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Mr. Harold R. Denton, Director
Office of Nuclear Reactor Regulation
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

RE: Show Cause Petition Pursuant to 10 CFR 2.206(a) In the Matter of Arizona Public Service, et al. (Palo Verde Nuclear Generating Station Nos. 1 and 2) Requesting Suspension of PVNGS No. 1 Operating License Pending Completion of Specified Corrective Actions and Institution of Proceeding on Corrective Actions at PVNGS Nos. 1 and 2. Docket Nos. 50-528, 50-529 (License No. NPF-34 and Construction Permit No. 142).

1. This petition is brought by the Coalition for Responsible Energy Education (hereinafter referred to as "Coalition") before the Director, Nuclear Reactor Regulation, pursuant to 10 CFR 2.206(a). The petition alleges that spray pond piping corrosion at Palo Verde Nuclear Generating Station (PVNGS) Nos. 1 and 2 constitutes an unreviewed safety question. The petition requests service upon Arizona Public Service (APS) of an order to show cause, pursuant to 10 CFR 2.202, why the low power operating license for PVNGS-1 should not be suspended and future licensing activity for PVNGS-1 and 2 deferred, pending completion of specific corrective actions and a proceeding initiated under 42 U.S.C. 2239(a).

DESCRIPTION OF PETITIONER

2. The Coalition for Responsible Energy Education is a non-profit citizen's organization founded in 1982 to address energy issues in Arizona through public education, research and litigation. The Coalition, through its officers and attorneys, has represented its members through show cause petitions and in meetings with the Commission, as well as in utility rate and financing hearings before the Arizona Corporation Commission. In January, 1985, the Coalition Board of Directors adopted the Palo Verde Intervention Fund as a special project of the Coalition. The Intervention Fund has previously participated in Atomic Safety and Licensing Board hearings on PVNGS-1, 2 and 3. The Coalition's membership consists of individuals and organizations residing in Arizona.

SUMMARY

3. In its "Evaluation of Spray Pond Weld Corrosion at PVNGS," filed with the Commission on April 3, 1985, Arizona Nuclear Power Project

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(APS, et al.) maintains that said corrosion does not constitute an unreviewed safety question. The Coalition has learned of information which contradicts that conclusion. The Coalition alleges that operation with existing and anticipated through-wall pitting of the spray pond welds due to microbiologically influenced corrosion (MIC) will:

(1) reduce the margin of safety below acceptable levels and result in essential cooling water system (ECWS) temperatures in excess of design criteria; and

(2) increase the probability of accident and malfunction of equipment important to safety through the potential for MIC contamination of other safety-related systems.

4. The Coalition further alleges that APS has failed to demonstrate that the MIC problem is or can be confined to the spray pond stainless steel piping, and to establish adequate means to prevent and monitor for further MIC activity. Indeed, based on its information, the Coalition alleges that APS' proposed corrective actions will prove counter-productive.

AUTHORITY

5. Title 10 of the Code of Federal Regulations 2.206(a) establishes the right of the public to petition the Commission, Director of Nuclear Reactor Regulation and other specified directors to institute proceedings pursuant to 10 CFR 2.202 to modify, suspend or revoke a license or for other relief as may be proper. Such a petition must specify the relief requested and set forth the facts that constitute the basis for the request. The Commission may, pursuant to 10 CFR 2.206(a), institute such a proceeding by serving upon the licensee an order to show cause.

6. 10 CFR 2.206(b) establishes that the appropriate director shall institute said proceeding or advise the person requesting said proceeding in writing of the reasons for denying the request "within a reasonable time."

7. The Atomic Energy Act of 1954 gives discretion to revoke, suspend or modify the license or construction permit of an NRC licensee:

> A license or construction permit may be revoked, suspended or modified in whole or in part... because of conditions revealed by the application for license or statement of fact or any report, record, inspection, or other means which would warrant the Commission to refuse to grant a license on an original application; or for failure to construct or operate a facility in accordance with the terms of the construction permit or license or the technical specifications

> in the application; or for the violation of or failure to observe any of the terms and provisions of this chapter or of any regulation of the Commission.

42 U.S.C. 2236. Notwithstanding the discretionary aspect of this statute, the NRC has a mandatory duty to exercise its authority when necessary and is required to determine that there will be adequate protection of the public health and safety. See Natural Resource Defense Council vs. U.S. Nuclear Regulatory Commission, 528 F.2d 166 (2d Cir. 1978).

8. The Director and Commission are not obligated under 10 CFR 2.206 to grant the requested relief nor to hold a formal hearing on the request. Although such action is discretionary, the Supreme Court has determined that the Atomic Energy Act mandates that "the public safety is the first, last and permanent consideration in any decision on the issuance of a construction permit or a license to operate a nuclear facility." Power Reactor Co. v. Electricians, 367 U.S. 196, 402 (1961), quoting In Re Power Reactor Development Co., 1 AEC 128, 136 (1959). How the NRC fulfills this mandate, particularly in determining the benefits of a discretionary hearing, is discussed *infra*.

9. First, a hearing should not be ordered when to do so will result in the reconsideration of issues:

> Parties must be prevented from using 10 CFR 2.206 procedures as a vehicle for reconsideration of issues previously decided, or for avoiding an existing forum in which they more logically should be presented.

Consolidated Edison Co. of New York, et al. (Indian Point Units 1, 2 and 3), CLI-75-8, 2 NRC 173, 177 (1975).

10. The instant case deals with an unreviewed safety question first identified in March, 1985, and has never been previously decided. There are no existing forums. An operating license has been issued for PVNGS-1, and was issued prior to discovery of the spray pond MIC situation. Consideration of full-power operation has been scheduled for May 23, 1985 (50 Fed. Reg. 18612 [May 1, 1985]). Normally, consideration of full-power operations would not constitute an adjudicatory forum in which all the issues raised herein could be addressed. The Coalition does not seek to reexamine the issues reviewed in granting the PVNGS-1 and 2 construction permits and PVNGS-1 license (i.e., *if* APS can meet NRC requirements), but rather, the consideration of *whether* the licensee now meets and will continue to meet the requirements of said permits and licenses, the Safety Analysis Report (SAR), and the Rules and Regulations

of the NRC, and further, if there is reasonable assurance that operation in the current state will not jeopardize the public health and safety.

11. In the instant case, there is no existing forum for determination of issues affecting the prudency of operation of PVNGS-1 in its current state. The risk of increasing the probability of malfunction of equipment important to safety through MIC contamination of additional systems arises with the operation of PVNGS-1 in its current state; accordingly the Coalition petitions for postponement of initial criticality until such time as this issue is resolved. Even more urgently, the increased risk of accident resulting from operation with currently identified and possible additional MIC arises particularly upon full-power operation. Therefore, the Coalition prays that any vote on full-power operation of PVNGS-1 should be delayed until such time as this issue has been resolved. The prolonged period of low-power testing, power ascension and analysis to be undergone prior to actual full-power operation provides an extended period of time during which this issue can be resolved without negatively impacting PVNGS in any way, economically or otherwise. Definitely, the public safety would be best served, therefore, by such a delay.

12. In Indian Point, supra, the Commission considered what existing forum might be best suited to address the matters at issue. Neither the deliberations on full-power operation of PVNGS-1 nor the NRR's recently announced and pending investigation of the spray pond MIC situation constitute the logical forum, as they are not contested case proceedings in which the petitioner, the Coalition, could raise its concerns. A request for hearing and petition to intervene at this stage pursuant to 10 CFR 2.714 would be extremely untimely. When the Atomic Safety and Licensing Board hearings were held and the operating license application noticed, the MIC condition was unknown or non-exitent.

13. The fact that the PVNGS-1 operating license has been issued and other procedural steps completed should not jeopardize this petitioner's right to a fair consideration of the issues raised herein. The provisions of Indian Point merely address the question of existing forums; they do not alter the fact that a utility with a construction permit or low-power operating license bears the burden of proof:

> We think it ineluctable that a utility must bear the burden of proving compliance with the Commission safety regulations not only at the beginning and end of the nuclear licensing

> process - but, as in this case - when called upon at some interim point to "show cause" why a construction permit should not be lifted for unsafe construction practices. Where nuclear power plants are involved, public safety is indisputably better served if a utility must stop construction practices it cannot prove safe; a decision that it may continue those practices because someone else cannot prove them unsafe is manifestly not one which places public safety considerations first.

Consumer Power Company (Midland Plant, Units 1 and 2), ALAB-315, 3 NRC 101, 104 (1976). Clearly, the same reasoning applies to operating practices or conditions as to construction practices. The point is that the paramount importance of public safety places the burden of proof on the licensee. A petitioner need only provide the NRC staff with "sufficent reason" to look into the matter of suspension of a license or other relief, but is not required to assume the burden of proof itself. Indian Point, supra. The public's right to due process of law, as well as public safety, dictates that this should be so.

14. A petitioner, however, has some responsibility to prove its case:

> [T]he standard to be applied in determining whether to issue a show cause order is, as we have said in Indian Point whether "substantial health or safety issues [have] been raised...." A mere dispute over factual issues does not suffice.

Indian Point, supra at 177. Another test against which any request for a discretionary hearing must be judged is whether such a proceeding would serve any "useful purpose." Public Service of Indiana (Marble Hill Nuclear Generating Station, Units 1 and 2), CLI-80-10, 11 NRC 438, 443 (1980). The dissenting opinion in Marble Hill suggests a two-fold interpretation of "useful purpose," the first of which is the public's right to know the risk with which they live (considered to be predicated on widespread citizen interest).

15. In the instant case, such widespread citizen interest clearly exists and has been demonstrated, both in regard to Palo Verde generally and in regard to the specific issue of spray pond MIC. Citizen concern about Palo Verde has increased markedly since the 1982 Atomic Safety and Licensing Board hearings. At an August 24, 1983 meeting with Region V Director Jack Martin, a diverse spectrum of local citizens expressed concerns about both the economics and safety of PVNGS and the candor of APS and, indeed, the NRC. Those last concerns were particularly emphasized by media representatives in attendance, and were occassioned in part by PNO's not released to the press on the 1983 reactor coolant system failure at PVNGS-1. (See attached Exhibit 1.) Subsequently, plant construction quality and cost, APS quality assurance and manage-

ment control and competence, and nuclear plant safety and economics generally have all increased. In 1984, a poll by Arizona's leading newspaper, The Arizona Republic, found 49% of local residents surveyed "dissatisfied" or "very dissatisfied" with PVNGS quality of construction, compared to 22% who were satisfied." Another 1984 poll, by the independent research firm Behavior Research Center of Arizona, showed a plurality of residents favoring abandonment of PVNGS and a majority opposed to any future nuclear plant construction. (Exhibit 2.) Public concern about plant costs has culminated in initiation of a $2 million, four-state utility commission construction cost and prudency audit and acknowledgement by the chief executive officer of a major ANPP partner, Salt River Project, that construction of PVNGS was "a mistake." (Exhibit 3.) The state agency regulating APS rates, the Arizona Corporation Commission, expressed its concern about the current MIC situation by calling a special hearing on the question. A leading metropolitan daily, The Phoenix Gazette, editorially expressed its disapproval of the failure to inform the public of the MIC situation (two PNO's issued in March,1985, were not released to the media and eventual utility disclosure failed to reveal the full extent of the MIC, until the PNO's were released to the press by the Coalition), and of the potential impact on plant costs and safety of APS' proposed corrective actions. The editorial stated:

> Officials at the Palo Verde Nuclear Generating Station and the U.S. Nuclear Regulatory Commission seem to have a rather cavalier attitude about more defects that have been discovered at the facility.
> ...No problems, of whatever magnitude, can be tolerated at Palo Verde. It should go on-line in as perfect a condition as engineers and competent craftsmen can make it.

(The Phoenix Gazette, March 28, 1985; Exhibit 4.)

16. Most importantly, the "useful purpose" to be served by a discretionary hearing is the technical resolution of problems which results in a greater degree of safety afforded to the public. As interpreted by the "Proposed General Statement of Policy and Procedure for Enforcement Action," 44 Fed.Reg. 66754, October 7, 1980 (implementing 10 CFR 2.202 and 2.204), suspending orders can be used to remove a threat to the public health and safety. Specifically, suspension orders can be used when further work or operation would preclude or significantly hinder the identification and correction of potentially hazardous conditions, or for any other reason for which license suspension,

modification or revocation is legally authorized.

17. The primary test of "useful purpose" is based on what kind of regulatory action best serves the public welfare. As a general rule, the Commission has held that:

> public health and safety is best served by concentrating enforcement resources on actual field inspections and related scientific and engineering work as opposed to the conduct of legal proceedings.

Marble Hill, supra. The Appeals Board elaborated on these roles:

> [W]here the matter is not one of inevitability of harm but rather of the extent to which the applicant is carrying out its obligations, the Commission's enforcement arm comes into play. It is in the first instance an enforcement and not an adjudicatory function to make certain that license conditions are being satisfied. It is left to enforcement personnel to insure that an unnecessary or avoidable impact is not incurred because of the applicant's lack of diligence.

Public Service Co. of New Hampshire, et al. (Seabrook Station, Units 1 and 2), ALAB-356, 4 NRC 525 (1976). This notwithstanding, the Atomic Energy Act and the implementing regulations of the NRC recognize that the role of enforcement actions is limited by providing for legal proceedings. In the instant case, the petitioner, the Coalition, alleges that an unnecessary and avoidable impact will be incurred by operation of PVNGS in its current state; however, the situation is not one in which the diligence of the operating utility is a point of controversy. Rather, at issue is the technical resolution of problems which would result in a greater degree of safety afforded to the public. Inspection and enforcement activity has already occurred "in the first instance." The situation has advanced to the stage at which a technical determination must be made in favor of one of two courses: early preventative action to preclude an increase in the probability of equipment malfunction or accident, or operation in the current condition, which would preclude or significantly hinder the identification, limitation and correction of potentially hazardous conditions. The general issue is whether MIC in the PVNGS spray ponds constitutes an unreviewed safety question, which was not considered when the Commission issued a low-power operating license. 10 CFR 50.57(a3) and (6) provide findings required for issuance of an operating license:

> There is reasonable assurance (i) that the activities authorized by the operating license can be conducted without endangering the health and safety of the public,

> and (ii) that such activities will be conducted in compliance with the regulations of this chapter

and:

> The issuance of the license will not be inimical to the common defense and security or to the health and safety of the public.

It is precisely the effect on the public health and safety resulting from operating with the existing MIC and pitting conditions (unanalyzed at the time the operating license was issued) and from the likelihood of the creation of additional conditions inimical to the public safety that concerns the petitioner. In addition, it is manifest that previous management and enforcement activities were inadequate to prevent these circumstances from arising. On-going inspection activities have occurred and substantial questions remain. Finally, as discussed infra, the problem of MIC raises several questions on which scientific knowledge is limited or uncertain, and others in which expert scientific opinion is inadequately reflected in APS' "Evaluation" of April 3, 1985. The Appeals Board has explained two reasons to grant a petition for discretionary hearings:

> ...the NRC already provides a separate procedure, under 10 CFR 2.206, for any interested person to seek enforcement actions beyond those adopted;

and:

> [The request must] state specifically what additional facts might be uncovered by a public hearing that has not been or will not be by pending investigations.

Marble Hill, supra at 443. The specific information, based on a review of the state-of-the-art scientific understanding of MIC upon which this petition largely rests, is discussed infra. Generally, it is this information and a broader exploration of the complexity of MIC problems touching on this issue, which could best be brought out through the presentation of scientific opinion by expert witnesses in an adjudicatory procedure.

18. It should also be emphasized that the Coalition's information suggests that APS' "Evaluation" and proposed corrective action fail in several respects to reflect the scientific state-of-the-art on MIC including ways which are likely to prove counter-productive. (See discussion in "Statement of Facts," infra.) Moreover, APS' public statements on the situation - including characterizing it as a "non-problem" - have, not inappropriately, been characterized as suggesting a "cavalier attitude," such as to indicate an abdication of

knowledge and responsibility by the utility. As the Commission has stated:

> In large part, decisions about licensees are predictive in nature, and the Commission cannot ignore abdication of responsibility or abdication of knowledge by a licensee applicant when it is called upon to decide if a license for a nuclear facility should be granted.

Houston Lighting & Power Co. (South Texas Project Units 1 and 2), CLI-80-32, 12 NRC 281, 291 (1980).

STATEMENT OF FACTS

19. The following summary of the APS-ANPP position on the spray pond piping and weld corrosion at PVNGS-1 and 2 is drawn from APS' "Evaluation of Spray Pond Weld Corrosion at PVNGS," filed with the Director, Nuclear Reactor Regulation, on April 3, 1985.

20. APS has identified corrosion in over 80% of the welds on the stainless steel spray pond piping at PVNGS-1 and 2, through a combination of radiographic sampling and visual inspection. A small number of indications of corrosion were identified in base metal. APS estimates 60% through-wall penetration.

21. APS estimates that water leakage due to through-wall penetration under specified LOCA conditions, could increase essential cooling water temperature to as high as 124.6°F (pp. 5-6). The design criteria limit is 125°F.

22. APS has identified the probable cause of the pitting as MIC and the probable causative agent as Gallionella, on the basis of microscopic analysis of weld sections and analysis of the physical characteristics of the corrosion. APS concludes that the accumulation of stagnant water caused the Gallionella infestation.

23. As corrective action, APS proposes continuation of its current chemistry control and biocide treatment program. APS proposes to prevent future stagnation through routine operation of the spray pumps (aeration). APS proposes a monitoring program consisting of quarterly pressure drop measurements and re-radiographing welds at the first refueling outage.

24. To determine whether MIC has affected other safety related systems, APS visually examined 2 welds and 1 valve from the Unit 1 safety injection system and reviewed prior inspections, concluding that the MIC is isolated to the spray pond piping.

25. APS concludes that it has established means to prevent further pitting initiation and monitor flow, that operation in the current condition will not reduce the margin of safety or increase the probability of acci-

dent or malfunction of safety related systems, and therefore does not constitute an unreviewed safety question.

26. According to APS' calculations, spray pond operation under specified LOCA conditions could result in a temperature increase to within 0.4°F of design criteria limitations. By definition, the margin of safety built into the design criteria would thus be reduced. Moreover, APS acknowledges that it cannot predict the rate or extent of future pitting, and anticipates further through-wall leakage to develop. APS' calculations appear methodologically sound and conservative at first glance. However, APS' analysis is premised on the critical, non-conservative assumption that there will be no further incidences of spray pond piping MIC; i.e., that there will be no increase in the number and size of the indications of MIC. This assumption lacks clear empirical support. It can only be verified over time, through allowing the MIC condition to run its course, or averted, by removing the corrosion and its causative agent (Exhibit 8). Moreover, APS' statistical methodology for inferring the extent of corrosion in similar systems is vulnerable to error because it fails to account for site-specific differences that could affect the rate of MIC (Exhibit 8).

27. In addition, our information establishes that APS' analysis and proposed actions do not provide satisfactory assurance that other safety related systems have not been and will not become affected by the MIC.

28. As stated on page 3 of "Microbiologically Influenced Corrosion of Industrial Alloys" (Daniel H. Pope, et al.; Exhibit 5) and page 13 of Microbiologically Influenced Corrosion: A State-of-the-Art Review (MTI Publication Number 13; Daniel H. Pope, et al.; Exhibit 6), microorganisms related to MIC:

> ...may be motile which aids in migrating to more favorable conditions or away from less favorable conditions, e.g., toward food sources and away from toxic materials.

It should be noted that APS was in a position to have been aware of this information, Bechtel Power Corporation having forwarded a copy of the Pope, et al. abstract to APS on January 3, 1984, as part of the discussion of corrosion of buried piping at PVNGS. (Exhibit 5, cover letter.) Booth, (page 14, Exhibit 7) states that sulfer-oxidizing bacteria (e.g., Gallionella) "are all actively motile." Pope adds:

> The individuals can be widely and quickly dispersed by wind, water, animals, aircraft, etc., and thus the potential for some of the cells in the population to reach more favorable environments is good.

(Exhibit 5 at p. 4; Exhibit 6 at p. 14). Moreover:

> They (MIC organisms) have specific receptors for certain chemicals which allows them to seek out higher concentrations of those substances which may represent food sources. It is very important to understand that nutrients, especially organic nutrients, are generally in short supply in most aquatic environments; but that surfaces, including metals, adsorb these materials, creating areas of relative plenty. Organisms able to seek out and establish themselves at these sites will have a distinct advantage in such environments.

(Exhibit 5 at p. 3; Exhibit 6 at p. 13.) Gallionella (as well as other microorganisms associated with MIC) can be spread by water movement through plant systems connecting with the spray ponds, as well as themselves migrating to separate but connecting systems. (Exhibit 8, affidavit).

29. In order to avoid such spreading of MIC, among other reasons, it is generally highly advisable as a first step in a treatment and control program to remove the microorganisms and corrosion through replacing the corroded materials or through chemical or mechanical cleaning. Such replacement or cleaning activity should take care to remove both the microorganisms and all traces of corrosion in the under-deposit metal. (Exhibit 8.) Such treatment should also reflect awareness of the distinctions between the behavior and response to various treatment procedures of free-floating microorganism and tubercles. (Exhibit 6 at 64.) Biocides and other treatment methods which are effective against free-floating organisms may be ineffective against nodules.

30. The potential for innoculating other plant systems with Gallionella or other MIC agents if the established concentration cells are untreated is further supported by the rapidity with which such microorganisms can establish themselves in a new environment.

> They produce enormous numbers of individuals in a short time (generating times of only 18 minutes are known), thus allowing them under favorable circumstances to "bloom" and quickly "take over" an environment.

(Exhibit 5 at 4; Exhibit 6 at 13.) Moreover, innoculation by MIC organisms can be difficult to detect, setting up the potential for safety situations which are recognized only when a system is called upon in emergency circumstances, as the NRC has recognized:

> The nature of aquatic fouling in piping systems is such that it may go unnoticed, or not severely degrade system performance , until the system is called upon to function following an incident.

"Abnormal Occurence: Blockage of Coolant Flow to Safety-Related Systems and Components," 47 Fed. Reg. 21654 (May 19, 1982). (The discussion therein addresses both marine animal and MIC fouling.) The safety significance of such circumstances is addressed:

> In a nuclear power plant, it is imperative that the heat generated by the nuclear reactor and the components of safety systems be dissipated into the environs. This process is usually performed by transferring the heat being generated to various cooling systems via heat exchangers and then to a heat sink such as a river, lake or cooling tower. These processes are utilized during normal operations and subsequent to normal plant shutdowns or accidents. Failure to provide adequate cooling could result in severe damage to the safety-related components or systems designed to safely shut down the plant and to mitigate the consequences of a major occurence (such as loss of coolant accident, LOCA).

Federal Register, op cit. (At PVNGS, the spray ponds function as the ultimate heat sink.)

31. Concern with MIC involves both the degredation of system structural integrity or operating efficiency through pitting and leakage and fluid flow blockages. Gallionella can foul systems through the creation of tubercles which accumulate in pipes so as to plug them. (Exhibit 5 at 6; Exhibit 6 at 17.) Gallionella may also establish itself in areas where protective coating has been applied through exploitation of "holidays" (discontinuities) in the coating, as may other MIC microorganisms:

> There has been a recent increase in the use of plastics, e.g., epoxy resins. The application of such plastic coatings, however, suffers from the same general problems mentioned above; that is, imperfections provide sites where bacteria can establish themselves and influence or initiate corrosion. There is also the question of the permeability of plastic and other coatings to such substances as hydrogen sulfide, organic acids and various other corrosive chemicals. Therefore, these coatings, although removing the organism from direct contact with the metal may not, in reality, prevent corrosion due to the activities of microorganisms.

(Exhibit 6 at 35.) Once intiated, the corrosion process can become almost auto-catalytic, even if the causative agent is removed or killed, unless all corroded material is also cleaned or removed (Exhibit 8).

32. The foregoing establishes a dual safety concern created by the MIC situation at PVNGS: (1) whether the current levels of MIC in the spray ponds so reduces the margin of safety as to constitute a significant safety question; and (2) the effect of spray pond MIC on the entirety of systems serviced by the spray pond, particularly the likeli-

hood that operation will spread the MIC to other safety systems. The Coalition alleges that the current levels of MIC constitute a significant safety question, particularly for operation at higher power levels. Perhaps an even greater concern, however, is the additional risk of malfunctions created by operation of the system and the transportation of MIC organisms, malfunctions which may go undetected until the systems are needed for safe operation. The existence of that risk is certain. It is, however, difficult to quantify the extent of the risk for numerous reasons. The variable nature and uncertain effect of fluid flow rates is one such reason. Conditions of low fluid flow may be more favorable, and conditions of stagnation or no flow during outages or cycling may be most conducive, to the attachment of MIC-related organisms. As the NRC has noted:

> ...[I]t has been observed that relatively rapid fluid flow <u>tends</u> to prevent attachment of organisms whereas low flow rates or stagnant conditions favor befouling and concentration cell corrosion.

(IE Information Notice No. 85-30 [SSINS No. 6835]: Microbiologically Induced Corrosion of Containment Service Water System, April 19, 1985, at p. 2. Emphasis added.) This positive effect of rapid fluid flow is only a tendency, however, and may be mitigated against by several factors. Even relatively brief periods of low or zero flow can provide an opportunity for microorganism attachment. Microorganisms are able to lodge themselves is small areas which are less subject to the effect of flows, e.g., surface "holidays" (<u>supra</u>) or crevices and other small spaces in the system:

> They [MIC organisms] are small (from less than two-tenths to several hundred µm in length by up to two or three µm in width), a quality which allows them to penetrate crevices, etc., easily.

(Exhibit 5 at 4; Exhibit 6 at 13.) Significantly, APS recirculated the spray pond water regularly prior to identification of MIC, although it did not routinely operate the spray nozzles. Once the bacteria have set up in the form of nodules or tubercles protected by a slime film or ferric hydroxide excresences, the effectiveness of flushing is drastically reduced. (See Booth, Exhibit 7 at 41.) Flushing may again have a positive effect once the MIC organism has pitted through the metal, as APS has noted ("Evaluation," page 7). However, one then has to deal again with the free-floating organisms. Particularly if the diagnosed Gallionella concentration cells contain sulfate-reducing bacteria, the bacteria may form spores which can lie dormant for extended periods of time in systems or components, germinating when conditions are most favorable. (See Pope, Exhibit 5 at 6; Exhibit 6 at 14.) The adaptability of MIC-related organisms has been noted by the NRC:

> They have been known to tolerate a wide-range of temperatures (-10 to 90°C), pH values of 0 to 10.5, oxygen concentrations from zero to almost 100 percent O_2 and extreme hydrostatic pressure.

(IE Information Notice, op cit.) For all the foregoing reasons, the sole reliable preventative to MIC contamination of other safety systems and additional incidences of spray pond MIC is removal of the tubercles.

33. Increasing the concern over the potential for MIC infestation of other safety systems, MIC has been identified or possibly implicated in the past at PVNGS. APS identified MIC on the Unit 2 auxiliary feedwater pump in 1984. (Final Report DER 80-40, Exhibit 9.) However, APS' Final Report did not specify a causative agent. Bechtel Power Corporation has considered the possible role of MIC in the corrosion of buried spray pond and other piping at PVNGS. (Exhibit 5, cover letter, January, 1984.) Following failure of the Plasite lining in carbon steel piping connected to the spray ponds, "widespread rusting" was identified on the Unit 2 diesel generator jacket water and lube oil coolers. (Exhibit 10 at 1.) Although other hypotheses are also vaible, such rusting would be compatible with Gallionella. In the Final Report on auxiliary feedwater pump corrosion, APS stated:

> Whereas MIC bacteria probably exists in other safety-related systems at PVNGS, the conditions that existed in the auxiliary feedwater system are no more hospitable or inhospitable due to the startup flushing and testing.

(Exhibit 9 at p. 3.)

34. The foregoing establishes two concerns: (1) APS must determine whether MIC has initiated or MIC-related organisms have established themselves in other safety-related equipment, and (2) APS must establish that it has or reliably will implement techniques adequate to monitor for and control the potential for such spreading of MIC to other systems in the future. The spray ponds function as the ultimate heat sink, for safe shutdown as well as for the emergency diesel generators. Failure to isolate the current MIC condition to the spray pond piping will significantly increase the probability or severity of accidents and increase the likelihood of malfunction of other safety systems and components at PVNGS.

