B. 16 "Microbiologically Influenced Corrosion (MIC),"
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Introduction

The objective of this topical discussion is to describe the subject of Microbiologically Influenced Corrosion (MIC) as applied to LWRs.

"Microbiologically Influenced Corrosion (MIC)" refers to corrosion that results from the presence and activities of microorganisms. MIC can result from microbial processes that produce corrosive environments such as organic acids or lower valence sulfur. The modes of corrosion, which can result from microbiologically produced local environments, include general corrosion (GC), pitting (PIT), crevice corrosion, de-alloying, galvanic corrosion, intergranular corrosion (IGC), stress corrosion cracking (SCC), and corrosion fatigue (CF).

Generally, the environments produced in the process of MIC are of three types:

- Formation of colonies, which are sometimes of substantial size, within which additional transformations beyond the initial metabolic processes can occur. Such colonies also have some of the features of "crevices" with the additional feature of dynamic changes of internal chemistry.

- Reactions between microorganisms and nutrients, e.g. nitrite oxidized to nitrate, or sulfuric acid/reduced sulfate compounds generated by sulfate-reducing bacteria, with a change in the corrosion modes thereby enabled.

- Corrosion directly on metal surfaces.

The term "microorganisms" includes bacteria and fungi. Both produce metabolic products that are acidic, as well as other byproducts, including sulfides. Some of the byproducts can react with the immediate environment to form corrosive species, acids, etc. The range of temperatures for vitality or growth and metabolic activity of the two are different, with fungi having a lower temperature tolerance limit than bacteria. Bacteria and fungi also differ with respect to the ranges of optimal growth in the sense that fungi and bacteria can survive different ranges and sets of unfavorable conditions. The intensity of MIC and the associated products of the microorganisms depend mainly on the following influences:

- Temperature, with there being a narrow optimum temperature for growth of each species of organisms.

- Water is necessary to the metabolic processes of all microorganisms. Bacteria require liquid (e.g. a thin surface film of liquid on which a biofilm can grow) for growth, but fungi can grow at relative humidity of 60% or higher.

- Oxygen is the electron acceptor for aerobic organisms, but anaerobes can use a variety of other terminal electron acceptors, e.g., SO_4^{2-}, NO_3, Fe(III), Mn(IV), Cr(VI).

- Nutrients including carbon, sulfur, phosphorous, nitrogen, are required. Such nutrients must include the capacity for electron exchange involving oxidation and reduction reactions. In some cases where nutrient availability is limited, secondary metabolic byproducts may be involved in the overall microbiological process and sustain the corrosion.

- Flowing, especially slowly flowing, environments tend to favor the growth of microbes by providing a ready supply of nutrients (in particular, periodically flushed systems). Stagnant areas adjacent to flowing areas are particularly susceptible to MIC (e.g., dead legs in piping).

- Microorganisms can grow in natural and processed waters including marine, potable, distilled, and fresh.

- Some species, e.g. boric acid, are toxic to microbes in high concentrations.

General Features of Microorganisms Relative to MIC

The following general properties concerning microorganisms as applied to nuclear applications are taken from Pope:[1]

- Individual microorganisms are small (from less than two-tenths to several hundred micrometers (□m) in length by up to two or three µm in width) a quality which allows them to penetrate crevices, etc., easily. Bacterial and fungal colonies can grow to macroscopic proportions.

- Bacteria may be motile, capable of migrating to more favorable conditions or away from less favorable conditions, e.g., toward food sources or away from toxic materials.

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

- Microorganisms 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% atmospheres).

- Microorganisms grow in colonies, which help to cross-feed individuals and makes survival more likely under adverse conditions.

- Microorganisms can reproduce very quickly if field conditions are particularly favorable

- Individual cells 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.

- Many can quickly adapt to use a wide variety of different nutrient 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.

- Many form extracellular polysaccharide materials (capsules or slime layers). The resulting 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.

- Many bacteria and fungi 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. Spores may remain viable for hundreds of years and germinate on finding favorable conditions. In the natural environment, there is a difference between survival and growth. Microorganisms can withstand long periods of starvation and desiccation. If conditions are alternating wet and dry, microorganisms may survive dry periods but will grow only during the wet periods.

- Microorganisms 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). 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).

