44	ND	ND	.60	4.2	.47	See Below	.98	est'd 2-3%	See Below	.33	.66	8.5

Sulfide .01%
(Total) S 1.085
C 1.01
H .63

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	Not Determined	
Count		

METALLURGICAL ANALYSIS:
Location of Attack
Nature of Attack No preferential attack

TREATMENT
Mechanical None. Pipe replacement planned (SS)
Chemical
Compound
Concentration
Method of Addition
Effectiveness
Additional Mitigation Measures

CASE HISTORY 3: Carbon Steel

COMPONENT/SYSTEM Fire Protection System

MATERIAL Carbon steel (.06 C, 0.8 Cu, .40 Mn, .05 Mo, .05 Ni, .038 P, .05 Si, .015 S) 4″ SCH40

OPERATING HISTORY
~10 years' service

METHOD OF DISCOVERY
Pipe removed

DIAGNOSTICS
WATER: River Water

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:
Extent Pipe ~12% occluded (4″)
Size .64″ X 1.14″ X 1.25″
Shape ~Elliptical
Color Reddish Brown/Black upon initial removal
Location All azimuths
Density
Moisture Content Moist on inside (black paste)
Texture/Friability Hard outer crust; black paste inside
Other Outer portion hardened on drying: inner portion shrunk. Wall thickness reduced from .237 to .153 in.
Analysis: (by EDAX) %

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Chlorine	Carbon		P	Si
									Organic	Inorganic		
55	0.5	0.5	0.3	1.0	2.5	ND	1.3	.5	NR	NR	0.6	4.0

Outer layer of nodule .1%
} Sulfide
Inner layer of nodule .1%
Total sulfur of each = 1.76%

MICROBIOLOGICAL ACTIVITY:

	Deposit	Fluid Stream
Species	Not Determined	
Count		

METALLURGICAL ANALYSIS:
Location of Attack
Nature of Attack No preferential attack

TREATMENT
Mechanical None. Pipe replacement planned (SS)
Chemical
Compound
Concentration
Method of Addition
Effectiveness
Additional Mitigation Measures

FIGURE 3-1
Partially Occluded Carbon Steel Service Water Line
(Case History 1)

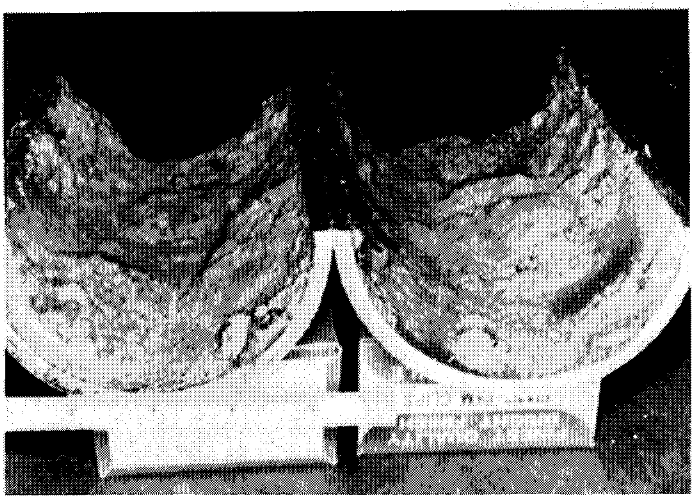
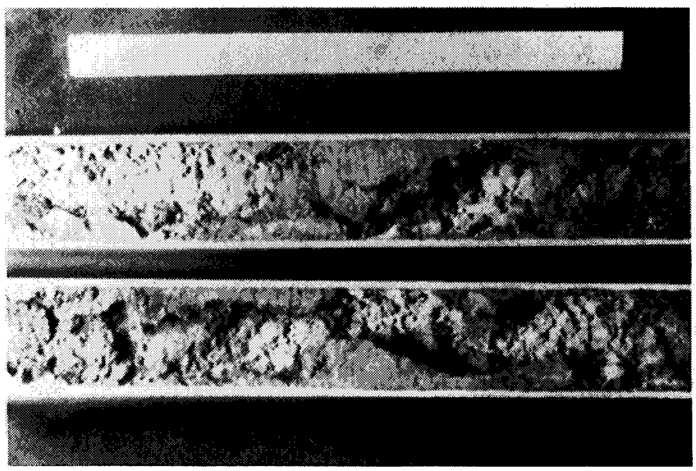


FIGURE 3-2
Heavily Occluded Carbon Steel Line
(Case History 3—Fire Protection System)



CASE HISTORY 4: Carbon Steel

COMPONENT/SYSTEM Fire Protection System

MATERIAL Carbon Steel. (99.49 Fe. .46 Mn) Small Diameter Pipe

OPERATING HISTORY
Water from deep reservoir

METHOD OF DISCOVERY
Corrosion Product Sludge on System Flushing.
Through wall pits.

DIAGNOSTICS
WATER:

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:

Extent
Size (Typical/Maximum)
Shape "Ringed" blisters
Color Black Sludge. Corrosion products from yellow/yellow-brown well in film to black and brown at outer extreme.
Location Random
Density
Moisture Content
Texture/Friability
Other Fe_2O_3 + Carbonates over $Fe_2(SO_4)_3$ & FeS
Analysis: %

	Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon	Mg	Ca	Zn
1.	85.19	ND	ND	ND	ND	9.54	ND	4.51	.70	NR	ND	.08	ND
2.	49.38	3.99				2.86		6.36	ND		3.99	32.70	.79

1. Cross-Section 2. Pipe ID ND = Not Detected NR = Not Reported

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	SRB	SRB in Water Supply
Count		

METALLURGICAL ANALYSIS:

Location of Attack Random Pitting under nodular oxides
Nature of Attack

TREATMENT

Mechanical None.
Chemical
  Compound Non-oxidizing biocide + dispersant
  Concentration
  Method of Addition
Effectiveness "Encouraging"
Additional Mitigation Measures Increased flow. Sampling station. pH >10.5

CASE HISTORY 5: Carbon Steel

COMPONENT/SYSTEM Service Water System—Radwaste Dilution Line

MATERIAL A155 KC55 C1.2, 30 in. pipe (.375 in. wall) Welded with E7018 electrodes using 1" wide backing rings.

OPERATING HISTORY
Five years' operation. Untreated river water. Primarily stagnant/low flow. Chlorine treatment had ceased.

METHOD OF DISCOVERY
1 inch drain line valve socket weld broke under stress and through wall hole at top of pipe. RT showed pitting in weld metal and under backing ring.

DIAGNOSTICS
WATER: ppm

pH	Conductivity	0_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	
5.9			7.5	<1			115	$C0_2$ 110		

See attached Table 3-1.

DEPOSITS:

Extent General. Normal rust - not significant.
Size (Typical/Maximum) N/A
Shape
Color Rust
Location Over pipe surface.
Density N/A
Moisture Content N/A
Texture/Friability N/A
Other N/A
Analysis: (water from deposits) %

*

as Fe_20_3 Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		$Mg0$ $Ca0$ $Si0_2$
									Organic	Inorganic	
99.15	ND	ND	ND		.11		**				.37 .06 .08

*pH 4.05
**Sulfate = .10; Sulfide = "Positive"

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	SRB activity verified	
Count	Not Determined	

METALLURGICAL ANALYSIS:

Location of Attack Severe pitting in crevices under backing rings; general pitting in pipe
Nature of Attack Pitting: maximum dimension = ½ inch diameter.

TREATMENT
Mechanical
Chemical NONE
Compound
Concentration
Method of Addition
Effectiveness
Additional Mitigation Measures Removed & replaced as possible.

Conclusion was that failure was due to crevice corrosion under backing ring, exacerbated by SRB activity in deeper crevice where the backing ring did not corrode away completely. Four additional service water problems observed in past 12 months. Three were small bore pipes plugged; influence of microbes not investigated. The fourth, a diesel standby service water pipe, exhibited nodules to .6 in. high x up to 2 in. diameter, Pit depths 6.5% → 58.1% of wall. In nodules see hydrated ferrous oxide. 2% S, 2-3% P, No Chloride, high silt, 20% organic. Nodules produced a low flow problem and corrosion reduced the wall. Pipe hydrolazed to remove nodules with good success. Pipe to be replaced due to loss of wall in pits.

TABLE 3-1
Chemical Analysis of Raw River Water (from Case History 5)

	Parts per million*
Total Solids @ 105° C	115
**Volatile Soilds @ 600° C	25
Fixed Solids @ 600° C	90
Total Alkalinity as $CaCO_3$ (methyl-orange)	45
**Hydroxide (as $CaCO_3$)	0
**Carbonate (as $CaCO_3$)	0
**Bicarbonate (as $CaCO_3$)	45
Free Carbon Dioxide	110
Total Hardness (grains per gallon)	1.9
pH	5.9
Silica (SiO_2)	12
Iron Oxide (Fe_2O_3)	0.5
Alumina (Al_2O_3)	0.1
Lime (CaO)	14
Magnesia (MgO)	2.7
Sulphate (SO_3)	*1
Chloride (Cl)	7.5
Soda (Na_2O)	8.7
Manganese (Mn)	0.04
Fluoride (F)	*0.1
Zinc (Zn)	*0.02

Fecal Coliform (MPN**/100 ml) *0.3
* None found if present less than
**Most probable number

FIGURE 3-3
Carbon Steel Service Water System Line with Through-wall Pits (Case History 5)

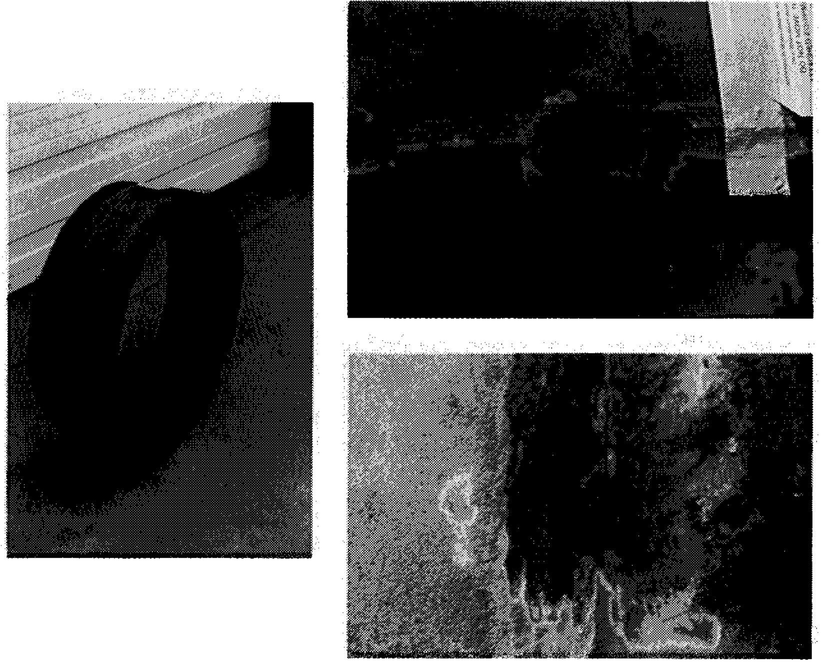


FIGURE 3-4
Corrosion at Pipe ID (Case History 5)

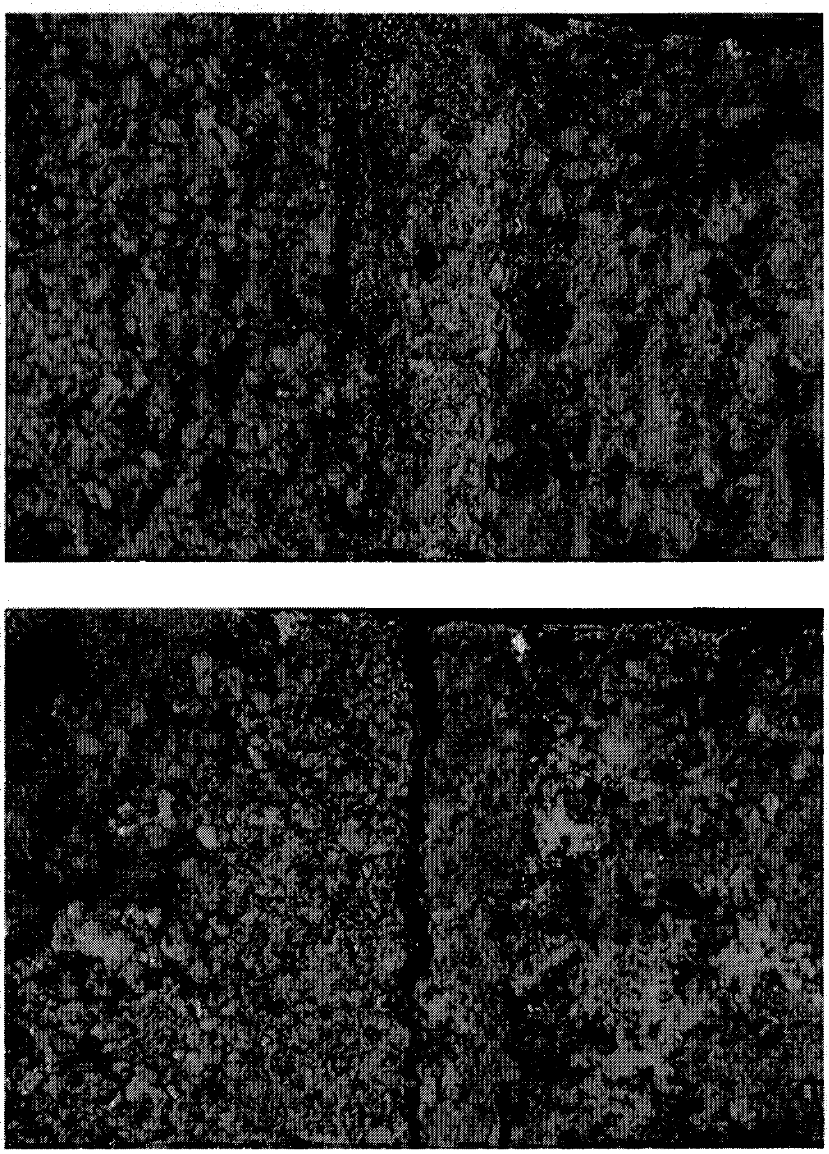
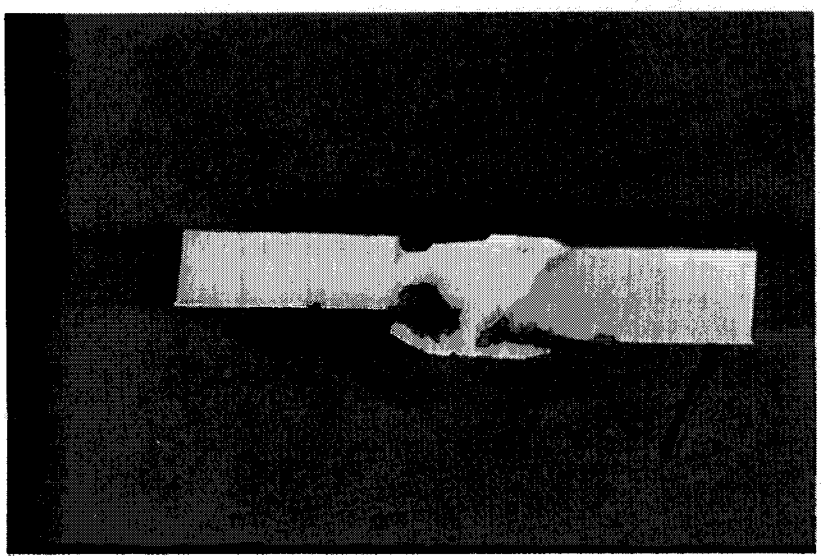


FIGURE 3-5
Cross Section of Corrosion (Case History 5)



CASE HISTORY 6: Carbon Steel

COMPONENT/SYSTEM ½ - 20 inch Pipe, Raw (Fresh) Water System

MATERIAL Carbon Steel. ASTM A106 Grade B. Various orientations.

OPERATING HISTORY
Fifteen years' plant operation, fresh water.

METHOD OF DISCOVERY
Maintenance on valves that would not isolate. Analyzed during five year test program.

DIAGNOSTICS
WATER: Temperature = 32°F to 85°F. ppm

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other Fe
								Organic	Inorganic	
7.2		7–11	8	5–13		1.4 NTU	2.4			0.2

See attached Table 3-2.