35. APS' analysis of the status of other plant safety systems in this regard, as described in its April 3 "Evaluation," is based for the most part not on contemporary visual inspection and other direct surveillance, observation and testing, but rather on review of prior inspections and operating performance. Given the rapidity with which Gallionella and other MIC-related organisms can establish themselves and initiate or influence corrosion and the capacity of MIC fouling of safety systems to go undetected absent specialized surveillance procedures, APS' analysis is inadequate.

36. APS' proposed monitoring program consists solely of monitoring spray pond pressure drop on a quarterly basis, and re-radiographing the previously examined welds at the first refueling outage. Again, given the rapidity with which MIC intiation can occur, more frequent and extensive monitoring is indicated. The NRC (Federal Register, op cit. at 21656) has identified a range of techniques and commented upon them:

> The Bulletin also asked licensees to describe their methods for preventing and detecting any future fouling at their plants. A combination of chlorination, heat treatment, flushing, backflushing and the installation of strainers were the preventative actions taken by most of the affected plants. Many of them routinely inspect the intake canal, the pump discharge strainers and the main condenser, cleaning them out as needed. Detection methods included surveillance programs comprised of visual inspections and measurements of flow, differential pressure, and temperature at various system locations. These actions by the licensees can be expected to have varying degrees of effectiveness depending on the frequency with which they are performed and the severity of the infestation present at and around the plant.

In addition to other forms of surveillance, system water and metals should be monitored on a routine basis for the presence of MIC-related microorganisms, both to identify incipient problems and to monitor the effectiveness of on-going treatment and control programs. Pope identifiies methodologies for such monitoring (Exhibit 6 at 66-69; Exhibit 8). A more intensive monitoring program than APS has proposed would aid in verifying the diagnosis of Gallionella as the causative agent. Ideally, APS should be required to obtain laboratory verification of its proposed treatment program in advance of implementation. This is important for two reasons: (1) the effectiveness of any treatment program depends upon the specific nature of the causative agent and the milieu in which the MIC is taking place, and (2) the presence of a given microorganism may mask the actual causative agent or agents, as discussed infra.

37. The mechanisms and role of Gallionella in MIC is not well-understood, according to Pope (Exhibit 6 at 17, 45). This increases the need for a treatment, control and monitoring program that is conservative on the side of safety. Gallionella is capable of direct oxidation, yet it may also create a microenvironment in the underdeposits of its nodules in which anerobic sulfate-reducing bacteria can initiate or influence corrosion (Exhibit 6 at 12, 23, 40-44). Sulfate-reducing bacteria, as well as Gallionella and other iron bacteria, may be associated with pitting such as characterizes the instant case. (Exhibit 6 at 32.)

38. As a case in point, Gallionella is aerobic and directly oxidizes ferrous iron in solution to the ferric state and effects the precipitation of ferric hydroxides. (Exhibit 7 at 41; Exhibit 5 at 5-6; Exhibit 6 at 17, 30.) While stagnant water conditions may facilitate the establishment of Gallionella infestation, aeration (such as APS proposes at PVNGS) is recommended only for sulfate-reducing, anaerobic bacteria. (Exhibit 7 at 52.) While aeration may increase the effectiveness of biocides in eliminating free-floating bacteria in the water, it is likely to prove counter-productive against Gallionella in the tubercle form. (Exhibit 6 at 44; Exhibit 8.) Oxygen can both cause Gallionella to "bloom" more rapidly and increase the oxidation rate and hence the degreee of corrosion. (Exhibit 8.) Inappropriate biocides can induce microorganisms to migrate to other systems as well, as noted <u>supra</u>. Therefore, laboratory testing will prevent a misdirected treatment program from actually worsening the MIC problem.

39. Oxidizers generally are resistant to a range of biocides (Exhibit 5 at 3-6; Exhibit 6 at 13-14, 34); and:

> Pope and coworkers and Costerton and coworkers and Characklis and coworkers have all pointed to the fact that the usefulness of many biocides in the control of organisms in fouling material is much more limited than it is in the aqueous part of the system. The other problem with certain of the biocides is that they will simply shift the microbial population from a "normal aquatic community" or "normal cooling system" community to very specialized communities, i.e., those which form slime or those which are through some other mechanism, able to be more resistant to biocides. This shift may cause a much more severe sliming or corrosion problem than might be encountered with a mixed microbial community.

(Exhibit 6 at 36-37.) (Indeed, it is a valid hypothesis that the on-going treatment program at PVNGS has actually had this effect in relation to the current MIC situation.) Gallionella sets up a "differential aeration" cell in which pH is altered (Exhibit 7 at 41). Eventual through-pitting may allow normal flushing to resume, as APS argues; but in the current state, aeration cannot penetrate the Gallionella tubercle but can encourage additional Gallionella MIC. Therefore, it is contra-indicated.

40. To overcome the foregoing difficulties, ensure maximum effectiveness of a proposed treatment program and prevent further infestation by the identified causative agent, Pope recommends elimination of the causative microorganism or microorganisms and the sites of corrosion, followed by treatment (Exhibit 6 at 44). Biocide application and chemical control programs alone are not generally effective unless accompanied by removal or cleansing of all corrosion (Exhibit 8). Booth also confirms that:

> ...a preliminary mechanical or chemical cleaning process may be essential before the application of a microbial inhibitor can become effective.

(Exhibit 7 at 50.)

41. The NRC has noted:

> ...[C]leaning and dry lay up, or periodic recirculation flushing, during extended outages to mitigate know [sic] biological activity would appear to be prudent alternatives.

(IE Information Notice, op cit.) However, in choosing between cleaning and flushing, the distinctions made <u>supra</u> between aerobic and anaerobic bacteria, free-floating bacteria and tubercles, etc., must be borne in mind. In the current case, thorough mechanical or chemical cleaning to remove deposits and underdeposit corrosion, or replacement of the corroded materials (removing the deposits) are the prudent courses. They are the conservative courses, in the sense that they clearly will prevent the intiation of additional corrosion which can create both safety hazards by reducing the effectiveness of safety equipment and increased long-term economic costs. By contrast, APS has failed to meet its burden of proof that its proposed corrective actions will have such positive effect and will not increase the probability of additional safety problems. Failure to take preventative actions that will avoid such degredation of safety systems and components where possible, or postponement of such actions until damage is done, is not a prudent course that puts public safety first. Operating the system in its present state, which is likely to spread the MIC problem, is not prudent. A more thorough inspection and analysis of the nature and extent of MIC at PVNGS and removal of the causative agent and the corroded material is the prudent course that best serves the public interest.

42. Given concern about the ability of APS to maintain ECWS temperatures within design criteria range and not reduce the margin of safety built into the design criteria to unacceptable levels, pipe replacement and/or rewelding represents the optimally prudent solution to the need to remove the Gallionella (or other microbial) infestation and underlying corrosion.

CONCLUDIONS OF LAW

43. 42 U.S.C. §2236(a) and 10 CFR 50.100 provide that a license or permit may be revoked, modified or suspended because of "conditions which would warrant the Commission to refuse to grant a license on an original application..."

44. 42 U.S.C. §2236(a) and 10 CFR 50.100 also provide that a license or permit may be revoked, modified or suspended "for failure to construct or operate a facility in accordance with the terms of the construction permit or license..."

45. The existence of the uncorrected MIC problem, the potential effect on other safety systems and the defective evaluation and corrective action proposals submitted by APS in the instant case (supra), fulfill the conditions of the Atomic Energy Act and Chapter 10 of the Code of Federal Regulations as set forth in paragraphs 43 and 44, supra, for suspension of a license or permit.

46. As the discussion in paragraphs 7 through 18, supra, establishes, the instant case meets the criteria for intiation of formal hearings. It should be pointed out that the relief requested (suspension of the license and permits for PVNGS-1 and 2, respectively, pending hearings and rework of the spray pond piping), is moderate and should not require a delay in Unit 1 initial criticality of more than one to two months, which delay is not unreasonable to protect the public health and safety. If the alternative relief suggested (deferral of a full-power decision until such time as these issues are addressed) alone were adopted, there would be no negative impact on PVNGS sheduling whatsoever, although the ability to prevent spreading of the MIC would be reduced.

RELIEF REQUESTED

47. WHEREFORE, Petitioners pray that the Director, pursuant to 10 CFR 2.202(a), Order the Arizona Public Service Company, et al., to show cause as to why Construction Permit No. 142 and License No. NPF-34 for PVNGS Projects 1 and 2, respectively, should not be suspended and a vote on full-power operation delayed, pending replacement of the corroded spray

pond piping, re-inspection of other plant systems, and development of a revised corrective action program in light of the information discussed above and any other relevant information; and

48. Initiate hearings on this issue, under 42 U.S.C. 2239(a).

Respectfully submitted,

Myron L. Scott

Myron L. Scott
COALITION FOR RESPONSIBLE
ENERGY EDUCATION

Dated this 6th day of
May, 1985.

AFFIDAVIT OF REPRESENTATION

TO WHOM IT MAY CONCERN:

Be notified that Myron L. Scott is Executive Director of the Coalition for Responsible Energy Education and Arizonans for a Better Environment.

The Executive Director, among his (her) other duties, is responsible for directing the activities of the litigation and research components of the Coalition for Responsible Energy Education and Arizonans for a Better Environment. The Executive Director may, under the Charter and By-Laws of the Coalition and A.B.E., represent those organizations in all legal matters and interface with the attorneys representing or assisting the Coalition and A.B.E. in all legal proceedings.

In particular, the Executive Director is authorized under the Charter and By-Laws and by vote of the Board of Directors to represent the Coalition for Responsible Energy Education in all proceedings before, petitions to and other matters before the U.S. Nuclear Regulatory Commission.

Done this 3rd day of May, 1985.

Barbara S. Bush

Barbara S. Bush
President, Coalition for Responsible
Energy Education and Arizonans for a
Better Environment

Myron L. Scott

Myron L. Scott
Executive Director, CREE/ABE

SUBSCRIBED ANS SWORN TO before me this 3rd day of May, 1985, by Barbara S. Bush and Myron L. Scott.

Lyn M Brewster
Notary Public

My Commission Expires:
May 22, 1988

EXHIBIT 1

Scotts Daily Prog. 8-25-83 P.1

Critics attack APS 'credibility gap'

By KEITH BAGWELL
Progress Staff Writer

The U.S. Nuclear Regulatory Commission and Arizona Public Service Co. came under fire for "totally lacking public credibility" Wednesday at a meeting in Phoenix with the NRC's new regional administrator.

Meeting with administrator Jack Martin were local critics of the $4.3 billion Palo Verde Nuclear Generating Station under construction 40 miles west of Phoenix and reporters from Arizona newspapers.

Martin said his background is in the NRC effort to develop nuclear waste disposal capability, and that he has limited knowledge of nuclear power plant operations and even less knowledge of Palo Verde specifics.

John Ahearn, state Residential Utility Consumer Board chairman and a former state corporation commissioner, said: "The operative word here is credibility. APS totally lacks it and the problem has been enhanced by the NRC. The words that come to my mind are intransigent, misleading, not forthcoming and misstatements."

Between mid-May and July 18, when APS conducted a "hot functional" test of Palo Verde's first reactor — then scheduled to begin operation in May 1984 — its cooling water pumps disintegrated, welds broke, pipes cracked and cooling water system problems were found.

Ahearn charged that the first news story about the problems appeared July 30 and even though APS officials had two extensive reports in front of them, they said damage was minor and there was only a "potential delay."

"Now, after being pushed to the wall, APS says there will be at least a six-months delay — that will cost consumers more for repairs and additional financing. NRC's reactions to such things must be significantly stronger," he said.

Jackie Meck, a former Buckeye mayor and member of the West Valley Agricultural Protection Council that has intervened in the NRC process leading toward a Palo Verde operating license, said APS never told area farmers of crop-damaging salt emissions from the plant's cooling towers and evaporation ponds and completely left them out of its Palo Verde environmental impact statement.

Yet, he said, the plant will emit "14,000 pounds of salt into the air every day, just from the cooling towers."

Such salt emissions, he said, are likely to damage extensively the 150,000 acres of crops farmed by West Valley's 55 members, reducing significantly their $90 million to $100 million in annual revenues.

Meck said APS officials say there is no problem with salt drift and refuse to address it. When APS board chairman Keith Turley was confronted at one meetng with the farmers, Meck said, he told them that if anything happens to their crops they can sue the utility, the state's largest and a 29.1-percent shareholder in Palo Verde. APS also is Palo Verde construction director and will be plant operator.

Renz Jennings, a farmer and former legislator, charged that APS officials wine and dine government and other industry officials, make charitable contributions, use "propaganda scare tactics" and intimidate workers to keep them quiet about Palo Verde construction problems.

Jill Morrison of the Palo Verde Intervention Fund said NRC's credibility problems mostly are due to its lacking on-site inspection of Palo Verde construction.

Martin said his agency lacks manpower and funds for more and better inspections and that its authority over nuclear power plants is limited by law to "the safety concerns that plants are built right and operated correctly."

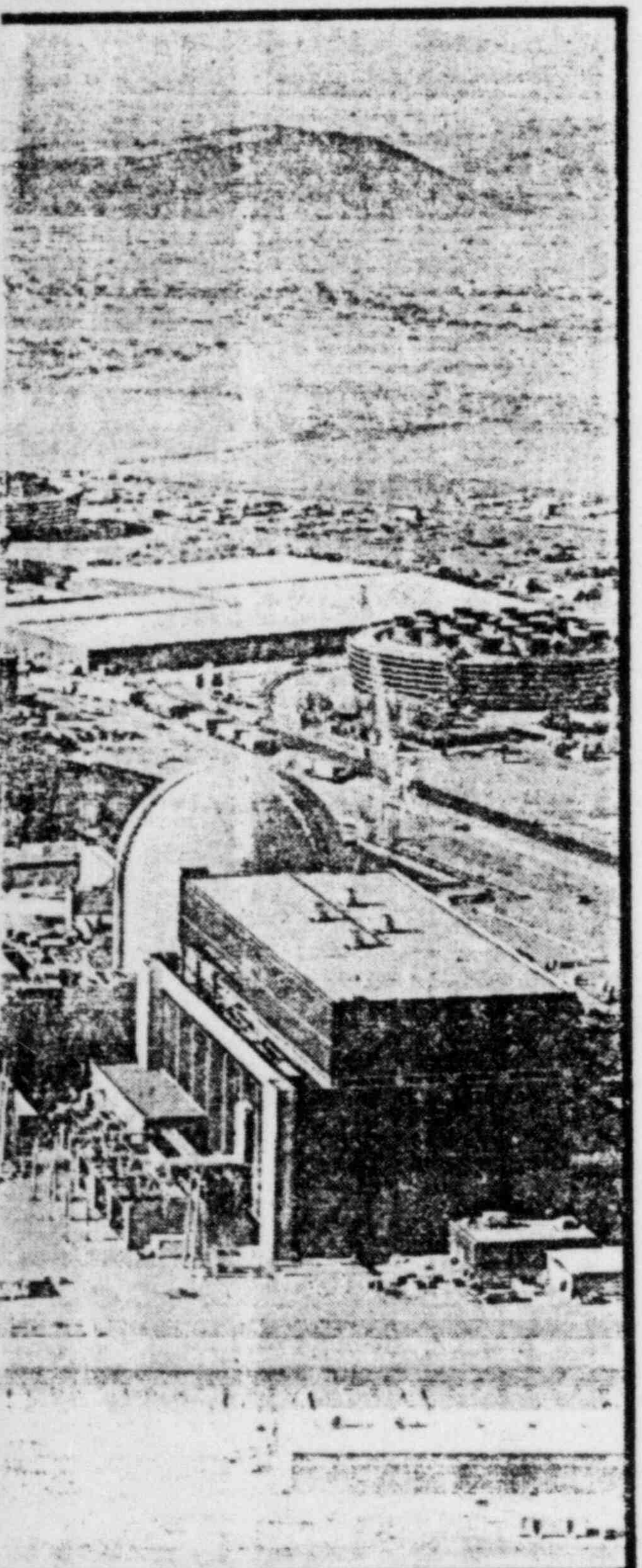
He said, "The government will have to reflect on all this . . . we will need all your help we can get . . . credibility relys on some good will and faith on everyone's part."

The Arizona Republic

Exhibit 2

Sunday, March 11, 1984

ARD
84 D
V41



apart. But they've got to get it into operation before we know if it's safe or not . . . Every piece

Palo Verde scores low Valleywide

Doubts are running rampant as state's first nuclear plant prepares to produce energy

Valley residents appear skittish about the construction of the Palo Verde Nuclear Generating Station.

Since July, they've been hearing about sabotage; damage in the primary reactor-coolant pumps during the first test; the Nuclear Regulatory Commission's finding of 15 construction problems, including four "significant deficiencies" for which the Arizona Public Service Co. may be fined; and allegations that records have been falsified and $1 million worth of tools buried.

That's not the stuff to put area residents at ease about the first nuclear plant in the state.

Assurances by APS that the 3,810-megawatt plant will be safe and the problems fixed apparently aren't soothing.

Almost half of the 601 people surveyed for the "Report Card" are dissatisfied or very dissatisfied with the quality of the plant's construction. There are more than twice as many dissatisfied people as satisfied people.

The survey showed 49 percent are dissatisfied and 22 percent are satisfied. The rest have no opinion.

Only one question on Palo Verde was asked: the level of satisfaction with the quality of construction at the plant.

Ed Van Brunt, APS vice president in charge of the

AZ. REP. 3-2-85 A-1

Palo Verde nuclear plant a mistake, SRP, APS admit

Top managers blame political climate, miscalculations

Jack Pfister

"Nuclear power has fallen from grace in this country."

By JOHN STAGGS
Arizona Republic Staff

The decision to build the Palo Verde Nuclear Generating Station has turned out to be a mistake, the chief executive officers of two Arizona utilities said Friday.

The assertion first was made by Jack Pfister, Salt River Project general manager, in an address to a Valley Leadership class. It later was seconded by Mark DeMichele, president and chief operating officer for Arizona Public Service.

APS is in charge of overseeing the construction of the plant.

In his address, Pfister said, "If I knew in 1973 what I know now, there's no chance I would have participated in Palo Verde. I wish it wasn't there."

He added that a coal-fired plant should have been built instead.

Program officials, saying the meeting was intended to be private, ordered a reporter to leave the session after he identified himself in asking a question.

Pfister's statement was made during Valley Leadership's 1985 Energy Day Program, attended by 40 people at the Valley Bank Center. The program, in its sixth year, brings together potential community leaders to identify and discuss Valley problems and solutions.

Pfister said that because of the accident in 1979 at the Three Mile Island nuclear-power plant in Pennsylvania, "nuclear power has fallen from grace in this country."

"No utility executive in his right mind would commit to a new nuclear plant today," Pfister said.

DeMichele, contacted late Friday, said that he agreed with Pfister's comments regarding the controversial plant.

"As I recall," DeMichele said, "what he (Pfister) said was that if he had the benefit of perfect 20-20 hindsight, we would not have gone into it. That's absolutely correct. But his point is that we did go into it and now we have to complete it. It's that simple."

DeMichele also said that in reporting Pfister's comments, *The Republic* had violated a 7-year-old agreement between the newspaper and Valley Leadership that comments made in the organization's classes were not for attribution.

In his remarks, Pfister said, "Going back to the early 1970s, it appeared the (nuclear) technology was sound. The estimates were that costs would be high for the nuclear plant, and the fuel costs would be relatively low, so the capital costs for fuel and operating would provide a 'bust bar' cost. That's the final cost as it goes off the transmission lines of the power plant," Pfister said.

"The bust-bar cost is very competitive with coal, particularly with the ratcheting that was going on with weather and air-quality requirements for the coal-fired plants. And, finally, one of the very attractive features of nuclear power was that it had little or no impact on the environment.

"Yes, there was radioactive waste being produced in the fuel cycle,

— Mistake, A2

Exhibit 3

Mistake

Continued from A1

but the experts in the area felt that was a technological problem that would be resolved, but they didn't understand the political implications of technological problems," Pfister said.

The SRP owns 23.1 percent of the nuclear plant, 50 miles west of downtown Phoenix. Arizona Public Service Co. owns 29.1 percent; El Paso Electric Co. owns 15.8 percent; Southern California Edison Co., 15.8 percent; Public Service Co. of New Mexico, 10.2 percent; and Southern California Public Power Authority, 5.91 percent.

Unit 1 of the triple-reactor plant has completed fuel loading and is expected to be operating at 100 percent capacity by the last quarter of this year. Unit 2 is expected to be operational next year, with Unit 3 a year later.

The $9.3-billion plant will be the biggest nuclear facility in the nation and the second-largest in the world. The largest is just outside Leningrad in the Soviet Union.

Pfister said, "Another reason SRP and APS were interested in nuclear power was that in the period from 1960 to 1973, we were growing at a rate of 11 percent annually. Our projections suggested that growth would go on indefinitely.

"So we began an aggressive campaign of additional coal-fired units. We were really concerned that perhaps we wouldn't meet the load (demand) as it developed in the area."

That was the environment in 1973 when APS and SRP made the decision to build three 1,270-megawatt nuclear units.

"Why did we make that decision? First of all, we had a water supply, and water is a key ingredient in the generation of electricity. One obvious water supply is the effluent that comes from the 91st Avenue sewage-treatment plant, and SRP and APS felt that would be an ideal water supply for a nuclear plant," Pfister said.

"It was an excellent site out there, from the geological standpoint. This area generally is a low area for earthquakes."

"Another major reason for selecting Palo Verde was the economics. All the studies that APS and SRP did at that time clearly demonstrated the choice was nuclear power. It was far more economical than coal-fired generation, and the prices were far more predictable at that time than coal because of the environmental" controversy, particularly in Western states," Pfister said.

Reliability, a major issue with any power plant, was another factor, he added.

"Other units were being sold by Combustion Engineering, so we would be the ninth or 10th unit of this size and model to go on line, and we thought we could learn by the technological evolution that comes about.

"Interestingly enough, those other units were canceled, so Palo Verde is the first of this model to come on line," Pfister said.

"But in 1973, when we made the commitment, it looked to us that we would be using an experienced product rather than the state-of-the-art product that we find ourselves with.

"Well, SRP and APS had a lot of competition as to who would be project manager and operating agent for the Palo Verde plant. And guess who lost? APS," Pfister said.

APS got the job.

Pfister later said, "But with 20-20 hindsight, if only I had known in 1973 what I know now, I never would have participated in Palo Verde. There's just no doubt about it. But I can't go back and make that decision. Palo Verde is there, its first unit is 100 percent complete. We've spent over $4.5 billion in the ground out there already. It needs to be completed. I wish it wasn't there, I really do, but there's nothing I can do to push it away."

In answering a question from his audience, he stated that in hindsight, he would prefer "a large, coal-fired generating station" in place of Palo Verde.

"Then the (1973) Arab oil embargo came and completely changed the dynamics in the electric-utility business," Pfister said.

"We had thought before that electricity price was inelastic. People would continue to use electricity no matter what the price. We found that concept was in error.

"Just like any other product in society, electricity does have price elasticity, and when prices go up, demand begins to go down," the SRP official said.

As a result of energy price increases due to the oil embargo, Pfister said, "our customers started using less, and we went from a load growth of more than 11 percent to one of less than 5 percent."

"Until 1979, things were looking good, until the accident at Three Mile Island. That was, I believe, the turning point in public acceptance of nuclear power," he said.

Exhibit 4

The Phoenix Gazette

Eugene C. Pulliam 1889-1975
Publisher 1946-1975

Eugene S. Pulliam
President

Darrow Tully
Publisher

Jay Brashear
Editor of The Editorial Pages

Lynne Holt
Managing Editor

Bill Shover
Community Services Director

Conrad A. Kloh
Director of Sales

Wm. R. Hogan
Director of Operations

"Where the Spirit of the Lord is, there is Liberty," II Corinthians 3:17

Editorials

These are the views of The Phoenix Gazette as an institution, thus are not signed by an individual writer.

Nuclear non-problems worrisome

Officials at the Palo Verde Nuclear Generating Station and the U.S. Nuclear Regulatory Commission seem to have a rather cavalier attitude about more defects that have been discovered at the facility.

The latest problem involves leaking welds in a backup cooling system, which may delay the scheduled May start-up of Unit 1. Eighty percent of the welds on stainless steel pipes in Units 1 and 2 are pitting and corroding, according to Arizona Nuclear Power Project officials. Some of the corroded welds, according to an NRC memo of March 11, have developed leaks. Palo Verde officials disclosed the corrosion problem in a recent newsletter but made no mention of the leaks.

Brad Parker, a spokesman for the nuclear project, said the pipes might not need replacing — even if they are leaking — because the water is not radioactive and simply would seep back into the ponds. "We're not planning to fix it," he said, "We say it's a non-problem."

The object of piping is to contain and move liquid. No reputable Valley plumber could get away with leaving leaks in an installation. And this so-called non-problem — the latest of many problems, some much more serious, has occurred at a triple-reactor nuclear plant whose latest cost estimate is $9.3 *billion*. The non-problem may continue and worsen, inasmuch as engineers suspect that a microorganism is attacking pipe welds.

No problems, of whatever magnitude, can be tolerated at Palo Verde. It should go on-line in as perfect a condition as engineers and competent craftsmen can make it.

EXHIBIT 5

January 3, 1984

Arizona Nuclear Power Project
P. O. Box 21666 - Mail Station 3003
Phoenix, Arizona 85036

Attention: Mr. Edwin E. Van Brunt, Jr.
APS Vice President, ANPP Project Director

Subject: Arizona Nuclear Power Project
Bechtel Job 10407
Bechtel Action Items Regarding
Corrosion Protection of Buried
Piping
File: E.16.05

Reference: (A) Letter B/ANPP-E-109836, December 12, 1983✓
(B) Letter B/ANPP-E-40378, February 7, 1979 —

Dear Mr. Van Brunt:

Our response to action items described in Conference Notes No. CN-E-1405 [Reference (A)] is summarized below. (Item numbers refer to Conference Notes item numbers.)

Item B.1

We have verified that the proposed locations of additional anode beds, rectifiers and related cathodic protection equipment do not interfere with the location of the low level radwaste storage facility, as shown on APS Drawing No. AO-A-RSS-A01, Revision 0, dated November 15, 1983, (Interim Onsite LLRW Storage Facility Plot Plan).

Item B.2

Three soils samples were analyzed in 1978, as referenced in our letter of February 7, 1979, [Reference (B)]. Ammonia was not listed as one of the constituents in the water extract sample. In general, ammonia compounds oxidize rapidly in aerated soil to form nitrates and are not retained in the soil as free ammonia. (Free ammonia in high concentrations could be corrosive to copper.) Also, we would not expect much ammonia, or its by-products, in the soil samples as the "farmland" that was used for pipeline backfill on the site did not include the first two to three feet of topsoil which was removed prior to use as backfill.

January 3, 1984

Item B.11

A list of all pipe isolating flanges installed, or to be installed, for the three units is enclosed. The list includes information regarding the drawing number and drawing coordinates to assist in the physical location of the flanges.

Item B.14

We are not aware of any alternate feasible methods available in the current technology to verify in situ external pipe wall thickness of buried piping. An inspection service is available (AMF Tuboscope of Houston) which utilizes a segmented pipeline "pig" which, with pressure from flowing fluid, travels through the pipeline being monitored. The "pig" carries an electromagnetic sensor which provides a magnetic flux over the entire 360° internal/external pipe surface. Deviations in wall thickness, such as corrosion pits, can be recorded for the total internal/external thickness without distinguishing between internal and external defects. This device would not be able to pick up anomalies where the depth of the defect is greater than four times the diameter. Also, this device is not yet available on the market for pipes less than six inches in diameter. Special piping manifolds need to be temporarily added to the piping systems to allow insertion and removal of the "pig" from the piping.

Another service (Corrosion Logging Service, Lafayette, Louisiana) is available to check continuity of coating/wrapping of buried pipelines by measuring piping electrical resistivity to ground. It would not be able to monitor the external coating protection of several pipes installed close together or one above the other. Although this monitoring method might be used to identify areas of defective coating on buried piping for future inspection purposes, actual exterior pipe wall conditions would still only be determined by excavation and visual inspection.

We believe that the current plan to excavate and visually inspect the known highly corrosive areas in the soil will provide a basis for determining the need for any additional monitoring or test plans. Hydrotesting can always be performed to verify adequacy of pipe wall thickness for excavated areas where some surface corrosion may have occurred.

Item B.15

There are no Bechtel standards regarding limit of concentrations for various chemicals in the soil. Also, we have found no specific industry wide Civil/Structural engineering codes regarding such limits. Industry wide standards refer to "engineered" requirements and relate to physical characteristics of the soil, such as bearing pressure, compaction, density, particle size, etc. Soils high in soluble salts, as determined at the Palo Verde site, are acceptable for use in engineered backfills.

