DEGRADATION OF CANDU FIRE PROTECTION SYSTEMS: PAST, PRESENT AND FUTURE

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Abstract

Recently, corrosion damage to the fire protection systems (FPSs) of some of the older CANDU® stations has been reported. This corrosion damage has resulted in through-wall penetrations and leaks Similar observations have been made in US nuclear power plants where the older stations have had to make significant and costly repairs because of localized through-wall corrosion (pitting) in their FPSs. As a result of both layout and operational practices, it is apparent that the FPS is often susceptible to microbially influenced corrosion (MIC) causing through-wall pitting. In this paper CANDU case histories will be reviewed to show the nature, extent and mechanism of the MIC in the FPS. The paper will conclude with recommendations from both a future and operational perspective to remedy the situation and prevent recurrence.

Introduction

Over the past few years a number of through-wall corrosion failures of fire protection system (FPS) piping in older CANDU units, have been reported. Failure analysis has often shown a build up of tubercles[1] of both microbial and non-microbial origins, associated with the failure site. In each case the cause of the failure has been attributed to microbially influenced corrosion (MIC). This problem is not unique to CANDU plants (or to power plants in general) and has been known for some time to be a major problem in many of the US pressurized water reactors (PWRs) and boiling-water reactors (BWRs) that are older than the CANDU stations currently operating in Canada.

Two aspects of system degradation are of concern in the FPS. First, the build up of corrosion product, tuberculation, on the inside of pipes can drastically reduce the diameter of the pipe and severely restrict the flow of water through the pipe. Second, microbial degradation of the material can lead to pitting and eventually to through-wall failures. Both forms of degradation are difficult to detect until leaks or loss of flow become apparent. Both forms of degradation will often be missed by the routine inspection programs currently employed by most stations to assess the condition of the FPS.

The Electric Power Research Institute (EPRI) has supported many initiatives to address the problem of MIC within the FPS over the last few years. Recognition of the potential problems by EPRI and many US utilities, led to the development of guidelines for the evaluation and treatments of corrosion and fouling in FPSs (EPRI 1999). The attention paid to the issue and the resulting guidelines marked a fundamental change in thinking. The first acknowledgment of the issue came in 1988 when Licina discussed MIC in nuclear power plant FPSs in the EPRI sourcebook for MIC in nuclear power plants (Licina 1988). However, although acknowledging the problem, it was suggested that, because of the difficulty of cleaning the system and implementing other large scale remedial methods, mitigation is prohibitively expensive compared to the perceived severity of the problem. This statement is no longer true with our improved understanding of the basic mechanism of the degradation and in view of today's operating environment.

The intent of this paper is to show that, through a basic understanding of degradation mechanisms as they apply to the FPS, simple but effective measures can be implemented in the system layout and operation to prolong the life of the FPS and lessen the risk of through-wall failures.

Degradation mechanisms

Microbially influenced corrosion does not proceed by a unique corrosion mechanism. Rather, the

[1] Mounds of corrosion product attached to pipe wall.

bacteria modify the local environment in such a way as to enhance the initiation or propagation of localized forms of corrosion such as pitting, crevice corrosion, or galvanic corrosion (Angell 1999). The bacterial actions that promote MIC are different for different alloys. Therefore, even though sulphate-reducing bacteria (SRB) have been implicated in the corrosion of many different metals, thereby suggesting a common mechanism, it is known that the mechanism of corrosion for carbon steel is very different from that for stainless steels and from that for copper alloys. However, because FPSs are normally constructed from carbon steel, the discussion in this paper will be limited to this material. Even considering only carbon steel, a number of different genera and species of bacteria have been implicated in its MIC. The large variety of bacteria involved, can conveniently be grouped into four diverse phenotypic groups:

- sulphate-reducing bacteria (SRB)
- iron-oxidizing bacteria (IOB) and manganese-oxidizing bacteria
- acid-producing bacteria (APB) or fungi
- slime (exopolymeric substance) forming bacteria

Microorganisms that form surface biofilms are capable of maintaining an occluded environment that is radically different from the bulk water in terms of pH, dissolved oxygen, and organic and inorganic species. In some cases, these interfacial conditions could not be maintained in the bulk medium at atmospheric pressure and room temperature. As a result, MIC can lead to the production of corrosion products that would not be predicted from abiotic experiments and thermodynamic analyses of the bulk water conditions.