DEPOSITS:
Extent Essentially 100% coverage in moving water; 0–10% in stagnant water
Size ½ inch tubercles typical; 1″ maximum.
Shape Spherical
Color Black-brown when hydrated; orange-brown when dehydrated
Location All carbon steel surfaces subject to moving water
Density 95 to 229 lbs/ft^3. Large density variations result from varying silt concentrations and various degrees of chemical/physical hydration.
Moisture Content High.
Texture/Friability Soft to moderately hard when hydrated; hard when dehydrated.
Other
Analysis: %

Fe[1]	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		SiO_2[2]
									Organic	Inorganic	
75											25

1. As hydrated Fe_2O_3.
2. Less than 1% other oxides (CO_2, SO_3, P_2O_5, CaO, MgO, CuO, ZnO, Cr_2O_3).

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	Siderocapsa	Siderocapsa, SRB (.001 of Siderocapsa)
Count	Undetermined	790 colonies/100 ml Water

METALLURGICAL ANALYSIS:
Location of Attack General
Nature of Attack Bacteria deposition. Tubercle formation/pitting. Average corrosion rate = 0.5 → 4 mpy. Pitting corrosion rate = 2 → 9 mpy. Worst case pitting rate = 100 mpy.

TREATMENT
½″ → 2½″ Lines: Replace with more resistant material (copper, stainless steel)
3″ → 8″ Lines: Sandjet and apply polyamide epoxy coating.
Replace with resistant material.
Greater than 8″. Monitor corrosion with UT and ensure adequate flow rate. If the tubercles are left alone and anaerobic bacteria are *not* present, pipe integrity will not be significantly affected.

Other Treatments: Closed loop operation
Chlorination (initial system service only. Ineffective after tubercles are established).
Increase flow rate.

Treatments to Avoid: Pigging/chemical cleaning (if not followed with coating).

NOTES:

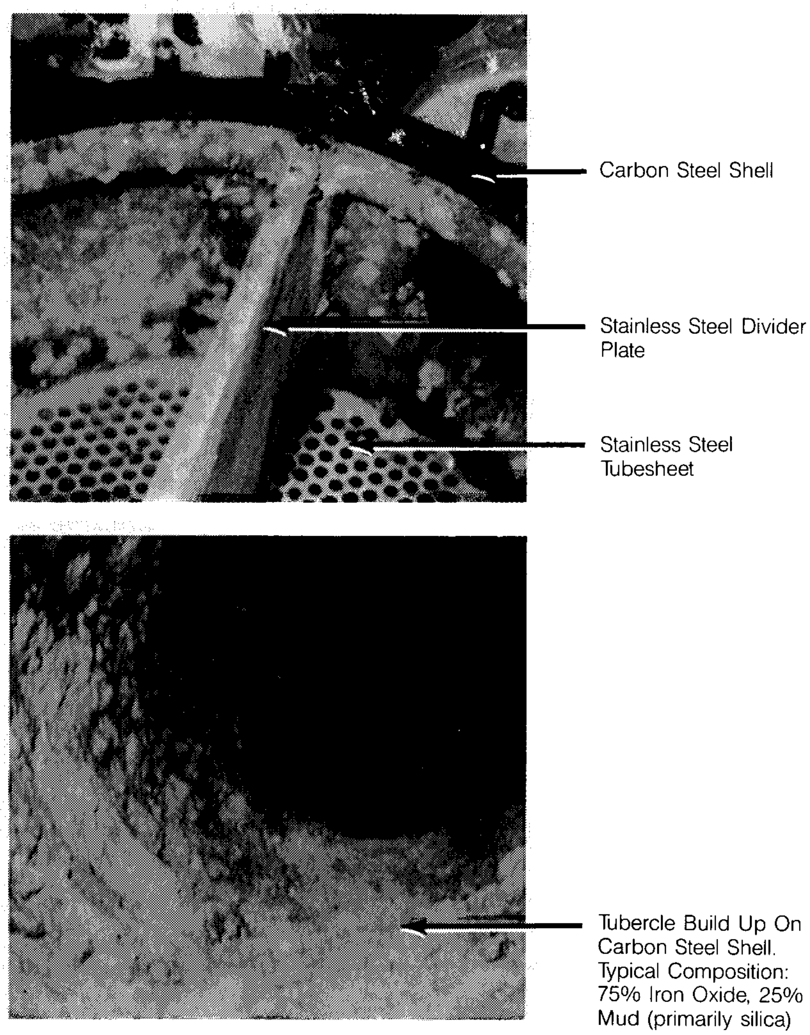
1. Typically, for 10 volumes of oxide found on pipe walls, 1 volume of metal is lost.
2. Deposition can result from:
    Corrosion of base metal
    Deposition from oxide in water
    Combination of corrosion and deposition.

   For this plant, corrosion of base metal was the primary mechanism.
3. Flow rate significantly affects aerobic corrosion rates:
   0 to 2 fps → LOW
   2 to 7 fps → HIGH
   Above 7 fps → LOW

TABLE 3-2
Typical Water Chemistry Analyses at Three Different Locations (Case History 6).

	Monitor 7	Plant Discharge	Monitor 3
Temperature	65.0	68.7	62.5
Dissolved Oxygen, mg/l	9.70	9.15	9.45
pH	7.42	7.32	7.34
Alkalinity as $CaC0_3$, mg/l	43.0	40.0	40.8
Calcium Hardness as $CaC0_3$, mg/l	17.1	20.8	16.4
Total Hardness as $CaC0_3$, mg/l	49.8	60.8	48.0
Total Phosphate as P, mg/l	0.022	0.024	0.017
Turbidity, NTU	1.5	2.0	1.2
Total Suspended Solids, mg/l	4.0	3.7	2.5
Total Solids, mg/l	92	118	88
Chloride, mg/l	7.25	9.30	6.75
Chromium, mg/l	<0.002	<0.002	<0.002
Copper, mg/l	<0.02	0.07	<0.02
Iron, mg/l	0.14	0.14	0.11
Sodium, mg/l	6.51	8.62	5.58
Sulfate, mg/l	9.4	21	9.2
Zinc, mg/l	<0.02	0.04	0.03

FIGURE 3-6
Tubercles on Heat Exchanger Shell (Case History 6)



Tubercles on Heat Exchanger

CASE HISTORY 7: Carbon Steel

COMPONENT/SYSTEM Riverwell

MATERIAL A-53 Grade B, 4″ Std. Wall. Horizontal orientation. Buried.

OPERATING HISTORY
Continuous flow at ~ 75 gpm.

METHOD OF DISCOVERY
Pinhole leaks noted by UT examination.

DIAGNOSTICS
WATER: (from a deep well). ppm

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Fe
								Organic	Inorganic	
7.1			15	110						12.4

Total Alkalinity 330 mg/l; Total Hardness (as ppm $CaCO_3$) 302

DEPOSITS:
Extent
Size (Typical/Maximum)
Shape
Color
Location
Density
Moisture Content
Texture/Friability
Other
Analysis: %

Fe	Mn	Ni	Cr	Cu	Al	Ti	S^*	Cl^-	Carbon		Other Ca
									Organic	Inorganic	
45.2	0.02						0.56				0.18

* Total Sulfur: Sulfur as Sulfate = 0.15%

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species		Siderocapsa Treubii
Count		17 colony forming units/ml

METALLURGICAL ANALYSIS:
Location of Attack
Nature of Attack

TREATMENT
Mechanical Pigged every two years
Chemical
Compound
Concentration
Method of Addition
Effectiveness
Additional Mitigation Measures

Comments:
Leaks initially attributed to anaerobic corrosion (SRBs). No SRBs were noted on analysis of water.

Also observe plugging of carbon steel and 304 and 316 stainless steel lines in gland flushing system but no through-wall corrosion. Heat exchangers which use river water do not exhibit deposition problems. This is attributed to a scouring action of particulates (sand) in the water.

CASE HISTORY 8: Copper-Nickel

COMPONENT/SYSTEM Stator Cooler

MATERIAL 90-10 Cu-Ni (ASTM B111). 5/8 X .049″ wall.

OPERATING HISTORY
Pre-Service

METHOD OF DISCOVERY
Leaks in Heat Exchanger tubes (through wall pits). Numerous shallower pits.

DIAGNOSTICS
WATER: Source: Clarified River Water

ppm

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	
7.8	630μmho/cm	8	29	140	<.1/4.0	10 NTU	unknown	unknown	unknown	

DEPOSITS:

Extent Slime: organic. Approx. 12 pits in 3 foot length
Size (Typical/Maximum) Not Reported
Shape Mounds
Color Green/Light green: Gray beneath
Location Everywhere
Density Not Reported
Moisture Content Not Reported
Texture/Friability Not Reported
Other Mounds: No cracking. Round bottom pits
Analysis: (By EDAX)

	Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other		
										Organic	Inorganic	P	Ca	Si
1.	M	m	M	-	M	m	-	m	m	NR	NR	m	m	M
2.	M	-	M	-	M	-	-	-	m	NR	NR	m	m	m
3.	m	-	M	-	M	m	-	m	M	NR	NR	m	m	m

KEY: 1. Loose Deposit 2. Thin Shell over Pit 3. Nodules; M=Major, m=minor, NR=Not Reported

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	Filamentous & Rod Shaped	
Count		

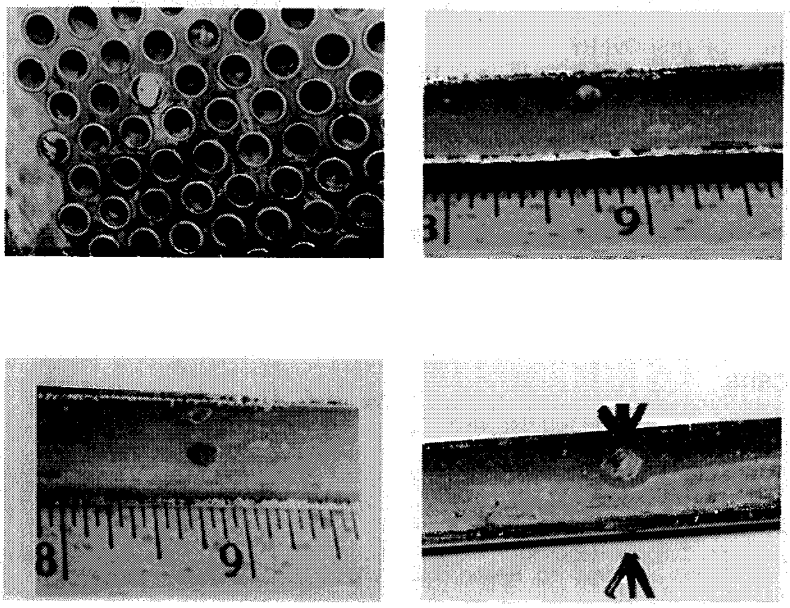
METALLURGICAL ANALYSIS:

Location of Attack
Nature of Attack Pitting. No preferential attack.

TREATMENT

Mechanical
Chemical 12% sodium hypochlorite addition for 10 minutes, twice a day (20 minutes, three times a day in warmer seasons).
  Compound
  Concentration
  Method of Addition
Effectiveness
Additional Mitigation Measures

FIGURE 3-7
Corrosion Products and Pits from Cu-Ni Heat Exchanger (Case History 8)



CASE HISTORY 9: Copper-Nickel

COMPONENT/SYSTEM Open Loop HXs

MATERIAL 70-30 & 90-10 Cu-Ni Tubes

OPERATING HISTORY
Water from deep reservoir (Pre-op)

METHOD OF DISCOVERY
Leaks

DIAGNOSTICS
WATER:

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:
Extent Less under chloride deposits
Size
Shape Blisters
Color Green. Red. Brown (90/10), Orange - Red (70-30)
Location Random over circumference
Density
Moisture Content
Texture/Friability
Other
Analysis: Corrosion Products wt%

	Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Ca	Si
										Organic	Inorganic		
*	3.6	ND	26.6	ND	62.9	ND	ND	.97	2.90	ND	ND	1.70	.97
**	.5–6.0	ND	3.3–12.5	ND	71.7–87.5	.80–1.39	ND	.30–.88	.52–2.2	ND	ND	.09–1.30	.37–2.63

* 70-30 Cu-Ni
** 90-10 Cu-Ni

MICROBIOLOGICAL ACTIVITY:

	Deposit	Fluid Stream
Species		SRBs known to be in reservior
Count		

METALLURGICAL ANALYSIS:
Location of Attack General over tubes.
Nature of Attack Random pitting; General Corrosion; denickelification

TREATMENT
Mechanical Yes
Chemical
Compound Chlorine (Some testing of non-oxidizing biocides & penetrating dispersants)
Concentration
Method of Addition
Effectiveness
Additional Mitigation Measures Avoidance of stagnant areas. Increased duration of chlorine treatments

CASE HISTORY 10: Stainless Steel

COMPONENT/SYSTEM Spray Pond Piping; Tanks

MATERIAL 316L SS (Weld Metal): 304 (Base Metal)

OPERATING HISTORY
Water from Spray Ponds.

METHOD OF DISCOVERY
Vertical rust streaks above & below girth welds

DIAGNOSTICS
WATER:

pH	Conductivity	0_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:
Extent
Size
Shape Conical
Color Black, Reddish Brown, Yellowish Brown
Location on Floor of tanks - pits beneath
Density
Moisture Content
Texture/Friability
Other
Analysis:

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other
									Organic	Inorganic	

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	Gallionella	
Count		

METALLURGICAL ANALYSIS:
Location of Attack Most in WM
Nature of Attack In 316L; austenite attacked

TREATMENT
Mechanical None
Chemical
Compound Sodium/Calcium Hypochlorite for pH<8; Bromine compounds pH>8; $Cl_2(g)$; ozone; H_20_2
Concentration
Method of Addition Continuous
Effectiveness
Additional Mitigation Measures pH to > 10; T to > 160°F; Intermittent pump operation; Dry lay-up

FIGURE 3-8
Through-wall Pits in Stainless Steel Piping (Case History 10)

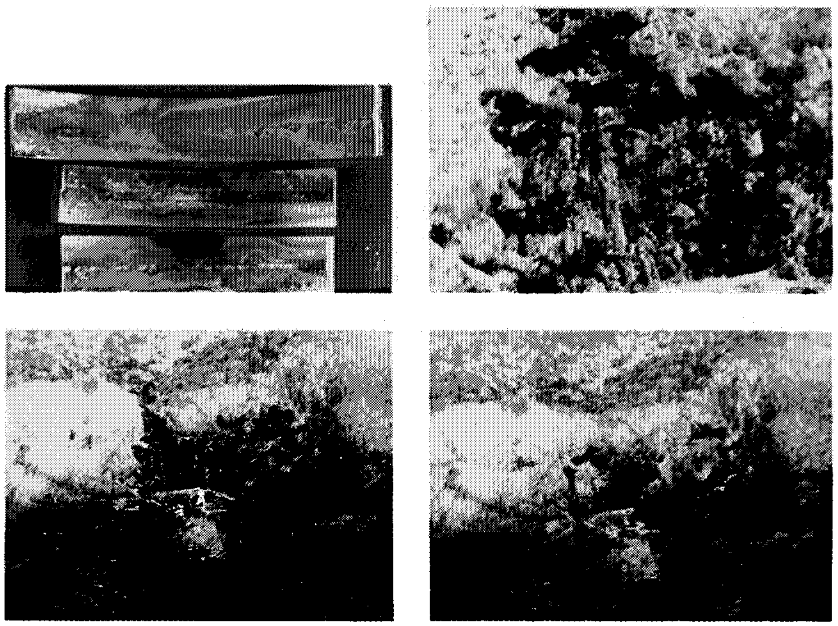


FIGURE 3-9
Preferential Attack of Austenite in Stainless Steel Weld Metal (Case History 10)

