WSRC-MS-99-00601

Criteria for Corrosion Protection of Aluminum-Clad Spent Nuclear Fuel in Interim Wet Storage

James P. Howell
Westinghouse Savannah River Company
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

Abstract

Storage of aluminun-clad spent nuclear fuel at the Savannah River Site (SRS) and other locations in the U. S. and around the world has been a concern over the past decade because of the long time interim storage requirements in water. Pitting corrosion of production aluminum-clad fuel in the early 1990's at SRS was attributed to less than optimum quality water and corrective action taken has resulted in no new pitting since 1994.

The knowledge gained from the corrosion surveillance testing and other investigations at SRS over the past 8 years has provided an insight into factors affecting the corrosion of aluminum in relatively high purity water. This paper reviews some of the early corrosion issues related to aluminum-clad spent fuel at SRS, including fundamentals for corrosion of aluminum alloys. It updates and summarizes the corrosion surveillance activities supporting the future storage of over 15,000 research reactor fuel assemblies from countries over the world during the next 15-20 years. Criteria are presented for providing corrosion protection for aluminum-clad spent fuel in interim storage during the next few decades while plans are developed for a more permanent disposition.

Keywords: Aluminum-clad, pitting corrosion, Savannah River Site (SRS), IAEA,

Introduction

Processing of aluminum-clad nuclear fuel was suspended at the Savannah River Site (SRS) and other locations within the DOE Complex in late 1989 due to safety upgrades and the U.S non-proliferation policy. Spent production fuel normally stored in water-filled basins at SRS for 12-18 months while awaiting processing, accumulated several years of exposure in less than optimum water conditions. Pitting corrosion of the aluminum resulted in breach of the cladding.[1] Corrosion surveillance tests in the reactor storage basins conducted over several years provided a basic understanding of the mechanisms of corrosion.[2-4] Recommendations were implemented to improve basin water quality and as a result, no new pitting corrosion has been seen since 1994. Today, with the restart of SRS canyon separations facilities, most of the old production fuel has been processed and new shipments of foreign and domestic research reactor spent fuel are being put into interim wet storage in the L and RBOF basins at SRS.

The knowledge gained from the corrosion surveillance testing and other investigations at SRS over the past 8 years has provided an insight into factors affecting the corrosion of aluminum in relatively high purity water. This paper reviews some of the early corrosion issues related to aluminum-clad spent fuel at SRS and and provides fundamentals for corrosion of aluminum alloys. It updates and summarizes the corrosion surveillance activities which will continue to support the storage of over 15,000 research reactor fuel assemblies from countries over the world during the next 15-20 years. Criteria are presented for providing corrosion protection over the next few decades for aluminum-clad spent fuel in interim storage as plans are developed for a more permanent disposition.

Spent Fuel Storage History

Storage of spent fuel at SRS has been successful over the 50 years of plant operations. Irradiated aluminum-clad production fuel has been stored in water-filled basins connected to the P, K, and L-Reactors while awaiting processing. Foreign and domestic research fuel has been traditionally stored in the Receiving Basin for Off-Site Fuels (RBOF) basin. The water in these basins is currently being maintained at a conductivity of 1-3 µS /cm using mixed-bed, continuously operated deionizers.

Corrosion concerns on the spent fuel have been minimal over the years of fuel storage. The water conductivity was maintained in the 60-70's µS /cm range in the 1970 through late 1980's using portable mixed bed deionizers. Some pitting was reported on aluminum-clad tritium target materials, but this was attributed to material defects and fabrication concerns.

Over 200 Metric Tons Heavy Metal (MTHM) of aluminum-clad fuel and target materials were stored in the basins at SRS in the early 1990's.[5] The aluminum cladding alloys were 30-mil thickness and primarily Types 1100, 8001, and 6061. The core materials were generally depleted uranium metal or uranium-aluminum alloys. With the suspension of processing and extended storage times, nodular corrosion product became visible on the aluminum cladding of Mk 22 assemblies in the K-Reactor basin and on the Mk 31A target slugs in L-Reactor basin as shown by Figures 1-2. Sampling and analysis of the corrosion products from the spent fuel cladding showed that cesium-137, uranium, plutonium, and other fission products were present. The cesium level was continuously monitored through water analysis and was continuously removed by the mixed-bed deionizers. The cesium-137 level in the water was always maintained well below the administrative limits set for the basins. The water chemistry in the basins at the time when corrosion was most aggressive in the basins showed the chloride ion concentration at 8-14 ppm and a conductivity of 160-175 µS /cm.

The factors believed to have played the most important role in the corrosion of aluminum-clad spent fuel in the reactor basins at SRS are:

- High basin water conductivity (100-180µS/cm).
- Aggressive basin chemistry (20 ppm Cl^-).
- Sludge (contains Fe, Cl, etc., ions in 10X water concentrations).
- Galvanic couple between stainless steel bucket and aluminum.
- Galvanic couple between aluminum and uranium.
- Scratches and imperfections in cladding.
- Relatively stagnant water.

The RBOF basin at SRS stores spent fuels from research reactors around the world. Corrosion of fuel in this basin has never been an issue over the 37 years of operations. In this basin, water purity is maintained by continuous mixed-bed deionization. Impurity concentrations are maintained in the parts-per-billion (ppb) range and the water conductivity is usually stable in the 1-3 µS /cm range. The cesium-137 levels in the RBOF basin are generally higher than in the reactor basins because of failed fuel from the research reactors around the world being stored in the basin.