Sulphate-Reducing Bacteria

Of all the diverse bacteria involved in corrosion, sulphate-reducing bacteria have received the greatest attention. This heterogeneous group of bacteria is capable of using sulphur compounds as their terminal electron acceptor. The majority of SRB are incapable of normal aerobic oxidation where oxygen is the terminal electron acceptor. As a result, the SRB are often classified as strict anaerobes although oxygen is not toxic to the cells and merely inhibits growth. The precise mechanism of SRB corrosion continues to receive considerable attention. Sulphate-reducing bacteria survive and grow in pipes either in anaerobic niches under deposits such as iron oxide or within a biofilm under a layer of aerobic bacteria.

In the case of carbon steel, three basic mechanisms have been suggested for the corrosion that results from the presence of SRB:

- *cathodic depolarization.* Bacterial consumption of cathodically produced hydrogen promotes iron dissolution at the anode.
- *metabolic sulphide, by generating/renewing the cathode.* It has been suggested that a galvanic corrosion cell can be established because iron sulphide is cathodic to metallic iron. Also, the deposition of a conductive corrosion product might offer an increased surface area for the cathodic reaction.
- *metabolic regulation of local pH.* This model suggests that the metabolic products of SRB are able to regulate the pH of their local environment. This can result in a pH value in the region underneath a bacterial colony that is lower than that of the surrounding non-corroding area (cathode).

It is widely recognized that in laboratory studies, none of the above mechanisms has been able to account for the high corrosion rates occurring or observed in the field (Hamilton, 1985). This situation is most likely the result of microbial corrosion being the complex and synergistic interaction of a number of corrosion mechanisms caused by a number of different bacteria.

Iron-oxidizing Bacteria

The chemoautotrophic[2] iron bacteria that derive energy from the oxidation of iron (II) to iron (III) have also been shown to be involved in MIC. These bacteria, through oxidation, deposit insoluble iron (III) hydroxide. This process does not directly cause iron metal to corrode. Only iron already oxidized to iron (II) is further oxidized to iron (III). It is the end product iron (III) hydroxide that is insoluble and precipitates out that leads to the formation of tubercles on carbon steel surfaces, which create conditions for corrosion. Oxygen diffusion will be limited in these areas setting up conditions for differential aeration cells. At the same time the tubercles can also provide

[2] Chemoautotrophic–an organism that is capable of using CO_2 as a source of cell carbon and derives its energy from inorganic substances.

anaerobic niches in which the anaerobic SRB can grow.

Acid-producing Bacteria

Recent MIC studies have drawn attention to an enormously diverse phenotypic group of bacteria called the acid-producing bacteria (APB). Many aerobic bacteria are known to produce organic acids under microaerophilic[3] conditions. In addition to these bacteria, the anaerobic members of the genera *Clostridium* and *Bacillus,* which are also known to produce organic acids, have been implicated in MIC. Also, there are members of the *Thiobaccillus* family and others that are capable of producing mineral acids and can drop local pH to 1. For mild steel, once the pH drops below 4, the general corrosion rate significantly increases. Under normal conditions general corrosion is not likely to cause failures because the materials will have been selected, and corrosion allowances set, taking general corrosion rates into account. However, when general corrosion is unexpectedly increased, for example by the presence of low pH conditions, general corrosion can become a concern. Also, it should be noted that when these low pH's are produced by bacteria they can be extremely localized in nature and lead to "localized" corrosion resulting in pitting and, ultimately, through-wall failures.

Exopolymeric-substance-Forming Bacteria

Various mechanisms have been proposed for the role of bacterial exopolymeric substances in corrosion processes. As has already been noted, biofilms can generate marked differences in the level of dissolved oxygen at the substratum interface with the biofilm and the bulk solution. Investigations using high-resolution techniques have shown that in the case of carbon steels and possibly stainless steels, biofilms can result in differential oxygen cells that lead to localized corrosion (Angell et al., 1995; Little et al., 1996).