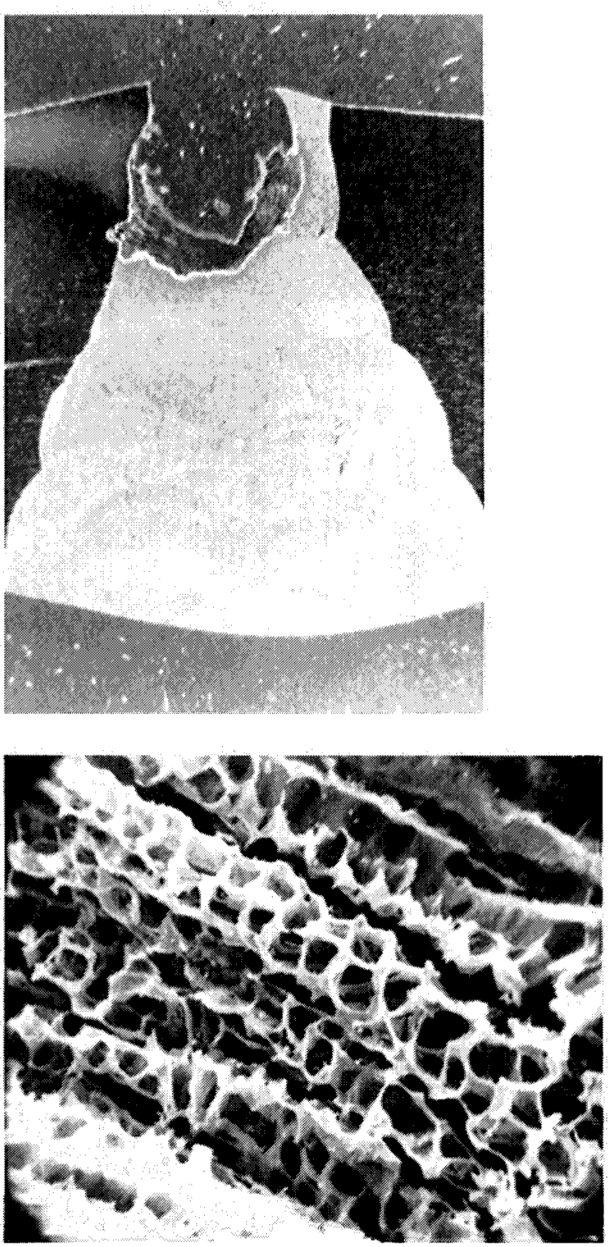
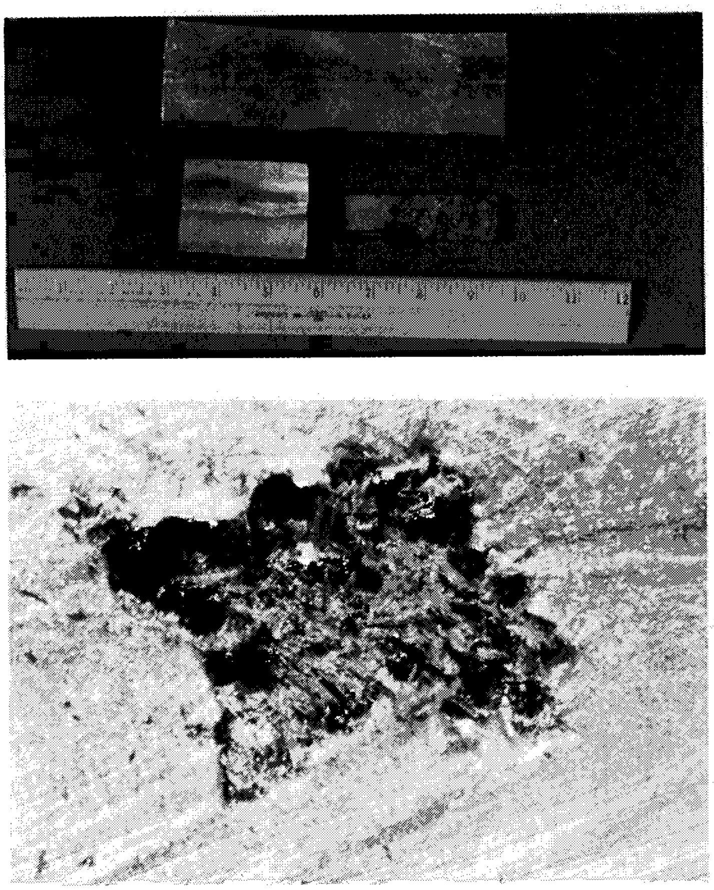


FIGURE 3-10
Pitting of Stainless Steel Tank (Case History 10)



CASE HISTORY 11: Stainless Steel

COMPONENT/SYSTEM Service Water - Containment Fan Coolers

MATERIAL 304 SS Pipe 6″ SCH10 (Pipe with .066% carbon; Fitting with .019%)

OPERATING HISTORY
Intermittent use system. Artificial lake water source (known to contain slime formers, iron bacteria, and SRBs)

METHOD OF DISCOVERY
Small leak (weeper). More extensive visual & RT showed ~10% of welds with pits (>50). Temporary repair → weld on (316L) sleeve.

DIAGNOSTICS
WATER: Very soft

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	
5.0										

DEPOSITS:	SAMPLE 1 (Pipe-Pipe Weld)	SAMPLE 2 (Pipe-Fitting Weld)
Extent		
Size		
Shape		
Color	Reddish-Brown	Black over Reddish-Brown
Location		
Density		
Moisture Content		High (Fresh)
Texture/Friability	Soft outer layer; hard, tenacious inner layer.	Soft, slimy outer layer; harder inner layer.
Other Analysis:	EDAX/Emission Spectroscopy	

	Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other		
										Organic	Inorganic	Si	Ca	P
1.	M	M	-	M	-	m	-	m	m	NR	NR	m	m	-
2.	M	-	M	M	-	-	m	m	m	NR	NR	m	-	m
3.	M	M	-	M	-	-	-	-	-	18%	NR	-	-	-
4.	M	M	M	M	M	M	-	M	M	19%	NR	M	M	-

M = Major. m = Minor. - = Not Detected. NR = Not Reported.
1. Sample 1, ID Deposit. 2. Sample 1, Corrosion Deposit 3. Sample 2, Black Deposit
4. Sample 2, Reddish-Brown Deposit (No differentiation between major and minor constituents in EDAX analysis for this sample).

MICROBIOLOGICAL ACTIVITY:

	Deposit	*Fluid Stream*
Species	Pseudomonas, Gallionella. SRBs.	Lake Water showed slime formers, iron bacteria, SRBs.
Count	Not Reported	Not Reported

METALLURGICAL ANALYSIS:
Location of Attack Sample 1:HAZ and Weld Metal; Sample 2:HAZ only (Pipe side only)
Nature of Attack Intergranular in HAZs. Preferential attack of ferrite in weld metal

TREATMENT

Mechanical None. Eliminate stagnant zones by design & periodic flow jogging.

Chemical

Compound Plan to use H_20_2

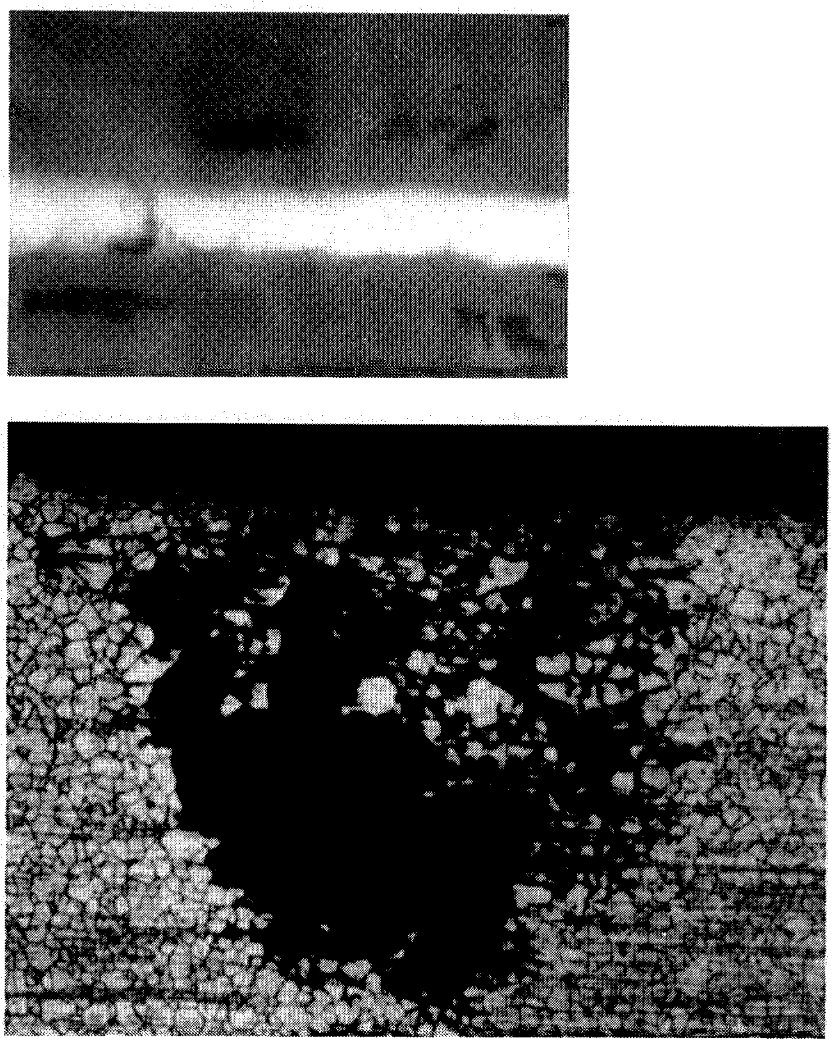
Concentration Planned @ 100 ppm

Method of Addition

Effectiveness — Subsequent stagnant conditions resulted in increased pitting

Additional Mitigation Measures Sleeves as leak barriers/structural reinforcement. Saw new pits at location of HAZ where sleeves had been welded onto pipe. Will replace piping at next outage. Until then will modify as limited closed loop operation and add H_20_2 @ 100 ppm, possibly higher concentration.

FIGURE 3-11
Radiograph and Photomicrograph Showing Pitting in Heat Affected Zone of Stainless Steel Pipe (Case History 11)



CASE HISTORY 12: Stainless Steel

COMPONENT/SYSTEM Makeup Water (Demin.)

MATERIAL Type 304 SS Pipe, 8″

OPERATING HISTORY
Hydrostatically tested (well water), drained (not dried). Sat idle for 15 months.

METHOD OF DISCOVERY
Leaks noted on trial run of demineralizer

DIAGNOSTICS
WATER:

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other
								Organic	Inorganic	

DEPOSITS:
Extent At butt welds within 8–9″ diameter ring (Bottom of pipe - incomplete drainage). All pits between 4 and 8 o' clock positions.
Size Mounds to ¾″ over pits.
Shape Conical.
Color Rust colored ring with multi colored "corona" inside; shiny, deposit-free area at center.
Location All at HAZ or in weld metal of butt welds except one pit about .7″ from weld.
Density Porous
Moisture Content
Texture/Friability
Other
Analysis: (Qualitative EDX)

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other
									Organic	Inorganic	
Yes	No	No	Yes	No	Yes	Yes	No	Yes*			Si,K Ca

* Significant concentration

MICROBIOLOGICAL ACTIVITY:

	Deposit	Fluid Stream
Species	Iron Oxidizing (NOT Gallionella)	
Count		

METALLURGICAL ANALYSIS:
Location of Attack [Refer to Figure 3-12 for location designations]. In weld metal (A,F,G), at fusion line (B), and in HAZ (C,D,E). Some pitting as much as .7″ away.
Nature of Attack Preferential attack of delta ferrite

TREATMENT

Mechanical Welds repaired. Recommendations for hydro/flushing with ozonated water or use of pneumatic testing as practical

Chemical Recommendation to use borate additions (to several hundred ppm) plus increasing pH to >10.5 in addition to ozonation.

Compound

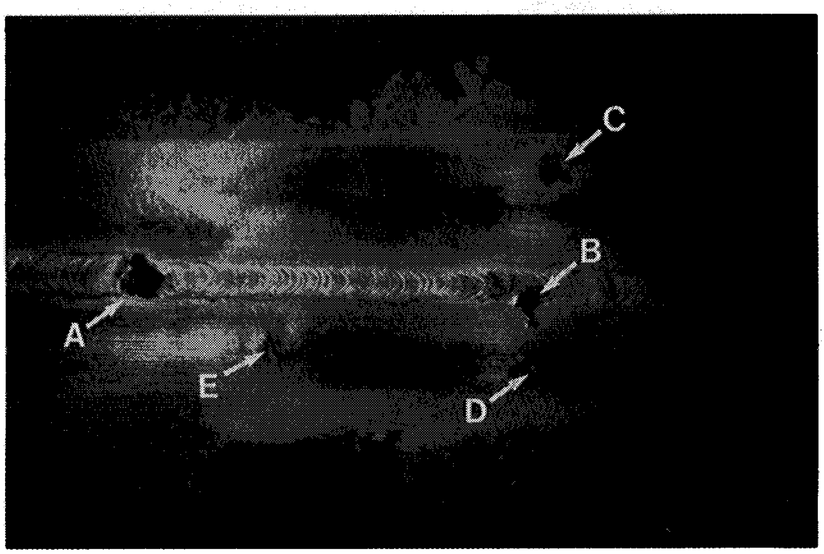
Concentration

Method of Addition

Effectiveness

Additional Mitigation Measures

FIGURE 3-12
Pre-Service Failure of Stainless Steel Pipe (Case History 12)



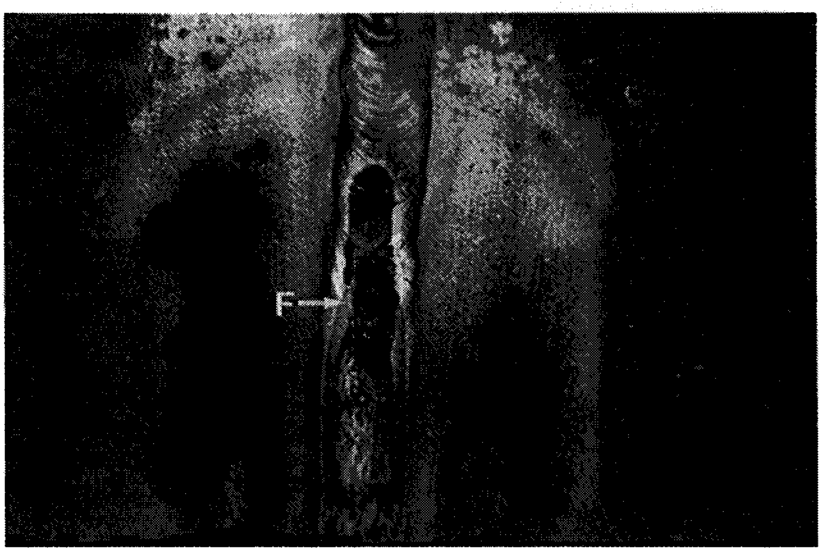
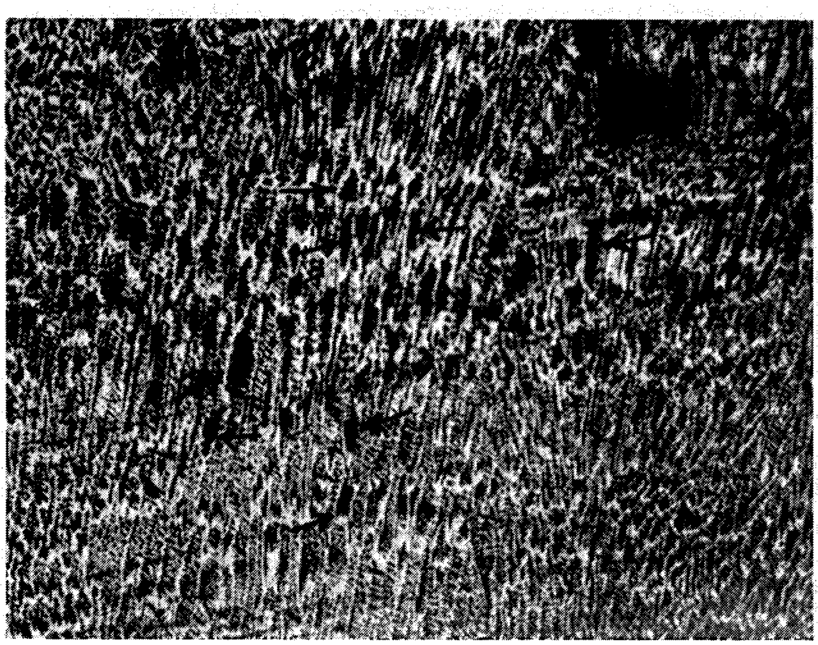


FIGURE 3-13
Preferential Attack of Delta Ferrite in Stainless Steel Weld Metal (Case History 12)



CASE HISTORY 13: Stainless Steel

COMPONENT/SYSTEM Laboratory Test to Simulate Stainless Steel Tank.

MATERIAL 304L Stainless Steel. Placed vertically in container.

OPERATING HISTORY
Welded plate was placed in a container of raw well water and allowed to stand undisturbed for a period of six weeks.

METHOD OF DISCOVERY
Formation of brown nodules occurred within 1.5 to 2 weeks. One nodule at the top edge of the plate grew rapidly to a diameter at its base of .5″ and a height of .375″.