Aluminum Corrosion

The factors promoting the corrosion of aluminum are complex. In many cases, they operate synergistically. These factors, including fundamentals and mechanisms have been discussed in detail in a previous NACE paper.[3] Some of the most important factors which affect the corrosion of aluminum alloys and aluminum-clad spent fuel are presented here for background to the criteria for protection.

Oxide Films on Aluminum

Aluminum is one of the most thermodynamically reactive metals and owes its excellent corrosion resistance to the protective oxide film formed and strongly bonded to its surface. When the film is damaged under conditions that self-healing does not occur, localized corrosion in the form of pitting or intergrannular attack can occur.[6] In water at temperatures about 60-70 ^{0}C, the amorphous barrier oxide on aluminum thickens with the formation of the crystalline hydrated oxide phase, Boehmite ($Al_2O_3{\cdot}H_20$). After days of immersion the crystalline phase Bayerite ($Al_2O_3{\cdot}3H_20$) is formed. At and above 70 ^{0}C, the oxide films formed on aluminum are predominately Boehmite.

The overall reaction for aluminum corrosion in water is given by the equation:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \tag{1}$$

Influence of Water Composition

The major factors believed to influence the pitting of aluminum alloys are: conductivity, pH, bicarbonate, chloride, sulfate, and oxygen content.[6] Because of the inter-relationship of the composition and service factors, it is difficult to predict the influence of the water from a table of water composition alone. A number of studies conducted in synthetic water containing several metal and salt ions alone and in combinations have found that the corrosion of aluminum was accelerated by combinations of salts of copper, chlorides, and bicarbonates, over single impurities.[7-9]

Conductivity

As most of the corrosion processes involving the aluminum-clad fuels in storage basins are electrochemical, and corrosion depends on the nature of the electrolyte. For basin water, the conductivity plays a key role in the flow of electrons and electrical current in the process. The amount of metal removed by corrosion is directly related to the current flow. By increasing the resistance of the water, the corrosion of the aluminum can be reduced. Very pure water has a high resistance to the flow of current and is much less corrosive than impure or natural waters. Conductivity is defined as reciprocal of specific resistivity:

$$C\ (\text{specific conductivity}) = \frac{1}{R\ (\text{specific resistivity})} \tag{2}$$

Where the unit for C is 1/ohm-cm or mho/cm. A smaller popular unit is μmhos/cm. In International Units, 1 μmhos/cm =1 μS/cm where S is the unit Sieman.

Extremely pure water with a conductivity of less than 1 μS/cm can be produced by deionizaton for atomic energy purposes. Type 1 reagent-grade water can be produced by deionization, distillation, reverse osmosis, or combinations of these techniques to a conductivity level below 0.1 μS/cm. Natural lake waters in some areas such as Lake Ontario, Canada have a typical conductivity of about 270 μS/cm as compared to 40,000 μS/cm for seawater.[10]

Effect of pH

Aluminum is passivated and protected by its oxide film in the pH range of about 4-8.5. The limits vary somewhat with temperature and the specific form of oxide present, and with the presence of substances that can form soluble complexes or insoluble salts with aluminum. The oxide coating is soluble at pH values below 4 and above 8.5. General corrosion in distilled water at 60 ^{0}C has been shown minimum at pH4 rising slightly in the passive range and faster between pH 9 and 10. For pitting corrosion, which is the predominant mechanism for aluminum in water, the pitting potential in chloride solutions has been found to be relatively independent in the range of 4-9.[11] Godard indicated that a deviation from neutrality (pH7) on both acid and alkaline sides could increase the rate of pitting in fresh waters.

The corrosion rate is often more dependent on the specific ion that causes the pH than on the pH itself. For example, aluminum is not rapidly attacked by concentrated nitric acid at a pH of 1, or by glacial acidic acid at a pH of 3, but is rapidly corroded by hydrocloric or phosphoric acid at a pH of 4. On the alkaline side, aluminum is resistant to ammonium hydroxide at pH 13, but is corroded rapidly by sodium hydroxide at pH of 11. The probable reason for this behavior lies in the composition of the corrosion product and their tendency to form protective films on the aluminum surface.[6]

Effect of Impurities

The rate of corrosion of aluminum alloys and their tendency for pitting is controlled by the protective oxide film formed on the aluminum surface. The corrosiveness of basin water is influenced to a large degree by the ability of impurity ions to penetrate the oxide film and attack the aluminum metal. Sverpa found that the penetrating power of anions in decreasing order to be chloride, bromide, iodide, fluoride, sulfate, nitrate, and phosphate.[12]

For aluminum, pitting corrosion is most commonly produced by the halide ions, of which chloride (Cl^-) is one of the frequently encountered. An increase in the chloride concentration of a solution has been shown to decrease the pitting potential of aluminum. Chloride breaks down the protective oxide film and inhibits re-passivation. It stimulates the metal dissolution. It is difficult to specify a chloride limit below which pitting corrosion does not occur because of the synergistic reactions that take place with other anions in the water.

Heavy metal ions such as copper and mercury are very aggressive toward the pitting corrosion of aluminum alloys. The aluminum reduces the ions of copper, mercury, lead, etc. These ions can plate out on the aluminum and form localized galvanic cells with the aluminum becoming the anode and the heavy metal becoming a very effective cathode.

Water hardness or softness as measured by the carbonate content is another important factor in determining the aggressiveness of the water toward pitting corrosion of aluminum. The bicarbonate ion alone, at concentrations up to 300-400 ppm has been shown not to pitting, but in combinations with chloride and copper, calcium carbonate ions has led to intensive pitting.[8-9] At low bicarbonate levels, voluminous corrosion products were dispersed in solutions around the pits. With increased concentrations of bicarbonate, harder, thicker caps of nodular corrosion products were formed which firmly adhered to the pits.

