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EVIDENCE OF MICROBIALLY INFLUENCED CORROSION OF BORAL USED IN SPENT FUEL CANISTERS

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ABSTRACT

Approximately six years after the TMI accident, the reactor vessel was opened and the defueling process was initiated. Within months after defueling had begun the turbidity of the water increased and visible biomass growth could be seen on the reactor walls. Samples collected showed the presence of viable microbial cells. The population was separated into pure culture isolates.

Both laboratory and canister corrosion tests were performed on selected materials in a variety of biological environments; results of these tests are discussed here. For example, the weld metal and heat-affected zone of welded 304L SS are less resistant to corrosion than the base metal, which is very resistant in all environments tested. Type 1100 Al exhibited severe pitting attack in many environments. The aluminum in Boral, a composite of aluminum and boron carbide, was even more severely attacked than 1100 Al itself, probably as a result of microbially mediated galvanic corrosion.

INTRODUCTION

After approximately six years from the time of the Three Mile Island (TMI) nuclear reactor accident (March 1979), the plenum of the damaged reactor vessel was removed. The engineering feat of defueling was then initiated. The defueling operation was designed to be accomplished manually. A platform was built and placed over the top of the vessel. Through a slot in this platform tools were suspended into the 20-25 feet of water to the surface of the rublized core. Crews operated these hydraulic actuated tools from the platform using visual references supplied by a suspended camera and high intensity light.

The core debris was grabbed by the tool and lifted. Near the surface a carousel contained a number of canisters which received the debris. This operation was also performed by visual reference. Once the canister was full of debris it was removed from the reactor vessel and stored until it was prepared for rail shipment in a cask to the INEL facility.

The canisters arriving at the INEL were unloaded, checked, and then placed in a rack in a pool at one of the facilities. Each canister was fitted with a tube and filled with demineralized water. Over 300 canisters were required to accomplish the defueling operation. These canisters are expected to remain submerged in the pool for 20 to 30 years.

This paper discusses the microbial problem associated with the defueling operation, their isolation and some of the microbial influenced corrosion testing that was performed with the mixed population.

METHODS AND MATERIALS

Standard microbial techniques were used on location in sampling the TMI reactor vessel water. The inoculated media were then transported to the INEL where isolation and dilution of the radioactivity was accomplished. API characterization tests were used to establish genera.

The storage canisters were fabricated from stainless steel (SS) with a number of other materials being used in the design. The tests reported here are for 304L SS (in the welded and unwelded conditions) boral (a composite consisting of boron carbide powder dispersed in aluminum and clad with aluminum), and 1100 aluminum.

Glass bioreactors were used for the laboratory study, coupons of the test materials were attached to a SS basket. After assembly the bioreactors were autoclaved or sterilized with ethanol. The nutrient media was added to the sterile bioreactors followed by inoculation with the appropriate organisms, under aerobic and anaerobic conditions. The organisms were those collected; from TMI reactor, from the INEL (Test Area North) Pool 1 and known sulfate reducing bacteria. The bioreactors conditions

reducing bacteria. The bioreactors conditions were maintained using flowing air for the aerobic and sterile control tests and nitrogen for the anaerobic test. The tests were run at 30° C, and ambient pressure, and as long as 10 months.

A TMI canister, 136B, was used to preform a long term biocorrosion test. This canister was filled with demineralized water that was amended to profile the actual reactor vessel water composition. Organisms were added along with 70 ppm of carbon in the form of organic acids. The test ran for 30 months.

RESULTS

ISOLATION OF MICROORGANISMS FROM THE TMI REACTOR COOLING SYSTEM (RCS):
Approximately two to three months after the cover was removed, crews noticed the appearance of filamentous material hanging from the walls of the vessel. Although the water visibility in the vessel still permitted visual contact with objects some twenty feet below, specially designed filter canisters began plugging at an abnormally fast rate with very little total solids entrained. Visibility was monitored weekly as well as the microbial count which eventually reached a population density of 10^3 to 10^4 cells per milliliter. Within two to three months after the first observation of the filamentous growth (January 1986) the visibility decreased to an extent that visual reference of objects at the surface of the debris could not be made even with a submerged camera. Visibility had deteriorated to less than six inches. Defueling operations ceased due to low visibility.