DIAGNOSTICS
WATER: Raw well water.

ppm

pH	Conductivity	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity	Total Solids	Carbon		Other Alk.
								Organic	Inorganic	
8.0	800 μS/cm	-	70	17	<.05	<1 NTU	640	1	-	268

Total Hardness = 35 ppm

DEPOSITS:

Extent One large and several small deposits formed on the plate in the HAZ
Size .5″ Diameter × .375″ high
Shape Hemispherical
Color Brown, reddish brown deposit. After removal, a reddish brown, tightly adherent concentric ring of stain remained
Location HAZ
Density
Moisture Content
Texture/Friability
Other
Analysis: Not performed

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other
									Organic	Inorganic	

MICROBIOLOGICAL ACTIVITY: See note 1.

	Deposit	*Fluid Stream*
Species		
Count		

METALLURGICAL ANALYSIS:

Location of Attack HAZ
Nature of Attack Pitting. 3/16″ pit had developed in 6 weeks under the large deposit. Previous attack of this type showed preferential attack of ferrite.

TREATMENT

Mechanical Hydrolazing of piping and components which have suspected MIC.

Chemical

Compound Hydrogen peroxide

Concentration 50–200 ppm.

Method of Addition Mix in tank or reservoir of demineralized flushing water.

Effectiveness Positive control measure in pure water while hydrogen peroxide residual is present.

Additional Mitigation Measures Drain/dry piping through low points during construction/layup. Ozonation or chlorination of water source. Minimizing or eliminating stagnant conditions. Monitoring bacteria level in bulk water.

Note 1: The species was not specifically determined during this test, however, based on the appearance and type of attack, Gallionella were believed to be the primary influence. Stains and the pitting, characterized by an almost imperceptible surface pinhole with a large subsurface cavity, were confirmed to be due to Gallionella in actual piping or component degradation of this type.

Summary: This test was performed in an attempt to better understand the rate of degradation by reproducing conditions which had actually existed in plant piping or components where MIC, specifically Gallionella, had caused previous failures. As a result, we now have a strong basis for training and procedures to stress the importance of avoiding the introduction and stagnation of raw well or reservoir water in systems even for short periods of time. Pinhole leaks can be predicted/expected to occur as soon as six weeks after these conditions.

CASE HISTORY 14: Stainless Steel

COMPONENT/SYSTEM Main Condenser

MATERIAL 304 SS. (A249 welded tubes, .875″ OD × .028″ wall).

OPERATING HISTORY
Restart following three month outage. Unit filled with cooling water about one week after shutdown, but incompletely drained. No attempt was made at drying.

METHOD OF DISCOVERY
Leakage of cooling water into boiler cycle water on startup. Detailed examination by sonography and eddy current test.
Nearly 100 leaking tubes were found; over 60% of tubes showed pitting.

DIAGNOSTICS
WATER: Water from Cooling Pond; historically a high scaling water. Previous treatments with formic acid fill and soak and HCl cleanings to remove scale; determined to be only partially effective as chips of loosened scale had plugged some tubes.

February, 1987, ppm

pH	Conductivity µS/cm	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Turbidity NTU	Total Solids	Carbon		Other
								Organic	Inorganic	
8.0	1085	11.6	37**	217	<0.1/3.8	9.5	681	15*	23	-

*4-81 **1-79

DEPOSITS:

Extent Confined to first three feet of condenser tubes. Intermittent. Some tubes plugged with $CaCO_3$ deposits; especially those in upper sections of the condenser.
Size About 1/4″ diameter maximum of distinct nodules. Many tubes completely covered.
Shape Not distinct. Tight along tube wall.
Color Some $CaCO_3$; some mud-like deposits.
Location Mostly near bottom of tubes, between 4 and 8 o'clock positions. About 95% confined to first 3 feet of tubes. Crevice noted (one sample only.)
Density Not reported.
Moisture Content Not reported.
Texture/Friability $CaCO_3$ deposits hard and fairly tenacious. Other deposits not reported.
Other Pits generally smooth contoured.
Analysis: (Deposit average, EDAX)

	Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other	
										Organic	Inorganic	Ca	Si
1.	M	-	M	M	-	m	-	-	-	ND	ND	M	M
2.	M	-	M	M	-	m	-	M	-	ND	ND	M	m
3.	M	-	M	M	-	m	-	m	M	ND	ND	M	M

NOTES: 1. ID surface. 2. Inside pit 3. Along weld seam
Analysis of a typical deposit given in attached table.
M = Major m. = *minor ND* = not determined

MICROBIOLOGICAL ACTIVITY: See note 1.

	Deposit	*Fluid Stream*
Species	Probably SRB. Clostridium, & Bacillus.	SRB. Iron Bacteria
Count	Not Determined	Not Determined

METALLURGICAL ANALYSIS:

Location of Attack Through-wall pits and shallow pits, mostly in lower half of tube.

Nature of Attack No preferential attack noted. Crevice attack at one weld observed; not associated with microbes.

TREATMENT

Mechanical Not reported. Water jets used for clean-up prior to failure analysis.

Chemical Formic acid soaks and on-line HCl washes continued as done prior to this incident. Sodium Hypochlorite. Methylene bis-thiocynanate added once as a sterilization method prior to return to service.

Compound Acid cleaning to remove scale. Formic acid done as a soak; HCl done on-line. Intermittent chlorination. Methyl bis-thiocynanate added as a fill and soak for 48 hours before return to service.

Concentration Chlorine concentration not specified. MBT added to give 20 ppm (decayed over 48 hours).

Method of Addition Chlorine through diffusers. Inject chlorine for 30 minutes prior to any outage. Increased circulating water velocity, hypochlorite concentration and injection time. Decreased pH to adjust Langelier Index to slightly corrosive.

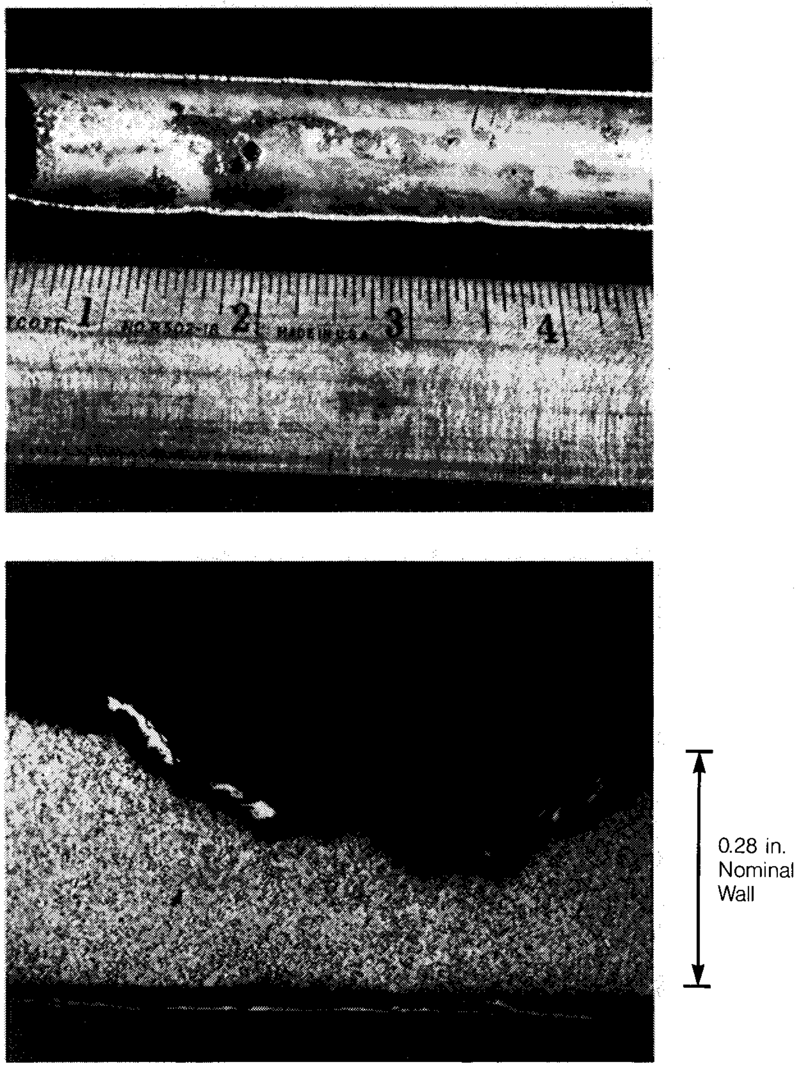
Effectiveness Satisfactory operation since coating and greater attention to system.

Additional Mitigation Measures Sandblasted and epoxy coated first 3½ feet of condensor tubes.

TABLE 3-3
Case History 14

Parameter	*Weight %*
Chloride, Cl^-	0.003
Phosphate, P_2O_5	0.05
Sulfate, SO_3	0.5
CuO	0.006
Fe_2O_3	0.14
K_2O	0.015
MnO	0.019
NiO	0.006
ZnO	0.004
SiO_2	0.2
Insoluble	0.1
Al_2O_3	0.05
Cr_2O_3	0.003
MgO	1.39
Na_2O	0.04
CaO as $CaCO_3$	97.1

FIGURE 3-14
Typical Pitting in First 3 Feet of Stainless Steel Condenser Tube (Case History 14)



CASE HISTORY 15: High Nickel Alloys

COMPONENT/SYSTEM Shutdown Cooler & Moderator Cooler

MATERIAL Incoloy 800, Incoloy 825, Monel 400

OPERATING HISTORY
Untreated lake water. Some mud, clams, etc.

METHOD OF DISCOVERY
Visual

DIAGNOSTICS
WATER: Turbidity, Total Solids, Carbon (Organic & Inorganic)

ppm

pH	Conductivity µS/cm	O_2	Cl^-	$SO_4^=$	$NO_2^-/NO_3^=$	Na	K	Ca	Mg	Silicon	Alkalinity	Other
8.0	310	ND	28.0	30.0	ND	15.0	2.1	41.0	8.4	0.5	94.0	*
7.8	210	ND	5.7	15.0	ND	3.3	2.0	24.0	6.9	1.5	81.0	**

* Lake #1 ** Lake #2

DEPOSITS:
Extent
Size
Shape
Color
Location
Density
Moisture Content
Texture/Friability
Other
Analysis:

Fe	Mn	Ni	Cr	Cu	Al	Ti	S	Cl^-	Carbon		Other
									Organic	Inorganic	

MICROBIOLOGICAL ACTIVITY:

	Lake #1		*Lake #2*	
	Winter	*Summer*	*Winter*	*Summer*
Species - Total Count, cm^{-3}	10^4	10^6	10^3	5×10^4

METALLURGICAL ANALYSIS:
Location of Attack None noted
Nature of Attack

TREATMENT
Mechanical None
Chemical None
Compound None
Concentration None
Method of Addition None
Effectiveness
Additional Mitigation Measures Test program in place (coupons). Will continue to monitor.

4

EFFECTS OF MIC ON STRUCTURAL MATERIALS

CARBON AND LOW ALLOY STEELS

MIC effects on carbon steel may result in random pitting, general corrosion, or severe hydraulic effects due to formation of tubercles and massive corrosion product deposits. Carbon steels are frequently used in raw water service and are thus commonly exposed to potential microbial influences under both aerobic and anaerobic conditions. Pitting under tubercles is common and exhibits no preference for a particular microstructural constituent. While the pitting typically observed in stagnant water where microbes do not play a role tends to be confined to crevices or to follow gravity, pits in carbon steel resulting from MIC can appear anywhere around the circumference of a pipe, and on both horizontal and vertical surfaces of tanks. Tubercle formation appears to be a necessary although not a sufficient condition for pitting. Pitting results as differential aeration and concentration cells are set up by mechanical (i.e., tubercle formation) and chemical influences (oxygen depletion, concentration of chlorides, or reduction of sulfate and the resultant effects on cathodic depolarization) of the microbial activity. Mechanical crevices resulting from design (e.g., thermal sleeves, weld backing rings, gaskets) or fabrication (incomplete penetration at welds) produce environments conducive both to growth of bacteria and localized abiotic corrosion. The result is often enhanced MIC effects.

Aerobic bacteria such as Gallionella, Siderocapsa, Sphaerotilus, Leptothrix, and Crenothrix can enhance corrosion by formation of differential aeration cells as oxygen deficient conditions are created under the microbial colony at the steel surface. Further, these bacteria tend to concentrate chloride and manganese in their metabolic process. These organisms also convert the soluble ferrous ion to the less soluble ferric state with resultant deposition of ferric hydrate; a significantly less dense product than the more protective magnetite film. The deposited hydrated product (typically iron deposition from the water rather than from the underlying surface [11]) provides an environment conducive to the growth and reproduction of these and other microorganisms. The result is a tubercle on the metal surface which supports its own little ecosystem (Figure 2-4). Aerobic organisms live and breed on the water side of the tubercle while creating a nutrient source and, more importantly, anaerobic conditions for other organisms at the metal surface. The hard-shelled tubercle also protects the colony below from mechanical effects and impedes the ingress of corrosion inhibitors to the metal surface or biocides to organisms living inside the tubercle. The resulting (chemical) corrosive species at the metal surface may include ferric and manganic chlorides resulting from concentration of chlorides, iron, and manganese. Production of permanganate ion via the oxidation of manganese during chlorination may also accelerate corrosion. Once tubercles have been established, the metabolic activity of the aerobic bacteria may be seen to be incidental to the corrosion process. Under-deposit corrosion conditions resulting from the concentration cells will proceed as will the corrosive effects of the more insidious SRBs harbored by the protective shell of aerobes.

Anaerobic corrosion under the influence of sulphate reducing bacteria is a well recognized phenomenon [3, 4, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 33] although the precise mechanism is subject to considerable debate. (See Section 2). The key feature to keep in mind is that SRB activity can be significant in aerated environments while sheltered from the bulk environment by tubercles of hydrated iron oxides and iron oxidizing bacteria. Attack under tubercles can proceed extremely rapidly (rates of 100 mpy or more [31,34]) as a result of the SRB. The pervasiveness of the sulfate reducing bacteria and their potentially devastating effects on steels in essentially all industries produce a powerful economic effect [6].

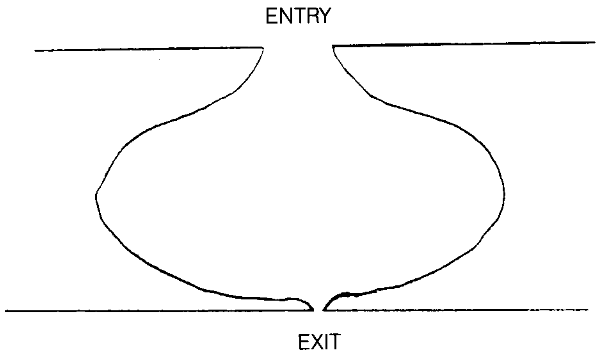
While penetration due to corrosion is the common concern with MIC in many industries such as petroleum production or pulp and paper, an additional concern with carbon steels in power generation is associated with hydraulic effects. For example, thick deposits of corrosion products on pipe interiors can reduce the available flow area significantly; to the extreme of complete blockage of pipes [4, 11, 31, 35]. Deposits with densities as low as 10% of that of the parent metal have been observed in raw water applications [31]. Two problems result. The immediate problem is that pressure drop increases dramatically, and in some cases will be such that cooling flow to critical equipment will be insufficient (See Case Histories 1-3, and Reference 35). Removal of the deposit (mechanical methods required, see Section 7) alleviates the flow difficulties in the near term, however, unless the cause of the corrosion problem has been removed, deposits will begin to reform rapidly and accelerated attack of the pipe wall in areas previously covered by the massive deposits will occur, jeopardizing the integrity of the pipe. Generally, tubercles are comprised of corrosion products from upstream locations, microbes, their mucilaginous exopolymer, and other debris. In some situations, however, the bulk of the iron in the tubercle can come from the corrosion occurring beneath the tubercle itself. In this latter case, removal of the tubercle without destruction of the iron oxidizing organisms can result in an increased corrosion rate (and damage at the prior location of the tubercle) as fresh metal is exposed under aerobic conditions. This effect was noted by Metell [31] following pigging of carbon steel lines.

In many environments where MIC is a problem, corrosion in sterile water of the same chemistry would also be high although not likely to be a localized phenomenon or one producing massive corrosion products. In such environments, the presence of microbes exacerbates the corrosive effects by producing much more rapid local perforations of the pressure boundary and the potential for flow blockage.