Studies by Draley have shown that the presence of sulfate at 50 ^{0}C and 70 ^{0}C reduces the corrosion rate of aluminum.[13] The sulfates decreased the oxide film thickness formed as the concentration of sulfates increased. The thinner the film, the more susceptible the base metal is to corrosion.

Surface waters and storage pools are normally saturated with oxygen, but if there were areas of a spent fuel storage pool where oxygen was reduced, it would likely diminish the corrosion rate of aluminum. Measurements of dissolved oxygen in the storage basins at SRS found the water to be saturated at 10.9 ppm and constant with depth.

Corrosion Mechanisms

In the wet storage of aluminum-clad spent nuclear fuel, there are a number of corrosion mechanisms, which potentially come to play. The most important of these as they pertain to the aluminum-clad alloys are discussed below.

General Corrosion. The general corrosion behavior of aluminum in high purity water is very good. There is not a gradual thinning of aluminum as occurs with steel and this mechanism has not been a problem in spent fuel storage basins.

Galvanic Corrosion. Galvanic corrosion occurs when a metal or alloy is electrically coupled to another metal, usually dissimilar, in the same electrolyte. Galvanic corrosion is evident through fuel storage basins. During galvanic coupling corrosion of the less corrosion resistant metal increases and the surface becomes anodic, while corrosion of the more corrosion-resistant metal decreases and the surface becomes cathodic. Factors affecting galvanic corrosion are area ratios, distance between electrically coupled alloys, and geometric shapes. Galvanic corrosion of the anodic metal usually takes the form of general or localized corrosion.

Crevice Corrosion. Crevice corrosion of aluminum alloys is highly localized corrosion occurring on closely fitted surfaces upon entry of water into the crevice. The general theory is that s complex mechanism exists in which chloride ions are drawn into the crevice as metal dissolution occurs and acidic conditions exist. Aluminum, which depends on a passive film for corrosion protection, is particularly susceptible to crevice corrosion. Crevices between fuel hangers and fuel as well as in storage buckets and storage racks form many possibilities for crevice corrosion to occur.

Pitting Corrosion. The primary mechanism for corrosion of aluminum-clad fuel and target materials in wet storage in the U. S. and around the world has been pitting. Pitting is a localized form of corrosion in which metal is removed preferentially at point locations on the surface to develop cavities or pits. The attack is generally limited to small areas while the remaining surface is relatively unaffected. Pitting requires the presence of an electrolyte and in the case of fuel storage basins, less than optimum deionized water serves this purpose. Pitting is most common in metals that are covered with an adherent film. The pits tend to develop at defects or flaws in the surface of the film and at sites of mechanical damage where it is unable to repair itself.

Pitting, like general corrosion has been shown to proceed by an electrochemical process. The pitting is caused by electrochemical differences at two adjacent locations at the metal-liquid interface. An individual pit is, therefore, a local cell with its own anode and cathode.

The pitting can be described as an autocatalytic process. The corrosion processes within a pit produce conditions that are both stimulating and necessary for continuing activity of the pit. In a situation where metal is being pitted by an aerated chloride-containing electrolyte, rapid dissolution occurs within the pit, while oxygen reduction takes place on the adjacent surfaces. The rapid dissolution within the pits tends to produce excess charge in this area and results in the migration of chloride ions into the pit to maintain neutrality. Thus in the pit, there is a high concentration of metal chloride and a high concentration of hydrogen ions. As a result, the pits become more acidic, reaching low pH levels and stimulating further dissolution of most metals.

The rate of penetration of pits in aluminum decreases rapidly with time Aziz and Godard found that the pitting rate cure follows a cube-root law, given by:[14]

$$d = Kt^{1/3} \qquad (2)$$

where d = maximum pit depth, t = time, and K = constant depending on the particular alloy and the water conditions (composition, temperature, velocity, etc.). One can see that doubling the wall thickness of the metal can increase the time for perforation by a factor of eight.

The most undesirable result of pitting corrosion of spent fuel cladding is the perforation of the barrier material that protects the fuel core. This allows the release of the radioactive products such as uranium, plutonium, and cesium 137 to the basin water as the core corrodes. Build-up of this radioactivity in the basin water can ultimately lead to high radiation levels and exposure to personnel working around the basins.

Corrosion of Uranium Metal and Uranium-Aluminum Alloy Fuel Core

Most of the Foreign Research Reactor and SRS production fuel and target materials are clad with aluminum alloys, but the active core of the fuel is uranium metal or a uranium-aluminum alloy. Once the 30-mil cladding (some foreign fuels have 15-mil clad) is breached, the active core material is exposed to water. The Mark 31A target slugs stored in the SRS basins had an 1100-aluminum alloy cladding and a uranium metal core. When the cladding was breached during the first two years of storage, the corrosion continued into the uranium metal core material producing voluminous uranium oxide corrosion product as seen in Figure 1.