During this time samples had been taken by the defueling contractor and the presence of microbial growth was confirmed. The initial work involved determining the numbers of cells, what substrates were being metabolized, developing permitable ways of eradicating the viable cells and restoration of the visibility.

Several media were taken to the TMI facility. Samples from the reactor vessel were obtained from their staff and aliquots were transferred into the media. These were then sent directly to our facility and transfers were made in our hot cells into similar fresh media about every 10 days until the radioactivity was diluted to levels required by 10 CFR 20. These "cold" cultures were then taken to our labs for further characterization and testing.

The samples taken at TMI were taken at two depths and from several other objects that had been in the reactor vessel or had been in contact with water from the vessel. All samples tested positive for organisms and the microbial results of the two depth samples are shown in Table 1. Isolates were obtained in pure culture from these samples and further characterized as to their gram stain reaction, morphology and biochemical tests.

TABLE 1. ORGANISMS FROM VARIOUS DEPTHS IN THE REACTOR VESSEL

MEDIA	SAMPLES RCS-307 FT	SAMPLES RCS-327 FT
AEROBIC		
Diatom	+	-
Zooglea/thiosulfate	+	+
Zooglea/thiosulfate cit/lac pH 3.0	-	-
Czapek and ampilcillin	+	+
Nutrient broth (1/3 strength)	+	+
Thiobacillus	-	-
Nitrate utilization	+	+
ANAEROBIC		
Nutrient broth (1/3 strength)	+	+
Zooglea/NH_4SO_4 lactic acid	+	+
Mineral salt/ glucose	+	+

Growth indicated by "+" after 10 days.

Organisms were also isolated from an "O" ring, DE filters and RCS tool.

REACTOR VESSEL PROBLEM:
The defueling process could not proceed at an expeditious rate if water clarity could not be maintained. An engineering fix to this menacing problem was scoped. A list of possible solutions was developed, Table 2. Some of these solutions were tested in a number of labs around the U.S. and others were eliminated without testing.

Potential solutions also had to contend with the extensive quantity of radioactive material, strict NRC water quality guidelines, and the physical size and configuration of the RCS.

Another question which had to be answered was what substrates were sustaining the population. The water chemistry was closely monitored on a

TABLE 2.	
RCS ERADICATION SOLUTIONS	TEST VIABILITY
Filtration	Plugged rapidly
Ozone	No circulation in res, destroyed in ionizing field
Heavy metals, e.g., Ag	Microbial resistance extremely high, Ag>100 times recommended dose
Chlorinated hydrocarbon	Increased potential for corrosion
Sulfones/thiozoles	Organisms tolerance and increased potential for corrosion
Centrifugation	Attempted not practical
Pressure	Tested did not erradicate the organisms
Temperature	Not operational possible
pH	Boron buffered water
Hydrogen Peroxide	Selected for application

routine basis during the defueling operation. A typical profile of the non-radioactive components was also determined. The major change in the water chemistry after defueling was initiated, occurred in the area of total organic carbon, (TOC). Prior to defueling, the TOC levels were lower, less than 15 ppm. The increase in carbon was traced to the defueling tools. These tools were hydraulically activated and had developed leaks. The fluid seeped into the RCS increasing the TOC level over 50 ppm.

The hydraulic fluid was a two component lubricant composed of long chained alcohols in an ether linkage to butanol and borated ester. Seventy-five percent of this fluid contained the butanol ether compound which contained 37 carbon atoms per molecule. The remaining twenty-five percent, the borated ester, contained 30 carbon atoms per molecule. An estimated 5 gallons or more of this fluid had leaked into the RCS. Apparently some or all of the organisms were able to metabolize one or both of the components.