Item C.1

Enclosed is a copy of a paper presented at the National Association of Corrosion Engineers meeting in April, 1983. The "state of the art" of microbiological influenced corrosion (MIC) of industrial alloys is presented. The general conclusions of the paper indicate that, although "MIC of several classes of alloys is well documented - - - - - data on the extent of the MIC problem relative to corrosion problems in general are largely unavailable."

Action Item B.5 (cathodic protection schedule), and Item B.10 (rationale for the Palo Verde Project cathodic protection design) will be addressed in separate correspondence. Action Items B.8 (isolating flange jumpers) and Item B.13 (coat and wrap balance of stainless steel piping) are in progress.

Please advise if additional information and/or clarification is required.

Very truly yours,

BECHTEL POWER CORPORATION
Original Signed By Burt Aley
for W. H. WILSON
W. H. Wilson
Project Manager
Los Angeles Power Division

J. Aley
RWG:lrw

Enclosure: (1) List of Piping Systems Isolating Flanges (1 page, 4 copies)
(2) Microbiologically Influenced Corrosion of Industrial Alloys (NACE technical paper) (8 pages, 4 copies)

PAPER NUMBER
247

CORROSION 83

*The International Corrosion Forum Sponsored by the
National Association of Corrosion Engineers
Anaheim Convention Center, Anaheim, California
April 18-22, 1983*

MICROBIOLOGICALLY INFLUENCED CORROSION OF INDUSTRIAL ALLOYS

by
Daniel H. Pope[1], David J. Duquette[2],
Arland H. Johannes[3], Peter C. Wayner[3]
[1]Department of Biology and Fresh Water Institute,
[2]Department of Materials Engineering,
[3]Department of Chemical and Environmental Engineering
Rensselaer Polytechnic Institute
Troy, N.Y. 12181

ABSTRACT

A multidisciplinary group of scientists at Rensselaer Polytechnic Institute was asked by the Materials Technology Institute of the Chemical Process Industries to survey the available literature on Microbiological Influenced Corrosion (MIC) and to report their findings relative to the evidence for MIC of iron and mild steels, stainless steels, copper alloys, aluminum and its aluminum alloys, nickel-chrome alloys, and titanium. Further the group was asked to report the state of the information relating to the mechanism(s) whereby MIC of each material occurs, methods of prevention and methods of detection in the laboratory and in the field. Finally, they were asked to develop a list of priority areas for research.

The group found evidence in the literature for MIC of all alloy groups except nickel-chrome and titanium. Detailed mechanisms for MIC are generally unknown. Protection from MIC and reliable methods of detecting it are not generally available. Details and suggested research areas are discussed herein.

INTRODUCTION

The purpose of this paper is to present the findings of a multidisciplinary study group constituted by the Materials Technology Institute of the Chemical Process Industries to evaluate the state of the art with regard to microbiologically influenced corrosion (MIC). This group was asked to study the available literature and to write an interpretative document which attempted to answer the question: Is there sufficient evidence in the literature to conclude that MIC, of any kind, occurs in various metals and alloys? The alloys of interest included the mild steels, stainless steels, copper alloys, aluminum and aluminum alloys, nickel alloys and titanium. In cases where the answer was in the affirmative the available information for each group of alloys was to be evaluated with regard to the following:

---

a. What are the physical and chemical conditions under which the MIC of a particular type of alloy occurs?

b. Which type(s) of organisms are involved?

c. What is the mechanism(s) whereby MIC occurs?

d. What methods can be used to detect MIC in the laboratory?

e. What methods can be used in the field to detect MIC?

f. What methods can be used to prevent MIC?

g. What research needs to be done?

Finally, the group was asked to evaluate the general MIC situation and make recommendations as to what research area(s) should receive the most attention in the near future in order to best advance the understanding of the prevalence, causes, detection and control of MIC.

GENERAL REMARKS REGARDING THE LITERATURE USED:

There is a good deal of literature on MIC. However much of it deals with reports of case histories, or observations incidental to the main study, with poor documentation regarding the physical, chemical and especially microbiological conditions under which it occurred. It should be noted that this was not usually the fault of the observer since very few qualified environmental microbiologists or corrosion experts have addressed themselves to the questions of MIC. Furthermore the techniques for dealing with many of the organisms involved have been adapted primarily from the area of clinical microbiology and are, in many cases, not adequate for dealing with the organisms involved in MIC, their isolation, growth, identification, or an evaluation of their role(s) in the corrosion process(es). A significant portion of the literature was available only in foreign languages . Much of this literature was not used directly in writing the report since it was possible to establish an adequate case for MIC of most alloys from the available English language literature. It should be noted however that there are at least two excellent reviews available, one in French (1) and one in Swedish (2).

There are also several English language review articles and books available which deal with MIC in a variety of ways. Reviews by Miller and Tiller (3) and Iverson (4) and Booth and Wormwell (5) and books by McCoy (6) and Postgate (7) were especially helpful.

A large percentage of the available literature deals with the area of corrosion of irons and steels by anaerobic, sulfate reducing bacteria, and spans a long period of time in which many different techniques were used. It represents therefore not only the area in which the most is known but also the area where most controversy still persists. For that reason this area has received the most attention herein. For other alloys, e.g., Monel and titanium, there is very little available in the open literature. Therefore the conclusions reached by the present study group for these alloys should be recognized as being based on limited data, and the dangers inherent, in such, realized. Finally, it should be stressed that the purpose of the study was to evaluate the "state of the art" with regard to MIC and not to produce an exhaustive compendium of available literature.

The rest of this article will be a summary of the findings of the study group. These are presented by alloy grouping for each major element. Finally, the general conclusions of the group regarding MIC research priorities are presented.

EXAMPLES OF MICROBIOLOGICAL CORROSION

Two examples of MIC are shown in Figures 1 and 2 along with a brief description of the cases to give the reader a better idea of what will be discussed below.

General remarks regarding the characteristics of microorganisms as they relate to MIC.

1. They are small, (from less than two-tenths to several hundred micrometers (µm) in length by up to two or three µm in width), a quality which allows them to penetrate crevices, etc., easily.

2. They may be motile which aids in migrating to more favorable conditions or away from less favorable conditions, e.g., toward food sources or away from toxic materials.

3. They have specific receptors for certain chemicals which allows them to seek out higher concentrations of those substances which may represent food sources. It is very important to understand that nutrients, especially organic nutrients, are generally in short supply in most aquatic environments; but that surfaces, including metals, adsorb these materials, creating areas of relative plenty. Organisms able to seek out and establish themselves at these sites will have a distinct advantage in such environments.

4. They can withstand a wide range of temperatures, (at least -10 to 99°C) pH, (about 0 - 10.5) and oxygen concentrations (0 to almost 100% O_2 atmospheres).

5. They can grow in the form of colonies which helps to cross-feed the individuals in the colony and make the survival of at least some members of the "colony"

more likely under adverse conditions.

6. They produce enormous numbers of individuals in a short time (generation times of only 18 minutes are known), thus allowing them under favorable circumstances to "bloom" and quickly "take over" an environment.

7. The individuals can be widely and quickly dispersed by wind and water, animals, aircraft, etc. and thus the potential for some of the cells in the population to reach more favorable environments is good.

8. Many can quickly adapt to use a wide variety of different food sources. For example *Pseudomonas fluorescens* can use well over 100 different compounds as sole sources of carbon and energy, including sugars, lipids, alcohols, phenols, organic acids, etc. This give them tremendous advantages in a constantly changing environment.

9. Many can form extracellular polysaccharide materials (capsules or slime layers) which, where accumulated, are widely recognized as causing problems in heat transfer, fluid movement, and in creating sites where MIC can occur. The slimes are sticky and trap organisms and debris (food), resist the penetration of some toxicants (e.g., biocides) or other materials (corrosion inhibitors) and hold the cells between the source of the nutrients (the bulk fluid) and the surface toward which these materials are diffusing. It also means that the organisms may be able to adapt to lower concentrations of certain nutrients, since although in low concentration, they will be moving *by* (not along with) the cells and are therefore almost always present to at least a minimal level. The presence of the microbial film ultimately may lead to macrofouling (barnacles, etc) which can also affect heat transfer, fluid flow and provide corrosion sites.

10. They produce spores which are very resistant to temperature (some even resist boiling for over 1 hour), acids, alcohols, disinfectants, drying, freezing, and many other adverse conditions. These may last for hundreds of years and then germinate on finding favorable conditions.

11. They are resistant to many chemicals (antibiotics, disinfectants, etc.) by virtue of their ability to degrade them or by being impenetrable to them (due to slime, cell wall or cell membrane characteristics). It is also important to note that such resistance may be easily acquired by mutation or acquisition of a

plasmid (essentially by naturally occurring genetic exchange between cells, i.e., genetic engineering in the wild).

12. Many species produce a wide variety of organic acids e.g., formic, succinic, which may initiate or accelerate corrosion of many types of metals.

13. Some species, produce mineral acids (e.g., *Thiobacillus thiooxidans*, which produces H_2SO_4) which are extremely corrosive.

14. Several bacteria metabolize NO_3^-, sometimes used as a corrosion inhibitor. Some (e.g., *Pseudomonas* spp.) reduce it to N_2 gas which leaves the system. They will do the same to NO_2^-. Other organisms convert NO_3^- to NO_2^-. Several types of soil and water organisms (*Nitrosomonas*) oxidize NH_3 to NO_2^-, and then others (*Nitrobacter*) oxidize the NO_2^- to NO_3^-.

15. Many organisms form NH_3 from the metabolism of amino acids. This forms ammonium ion in solution which may play a role in the corrosion of certain alloys, e.g. copper alloys.

16. They produce many enzymes, some of which may be excreted outside the cell, and which act on substances outside the cells. One such, hydrogenase has been reported as important in the corrosion of the iron and steels, presumably due to depolarization of the cathodic sites.

17. Many organisms produce CO_2 and H_2 as a result of their fermentative type of metabolism. Carbon dioxide in solution becomes carbonic acid and could thereby enhance corrosion. Hydrogen could depolarize metals such as stainless steel or may even cause embrittlement.

18. Many bacteria (belonging to several genera) which normally use organic carbon compounds as carbon and energy sources can use H_2 gas as their energy source and CO_2 as their carbon source and live chemoautotrophically (without organic sources of carbon and energy). This could result in a depolarization of the cathodic sites on steels and promote corrosion. This is one of the proposed mechanisms whereby sulfate reducers (e.g., *Desulfovibrio desulfuricans*) obtain their hydrogen for sulfate reduction. It has been suggested that this could promote cathodic depolarization and corrosion of the steels in anaerobic environments.

19. Some bacteria can oxidize or reduce metals or

metallic ions directly. For example some * (*Gallionella*, *Spherotilus*) oxidize Fe^{+2} to Fe^{+3}. The ferric compounds precipitate in a sheath around the cells. These can accumulate as tubercles in pipes and plug them. Concentration cells are easily formed under these deposits with corrosion resulting. Whether the removal of the Fe^{+2} directly affects the corrosion of the metal or not is unclear. It is clear, however, that if these organisms "co-accumulate" ferric or ferrous ions with chloride or other such ions, aggressive mixtures could result. Other organisms (e.g., *Pseudomonas* spp. from oil wells and bacteria from marine sediments) have been shown to reduce ferric iron to the more soluble ferrous form. It has been suggested that this strips off the ferric compounds which normally stabilize the surface of mild steels, leaving it reactive. Corrosion is thus accelerated. Other bacteria can oxidize or reduce manganese. This along with the iron transformations listed above, is the cause of considerable tubercle formation and subsequent fouling or occluding of pipes, and probably deposit associated corrosion by species such as the sulfate-reducing bacteria. Many organisms which transform iron also transform manganese. It has been suggested that some of these can reduce iron through the mediation of catalases and hydrogen peroxide. Yet other organisms are reported to metabolize chromium, possibly aiding in the corrosion of stainless steels.

20. They form synergistic or mutualistic communities with other bacteria, fungi, algae, plants and animals. The result is that the community can accomplish things that the individuals alone cannot perform, e.g., certain fungi break down wood to organic acids and consume O_2 which provides the food and anaerobic conditions required by *Desulfovibrio* spp. These communities also change their structure, dominant species, etc. to meet changes in the external or internal environments. The community also provides protection for individuals, e.g., anaerobes from O_2 or biocide sensitive organisms from biocides, otherwise subjected to these adverse (from the point of view of the organism) factors. The community therefore increases greatly the potential of microorganisms to accomplish many feats otherwise not possible, among them the corrosion of many types of metals.

THE CASE FOR MIC OF IRON AND MILD STEELS

Corrosion under Anaerobic Conditions:

There is a large body of evidence that sulfate reducing bacteria (SRB) are an important factor in the corrosion of iron and mild steels in anaerobic conditions (see references 3, 4, 5, 7 for detailed reviews of subject). This can occur in underground installations where localized anaerobic conditions are present, e.g., under a tubercle or under a thin biofilm. There are numerous reports of such occurrences from both freshwater and saline systems, involving a number of different genera and species of SRB's.

The SRB's, as a group, are found in a great many different natural environments, including many types of soils and sediments, fresh, brackish and salt waters, natural hot springs, oil and gas wells, sulfur deposits, salt pans, guts of at least some insects and ruminants (sheep, cows, etc.) and on corroding iron. They tolerate temperatures from ≤5 to 75°C, a pH range of about 5 to 9.5, a wide range of osmotic conditions, and hydrostatic pressures of at least 1×10^5 kPa. They survive but do not grow under aerobic conditions (7).

The controversy in this area revolves around the mechanism(s) whereby the SRB's influence the corrosion of iron and mild steels. Several groups of investigators (see Miller and Tiller, 3; and Booth, 5; for example) seem to currently believe that SRB's cause (or accelerate) such corrosion by removing hydrogen from cathodic sites, resulting in cathodic depolarization.

The equations of Von Wolzogen Kuhr and Van der Vulgt (8) form the basis for this proposed mechanism. They are as follows:

$$4\ Fe^{\circ} \longrightarrow 4\ Fe^{+2} + 8\ e^{-} \qquad \text{anodic reaction} \tag{1}$$

$$8\ H_2O \longrightarrow 8\ H^{+} + 8\ OH^{-} \qquad \text{electrolytic dissociation of water} \tag{2}$$

$$8\ H^{+} + 8\ e^{-} \longrightarrow 8\ H \qquad \text{cathodic reaction} \tag{3}$$

$$SO^{-2} + 8\ H \longrightarrow S^{-2} + 4\ H_2O \qquad \text{cathodic depolarization (by SRB)} \tag{4}$$

$$Fe^{+2} + S^{-} \longrightarrow FeS \qquad \text{corrosion product} \tag{5}$$

$$3\ Fe^{+2} + 6\ OH^{-} \longrightarrow 3\ Fe(OH)_2 \qquad \text{corrosion product} \tag{6}$$

$$4\ Fe + SO_4^{-2} + 4\ H_2O \longrightarrow 3\ Fe(OH)_2 + FeS + 2OH^{-} \qquad \text{overall reaction} \tag{7}$$

Some workers (Booth et al. 9) reported that corrosion rates were increased with increasing metabolic rates and were dependent on the level of ferrous iron in the surrounding medium. The most active corrosion occurring when enough Fe^{+2} was produced to react with all the H_2S produced and prevent the formation of a protective sulfide film.

The role of the enzyme(s) hydrogenase(s) which facilitate(s) the reactions:

$$H_2 \longrightarrow 2H \longrightarrow 2H^+ + 2e^-,$$

whether from SRB's or not, is not clear, since not all strains showing hydrogenase activity cause corrosion, and the hydrogenase levels were not always correlated with the rate of corrosion (9).

Finally, Iverson (10), has reported that *Desulfovibrio desulfuricans* produces a highly corrosive metabolic product which is the major factor responsible for anaerobic corrosion of iron and mild steel by that organism.
The study group has concluded that:

i. The evidence for cathodic depolarization is quite convincing

ii. The roles of hydrogenase and ferrous ion in solution are poorly understood

iii. The extent to which the various mechanisms are operative is dependent upon environmental conditions e.g., levels of Fe^{+2}, numbers and types of organisms present.

iv. The metabolic product mechanism as proposed by Iverson (10) is intriguing but needs further documentation.

It was also concluded that there are a variety of other mechanisms whereby various microbes could cause MIC of iron and mild steel under anaerobic conditions, these include:

1. The production of corrosive metabolic products such as organic or inorganic acids.

2. The formation of ion concentration cells.

3. The production of ammonia.

4. The prevention by the very presence of the biofilm, of corrosion inhibitors from reaching the areas of active corrosion.

Corrosion under Aerobic Conditions

The case of sulfuric acid production by *Thiobacillus thiooxidans* from the oxidation of elemental sulfur or reduced sulfur compounds is well established.

The production of organic acids could have the same corrosive effects and could be produced by a wide variety of aerobic and facultatively anaerobic (live with or without oxygen) organisms. The growth of various microbes or microbial communities (e.g., tubercle forming iron bacteria and associated organisms) and/or their metabolic processes (e.g., consumption of O_2 and production of CO_2 during respiration) result in the formation of oxygen and ion concentration cells and acidification of localized environments. Indirectly, they also form good conditions for the growth of SRB's.

General methods for sampling, detecting, enumerating and testing for various microorganisms involved in MIC are discussed by Pope et al. (11).

Specifically for the mild steels and iron one would test for SRB's, by culture, microscopic (fluorescent antibody) or biochemical techniques (identification of specific unique compounds, see White, 12). Additionally one could test for the presence of H_2S by chemical means. Tubercle forming organisms (e.g., Gallionella) may be identified by microscopic or biochemical means. Acid producing organisms can be identified using routine test procedures (11).

Prevention of MIC in mild steel and iron, like that of most other alloys, revolves primarily around trying to prevent the occurrence, growth and metabolic activities of MIC causing microbes in the vicinity of the metals. Many times this involves attempts to kill or inhibit the microbes using chemical means.

It should be stressed in this regard that many such chemicals do a very good job of killing organisms in the bulk water phase, but are much less effective in penetrating slime (biofilms) and killing the organisms therein. The importance of biofilm to the MIC processes should be apparent from the foregoing discussions. Therefore the understanding of the processes whereby such film develop; their properties, especially with regard to mass transport, ion concentration, etc; and the way in which they react with biocides and anti-corrosive chemicals is essential to the prevention of MIC of many types.

Another prevention method is to cathodically protect at about -0.95V (relative to a saturated $Cu/CuSO_4$ electrode). This has apparently been quite successful.

Coatings of a variety of types can be used, although their use in many water side applications is quite limited. Also, if holidays develop in these, they can become very active corrosion sites and result in rapid penetration.

A common method for preventing anaerobic, SRB related corrosion is to surround the pipe or other such structure with materials which create an environment less permissive of MIC.

Such methods usually involve surrounding structures or pipes with gravel or chalk to provide drainage and better aeration.

- Research still needs to be done to:

  a. develop simple, reliable methods for telling whether or not the corrosion seen is MIC related.

  b. use the methods developed to assess the extent of the MIC problem in industrial and other applications.

  c. understand how biofilm form and to develop better ways of preventing biofilms from forming. Since if formation is prevented, several types of MIC can be prevented.

  d. work out the mechanisms whereby the SRB's promote corrosion of the mild steels and iron since that understanding should help lead to prevention or cures.

THE CASE FOR MIC OF STAINLESS STEELS

The study group feels that there is a good case for MIC of stainless steels which involves the ability of microbes to form films, with crevices resulting, and to modify the environment within the crevice. This may often take the form of accelerating the corrosion process.

Many organisms will as a result of consuming O_2 and producing CO_2 create O_2 concentration cells and produce carbonic acid, both corrosive to stainless steels. Many of these organisms also produce organic acids under the biofilms. These are potentially corrosive.

Bacteria which oxidizes ferrous to ferric ions and/or manganous to manganic ions (e.g., *Gallionella*, *Sphaerotilus*) probably cause the co-accumulation of chloride ions (to acheive charge neutralization) in the region e.g., a crevice. This will result in the formation of acidic ferric chloride and manganic chloride solutions which are highly corrosive to stainless steels. This MIC is often seen in the form of severe pitting (see Tatnall, 13, and Kobrin, 14). *Pseudomonas* spp. have in some cases been associated with corrosion of stainless steels, although their specific roles, beyond slime formation and general biofouling is yet to be defined. Species of *Aerobacter*, *Clostridium*, *Flavobacterium*, *Bacillus*, *Desulfovibrio* and *Desulfotomaculum* have also been reported as isolated from slime associated with corrosion deposits on stainless steel (J.G. Stoecker personal communication and Tatnall, 13).

As mentioned above it is quite certain that microbes, by forming a slime layer, produce a crevice in which regions of the normally passive film damaged by mechanical means or through halide attack go unrepaired perhaps due to the consumption of oxygen by the biofilm thus preventing the oxygen in the external environment from reaching the interior of the crevice.

Another consequence of the oxygen depletion is the growth of the SRB's in crevices resulting in corrosion as described in the section on mild steels.

Another possible corrosion mechanism is through the apparent ability of certain microbes to fix the redox potential of Fe^{+2}/Fe^{+3} and/or Mn^{+2}/Mn^{+4} at the metal surface. They may therefore polarize the surfaces of the metal to a potential at which Fe^{+3} or Mn^{+4} exists. The resultant $FeCl_3$ and $MnCl_4$ solutions are as discussed above, very aggressive to stainless steels. Methods of detection and prevention for MIC of stainless steels are much like those for mild steel (see above). Areas in which research is needed, in addition to those already described for iron and mild steels, include studies on the stability of passive films, especially in the presence of organic acids. The role of *Gallionella* in the corrosion of stainless steels, should be examined in more detail. The ability of organisms to fix electrochemical conditions seems especially intriguing and potentially very important.

THE CASE FOR MIC OF ALUMINUM AND ALUMINUM ALLOYS

The study group has concluded that accelerated attack of aluminum or its alloys was demonstrated in almost all of the test systems in which microorganisms have been tested for MIC of these materials. This has included almost all tests of the abilities of pure cultures of bacteria and fungi to cause MIC of these materials. This may indicate that aluminum is very susceptible to MIC.

The best studied cases of MIC of aluminum and its alloys are those involving fuel-water two phase systems in aluminum alloy fuel tanks. Attack can occur under aerobic or anaerobic conditions, and is usually at the bottom of the tank (water phase) and at the fuel-water interphase. Colonies or mats of the organisms can often be observed on the metal surface. In some cases volcano-like tubercles have been observed from which gas bubbles were evolved.

Organisms shown to be involved in MIC in these cases include (15, 16)

Bacteria
Pseudomonas aeruginosa
Aerobacter aerogenes
Clostridium species
Desulfovibrio desulfuricans
Micrococcus species
Sphaerotilus natans

Fungi
Penicillium luteum
Aspergillus flavus
Spicaria species
Hormodendrum hordei
Cladosporium species

Corrosion of aluminum alloys in single phase aqueous systems has not been studied nearly so exhaustively. However, Tiller and Booth (17) did show that several SRB cultures accelerated the corrosion rate by 3-100 times the rate found in sterile medium. Willingham and Quinby (18) showed a similar acceleration of weight loss for SRB's in sea water aluminum test systems. Corrosion in both these tests was of the pitting type, rather than the generalized type observed with iron in the same cultures.

Five primary mechanisms have been proposed whereby MIC of aluminum and its alloys occurs (19). Each has research results which support it; and each may play a role in the overall MIC seen in different environments. These are:

(1) Depletion of natural inhibitors
(2) Production of corrosive compounds
(3) Creation of oxygen and/or ion concentration cells
(4) Cathodic depolarization
(5) Extracellular enzyme activity and metabolization of
    alloy constituents.

Identification in the laboratory and field may initially involve the observation of volcano-like tubercles and/or pitting corrosion associated with microbial colonies or mats. Sampling, cultivation and identification of the organisms involved is accomplished by methods discussed above (see iron and mild steel section above and 11).

Prevention of MIC of aluminum and aluminum alloys should involve better handling procedures for fuels and fuel additives. In addition, as discussed above, biocidal compounds able to effectively penetrate colonies, tubercles, and slimes must be developed.

Research should concentrate on prevention and definition of the mechanisms involved.

CASE FOR MIC OF COPPER ALLOYS

The case for MIC of copper alloys is more poorly documented than for steels or aluminum. This may be, in part, a reflection of the fact that many people have believed copper ions and salts formed by copper alloy corrosion to be lethal to most, if not all, microorganisms (20). This is now known to be erroneous. For example Thiobacillus thiooxidans can withstand copper concentrations as high as 2% (21).

The study group has concluded that MIC of at least some copper alloys does occur. In most reported cases of presumed MIC of copper alloys, pitting was observed under microbial colonies or tubercles (see Grout et al., 22; Bengough and May, 23; Rogers, 24). The addition of nutrients accelerated such corrosion in one test with 2 to 10 times the normal rate being observed (24) while mixed cultures appeared to cause more severe corrosion than pure cultures (8).

Several mechanisms have been proposed to explain MIC of copper alloys.

a. Through the production of corrosive substances e.g., CO_2, H_2S, NH_3, organic or inorganic acids.

b. Through the production, by microbes, of metabolites (e.g. disulfide) which act as depolarizers or catalysts of corrosion reactions.

c. Through the microbial metabolic transformation of sulfur compounds, anaerobically, producing mercaptans and disulfides.

It is interesting to note that apparently healthy biofilms were not often associated with corrosion problems (but rather heat transfer problems) whereas when decomposition processes began(during which H_2S, NH_3, CO_2 are produced) corrosion problems were observed.

SRB's were shown to corrode copper alloys in underground pipe installations, probably through the production of H_2S. It is proposed that this ordinarily forms a protective sulfide film on the surface of the metal, which is more noble than the ordinary film found in the sulfide containing environments. However, subsequent breaks in the film would expose areas where pitting or stress corrosion cracking might occur, with the sulfide film acting as the site of the cathodic reaction.

Methods for the detection and isolation of organisms for suspected MIC of copper alloys follow the same general procedures as that outlined for MIC of iron and steels (see above). Care should be taken however to exclude copper from the initial isolation media, unless one is looking specifically for copper resistant strains of microbes.

Methods of control again revolve around water treatment and must include the development of new means of dispersing slimes and/or preventing their formation.

Water treatment to remove sulfur compounds may help, and be feasible, under certain circumstances.

Research needed again involves the development of better means of detection, and prevention, as well as defining the mechanisms whereby it occurs.

THE CASE FOR NICKEL-CHROMIUM ALLOYS AND TITANIUM

No cases could be made for MIC of these materials from the available literature. All trials reported to date indicate that they are resistant to the types of MIC familiar to the scientific and engineering communities at the present time.

GENERAL CONCLUSIONS

MIC of several different classes of alloys is well documented, whereas the specific mechanisms for most are poorly defined. The sulfate reducing bacteria seem to be involved in at least some form of MIC of most of these alloys. It is also obvious that the formation of colonies, slimes, mats and tubercles on the surface is a major fact contributing to MIC of most alloys, whether by production of oxygen and ion concentration cells, cathodic depolarization, acid production and concentration under the film, by halide accumulation, by direct metal transformation by the organisms or some other mechanism. It is also apparent that few good simple methods are available for the reliable confirmation of suspected MIC in the field. Methods for "curing" or preventing MIC, short of replacement with more resistant alloys seem largely unavailable. Data on the extent of the MIC problem relative to corrosion problems in general are largely unavailable.

The areas for research needed fall into two main categories "technological" and "scientific". The former being those practical approaches required to identify, correct, and/or prevent MIC. The latter being a description of the specific mechanisms involved and the development of new means (alloys, chemicals, etc.) to combat MIC.

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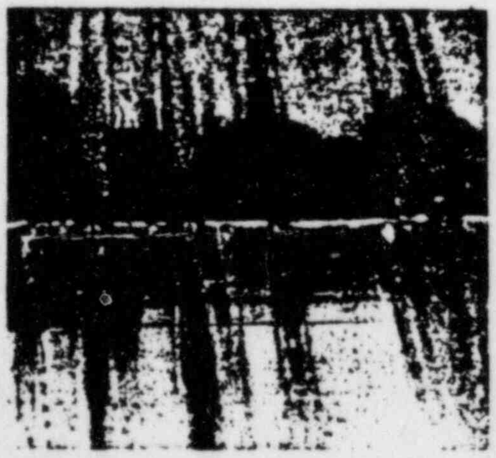

Fig. 1 - Rust colored vertical streaks and pitting along weld ear in 304 stainless steel tank.