STAINLESS STEEL

Stainless steels of the basic 18-8 composition are commonly used in nuclear power plant construction in applications where corrosion resistance is required. They provide the added benefit of high toughness and demonstrated leak-before-break margin in wrought and welded forms. These materials are used extensively in high purity aqueous environments such as the reactor coolant system, emergency systems, reactor auxiliary systems, and, in many plants, in the feedwater train and condenser. Stainless steels may be subjected to microbial influenced attack in preoperational testing when untreated or potable water is used, in components which process raw water, as a result of condensation, or in high purity water environments with microbial activity. As noted by Pope [4] and Stoecker and Pope [36], deionized water can contain significant quantities of microbiological activity. MIC of stainless steel is characterized by pitting, most commonly at weldments. Through-wall pitting with resultant small leaks is the most common consequence of MIC of stainless steels. The preferential attack at welds has generated some concern with the potential magnitude of the problem as evidenced by NRC I&E Bulletin 85-30 [2] and INPO Significant Event Report 73-84 [1]. Pits often exhibit very small entrance and exit penetrations with very large subsurface cavities as illustrated in Figure 4-1. (See also [3, 4, 7, 9, 13, 27]). Tatnall [7] cautions that the same pit shape can be produced when manganese rich deposits contact chlorinated water whether bacteria are present or not. (This appears to be the result of the combined action of chloride and permanganate ions.) Pits may be associated with attack of the weld metal, generally near the fusion line, or with sensitization in the heat affected zone (Figure 3-11). Base metal attack is much less common, although such attack has been observed [3, 37]. The two phase weld metal appears to be the most susceptible area although the relative susceptibilities of the austenite and delta ferrite phases have not been clearly defined. As shown in Case History 10 in Section 3 and in [25, 37, 38], in some situations, the austenite is attacked preferentially. In other applications (Case Histories 11, 12, and 13 and [3]), the delta ferrite is removed and the austenite unattacked.

FIGURE 4-1
"Tunneling" Pit Observed In Stainless Steel



Iron oxidizing bacteria such as Gallionella and Siderocapsa are most commonly associated with MIC of stainless steels and the type of pits described above. In those instances where SRB activity has been associated with stainless steels, pitting was still the primary form of corrosion, however, the pit morphology was distinctly different. In the presence of SRBs, round bottom, broad pits were observed rather than the bottle-shaped variety [7, 9].

COPPER BASE ALLOYS

Copper base alloys such as 70-30 and 90-10 copper-nickels, brasses, aluminum bronzes, and admiralty brass are used in nuclear plant service in various heat exchangers ranging from pumps and valves to small coolers to feedwater heaters to main condenser units. All of these alloys are susceptible to MIC despite copper's reputation as a material toxic to common biofouling organisms. Copper alloys do indeed exhibit superior resistance to both macro- and micro-fouling [39, 40], however, pitting, plug dealloying, and ammonia-induced stress corrosion cracking attributable to the influence of microbiological activity have been reported as noted in Section 3 and references 4, 26 and 41. All of the commonly used copper alloys appear to be susceptible to MIC. Microbial corrosion effects on copper and its alloys involve attack of the corrosion film by the metabolic products of the particular organisms. Ammonia is a common waste product whose effect on copper-based alloys is well known. Organic acids, produced by many organisms, can also attack copper. Sulfides produced by the sulfate reducing bacteria are particularly potent [26, 42].

Sulfate reducing bacteria can produce hollow, hemispherical tubercles with pits of essentially the same size and shape underneath [3, 7]. Sulfide contents less than 0.2 ppm have been shown to produce a significant increase in pitting of copper [26]. No minimum "safe" level of sulfide has been identified. In sulfide polluted waters, pits tend to be irregular and angular in shape as opposed to the nearly hemispherical shape associated with classical pitting. A non-protective, sulfur doped oxide is produced upon exposure to sulfide-containing solutions. This phenomenon can occur during periods of lay-up or operation. When dissolved oxygen in the water subsequently contacts this non-protective film, accelerated corrosion results.

A second effect that can plague copper alloys and may sometimes be attributable to MIC, is an erosion-corrosion phenomenon. Partial blockage of heat exchanger tubes from corrosion product debris or Asiatic clams that leads to high local velocity can repeatedly strip the protective film from the tube interior surface and lead to a rapid deterioration.

HIGH NICKEL ALLOYS

High nickel alloys such as the Monels, Incoloys, and Inconels are generally specified for applications where a very high degree of corrosion resistance is required. Most LWR applications of these materials are restricted to critical areas such as PWR steam generators. Heat exchangers such as the moderator coolers in heavy water reactors may also utilize the corrosion resistance and favorable physical properties of the high nickel alloys. Even with the high resistance to pitting in oxidizing environments, including high chloride environments, exhibited by these materials, several case histories imply that resistance to MIC may not be significantly greater than that of stainless steel [3, 7, 13]. In at least one instance in the chemical process industry, 90-10 copper-nickel was specified as a replacement for nickel for resistance to MIC [7]. The supporting study for this material selection concluded that Type 316 stainless steel and Hastelloy C were more resistant to MIC-induced pitting than Monel 400 and Hastelloy B and both exhibited far superior resistance to that of nickel. Corrosion as influenced by microbiological activity is manifested by pitting and leaks. The appearance of hemispherical tubercles with hemispherical pits beneath is very similar to that observed for copper-nickel alloys [7]. Monels have shown susceptibility to pitting and denickelification in the presence of Pseudomonas in hard water [13].

Nickel-chrome-moly weld metal *may* exhibit greater resistance to stainless steel weld metal. Stein [43] has observed attack in the heat affected zone of a Type 316 stainless steel component while the adjacent Inconel 625 weld metal was unattacked. Additional testing to evaluate and confirm this observation is required.

OTHER MATERIALS

Other materials that have been used in nuclear applications include titanium for various heat exchangers, "super stainless steels" such as AL-6X, polyvinyl chloride pipe (both with and without fiberglass reinforcement) and various coatings and linings including polymers (especially epoxies), natural and synthetic rubber, and concrete. Titanium appears to be the most MIC resistant metal examined to date [4]. The extremely stable oxide film is highly protective in a variety of environments that apparently include all local environments established by micro-organisms. Titanium is susceptible to biofouling [39, 40] and its use may be limited by these considerations. The expense associated with specification of titanium is great although not prohibitive as evidenced by the increasing use of the material in critical heat exchanger applications including the main condenser. Service data on MIC of titanium are scarce which may also be a contributor to the apparent resistance of the material. In light of this consideration, titanium should not (yet) be considered *the* materials solution to MIC problems.

The highly pitting resistant stainless steels such as AL-6X are not immune to MIC although they may be significantly more resistant than the standard 18-8 grades [4]. Failure modes are the same as for the standard austenitic stainless steels—pitting generally associated with weldments. Ferralium 255, a duplex stainless steel with a high resistance to pitting in acidic and chloride contaminated environments has also exhibited corrosion in stagnant saltwater containing Gallionella, Pseudomonas, Sphaerotilus, and Desulfovibrio [13]. No hard data were presented to specifically link the observed pitting with the presence of the bacteria, however, the appearance of the pits and associated reddish-brown streaks was very similar to that observed for attack of stainless steel welds in the presence of Gallionella.

The use of non-metallic piping can eliminate MIC concerns but brings about different problems. For example, PVC pipe may be substituted for carbon steel in various supply and waste lines, however, seismic considerations eliminate it from contention in all but the smallest diameters. Use of fiberglass reinforced pipe can provide greater stiffness but Code acceptance and toxicity considerations in the event of fire may disqualify its use. The weight of concrete pipe eliminates this otherwise useful alternative material for all but large diameter, underground lines. Further, sulfur oxidizing bacteria can rapidly deteriorate concrete, especially at joints.

Polymeric coatings are often used on both carbon and stainless steels in applications where maintenance is difficult, component size is large and use of higher alloyed material is prohibitively expensive, or as a refurbishment procedure. Obviously, coating holidays cannot be tolerated for corrosion concerns of all sorts. Coal tar based and synthetic epoxies both improve resistance to MIC [4, 11, 27, 30, 38, 44] while sulfide diffusion through PVC coatings can result in attack of the base metal even though the coating and interface remain intact [14]. Laboratory studies show that wax, asphaltic coatings, polyethylene and polyvinyl can be attacked in pure cultures while coal tar formulations are not [45]. Biocidal constituents in the coating itself do not appear to improve resistance [16]. Pigments in epoxy coatings may provide a nutrient source for bacteria that actually increase the rate of attack [15]. Cement coatings (typically used inside large diameter carbon steel pipelines) can be effective, however, grouted joints or flaws related to high temperature exposure (e.g., lining areas near weld locations) can be the site of local failures totally unrelated to MIC with the subsequent result that accelerated corrosion at the location of the coating failure by MIC (or other causes) may follow. Cement linings may also be attacked by sulfur oxidizing bacteria such as Thiobacillus [11, 18, 23, 46]. Finally, weight considerations limit the usefulness of cement lined pipes.

5

COMPONENTS

Brief discussions are provided of several types of nuclear plant components and systems which often experience MIC. This list is not intended to be comprehensive; merely to provide a general discussion of the materials and operating conditions over which MIC is observed in power plant service.

FIRE PROTECTION SYSTEM

Although not classified as a safety related system, the fire protection system must be proven to be operable and reliable prior to plant operation and throughout the operating cycle. The fire protection system piping (much of it buried), valves and pumps are typically constructed from carbon steel. Pipe sizes may range from over 30 inches to less than one inch. Miles of small bore piping may be involved. Raw water or potable water (from local municipalities) is commonly used throughout the system although some plants have modified their systems to utilize treated water from on-site storage tanks. Stagnant conditions are the norm for this standby system.

Conditions are nearly ideal for macrofouling, microfouling, and MIC. All three effects can serve to decrease flow at hydrants, hoses, and sprinklers such that system effectiveness is lost. MIC can affect system performance by deposition of low density corrosion products and/or as a result of through-wall pitting of pipes (attack from both the ID and OD is a concern for buried pipes). Both effects have been observed in practice (see Section 3). Mechanical cleaning is difficult due to accessibility limitations. The cost of wholesale materials changes is prohibitive although treatment of the main water supply, particularly the initial fill water, would be expected to improve performance. Use of materials more resistant to plugging by corrosion products (e.g., stainless steel) in key locations might also prove to be justified. Increasing pH to greater than 10 and incorporating provisions for periodic (e.g., annual) flushing should also serve to prevent MIC in most cases.

HEAT EXCHANGERS

Heat loads from various pieces of nuclear power plant equipment are transferred to the plant's ultimate heat sink by a variety of paths through "essential" and "non-essential" heat exchangers. Cooling water in contact with the equipment may range from demineralized, deoxygenated water to untreated brackish or seawater, generally depending upon the safety function of the equipment in question. Corrosion, including MIC, must be a consideration in all of these environments.

Raw water cooled components from the main condenser down to the small, intermittent operation heat exchangers associated with some instrument lines, are subject to fouling from silt or mud, biofouling and MIC. In many of the larger, continuous flow heat exchangers (e.g., condenser), fouling is the major problem [47]. Corrosion, of organic and inorganic origin, can occur under these macro-deposits. Smaller heat exchangers, particularly those subjected to stagnant or low flow conditions over much of their life in untreated water, are particularly susceptible to MIC. Copper-base alloys (e.g., brasses, aluminum bronze, admiralty metal, and 70-30 and 90-10 copper-nickel) and stainless steel are commonly used for heat exchanger tubes. Muntz metal, carbon steel, and stainless steels are often used for tubesheets with the these tubing materials. Carbon steel is most often used for the heat exchanger shell and tube supports. High nickel alloys (e.g., Alloy 800 and Monels) and titanium are used for special applications. These materials, particularly titanium, are seeing increased usage in condensers and service water cooled heat exchangers.

Through-wall pitting of tubes or attack at the tube-tubesheet area is the most common manifestation of MIC failures in heat exchangers. As noted in Section 3, Cu-Ni tubes may be subject to random pitting and denickelification under deposits of iron oxidizing bacteria and SRBs. Evidence of ammonia induced stress corrosion cracking has been observed in admiralty brass condenser tubes under thick deposits of scale and organics [4]. In the same heat exchanger, deposits of iron oxide and iron sulfide were also noted on the carbon steel shell and tube supports. Stainless steel heat exchangers also are subject to failure due to MIC [3, 7, 13, 48, 49]. Monel tubes have exhibited pitting and apparent denickelification in hard water [13].

Heat exchanger tube walls and tube-tubesheet joints are critical boundaries for isolation of high purity water systems from the more heavily infested raw water systems. Many essential components are cooled by a demineralized water loop which is in turn cooled by raw water. A heat exchanger with the high purity water on one side of the tubes and raw water on the other is common to the two systems. In the event of a leak in the heat exchanger, raw water may be introduced to the high purity stream. While inorganic contaminants are unlikely to cause problems in the higher purity loop simply because they are unlikley to be introduced in sufficient quantity, microbes could cause problems in the higher purity loop as they attach themselves to tube or pipe walls and multiply. This scenario will take time and is not considered a likely cause of failure for critical equipment but does illustrate how contamination of systems and components within the containment, and the potential for the failure by known corrosion mechanisms could occur as a result of seemingly minor leaks in a heat exchanger.

TANKS

Tanks can be particularly susceptible to MIC since stagnant conditions are the norm. Tanks of both carbon steel and stainless steel construction may be hydrostatically tested in the field, often with untreated water, then left with standing water until system commissioning. Microbes can become well established during this time and may often lead to through-wall pitting prior to service as given in Section 3 and in References [3, 4, 6, 15, 36]. Mounds to several inches high, though atypical, have been observed on stainless steel tank bottoms with pits beneath. Pitting has also been observed on the vertical surfaces of tanks with the characteristic rust colored streaks emanating from these locations. The effects are the same on carbon steel tanks, also as a result of the influence of iron oxidizing bacteria and SRBs.

Use of biocide treated water for hydrostatic testing with subsequent attention to drying operations prior to commissioning should help to prevent MIC. Where possible, biocide additions or maintenance of a high pH (>10) should be considered in service.

ESSENTIAL SERVICE WATER SYSTEM

This system is typically constructed from carbon steel (although replacements may be stainless), with stainless steel piping in components closer to the reactor itself. Heat exchangers may be tubed with copper alloys or stainless steel. The system provides service water to cool critical components throughout a typical nuclear plant. Many key components may not be cooled directly via this system but heat is transferred from a high purity water system (i.e., a closed loop) to the Essential Raw Cooling Water (ERCW) system via a heat exchanger. The ERCW system may utilize untreated water, clarified raw water, or raw water that has been treated with a biocide. Analogous to the fire protection system, system function (in this case cooling capability) may be jeopardized as a result of MIC; either due to occluded pipes resulting from massive deposition and/or via through wall pitting. Although the degraded flow condition is not itself a plant safety issue, the degradation in heat removal capabilities from safety related equipment is involved. As noted previously, heat exchanger leaks can introduce biological contamination to high(er) purity cooling water circuits with the possibility of MIC of safety-related components. Mechanical cleaning of the system may be difficult since accessibility can be limited. Since many service water systems are once-through systems, chemical or biocidal treatment may also be limited by effluent limits.

6

DIAGNOSIS

Proper diagnosis is particularly important in situations where MIC is suspected since treatments for MIC can be expensive in terms of time, equipment, materials, and environmental impacts. Since treatment for MIC often involves the addition of oxidizing agents to the environment, an improper diagnosis may aggravate the prevailing corrosion environment by accelerating corrosion at existing oxygen concentration cells. In this light, diagnostic procedures should attempt to prove that corrosion can be explained by causes other than those involving microbial activity. MIC should be concluded as the cause of, or a contributor to, the observed attack only if the situation cannot be explained by other means.

Many characteristics of MIC are readily detected by sight, smell, and touch. The general appearance of the attacked region—the shape of deposits or penetrations, characteristic colors, and, in many situations, the location of the attack can be indicative of MIC. For example, sulfate reducing bacteria produce characteristic black deposits of iron sulfide on steel and stainless steel. Carbon or low alloy steels may have pits covered by a hard crust (especially if the deposit has been allowed to dry out) with a soft, black paste inside the crust [11]. A rounded gouge or pit and black FeS at the center, surrounded by a dark outer ring and a bluish inner ring with shiny metal beneath are associated with SRB attack of stainless steel. Iron oxidizing bacteria typically result in brown or reddish-brown deposits. Through-wall penetrations of stainless steel due to Gallionella or other iron oxidizers generally result in rust colored streaks emanating from the penetration and going both up and down. Deposits are typically low conical shapes, generally less than 1/4 inch high, but can be very large (to several inches in diameter). Massive brown or red-brown deposits on carbon steel tanks or in carbon steel pipes typify the effects of iron oxidizers. These deposits are generally hemispherical but in pipes can grow together such that individual deposit shape is lost. A strong yellow color on any of the structural materials can indicate the action of sulfur oxidizing bacteria such as Thiobacillus or Beggiatoa. Ferrobacillus, another sulfur oxidizer, generally produces brown precipitates of ferric sulfate and can give locally acidic conditions (to pH 2) [32].