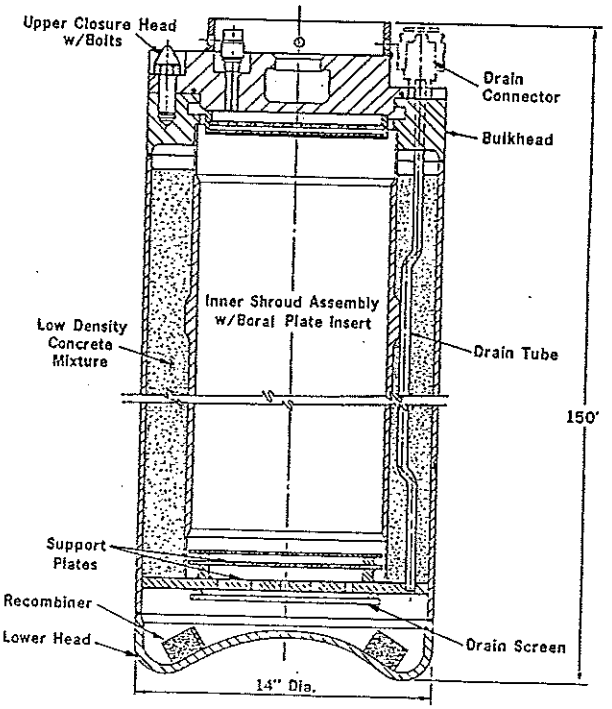
The installed defueling filtering system was designed to handle suspended fines, a result of fuel debris disturbances during defueling. The filter canisters were an elaborate one piece system capable of handling a substantial loading. The filter canister contained a sintered steel mesh with a 5 micron pore size. However, these filter canisters quickly plugged with little loading. There was no mechanism for backflushing.

Three months after the defueling operation had begun the visibility decreased to less than several inches and the operation had to stop. The decision was made to attempt a biocide treatment using hydrogen peroxide. Testing at the facility using this agent showed good biocidal activity at low levels of peroxide, 200 ppm.

After several additions of peroxide, the installation of a sand filter and water coagulant system, water clarity was restored to several feet or more and the defueling operation continued until all the debris had been removed.

BIOCORROSION CONCERN:
The INEL facility was chosen to store the canisters which received the core debris. The canisters are a complex container made with a stainless steel exterior shell, see Figure 1.

Figure 1. Fuel Canister



Since the core debris is highly radioactive and the canisters are to be stored for many years submerged in water at a facility that has other project work ongoing, it is essential that leaks do not occur during storage. The storage conditions for the canisters includes filling them with water on arrival after shipment from TMI. If organisms were viable inside the canister there would not be any means of determining what physical changes were taking place. Many reports in the literature indicate that stainless steel and other alloys are attacked by microorganisms and as a result the corrosion of these materials is accelerated. Although the pool water in which the canisters are stored is not sterile, visual contact of the majority of the canisters will be possible and the history of the pool has not shown any microbial influenced corrosion (MIC).

Therefore, a sterilization program was initiated to be performed on the canisters before they left TMI. This treatment included the dewatering of the canisters followed by circulation of a hydrogen peroxide solution through the canister before being placed in the cask for shipment via rail. The sterilization treatment lasted for 60-90 minutes with a peroxide solution of 200 ppm. This level of peroxide was chosen because it had been used to control growth of the organisms in the reactor vessel. Once a month additional peroxide was added to the vessel in order to maintain some level of visibility. Higher levels which probably would have been more effective in killing the cells were shown to cause the release (dissolve) additional radioactive material from the surfaces of the core debris. As a result, the levels of exposure would be greater to the personnel and a level of 200 ppm was selected.

A canister was selected for testing after its arrival to the INEL facility as to the sterility of the water which remained inside during shipping. Canister 153 was carefully opened inside the hot cell. All the surfaces which might come in contact with the water that was inside were flushed with 95% ethanol. The collection container had been autoclaved. The collected water sample was transferred to a lab and 1.0 ml aliquots were transferred to different media. Growth occurred in all eight media. Characterization tests were done on the isolate and the results match those for TMI isolate #10.

This isolate was cultured and tested as to the tolerance to hydrogen peroxide. Cells were centrifuged at 4° C and resuspended in mineral salts media with and without boron. An aliquot of cells were then added to a media containing 100 or 200 ppm of hydrogen peroxide. A stability of hydrogen peroxide was done in the presence of boron and without boron. The disappearance of hydrogen peroxide was observed in the flasks that received live cells, shown in Figure 2. Cell viability was checked on two different aged population of this isolate. All tests showed that cell viability was maintained even in the presence of peroxide for many hours.