Applications to LWRs

MIC is relatively common in LWR systems such as fire water, service water and low temperature cooling water systems and components, and typically occurs in light water plants in two general locations. One is on external surfaces where there is moisture and other materials, such as organic debris buildup; deposits containing animal droppings, and slimes; secretions; etc. which contain nutrients suitable for bacterial or fungal growth. The second occurs on internal surfaces in low temperature components; primarily those where water is flowing slowly or is periodically flushed; both situations provide a good supply of nutrients for microbiological activity and growth. This is particularly true for systems where deposits can build up, and where these deposits could accumulate bacterial or fungal populations by exposure to water that has been air-exposed.

Truly stagnant systems with no replenishment of nutrients (e.g. not exposed to air) are not favorable for significant MIC activity. Vertical deadlegs, with water flowing by the end of the deadleg, are areas particularly at risk for bacterial growth. It should be noted that periodic flushing, by introducing nutrients and bacteria, is one of the major factors in promoting MIC in piping and tanks. Usually this flushing is carried out for testing purposes and consideration should be given to reducing the frequency of such testing to minimize the risk of MIC. Chemicals that are common in LWR waters can affect the growth of microorganisms, for instance hydrazine and boric acid. MIC is often associated with fouling, the fouling being a combination of bacterial colonies and associated corrosion products, and the MIC damage found under the deposits. These deposits can be significant, resulting in blockage of piping and much reduced water flows MIC and MIC-related fouling have been found in a wide range of systems, from fire protection and service water systems to ECC storage systems and spent fuel pools.

There are several key chemistry-related factors that may affect microbial activity in LWRs:

1. Temperature and pH

Hyperthermophiles (bacteria that can extend their temperature range above that typically found in most water systems) can grow up to a temperature of 110°C. In effect this defines the upper limit for MIC activity, although in practice MIC is rarely found at temperatures above 60°C. Bacteria can grow over the pH range from 0 to about 10.5, in effect the entire spectrum of pH found in LWR systems. Thus the temperature and pH ranges that can sustain microbial activity cover most of the conditions found in LWR low temperature systems.

2. Boric acid

Many LWR systems are borated, and thus are sometimes regarded as protected against microbial activity. The acute boron toxicity level for bacteria is between 8-340 mg/L. Bacteria have a low sensitivity to boron. Metabolism of boric acid is thermodynamically unfavorable. There are no known bio-transformations of borate. Thus borated systems at low temperature may be able to sustain microbial activity at boron concentrations below a few hundred mg/L.

3. Hydrazine

There is relatively little literature concerning the effect of hydrazine on bacterial growth under LWR conditions. Addition of hydrazine to low temperature systems, while common, is not an effective protection against rapid changes in oxygen concentration because the reaction of hydrazine with oxygen at low temperatures is slow, but nevertheless some low temperature recirculated systems do contain hydrazine as an oxygen scavenger. Based on limited data, then, hydrazine sulfate at 1mM is known to be an inhibitor for bacterial utilization of amino acids, although some growth was observed. Hydrazine can be metabolized to nitrogen gas by some nitrifying bacteria or reduced to ammonia by nitrogenase isolated from a nitrogen-fixing bacterium. Only concentrations below 1 mg/liter were completely degraded. Higher concentrations were inhibitory. It seems likely therefore that low temperature systems in LWRs containing a few mg/L (ppm) of hydrazine would be protected against microbial activity and corrosion, whereas for LWR systems containing less than this level of hydrazine, microbial activity would be possible.

Overall it appears, based on limited data, that in LWRs MIC is possible in systems operated with stagnant or intermittent flows and at temperatures less than 100°C, and containing low levels of hydrazine (less than a few ppm). Low levels of boric acid or borate appear to inhibit MIC, and thus systems containing boric acid are likely protected against MIC.

Over the past 5 to 10 years there has been an increase in reported incidences of MIC-related degradation, especially of underground systems and systems which have been flushed regularly as part of a testing program (for instance fire water systems and safetyrelated systems), a practice that renders carbon steel piping susceptible to MIC. This has led to leakage of underground piping, plugging of heat exchangers and fire protection piping, plugging of strainers with bacterial growth, failure of tensioning cables, etc. In short, in any low temperature location where deposits and bacteria can build up, and especially where periodic replenishing of nutrients can occur, as with flushing of piping, carbon steel components can degrade through the action of MIC. This experience has led to the increasing use of plastic or epoxy piping in low temperature, low pressure systems. Such piping is immune to MIC degradation, although it may still be susceptible to buildup of deposits caused by microbial activity.

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References for B.16

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[2] ND Luchini, GA Broderick and DK Combs, "In Vitro Determination of Ruminal Protein Degradation Using Freeze-Stored Ruminal Microorganisms," *J Animal Science 74*, 1996.