Fig. 2 - Open "gouging" type corrosion of 304 stainless steel flange. This occurred unger slime deposits harboring Desulfovibrio sulfate reducing bacteria.

EXHIBIT 6

MTI PUBLICATION NO. 13

MICROBIOLOGICALLY INFLUENCED CORROSION: A STATE-OF-THE-ART REVIEW

by
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Rensselaer Polytechnic Institute
Troy, New York

June, 1984

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FOREWORD

In recent years substantial interest in microbiologically influenced corrosion (MIC) has arisen in the chemical process industries. This is evident in the formation of various NACE Committees, on-going programs within the Corrosion Control Engineering Joint Venture abroad and countless international symposia on the subject. While some enlightened individuals, including Frank LaQue, formerly with INCO, and Warren Iverson of NBS, have been writing about the subject for decades, most materials and corrosion engineers remained oblivious to MIC.

Many of us were shocked out of our complacency in the 1970's when we began to see a puzzling parade of corrosion failures which were not explained by "classic" corrosion mechanisms. MIC was identified as a probable cause. Case histories continue to mount but our understanding of, and ability to control, MIC lags. Funding for basic research has been minimal because some in the corrosion community still maintain that MIC does not exist or is not a significant problem. This project is an attempt to answer three questions:

(1) Is MIC a valid phenomenon?
(2) If so, is it a widespread problem in the CPI?
(3) Does adequate technology already exist to combat it?

This report answers yes, yes and no, respectively, and further emphasizes the need for additional basic work. In response, the MTI is sponsoring the development, by Dr. Pope and associates, of field and laboratory test kits to identify sulfate reducing bacteria. The method should be readily expandable to the detection of other species as well. It is expected that preliminary kits will be available for use by member companies in the near future.

Finally, we wish to mention that Dr. Arthur J. Freedman was originally chairman of the Task Group. After he left Nalco to become an independent consultant, he was retained as a consultant to the Task Group, and did, in fact, provide much of the detailed liaison work to see this through. Our thanks for his continuing assistance.

R. E. Tatnall
Chairman, Task Group No. 26
Technical Advisory Council

SUMMARY

A multidisciplinary group of scientists at Rensselaer Polytechnic Institute was asked by the Materials Technology Institute of the Chemical Process Industries, Inc., to survey the available literature on Microbiologically Influenced Corrosion (MIC) and to report their findings relative to the evidence for MIC of iron and mild steels, stainless steels, copper alloys, aluminum and aluminum alloys, nickel-chromium alloys, and titanium. Further, the group was asked to report the state of the information relating to the mechanism(s) whereby MIC of each material occurs, methods of prevention and methods of detection in the laboratory and in the field. Finally, they were asked to develop a list of priority areas for research.

The group found evidence in the literature for MIC of all alloy groups except nickel-chromium and titanium. Detailed mechanisms for MIC are generally unknown. Protection from MIC and reliable methods of detecting it are not generally available. Details and suggested research areas are discussed herein. It is suggested that development of methods for identifying corrosion as MIC and using these to ascertain the prevalence of MIC in chemical process industry environments is the technological research area requiring the most immediate attention. Scientific studies designed to elucidate the specific mechanisms of MIC should also receive a high priority.

CHAPTER 1
INTRODUCTION

The purpose of this report is to present the findings of a multidisciplinary study group constituted by the Materials Technology Institute of the Chemical Process Industries, Inc., to evaluate the state of the art with regard to microbiologically influenced corrosion (MIC). This group was asked to study the available literature and to write an interpretative document which attempted to answer the question: Is there sufficient evidence in the literature to conclude that MIC, of any kind, occurs in various metals and alloys? The metals of interest included the mild steels, stainless steels, copper alloys, aluminum and aluminum alloys, nickel alloys and titanium. In cases where the answer was in the affirmative, the available information for each group of alloys was to be evaluated with regard to the following:

(1) What are the physical and chemical conditions under which the MIC of a particular type of alloy occurs?
(2) Which type(s) of organisms are involved?
(3) What is the mechanism(s) whereby MIC occurs?
(4) What methods can be used to detect MIC in the laboratory?
(5) What methods can be used in the field to detect MIC?
(6) What methods can be used to prevent MIC?
(7) What research needs to be done?

Finally, the group was asked to evaluate the general MIC situation and make recommendations as to what research area(s) should receive the most attention in the near future in order to best advance the understanding of the prevalence, causes, detection and control of MIC.

General Remarks regarding the Literature Used

There is a good deal of literature on MIC. However much of it deals with reports of case histories, or observations incidental to the main study, with poor documentation regarding the physical, chemical and especially microbiological conditions under which it occurred. It should be noted however that:

(1) In the cases reported in the literature and dealt with in this study, this was usually not the fault of the observer since it was usually the case

that the observer(s) were not trained in environmental microbiology and corrosion, i.e., there was not an interdisciplinary approach to the case study.

(2) In many cases the techniques used in the study were adapted primarily from the area of clinical microbiology and are inadequate for MIC investigations.

(3) Some cases of MIC may have been successfully identified and dealt with by qualified persons in various industries, e.g., the water treatment industry, but reports regarding these are generally unavailable and could not therefore be dealt with herein.

A significant portion of the literature was available only in foreign languages. Much of this literature was not used directly in writing the report since it was possible to establish an adequate case for MIC of most alloys from the available English language literature. It should be noted however that there are at least two excellent reviews available, one in French(1)* and one in Swedish.(2)

Also several English language review articles and books are available which deal with MIC in a variety of ways. Reviews by Miller and Tiller,(3) Iverson(4) and Booth and Wormwell(5) and books by McCoy(6) and Postgate(7) were especially helpful.

A large percentage of the available literature deals with the area of corrosion of irons and steels by anaerobic, sulfate-reducing bacteria, and spans a long period of time in which many different techniques were used. It represents therefore not only the area about which the most is known but also the area where most controversy still persists. For those reasons this area has received the most attention herein. For other alloys, e.g., Monel and titanium, there is very little available in the open literature. Therefore the conclusions reached by the present study group for these alloys should be recognized as being based on limited data, and the dangers inherent in such, realized. Finally, it should be stressed that the purpose of the study was to evaluate the "state of the art" with regard to MIC and not to produce an exhaustive compendium of available literature.

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* References appear on page 70.

The rest of this report consists of a chapter on the ways in which microbes can influence corrosion and chapters presenting the case for MIC for each alloy group. Alloys are grouped according to major element. The general conclusions of the study group regarding MIC and needed research priorities are presented in the last chapter.

Finally, an outline of procedures for sampling where MIC is suspected is presented in the Appendix.

Examples of Microbiological Corrosion

Two examples of MIC are shown in Figures 1 and 2 along with a brief description of the cases to give the reader a better idea of what will be discussed in the following chapters.

Figure 1

Rust colored vertical streaks and pitting along weld seam in 304 stainless steel tank.

(Reprinted with permission:
G. Kobrin, Materials Performance, 15, July 1976, p 42.)

Figure 2

Open "gouging"-type corrosion of 304 stainless steel flange. This occurred under slime deposits harboring Desulfovibrio sulfate reducing bacteria.

(Reprinted with permission:
R. E. Tatnall, Materials Performance, 20, September 1981, p 34.)

CHAPTER 2
CORROSION: EXPLANATIONS INVOLVING MICROORGANISMS

Introduction

The intent of writing this chapter is to present a brief description of microorganisms and the way in which their structure and function may relate to the corrosion of metals. Details of mechanisms or proposed mechanisms for specific organisms or materials will be found, for the most part, in various research reports published elsewhere.

Microorganisms are generally thought of as those organisms which are too small to be clearly perceived using only the unaided human eye. The major divisions of this microbial world are protists and monera. The protists are the algae, fungi and protozoa. These are all eukaryotic (have true nuclei) and have certain other characteristics in common. The monera are the bacteria and blue-green bacteria (formerly classified as blue-green algae) both of which are procaryotic (have no true nucleus) and share certain other common properties.

The Algae

The algae are eukaryotic, photosynthetic organisms, relatively large, sometimes motile and usually colored. They include the green and yellow algae and the dinoflagellates and diatoms all of which are unicellular, although many form filaments or colonies. The algae also include the red and brown algae which are plant-like (kelp, etc.) and do not concern us much in the present connection.

The algae, as a group, can tolerate conditions of very high to very low light intensity, some even growing slowly (and nonphotosynthetically) in the dark. They can grow over a pH range of about 5.5 to 9.0, although rare strains may tolerate a wider range. The temperature range for survival is from much less than 0° C (32° F) to somewhat over 40° C (104° F) while the range for good growth is from about 10° to 35° C (50° to 95° F). Many marine strains are of course forced to grow only at temperatures less than 5° to 10° C (41° to 50° F) since they occur in permanently cold water, e.g., arctic. Since they produce oxygen when exposed to light, algal cells are usually in a relatively oxygenated environment. They do not, however, like environments where both high O_2 and low CO_2 levels are found (such as in algal blooms) and may die under these conditions. They tolerate a wide range of salinities, from distilled water to saturated brine.

The algae generally have simple nutritional requirements; light, water, air and a few inorganic nutrients of which phosphorus for fresh water and nitrogen for marine organisms are usually limiting to growth. Where the limiting nutrient is supplied in excess, rapid growth of large amounts of algae (a "bloom") may result. Inorganic trace elements, Fe, Mn, Mg, etc., are required in very small amounts. Some strains also require vitamins or other organic factors in trace amounts. The algae (along with the blue-green bacteria, see below) are widely recognized as agents which can cause severe fouling problems (slime, reduction in heat-transfer rate, plugging of tubes, etc.). These fouling problems whether caused by algae, fungi or bacteria can also be the source of many problems related to corrosion, since they can lead to the formation of concentration cells involving O_2, various ions, etc., due to the fact that the diffusion of these materials through a biofilm will usually be at a different rate than to the bare surface of the metal itself. Alternatively, the biofilm community may actively concentrate such materials within itself, transport them through the biofilm to the surface or exclude them from the film altogether. Each of these could theoretically lead to the rapid development of concentration cells in and/or around the biofilm. Also important is the fact that these films can prevent the diffusion of certain biocides and of corrosion inhibitors to the surface of the metal.

Algae must be considered as important to MIC in yet another general way; that is, they along with higher plants are primary producers of the food necessary to support the growth of bacteria and fungi in the biosphere. Therefore if the system under consideration is lighted and/or downstream of algae, or points where manufacturing plant products are being discharged (pulp mills, etc.), this will affect the ability of bacteria, etc., to cause MIC at the site of interest. This is of course an indirect, but nevertheless important role for algae, and indeed plants in general, in MIC.

Specific metabolic activities by which algae might cause MIC might include the production of gaseous oxygen and the production of corrosive chemicals.

In the light, algae, like the blue-green bacteria and higher plants, produce O_2 during photosynthesis. The O_2 so produced can accumulate within the biofilm to quite high concentrations and result in a much larger difference in O_2 concentrations between these sites and adjacent sites not covered by algae. This O_2 could also depolarize the corrosion reaction, leading to increased corrosion rates. It should be noted that this condition will reverse itself at night since algae consume O_2 (respire) in the dark.

Many algae also excrete organic acids which can accumulate to relatively high concentrations in films and cause corrosion by creating localized areas of low pH, thereby removing the passivating or protecting layer of corrosion products.

The Fungi (yeasts and molds)

The yeasts are unicellular, generally reproduce by budding (although some divide by fission) and are relatively large. They appear to be of minimal importance in the context of corrosion of metals, as they are rarely found in large numbers in most aquatic systems. Their roles in the deterioration of wooden vat materials, etc., should be considered elsewhere.

The molds are a very diverse group of microbes which may be filamentous (e.g., bread molds, Figure 3) or colonial. They are non-photosynthetic and require O_2 and organic compounds for growth. They are nutritionally diverse, using a wide variety of compounds including wood as food sources. They produce an enormous variety of end products from alcohols and organic acids to antibiotics. The pH range for growth is about 2 to 8 with the optimum around 6 for most species. Temperature ranges for growth are from about 0° to 60° C (32° to 140° F), although most only grow in the range of about 10° to 35° C (50° to 95° F). The molds reproduce by cellular division, fragmentation (falling apart into individual cells which can start new colonies), asexual spore formation and many by sexual means. The spores are generally very tolerant of desiccation and

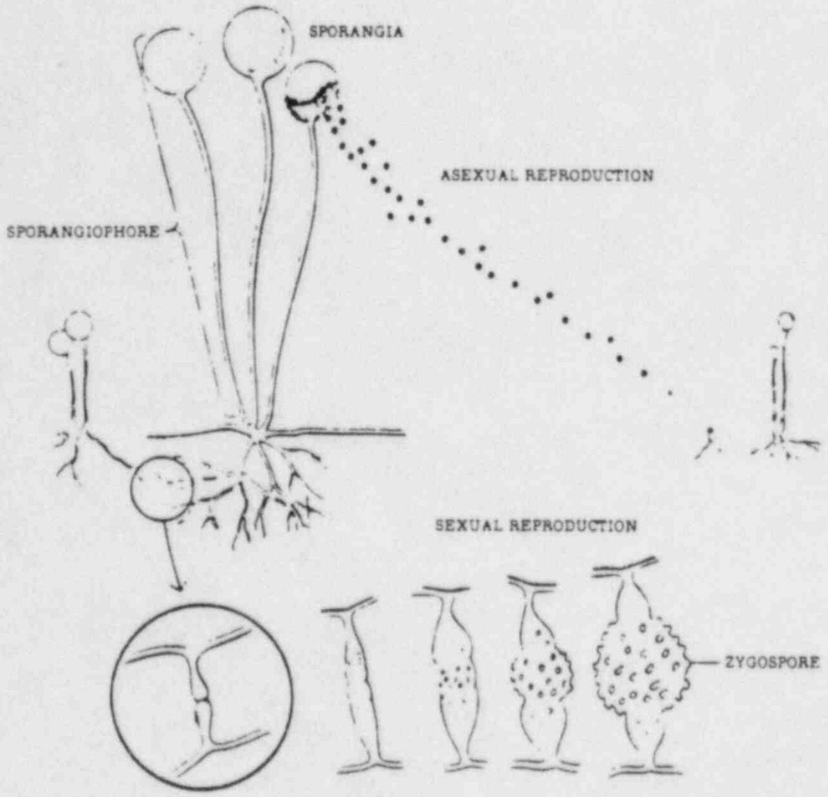

Figure 3

Asexual and sexual reproduction in the common black bread mold Rhizopus. The mold consists of branched hyphae, including rhizoids, which anchor the mycelium, stolons which run above ground; and sporangiophores. At maturity, the fragile wall of the sporangium disintegrates, releasing the asexual spores, which are carried away by air currents. Under suitable conditions of warmth and moisture, the spores germinate, giving rise to new masses of hyphae. Sexual reproduction occurs when two hyphae from different mating strains come together, forming gametangia, which fuse to form a thick-walled, resistant zygote, commonly called a zygospore. After a period of dormancy, the zygote undergoes meiosis and germinates, producing a new sporangium.

(Reprinted with permission:
Helena Curtis, Biology, 2nd Ed., Worth Publisher, Inc.,
New York, NY, 1975, p 322.)

somewhat more resistant to certain chemicals than are the vegetative cells. They may remain viable but dormant for many years until favorable conditions are encountered. They can also be transported in water, wind, etc., for long distances.

Fungi are important as they can form large masses of filaments which may trap other material. This can quickly cause a worsening of fouling problems with the resultant effect on corrosion that fouling may entail (see algae, above).

As with the algae, fungi produce many potentially aggressive metabolic by-products, especially the organic acids (established as a cause of corrosion of aluminum aircraft fuel tanks). Their role in the establishment of O_2 concentration cells would however be related to their consumption of O_2 rather than its production (as would be the case with the algae). They also break down complex polymers, like those found in wood with the concomitant release of various by-products which may serve as nutrients for organisms more directly involved in corrosion processes. Thus they are very important in systems containing wood or wood products.

The Protozoans

These are eukaryotic and may be amoeboid, flagellated or ciliated. There have been no reports of the involvement of protozoa in the corrosion of metals. As predators on bacteria and algae, they may have a potential role to play in preventing corrosion caused by these organisms. It is of interest to note that some pathogenic species have been found in thermal effluents from heat exchangers.

The Bacteria

A generalized diagram of a bacterial cell is shown in Figure 4. They may be spherical, rod shaped, filamentous, helical or colonial. Most reproduce by dividing the cell in half, a process known as binary fission. They are generally small, usually about 0.2 to 5 micrometers (μm) wide by 1 to 10 μm in length, although some filaments may be several hundred μm in length. The cells are generally colorless when viewed as individuals (except for the blue-green bacteria, the green and purple sulfur bacteria and the purple non-sulfur bacteria which are red to purple in color)

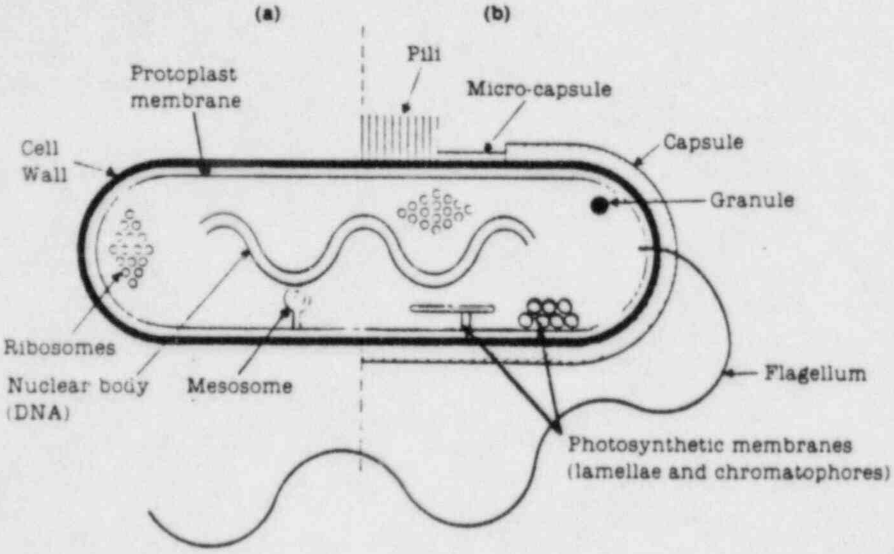

Figure 4

Cross section of a generalized bacterial cell showing (a) essential and (b) inessential structures.

(Reprinted with permission: J. Mandelstam and K. McQuillen, Biochemistry of Bacterial Growth, 2nd Ed., Halsted Press, New York, NY, 1973, p 64.)

Bacteria may live at relatively cold temperatures [the psychrophiles, from less than 0° to about 25° C (32° to 74° F)], at moderate temperatures [the mesophiles, from about 15° to 45° C (59° to 113° F)], at relatively high temperatures [the thermophiles, from about 45° to 75° C (113° to 167° F)] or at extremely high temperatures [the extreme thermophiles, from about 75° to 99+ ° C (167° to 210+ ° F)].

Bacteria, as a group, can grow over the pH range from about 0 to 12. They can be obligately aerobic (require O_2 to survive and grow), microaerophilic (require low O_2 concentrations), facultative anaerobes (prefer aerobic conditions but will live under anaerobic conditions), or obligate anaerobes (will grow only under conditions where O_2 is absent). It should be emphasized that some of the latter organisms may survive aerobic conditions for quite a while. Also note that, for a microorganism, anaerobic conditions may be quite easily found in what are thought to be generally aerobic environments. Often these anaerobic microenvironments are in, or under, films, in particles of debris, inside crevices, etc.

As a group, the bacteria may use almost any available organic carbon molecules, from simple alcohols or sugars to phenols to wood or various other complex polymers as food (heterotrophs) or they may fix CO_2 (autotrophs) as do plants. The heterotrophs may use a wide variety of (almost any) organic molecules as energy sources. The autotrophs may oxidize reduced inorganic compounds, elements or ions (e.g., NH_3 or NO_2^-, CH_4, H_2, S^0, Fe^{+2}, Mn^{+2}, etc.), most as sources of energy. A few may use light as a source of energy. These organisms may use organic molecules for carbon (food) sources (the photoheterotrophs) or CO_2 as a carbon source (the photoautotrophic blue-green bacteria). The nutritional requirements of these organisms, therefore range from very simple (blue-green bacteria) to very complex (such as the obligate parasites which require a living host of a specific type). Most fall in between these extremes and require a limited number of organic molecules, moderate temperatures, moist environments and near neutral pH.

The bacteria have many unique properties, some of which may be important in the corrosion process:

(1) They are small, (from less than two-tenths to several hundred μm in length by up to two or three μm in width), a quality which allows them to penetrate crevices, etc., easily.

(2) They may be motile which aids in migrating to more favorable conditions or away from less favorable conditions, e.g., toward food sources or away from toxic materials.

(3) They have specific receptors for certain chemicals which allows them to seek out higher concentrations of those substances which may represent food sources. It is very important to understand that nutrients, especially organic nutrients, are generally in short supply in most aquatic environments; but that surfaces, including metals, adsorb these materials, creating areas of relative plenty. Organisms able to seek out and establish themselves at these sites will have a distinct advantage in such environments.

(4) They can withstand a wide range of temperatures [at least -10° to 99° C (14° to 210° F)], pH (about 0 - 10.5), and oxygen concentrations (0 to almost 100% O_2 atmospheres).

(5) They may utilize O_2, NO_3, CO_2, SO_4 and perhaps other compounds as the final electron acceptor in their respiratory metabolism. The reaction products, H_2O, NO_2^-, N_2, CH_4, H_2S can be important in many ways. Especially important here is H_2S since it is known to be involved in the corrosion of many metals (see following chapters).

(6) They can grow in the form of cell aggregates ("colonies") which helps to cross-feed the individuals in the colony and make the survival of at least some members of the "colony" more likely under adverse conditions.

(7) They produce enormous numbers of individuals in a short time (generation times of only 18 minutes are known), thus allowing them under favorable circumstances to "bloom" and quickly "take over" an environment.

(8). The individuals can be widely and quickly dispersed by wind, water, animals, aircraft, etc., and thus the potential for some of the cells in the population to reach more favorable environments is good.

(9) Many can quickly adapt to use a wide variety of different food sources. For example, Pseudomonas fluorescens can use well over 100 different compounds as sole sources of carbon and energy, including sugars, lipids, alcohols, phenols, organic acids, etc. This capability gives them tremendous advantages in a constantly changing environment.

(10) Many can form extracellular polysaccharide materials (capsules or slime layers) which, where accumulated, are widely recognized as causing problems in heat transfer, fluid movement and in creating sites where MIC can occur. The slimes are sticky and trap organisms and debris (food), resist the penetration of some toxicants (e.g., biocides) or other materials (corrosion inhibitors) and hold the cells between the source of the nutrients (the bulk fluid) and the surface toward which these materials are diffusing. It also means that the organisms may be able to adapt to lower concentrations of certain nutrients, since although in low concentrations, they will be moving by (not along with) the cells and are therefore almost always present to at least a minimal level. The presence of the microbial film ultimately may lead to macrofouling (barnacles, etc.) which can also affect heat transfer, fluid flow and provide corrosion sites.

(11) They produce spores which are resistant to temperature (some even resist boiling for over 1 hour), acids, alcohols, disinfectants, drying, freezing and many other adverse conditions. The spores may last for hundreds of years and then germinate on finding favorable conditions.

(12) They are resistant to many chemicals (antibiotics, disinfectants, etc.) by virtue of their ability to degrade them or by being inpenetrable to them (due to slime, cell-wall or cell-membrane characteristics). It is also important to note that such resistance may be easily acquired by mutation or acquisition of a plasmid (essentially by naturally-occurring genetic exchange between cells, i.e., genetic engineering in the wild).

(13) Many species produce a wide variety of organic acids e.g., formic, succinic, which may initiate or accelerate corrosion of many types of metals.

(14) Some species produce mineral acids (e.g., *Thiobacillus thiooxidans*, which produces H_2SO_4) which are extremely corrosive.

(15) Several bacteria metabolize NO_3^-, sometimes used as a corrosion inhibitor. Some (e.g., *Pseudomonas* spp.) reduce it to N_2 gas which leaves the system. They will do the same to NO_2^-. Other organisms convert NO_3^- to NO_2^-. Several types of soil and water organisms (*Nitrosomonas*) oxidize NH_3 to NO_2^-, and then others (*Nitrobacter*) oxidize the NO_2^- to NO_3^-.

(16) Many organisms form NH_3 from the metabolism of amino acids. NH_3 converts to ammonium ion in aqueous solution and may play a role in the corrosion of certain alloys, e.g., copper alloys.

(17) They produce many enzymes, some of which may be excreted by the cell, and which then act on substances outside the cells. One such enzyme, hydrogenase, has been reported as important in the corrosion of iron and steels, presumably due to depolarization of the cathodic sites.

(18) Many organisms produce CO_2 and H_2 as a result of their fermentative type of metabolism. Carbon dioxide in solution becomes carbonic acid and could thereby enhance corrosion.

(19) Many bacteria (belonging to several genera) which normally use organic carbon compounds as carbon and energy sources can use H_2 gas as their energy source and CO_2 as their carbon source and live chemoautotrophically (without organic sources of carbon and energy). By living in this manner, they could cause depolarization of the cathodic sites on steels and promote corrosion. This is one of the proposed mechanisms whereby sulfate reducers (e.g., *Desulfovibrio desulfuricans*, see Figure 5) obtain their hydrogen for sulfate reduction. It has been suggested that, in so doing, they could promote cathodic depolarization and corrosion of steels in anaerobic environments.

(6000X)

Figure 5

Electron micrograph of Benghazi strain of Desulfovibrio af.
Gold-shadow-cast.

(Reprinted with permission: Marcel Dekker, Inc.
H. L. Ehrlich, Geomicrobiology, Marcel Dekker, Inc.,
New York, NY, 1981, p 263.)

(20) Some bacteria can oxidize or reduce metals or metallic ions directly. For example some species (Gallionella, Figure 6 and Sphaerotilus, Figure 7) oxidize Fe^{+2} to Fe^{+3}. These ferric compounds then precipitate in a sheath around the cells, and can accumulate as tubercles in pipes and plug them. Concentration cells are easily formed under such deposits with corrosion resulting. Whether the removal of the Fe^{+2} directly affects the corrosion of the metal or not is unclear. Other organisms (e.g., Pseudomonas spp. from oil wells and bacteria from marine sediments) have been shown to reduce ferric iron to the more soluble ferrous form. It has been suggested that this bacterial action strips off the ferric compounds which normally stabilize the surface of mild steels, leaving it reactive. Corrosion is thus accelerated. Other bacteria can oxidize or reduce manganese which, along with the iron transformations listed above, is the cause of considerable tubercle formation and subsequent fouling or occluding of pipes, and probably deposit-associated corrosion by species such as the sulfate-reducing bacteria. Many organisms which transform iron also transform manganese. It has been suggested that some of these organisms can reduce iron through the mediation of hydrogen peroxide and catalases (enzymes capable of breaking down hydrogen peroxide into oxygen and water). Yet other organisms are reported to mediate changes in the oxidation state of chromium, possibly aiding in the corrosion of stainless steels.

(21) They form synergistic or mutualistic communities with other bacteria, fungi, algae, plants and animals. Such communities can accomplish things that the individuals alone cannot perform, e.g., certain fungi break down wood to organic acids and consume O_2 which provides the food and anaerobic conditions required by Desulfovibrio spp. These communities also change their structure, dominant species, etc., to meet changes in the external or internal environments. The community also provides protection for individuals, (e.g., anaerobes

(1280X)

Figure 6

Gallionella. Note the small cell attached laterally at the tip of each of the twisted stalks.

(Reprinted with permission: Marcel Dekker, Inc.
H. L. Ehrlich, Geomicrobiology, Marcel Dekker, Inc., New York, NY, 1981, p 180.)

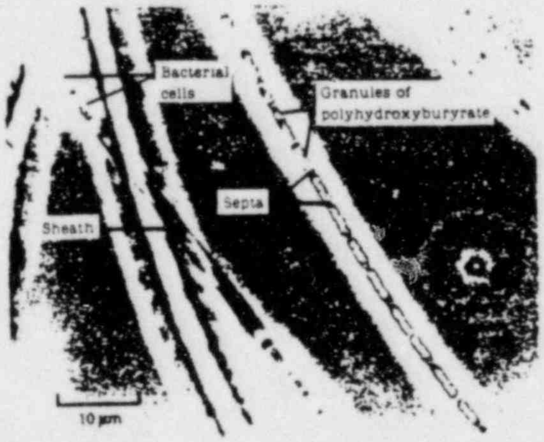

Figure 7

<u>Sphaerotilus</u> species, a sheathed bacterium.
(Phase contrast photomicrograph courtesy:
J. T. Staley and J. P. Dalmasso.)

from oxygen or biocide-sensitive organisms from biocides) which would otherwise be subjected to adverse (from the point of view of the organism) factors. The community therefore increases greatly the potential of microorganisms to accomplish many feats otherwise not possible, among them the corrosion of many types of metals.