An excellent description of classical corrosion of uranium is provided by the work done in the late 1950's.[15] In general, once the clad has been penetrated by pitting corrosion, the compounds formed by the nickel bonding layer between the aluminum and the uranium may become slightly anodic to the aluminum and result in undercutting of the cladding by galvanic corrosion when exposed to the basin water. When uranium is metallurgically bonded to aluminum by a material like nickel, it corrodes somewhat more rapidly than bare uranium, but the increase in rate is more than offset by the smaller, restricted area of attack. The good bonding minimizes exposure of the uranium to the water. The corrosion of uranium in water can be expressed by the reaction:

$$U + 2H_2O \rightarrow UO_2 + 2H_2 \qquad (1)$$

The corrosion can be divided into two stages: an initiation stage, corresponding to the induction period observed in the corrosion of bare uranium, and a propagation stage. The initiation stage usually is an unpredictable length. There is generally absence of any significant swelling, but occasional bubbles of hydrogen may be evolved, and the pinhole in the aluminum may be discolored by small particles of UO_2. The propagation stage is characterized by the growth of a blister at the pinhole. Once swelling starts, the blister grows at a fairly steady rate until the accumulated uranium oxide causes the cladding to split. After the cladding splits, the $UO_{2\ is}$ released into the water and a larger area of the metal is exposed to attack. If the uranium core is of sound metal and the bond layer has no flaws or discontinuities, the blister is usually localized at the pinhole and has a mountain-like profile.

If the uranium contains stringers of voids or rolling seams, diffusion paths are provided for the hydrogen resulting from attack at the pinhole. Because of the small diameter of such flaws in uranium, the hydrogen can diffuse through them more rapidly than water, steam, or air. When the hydrogen encounters a site susceptible to attack (not protected by oxide), uranium hydride can be formed. This hydride attack is characterized by the appearance of a blister at a distance from the original pinhole. Since uranium hydride forms rapidly and has a lower density, the hydride blister almost always grows more rapidly than the original blister at the pinhole in the cladding, and the cladding usually splits first at the hydride blister. The splitting of the hydride blister exposes uranium hydride to water, with the formation of UO_2 and hydrogen, and simultaneously exposes a large area of uranium to attack. The uranium hydride attack is generally more rapid than the direct attack of uranium by water.

The Mark 22 fuels used in the SRS reactors contained two concentric aluminum-clad fuel tubes using an enriched uranium-alloy core. This alloy core consisted primarily of particles of UAl_3 and UAl_4 embedded in an aluminum alloy matrix. The nominal distance between larger particles was generally in the range between 1.5 to 45µm (0.06-1.8 mil.) The particles were broken up after the extrusion process. Corrosion of this alloy based on preliminary electrochemical laboratory tests was found to be similar to an aluminum alloy, itself. The corrosion rate of 8001 aluminum was measured at about 0.175 mpy compared to 0.171 mpy for the UAl_4 alloy.[16] The release of cesium from this type fuel is expected to be much slower than that from uranium metal.

Corrosion Surveillance at SRS 1992-2000

In order to develop a fundamental understanding of the corrosion problems with aluminum-clad spent fuel in the SRS wet storage basins in early 1992, a corrosion surveillance program was implemented. The program consisted of in-basin tests using corrosion surveillance coupons and laboratory electrochemical tests. Information obtained from these programs provided the basis for recommendations for improvements to plant equipment and basin operations to mitigate corrosion of the spent fuel.

Component Immersion Tests

These test were initiated in early 1992 after corrosion coupon scoping tests indicated that water in the reactor basins was aggressive to the corrosion of aluminum alloys used in the cladding for SRS fuel and target materials. Actual un-irradiated fuel and target tubes from a Mark 22 fuel were cut into 6 inch long cylinders and nested together like real fuel assemblies. The individual fuel and target tubes were pre-oxidized in deionized water to give about 1-micron thickness of Boehmite phase oxide on the surfaces. A total of 6 nested coupons were placed on a rack that could be lowered into the basin water at a depth of 3-6 below the surface. After various exposure times, two coupons were removed and metallography done on any pitting that was found. Two additional nested coupons were added to the rack and re-immersed in the basin. Corrosion racks were initially placed in the K-Reactor basin and expanded to L, P, and RBOF by early 1994.

The Component Immersion Tests have continued from 1992-2000. Results of these withdrawals can be seen in Table 1. Coupons were withdrawn more frequently early in testing, as the basin water was more aggressive before positive steps were taken to mitigate the corrosion. Early withdrawals in K-basin during 1992 showed that pitting through the 30-mil clad occurred in as little as 45 days. At the time of this exposure, the water in K-basin had a conductivity of about 180 µS/cm with 8 ppm chlorides. With pitting very aggressive in K-basin and earlier scoping tests indicating that the other reactor basins were equally aggressive, immediate steps were taken to continuously deoinize all basins. With further deionization of the basins and conductivity levels lowered to the 100-125 µS/cm range, no pitting was seen in K and L-basins. With continuous deionization of the RBOF basin and the conductivity maintained in the 1-3 US/cm range, no pitting has ever been seen on corrosion surveillance coupons. When conductivity of the P-basin reached 165 µS/cm pitting re-appeared on fuel in that basin.

SRS Research Reactor Corrosion Surveillance Program

The L-Reactor basin at SRS was refurbished to receive a large number of the aluminum-clad research reactor assemblies from both domestic and foreign sources over the next 20 years. With this refurbishment, a comprehensive corrosion surveillance program was developed to directly support the new extended fuel storage activity at SRS. This program was initially for basin to demonstrate that this storage basin could provide a suitable environment for long term interim storage of aluminum alloys after the basin upgrades during 1994-1996. The RBOF basin, shown in Figure 3, with its superb water quality over the years of operations and extremely low conductivity did not experience the pitting corrosion problem seen in the reactor basins in 1992-1993. However, the new surveillance program was implemented in this basin to provide additional data to supplement the existing Component Immersion Program.