Deposits can be located on horizontal or vertical surfaces. In pipes, deposits and the associated pits are likely to appear anywhere around the circumference so long as the entire circumference has been wetted over the bulk of the exposure period. Microbial colonies are frequently found at the bottom of tanks that had been incompletely drained, in low spots of piping systems where water remained after draining, or where condensation collected in pipes, tanks, or beneath other fluids such as fuel oil or solvents.

Fresh and wet deposits generally feel slimy and exhibit the most distinctive color. Deposits with reduced products of sulfur will also generally have the distinctive smell of H_2S. Acidification of drier, less fresh deposits will produce the same odor if sulfides are present. Bacterial deposits are typically soft or friable, in comparison to oxide or mineral deposits.

Visual inspections as noted above are useful for detecting through-wall penetrations from the outside, evaluating the inside of readily accessible systems during shutdowns, or as initial steps in failure analyses. The interior of some piping systems (e.g., Service Water) can be examined by remote camera. For most nuclear systems which may be affected by MIC, an assessment of damage by quick nondestructive techniques which can be performed from the outside of pipes or vessels is desired. Radiography has been used effectively to detect pitting at stainless steel welds (see Section 3 and [3, 9, 15]) and can also detect pitting in carbon steels, copper base alloys, and high nickel alloys. Other volumetric examination methods such as ultrasonic or eddy current testing have occasionally been applied successfully to the detection of pitting due to MIC. These techniques are useful for detecting and monitoring the growth of a defect, but they obviously cannot ascertain whether the defects are the result of microbes.

INITIAL ASSESSMENT

A standard format much like that shown throughout Section 3 of this report is recommended for collection of data pertinent to suspected instances of MIC. Background information such as materials of construction, fabrication methods, and operating history (e.g., stagnant, low flow or intermittent operation, water source, water treatment if any, lay-up methods, and operating time) can yield significant insights into potential microbiological influences. Any significant differences between the system's first exposure to water and the plant's operating time should be noted. If the system can be opened to allow visual inspection, detailed visual examination should be performed. Time between cessation of the service condition and the examination should be noted to benchmark potential dry-out or aging of the surface prior to the examination. Similarly, any history of mechanical cleaning operations and potential disruption of surface condition will be important in assessments of MIC. The existence of any deposits, their location, shape, color, and any layering tendencies should be noted. The moisture content of the surface, a key indicator of freshness, should also be noted. All observations of color, texture, and friability of deposits must be evaluated relative to the freshness of the sample. Location of any discernible corrosion (pitting or general) and any markings in the vicinity (e.g., concentric rings on stainless steels, build up of corrosion products on copper-nickel) should also be recorded.

WATER SAMPLING

Ideally, the aqueous environment will be well characterized prior to any investigation of suspected MIC. Sampling of the water at the intake point and immediately upstream and downstream of the component of interest will provide optimum background. For microbiological sampling, flow-through methods are strongly recommended. Random grab samples are satisfactory for a general water chemistry determination but provide unreliable results relative to microbes. Filtering a process stream with polypropylene cartridges (Tatnall [7] suggests a 350μm rating) for a period of one day to two weeks or more is suggested as a better method. Seasonal variations in microbial content, oxygen, and critical nutrients can be significant. Sampling on a monthly or bi-monthly basis should be sufficient to assess these effects. Turbidity, color, and odor can provide a qualitative indication of the microbial activity in the water [4]. Organic carbon and microbial counts (total and specific) of the sample serve to quantify the assessment. From the corrosion viewpoint, a complete water analysis (semi-annually; quarterly following changes in the upstream water supply, drought, etc.) will assist in separating corrosive effects of the water itself from any potential microbial influence. Salinity, hardness, pH, total conductivity, total and dissolved solids, dissolved oxygen, chloride, sulfate, nitrate, nitrite, and total carbon should be included as a minimum in the analysis. Systems that are being treated with a biocide should also include determination of biocide concentration on a regular (e.g., quarterly) basis. Pope [4] would add iron, manganese, ammonia, total sulfur, and carbonates to this list.

The absolute value of a microbial count is of itself of little value unless the number of microbes detected is zero. Sampling of the fluid stream is not necessarily indicative of the numbers or activity of organisms at the metal surface where MIC damage is done. Sampling of the fluid stream can be useful to identify heavily infested systems and select areas for further investigation, evaluating the effectiveness of biocide treatments, locating areas where microbes may be reproducing rapidly, and detecting trends over time (years) to focus sampling.

SOLIDS SAMPLING

Once the area of interest has been examined visually, samples may be removed for detailed chemical and microbiological examination. Typically, deposits, tubercles, or volumes of corrosion product in the vicinity of the corrosion site will be the areas of interest. Additional visual examination of the under-deposit areas and removal of samples for metallurgical analysis may follow. Removal of deposits requires great care to assure that the deposit is not physically damaged nor chemically or biologically contaminated. Samples should be removed using a sterilized stainless steel spatula (sterilized by soaking in alcohol then burned) and placed in a sterile glass or plastic container with a tightly fitting lid. No water or other fluids should be added to any samples. If a sample is dry upon removal it should be kept dry. If wet, the sample should be kept moist by adding a wet paper towel to the sterile chamber. Either water from the sampled area or *sterile* distilled water should be used as the moisture source.

Samples for microbiological analysis should be refrigerated or stored on ice until the analysis can be performed. Microbiological analysis should be performed as soon as possible but not more than 24 hours after sample removal. If a sample must be stored for longer than 24 hours, freezing or chemical fixing (2% formaldehyde buffered with marble chips; isopropyl alcohol if freezing or formaldehyde are unavailable) should be considered. Chemical analysis can utilize the same sample or a portion of the sample collected for microbiological analysis. The same sampling techniques will prevent chemical contamination. In the event that chemical analysis requires treatment of the sample with acid upon removal, separate samples should be taken for microbiological, metallurgical, and chemical analysis.

Samples for metallurgical analysis should typify the areas with attack such that the failure mode and physical and chemical characteristics may be determined. Chemical contamination of surfaces (particularly by sulfur, halides, and organics) must be avoided. Cutting should be done so that corrosion products are retained. The sample must not be subjected to overheating or excessive vibration. If possible, cutting should be done dry at low speeds. Following removal, metallurgical samples should be physically protected but need not be kept moist.

Metallurgical examination by low power optical microscopy followed by scanning electron microscopy will serve to characterize the details of the appearance of the corrosion site. These techniques can serve to define the location and morphology of any attack. Examination of a cross-section should focus on identification of the nature of the attack; usually pitting in the case of MIC. The general nature of the pits (round vs. angular or flat bottomed), their shape (small entry and exit holes with bulbous cavity beneath, any changes in direction of pit propagation) should all be noted. Intergranular attack or preferential attack of one phase (e.g., attack of austenite or delta ferrite in stainless steel welds) should also be characterized.

DEPOSIT ANALYSIS

Used in conjunction with historical information surrounding the suspected MIC, visual examination of the attacked area, and metallurgical characterization of the failure mode, chemical analysis of the deposits provides a powerful confirmatory tool. Microbial induced corrosion leaves a particular set of chemical fingerprints that can be used to determine whether or not MIC was at work. Elemental analysis by X-ray fluorescence, energy dispersive X-ray spectroscopy, atomic absorption, or wet chemistry techniques coupled with a determination of the amount of organics (e.g., by loss on ignition) provides a useful insight into the cause of the corrosion.

An organic carbon content of 20% or more indicates likely microbial involvement. More specifically, manganese and chloride concentrations in the deposit coupled with a high iron (especially for non-ferrous metals) would indicate the likely influence of iron oxidizers such as Gallionella or Siderocapsa. High sulfur contents, black slimy deposits and the smell of H_2S would indicate the presence of SRBs. High sulfur with yellow deposits and locally acidic conditions would implicate sulfur oxidzers. When a properly collected and maintained sample exhibits a very low organic content and essentially no enrichment in sulfur or chloride (as compared to the base metal and/or the water analysis) is noted, MIC is unlikely to have been a contributor to the corrosion.

MICROBIOLOGICAL ANALYSIS

A carefully prepared and preserved specimen may be examined for life forms known to produce corrosion. Determination of a total bacterial count can be achieved readily by using a "dipstick" [3, 4, 7], or culturing the organisms on a commercially available medium. As Pope [4] notes, such cultures detect only a small fraction of the organisms in the sample (as little as .001% or even less to a maximum of only 10%), are not organism-specific, do not support growth of such important organisms as Gallionella and SRBs, and require an incubation period for anything to show up. Use of a "selective" culture media to selectively grow certain microbes helps to alleviate some of these problems. The selective analysis can be an on-site microscopic examination to verify that specific microbes are indeed in the water or deposit. Certain microbes such as Gallionella or Desulfovibrio may be identified by relatively low power epifluorescence microscopy. Note that in all cases, these techniques only verify the presence of viable bacterial colonies. They can only provide supporting information to the supposition that the microbial activity was associated with corrosion.

Detection of specific biochemical constituents can provide somewhat greater insight into the types of organisms present in a deposit or corroded sample. Highly sophisticated techniques such as Fourier transformed IR spectroscopy [50], gas chromatography and mass spectroscopy, measurement of the amount of DNA/RNA in a sample, or highly specific separations and transformations of chemical substances performed by microbiological specialists can provide valuable information in laboratory studies but are probably impractical for field evaluations. Determination of the amount of ATP (adenosine triphosphate) has been used in many evaluations to estimate the total number of organisms (see for example [32]). Pope [4, 51] cautions that unless this method is applied very precisely, the results will be suspect. Analysis for specific metabolic products such as ammonia, hydrogen sulfide, and various organic or inorganic acids can give some indication into metabolic activity although many such substances can be produced by other means. Measurement of corrosive materials such as these may be useful in the determination of corrosion mechanisms although their presence does not positively indicate MIC. Recent work by Pope, Siebert, and others under the auspices of NACE subcommittee T-3J has attempted to combine chemical and metallurgical evidence of known MIC to establish a definitive "fingerprint" of MIC.

Microscopic techniques have been augmented by the use of fluorescent dyes which stain constituents unique to living organisms and epifluorescent microscopy. Small samples can be collected, dried, heat fixed and stained for viewing in the epifluorescence microscope. Pope [4, 51] has proposed this technique as a relatively cheap and rapid method for field identification of specific bacteria types. Electron microscopic identification of microbes on a sample with suspected MIC has the advantage of high resolution and can couple microbiological and metallurgical analyses on a single sample, provided that the sample was carefully fixed and dried.

CORROSION MONITORING CONSIDERATIONS

All discussion of diagnostic procedures to this point has dealt with materials removed from operation. Investigation of MIC may, and, in many situations, should, involve monitoring of side streams or the main flow path for electrochemical potential or corrosion of test pieces. Candidate replacement materials may be tested under prototypic conditions in this way while the use of various electrochemcial methods or corrosion coupons can give an estimate of corrosion rates of piping or vessels. Flow velocities should match those of the component being evaluated. Coupon surfaces should also be prototypic. Flanged pipe spools provide the best mock-up of operating condition and are recommended for replacement material evaluations. Electrochemical methods that do not disturb the corrosion process are recommended (e.g., monitoring of corrosion potential with time). These and other techniques have been used successfully in the laboratory [13, 52, 53]. Commercially available electrodes have been discussed elsewhere [7].

7

TREATMENTS

Once a positive diagnosis of MIC has been made, a treatment program may commence. Treatments fall into three general categories: mechanical cleaning, chemical water treatment, and engineering and operational controls. Mechanical methods are used to physically remove deposits from material surfaces; either on an as-needed basis or semi--continuously. In this way, impediments to flow are removed and physically attractive sites for further organic and inorganic material deposition are eliminated, while microbial consortia are destroyed permitting biocides and corrosion inhibitors to reach the microbes and metal surfaces. Some mechanical cleaning methods expose bare metal, preparing the surface for the application of protective coatings. Chemical water treatments as considered here include the use of biocides, corrosion inhibitors, and dispersants. Biocides may be oxidizing or non-oxidizing agents with additions made continuously or as a slug. Biocides are often used in combination with one another to increase their effectiveness, decrease effluent concentrations, or reduce costs. Biocides may also be used in conjunction with dispersants to prevent accumulation of deposits. Inhibitors may be used independently or along with biocides or dispersants for corrosion control. References 54 and 55 illustrate typical chemical additions to power plant water chemistry. Engineering and operational controls may involve draining and drying of dead legs and low spots in piping systems and tanks wherever possible or elimination of stagnation by periodic operation of pumps or valves. Engineering approaches to the elimination of MIC may also include system modification to provide closed loop operation of particularly critical areas where such rework is possible. Other considerations include alternative methods of microbial control such as the use of ultraviolet radiation or a combined mechanical/thermal treatment such as backwashing with higher temperature streams.

MECHANICAL METHODS

Mechanical cleaning of affected surfaces provides the initial phase of treatment for known occurrences of MIC. Since MIC is always associated with biofilms on the metal surfaces, the first and obvious action should always be to remove the film. Often, such films are extremely tenacious and can render biocides or corrosion inhibitors completely ineffective.

Piping systems and heat exchangers may be cleaned using metal or vinyl pigs which are propelled along the inside of the pipe or tube by pressurized gas or water. Straight sections and smaller bores are most amenable to the use of pigs. Piping runs uninterrupted by valves, diameter reductions, or many changes of direction may be cleaned in this manner so long as access ports for insertion and removal of the pig are provided. Straight tube heat exchangers are also readily cleaned by this method. Brushes may be used in similar applications and are particularly useful where shapes are more irregular and greater control of the process via manual manipulation is desired [55, 56]. Several examples are noted in Section 3.

Sponge ball cleaning systems provide a semi-continuous method for mechanical cleaning water systems. Sponge rubber balls (available in various stiffnesses, with and without abrasive coating) of a diameter slightly larger than the pipe or tubes to be cleaned are periodically introduced into the fluid stream, pass through the pipework and tubes, then are collected in a downstream area of the system and cycled back into the injection area. This type of on-line cleaning system is frequently installed to maintain the circulating water side of condensers where fouling from mud, silt, or biomass is a common problem [47, 57]. Sponge ball cleaning alone can improve fouling control, however, its use in conjunction with chlorination has also been shown to be effective in controlling corrosion [39]. One problem associated with this method of cleaning is the risk of increased corrosion due to overzealous use and subsequent removal of protective films. Miscellaneous system related malfunctions are the more common problem. Unreliable operation (often due to poor maintenance practices) has been identified as a major concern related to mechanical control of condenser biofouling; one that requires additional study [47].

Other mechanical cleaning methods rely upon fluid movement or transfer of pressure pulses to remove biofilms. Air bumping pulses high pressure air through a pipe to remove deposited material. This technique effectively removes loose deposits, generally in preparation for other more thorough cleaning processes. Methods that utilize solids suspended in a fluid stream may be effective in situations where deposition on pipe or vessel surfaces is not severe. With relatively thin films, the abrasive particles will flow along the film and effectively remove it rapidly. The Sandjet process, which involves suspending sandblast material in a dry nitrogen carrier, was shown to be particularly effective in preparing surfaces for subsequent coating [31]. The use of high pressure water sprays (hydrolazing) has been used extensively for removal of deposits in preparation for subsequent chemical treatment, for nodule removal following intensive biocidal treatment (e.g., ozone), or as the singular removal technique. (see Section 3). Improvements to the hydrolazing process have primarily been associated with allowing equipment to access smaller and more remote areas of a system. The disadvantage with hydrolazing and all of the other mechanical methods that rely upon fluid streams are that they must be done off-line and single setups are limited to areas without many changes in direction or bore. When abrasive particles are used, an additional step, collection, is required as well.

CHEMICAL TREATMENTS

The area of chemical treatment is one where treatment of MIC deviates significantly from that for other forms of corrosion. The involvement of living organisms in the corrosion process requires that they continue to be controlled even after a treatment has been made that has removed the corrosive condition. Consortia of microbes may reform even after mechanical and/or chemical treatment unless the fluid stream is treated to prevent their growth. Interruption of chemical treatment can permit the microbes to re-establish themselves in the fluid stream and on surfaces. Resumption of the chemical treatment may then be insufficient to prevent further corrosion. Chemicals commonly used for treatment and control of MIC can be classified as biocides, dispersants, and corrosion inhibitors. For the purposes of this document, they will be discussed separately even though many of the commonly used chemicals actually perform more than one of these functions.