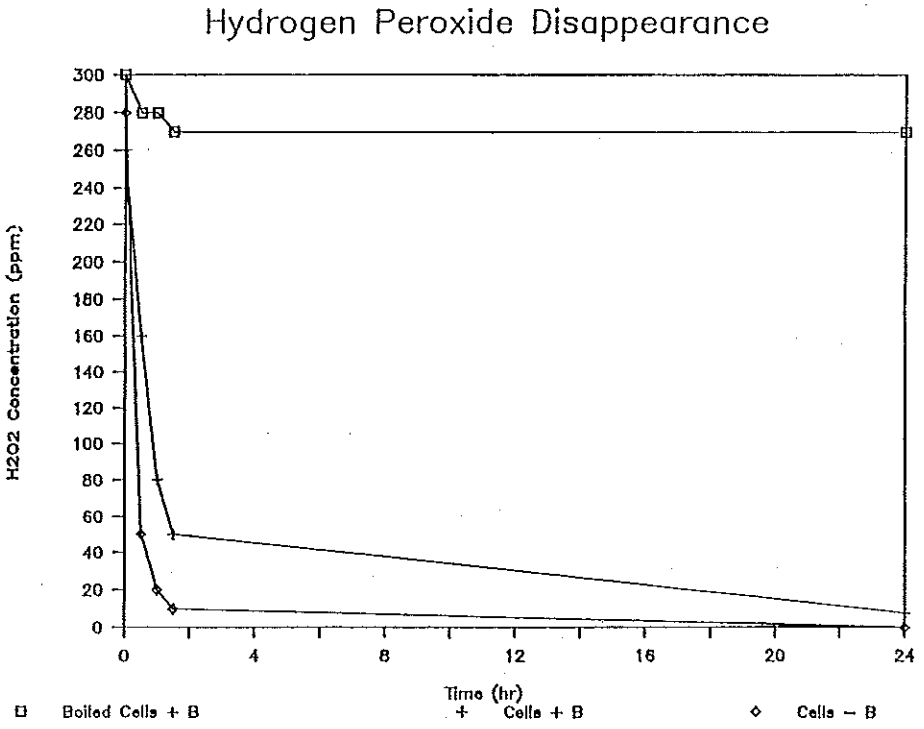


Figure 2. Disappearance of hydrogen peroxide with a cell suspension of isolate from the canister.

Another canister was selected for examination after several additional shipments had arrived. Canister 160 showed no viable cells were present in the entrained water.

Lab Tests:
To determine if the mixed population isolated from the RCS could cause MIC, laboratory studies using small glass vessels (1 and 2 liters) were set up to study the affects of the organisms on the various canister materials. The coupons of boral, aluminum, 304L stainless steel (SS) and welded 304L SS were wired to the stainless grating. The entire flask was sterilized and the media was sterilized separately cooled and then aseptically added to the flasks. The flasks were then inoculated with an aliquot of organisms, from the TMI population, or the canister 153 isolate. The Test Area North (TAN) flasks received centralized water and the other media supplements. A test matrix and evaluation scheme are shown in Table 3.

TABLE 3. LABORATORY TEST PLAN

	TAN WATER W/O NUTRIENT	TAN WATER W/NUTRIENTS
TMI ORGANISMS[b]	Flask 21	25
TAN ORGANISM	Flask 22	27
CANISTER D-153 ISOLATE[b]	Flask 24	28
CONTROL	Flask 23	26

a. Media: 2 liters of TAN WATER, 200 ml of 3x nutrient broth and 7.5 ml of 1% Lactate/Citrate/Sodium Sulfate and Sodium Thiosulfate.

b. 50 ml of cell suspension of TMI organisms or canister 153 isolate cells were centrifuged and resuspended in mineral salt solution (sterile).

Over the longest testing period of 323 days dramatic changes took place in some of the flasks. Bacterial action in the reactors resulted in the formation of biofilms on the surface of the vessels, baskets, and coupons. In flasks copious white-cream colored precipitates formed and settled to the bottom of the reactors. MIC resulted in the formation of large amounts of inorganic matter, largely hydrated aluminum oxides. These tended to form thick scales on the coupons and on internal reactor parts. In many cases large tubercles were formed, especially on the boral and aluminum coupons. In some cases adjacent coupons responded differently, in one case one aluminum coupon was essentially free of corrosion and scaling while an adjacent coupon was very badly corroded and had a thick deposit of organic and inorganic matter on it surface.