The Research Reactor Corrosion Surveillance Program was designed to support the receipt of both domestic and Foreign Research Reactor (FRR) fuels. The corrosion monitoring program concentrates on aluminum alloys that are typical of cladding materials for spent foreign reactor fuel. Other alloy-clad fuels like Zircaloy and stainless steel are likely to go to another DOE storage basin in Idaho and are not included in this program. In addition to providing data to support fuel receipts at SRS, results from this program feed directly into the IAEA sponsored corrosion surveillance activities for research reactor aluminum-clad spent fuels.

The testing for this program began in both L-Reactor basin and in RBOF in January 1996. This was deemed adequate lead-time to determine the suitability of the reactor basin water for the extended storage of the FRR aluminum-clad materials. Data from this program and laboratory corrosion testing programs provide a technical basis for maintaining and improving basin management practices, establishing operational limits, and will aid in the prediction of fuel storage performance in the basin.

Corrosion Racks and Test Coupons. The corrosion samples are 31.75 mm (1 1/4 in.) circular disks of 3.175 mm (1/8 in.) thickness with a hole in the center designed to fit over the insulated stainless steel rod rack. Plastic insulators separate individual samples. The coupons are not pre-oxidized at elevated temperature in water, but have the normal air formed oxide. This condition should make them more sensitive to any water chemistry changes. Four basic types of corrosion specimens are being tested in the L-basin and RBOF water environments:

- Standard alloy circular disk.
- Welded alloy circular disk.
- Galvanic couple alloy circular disk with a 4:1 cathode to anode area ratio.
- Crevice alloy pairs.

Based on the current inventory of fuel in the RBOF basin and the available information for incoming research reactor fuel, 1100, 6061, and 5086 aluminum alloys are the primary cladding alloys expected to be stored in the basin. Welded and galvanic samples will concentrate on the 1100 and 6061 alloys. Some 304L stainless samples are included in galvanic couple tests to represent potential interactions that have typically existed over the years in most storage basins around the world. Multiples of each type coupon are included on each corrosion rack. Each rack contains 60 samples. A typical rack is shown in Figure 4.

Schedule for Withdrawal and Analysis. Eighteen corrosion racks are available for the SRS Research Reactor Corrosion Surveillance Program. Twelve racks are immersed in two different areas of L-basin. Six racks are immersed in the RBOF basin to support the program that is currently scheduled to last for twenty years. The corrosion-monitoring program was designed to provide data after six months, one year, two years, five years, ten years, and twenty years of exposure. Duplicate racks are scheduled for examination at the end of each pre-determined exposure time. The first three withdrawals up through two years of exposure were designed to provide an early indication of the aggressiveness of the storage environment on the aluminum coupons.

Along with color photography and metallurgical examination of the specimens, a detailed characterization of the basin water during the exposure period will be obtained from the existing water sampling and analysis program. The water conductivity, pH, chloride, nitrate, nitrite and sulfate content will be recorded.

Results. A total of six racks were withdrawn from the two basins during 1996-1997. These racks were withdrawn after six and 12 month's exposure. No pitting was observed except where embedded iron particles were found on 4 specimens from polishing by the vendor.

Three additional racks were removed from L-basin and from RBOF in early 1998 after 2 years of exposure in water conditions that generally ranged from 1-3 µS/cm conductivity with a chloride ion content in the parts-per-billion range. No pitting was observed on these racks. Some mild surface oxidation was seen on all coupons. Some mild surface reaction was seen in the crevice area of the stainless/aluminum galvanic couple samples.

A new simplified corrosion rack was designed in early 1999 to supplement the existing program. The new rack contained a reduced number of wafer samples of the aluminum alloys, with crevice and some galvanic samples. This rack was designed to be use to fill in the gaps for years in which there were no scheduled withdrawals in the original program. Fifteen additional racks were immersed in RBOF and L-Reactor basins in February 1999 and a new schedule for withdrawals made. The new schedule calls for a minimum of one withdrawal each year over the 20-year program.

Improvements to SRS Fuel Storage

With the aggressive nature of the water in K-Basin having been demonstrated by the pitting corrosion of the coupons during the corrosion tests and by the visual inspections of the fuel and target materials in the basins, a concentrated basin cleanup effort was initiated in the basins during 1993. Through a Basin Management Team consisting of reactor engineering, operations, and SRTC technical personnel, extensive manpower and resources were devoted to activities designed to improve basin storage conditions.

Based on initial observations and understanding on what was driving the corrosion processes, recommendations were made to improve the water quality. The effort initially started in the K-Basin with extensive deionization of the basin water that had approached 180μS/cm. Using the portable mixed-bed deionizers, the conductivity and impurity concentration of the water was slowly lowered. K-basin conductivity reached as low as about 125 μS/cm by early 1995.

Extensive deionization occurred in L-basin during early 1994 reaching a low of about 96 μS/cm from a high of over 160 μS/cm. The chlorides in this basin were lowered from about 18 ppm to 11 ppm by the deionization. Due to limited availability of deionizers, no special cleanup efforts were initiated in P-basin until the conductivity reached about 165 μS/cm and some pitting was seen on the aluminum corrosion surveillance coupons in that basin. After a concentrated deionization campaign, the conductivity of the P-basin was lowered to the 85 μS/cm range and no further pitting was seen. P-basin has since been closed and all fuel transferred to the other basins.

In July 1995, a vendor was contracted to accelerate the deionization of the SRS basins. Using mixed-bed deionization equipment that was installed in the L-basin, the water conductivity was lowered from about 110 μS/cm to below 8 μS/cm in 2.5 months. After releasing the vendor deionizer to go to K-basin, the SRS portable deionization equipment was used periodically to further lower the conductivity to about 1.8 μS/cm by March 1996.