Tubercles

Tubercles can be defined as a mound of corrosion product. It should be recognized that for carbon steels there are two types of tubercle that are differentiated by their mode of formation, which leads to distinctive differences in their morphology. "Classical MIC type" tuberculation occurs when iron oxide is deposited by the microbial oxidation of soluble iron (II) within the bulk water to form insoluble iron deposits (III) on the surface of the pipe. As the new material is generated on the outside of the tubercle, this results in the centre being hard and the extremities being softer. Another characteristic feature, resulting from the mode of formation, is that MIC tubercles are often layered when viewed in cross-section (Figure 1).

Figure 1. Cross section through a MIC tubercle, from FPS piping, showing layered morphology

The other form of tuberculation is the result of an electrochemical process whereby iron metal from the pipe wall is oxidized to iron hydroxide corrosion products that are deposited to form a tubercle. In this case, the fresh material is generated at the centre of the tubercle that is therefore soft and the older material at the extremities causes the tubercle to have a hard outer shell. However, it is not always clear what has caused this "localized" corrosion. It is possible that this is still MIC, but in this case the role of the bacteria would have been to create either some form of differential aeration, or ion concentration cells by one of the mechanisms noted above. It should be noted that there are also numerous other non-microbial mechanisms by which such localized corrosion could occur. This non-MIC tuberculation obviously requires the presence of oxygen for the growth of the tubercles. Therefore, in a stagnant system, the growth of tubercules is limited by the ingress of oxygen to the system.

[3] Growth under very low levels of oxygen, where oxygen is still the terminal electron acceptor.

Once all the oxygen in the water has been consumed, no further corrosion can take place and tubercle growth is halted.

MIC and FPS

As a designated safety system it is required that the FPS of a nuclear plant be available at all times. However, as a non-nuclear system, with no production function. the FPS often does not receive a high priority for proactive maintenance. This trend is also, in part, due to the assumption that nothing changes if it is not being used. This, however, is not the case for the FPS, where even a highly degraded system can appear to be in excellent condition based on an external visual examination. From the discussion in the preceding sections, it is evident that FPSs are particularly susceptible to MIC, specifically during the periods of regular but intermittent use, typical of normal FPS operation and testing.

Fire protection systems are almost exclusively constructed from carbon steel. Carbon steels are susceptible to general corrosion and, to tuberculation.

The make up water is generally lake water which normally has a significant microbial population that acts to inject potential MIC bacteria to the system. Lake water also has an elevated level of microbial nutrients over potable or de-ionized water. Within nuclear plants, the FPS is rarely a truly stagnant system but rather a system that is exposed to intermittent flow. Another factor is that because of the often elevated temperatures encountered within a nuclear facility: during the periods of stagnation the temperature of the water in the pipes is elevated to around 30°C, which is optimal for the growth of many of the bacteria associated with MIC. Elevated (warm) temperatures are also known to cause an increase in the rate of corrosion processes in general.

Periods of stagnation also promote the growth of the anaerobic bacteria such as SRB that produce sulphides at the metal surface. When the system is allowed to flow again, new water with a fresh supply of nutrients, bacteria and oxygen enters the system promoting conditions that lead to pitting. The cmbined presence of sulphide and oxygen leads to particularly corrosive conditions.

Materials considerations

As noted above, FPSs are normally constructed from carbon steel which is susceptible to corrosion under service water conditions. Also it is known that welds, and in particular crevices, are areas where accelerated corrosion can occur. Although some nuclear plants in the United States have considered the use of the more corrosion-resistant materials such as AL6XN, such materials are not considered necessary, particularly when it is remembered that carbon steel performs adequately in most non-nuclear utilities if maintained correctly (this difference which is considered to be a particular feature of nuclear system operations, will be discussed later).

Notwithstanding the comments above regarding corrosion-resistant materials, a few simple changes to the present materials of construction can reduce the chance of microbial degradation. First, the use of seamless piping rather than seam-welded piping can eliminate a site (the longitudinal weld), that has been shown to be susceptible to MIC failures. Also the use of butt welds rather than socket welds and elimination of backing rings will help to reduce the number of crevices that may also undergo increased levels of corrosion.