AISI type 304L stainless steel(SS) was the major structural material in the canisters and was selected on the premise that thirty year corrosion would be minor. Only minor evidence of corrosion was observed on welded coupons from sterile environment, no corrosion was observed on unwelded SS coupons.
Boral is a composite consisting of boron carbide, B_4C and aluminum. Electrochemical measurements have shown the aluminum is anodic with respect to B_4C and this contributes to galvanic attack of the aluminum. This attack has been seen as pitting of the aluminum cladding, as extensive wasting of the aluminum in the B_4C-Al composite, and as hydrogen blistering at the interface between the cladding and the B_4C-Al composite, (see Figure 3).

The worst cases of metal deterioration occured with the boral. In Figures 4 and 5, the weight losses are shown for boral and aluminum coupons. In the flasks which contained the nutrients, the weight loss after 323 days from the boral coupons was generally greater than

Figure 3. A blister Boral Coupon.

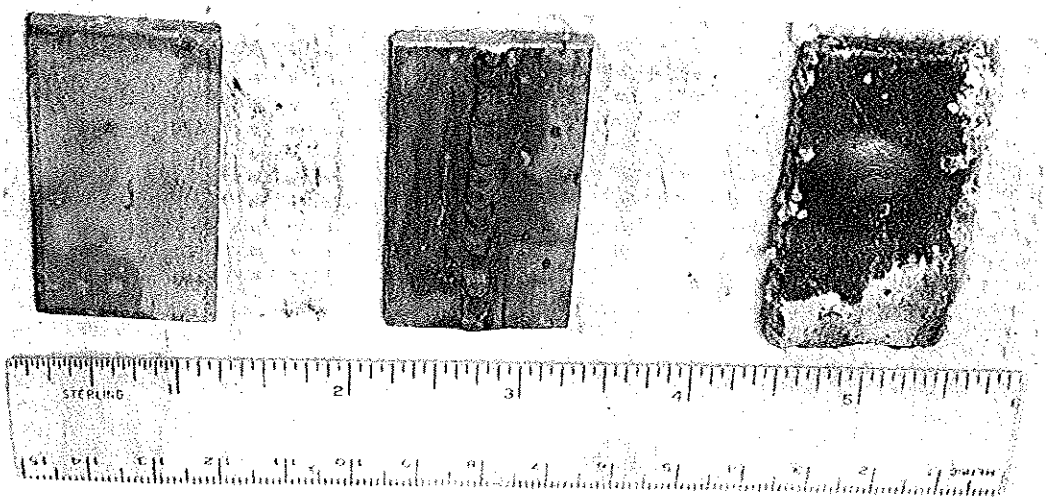


Figure 4. Weight loss of boral.