In October 1995, the vendor equipment was installed in the K-basin and by February 1, 1996 all sections of the basin were down to a conductivity level below 10 μS/cm. Westinghouse purchased the deionization equipment from the vendor after the contract was completed. With continuous operation through March, the conductivity was further reduced to the 2.5 μS/cm range. The anion concentrations in the L and K-basins, typically chlorides, nitrates, and sulfates, were reduced to about 0.5 ppm by the vendor deionization.

As part of the cleanup activities in the reactor basins, a Disassembly Basin Upgrade (DBU) Project was initiated in 1994.[5] This project initially was to include three new permanent deionizers for the K and L-basins, sludge removal from the basins, and new aluminum storage racks for L and K-basins. The new DBU deionizer system began operating in both L and K-Areas on June 3, 1996. The new systems are designed to operate continuously at a flowrate of approximately 200 gpm through four vessels that are connected in series. The first two vessels contain 50 cubic feet of mix-bed resin, the third vessel holds 70 cubic feet of cation resin, and the final vessel contains 50 cubic feet of anion resin. With continuous deionization by the new DBU system, the conductivity and chemistry of the L and K-basins is routinely maintained at 1-3 μS/cm and is below 1 μS/cm for much of the time.

During 1994-1996 an extensive campaign of sludge removal was put into place. Underwater vacuum cleaning equipment was developed and used to remove sludge, several inches thick in some places, from the basin floor and other horizontal surfaces. The sludge is predominately iron oxide, aluminum oxide and other impurities which can set up localized anodic-cathodic sites on the aluminum clad fuel. In addition, some of the impurities like chloride can be concentrated several times the levels in the basin water.

The effort to clean up the basins has had a significant impact on the quality of spent fuel storage. With the basins routinely operating with a conductivity near 1 μS/cm and impurity concentrations in the ppb range, no new pitting corrosion has been seen on SRS fuel since 1994. In addition, fuel processing has been resumed at SRS and the worst of the old, corroded production fuel has been removed from the basins and reprocessed at this time.

Criteria for Corrosion Protection of Aluminum-Clad Spent Nuclear Fuel

Most of the fuel used in research reactors of eastern and western countries is fabricated with a uranium-aluminum alloy core protected by an aluminum alloy cladding material. A small percentage of the fuel is clad with stainless steel, zirconium, or other alloys. Fuel is regarded as spent nuclear fuel (SNF) regardless of burnup when it is discharged from the reactor core for the final time. It is then normally placed in pools for cooling and interim storage until a final disposition is made. Some of this aluminum-clad spent fuel has been in water storage for more than 40 years and remains in pristine condition while other fuel has been severely degraded by pitting corrosion. Pitting corrosion of the fuel can lead to breach of the cladding material and release of radioactivity to the storage basin. The criteria presented in this paper provide guidelines for optimizing corrosion protection for aluminum-clad spent nuclear fuel in wet storage pools and include recommended water chemistry, operational practices, and other basin management techniques for extended interim storage. The principles applied to obtain optimum water quality will also result in low corrosion rates for the other cladding alloys used with research reactor fuel.

Research reactor spent fuel is being stored in water filled basins around the world under a wide variety of storage conditions. Many of the pools have water purification equipment that maintains the water at high purity levels. In these basins, aluminum-clad fuels have been stored for 25-35 years without corrosion problems. Other storage pools are small and do not have high quality water. For these pools, corrosion of aluminum clad SNF has been a concern. As a part of the U.S. Department of Energy's decision to return foreign research reactor spent fuel to the United States, over 1700 aluminum-clad assemblies have been inspected for corrosion and mechanical damage.[17] The condition of assemblies has ranged from pristine, with no visible corrosion, to severe and localized nodular corrosion with pitting. Approximately 7% of the assemblies inspected showed pitting, which was judged to be through the aluminum clad into the core of the fuel.

Guidelines

The corrosion of aluminum-clad spent nuclear fuel is dependent on a number of interrelated factors. Many of the metallurgical factors are already inherent in the spent fuel when the reactor operator receives the fuel from the fuel fabricator for irradiation. Factors such as alloy composition, heat treatment, microstructure; nature and thickness of the protective oxide coating, inclusions and impurities in the alloy, and cold work play a role in the corrosion process, but are not controllable during wet storage. The recommended guidelines presented in this paper apply to the environmental and service related factors that are normally controllable and can be used to optimize the corrosion protection of the aluminum-clad fuel during interim wet storage.

These guidelines are designed to prevent breach of this clad and subsequent corrosion of the fuel core. Most of the research reactor fuel is fabricated from uranium-aluminum alloy and this type of fuel exhibits a corrosion behavior similar to aluminum. Therefore, implementation of these guidelines should also minimize corrosion of the fuel core. The corrosion of a metallic uranium core is a much more rapid chemical reaction than that for a uranium-aluminum alloy fuel, but would still be reduced by implementation of these recommendations to protect the aluminum clad.