Piping layouts

Microbially Influenced corrosion is enhanced with elevated levels of both oxygen and nutrients, therefore the less water that flows through a system the less MIC will occur. Piping layouts within nuclear plants often contain a buried primary ring main that feeds another ring main within the service and turbine buildings. In order to ensure adequate water flow for fire fighting there are normally a number of paths through which the water can flow. As yard hydrants are often used for purposes other than fire fighting, it is important to ensure that water does not flow through the buildings when it is being used at external locations. The simplest way to control this is by the installation of check valves at each location where water enters a building, allowing water to freely flow in, but not out.

Figure 2. 3-inch riser from a FPS showing extensive build up of corrosion product (tuberculation)

In no circumstance should the piping be designed in such a manner that water constantly flows past a dead-leg (section of pipe in which water does not normally flow). Figure 2 shows the results of a plant where the ring main was exposed to constant flow. Extensive build up of corrosion products (tuberculation) was found to have occurred in the headers and risers that were essentially dead-legs connected to the ring main. In this case a 3-inch riser is almost totally blocked. It was determined that oxygen and nutrients were constantly diffusing from the colder ring main into the stagnant dead-leg. As this cold water reached the warmer riser, a small convection cycle was established that allowed mixing in the section of the riser below the header with optimal conditions for tubercle formation. It is felt that in this case the elimination of flow in the ring header should significantly reduce the level of corrosion and tuberculation seen in the headers and risers.

As part of the design of the system, provision should be made for both monitoring the system and any treatments that might be necessary to maintain the system. From the monitoring perspective it is necessary to provide points at which the system can be accessed in order to take samples of the bacteria growing as biofilms on the internal surface of the pipe. This can range from sophisticated devices containing removable coupons to simple pipe spool pieces in a side-steam that can be valved out of the system.

Within the design and piping layout, provision should be made to allow chemical cleaning and other treatments to be applied. To effectively clean and apply treatments, it should be possible to isolate sections of the system in order to cycle cleaning solutions through the isolated section of pipe.

Operational considerations

As noted above, in order to minimize corrosion within the FPS, it is important to limit the amount of nutrients and oxygen that are introduced into the system in water; therefore the system should be operated to maintain stagnant conditions. In many utilities, the FPS may be regarded as a ready source of high-pressure water, and as such it is used for operations such as cleaning of heat exchangers. Such applications should be discouraged because each additional use of the water increases the flow of water, and hence nutrients and oxygen, through the system, leading to increased corrosion levels. Such alternative uses are often in violation of various codes that restrict the use of the FPS water to fire fighting.

Perhaps the most significant operational procedure that distinguishes nuclear plant FPS operation from FPSs in other industries is the routine flushing of the fire hose cabinets (FHCs). This flushing varies among stations and tends, on average, to be either biannual or annual. Such flushing is often specified in the stations' operations manual as a specific system call-up. However, there is limited basis for such routine flushing based on either the National Fire Protection Association (NFPA) or National Fire Code of Canada.

Sentence 6.4.1.6.(1) of the National Fire Code of Canada requires the flow testing of standpipe and hose systems at intervals not greater than 5 years. The test is to take place at the most remote (based on flow path) hose connection of each standpipe/hose reel zone. In addition sentence 6.4.1.6.(2) states that if during the flow test there is any indication of the presence of debris in the piping, the entire system shall be flushed of foreign material. Concurrence with this standard may be found in NFPA 25 (3-3.1.1).

Some stations have used these quotes as the basis for biannual flushing, noting that each time they flush the system debris is found. However, recent experience where water samples were being drawn for microbial analysis of the FPS it was noted that debris was present 4 to 6 weeks after the FHCs were flushed, indicating that debris accumulates in far less than the 6 months currently used as the minimum period between FHCs flushes. Confirmation by one CANDU station with NFPA has confirmed that routine flushing of the FHCs is not required under the above code. It is therefore recommended that stations examine the possibility of increasing the interval between FHC system flushes. Consideration should be given to either 3 or 5 year periods between flushing, in order to enable the system to remain stagnant for as long as possible and minimize the level of degradation experience.