It should be emphasized here that the community is a primary reason why pure-culture-laboratory tests often do not adequately reflect the real world situation. The results of such laboratory screening types of tests should not be extrapolated to field conditions without adequate tests and follow-up in real world operating situations. Ideally, more laboratories will begin to consider films, communities, debris and MIC, etc., when designing test systems for biocides or corrosion inhibitors. It should be noted that there are many people operating in industrial settings (e.g., the water treatment industry) who are undoubtedly aware of the above problems and apparently deal with them effectively. Reports of their activities are however not generally available.

CHAPTER 3
THE CASE FOR MICROBIOLOGICALLY INFLUENCED CORROSION OF IRON AND STEEL

Introduction

The role of microorganisms in corrosion of iron and steel has been the subject of numerous articles and a number of excellent review articles on this topic are currently available, including those by Iverson(4) and Miller and Tiller.(3) In addition there are a number of books available which have much useful information relating to the subject of corrosion in general and to the question of the role of microorganisms in mineral cycling and in the corrosion of metals. These include books by McCoy,(6) Neilands,(8) Postgate,(7) Fenchel and Blackburn,(9) Ehrlich(10) and Weinberg.(11)

Recognition that microbes play a role in the corrosion of metals buried in the ground or immersed in water occurred as early as the late 19th century. Gaines(12) early in the 20th century, was one of the first to suggest that iron bacteria and sulfur bacteria might be responsible for the corrosion of ferrous metals buried in soil. Von Wolzogen Kuhr and Van der Vulgt(13) were among the first to attempt to provide a mechanism to explain the corrosion of metals in soils due to the action of sulfate-reducing bacteria. The concept of MIC of iron and steel is intimately linked with the development of an understanding of sulfate reducing bacteria, their physiology, biochemistry and ecology. This is not to imply that the sulfate-reducing bacteria are the only bacteria involved in MIC of iron and steel; however, it has certainly been the most widely observed instance of MIC in these materials and is the one which has received the most detailed attention in terms of the number of cases observed in the field, the number of field trials attempted to define conditions under which it occurred, and the number of laboratory experiments which have been done to determine the mechanisms whereby it occurs.

There has been a recent upsurge in the number of reports of various types of MIC involving iron and steel, and in the level of interest in the topic shown by members of especially the chemical process, petroleum and water treatment industries.(14-18)

The remainder of this chapter is an attempt to briefly describe the current state of the information on microbiological involvement in the corrosion of iron and steel, excluding the stainless steels which are covered in a separate chapter.

Microorganisms involved in Microbiologically Influenced Corrosion of Mild Steel

The best known group of organisms involved in the corrosion of iron and steel are the sulfate-reducing bacteria. These fall currently into three genera (a genus may contain one or more species of organisms which are very much alike) Desulfovibrio, Desulfotomaculum and Desulfomonas. The species of organisms in the genus Desulfovibrio are the best known, probably because they are the easiest to isolate, are mesophilic [grow at temperatures of about 10° to 40° C (50° to 104° F)] and are perhaps the most wide spread. The organisms in this genus can be terrestrial, fresh water or marine (require sodium) and do not form spores. They are, like all of the other sulfate reducing bacteria, anaerobic. Earlier names for this genus were Spirillum, Sporovibrio, Microspira and Vibrio. The organism about which most is known is Desulfovibrio desulfuricans.

Desulfotomaculum strains can be mesophilic or thermophilic (have the ability to grow at elevated temperatures). The best known of these is probably Desulfotomaculum nigrificans, an organism which is reported in much of the literature as Clostridium nigrifircans. All of the Desulfotomaculum species form spores, which are dormant forms of the organisms resistant to many harsh environments. The Desulfomonas appear to be quite similar to the Desulfovibrio. An excellent source for more information on the sulfate-reducing bacteria is the book by Postgate.(7)

The other microorganisms which are mentioned most commonly with regard to their role in the corrosion of iron and steel are the bacteria in the genus Thiobacillus. These organisms have the ability to oxidize reduced forms of sulfur with the subsequent production of sulfuric acid. The mechanism(s) whereby this acid produces corrosion is well established in the general corrosion literature and involves the destabilization of otherwise protective corrosion-product films.

The case for corrosion of iron and steel by the bacterium Thiobacillus ferrooxidans is straightforward. This organism oxidizes ferrous iron to ferric iron to obtain energy.

The other major group of organisms which have been reported as important in the corrosion of iron or steel are the so-called iron bacteria. This group includes the organisms in the genera Gallionella, Leptothrix, Sphaerotilus, Crenothrix, Clonothrix and Lieskeella.(10) Those most commonly reported in connection with the formation of raised "growths" on the surface in iron water pipes and water mains, and as possible agents of MIC in various industrial situations have been Sphaerotilus and Gallionella. The role of these microorganisms in MIC seems to involve their presence in (their formation of?) deposits or tubercles, under which various types of corrosion can occur. These organisms and mechanisms are discussed in more detail below.

Recently another group of organisms has been identified as important in the corrosion of mild steel. These are the Pseudomonas or Pseudomonas-like organisms which have been reported as having the ability to reduce ferric to ferrous iron.(19-22) These organisms have been found in various freshwater and marine environments and appear, in many cases, to be the organisms which ordinarily use oxygen or nitrate as final acceptors of electrons in their respiratory metabolism, but which can in the absence of these substances turn to ferric iron as an alternative electron acceptor for respiratory activity. It has been reported(19-21) that a ferric-iron-reducing Pseudomonas strain isolated from crude oil has the ability to depolarize anodic sites and also to remove a protective amorphous coating from the surface of mild steel, thereby exposing bare metal to the environment and increasing corrosion rates.

There have also been several reports of the importance of other aerobic and facultatively anaerobic organisms (like to grow in aerated conditions but will grow under anaerobic conditions) in the corrosion of ferrous metals. Several of these, including Escherichia coli, Bacillus megaterium, Serratia marcescens and Salmonella typhimurium have all been reported to promote the oxidation of iron.(23) It has been suggested by some investigators that this is due to the ability of these organisms to produce organic acids as metabolic end-products. Other investigators[24] report that the enzyme, hydrogenase, possessed by some of these organisms is responsible, perhaps by removal of hydrogen, thus causing depolarization of cathodic sites. This is discussed further below.

Physical and Chemical Conditions under which Microbiologically Influenced Corrosion of Iron and Steel Occurs

The temperature range within which MIC can occur in iron and steel is broad. The temperature can vary from approximately freezing (at such low temperatures most metabolic processes, e.g., organic acid production, can occur although quite slowly) to 45° to 75° C (113° to 167° F) at which thermophilic organisms, such as Desulfotomaculum, can be active.

The availability of oxygen determines in large part the kinds of metabolic activities which can be performed. In strictly anaerobic conditions such reactions as sulfate reduction, nitrate reduction, ferric iron reduction and production of organic acids by a variety of microorganisms will occur quite readily. In aerobic environments the production of sulfuric acid by Thiobacillus and the oxidation of ferrous iron will occur. Some forms of MIC will therefore probably occur over a wide range of O_2 concentrations, i.e., zero to almost saturation.

The pH range in which MIC of these materials can occur is also very broad. It ranges from approximately zero, in the cases where acid tolerant organisms like the Thiobacilli are involved, to neutral or slightly alkaline conditions, where a great variety of organisms can grow, up to about pH 10.5 where some organisms (e.g., Nitrobacter) can grow.

The various bacteria which are potentially involved in the corrosion of iron and steel can tolerate a wide variety of other conditions. For example, salinities may range from approximately zero, i.e., distilled water, to saturated brines. Some microorganisms can tolerate high concentrations of materials, e.g., biocides and copper ions, which are very toxic to a great many other microorganisms. These microorganisms will therefore represent possibilities for corrosion of iron and steel under a variety of extreme conditions. For a more general discussion of the mechanisms of resistance in microorganisms, see the introductory chapter on microorganisms and also references 25 and 26.

It should also be remembered (see Chapter 2, Corrosion: Explanations Involving Microorganisms) that bacteria as a group use a great variety of organic compounds (e.g., cellulose, alcohols, acids, etc.) as carbon and energy sources, while others use light or reduced inorganic compounds (Fe^{+2}, NO_2^-, CH_4) as energy sources, with CO_2 or organic compounds serving as the carbon source.

Again, it should be noted that many cases of MIC are probably associated with biofouling material (biofilms, slime). Fluid flow patterns are therefore important considerations since, for example, where fluid velocity prevents the formation of a film of the required thickness to achieve MIC, no MIC of that (those) type(s) will be seen. In other cases where the film is "protecting" the surface, removal of a portion may expose active sites.

Mechanisms involved in Microbiologically Influenced Corrosion of Iron and Mild Steel

Corrosion under Anaerobic Conditions. Certainly the best documented case for MIC is that for mild steel and iron under anaerobic conditions by sulfate reducing bacteria (SRB). There is an enormous amount of literature on this subject and the reader is encouraged to read much more of the detail than can be presented here, e.g., the reviews by Iverson(4) and Miller and Tiller(3) and for an understanding of the ecology, physiology and biochemistry of the SRB, a relatively recent work by Postgate.(7)

There seems to be little doubt from the numbers of case histories presented and the literature reporting the corrosion of pipes in underground locations, that the SRB are involved in corrosion processes. The major point of dispute is the specific mechanism(s) whereby this corrosion occurs. The main items of contention seem to revolve around the following:

(1) The failure of laboratory experiments to reproduce the rates of corrosion observed in the field;

(2) The role of hydrogenases (enzymes capable of performing the following reactions, $H_2 = 2H = 2H^+ + 2e^-$), in the process;

(3) The role of SRB and other organisms in cathodic depolarization;

(4) The influence of iron concentrations in the solution on the corrosion rate; and

(5) The role of the organisms in the formation and production of a protective sulfide film.

The following equations are those originally proposed by Von Wolzogen Kuhr and Van der Vulgt(13) to explain the mechanism of cathodic depolarization:

$4\ Fe - 4\ Fe^{+2} + 8\ e^-$	anodic reaction	(1)
$8\ H_2O - 8\ H^+ + 8\ OH^-$	dissociaton of water	(2)
$8\ H^+ + 8\ e^- - 8\ H$	cathodic reaction	(3)
$SO_4^{-2} + 8\ H - S^{-2} + 4\ H_2O$	cathodic depolarization (by SRB)	(4)
$Fe^{+2} + S^{-2} - FeS$	corrosion product	(5)
$3\ Fe^{+2} + 6\ OH^- - 3\ Fe(OH)_2$	corrosion product	(6)
$4\ Fe + SO_4^{-2} + 4\ H_2O -$ $3\ Fe(OH)_2 + FeS + 2\ OH^-$	overall reaction	(7)

Mara and Williams(27) reported a direct linear relationship between weight loss by cast iron and five different steels during corrosion by hydrogenase-positive (produce the enzyme hydrogenase) SRB's, and the carbon content of the alloys. Further the rate of weight loss was reported as increasing in iron-poor media. The latter result suggested to the authors that the corrosion rate would be proportional to the number of available cathodic sites on the surface of the metal.

Ashton et al.,(28) using the facultatively anaerobic Escherichia coli, found that corrosion of six different iron-carbon alloys in anaerobic environments was attributable to the activities of the bacteria, but not related to the amount of nitrate reduced nor to the carbon content of the alloys. They did report that the corrosion rate was reduced by the formation of a protective Fe_3O_4 film.

King et al.(29) reported that a protective FeS (Mackinawite, FeS_{1-x}) film formed on ferrous metals from the reactions of H_2S produced by SRB's with the iron. The rate of breakdown of the film was reported to be proportional to the concentration of iron in solution, as was the rate of corrosion after film breakdown. Film breakdown was associated with the conversion of FeS_{1-x} (Mackinawite) to hexagonal Fe_3S_4 (Symthite) and $Fe_{1-x}S$ (Pyrrhotite) and not to cubic Fe_3S_4 (Greigite).

Booth et al.(30) showed that the corrosion rates of mild steels were increased with increased metabolic rates of the SRB's in the test system. Further, the corrosion rates were dependent on the nature of the sulfide film on the surface, most rapid corrosion occurring when sufficient ferrous iron was present in the medium to react with all of the H_2S produced by the SRB's and thus to inhibit the formation of the protective iron sulfide film on the metal surface. Finally, they reported no good correlation between the hydrogenase activity of a given strain and the rates of corrosion. This result is in contrast with that reported by Booth and Wormwell,(24) who found a linear relationship between the rate of corrosion and hydrogenase activity of the strains employed.

Salvarezza and Videla(31) reported that introduction of steels into sea water containing SRB's resulted in a change in pitting and corrosion potentials to more active values, but that similar results could be obtained with artificial sea water with added sulfide ions or SRB's. They also concluded that the breakdown in passivity was due directly to the metabolic production of H_2S by these SRB's and that it occurred most easily under anaerobic conditions. Gaylarde and Johnson,(32) on the other hand, reported that the direct adsorption of SRB's on metal surfaces allowed the production and maintenance of thicker, sulfide-rich precipitates than that which formed when the medium was also allowed to interact with the metal surface. The deposits associated with SRB's were hard to remove, in contrast to the "fine" deposits found in the absence of SRB-metal surface interactions. They suggested that the role of H_2S itself is minimal and that it is either cathodic depolarization or the production of high molecular-weight metabolic products which may be responsible.

Miller and Tiller in their 1970 review article(3) state that "the available evidence suggests that factors controlling anaerobic microbiological corrosion are: (a) the utilization of hydrogen by sulfate reducing bacteria (and possibly by other microbes that possess a suitable enzyme system); (b) cathodic depolarization by precipitated ferrous sulfide; (c) the prevention of formation of protective sulfide films in the presence of excess ferrous ions; (d) anodic stimulation by the sulfide ions; and/or perhaps (e) the formation of local concentration cells." They further stated that (a) and (b) above were most important and were perhaps interrelated to some extent, in a way that was not fully understood. Postgate, in his 1979 book on the SRB's,(7) has concluded that anaerobic corrosion of cast iron is brought about by SRB's and has three main characteristics:

(1) It is restricted to anaerobic environments such as clay or waterlogged soils.

(2) The corroded metal tends to be pitted rather than evenly corroded, indicating that corrosion is not self-stifling.

(3) If the alloy is cast iron, it should—at the point of corrosion—show a graphitic structure, i.e., the metallic iron at the site is entirely removed but the graphite skeleton of the pipe often retains its original form.

Postgate further concludes that:

(1) The mechanism of anaerobic corrosion by sulfate-reducing bacteria was once controversial but is now largely understood and agreed upon.

(2) Hydrogen sulfide is in itself corrosive.

(3) The corrosion of metals by sulfide-producing bacteria other than SRB's has been recorded.

(4) The distinctive feature of corrosion by Desulfovibrio and Desulfotomaculum is cathodic depolarization.

He further states that "in underground corrosion the sulfate-reducing bacteria can remove the hydrogen film through their enzyme hydrogenase with the formation of both iron hydroxides and iron sulfide in the corrosion product."

There is considerable evidence that corrosion of ferrous metals occurs by mechanisms in addition to cathodic depolarization. Postgate(7) mentions several of these. They can be summarized briefly as: direct attack on iron by H_2S, with or without the formation of oxygen concentration or ion concentration cells, due to the presence of bacteria in or under tubercles or by actually forming the tubercles themselves. In addition, solid ferrous sulfide has been reported as being corrosive to iron and steel.(33) The extent to which a particular corrosive reaction or set of reactions dominates in a given location or environment depends on a variety of factors. These will include:

(1) The nature of the alloy surface;

(2) The presence or absence of dissolved iron in the medium, or the presence of organic matter capable of chelating iron or other metals in the surrounding water;

(3) The nature of the strain(s) of bacteria itself, since some tend to form a film on the metal and some do not;

(4) Whether the iron sulfide itself forms a film which can under some circumstances be protective; and

(5) Whether other ions such as sodium, chloride, nitrate, nitrite or phosphate are present.

Iverson, in a report[4] and also in a talk at a Canadian Institute of Mining and Metallurgy meeting in Toronto,[34] presented evidence that it is the formation of a highly corrosive (and as yet unidentified) metabolic product by Desulfovibrio desulfuricans which is the actual cause of corrosion of iron and steel in anaerobic conditions, and further that the cathodic depolarization theory for such corrosion could not account for the observed corrosion rates.

Therefore it can be seen that there are a large number of organisms and mechanisms involved (or possibly involved) in the corrosion of steel and iron under anaerobic conditions. The general mechanisms whereby corrosion involving the production of organic acids, mineral acids, ammonia and so forth occurs, as well as mechanisms involving the production of oxygen or ion concentration cells are not discussed in detail here as they have been discussed in some detail in previous chapters. However, it appears that these general classes of MIC mechanisms can occur on iron or steel quite readily under anaerobic or aerobic conditions and may involve a great many different types of microorganisms.

Finally, it should be stressed that in environments generally thought to be aerobic, a great number of microenvironments can exist which are anaerobic, or which are at times anaerobic due to fluctuating conditions within the overall system. It is important to realize that in these microenvironments many of the same types of corrosion which are recognized to occur in grossly anaerobic conditions will also occur.

Microbiologically Influenced Corrosion of Iron and Steel in Aerobic Conditions. One mechanism in aerobic environments whereby microorganisms may cause corrosion of iron and steel is the case of Thiobacillus which, through its oxidation of sulfur compounds, produces acidic environments. The local pH around these organisms may be very low and the surrounding material may disintegrate quite rapidly. Likewise the production of organic acids by a variety of different organisms will corrode iron and steel materials in much the same way. It might be noted in this connection that some organisms are known which break down some of the types of coatings used on iron and steel pipe and that the breakdown products of these coatings may provide substrates to acid producers, ultimately resulting in the corrosion of the materials underneath. It might be noted also that holidays (breaks) in these coatings provide excellent starting points for the growth of microorganisms and/or anaerobic environments in what are otherwise generally considered to be aerobic conditions.

Other mechanisms whereby MIC occurs in the aerobic environments are the general cases of microbial growths and deposits on materials creating oxygen or ion concentration cells, which can result in corrosion explained by classical corrosion theory. These can lead to the corrosion of the materials either under the growth or around the perimeter of the growth. A good example of this is seen in the involvement of the iron bacteria which produce extensive ferric hydroxide deposits termed tubercles, especially inside of iron water pipes. Associated with these deposits are often very extensive areas of corrosion.

Methods of Detecting Microbiologically Influenced Corrosion of Iron and Steel in the Laboratory

The methods generally available for detecting MIC of iron and steel in the laboratory are related to the attempts to isolate or otherwise identify specific organisms involved in the corrosion processes. The most obvious are the culture of the SRB's, Thiobacilli, and the iron bacteria. Any standard reference giving microbiological methods will outline methods for the culture, or attempted culture, of each of these types of organisms. The culture of other microorganisms capable of producing organic acids or producing sufficient biological growth in slimes, to allow for the development of oxygen concentration cells, ion concentration cells and the like is a fairly straightforward matter. These methods can also be found in standard reference volumes.

Another approach is to attempt to identify, through various microscopic means, the types of microorganisms involved in the suspected MIC. The iron bacteria can often be identified by simply observing the material under the light microscope. An example of such an organism is shown in Figure 6. The general value of the light or phase microscope in a "first cut" determination of whether one has an MIC problem or not cannot be overestimated. This simple technique allows a rapid determination of the general types of microorganisms present and the general magnitude of the populations. One can also, with some experience, identify many of the microorganisms by simply observing them under the microscope or with the help of simple staining procedures. Further one can get an idea from the appearance of the materials in the specimen as to what is happening in the areas suspected of having MIC.

There are a variety of chemical and biochemical means for attempting to ascertain whether microorganisms are present or to ascertain what specific microorganisms are present. These techniques might take the form of trying to identify specific chemical species, that is, the presence of H_2S, H_2SO_4, organic acids, etc. Alternatively, one can look for specific molecules which identify various microorganisms. This may take the form of identifying lipids which are characteristic of fungi, algae or bacteria or by the identification of lipids specific for sulfate-reducing or other bacteria. A good discussion of the latter biochemical methods is to be found in the article by White.(35)

Another useful technique is the fluorescent antibody procedure. In this procedure antibodies directed against a specific organism, e.g., a particular sulfate-reducing bacterium, are produced in rabbits or other animals, and purified and chemically linked to a fluorescent dye. A suspected MIC specimen is then removed, placed on a microscope slide, stained with the reagent containing the fluorescently labeled antibody to the SRB, processed and viewed under a fluorescence microscope. The numbers of organisms reacting with the antibody can then readily be enumerated. For a further discussion of many of the above culture and microscopic techniques, the reader is directed to an article by Pope et al.(36)

It is impossible to identify, beforehand, which technique(s) should or could be used either in the laboratory or in the field to give the most information.

All have their advantages and disadvantages and all should be tried (the simplest first, perhaps) until the investigator is satisfied with the evidence. Also a little experience and thought about the chemical and physical conditions should alert the investigator to the possible types of microbes to be found, and therefore help him to choose a method(s).

Methods of Detecting Microbiologically Influenced Corrosion of Iron and Steel in the Field

An important point to make in connection with the detection of MIC of iron and steel in the field is that very careful observations of the suspected sample of MIC and the physical and chemical conditions in and surrounding these samples must be made and recorded. It is especially important to note:

(1) Whether there is blistering or tuberculation and the patterns thereof;
(2) The appearance of the metal (bright?, black?) underneath in tubercles;
(3) The color of the fouling and/or corrosion product;
(4) The presence or absence of the H_2S odor in the general environment (soil, water) or from the corrosion product upon adding a few drops of HCl;
(5) The general conditions of water (chemistry); and
(6) The types of materials in use.

If it is suspected that the MIC is due to Desulfovibrio or other SRB's, it is important to attempt to establish that there are in fact anaerobic conditions surrounding the MIC area. It would also be important to establish whether H_2S or FeS were present in the area. Additional useful tests are to determine general bacterial populations by viable plate counts, whether there were SRB's or other anaerobic bacteria present or whether there were strict aerobes present, each of these being important indicators as to the conditions in the area. It would also be important to note whether the corroded metal was generally corroded or whether it was pitted, since the latter condition could be indictative of SRB related corrosion.

If one suspects that the MIC is related to the Thiobacilli, then it would be important to determine whether sulfur is present in the environment and in what forms, i.e., as elemental sulfur, as H_2S or H_2SO_4. These determinations can be made by straightforward chemical methods. Also important is an attempt to culture the Thiobacilli. This can be done by methods as outlined in any general microbiological-methods reference work. In addition the pH should be measured, since a low pH would be one indication of the presence of Thiobacilli. Finally the conditions should be aerobic, so a determination of the level of oxygen would be important. Electrodes, chemical analysis or redox dyes can be used depending on the conditions.

If it is suspected that MIC is related to the production of organic acids by one or more bacterial types, then one should measure, if possible, the pH in the local environment surrounding the corroded area (a contact pH electrode is useful for this), take samples for analysis for organic acids, and attempt to culture as many of the bacteria as possible from the samples using ordinary culture techniques. An additional procedure which is often helpful is to collect some corrosion product, inoculate it into a growth medium containing one or more fermentable carbon sources (e.g., glucose) and use a pH indicator to determine whether the potential MIC microbial community can in fact produce acids as a result of their metabolism. The MIC environment could be anything from aerobic to anaerobic and still contain organisms whose metabolism produces organic acid by-products, so although this procedure is not indicative of specific types of organisms being present it is still quite useful. It would also be wise to measure the oxygen levels at the site, if possible.

If MIC is suspected as being related to the formation of tubercles then of course one would want to observe the MIC for the presence of tubercles. One or more should be removed and the area underneath observed for bright areas indicating active corrosion. The presence of H_2S and/or metal sulfides or blackening of areas under the tubercles would indicate the presence of SRB's. It would be important to analyze the tubercle material and surrounding material for the presence of iron bacteria or other bacteria which may be responsible for the formation of the tubercle. Microscopic analysis to demonstrate the presence of the iron bacteria may be the most fruitful and direct way. Culture techniques, as mentioned above, for the general types of bacteria present in the tubercles should be used. Chemical analysis to show an association of organic acids or inorganic acids with tubercles would also be suggestive of the presence of bacteria capable of causing MIC, and one should therefore try to analyze for these if possible.

Methods for Controlling Microbiologically Influenced Corrosion of Iron and Steel

Although a variety of approaches are currently in use to try to combat corrosion, none of them seems to have been designed specifically to prevent the occurrence or activities of organisms involved in MIC. Most biocides seem to have been designed more to prevent the growth of the organisms and the associated problems of sliming and heat transfer loss than to prevent corrosion by them. It should be noted however that control of slime will prevent many types of MIC.

In general the methods of preventing or retarding corrosion can be lumped into two major categories: (1) using noncorrodible materials and (2) using corrodible materials with some other kind of condition(s) being imposed. Using noncorrodible materials certainly is an excellent solution provided that the materials are obtainable in the form that is required, not prohibitively expensive for the use required, and have the qualities necessary to be resistant to any other conditions besides the possible MIC in the environments being used. In many instances it is simply not economically feasible to use materials such as titanium or nickel-base alloys, which might be more resistant to the types of MIC seen than are iron or steel. The second alternative, that is, using corrodible materials will require, if used in an aggressive environment, the application of additional measures to counteract the effects of MIC. These countermeasures fall into four groups which are discussed in the following paragraphs.

One approach is through modification of the environment. This involves the modification of the localized environment around the iron or metal structure or pipe such as to create a local environment which will be less likely to support MIC. An example of this type of approach is the procedure of surrounding pipes in otherwise anaerobic soils with gravel or chalk to provide drainage and better aeration of the soils. Another example would be to modify the pH of the surrounding environment to prevent certain organisms from growing or performing certain types of metabolic activities. This might be done, for example, by adding carbonate-type rods to in-ground installations to prevent acid accumulation.

A second method is the application of protective coatings. These coatings usually fall into the categories of coal-tar-base materials, asphaltic bitumen-based materials, concrete, zinc, lead or plastics. Romanoff(37) reported that the coal-tar and asphaltic coatings have been quite successful in protecting underground steel structures and pipes. Speller(38) found that cement coatings applied over steel were quite effective. Wagner(39) reported that polyethylene sleeving applied over cast iron pipe was effective in preventing corrosion. Dittmer,(40) however, reported greater weight losses in specimens of polyethylene-coated iron than in controls when both were exposed to SRB's.

It should be noted however that the application of various types of coatings to iron and steel (especially in the absence of cathodic protection) brings another whole set of MIC problems to the fore. Some of these coatings may be laid over reinforcements containing cellulosic materials which if attacked by microorganisms can produce organic acids and therefore decompose not only parts of the coating itself but cause extensive corrosion of the underlying metal. The application of coatings often leaves holidays (discontinuities) in the protective coatings which constitute areas where microorganisms can enter and form microcolonies very rapidly and result in very rapid corrosion at these localized sites. Cathodic protection may solve most of these cases (see below).

Zinc coating of steel pipes has been reported as preventing corrosion for extended periods of time. However, there are several cases where zinc coated metals have shown MIC. Coatings with other types of metal should be effective under certain conditions. However, again, imperfections or cracks in the coating are localities where very rapid MIC can occur. There has been a recent increase in the use of plastics, e.g., epoxy resins. The application of such plastic coatings, however, suffers from the same general problems mentioned above; that is, imperfections provide sites where bacteria can establish themselves and influence or initiate corrosion. There is also the question of the permeability of plastic and other coatings to such substances as hydrogen sulfide, organic acids and various other corrosive chemicals. Therefore, these coatings although removing the organism from direct contact with the metal may not, in reality, prevent corrosion due to the activities of microorganisms.

The third method is cathodic protection. Cathodic protection and the principles underlying its application to combat MIC are discussed in a very thorough way by Miller and Tiller in their review article.(3) These authors concluded that cathodic protection either alone or in combination with protective coatings seems to be a quite effective means of controlling the corrosion of iron or steel by the SRB's under anaerobic conditions. Booth and Tiller(41) did note, however, that effective protection by cathodic means requires the potential to be increased in the active direction to about -0.95 volt instead of the usual -0.85 volt (versus a saturated copper/copper sulfate electrode). Since these potentials cause the development of very alkaline conditions, pH may be the mechanism whereby protection is afforded. However, high alkalinity may cause other problems, e.g., cracking.