Water Chemistry. Maintaining high quality water chemistry in the fuel storage pool is the single most important factor in controlling corrosion of aluminum-clad spent fuel assemblies and other aluminum components stored in the pool. Treatment and purification of the water in the pool and any make-up water through filters and using ion exchange resins is essential to achieving optimum storage performance. The guidelines presented here provide the recommended water parameters to minimize pitting and other forms of corrosion on aluminum-clad spent fuel during extended interim wet storage:

Conductivity. The conductivity of the water in the fuel storage basin shall be maintained as low as achievable and in the range of 1-3 µS/cm for optimum corrosion protection. This level may be difficult to achieve in unlined pools. A level of 3-10 µS/cm may yield satisfactory results provided impurities like chloride ions are in low concentrations. There is some evidence that pitting may be suppressed below 50 µS/cm depending on other favorable conditions. Values near 200 µS/cm are known to be aggressive to pitting of aluminum.

pH. The pH shall be maintained in reactor pools in a range of 5.5 to 6.5. This pH level will minimize uniform corrosion. Pitting corrosion is relatively independent over this pH range. Tight control of the pH is essential for reactors that have the core and fuel storage basin sharing the same cooling water. For away from reactor storage pools, a somewhat wider range of 5.0-8.0 may be permissible. Irradiation is known to reduce the stability range of the protective oxide and can result in extensive turbidity from precipitation of aluminum hydroxide from the water.

Chloride (Cl). The chloride ion content of the water shall be maintained as low as achievable and less than 1 ppm for optimum corrosion protection. This level is generally achievable if water conductivity is maintained in the 1-3 μS/cm range. Chloride ions break down the passive film on aluminum and promote metal dissolution.

Sulfates (SO_4). The total sulfate ion content of the water shall be maintained at less than 1 ppm for optimum corrosion protection. However, for unlined pools where chemistry is hard to control, a level at or below 10 ppm should give satisfactory protection. An increase in sulfate concentration results in a decrease in thickness of the protective oxide film with a corresponding increase in the susceptibility to pitting corrosion.

Heavy Metals**.** The concentration of copper (Cu)**,** mercury (Hg)**,** silver (Ag), and other heavy metal ions shall be maintained at or below 0.02 ppm. Heavy metal ions are extremely aggressive to the pitting corrosion of aluminum as they can plate out readily forming strong galvanic cells. These ions have strong synergistic reactions with chloride, bicarbonate, and calcium ions. Reduced metals in the basin sludge or particulate in solutions can form galvanic cells leading to localized corrosion when the particles are in contact with the aluminum.

Other Impurities. Impurity ions such as iron (Fe), aluminum (Al), nitrates (NO_3), nitrite (NO_2) shall be maintained at levels as low as possible. Normal deionization of the water in the storage pool to 1-3 μS/cm should keep these impurities to the 1 ppm or lower level. Any addition of cations or anions to the water increases the water conductivity and offers less resistance to the flow of corrosion current from the aluminum-clad.

Hardness. Maintain carbonate hardness of the water at 60 ppm or less when possible**.** Carbonate (CO_3^-) and bicarbonate ions (HCO_3^-) and can react synergistically with chloride and copper and lead to intensive pitting of aluminum. Soft water as defined by a carbonate content of 60 ppm or less is less aggressive to aluminum corrosion than hard water at a carbonate content of 60 ppm or greater. Continuous deionization of the basin water softens the water as it removes calcium carbonate and other ions contributing to the hardness.

Temperature. The water temperature shall be maintained at 40 ^{0}C or below. The rate of pitting at pitting at 40 ^{0}C has been found to be 5 times the pitting rate at 25 ^{0}C. The density and probability of pitting has been found to increase with temperature. The corrosion rate of uranium metal increases dramatically with increasing temperature.

Radiation Effects. Gamma radiation from irradiated fuel assemblies, cobalt-60 or radioactive cesium sources can have some effect on materials stored in fuel storage pools. The gamma fluxes, however, have little effect on the properties of the metal cladding and the radiation field does not seem to promote any significant increases in corrosion of the metals in wet storage. Gamma fields can deteriorate components subjected to radiolytic decomposition like neutron absorbers that include organic materials and rack configurations that trap water that subsequently forms gas pressure from radiolyic decomposition.

Operational Practices

Water Circulation. Avoid stagnant areas of water in the fuel storage basin. Ensure that the water is circulated to provide movement over the stored fuel assemblies. As an example, a linear flow rate over the aluminum surface as little as 2.4 meters per minute has been shown to suppress pitting on some aluminum alloys.

Sludge Removal. Do not allow sludge to accumulate in the water of the fuel storage basin. Remove on a periodic basis by vacuuming or other methods. This material can concentrate chlorides, heavy metals, etc. and deposit on fuel assemblies initiating pitting of the aluminum clad.

Filtration. Mechanical filters or resin beds shall be used to control suspended solids or particulate material in the basin water before it turns into sludge. Deionization of the water helps to accomplish this.

Skimmer System. Debris and other species floating on the water surface of fuel storage pools shall be removed by a skimmer system or other means. This material can settle on surfaces of fuel cladding and cause pitting corrosion.

Crevices. Avoid crevices between the aluminum-clad assemblies and the fuel storage racks or hangers. Low pH water conditions, concentration of chloride ions, and oxygen concentration cells in these crevices can lead to accelerated corrosion of the cladding.

Galvanic Couples. Avoid contact between aluminum-clad fuel assemblies and dissimilar metal storage racks or hangers. Use aluminum storage racks or provide non-conducting insulators whenever possible. Aluminum-clad fuel coupled to stainless steel racks or hangers will accelerate pitting corrosion of the aluminum.

Handling of Spent Fuel**.** Avoid handling fuel assemblies with sharp edged tools as scratches in the oxide coating of irradiated fuel serve as pitting initiation sites when in the storage basin. Minimize, as much as possible, mechanical damage and surface scratches on fuel element surfaces during discharge from the reactor core and during subsequent fuel handling and storage operations.