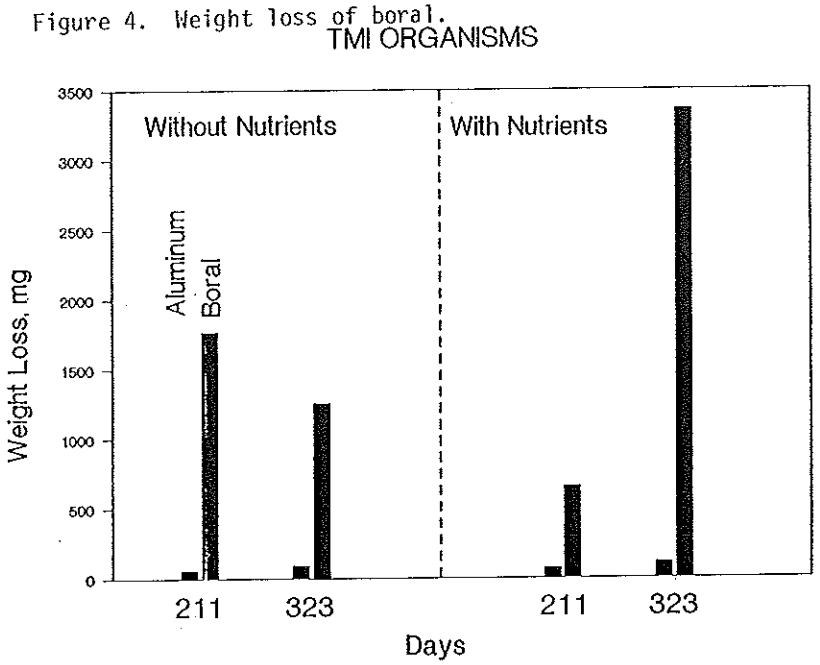
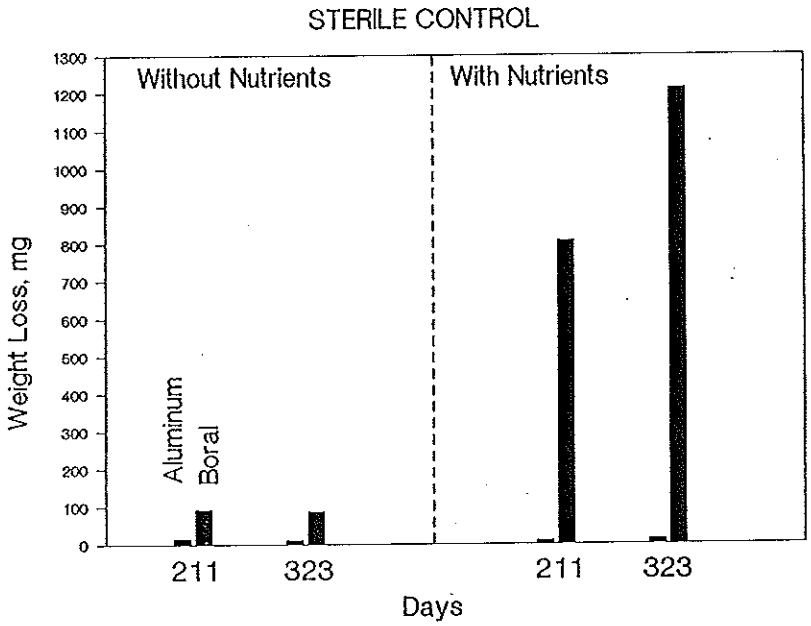


Figure 5. Weight loss of controls.



the other set. However, at the 211 day sampling period more weight loss was detected in the non nutrient media set. The aluminum coupons did not show the same trend as the boral.

The controls became contaminated during the 97 days sampling period. Corrosion of the boral occurred quickly in the nutrient flasks and to a much slower degree in the non nutrient.

The flasks containing the TAN organisms also showed corrosion in the boral and the aluminum.

Canister 136B Tests:

An actual fuel canister was shipped to the INEL empty after being dewatered at the TMI. This canister numbered D-136B was set up in a hot cell. The design features of the fuel and filter canisters is shown in Table 4. The interior was divided into nine verticle chambers in a 3 x 3 array using expanded stainless steel. Each chamber was about 2.5 x 2.5 x 140 inches long and was open at the top of the canister. Racks to hold test samples were constructed so that they would fit into

TABLE 4. CANISTER DESIGN FEATURES		
	Type of Canister	
	Fuel	Filter
Overall length (max.)	150.0 in.	150.0 in.
Outer diamter (nom.)	14.00 in.	14.00 in.
Canister contents	Up to partial fuel assemblies	Small fines 0.5 to 800 microns
Total inside free volume	6.75 ft^3	9.94 ft^3
Usable volume	6.45 ft^3	6.89 ft^3
Debris denstiy range[a]	215-400 lb/ft^3	169-431 lb/ft^3
Loaded canister wt. (Max.) Dewatered in air	2800 lbs	2040 lbs[b]
Empty canister wt. (nom.) In air	1230 lbs	1440 lbs
Bottom head design	Reversed dish	Reversed dish

a. Provided by GPUN.
b. Based on 500 lbs payload and 100 lbs water remaining after dewatering.

the chambers. The racks were divided vertically into six section, A-F. Sections A, C, and E were plates to which stainless steel and aluminum coupons were bolted. PTFE washers were used that would promote crevice corrosion test the materials for susceptibility to this form of attack. Sections B and D held expanded stainless steel baskets into which Boral, Licon, Boron carbide pellets, EPDM, and Boroflex I samples were placed. Section F was reserved for biological monitoring samples.