The fourth method is through the use of microbial inhibitors. The use of various inhibitors to stop the occurrence, growth or metabolic activities of a variety of microorganisms is a well established practice. There are a wide variety of these biocides in use today including oxidizing compounds such as chlorine or hypochlorite, ozone and chlorine dioxide; various organic biocides such as the organotins, quaternary ammonium compounds, dibromonitrilopropionamides (DBNPA), isothiazolins and a variety of others. Many of these biocides are very effective in the control of organisms when they are suspended in an aqueous medium; that is, when they are occurring as single cells or as small clumps of cells in the medium. The control therefore of organisms in the water itself is usually a reasonably simple task compared with the real problem which is control of the organisms in the biological films on the surface of the materials. The latter situation is much more difficult to deal with, the concentration of biocide required to effect killing or control of the organisms under this situation often being many times the concentration necessary to kill the organisms in an aqueous phase. Pope and coworkers(42-44) and Costerton and coworkers(45) and Characklis and coworkers(46) have all pointed to the fact that the usefulness of many biocides in the control of organisms in fouling material is much more limited than it is in the aqueous part of the system. The other problem with certain of the biocides is that they will simply shift the microbial population from a "normal aquatic community" or "normal cooling system" community to very specialized communities, i.e., those which form slime or those which are through some other mechanism, able to be more resistant to the biocides. This shift may ultimately cause a much more severe sliming or corrosion problem than might be encountered with a mixed microbial community. Certain organisms such as the Pseudomonas-type organisms are noted for their ability to form slime and for their resistance to a great variety of chemicals. In fact, they are able to break down and use as foodstuffs some of the biocides which are ordinarily used to kill other organisms. One partial solution to this problem, currently in wide use, is to switch biocides to prevent build-up of "biocide-resistant" types of organisms.

Research needed in the Area of Microbiologically Influenced Corrosion of Iron and Steel

It is clear that microorganisms can play an important role(s) in initiating and/or accelerating corrosion of all steels. However, the specific mechanisms of attachment and/or enhancement are still not clearly understood. For example, after considerable study the exact mechanism whereby SRB's cause corrosion of iron and steel is still open to question. The question of whether other organisms which produce H_2S but which are not sulfate reducers can produce the same sort of symptoms needs to be studied. Very little research has been done on the matter of how organic acids cause corrosion. The relative problems represented by different organic acids must be addressed. The role(s) of other materials such as ammonia, nitrite, nitrate, etc., which are very common metabolic intermediates from a variety of microbes, needs to be further elucidated. Certainly the recent discussions relating to the ability of certain microorganisms, including certain of the Pseudomonas spp., to actively reduce ferric to ferrous iron needs to be intensively investigated to determine the importance of this capability in the corrosion of iron and steel under a variety of conditions. Finally, we feel that it is extremely important that a group of investigators be given an opportunity to investigate cases in a variety of industrial situations where MIC is suspected. This group would need to examine the situation from microbiological, metallurgical, environmental and process points of view and to do thorough work-ups relative to the microbiology and chemistry of the water and MIC products, electron microscopy and other types of metallurgical analysis all of which should be designed to confirm whether these are cases of MIC or not.

The area in which research might do the most toward helping to estimate the magnitude of the MIC problem and ultimately lead to the best chance for understanding and controlling it is the area of developing rapid methods for identifying MIC and the organisms involved, in the field. Such methods might certainly take the form of sampling kits for microbiological or chemical analyses or the use of the fluorescent antibody techniques. In addition, on-line detection methods, somewhat similar to the "bug-pots" in use at DuPont,(47) might be used. Electrochemical methods (linear polarization) might be developed to assess whether MIC is occurring under the conditions in the plant being studied.

Much more research needs to be done under controlled laboratory conditions, using biochemical, molecular, genetic and genetic engineering techniques to define the exact role of microorganisms in the various types of microbiological corrosion processes.

Finally, the ultimate goal of being able to prevent MIC must be addressed. One of the most important areas in this regard is the development of methods, be they chemical or otherwise, to prevent the sorption of organics and/or attachment of organisms to the metal surface, since most cases of MIC can be prevented if these processes can be controlled. Also in this regard, we must find ways to disassociate preformed biological films from the surfaces of metals, since clean surfaces will under most conditions offer much less opportunity for MIC.

A prioritized list for research needs relative to MIC of iron and steel is essentially the same as for MIC in general. That list is given in the last chapter: General Conclusions and Research Needs.

CHAPTER 4
THE CASE FOR MICROBIOLOGICALLY INFLUENCED CORROSION OF STAINLESS STEELS

Introduction

Stainless steels are iron-chromium alloys in which 12 to 30 weight percent chromium is added to iron to impart corrosion resistance. In general they are resistant to oxidizing media unless such media contain significant amounts of halide, (particularly chloride) ions. However, they are not particularly resistant to reducing environments. Since for aqueous solutions, dissolved oxygen is often the oxidant which induces passivation, areas of alloy surfaces in contact with an environment which is depleted in oxygen and also in contact with passivated surfaces often show abnormally high corrosion rates. Thus, crevices where oxidant availability is generally low, are particularly prone to corrosion. Additionally, if crevices become acidified, for example by the incursion of halides, corrosion rates in the crevices may be increased considerably.

Metallurgically, the stainless steels are usually divided into four categories: austenitic, ferritic, martensitic and duplex. The most common alloys used in chemical process applications are the austenitic alloys. These alloys contain 12 to 25% chromium and 8 to 35% nickel. The addition of nickel stabilizes a face-centered-cubic crystal structure which improves ductility and workability. Common alloys in this family are Types 304 stainless steel (18 Cr - 8 Ni), 316 stainless steel (with approximately 2% Mo added to improve resistance to chloride ion), 304L and 316L (very-low-carbon grades of 304 and 316, respectively) and the less frequently used 317 stainless steel (approximately 3 to 4% Mo).

Modern melting techniques allow high purity ferritic alloys consisting of Fe, 11 to 30% Cr, and 0 to 4% Mo, to be produced. Some of these alloys show good resistance to pitting corrosion, stress-corrosion cracking and general corrosion in oxidizing environments. However, considerable research remains to be performed before they are generally accepted as replacements for austenitic alloys.

The third class of alloys, the martensitic stainless steels, are generally used for applications where high strength and moderate corrosion resistance are required, e.g., steam turbine blades, aircraft compressor blades and cutlery. There are no references to MIC of these alloys and it is unlikely that they would generally be used in chemical process environments which contain significant numbers of bacteria.

The fourth class of alloys, the duplex steels are phase mixtures of ferrite and austenite. They have recently become available as wrought materials (sheet, plate and pipe). They show good resistance to intergranular stress-corrosion cracking and localized corrosion with improved strength when compared to either single-phase austenitic or ferritic steels. Additional duplex structures have traditionally been utilized in weldments for normally austenitic structures to inhibit many of the problems of tearing which sometimes occur in single phase alloys upon cooling after welding.

Microorganisms involved in Microbiologically Influenced Corrosion of Stainless Steels

Microbiologically influenced corrosion of stainless steels, particularly of the 300 series, has been reported by a number of authors.(16,48-52) It should be noted, however, that several investigators have reported observing little or no attack on these alloys in experiments where MIC was specifically studied and where mild steel was shown to be corroded.(54,55) Perhaps the area of largest controversy vis-a-vis stainless steels relates to the involvement of MIC in crevice corrosion; the question is whether it is simply a classical crevice corrosion problem with the biomaterials being involved in the screening of oxidants, or whether there is a true accelerative effect by these biological elements on the corrosion rates.

Reports of accelerated corrosion of stainless steels associated with microorganisms began to appear in the early 1970's. Many of these reports did not detail the specific types of organisms involved in MIC, but rather, only indicated that bacteria or some other organisms could be identified as causal to the corrosion problems. Of the microbes identified with corrosion of stainless steel, aerobic iron- and manganese-oxidizing bacteria were associated with pitting in 304 and 316 stainless steels.(16,48) In these cases it was believed that the bacteria oxidized ferrous (Fe^{+2}) and manganous (Mn^{+2}) ions to ferric (Fe^{+3}) and manganic (Mn^{+4}) ions which when combined with ambient chlorides, resulted in pitting. In the cases reported, virtually all of the pitting was associated with weld seams.(16) However, it should be noted that, in this case, preferential corrosion of the ferrite phase was observed, suggesting a more complicated explanation. The preferential corrosion of delta-ferrite in duplex weldments has been reported in at least two other independent studies. In a NASA study, corrosion of 321 stainless steel (Fe - 18 Cr - 8 Ni - Ti) was reported to have been attributed to microorganisms derived from human feces or from bath water inoculated with bouillon.(52) However, while a variety of organisms were isolated, no direct causal relationship between individual bacterial species and corrosion was identified.

There are few reported observations of sulfate-reducing bacteria (SRB's) involved with the corrosion of stainless steels. Only two cases of extensive corrosion in CPI environments involving 304 and 303 have been reported. However, several reports of similar cases are available from other industries (e.g., pulp and paper). Corrosion was observed on carbon steel, stainless steels and galvanized steel in the same system.(16,48) Both SRB's and Sphaerotilus were identified. The results suggested that corrosion of the stainless steel may have occurred due to oxygen and or acid concentration cells created by sludge buildup. In this case then, the action of the bacteria may have been to create an occluded cell geometry rather than to intrinsically corrode the alloy.

In a recent report, Pseudomonas, Sphaerotilus and Desulfovibrio were shown to be associated with slime which covered corroded areas on stainless steel.(48) It was suggested that the slime formers set up anaerobic conditions in which the metabolic products of Desulfovibrio accumulated and acted to destroy the passive film. In a second study cited in the same reference, corroded areas of a 304 stainless steel pump impeller were covered with slime deposits which contained Pseudomonas, Aerobacter, Flavobacterium and/or Bacillus types of bacteria. Desulfovibrio, Desulfotomaculum and/or Clostridium species were identified as occurring in or under the slime. Gallionella was also identified as causing corrosion at welds in 304 stainless steel in yet another case study cited in the same reference (J. G. Stoecker, personal communication, R. E. Tatnall).

It should be noted, however, that other studies have indicated no effect of the SRB's, in the absence of slime, on corrosion of stainless steels.(51,53)

Mechanisms involved in Microbiologically Influenced Corrosion of Stainless Steels

Stainless steels and other "passive" alloys rely on a thin (virtually transparent) surface film to provide resistance to corrosion. This film requires oxidizing conditions for stability, both to initiate passivity and to repair subsequent chemical or mechanical damage to the film. It is for this reason that stainless steels are particularly susceptible to crevice corrosion. The passive film is set up by reduction of oxygen in solution according to the reactions:

$$Me - Me^{++} + 2e^{-} \qquad (1)$$

$$1/2\ O_2 + H_2O + 2e^{-} - 2OH^{-} \qquad (2)$$

$$Me^{++} + 2OH^{-} - Me\ (OH)_2 \text{ (probably precipitated film)} \qquad (3)$$

Alternatively, some investigators believe that oxygen alone, reacting with the alloy surface, is sufficient to induce passivity. In either case, oxygen is generally required to initiate the film and, if the film is damaged, to repair it. In non-halide environments film repair is usually not a problem since crevices, being essentially stagnant areas, do not create conditions where the passive film is damaged. However, when mechanical action, such as fretting, occurs in the crevice, high corrosion rates may be observed. An additional problem is presented by the halides which, when present, can chemically damage the passive film. If insufficient oxygen is available to reform the film, corrosion may be initiated. Even if the nominal bulk chloride concentration is extremely low, the chloride concentration in the crevice may increase considerably due to continued metal dissolution. Since in this process, no oxygen is available to produce hydroxide ion, dissolved metal ions will react with available hydroxide, and a charge imbalance of Me^{++} and H^{+} ions will arise. Chloride ions which are more mobile (due to concentration gradients) than hydroxide ions will diffuse into the crevice, and will react with the metal ion and water according to the reaction:

$$Me^{++} + 2Cl^{-} + 2H_2O - Me(OH)_2 + 2H^{+} + 2Cl^{-}$$

This halide acid environment further destroys passive films resulting in high corrosion rates in the crevice.

It is tempting to associate all MIC of stainless steels with simple crevice mechanisms, where slime producers are simply effective creators of crevices. i.e., between the slime and the metal surface. However, there is evidence that the microbes create a further accelerative effect which catalyzes the corrosion reactions to a greater degree than is explained solely by the mechanism of a simple crevice. For example. the following scenario has been proposed(48) for situations where sulfate-reducing bacteria are present in aqueous solutions:

(1) Slime formers attach to the metal surface and multiply especially in regions of low fluid velocity, such as at joints and at other stagnant areas.

(2) As the deposit grows, it traps particles from the water. These include many aerobic bacteria, including the iron bacteria, which subsequently consume oxygen, creating the anaerobic conditions required for classical crevice corrosion. Thus, the bacteria at this stage accelerate the rate of oxygen depletion and the formation of the crevice.

(3) Any SRB's present may grow and concentrate in the anaerobic zones and will attack the ferrous alloy in much the same manner as they would attack mild steels (see Chapter 3).

Another possibility by which microbes may accelerate localized corrosion processes of stainless steels is suggested by the presence of metal concentrating/oxidizing microbes. These bacteria apparently fix the Fe^{+2}/Fe^{+3} or Mn^{+2}/Mn^{+4} redox potential at the metal surface. Accordingly, they may polarize the surface of the metal to a potential which exceeds the critical breakdown potential and/or accumulate chlorides in the crevice region. The latter situation would be expected to arise if the migration of chloride ions into the crevice is driven by the requirement to neutralize the increased charge created by the higher oxidation state of the metal ion. Thus the crevice environment is, in reality, a $FeCl_3$ or $MnCl_4$ solution, both of which are known to be highly damaging to the normally protective passive film. This would be analogous to the conditions employed in localized corrosion tests in which inorganic $FeCl_2/FeCl_3$ combinations are used to accelerate (and to assess) the pitting resistance of stainless steels.

It should be stated that few mechanistic studies of MIC of stainless steels have been conducted, and the specific processes by which bacteria may increase corrosion rates are still open to question.

Methods of Detecting Microbiologically Influenced Corrosion of Stainless Steels in the Laboratory and in the Field

The bacteria suspected of involvement in corrosion of stainless steels are essentially those associated with corrosion of mild steels. (In the absence of passivity, stainless steels behave essentially like mild steels). Accordingly, the methods of detection are outlined in the chapter of this report related to mild steels and in the Appendix.

Methods for Control of Microbiologically Influenced Corrosion of Stainless Steels

Controlling MIC of stainless steels can be accomplished by the obvious techniques of either eliminating the bacteria, eliminating the sites where crevices may occur, or by coating surfaces with alloys which are more resistant to localized corrosion. The first of these can theoretically be effected by appropriate biocide additions, but this has proven to be difficult if not impossible to accomplish in actual operating conditions. In theory it is also possible for some biocides to encourage attachment of some organisms, thereby promoting fouling and perhaps subsequent MIC. Additionally, there are presently no uniformly accepted guidelines which can be used to determine appropriate biocide levels to prevent MIC. With regard to geometric effects, the elimination of gaskets, joints, stagnant areas, etc., is often not possible in engineering design. However, when possible, surfaces should be smoothed to help discourage bacterial attachment. Finally, overlaying or lining with higher chromium or higher nickel alloys may prove to be an effective method for controlling MIC if crevices are inevitable. Several other suggestions for controlling MIC are contained in the general article on the fundamentals of MIC by Tatnall.(56)

Research needed in the Area of Microbiologically Influenced Corrosion of Stainless Steels

The research areas described in the section of this report dealing with iron and steel certainly apply to the stainless steels. In addition, however, the stability of passive films should be examined, particularly in the presence of organic acids such as those often produced by microbes. It has been reported, for instance, that the resistance of stainless steels to localized corrosion is very much reduced when organic solvents are present.(57) The specific role of microbes such as *Gallionella* must be assessed. For example, in the section entitled Proposed Mechanisms, it was suggested that the Fe^{+2}/Fe^{+3} and/or Mn^{+2}/Mn^{+4} redox potentials might directly affect the corrosion potential of an alloy and possibly lead to enhanced chloride levels. Thus the ability of microbes to fix electrochemical conditions needs to be addressed. Mechanistic studies aimed at understanding the specifics of MIC might be one of the most fruitful, ultimately leading to control of corrosion of nominally "corrosion resistant" alloys.

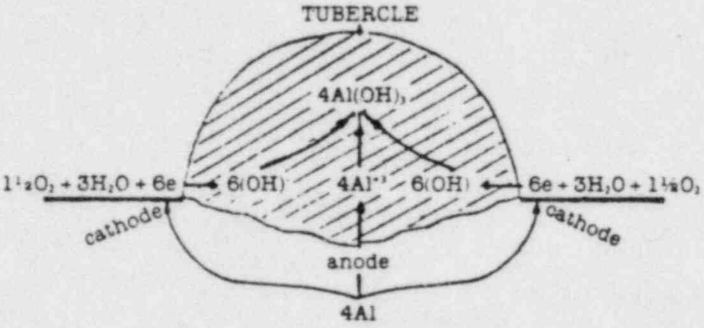

Figure 9

Diagram of oxygen concentration cell formed by tubercle.(64)

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CHAPTER 9
GENERAL CONCLUSIONS AND SUGGESTED AREAS FOR RESEARCH

It is the opinion of the study group that MIC of several different classes of alloys is well documented in the literature whereas the specific mechanisms for most are poorly defined. The sulfate-reducing bacteria seem to be involved in at least some form of MIC of most of these alloys. It is also clear that the formation of colonies, slimes, mats and tubercles on surfaces is a major contribution to MIC of most alloys. (It should be noted here that a decided effort to inform field engineers of the differences between free-floating and attached organisms and the problems caused by each should be made.) Enhanced corrosion under these formations may occur by production of oxygen and ion concentration cells, cathodic depolarization, acidification, halide accumulation or by direct metal/ion transformation by the organisms, etc. It is also apparent that few good simple methods are available for the reliable confirmation of suspected MIC in the field.

In the literature available for review, reports of methods for the prevention of MIC (short of replacement with more resistant alloys) are largely unavailable. This probably does not adequately reflect the situation since presumably many cases of MIC are successfully treated by chemical water treatment methods with the results never published. It is hoped that ways will be found for reports on such "success stories" to be published in the open literature. Data on the extent of the MIC problem relative to general corrosion problems also are largely unavailable. For example, there may be many cases of accelerated corrosion, due to contributions from MIC, which have been improperly diagnosed due to ignorance of the possibility of the problem.

The areas in which research is needed fall into two main categories "technological" and "scientific." The former are those practical approaches required to identify, mitigate and/or prevent MIC. The latter consists of a description of the specific mechanisms involved and the development of new means (alloys, chemicals, etc.) to combat MIC. (Note that specific recommendations for each alloy type are given at the ends of the chapters dealing with alloy systems.)

A prioritized list is as follows:

A. Technological

1. Develop reliable, simple (and hopefully inexpensive) means for detecting MIC in the field. In situ probes, test kits, etc., should be developed.
2. Develop quantitative or semiquantitative estimate of the extent of the problem using the methods made available above.
3. Develop adequate antifouling and slime dispersing agents.

B. Scientific

1. Investigate SRB's in greater detail, as they are obviously very important to MIC of many metals.
2. Study the role of organic acids, particularly those produced by microbes, in the corrosion of various alloys.
3. Determine the ability of microbes to fix electrochemical potential parameters, e.g., on metal or alloy surfaces.
4. Perform biochemical/genetic studies of the microbes involved in MIC.
5. Investigate the possibility of biological solutions to MIC problems, for example, enzyme treatments, use of bacteriovores, etc.

It should be emphasized that, while somewhat arbitrary priorities have been assigned in these lists, it is, at best, difficult to assign specific priorities. Rather, the priorities assigned in the "Technological Research Areas" should be considered as evolutionary with Item 1 being required before Item 3 can be addressed. Similarly, the "Scientific Research Areas" are often specific to certain metal/environment couples and should probably be treated rather independently.

APPENDIX
PROCEDURE FOR OBTAINING AND PRESERVING SAMPLES WHERE MICROBIOLOGICALLY INFLUENCED CORROSION (MIC) IS SUSPECTED AS BEING INVOLVED

A. Observations in the Field

1. It is very important that the conditions to which a sample is normally exposed be accurately recorded in order to obtain the maximum amount of information from the sample analyses. At a minimum, data should be obtained for:
    a. Temperature or temperature range in the system
    b. pH of the system
    c. Type of material(s) in the system, e.g., 304 stainless heat exchanger
    d. Type of water being used, e.g., fresh, brackish, marine
    e. Operating conditions including shut downs, cleanings and other unusual events
    f. Chemical treatment used, if any
    g. Water or process chemistry
2. Almost any other observations which can be made will be useful, e.g., conductivity, turbidity, suspended solids, organic loads, "downstream from a pulp mill," etc.

B. Preparing for Sampling

1. Try to set up for sampling <u>before</u> the need arises, i.e., be prepared to take advantage of unexpected sampling opportunities as they arise.
2. Try to let the laboratory staff doing the analyses know as far in advance as possible that samples will be sent, how many, what type, etc.
3. If microbiological analyses are to be done, have available shipping containers, ice and arrangements for immediate transport of the sample to the laboratory. Getting the sample to the laboratory <u>as soon as possible is critical</u>, within 12-24 hours is a must (see D below).

4. If it is decided that the samples will probably not be analyzed within 12-24 hours then it is suggested that the samples be killed and processed for light and electron microscopy and chemical analyses (see D below).
5. The best procedure is to combine the above and send both live and preserved samples.

C. Taking the Sample—General

1. Samples of water, or scrapings from the area, nodules, tubercles or sections of material containing suspected MIC should be taken as soon as possible after disturbing the "normal operating conditions."
2. Samples should be taken in, or put into clean, sterile, glass or plastic containers.
3. Water samples are best taken from a "flowing stream" situation with minimum disturbance to the other components of the system, i.e., sediment or slime. Water samples are most useful when accompanied by other evidence of MIC, e.g., tubercles.
4. Scraping of some samples (tubercles, slime, etc.) is best done with sterile utensils, e.g., spatulas or spoons. Simply dipping in alcohol and burning off the excess will sterilize them. Swabbing is best done with sterile cotton swabs or gauze squares.

D. Water Samples—Unpreserved

1. These are useful for microbiological, microscopic and chemical analyses.
2. Samples must be placed in a sterile container, capped, refrigerated and put on ice (not dry ice) and delivered or shipped to the laboratory as soon as possible. Analysis in the laboratory should begin no more than 12-24 hours after collection. Samples must be kept cold (0° to 4° C) until analysis is complete.

E. Water Samples—Preserved

1. These are useful for optical and electron microscopic analyses and for some chemical analyses.
2. For routine analyses, preservation with approximately 2% formaldehyde is generally satisfactory. Add 1 part commercial formalin to approximately 20 parts of water sample. The formalin should be neutralized (to pH 7.0) with KOH or NaOH before use.
3. For electron microscopy:

   Add 1 volume of a 4% paraformaldehyde - 5% glutaraldehyde fixative solution (see below) to 1 volume of sample, put on ice and ship to laboratory as soon as possible.

   Prepare the fixative solution as follows:

   a. Take appropriate precautions to avoid getting on skin or inhaling
   b. Dissolve 4g paraformaldehyde in 25 ml distilled water
   c. Heat solution while stirring
   d. Cool to room temperature
   e. Add 10 ml 50% glutaraldehyde solution
   f. Bring final volume to 100 ml with filtered buffered water

   Prepare buffered water as follows:

   NaH_2PO_4 6.41 g
   $Na_2HPO_4 \cdot 7H_2O$ 4.31 g
   Distilled-deionized water 100 ml
   Filter through 0.2 μm or 0.22 μm membrane filter into sterile container, seal and refrigerate until use.

F. Samples of Tubercles, Sediment, Etc.—Unpreserved

1. These should be as undisturbed as possible and kept so during transit.
2. Guidelines for use of sterile sampling utensils, vessels, refrigeration and rapid analyses (see above) should be followed.
3. Be certain that the samples do not dry out before analysis. Place in moist container or, if appropriate, cover with water from the site.

G. Samples of Tubercles, Slimes, Etc.—Preserved

1. Routine analyses: Bring the solution covering the specimen to 2% final concentration formalin (see E above).
2. Electron microscopy: Add samples to a 2% paraformaldehyde - 2.5% glutaraldehyde solution (see E-3 above).

H. Sampling Kits Available

1. Kits for all types of sampling can be made available on a cost reimbursable basis. One such source of kits is Dr. D. Pope, (518) 270-6757.

Exhibit 7

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1. Introduction

Microbial intrusion into the field of corrosion does not involve any new form of corrosion process. Corrosion can be defined as an electrochemical process whereby part of the surface of the corroding substrate is oxidised and transferred from the solid state into solution, accompanied by the simultaneous reduction of some component of the corrosive environment. This definition remains valid whether microbiological influences are at work or not.

There are essentially two ways in which microbes are involved in corrosion processes. Firstly, by virtue of their growth and metabolism, they can introduce into an otherwise innocuous system, chemical entities such as acids, alkalis, sulphides and other aggressive ions which will render the environment corrosive. Secondly, microbes may enter *directly* into one or more of the electrochemical reactions at the surface of the substrate, thereby initiating or accelerating an electrode reaction already potentially present. Alternatively, the presence of the organism and its entry into the electrode reaction may provide a different pathway for a familiar process. If these points are borne constantly in mind, much of the "mystique" that has bedevilled this subject for many years will disappear.

NOMENCLATURE

Confusion may arise over the nomenclature of micro-organisms. A micro-organism is classified and named according to its known characteristics and physiological and biochemical behaviour. All too frequently, in the light of new knowledge, it becomes necessary to reclassify a particular organism. This has often happened to organisms involved in corrosion, and the same organism may be encountered in the literature under a variety of names.

The sulphate-reducing bacteria, for example, which include the most important and most frequently-encountered bacteria in the corrosion field, may be found under the name of *Spirillum*, *Microspira*, *Vibrio*, *Sporovibrio*, *Desulfovibrio*, *Clostridium* and *Desulfotomaculum*.

In this account, names used are those in general use at the time of writing; in referring to earlier literature, the nomenclature used therein is changed to that now current.

2. Micro-organisms of Importance in Corrosion

Micro-organisms covering a wide range of genera and species are encountered in corrosion problems, but the most familiar and important ones have one feature in common; sulphur and/or its compounds play a vital part in their metabolism and they are intimately concerned with the sulphur cycle in nature.

The natural sulphur cycle is illustrated in simplified form in Fig. 1. The upper part of the main cycle is relevant to the understanding of microbial corrosion, together with the "short-circuit" in which sulphate may be reduced to sulphide without going through the organic sulphur compounds.

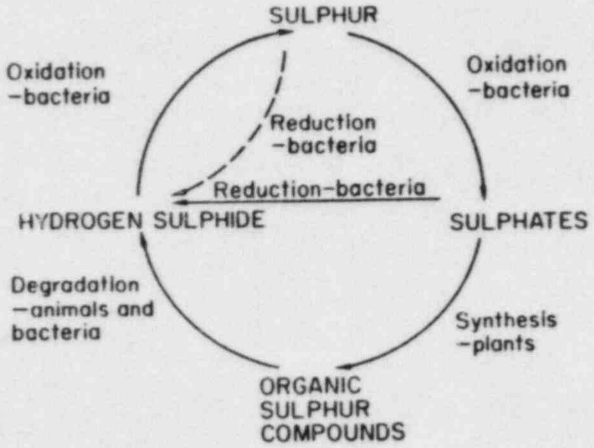

Fig. 1 The sulphur cycle in nature.

The portion of the main cycle concerned is the province of the *sulphur-oxidising bacteria*; the short-circuit is that of the *sulphate-reducing bacteria.*

SULPHUR-OXIDISING BACTERIA

The oxidation of sulphur, thiosulphate, sulphite and several polythionates to sulphate, with the simultaneous production of strong acid, is carried out by a group of bacteria of the genus *Thiobacillus*; three species, *Th. thioparus*, *Th. thio-oxidans*, and the graphically-named *Th. concretivorus*, find a place in corrosion phenomena. They are all stubby, rod-shaped bacteria, measuring 0·5 μ by 1·0 to 3·0 μ; they are aerobic (requiring the presence of oxygen for growth) and obligately autotrophic, meaning that they synthesise all their complex organic compounds (proteins, carbohydrates, etc.) from inorganic starting materials, and are unable to make use of organic materials as foodstuffs. Cell carbon is derived from carbon dioxide, nitrogen from ammonium compounds, etc.