Water Source

The primary function of the FPS is to provide large quantities of water to fight fires. Obviously, an on-site water treatment plant would not be able to supply such quantities of water. Also, the use of treated water for fire fighting is not required nor economic. Therefore water for the fire protection system is normally untreated, or minimally treated, water either drawn from the same intake as the service water, or from an alternative fresh water source[4]. Such water normally contains a healthy diverse flora of microorganisms as well as moderate levels of microbial nutrients, all of which enhance the possibility of microbial degradation.

While it is not desirable to use treated water for fire fighting purposes, in order to prolong the life of the system it is recommended that consideration be given to limited water treatment. This treatment could take the form of addition of a biocide directly to the FPS each time the fire pumps are activated. Alternatively another treated water source could be used for make up and testing purposes. This water should be of potable quality, at least. A better option available to many nuclear plants is to use a source of high pH (> 9.5) water, which is known to inhibit microbial action and to minimize carbon steel corrosion.

Monitoring the FPS

Traditionally FPSs have been designed and operated based on the prevailing codes for FPSs, with little consideration of potential degradation mechanisms. As a result, problems—which range from flow restriction, where plants have not been able to meet the mandated flow tests to through-wall leaks—are being encountered as plants age. Because of the development of problems internally and the closed nature and sporadic use of the systems, such problems have often come as a surprise to station staff.

Many of the problems that have occurred could have been predicted through some simple monitoring programs. At the lowest level, the common observation that the water from the FHCs is black and smells of sulphide is indicative of microbial action occurring within the system. Also problems with seating valves after flushing and flow tests can be indicative of tuberculation occurring within the system. This is particularly the case when examination or replacement of passing valves reveals the presence of "chunks" of corrosion products – tubercles.

Routine analysis and trending of the microbial activity within the FPS by using a MIC index such as that described by Lutey and Stein (1998) can give station personnel either added assurance that there is no problem or a warning that a problem exists. For any microbial analysis to be effective it is necessary to obtain samples of the biofilm populations within the piping system. Obtaining suitable samples is not a simple matter, with the current design of FPS. However, because of the stagnant nature of the system, AECL has recently been able to obtain representative water samples. Although swab samples are preferred, it is reasoned that extended periods of stagnation allow a measure of equilibration between the sessile (attached) and planktonic (free swimming) populations. Thus a water sample should provide an effective measure of bacterial activity. It is strongly recommended however that stations make provision for collecting samples of the sessile bacterial populations, either through the installation of sampling locations, using side loops etc., that can be valved out for sample collection, or provision can be made for sample collection whenever the system is open for maintenance.

Concluding Remarks

The following quote from the EPRI guidelines (EPRI 1999), is an appropriate conclusion; "The operating philosophy of each individual fire system will dictate the number of problems encountered and the cost of the treatment expected. If a fire system is used only to combat fires and is treated to limit biological

[4] In no circumstance should sea or brackish water be used in unprotected carbon steel pipes.

growth and corrosion when makeup is necessary the system will perform without complication for the life of the plant. On the other hand if the system is subjected to cyclic use, through-wall failures and general occlusion with significant flow blockage in small diameter piping can be expected."

Until recently most FPSs have not been given sufficient attention to corrosion control because of the assumption that it will always be available. Recent incidents of through wall failure have alerted a number of stations to the need for greater attention to the system. In order to aid in the process of maintaining the FPS in a routinely-available operational state the following concluding recommendations are made:

- Avoid the use of seam welded pipe
- Minimize the creation of crevices through the use of butt welds (rather than socket welds) and limit the use of threaded joints in smaller pipe.
- Use check valves where pipes enter buildings from a ring main header to prevent water from flowing through the building.
- Install microbial biofilm monitoring devices.
- Install isolation valves and connection points to allow chemical cleaning or biocide treatment to sections of piping.
- Limit the use of the FPS water to fighting fires.
- Increase the time between routine flushing of FHCs, (suggest 3 to 5 years).
- Attempt to use a water source that allows the use of biocide treatment, for make-up and test purposes.
- Conduct routine monitoring of the FPS to trend microbial activity.

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