The microbial inoculum was produced from the TMI organisms grown in two different media. One medium was 1/3 strength nutrient broth and was grown under aerobic conditions. The second medium was a mineral salts broth with 1000 ppm each of lactic acid, citric acid, sodium sulfate, and sodium thiosulfate grown under reduced aerobic conditions. The cells were centrifuged for 15 minutes at 5000 rpm then resuspended in mineral salts. These inoculums were taken to TAN and on August 13, 1986 were introduced into the canister.

At the end of three, six, twelve and eighteen months, corrosion coupons and aliquots of water were taken for microbial analyses. Scrapes from these coupons were placed into media to determine if viable cells were present. Aerobic and anaerobic systems were both used for bacterial evaluations, e.g., Czapek, nutrient broth, and mineral salts with sulfate, lactate, and citrate. Samples were plated onto solid media to determine the number of viable isolates remaining.

At the 6, 12, and 18 month interval, microbial enumeration was done. Several media were used to determine the viable population in the bulk water. Viable cells were found during all the testing periods. Even after 18 months both aerobic and facilative anaerobic organisms were found.

The examination of the various materials at each sampling period showed little to no corrosion during the first 12 months. Some small brownish spots were observed along with a thin scale deposit in a few areas on some of the SS coupons. At the 18 month sampling, again some discoloration was observed on small areas of the welded 304L SS, no pitting was observed.

The aluminum coupons during the first twelve months showed some thin grey scaling and very small and shallow pitting. At 18 months numerous small pits could be seen on most coupons and there were a couple of deep pits observed.

The boral coupons began showing pitting by the twelve month sampling. There were also deposits of white and grey scale on some of the coupons similar to the ones observed in the accelerated tests. At the 18 month sampling period several boral coupons showed the presence of blisters and some encrustations.

DISCUSSION

The microbial presence in the RCS could have occurred at the time of the accident. During the loss of coolant emergency, river water was directly pumped into the vessel or the containment buidling. Although the radiation field as well as the temperature were extremely high during those times, some areas may have been partially shielded. No matter how the organisms become introduced to the RCS, the radiation field was high and time in that field was prolonged. Organisms have been shown to survive very high single doses of radiation 2 to 100,000 rads and one genera has survived $3.5/10^6$ rads. The radiation field near the rubblized core was greater than 1000 rads per hour.

These organisms not only survived in a high radiation field for prolonged periods but also grew in this environment, under restricted nutrient conditions. Preliminary evidence indicates that at least two isolates could metabolize one or both of the hydraulic fluid components.

Turbidity in the RCS water caused a loss of time and eventually shut down the defueling operation. All filtration was based on the utilization of the filter canisters. When they plugged quickly and filtration via the filter canister system was discontinued, no means existed to restore the water clarity.

A biocide treatment was selected from all the alternatives that were proposed and tested. Hydrogen peroxide was finally selected from a number of suggested compounds. The use of peroxide was viewed favorably because no residual carbon, halogen, sulfur or nitrogen by-products would be produced. All our studies showed that peroxide would not eliminate the population at the 200 ppm level, that level was chosen and additions of peroxide to the RCS were made several times.

Two canisters were tested on arrival at the INEL for the presence of live microorganisms inside. The first canister checked, # 153, tested positive. The organism was isolated and shown to be similar to TMI-10 isolate. Several tests were done with the biocide, hydrogen peroxide, at the level used for disinfection (200 ppm). It was determined that the organism survived very well and all the isolates were tested for the presence of catalase. Many organisms had catalase and several isolates tested very positive for that enzyme.

Two accelerated corrosion tests were set up and a canister was supplied to be utilized as an actual container for corrosion testing over a long time period. The first test used a mixed population of TMI organisms, rich synthetic media under aerobic and anaerobic conditions. Severe deterioration of both the boral and aluminum were observed. Very little discoloration of the stainless steels were observed and only a few small shallow pits were detected in the weld metal.

The second test involved nutrient media and TAN deionized water. This test was done under stagnant conditions using organisms from three sources, TAN, TMI, and the canister isolate. Growth occurred rapidly in all the flasks with the production of surface slime and submerged biomass on the glass, coupons and SS support structure.

Initially both test controls coupons remained clean and free of biomass. However, eventually all the controls became contaminated and growth could be detected in the glass flasks. Deterioration of the aluminum and boral also occurred in the control flasks.

The results of the second test indicate that open edged boral deteriorated substantially within the testing period. The coupons lost as much as 40% of their inital weight.