These bacteria are all actively motile, being propelled by a single polar flagellum when in young culture, but they may lose their motility with age. They do not form spores. They exist as single cells and do not tend to form chains or aggregates.

The net energy gain resulting from the oxidation of reduced sulphur compounds provides energy for the synthetic processes of the growing organism. The optimum temperature for growth is 25–30°C; the organisms exhibit some growth over the range 10–37°C and are ? killed at about 55–60°C.

Differences between the three important species may be summarised as follows:

Th. thioparus oxidises thiosulphate to sulphate and sulphur as its main energy-producing reaction. The oxidation does *not* involve tetrathionate as an intermediate, and in this way it differs from the other two. *Th. thioparus* will also oxidise elementary sulphur to sulphate but will not oxidise sulphide. The oxidation will begin at a pH of about 7·8 and a fully-grown culture will reach a pH of around 4·5.

Th. concretivorus will oxidise thiosulphate *with* tetrathionate as intermediate; it will also oxidise sulphur and sulphide. The optimum pH for the growth of the organism is between 4 and 2, but slow growth may continue to an ultimate pH of about 1.

Th. thio-oxidans will produce even stronger acid, reaching a pH of 0·6 or less, and it will continue to live in a more acid medium than any other organism yet reported.

All three organisms are widely distributed in nature, being found in muds, soils and water.

DETECTION TEST

A simple test is recommended by Starkey(29) for detecting the presence of these bacteria in suspect material, using a mineral salt medium of the following composition:

$(NH_4)_2SO_4$	3 g
KH_2PO_4	3 g
$CaCl_2$	0·25 g
$MgSO_4$	0·5 g
$FeSO_4$	0·01 g
Distilled water	1 dm^3

This medium is dispensed conveniently in 100 cm^3 quantities in 250 cm^3 Ehrlenmeyer flasks. About 1 g of elementary sulphur is sprinkled on the surface of the contents of each flask, and the flasks are closed with loose plugs of non-absorbent cotton wool. The flasks are sterilised by steaming for one hour on each of three successive days, taking care that the sulphur remains floating on the surface of the liquid. (If the sulphur sinks, the efficiency of the medium is greatly reduced.) The pH of the medium is adjusted with sterile hydrochloric acid or caustic soda to a suitable value (7·5 for *Th. thioparus* or 5·0 for the others) and a flask is inoculated with about 1 g or 1 cm^3 of the material to be tested. The flask is then incubated in air at 30°C and the pH measured at intervals over a period of 4 days to 2 weeks. An abrupt drop in the pH of the medium indicates growth of thiobacilli and their presence in the inoculum.

SULPHATE-REDUCING BACTERIA

The reduction of sulphates to sulphides is effected by sulphate-reducing bacteria of the genera *Desulfovibrio* and *Desulfotomaculum*.

The genus *Desulfovibrio* comprises five species, four of which influence corrosion. All are curved rods (they may occasionally appear straight), sometimes sigmoid or spirilloid (Plates I, II). All are obligate anaerobes, i.e. they will not grow in the presence of even traces of oxygen. They grow well at temperatures between 25 and 44°C, and at pH values between about 5·5 and 9 (optimum pH 7·2 approx).

The three species *D. vulgaris*, *D. desulfuricans* and *D. salexigens* are all about 0·5–1·0 μ by 3·0–5·0 μ in size, and are actively motile, being propelled by a single polar flagellum. *D. salexigens* has an absolute requirement for about 2·5 per cent sodium chloride, but the other two species can be trained to grow in either fresh or salt water conditions. The species *D. africanus* is larger, a sigmoid rod 0·5 μ by 5–10 μ; it is rapidly motile, with a polar flagellum at each end.

The genus *Desulfotomaculum* comprises the spore-forming sulphate-reducers; it contains three species, two of which

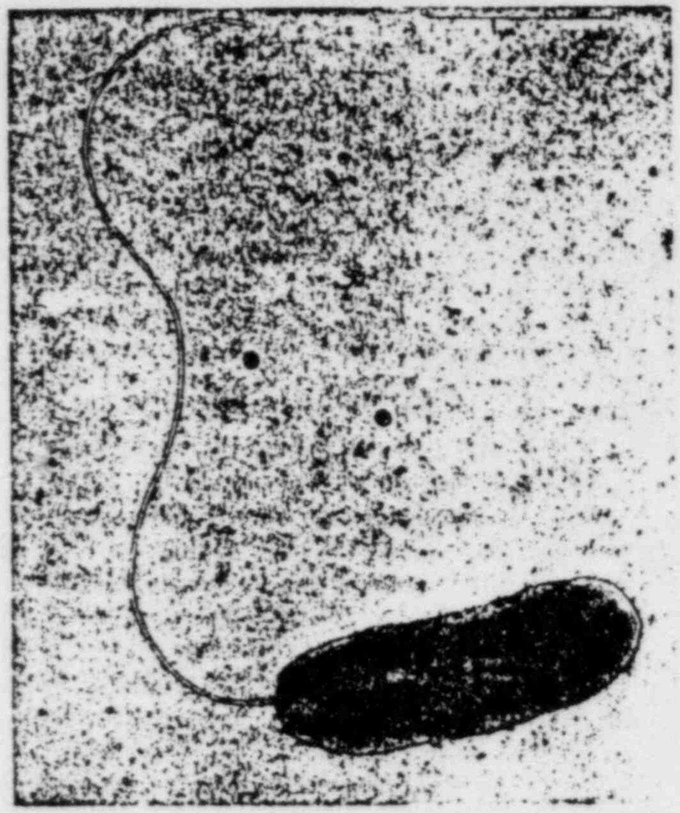

Plate I Electron micrograph of "Desulfovibrio vulgaris" (Hildenborough)—usual form. By courtesy of the National Physical Laboratory. Crown copyright.

are known to be involved in corrosion. These organisms are also obligate anaerobes; they are straight or curved rods, usually single but sometimes in pairs or short chains. They produce terminal or subterminal spores, accompanied by slight swelling of the cells; they are motile, using peritrichous flagella to give a "twisting and tumbling" motion which is easily distinguished from Brownian movement.

Plate II Spirilloid form of a mesophilic "Desulfovibrio". Crown copyright.

Dtm. nigrificans, formerly classified as *Clostridium nigrificans*, measures about 0·3–0·5 μ by 3·0–6·0 μ. It is thermophilic, with an optimum growth temperature of 55°C. Growth occurs even at 65–70°C, and the organism can be trained to grow at 30–37°C. *Dtm. orientis*, 1·5 μ by 5·0 μ, is a mesophile with optimum growth between 30 and 37°C and an upper limit of 42°C.

The pH range of *Desulfotomaculum* is similar to that of *Desulfovibrio*. All the sulphate-reducers are heterotrophic, i.e. they require an organic source of carbon. Energy for growth is supplied by the reduction of sulphate to sulphide. All the sulphate-reducers can effect this reduction at the expense of the corresponding oxidation of organic material; many of them can also effect it at the expense of

the oxidation of elementary hydrogen. The latter property governs, at least partially, the involvement of these bacteria in corrosion phenomena.

The vigorous growth of sulphate-reducers demands reducing conditions more rigorous than can be obtained simply by the exclusion of oxygen, and a redox-potential of around −100 mV (normal hydrogen scale) is necessary if the bacteria are to thrive. In the absence of interfering influences, however, even a marginal growth will produce sufficient hydrogen sulphide to reduce the redox-potential to a more favourable value, so that growth once begun tends to accelerate.

DETECTION TEST

There is again a simple test available for the detection of sulphate-reducers. In this case, the medium (due to Baars(30)) consists of:

KH_2PO_4	0·5 g
NH_4Cl	1 g
$CaSO_4$	1 g
$MgSO_4.7H_2O$	2 g
Sodium lactate	3·5 g
tap water	1 dm^3

The medium is sterilised by autoclaving and the pH adjusted to 7 to 7·5. About 1 g of the suspect material is placed in a sterile screw-capped bottle of about 10 cm^3 capacity, and the bottle is filled to the brim with the sterile medium. A small flamed crystal of ferrous ammonium sulphate is added (*c.* 10 mg), and the stopper is screwed home so that air is not trapped inside the bottle. (For liquid samples, double-strength medium is recommended, using equal volumes of this and the sample. For samples of a marine origin, the medium should be supplemented with 2·5 per cent sodium chloride.)

The bottle is incubated at 30°C (55°C for thermophiles). Presence of the bacteria is indicated by blackening of the medium due to the production of ferrous sulphide. 2 or 3 days incubation is often sufficient for heavily-contaminated samples; up to 21 days should be allowed before negative results are affirmed. An absolute minimum of time should elapse between sampling the suspect material and closing the culture bottle; this prevents undue oxidation by exposure to air and inhibition of any sulphate-reducing organisms present.

The sulphate-reducers are widely distributed in nature; using efficient technique, they can be isolated from most soils. They occur also in natural and polluted fresh and salt water, in hot springs, in oil wells, in temperate and in tropical environments; they have been found (including the thermophilic types) even in the Antarctic permafrost.

3. Bacterial Corrosion in the Presence of Oxygen

Corrosion due to the activity of micro-organisms in aerobic conditions is invariably the result of the production of a corrosive metabolite. Usually this is an acid, either mineral or organic.

A wide range of organisms may be concerned in corrosion of this type, but thiobacilli, the sulphur-oxidising bacteria, are by far the commonest and most important. Situations in which the bacteria have been unequivocally incriminated are comparatively rare, but it seems probable that this is often due to inadequate diagnosis of the cause.

When corrosion occurs in an environment containing a substantial amount of sulphuric acid, and there is no immediately-obvious explanation of its origin, thiobacilli should be suspected. The presence of the organism may be confirmed using the simple test already described, and an investigation of the circumstances of the corrosion will usually reveal the source of sulphur.

A typical example of this type of corrosion was experienced on a housing estate in South London, where gas pipes laid in a peaty soil were perforated by corrosion in little over a year. It was found that the soil had a pH of about 2, and a sample stored in the laboratory for about a week continued to become more acid, reaching eventually a pH of 0·6. Thiobacilli were shown to be active in the soil, and the source of sulphur was traced to the diffusion of hydrogen sulphide from a lower level; sulphate reduction was occurring in a layer of anaerobic clay, due to the action of sulphate-reducing bacteria.

CORROSION OF CONCRETE

There are several species of sulphur-oxidising bacteria with different optimum ranges, and it is possible for very low pH values to develop from conditions of near-neutrality (or even alkalinity) by successive dominance of the various types. Most metals susceptible to acid attack may be affected, but some of the most impressive examples of corrosion by this mechanism have involved concrete.

An example of concrete corrosion, investigated by Parker(23) in Australia involved concrete pipes carrying sewage; it demonstrated both chemical and microbiological processes at work. The pipes were not completely filled, and the concrete surface in contact with the air above the liquid was exposed to the combined action of carbon dioxide and hydrogen sulphide in condensate from the slightly warm and fermenting sewage. The carbon dioxide gradually reduced the pH from its original value of about 12·5 to around 8·5; the hydrogen sulphide was partially oxidised by the air to a mixture of thiosulphate and polythionates, which further reduced the pH to about 7·5.

In the early stages of the oxidation, while the pH was still around 10, a wide variety of organisms slowly oxidised thiosulphate and polythionates to polythionates and sulphate. When the pH had fallen below 9, *Thiobacillus thioparus* began to show significant activity, forming elementary sulphur, the pH continuing to fall to about 5. At this stage, *Th. concretivorus* and *Th. thio-oxidans* took over, oxidising the sulphur to sulphuric acid; this resulted in a rapid fall in pH to around 1, causing the concrete to disintegrate.

It is interesting to note that the almost unique conditions in a concrete sewer pipe are precisely those that favour development of these particularly destructive organisms.

Other examples of this type of corrosion have caused the collapse of massive concrete cooling towers. There are many cases of corrosion of building stone (Plate III), and the archaeological treasures of Angkor Vat, the ancient temples of Cambodia (Plate IV) are in great danger from the same cause. Although the phenomenon is comparatively unusual, its results can be spectacular.

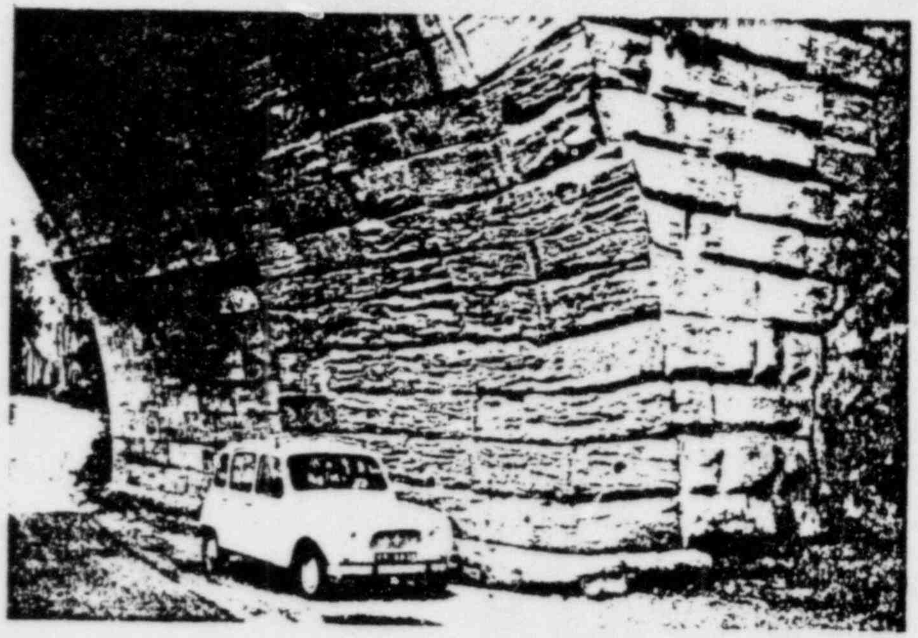

Plate III Acid corrosion of building stone. By courtesy of J. Pochon and C. Jaton.

CORROSION OF IRON AND OTHER METALS

The iron-oxidising organism, *Ferrobacillus ferro-oxidans*, another autotroph, is often found in association with thiobacilli, commonly in the vicinity of pyritic deposits, e.g. in mines. The organism derives energy for its metabolism from the reaction $Fe^{2+} \rightarrow Fe^{3+} + e$.

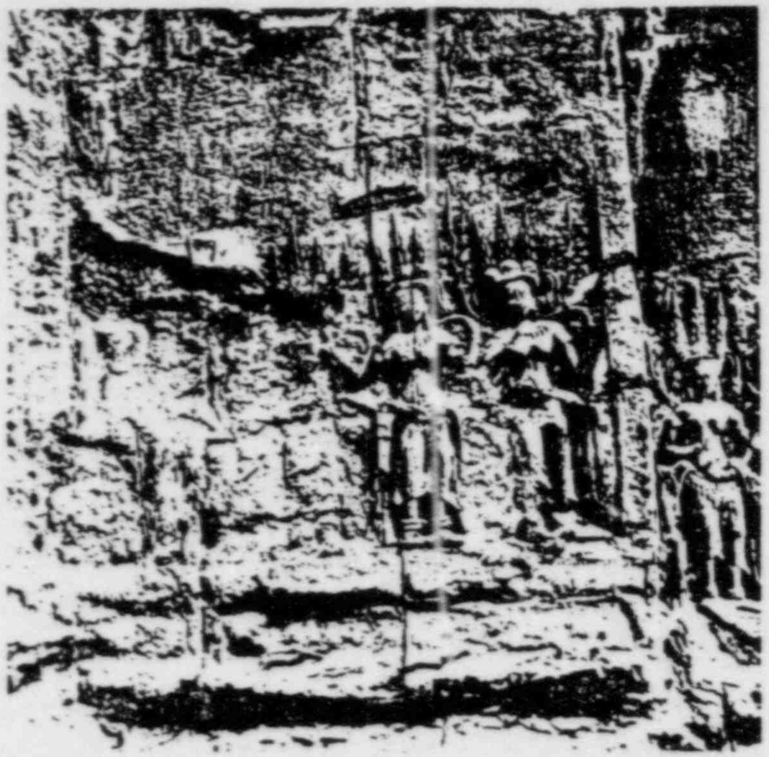

Plate IV Corrosion of historical monuments by sulphur-oxidisers in Cambodia. By courtesy of J. Pochon and C. Jaton.

The ferric iron produced in this way will oxidise sulphur compounds to sulphuric acid. About a million tons of sulphuric acid are contributed annually to the drainage area of the Ohio River as a result of oxidation by this organism of the pyrite in the mines of Western Pennsylvania. Severe corrosion of pumping and other mining machinery results from action of this sort. Problems have arisen even in museums, where mineralogical and palaeontological specimens based on a pyrite matrix,

often of great value and great beauty, have been destroyed by the action of these bacteria; the phenomenon is described as "fossil disease".

On the credit side, the activities of sulphur-oxidising bacteria have been put to constructive use. They have been used to accelerate the natural leaching of low-grade ores in the recovery of copper and uranium, and a considerable research effort is being made to improve the efficiency of the process.

For many years, an unusual form of corrosion of lead cable sheathing in underground situations was known as "phenol corrosion". It was believed to be caused by phenols in the tar-impregnated wrapping materials used as a protective for the lead, and much conflicting evidence accumulated on the corrosivity of phenolic compounds towards lead. Eventually, Coles and co-workers(16) showed that the real cause of the corrosion was the presence of organic acids of low molecular weight; these were produced by bacterial and/or fungal decomposition of cellulosic material in the wrapping material itself or in the soil. The use of cellulosic wrapping materials, such as hessian, as reinforcing insert for protective coatings is thus to be deplored.

Examples of organic-acid corrosion of iron, copper and aluminium associated with fungal growth have been reported. Allen *et al.*(31) have described the corrosion of steel in a sugar-beet factory, caused by *Lactobacillus*.

A potentially serious situation can arise by the development of acidity and consequent corrosion in aluminium fuel tanks on aircraft. A wide variety of organisms has been isolated from this unusual environment. *Aerobic* organisms include the fungus *Cladosporium resinae*; organic acids secreted by the organism have been blamed for this type of corrosion. The bacterium, *Pseudomonas aeruginosa*, an occasional human pathogen, may also make a significant contribution; Blanchard and Goucher(10) have isolated a high-molecular-weight corrosive substance of unknown composition from laboratory cultures.

Although most examples of bacterial corrosion in the aerobic environment can be identified as acid corrosion, there are instances of the production of alkali, especially ammonia. This was reported by Bengough and May(32) in 1924. More recently, workers in France(33) have demonstrated the accelerated corrosion of copper in the laboratory by cultures of *Flavobacterium hydrophilium*; no proven cases are known from the field.

4. Bacterial Corrosion in the Absence of Oxygen

IRON AND STEEL

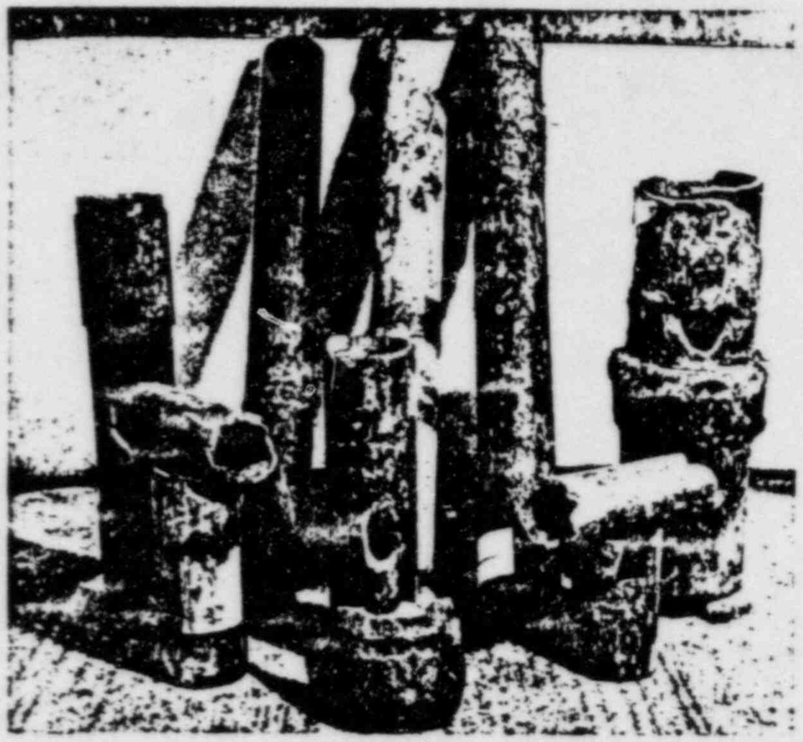

Plate V Cast-iron pipes from anaerobic soils. By courtesy of the National Physical Laboratory. Crown copyright.

Most instances of serious corrosion involving micro-organisms in the absence of oxygen (*anaerobic* conditions) concern iron and steel. Electrochemical considerations spoilage organism in canned foods. It has an optimum-growth temperature of 55°C and an ability to *survive* at very much higher temperatures (*c.* 80°C). It exists in both positive and negative hydrogenase strains.

The positive strains of *Dtm. nigrificans* behave in the same way as their mesophilic counterparts. They are seldom encountered in problems of corrosion in soil, rivers or the sea, but they appear frequently in corrosion of central-heating installations, heat exchangers and cooling systems operating at elevated temperatures.

NON-FERROUS METALS

Much of the emphasis in any consideration of corrosion problems is placed upon the corrosion of iron and steel. In recent years, however, it has become apparent that aluminium and its alloys are equally susceptible to microbiological corrosion. This is of particular concern to the aircraft industry, where cases of corrosion and failure of aircraft fuel tanks have been ascribed to the action of sulphate-reducing organisms (often in association with other micro-organisms).

Examples of the corrosion of copper, zinc and lead have also been described from time to time. In these cases, the effect may be a "secondary" one, caused by hydrogen sulphide. A low redox-potential environment is a good indication of corrosivity and of suitability for sulphate-reducing bacterial growth. It might be anticipated also that metals such as copper, zinc and lead would exert a toxic effect on the bacteria.

The corrosion rates of non-ferrous metals under reducing soil conditions measured by Denison and Romanoff(37) are substantial, and cannot be dismissed out of hand.

5. Corrosion due to Differential Aeration Situations set up by Bacteria

Consumption of oxygen in the course of metabolism is a feature common to all types of aerobic micro-organism. If microbial action is localised in the neighbourhood of a structure liable to corrosion (e.g. a pipeline) a "differential aeration" cell may be set up between those parts of the structure where the oxygen supply has been depleted and those parts where micro-organisms are not active, and the supply of oxygen remains unaltered. The oxygen-depleted regions will be anodic to the rest, and will become centres for the loss of metal. Tomashov and Mikhailovsky(27) consider that "long-line currents" set up in pipelines by such a mechanism account for much pipeline corrosion.

TUBERCLES

Aerobic iron bacteria, such as *Gallionella ferruginea*, oxidise ferrous iron in solution to the ferric state and effect the precipitation of ferric hydroxides. These organisms are common inhabitants of springs and brooks, and may find their way into water pipes. Precipitated ferric hydroxides can build up on the *internal* surface of a pipe to form hard excrescences known as "tubercles", which are firmly adherent to the metal surface.

A tubercle shields the surface of the pipe from contact with oxygen dissolved in the water, and the surface at the base of the tubercle becomes anodic to those parts of the internal surface of the pipe which are not covered by the deposit. Similar tuberculation phenomena have been described in which other types of iron-oxidising bacteria, e.g. *Leptothrix* and *Crenothrix* have been involved.(38) The relatively small area of anodic surface in these circumstances results in intense localisation of the corrosion, and water pipes are readily perforated.

The problem is often intensified by the fact that the anaerobic region at the base of the tubercle provides a suitable habitat for sulphate-reducing micro-organisms; they proliferate in this region and add their own contribution to the total corrosion. When a tubercle is chipped away, the area in contact with the metal is often rich in sulphide, and active vibrios can be isolated. The 1·5–2·5 per cent sulphide and 1,000 cells/gram reported by Butlin(39) is typical.

There are many other examples of sulphate-reducers taking advantage of the anaerobiosis created by the growth of aerobes. Well documented examples are given by Iverson,(20) in which sulphate-reducers were found in association with *Pseudomonas aeruginosa* and the fungus *Cladosporium*, the whole system being instrumental in bringing about corrosion of aluminium.

Sulphate-reducers are found beneath barnacles attached, for example, to the hulls of ships, where they find an anaerobic micro-climate similar to that provided by a tubercle. Other forms of marine fouling can yield similar conditions. Complex situations prevail at the surface of metal exposed to the waters of an industrialised estuary. Here, corrosion can be caused by water of varying salinity and oxygenation; sulphate-reducers may be active, generally at times of anaerobiosis and in localised situations beneath marine attachments and accretions of corrosion product. The formation and retention of accretions is influenced by movement and turbulence and it is often difficult to assess the importance of microbiological factors in the overall corrosion pattern (Plate X).

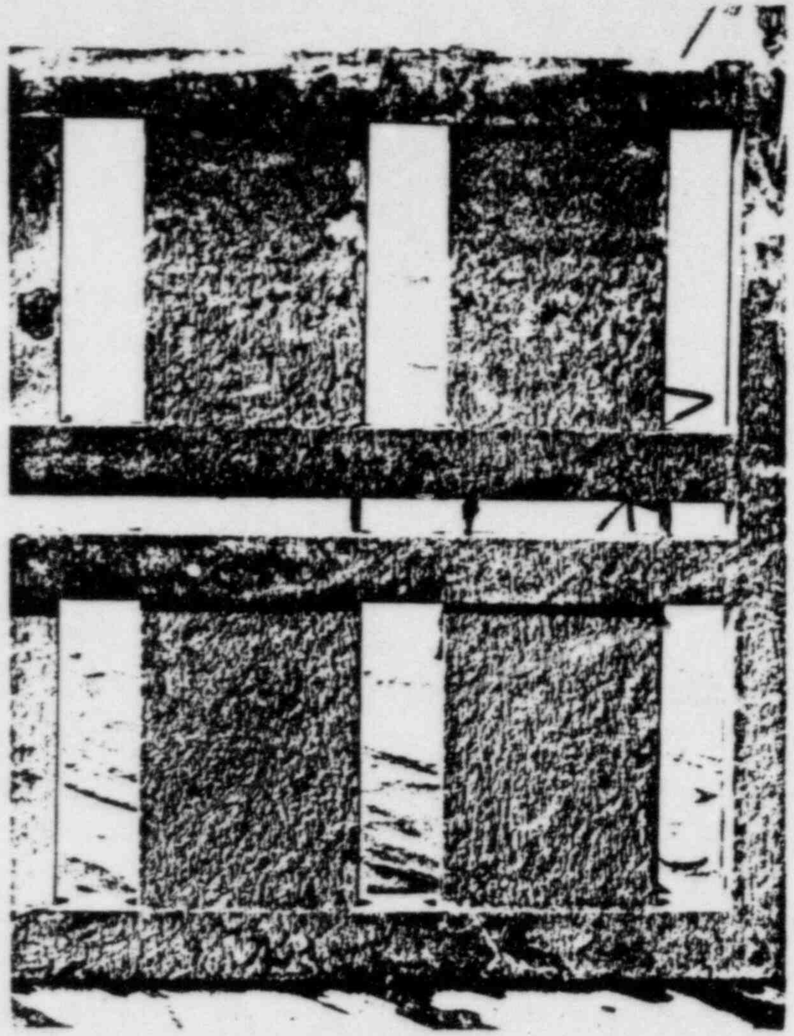

Plate X Bare steel specimens exposed to River Thames for 5 years. Note combination of corrosion and fouling. By courtesy of the National Physical Laboratory. Crown copyright.

7. Prevention of Microbial Corrosion

There is no universal panacea for the prevention of corrosion by micro-organisms, and the problem is usually approached more from the "corrosion" than from the "microbiological" viewpoint.

Elimination of the causative organisms is seldom practicable, except in closed systems, e.g. cooling systems and tanks; even then, precautions must be taken to minimise the risk of reinfection. A controlling additive must penetrate to all parts of the system. Bacterial action, particularly when anaerobes are concerned, is often concentrated in re-entrant crevices and stagnant corners of a closed system; it is commonly associated with deposits. A preliminary mechanical or chemical cleaning process may be essential before the application of a microbial inhibitor can become effective.