Biocides

Biocides should kill microbes and may disintegrate the biofilm in doing so. Chlorine, added as chlorine gas or sodium or calcium hypochlorite, is by far the most commonly used oxidizing biocide. Other oxidizing biocides which have been used in various applications include chlorine dioxide, bromine compounds, ozone, and hydrogen peroxide. Nonoxidizing biocides include acrolein, glutaraldehyde, isothiazolin, quartenary ammonia compounds and numerous other generic and proprietary formulations (see, for example, references 54 & 58). As reflected in Section 3, the oxidizing biocides, particularly chlorine, are by far the most commonly used biocidal agents in nuclear plants. Economics, simplicity of use, and the vast experience base (qualitative) are the overriding considerations for the utilization of chlorine [59]. Pope's recommendation that the effectiveness of biocides be tested against the organism(s) of concern "in a biofilm under real world conditions" is most pertinent [4]. The efficacy of chlorine or any oxidizing agent as a biocide must be balanced against its potential effects on corrosion, especially acceleration of localized corrosion at existing concentration cells.

The use of chlorine (added as a gas or a hypochlorite) is common practice for control of both microorganisms and clams in cooling waters. Philosophies vary as to whether continuous (i.e., daily or weekly) low level chlorination is superior to intermittent slug doses [55, 56, 59]. Chlorine is typically utilized for waters with pH in the range 6.5 to 7.5, possibly to pH 8 [60, 61]. At more basic pH, dissociation of chlorine or hypochlorite to the biocidal hypochlorous acid is significantly less [28]. At a pH greater than 7.5 or 8, bromine compounds may be more effective. A total residual chlorine level of 0.2 to about 1 ppm appears to be the norm. Present federal regulations on discharge limits for existing plants (Best Practicable Treatment) restrict the free available chlorine in the effluent to an average of 0.2 ppm with a maximum value of 0.5 ppm [59].

There is no standard method or single accepted level of chlorination for control of microfouling and corrosion in power plants. For example, Bartz, et. al. [55], in a survey of fouling and MIC in condensers from fossil fired plants indicated chlorination at levels from 0.2 ppm to 1 ppm for a variety of cooling waters. Pope [4] recommends continuous chlorination at the 0.2 to 0.5 ppm level and cites its success in prevention of further MIC in a Cu-Ni fan cooler application following a short term treatment at higher concentration. He also notes that addition of about 0.5 ppm following mechanical cleaning proved a satisfactory treatment for MIC in a Monel heat exchanger in a different study. Pope also notes that while slug doses of chlorine at 5 to 20 ppm for several minutes to an hour or so once per day killed microbial growth, 0.2 ppm can allow the growth of slime formers (with no mention made of any corrosive effects). In a carefully controlled study where iron oxidizing bacteria were determined to be responsible for corrosion of carbon steel, Metell [31] found a chlorine residual of 0.1 to 0.5 ppm was effective in controlling MIC. No details on the method of addition were given. Discussion with a foreign utility revealed their use of continuous chlorination at the 0.5 ppm level or slug doses at 5 to 20 ppm (one hour per day). Some utilities have found continuous chlorination unsuccessful for clam control (use of a non-oxidizing biocide or a molluscicide was superior), others have advocated intermittent chlorination, while still others advocated 0.5 to 2 ppm additions for half an hour, twice a week to be effective for controlling Asiatic clams. In a document prepared for the NRC, Neitzel, et. al. suggest that weekly, low level chlorination, augmented by continuous chlorination during clam spawning season, will effectively control slime formation and eliminate infestation and growth of clams [56]. Kobrin [3] notes that the use of shot chlorination (concentration, interval, and season of the application not specified) effectively controlled both clams and slime. No failures were observed in a component after eight years of service where failures had previously occurred in eight weeks.

Cooling water treatment for both MIC and biofouling in petroleum and chemical industries typically involves chlorination at the 0.5 to 1 ppm level with higher residual chlorine levels in extreme climates or with heavily infested waters. In one case study, corrosion coupons in the cooling water of a pharmaceutical plant had exhibited reasonable corrosion rates for years. Following an abrupt increase in the corrosion rate, sodium hypochlorite additions were increased to achieve a chlorine concentration at the high end of the range and corrosion rate dropped back to the original level [60]. In a chlorine minimization study, a utility attempted to decrease from a 1 to 3 ppm chlorine concentration to the 0.2 ppm level without success prompting them to switch to a chlorine enhancer (a chlorine-bromine product) [62]. Chlorine dioxide is a potential alternative to chlorine that may be more effective under specific conditions [63] but at a significant increase in cost.

In situations where microbial colonization has been established to the point that tubercles are visible on pipe or vessel walls, chlorine is unlikely to provide an effective treatment, particularly for any anaerobes such as SRBs attached to the surface. Costerton notes that "sessile bacteria . . . are rarely affected by levels of biocides that kill planktonic cells" [21]. Several failures have been noted following lay-up with chlorine concentrations at levels that would normally control biological growth [24, 48]. Use of chlorinated water following mechanical removal of tubercles would, however, be expected to provide an effective treatment.

Based upon these data, chlorination to a free chlorine residual of about 0.2 ppm or a total chlorine residual of 0.5 ppm is considered reasonable for nuclear plant cooling waters. A 0.2 ppm residual is probably adequate for maintenance of an already clean system with no disruption of the chlorination; 0.5 ppm is considered adequate for a more typical system that has already experienced some degree of biological infestation and periodically experiences failures of the chlorination delivery system. Continuous chlorination is preferred although chlorination once or more per day (an intermittent process in the strict sense) should prove satisfactory for control of MIC. Augmenting the base level of chlorination with shot chlorination (additions of the order of 5 ppm) on a daily basis during clam spawning season should provide satisfactory control of clams as well.

Some of the corrosion risks associated with the use of chlorine as a biocide have been discussed previously. Chlorine does change the electrochemical potential of the environment slightly such that a shift to more noble potentials with associated increases in corrosion can occur. For low level chlorination, no detectable change in corrosion performance is anticipated. Intermittent chlorination, especially with levels in excess of a few ppm may produce cyclic oxidation effects. At high temperatures, formation of chloride ion from hypochlorite or hypochlorous acid can occur. Chlorine may react with sulfites, other oxidizing agents (e.g., H_2O_2), or light to produce chlorides. Chloride can contribute to pitting of carbon and stainless steels at ambient temperatures and to stress corrosion cracking of stainless steels at slightly higher temperatures. Like other oxidizing agents (and some microbes), chlorine can cause iron (and manganese) to precipitate from solution as the ferrous ion is oxidized to the less soluble ferric (or manganic) state. The probability of pitting of carbon, low alloy, and stainless steels is increased [64, 65].

Ozone and hydrogen peroxide are more powerful oxidizing biocides with greater penetrating power than chlorine. Ozone has been used for treatment of existing MIC at a typical concentration of 0.2 ppm in water or a water fog, or at 1% in air to kill microbes under a grease layer [4]. Typical treatment times of 24 hours were sufficient to achieve essentially 100% kill in stainless steel, admiralty brass, and 90-10 Cu-Ni applications. A residual of ≤ 0.1 ppm on a continuous basis or about 5 ppm for a few minutes per day has been recommended for hydrotest water or for prevention of MIC [4]. Stoecker [66] suggests a 0.2 ppm level for hydrotest water. Ozone decomposes rapidly which makes it particularly desirable where effluent restrictions are of concern. Personnel safety considerations and the expense of ozonation equipment are balanced against these advantages. Ozone at concentrations greater than .25 or .30 ppm in air is injurious to personnel [28, 67]. In addition, iron or manganese can be precipitated from the water as soluble ferrous or manganous ions are oxidized to the less soluble ferric or manganic states. Ozone also rapidly degrades organic materials (e.g., silicones, epoxides, neoprene, and viton) that may be used as O-rings or linings in the system.

Hydrogen peroxide has many of the same advantages as ozone but is much cheaper and safer to use. Pope [4] recommends use at the 50–100 ppm level and notes that a 24 hour treatment at such a level shows the same killing power as a 2 hour/0.5 ppm ozone treatment. Some utilities have incorporated or proposed additions of hydrogen peroxide for control of algal and bacterial growths (See Section 3). The effects of hydrogen peroxide on structural metals are approximately the same as those of ozone or any other strong oxidizing agent. Hydrogen peroxide is stable for longer periods at ambient temperature and does not have the same adverse effect on rubber or polymers as ozone does.

Other biocidal agents such as glutaraldehyde and isothiazolin have been utilized as biocides but not nearly to the extent that chlorine has. They are most frequently used against aerobic organisms as encountered in cooling water applications and are also frequently used in oil field applications against anaerobic organisms such as the SRBs [60, 61, 68]. Their use in the once-through systems commonly encountered in power plants is limited by the necessity for relatively high concentrations (e.g., 50 ppm and above for glutaraldehyde) required for effectiveness and their expense.

Dispersants, Inhibitors, and pH Control

Other chemical treatments may be useful in treating MIC when used alone or along with biocides. Used in conjunction with biocides, dispersants may have valuable supplemental effects. Their use helps to remove organisms killed by the biocidal treatment along with nutrients and debris that may have become attached to the biofilm as they keep such materials suspended in the fluid stream. Used alone, dispersants may be useful for control of light siltation with minimal impact on the more tenacious biological deposits. An established biofilm (particularly a collection of tubercles on a pipe or vessel wall) can prevent corrosion inhibitors from ever reaching the wall and render them competely ineffective. Addition of most inhibitors to treat MIC is unlikely to have any effect at all unless the biological growth has been removed from the surfaces either mechanically or chemically and the microbial infestation has been controlled. [4, 7, 31]. Inhibitors such as chromates have biocidal properties of their own and can be effective in the treatment of MIC. Effluent limitations severely restrict their use. Modifications of water chemistry to provide more basic conditions ($pH < 10$ or 10.5) can provide an effective control, especially in systems that will remain stagnant for long periods that cannot be treated in any other manner have been reported as effective treatments for MIC. Borates may also have some merit for the control of microbial growth, although the mechanism for the effect is not clear.

Chemical Cleaning

Acid cleaning provides a means to remove tightly adherent tubercles and can thus eliminate sites for MIC or other under-deposit corrosion effects. When used in a properly controlled manner, existing deposits (of both organic and inorganic origin) may be removed completely with minimal removal of base metal. The freshly exposed metal surfaces may then be coated, painted, passivated, or treated in some other manner to prevent further corrosion effects. The cleaning procedure must be executed with great care to assure complete removal of tubercles or other deposits. Incomplete removal, poor flushing practice, or excessive reaction of the cleaning agent with the base metal may serve only to aggravate the microbial corrosion problem that cleaning was intended to alleviate. Similarly, unless the cause of the original corrosion condition is eliminated or controlled, exposure of fresh metal to the corrosive environment can result in greatly increased rates of attack.

ENGINEERING AND OPERATIONAL CONTROLS

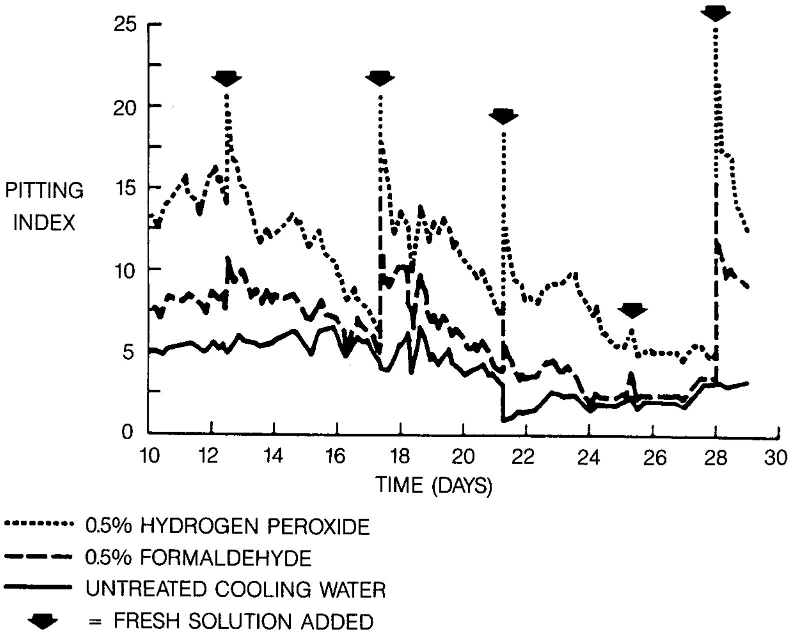
Modifications to operating parameters can effectively treat MIC but only in situations where biofilms are not already well established. Once biological consortia are established, their resistance to changes in fluid forces, aeration level, or modifications to the bulk environment generally require mechanical removal or treatment with a strongly oxidizing biocide. Where operational controls can be used, modifications to the flow pattern can dislodge some biofilms and may be effective in eliminating potential corrosion sites. Some general rules apply, however, the most appropriate operational treatment can be system specific.

Johnson [69] lists the basic guidelines for treatment and prevention of MIC in cooling water systems from design through construction and into the operational phase. The main thrust of his recommendations is that stagnant, untreated water should not be kept in contact with structural materials. The recommended actions to prevent problems, in decreasing order of desirability, are to drain (and dry), treat the water, or, as a last resort, establish flow on a daily basis. These intermittent flow conditions are intended to dislodge any biofilms early in their development such that cooperative communities of aerobes and anaerobes, known to be highly resistant to subsequent fluid forces or chemical treatments, cannot develop. Depending upon the materials, chemical environment, and microbiological factors involved, however, corrosion under intermittent flow conditions may be worse than those in a stagnant system. In other situations, a constant low flow or variable flow situation may exacerbate corrosion.

Metell [31] has shown that corrosion in carbon steel systems due to iron oxidizing bacteria may be strongly affected by flow rate. For example, at high flow rates, bacterial attachment was prevented while under stagnant conditions transport of oxygen to the aerobic bacteria was insufficient to support their growth. At low flow rates (2 to 5 feet per second) corrosion rates were increased. He also noted that under conditions of variable flow that MIC effects were a maximum, corresponding to the rate for optimum growth. Under intermittent flow conditions, MIC effects tended to present a magnitude more representative of the flow spectrum.

Fellers [70] has observed that under intermittent flow conditions, the instantaneous corrosion rate of carbon steels in oxygenated waters infested with iron oxidizing bacteria and SRB was a factor of 100 greater than that observed under stagnant conditions. The effect was attributed to the formation and breakdown of metal sulfide deposits. The rapid corrosion of copper alloys in oxygenated water following exposure to sulfide contaminated environments represents a similar effect. A situation phenomenologically equivalent to one of intermittent flow is represented in a laboratory test result from Tatnall [53] as shown in Figure 7-1. Each addition of fresh cooling water solution was accompanied by a sharp increase in the pitting index. Time of stagnation would be expected to be a key factor in this consideration. Very frequent (daily or more often if possible) jogging of pumps may alleviate the effect under the specific conditions as noted above.

FIGURE 7-1
LPR "Pitting Index" Rates During Portion of First Laboratory Tests



In all cases, a dry system will be more resistant to MIC than a wet one. Biocide treated water will provide greater resistance to MIC than untreated water. In general, MIC in a flowing systems will be less than that in a stagnant system. Intermittent flow provides the potential for cyclic oxidation and can produce the worst corrosion situation. This might be expected for copper alloys and for carbon steels where SRB activity is high. For stainless steels, intermittent flow conditions would be preferable to stagnation since the attachment of bacterial consortia will be minimized thereby reducing the effects of anaerobes. The effects of intermittent flow on total corrosion will be influenced by the purely chemical environment, the microbial species and their metabolic products, and such variables as the time between flow initation events. As a result, the use of intermittent flow to mitigate MIC should be considered only as a last resort, and then must be evaluated in detail for the specific system conditions. To paraphrase Johnson, "flow. . .at least daily,. . .is probably better than nothing". Note that several case histories in Section 3 indicate that elimination of stagnation was effective in preventing recurrence of MIC, however, no results of the use of periodic flow in treating MIC are reported.

Loop design modifications to permit periodic backwashing of surfaces with water or steam can be effective in treatment and prevention of MIC [4, 7, 15]. These treatments can be purely mechanical—for the purpose of removing biofilms and eliminating potential corrosion sites; or supplement mechanical removal with high temperature streams to kill the majority of the organisms. Design solutions have also proven effective in treating and controlling MIC when cooling water loops have been modified from a once-through configuration to a closed loop [7, 15, 56]. In a closed loop, water can be treated with biocides, dispersants, and inhibitors as desired to control organics and corrosion. Obviously, the modification of even a portion of a large cooling water circuit to permit the closer control permitted by closed loop operation represents a significant investment of resources. The costs of the design effort and hardware modification may be justified for some systems where reliability cannot be obtained in any other manner. Cost-benefit analyses may also reveal that such modifications are justified for selected areas of cooling water loops in lieu of massive materials replacements efforts utilizing expensive replacement materials.