INHIBITORS OF MICROBIAL ACTION

Inhibitors of microbial action are of two types. On the one hand, there are the "biocides" which actually kill the organisms; on the other hand, there are the "biostats" that maintain the organisms in a state of inactivity or "non-growth". The distinction between these two classes may be only a matter of concentration; a substance may be bacteriostatic at one concentration and bacteriocidal at a higher one. An efficient bacteriostat, however, may never become bacteriocidal.

An inhibitor for corrosion-producing organisms must possess the following properties:

(a) It must be reliable for the organism concerned. Considerable specificity is involved, and it is important that the causative organism is properly identified.

(b) The inhibitor must *retain* its inhibitory properties in the conditions prevailing, i.e. it must not be deactivated by any other substance likely to be present. It must be stable at the operating temperature of the relevant system and it must be a substance for which the organism cannot develop a tolerance. (The development of strains resistant to disinfection is well known, particularly in the medical field, where pathogenic organisms with an acquired resistance to antibiotics have become a serious problem.)

(c) The inhibitor must not itself display any corrosive action towards the system in which it is to be used.

Difficulties of various types may be encountered in using inhibitors against micro-organisms. The spore-forming thermophilic sulphate-reducer *Desulfotomaculum nigrificans*, for example can be controlled (bacteriostasis) by 0·25 ppm of chlorhexidine gluconate; the mesophile *Desulfovibrio vulgaris* requires 2·5 ppm, *D. desulfuricans* 10–25 ppm, and the obligate halophile *D. salexigens* will often tolerate 1,000 ppm.

Most of the sulphate-reducers are inhibited by 20–50 ppm of cupric ions, but this would not be tolerable (and would not be maintained) in protecting a structure based on ferrous metals. The thiobacilli (sulphur-oxidisers), on the other hand, will thrive in media containing up to 20,000 ppm of copper.

Chromates are good inhibitors of sulphate-reducers and are also good corrosion inhibitors, but they are toxic and tend to be dermatitic, rendering them undesirable in many applications.

In effect, every case requires individual consideration if biological control is to be used as the protective measure. Laboratory experiments may be useful in predicting the possible effectiveness of microbial inhibitors, but laboratory results cannot necessarily be extrapolated directly into field conditions. Field trials are an essential supplement.

METABOLITE REMOVAL

Sometimes, it is possible to control bacterial action by removal from the system of an essential metabolite. Elimination of sources of sulphur, for example, will stop the production of sulphuric acid by thiobacilli. In the complex system described earlier, thiobacilli obtained their sulphur via hydrogen sulphide from fermenting sewage; this might have been prevented by aeration of the sewage during its passage through the concrete pipe. Unfortunately, the damage has often been done beyond repair before it is realised that the problem exists.

OXYGEN

So far as the sulphate-reducers are concerned, the cheapest and most efficient inhibitor is air or oxygen, which is used to establish aerobiosis. Forced aeration of stagnant water has been used to control corrosion in tanks (and, incidentally, to banish offensive odours); the drainage of water-logged soils to improve aeration has been used to control corrosion of buried pipes. The laying of pipelines with a surround of gravel has proved effective, but care is necessary to ensure that such treatment provides a drain and not a sump. In the latter event, conditions may be worsened.

pH

Extremes of pH may be used for controlling sulphate-reducers. Outside the approximate pH range of 5·5–9, activity and growth are almost completely suppressed. Acidic conditions are undesirable from the corrosion point of view, but the maintenance of mildly-alkaline conditions can be helpful in the protection of iron and steel (such conditions can be dangerous in the case of metals that readily form complex anions). This technique has been used with some success by employing a lime or chalk backfill in a trench. There are other methods of providing high pH values in the immediate vicinity of buried metals (see page 55).

PROTECTIVE COATINGS

The commonest method of protecting metals against corrosion is the use of protective coatings, i.e. the interposition of an (ideally) impenetrable physical barrier between the metal and the corrosive environment. A wide range of coatings is available, and the most suitable for use in any given situation must be selected with due regard to the physical, chemical and biological characteristics of that environment.

The coating should not itself undergo degradation, a point sometimes forgotten. Kulman(22) has reported on extensive testing of coatings intended for underground use, and has shown many to be susceptible to attack by soil micro-organisms. Neoprene, asbestos, felt, petroleum wax and asphalt mastic coatings may all undergo some degradation in the soil. Coatings reinforced with cellulosic fabrics are particularly prone to attack. Coatings based on polyethylene or polyvinyl chloride, heavy coherent coatings based on bitumen or coal-tar pitch, with or without mechanical reinforcement by inert materials such as glass fibre, give good results and are relatively cheap to apply.

It is important that there should be a good physical bond between a coating and the surface it is designed to protect.

Moisture beneath a poorly-bonded coating may contain an assortment of micro-organisms, and conditions for the establishment of anaerobiosis are excellent. By the same token, the coating should be free from defects, pinholes and mechanical damage sustained after its application; it should have low absorptive capacity for water, and the outer surface should be free from protuberant reinforcing material liable to sustain any "wicking" action.

CATHODIC PROTECTION

Theoretically, the technique of cathodic protection of metals should be foolproof. Corrosion of the vulnerable surface is rendered impossible, as all anodic areas are eliminated by making the entire structure into the cathode of an electrochemical cell. The achievement of this state of affairs is a technology in itself.

Two techniques of cathodic protection are commonly employed: (1) the "sacrificial" method, in which the structure to be protected is electrically bonded to anodes of a more electronegative nature which are corroded preferentially, and (2) the "impressed current" method, whereby a direct current is passed into the protected surface, through the corrosive environment, from anodes of a remotely-situated inert or scrap metal material by means of a direct-current generator.

In normal circumstances, protection of steel is achieved when its potential is depressed to −0·850 volts (referred to the $Cu/CuSO_4$ electrode). Practical experience has shown that, in the presence of active sulphate-reducers and/or sulphides, it is necessary to depress the potential by a *further* 0·100 volts, i.e. to −0·950 volts ($Cu/CuSO_4$) to achieve the desired protection. This extra requirement is predictable from the thermodynamic considerations of Horvath and co-workers(18) and is further substantiated by laboratory experiments using pure cultures of the bacteria by Booth *et al.*(13)

The use of cathodic protection gives a bonus in so far as restriction of the action of the sulphate-reducers is concerned, since its application results in the development of alkaline conditions in the immediate vicinity of the surface. This has an inhibitory effect on the bacteria.

In order to reduce current drain from the protected system to an economic level, cathode protection is applied wherever possible in combination with a good protective coating. In such a case, the function of the cathodic protection is to cover any faults in the coating.

NATURAL PROTECTION

In 1950, in the course of archaeological excavations in York, a number of extremely well-preserved iron objects dating from the Roman occupation were unearthed from soil in which microbial corrosion would have been expected to have been very severe indeed (Plate XII). The same phenomenon has been observed in many other cases, and some museums—notably the Guildhall Museum in the City of London—have impressive exhibits of archaeological specimens preserved in this way. The soils in which these specimens are found are usually water-logged black clays and silts containing, in addition to the well-preserved iron, quantities of bones, leather and wood. For a long time, it was considered that preservation was due to the inhibition of the sulphate-reducing bacteria, abundant in the soils, by traces of tannins emanating from the leather and wood. Experiments showed, however, that tannins were not inhibitory to the bacteria unless the concentration was sufficiently high to shift the pH below a value of about 6. The "non-aggressive" soils concerned were always around pH 7 and contained only traces of tannins.

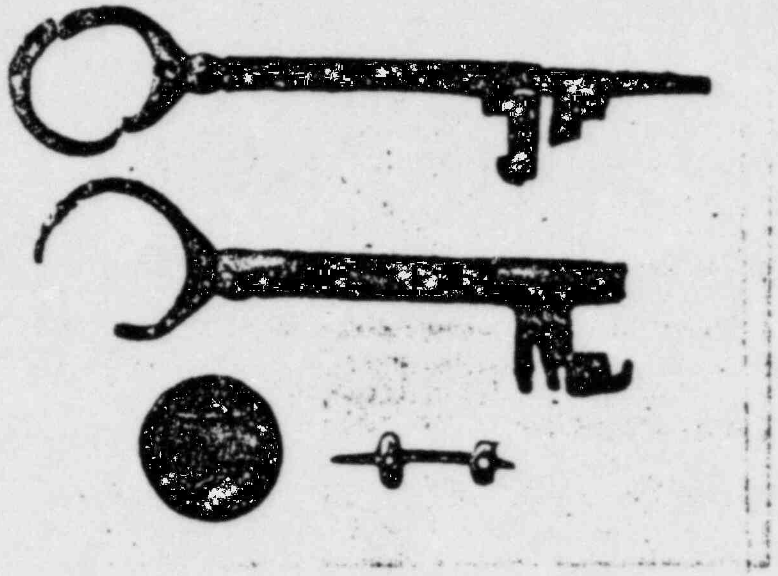

Plate XII Well preserved metal objects recovered from Hungate, York. By courtesy of the Department of the Environment. Crown copyright.

The preserved objects are covered with a thin, compact and strongly-adherent black film, often carrying a light-blue bloom. Analysis showed this coating to be largely of the basic ferrous phosphate, vivianite ($3FeO.P_2O_5.8H_2O$). Polarisation test on the objects revealed intense anodic inhibition of the escape of ferrous ions into solution. The general condition of the objects and the absence of any detectable quantities either of oxide or sulphide suggests that there had not been any appreciable corrosion in either aerobic or anaerobic circumstances before the vivianite coating was laid down; it can be inferred that this occurred soon after the time of burial.

We have no knowledge of the mechanism of formation of this highly efficient "natural" protective coating, nor whether its equivalent could be produced artificially. The conditions in which it arises are clearly very different from those in which industrial phosphate coatings are applied and from those to which iron articles are normally exposed in use. There is clearly scope for much useful work on this intimidatingly complex system; the results could be of immense economic importance.

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EXHIBIT 8

Memorandum: Telephone Conversation, April 19, 1985 (1:30 P.M. M.S.T.)
Between: Daniel H. Pope, Rensselaer Polytechnic Institute, Troy, N.Y.
and Myron L. Scott (affiant), C.R.E.E., Tempe, Arizona.

Prof. Pope's qualifications include authorship of Microbiologically Influenced Corrosion of Industrial Alloys, A State of the Art Review published by Materials Technology Institute, Columbus, Ohio, consultation for numerous contractors including Bechtel Power Corporation, and a contract with EPRI for a general text on MIC in nuclear power plants.

Pope stated that he is only generally familiar with the current MIC situation at Palo Verde, but could offer generic comments.

Pope identified five "concerns" in any alleged case of MIC:

1. Correct diagnosis of causative agent. Gallionella and MIC generally "over-diagnosed." Several other organisms could produce same or similar physical characteristics as gallionella. Mere presence of a microorganism insufficient to establish its role as causative agent. Others could be present. Indeed, gallionella nodules can provide a habitat for sulphate-reducing bacteria. Relatively few labs and technicians are qualified to accurately identify gallionella.

2. Accurate identification of causative agent essential to effective treatment. Treatment and monitoring must be specific to the verified causative agent. Improper identification can result in counterproductive action. Treatment that is effective for some bacteria might cause gallionella or other organisms to flourish.

3. Diagnosis and treatment efficacy should be verified experimentally. To confirm identification of causative agent and to verify effectiveness of proposed treatment program, the treatment should be tested experimentally on samples in the laboratory before field application.

4. Corrosion must be removed. "Whenever possible, as the first step, we must rid ourselves of the nodules and all underlying corrosion." Otherwise, treatment is likely to be ineffective and corrosion can spread. When it is impossible to physically remove all corroded areas, "I recommend thorough chemical cleaning, followed by treatment to keep it sterile." It is not enough to kill the bacteria. Corrosion in the under-deposits must also be removed or corrosion process can continue "almost autocatalytically."

5. Absolute followup monitoring on a frequent and regular basis. The correct monitoring technique is organism-specific.

In response to questions, Pope confirmed that gallionella could be transported through transfer of water or nodule materials to other systems. Verified that gallionella (and other MIC agents) could potentially be spread to "other, separate systems which are connected to the spray ponds" by piping, etc. Would recommend inspection and monitoring of other systems in all probability.

Pope asked nature of ANPP proposed corrective action which was read to him. "Why should you aerate if the causative agent is gallionella? Gallionella is aerobic; it requires oxygen." Aeration might make sense for sulphate-reducers, but not for aerobic, iron-oxidizing gallionella. When informed that ANPP proposed using spray nozzle circulation to reduce stagnation which led to MIC, Pope commented: "That may well be. But once it is established, oxygen will cause the gallionella to flourish."

"We have found few methods of treatment to be truly effective. Organic biocides are generally not effective." Chlorine in the form of chloride can be counterproductive, can cause some problems with stainless steel. Ozone treatment is "phenomenally successful, but should be preceded by cleaning out the corrosion." Cleaning (corrosion removal) and ozone are generally recommendable.

The foregoing is accurate to the best of my recollection and belief, and has been reviewed by Mr. Pope.

Done this 30th day of APRIL, 1985.

Myron L. Scott

Myron L. Scott

SUBSCRIBED AND SWORN TO before me by Myron L. Scott this 30th day of April, 1985.

Lyn M. Brewster

Notary Public

My Commission Expires:

May 22, 1988

Memorandum: Tele-con, April 30, 1985 (8:30 A.M., M.S.T.)
Between: Daniel H. Pope; Myron L. Scott (affiant)

Prof. Pope stressed that he was unfamiliar with the specifics of the PVNGS situation. Therefore, all his comments were general in nature, and based upon his statements in published work and statements at professional conferences. However, "based on what data there is in that (ANPP: "Evaluation of Spray Pond Weld Corrosion at PVNGS," April 3, 1985), there are some questions I have":

1. Who identified the causative agent as gallionella? Metallurgist was consulted, on Pope's personal knowledge. Metallurgist is qualified to analyse metal characteristics, and those characteristics could be compatible with gallionella. However, the same corrosion characterstics could be compatible with several other bacteria. Only a microbiologist specializing in the MIC field is qualified to make a positive diagnosis of the causative agent.

2. (Page 2) The "enormous number" of indications cited for the Unit 2 North spray pond not necessarily consistent with numbers for other ponds. Although not a statistical analyst, working knowledge of characteristics in field suggests such statistical exptrapolation prone to errors. Intervening variables likely to affect such calculations include site of each pond, flow rate differentials, etc.

3. (Page 5) Methodology for determining thermal impact appears methodologically sound and utilizes apparently conservative assumptions. However, the analysis is premised upon one critical assumption: APS "assumes there will be no further incidences. That there will be no increase in the number and size of the indications. That is something that can only be established over time, through regular metallurgical and microbiological monitoring."

The only other way to assure no further incidence is to make sure your treatment program has killed all the bugs and stopped the processes. Then you could still have metallurgical processes which could cause the corroision to worsen. Generally, we must rid ourselves of both the microorganisms and the corrosion."

Confirmed that replacement or cleaning is the indicated first step where feasible. Specific recommendations would tend to be site-specific. Frequently, biocidal treatment is ineffective unless preceded by cleaning. APS' "Evaluation" acknowledges by indicating (page 2) "pits are expected to continue to grow" at unpredictable rate.

Flushing could spread microorganisms to other isolated systems. Or microorganisms could migrate if not removed.

Chlorine has limited effectiveness against nodules. In an experiment reported to the National Disinfection Conference, Pope cultured small gallionella nodules on 304L stainless steel in five days using Troy city tap water. Nodule film was very thin, but some growth had occurred. Then treated with 3 parts-per-million and 10 parts-per-million chlorine. 3 ppm chlorine had no effect. 10 ppm penetrated the "exceptionally thin film" in three days. Further experimental work needed, but this experiment demonstrates that nodule film is resistent to chlorine to a measurable degree.

Absent cleaning, second best treatment program involves use of ozone. Ozone also is environmentally benign (doesn't produce THMs, etc.), appears to create fewer materials problems, and is demonstrably more effective in penetrating film and re-passivitizing stainless steel.

However, more experimental work required.

The foregoing is accurate and complete to the best of my knowledge and belief.

Done this 3rd day of MAY, 1985.

Myron L. Scott

Myron L. Scott

SUBSCRIBED AND SWORN TO before me by Myron L. Scott this 3rd day of May 1985.

Lyn M. Brewster

Notary Public

My Commission Expires:

May 22, 1988

EXHIBIT 9

Arizona Nuclear Power Project
P O BOX 52034 • PHOENIX, ARIZONA 85072-2034

(101) 2077 P

December 14, 1984
ANPP-31489-TDS/TRB

U. S. Nuclear Regulatory Commission
Region V
1450 Maria Lane - Suite 210
Walnut Creek, California 94596-5368

50-528
529
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Attention: Mr. D. F. Kirsh, Acting Director
Division of Reactor Safety and Projects

Subject: Final Report - DER 84-40
A 50.55(e) Reportable Condition Relating To Unit 2 Auxiliary
Feedwater Pump Has Corrosion.
File: 84-019-026; D.4.33.2

Reference: A) Telephone Conversation between J. Ball and T. Bradish on
June 5, 1984
B) ANPP-29867, dated June 29, 1984 (Interim Report)
C) ANPP-30566, dated September 19, 1984 (Time Extension)
D) ANPP-30930, dated October 23, 1984 (Time Extension)

Dear Sir:

Attached is our final written report of the deficiency referenced above, which has been determined to be Not Reportable under the requirements of 10CFR50.55(e).

Very truly yours,

E. E. Van Brunt

E. E. Van Brunt, Jr.
APS Vice President
Nuclear Production
ANPP Project Director

EEVB/TRB/nj
Attachment

cc: See Page Two

IE-27

FINAL REPORT - DER 84-40
DEFICIENCY EVALUATION 50.55(e)
ARIZONA PUBLIC SERVICE COMPANY (APS)
PVNGS UNIT 2

I. Description of Deficiency

The resolution of DER 83-66 required rework of all auxiliary feedwater pump impeller assemblies. Upon inspection by Bechtel Engineering at the Supplier's (Bingham-Willamette Co.) facility for rework as described in DER No. 83-66, it was noted that the impeller assemblies for Auxiliary Feedwater Pumps 2-M-AFA-P01 (turbine driven and 2-M-AFB-P01 (motor driven) had areas of corrosion with the turbine-driven pump having the greatest concentration. Analysis of the deposits indicated the presence of bacteria associated with "Microbiologically Influenced Corrosion" or MIC. Examination of the pump cases for these pumps also showed evidence of corrosion.

Nonconformance Reports (NCRs) MC-2229 and 2230 were initiated to document the condition for the pump cases. The corrosion on the pum rotating assemblies had been noted upon receipt of the assemblies at the supplier's shop. A separate inspection plan (Engineering log numbers M021-230 and 300) and Purchase Order Revision to P.O. 10407-13-MM-021 were initiated to determine the extent of corrosion on the rotating assemblies, and to determine if the assemblies' safety function had been adversely affected.

Evaluation

A. Background:

Microbiologically influenced corrosion is defined as the deterioration of a metal by corrosion processes which occur directly or indirectly as a result of the activity of living organisms.

Microorganisms that influence corrosion are found in soils, in natural waters such as well water, in oil wells, in silty river bottoms, in municipal sewage systems, and in numerous industrial environments. These living bacteria can be carried into a syste in dust or sand. There are various types of microorganisms that influence corrosion; some are anaerobic and others aerobic. The mechanisms whereby they influence corrosion vary with the type o microorganism and the type of material involved. The details of some of the mechanisms of MIC are not completely understood. Microbiologically influenced corrosion requires both moisture an nutrients to occur. It occurs in a pH range of 0 to 10.5 and only where the velocity is below 3 ft/sec. It can result from water being left in systems after hydrostatic test. Natural waters, particularly well waters, and soil, including airborne dust and sand contain several classes of microorganisms that thrive in mo[illegible] environments and greatly accelerate metal corrosion.

These bacteria, as with any living organism, require certain conditions for growth, including nutrients. Open cooling systems, such as cooling towers, have almost unlimited nutrient sources from the air and dead organisms after chlorination. In systems which carry demineralized water, only traces of nutrients are present after flushing has removed the dirt debris from the construction process. Therefore, those safety-related systems at PVNGS which carry demineralized water in unlined pipe do not have the most favorable conditions for MIC.

B. Inspection of Auxiliary Feedwater Pumps and Piping:

In order to determine the extent of damage from the effects of MIC in the auxiliary feedwater system and provide a basis for further inspection and repair, if necessary, NCRs MC-2229 and 2230 were interim dispositioned as follows:

1. Inspect with radiographs the areas in the auxiliary feedwat system piping which could be sensitive to MIC.
2. Inspect the pump casings using dye-penetrant examination an grinding to base metal.

The impact of MIC on the rotating elements was evaluated by Bingham-Willamette Co. in accordance with the inspection plan referenced above.

The inspection program per NCRs MC-2229 and -2230 showed no extensive corrosion of the pump casings from the observed corrosion. In addition, radiographs of weld metal, known to be particularly susceptible to MIC, showed no evidence of corrosion. Samples of water from the pump casings showed traces of MIC bacteria.

The pump rotating assemblies were examined by Bingham-Willamette Co. Any surface corrosion was removed by a sand-water slurry, and the components were dye-penetrant examined. Defects were noted and ground out to base metal. An evaluation of the conditions found showed that the ability of the rotating elements to perform their safety function was not adversely affected.

The turbine-driven pump had by far the greatest concentration of corrosion. This is attributed in part to the fact that the pump was never operated (non-availability of steam) and to an inadvertent condition which happened during startup flushing of the system. Both the suction and discharge lines from this pump were separately flushed with the pump isolated from this activity; however, as discovered later, some water had leaked into the pump and was left to stand in excess of six months. The pump was not drained after system flush because startup had no knowledge of this seepage. The pump had been approximately half full as indicated by the water line and existence of corrosion on only the lower portions of the pump casings.

During the Unit 1 auxiliary feedwater pump impeller assembly rework described in DER 83-66, this condition was not observed because these assemblies had not been exposed to a long period of standing water. The Unit 3 auxiliary feedwater pumps have not yet been exposed to water at PVNGS.

C. Root Cause:

The root cause of the condition was the undetected retention of flushing water in the feedwater pump casings after the startup flushing operation of the feedwater system. This stagnant water contained sufficient microorganisms, and nutrients, to initiate and sustain a microbiological influenced corrosion process.

II. Analysis of Safety Implications

Evaluations of the rotating elements by Bingham-Willamette Co. and of the pump casings by Bechtel Material and Quality Services have determined that the existence of MIC did not adversely affect the capability of the auxiliary feedwater system to perform its safety-related function.

The auxiliary feedwater system uses demineralized water. Although conditions for bacterial growth existed, no corrosion had occurred. If left undetected, additional use of the system would have eliminated the conditions for growth.

Whereas MIC bacteria probably exists in other safety-related systems at PVNGS the conditions that existed in the auxiliary feedwater system are no more hospitable or inhospitable due to the startup flushing and testing.

Based on the above, this condition is evaluated as not reportable under the requirements of 10CFR50.55(e) or 10CFR Part 21 since if left uncorrected would not represent a safety-significant condition.

III. Corrective Action

This problem is isolated to the Unit 2 auxiliary feedwater pumps.

In accordance with the final dispositions of NCRs MC-2229 and MC-2230, the Unit 2 pump cases were cleaned of corrosion.

All parts of the Unit 2 rotating assemblies will either be cleaned or replaced at the vendor's facility.

The PVNGS Startup Manager has been requested to assure that flushing procedures ensure adequate system cleanliness and to notify PVNGS chemistry whenever there exists the possibility that any safety-related system could be left in a wet, untreated condition for a period in excess of one week. PVNGS chemistry will assure that proper operating and lay-up water chemistries are maintaned to minimize the potential for microbiological and other forms of corrosion.

The PVNGS Operations Managers have been requested to review applicable operating procedures to assure that for shut down periods in excess of one week measures will be implemented to ensure that proper operating and lay-up water chemistries are maintained in safety-related systems to minimize the potential for microbiological and other forms of corrosion.

EXHIBIT 10

SSINS No.: 6835
IN 85-24

UNITED STATES
NUCLEAR REGULATORY COMMISSION
OFFICE OF INSPECTION AND ENFORCEMENT
WASHINGTON, D.C. 20555

March 26, 1985

IE INFORMATION NOTICE NO. 85-24: FAILURES OF PROTECTIVE COATINGS IN PIPES AND HEAT EXCHANGERS

Addressees:

All nuclear power reactor facilities holding an operating license (OL) or construction permit (CP).

Purpose:

This information notice is provided to alert recipients of a potentially significant problem pertaining to the selection and application of protective coatings for safety-related use, especially painting interior surfaces of pipes and tubing. It is expected that recipients will review the information for applicability to their facilities and consider actions, if appropriate, to preclude a similar problem occurring at their facilities. However, suggestions contained in this information notice do not constitute NRC requirements; therefore, no specific action or written response is required.

Description of Circumstances:

1. Spray Pond Piping

While making minor repairs to the spray pond piping system in 1982, Palo Verde Nuclear Generation Station Unit 1 personnel discovered delamination and peeling of the interior epoxy lining in three 24-inch-diameter 90° elbows. Examination of the remainder of the piping system showed similar lining failures in other elbows, such as 3-inch blisters that contained solvent, poor adhesion, soft film, and excessive film thickness. The spray pond is the ultimate heat sink for the Palo Verde Station. During a shutdown where the ultimate heat sink was needed, separation of the epoxy lining from the elbows could potentially cause a flow restriction in the piping system.

The epoxy coating specified was Plasite 7122-H, a product of Wisconsin Protective Coatings Company. This material is formulated to be applied by mechanical spraying equipment in layers 2-1/2 to 4 mils thick with sufficient time allowed for each layer to cure. The use of mechanical spray equipment provides a uniform and controlled coating film thickness. The straight sections of the piping system were coated in this manner. The multilayer mechanical deposition and curing of 12-15 mils of coating in the straight sections of pipe took 7 days, and no discrepancies similar to those in the elbows were found.

However, the elbows were coated in two layers using a hand-held gun. The lining was uneven with the coating up to 25 mils thick. Coating took only 3 days in December of 1980; this reduction in curing time can be critical, especially in the winter when chemical curing and solvent evaporation tends to be retarded. In addition, the elbows were capped after the final coating application and there was insufficient air necessary for curing.

A hand-held gun was used to spray the coating because of the shape of the elbow. There are other methods of applying epoxy coatings that are more controllable and use less solvent. Electrostatic spray uses less epoxy and solvent for the same coating thickness. Electrodeposition in a water solution provides the most uniform coating and does not use solvents. The fluidized bed method will provide the thickest epoxy deposit. Whatever application method is selected, epoxies are thermosetting materials and are normally cured by oven baking or infrared heating. Heating reduces curing time from several days to several hours.

The elbows were repaired by removing the deficient lining, preparing the surface by grit blasting, and recoating with Plasite 9009-IT. The repairs were acceptable and a final report was issued in January 1984.

2. Diesel Generator Heat Exchangers

While operating train A of the spray pond piping system in May 1984, Palo Verde Nuclear Generation Station Unit 2 personnel discovered an accumulation of epoxy material. The jacket water cooler, air after-coolers, and lube oil coolers of all the train A and train B diesel generator heat exchangers had extensive failure of the epoxy coating and resulted in complete blockage of the governor oil coolers.

The failures of the epoxy coating included severe blistering, moisture entrapment between layers of the coating, delamination, peeling, and widespread rusting. The epoxy coating specified was Plasite 7155-H. It is formulated to be deposited in thin layers using mechanical spraying equipment.

An evaluation of the deficiencies showed the presence of cutting oils on the heat exchanger surface before the coating was applied. It is a basic requirement to have a dry, oil-free surface before applying coatings. In addition, the surface was too smooth for the epoxy coating to adhere. Epoxy coatings are applied directly to the metal without a primer and it is necessary to slightly roughen the metal surface. Finally, the heat exchangers were sealed after spraying and there was insufficient air to complete the curing process. Repairs were successfully made with Plasite 9009-IT and a final report was issued in September 1984.

It should be noted that this information notice is not intended to imply that Plasite materials produced by Wisconsin Protective Coatings Company are unacceptable. Other applications using appropriately selected materials and application techniques have been successful.

No specific action or written response is required by this information notice. If you have any questions about this matter, please contact the Regional Administrator of the appropriate regional office or this office.

E L Jordan

Edward L. Jordan, Director
Division of Emergency Preparedness
  and Engineering Response
Office of Inspection and Enforcement

Technical Contact: P. Cortland, IE
(301) 492-4175

Attachment: List of Recently Issued IE Information Notices