Other Treatment Measures

Procedures for treatment of the fluid or the metal that cannot be readily categorized as chemical or mechanical methods include the use of ultraviolet radiation for disinfection of aqueous systems and cathodic protection of metallic members. UV water sterilizers can effect kills in excess of 90% in small systems provided that a filtration of the water has been done [71]. This type of system may be particularly attractive in test systems where comparisons of the corrosion observed in a natural water and sterilized water of *precisely* the same chemistry are desired. UV treatments may also be useful for selected systems (relatively small ones) in nuclear plants.

Cathodic protection for corrosion control is common practice in a wide variety of industries. Applied current systems are commonly used for OD protection of pipe while ID protection is more commonly achieved through the use of sacrificial anodes. Its applicability for treatment of existing MIC has not been satisfactorily demonstrated in power plants, however, the use of cathodic protection as a preventative measure has been explored. This will be discussed in Section 8.

8

PREVENTION

DESIGN

In order to prevent problems with MIC, system design must incorporate sound concepts for corrosion control including corrosion by mechanisms other than those influenced by microbes. Items to be considered are the water source including its pH, salinity, and hardness; typical temperature range; flow rates; the type of operation to be expected (continuous, intermittent, normally stagnant; once-through vs. recirculating); OD environment (e.g., buried pipe); levels of organic materials; and accessibility for cleaning and water treatments. Analysis of the raw water that will be handled by a system should also include determinations of organic carbon, dissolved and total solids, turbidity, iron, manganese, chloride, sulfate, nitrate and nitrite levels, and oxygen. A biological sample of the water source provides an indication of the type of organisms that may present problems.

As noted in many of the case histories and in the discussion of mechanisms, stagnant or low flow conditions are particularly amenable to microbial growth and subsequent corrosion. Where possible, the design should consider control of velocity to a range that will prevent or, at least, delay MIC. Generally, this approach will involve a lower limit on flow velocity such that particulates and organisms will tend to remain suspended in the fluid stream. Continuous flow is preferred to intermittent flow conditions. Dead legs should be avoided to the greatest extent practicable. When they are required, traps or drains should be considered in design to permit periodic draining and/or monitoring of contaminant levels. Detail design should also consider local areas likely to trap microbes. Crevices generated by weld backing rings may act as areas for accumulation of both organic and inorganic contaminants and thus contribute to corrosion (including MIC). For systems that typically remain stagnant for long periods (e.g., fire protection systems), provision for periodically flowing the sytem at a flow velocity sufficent to sweep sedimentation and organic deposits may contribute to the prevention or delay of MIC (see Section 3). Before intermittent flow is utilized as a mitigating treatment, the chemical and biological influences on corrosion of the system should be well understood.

Maintenance considerations should also be factored into system design. System design should consider the need for periodic removal of deposits by mechanical cleaning. For example, for systems likely to experience heavy deposition (MIC or otherwise), provide access ports for introduction of pigs, air bumping, Sandjetting, or hydrolazing equipment. Consideration of on-line cleaning systems (e.g., sponge ball cleaning) for heat exchangers and condensers is best done during the system design phase. Similarly, water treatment stations should also be incorporated into the system design. In the event that specifics of the water treatment, be it for biocide, dispersant, or corrosion inhibitor, are not clear at the design stage, provision for piping, power and space for a water treatment station can contribute significantly to the ease with which such treatment systems can be operated and maintained. System design should also consider provisions for assessing the adequacy and uniformity of cleaning processes. A number of the case histories presented in Section 3 allude to the inoperability of biocide addition equipment as at least a contributor to the observed MIC effects. As noted in Section 7, cathodic protection offers the ability to mitigate corrosion effects, including MIC. System design should allow application and ready maintenance of the cathodic protection as well.

Serious consideration to use of closed loop design should be considered for those circuits with a high susceptibility to MIC and with serious consequences of failure. In a closed loop, ingress of contaminants is more readily controlled and chemical additions are not restricted by effluent limits. This approach, although capital intensive, may prove to be the most economical approach in the long run for critical systems.

CONSTRUCTION AND MAINTENANCE

From the initation of the construction phase, through hydrostatic testing, and into operation, good housekeeping and cleanliness are critical to the prevention of MIC. Throughout construction, systems and materials should be drained of all water and dried. Material must be kept free of moisture and water, particularly in a stagnant condition. Similarly, dirt and construction debris should not be left in contact with materials, particularly in the presence of moisture. In the event that systems or materials have been stored in a wet and/or dirty condition, they should be rinsed or flushed with clean water, preferably water that has been biocide treated, then drained and dried. In large piping systems, drying may be performed by circulation of warm air or nitrogen gas and the moisture content of the gas monitored to assure that the desired dryness has been achieved. Selection of hydrotest water can be critical to prevention of MIC.

In the event that a system cannot be stored dry, either during construction or after start-up, proper attention to lay-up is critical. Various corrosion mechanisms that would not be active during operation often appear during lay-up as water chemistry controls may not be as stringent as during high temperature operation when greater attention is focused on impurity control. During lay-up, alternate wetting and drying may concentrate impurities. MIC is particularly insidious in this regard as the "impurities" of concern are produced by living, multiplying organisms. During lay-up, microbial growth may proceed unimpeded as fluid forces that remove attached organisms from pipe or vessel surfaces are absent. Additions of corrosion inhibitors and biocides made after lay-up are unlikely to be effective as distribution throughout the system is limited. Finally, biocides will be depleted by chemical decomposition or in destroying the microbial life. Proper attention to the initial levels of additions and to their maintenance within the effective range is critical to avoid MIC. A number of the case histories in Section 3 (particularly the pre-operational failures) and in the references [3, 7, 9, 13, 15, 36, 48] will attest to the necessity of proper lay-up.

Probably the second most common source of MIC-related events noted in Section 3 is related to improper operation of chlorination equipment; a condition frequently attributable to improper maintenance and attention to the operation of the injection system. This item may be key in the utilization of chlorine or hypochlorite for treatment and control of MIC. Proper attention to biocide injection equipment may be more important to the success of a treatment program than any other single consideration.

MATERIALS SELECTION

With the present state of knowledge, MIC problems do not appear to be avoidable by materials selection. While titanium (and possibly zirconium and tantalum) does appear to be more resistant to MIC than the commonly used structural materials, it is expensive, is not available in many product forms required for power plant components, and is prone to biofouling to a significantly greater extent than copper alloys, steels or stainless steels [40].

Varying degrees of resistance to MIC for the commonly used materials do appear; however, the total impact of a materials substitution must be evaluated. For example, stainless steels exhibit an inherently greater resistance to MIC than carbon or low alloy steels as evidenced by the fact that stainless steels rarely exhibit microbiologically influenced corrosion away from weldments and do not appear to be nearly so prone to plugging with corrosion products as do carbon steels. In systems where the water is relatively corrosive (i.e., independent of microbial activity), iron loss to the system from stainless steel upstream will be less than for carbon steel, formation of tubercles involving microorganisms will be less likely, and concerns with blockage of pipes will probably be avoided. Further, since welds are the primary areas of concern with stainless steels, alternate filler metals (fully austenitic, iron or nickel based) or additional preventive treatments such as cathodic protection may satisfactorily protect the welds and in doing so protect the entire structure. On the downside, the corrosion of stainless steels under MIC is highly localized leading to through-wall pitting and leaks, just as for carbon steels. Further, the time to achieve the first through-wall penetration may not be significantly different for stainless steels. If failure is defined by leakage, the higher alloyed material in this case would not have produced any improvement in performance. In most cases, substitution of stainless steel for carbon steel can only "buy time" relative to the onset of through-wall pitting. In at least one case, substitution of a "lower alloyed" material (copper-nickel) for a presumably more corrosion resistant one (nickel and Monel) has provided improved resistance to MIC [3]. Obviously, materials selection for resistance to MIC is not straightforward.

Non-metallic materials such as PVC, with and without fiberglass reinforcement, concrete, and various linings and coatings may also be specified as a preventive measure against MIC. Considerations of weight (concrete and concrete lined steel pipe), seismic response (PVC) and fire resistance (PVC) enter into selection of these alternate materials. Biofouling may also be a severe constraint on their use. Certain organisms (e.g., sulfur oxidizing bacteria) can rapidly deteriorate concrete and cemented linings (see Section 4). Coal tar based and synthetic epoxies may also be specified to improve resistance to MIC [4, 11, 44, 66]. On an application-specific basis, selection of various non-metallic materials as pipes or coatings may prevent MIC-related failures.

WATER SOURCES

In operation, few options exist relative to the water source. A service water or cooling water system that utilizes raw water is essentially limited to that environment. While the potential perils of handling raw water are well documented, deionized water or condensate may also harbor microbes with resultant potential for failure [36]. Design modifications to provide closed loop operation offer an extension of the water treatment capability; in effect, permitting the water source used in operation to be modified.

The water sources for hydrostatic test and any lay-up prior to operation are not necessarily limited by the plant design. Many of the MIC case histories presented in Section 3 and in various references were a direct result of microbial activity introduced during pre-operational activities and can be traced to the water source chosen for hydrotest or other construction-related operations. Water treated with biocides may be stored on site and reused as required. Continuous chlorination to produce a total residual chlorine level of 0.5 ppm (minimum) or shot chlorination at 5 to 20 ppm, ozonation (0.1 to 0.2 ppm residual for continuous treatment or 5 ppm slug dose), or 50 to 100 ppm hydrogen peroxide would all be expected to provide sufficently disinfected hydrotest water. Draining and drying of the system or component following testing is still strongly recommended. [3, 4, 13, 66, 69]. Water from a similar treated source should also prove suitable for lay-up. Lay-up considerations will be discussed in greater detail in the next section.

WATER TREATMENT

Biocide additions to water for pre-service tests, lay-up, and during operation can be a first line of defense against MIC. As noted above, the use of an oxidizing biocide such as chlorine, ozone, or hydrogen peroxide is strongly recommended for water used for hydrostatic testing. Continuous or slug doses of one of these same additions or the use of a non-oxidizing biocide (glutaraldehyde, isothiazolin, etc.) for operation will also act as a prophylactic measure. Effluent limits may determine the biocides and concentrations that are usable for a particular system. Sterilization/disinfection of make-up demineralized water is a critical first step in the prevention of MIC in all demineralized water systems. Attention to this step will limit MIC problems considerably and avoid concerns for many of the plant systems critical to safety.

A 0.2 ppm total chlorine residual is probably adequate for maintenance of a system known to be clean; 0.5 ppm is suggested for a more typical system subject to periodic disruption in chlorine delivery or one which has experienced prior biological infestation. The effectiveness of chlorine, whether added as sodium or calcium hypochlorite or as chlorine gas, will be greatly diminished above pH 8. Use of bromine compounds in these more basic waters will provide better microbial control. Shot chlorination is not recommended as a typical prevention measure, however, additions of 5 to 20 ppm chlorine during spawning periods may provide a valuable supplement to continuous low level chlorination for clam control. Ozonation to a residual of about 0.1 ppm or 5 ppm for a few minutes per day has been advocated as a MIC preventative level [4]. Hydrogen peroxide additions to provide a 50 to 100 ppm level with maintenance on a daily schedule is another alternative. All of these oxidizing biocides are "indiscriminant" oxidizers meaning that they will oxidize any organics in the water. Proper monitoring of residual levels is required to assure proper effectiveness. Similarly, all of these agents will modify the oxidizing potential of the fluid and can affect structural materials. Ozone is particularly damaging to rubber and various seal materials. Decomposition of chlorine to chloride ion at elevated temperature may be damaging to carbon steels and stainless steels. Use of non-oxidizng biocides, especially if used in conjunction with a dispersant, may prove to be effective in preventing MIC. Closed loop systems are the most likely candidates for such treatment.

Corrosion inhibitors are generally ineffective for the treatment of existing MIC conditions but may prove useful as preventive measures so long as microbial growth is controlled by a biocide or other means. In order for an inhibitor to be effective, it must reach the metal surface and act to retard the half-reaction controlling corrosion. Some inhibitors (e.g., chromates) have biocidal properties and can be effective in preventing MIC. Inhibitors may be particularly valuable for the treatment of water for lay-up conditions. The premise in this case is that the lay-up environment will be treated with a biocide to control microbiological activity while the inhibitor will act to control dissolution (anodic reaction) or cathodic effects as appropriate for the particular environment. In the event that untreated water must be used for hydrostatic testing or lay-up and more "proper" measures cannot be taken for control of microbial activity, increasing the pH to above 10 will retard the growth of most microbes and may be sufficient to slow down MIC. In all cases, EPA effluent restrictions may limit the types and concentrations of inhibitors that may be utilized.

OTHER TREATMENTS

Alternative procedures for treatment of the fluid or the metal such as the use of ultraviolet radiation for disinfection of aqueous systems and cathodic protection of metallic members are discussed in Section 7 as treatments for existing MIC and will be discussed in the context of preventative measures here. UV water sterilzers can effectively kill microbes in small systems provided that a filtration of the water has been done [71]. UV treatments may be useful for selected systems (relatively small ones) in nuclear plants.

Cathodic protection for corrosion control is common practice in a wide variety of industries and has been effective in control of MIC [7, 9, 18, 27, 66]. For example, Tatnall [38] has reported successful use of cathodic protection following repair of a carbon steel tank. Sacrificial anodes of zinc, magnesium, and aluminum appear to prevent corrosion in systems with known MIC, however, the protected area was limited to the area in the immediate vicinity of the anode [31]. Since microbial activity affects the local electrochemical conditions, cathodic protection schemes can be effective for treatment of known MIC or as a preventative measure. King, et. al. have implied that cathodic protection has effectively prevented MIC in a large number of pipelines and vessels even in environments where MIC might be expected and, perhaps, given users the sense that microbial influenced attack may be ignored [44]. For proper application of the method, the mechanisms involved in MIC must be well understood. In addition, the proper application systems (e.g., impressed current vs. sacrifical anodes, power requirements, maintenance needs) for local protection and for protection of large areas must be defined.

MONITORING

Although not strictly a preventive measure, monitoring of the environment and its corrosive effects should be considered in any MIC-control program. Monitoring of source and effluent streams and corrosion of plant components or surveillance coupons provides important data on the effectiveness of the treatment program and can alert the operator to changes in either the environment or the corrosion response of materials. As discussed in Section 6 sampling of the fluid stream should be based upon flow-through sampling when determinations of microbe populations or types are of concern. Representative samples of the chemical condition of the water may be collected from a flow-through sampler or via grab sampling. Filtering of the process stream past polypropolene cartridges [7] provides a staisfactory method for collection of microbes. Monitoring the biocide level at the exit of key systems should provide reasonable assurance that: 1) the biocide injection system is working, 2) the proper biocide level is being maintained, and 3) no unexpected organic intrusion has occurred. A bi-weekly check of this sort should be adequate for most systems. Microbiological counts of the influent and effluent on a quarterly basis can also provide information on any significant changes in the microbial population. The focus in these measurements should be on any major changes from prior measurements or large (positive) differences between outlet and inlet streams. Electrochemical probes, inserted into the process stream, can indicate corrosion potential. Correlations between shifts in this potential and biofilm formation may be utilized as a corrosion monitor. Tatnall

[7] and DeMonbrun [72] have reported success with a commercially available electrochemical monitor.

Augmented in-service inspection of suspect areas using radiography or ultrasonic techniques can provide up-to-date information on the condition of plant components. Such inspections should be focused on areas of known MIC, or locations which are likely to be susceptible (e.g., stagnant areas, welds in stainless steel systems, designed-in or built-in crevice locations that can harbor microbes). The existence of MIC and the propagation rates of any occlusion or pitting may be monitored in this fashion.

Corrosion coupons or spool pieces are used in various industries to monitor corrosion in the actual process environment during plant operation. Removable coupons are often located in accessible areas of the plant to provide an accurate measure of corrosion of existing or candidate alternate materials. Use of similar coupons in side streams from the main process environment simplifies insertion and removal and can also provide a test site for evaluations of treatments without interfering with plant operations. Spool pieces provide an even better assessment of candidate materials and treatments as localized flow geometries and resultant biological attachments may be precisely mocked up. Qualification of any alternate material should be based upon actual operation in a similar facility or as a spool sample in the environment which it will experience.

9

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