Microbiological Activity. Do not add chemicals containing chlorides or other halogens such as sodium hypochlorite (NaOCl) to the water in storage basins for control of algae, bacteria, or turbidity without first testing for compatibility with the fuel, basin lining, or other basin components. The chloride in many of the chemicals will destroy the passive film on aluminum and cause aggressive pitting corrosion.

Biofilm Formation at Air/Water Interface. The bath tub ring often formed at the air/water interface around the sides of the basin is likely a biofilm of microbial activity. This film acts like a trap and is known for concentrating cesium and other radioactive isotopes contained in the basin water. This biofilm should be removed mechanically by wet brushing using water to hold down any airborne activity. A 35% solution (200mL in 700 gal) of hydrogen peroxide (H_2O_2) has proven effective in killing microbial activity and could be used to assist this removal without corrosive attack on aluminum alloys.

Basin Lighting Conditions. The lighting conditions shall be maintained as low as practical in and around the basin area. High levels of lighting promote microbiological growth activity in the water. Ultraviolet lighting can be used to suppress microbiological activity associated with filters, etc. However, sidestream ultraviolet light systems are used primarily for planktonic activity and are not effective on sessile colonies.

Make-up Water. Additions of water to the fuel storage pool should be of a quality equal to or better than the existing pool water. Deionized water shall be used whenever possible.

Radionuclide Activity in the Basin Water. Radionuclide activity in the basin water leached from the spent fuel shall be monitored and controlled to levels deemed to be safe for personnel working in the surrounding area. Continuous deionization of the water removes alpha and beta-gamma radioactivity from the water. Fission products such as Cesium-137 and other radionuclides may be found in the water from the storage of failed spent fuel elements or breach of clad. Special materials such as zeolite can be used in the ion exchange type purification system to specifically target these radionuclides for removal.

Water Sampling Plan. Maintaining water purity levels to the strict guidelines presented here is vital for successful operation of a wet storage fuel facility. Basin water quality is monitored through sampling, and trending sampling results. All the major water parameters such as pH, conductivity, and chlorides shall be measured on a periodic basis consistent with good basin management practices. Weekly monitoring is recommended, but this interval can be established by the basin operator and is dependent on pool conditions. Other impurity ions such as sulfates, nitrates, nitrites, copper, mercury, iron, and aluminum shall be measured quarterly as a minimum. Temperature shall be monitored daily. The alpha and beta-gamma radioactivity measurements in basins storing spent fuel shall be made on a frequency basis established by individual requirements. An increase in radioactivity is an indicator of corrosion. Permanent records shall be kept and analytical results trended.

A baseline evaluation of microbiological activity in the basin shall be made from a sampling of the basin water. Analysis shall include counts of hetrotrophic, acid producing, anaerobic, and sulfate reducing bacteria. This baseline can be use to compare with analysis of bacteria at some later time.

Corrosion Surveillance Program. A long-term corrosion surveillance program shall be implemented in the fuel storage pool to monitor the aggressiveness of the basin water toward the corrosion of aluminum alloys. Details for specific site programs can be tailored for the individual sites, but should contain the generic elements described in this paper. A typical program has been implemented in a number of countries with research reactor fuel.[18] Corrosion racks with coupons manufactured from aluminum alloys typical of the spent fuel cladding shall be immersed in the water near the stored aluminum-clad spent fuel. Standard corrosion coupons, either round or rectangular shaped shall be used. Multiple coupons representing individual aluminum alloys, crevice corrosion coupons, and galvanic coupons shall comprise each rack. The coupons shall not be pre-oxidized other than air-formed oxide normally found on the surface. This insures some conservatism.

A schedule for withdrawal of these coupons shall be formulated based on the length of time fuel is expected to be in the basin and the total number of corrosion racks available for testing. As a minimum there should be enough racks available to obtain data after 6 months, one year, and two years to provide an early indication of the aggressiveness of the storage environment on the aluminum coupons. Depending on the expected storage life of the fuel, the surveillance program should continue. For a twenty-year program, withdrawals could be extended to 5 years, ten years, and twenty years exposure time. If the water conditions are more aggressive, additional racks may be required and more frequent intervals of withdrawal may be necessary. Ideally, however, enough racks should be purchased to permit at least one withdrawal each year.

Metallographic evaluation of the corrosion coupons shall include pitting density and maximum pit depth. Knowing pitting depth and exposure time, the pitting rate may be calculated. Video and still color photography shall be used to document the withdrawals. Data from the water analyses taken during the exposure periods should be correlated with the corrosion observations on the coupons to explain the test results.

Records Management Program. Data from the individual basin water chemistry and corrosion surveillance programs shall be maintained at the individual sites.

Conclusions

The storage of aluminum-clad spent nuclear fuel in less than optimum quality water can result in aggressive pitting corrosion. This corrosion was a concern at SRS in the early 1990's, but an aggressive Basin Management program resulted in significantly improved storage conditions and no new pitting has been seen in the reactor basins since 1994.

The knowledge learned from these basin cleanup activities and the corrosion surveillance program, underway since 1992, have provided a basic understanding of the important factors affecting the corrosion of aluminum-clad fuel. The criteria for corrosion protection of this fuel have been presented in this paper. Even though there are a number of important factors affecting this corrosion and some act synergistically, the key to improved and extended storage is based on improved water quality conditions. Improved water quality through continuous deionization results in low water conductivity and low impurity concentrations of important corrosion causing species like chloride ions. Aluminum-clad spent fuel can be stored safely and with minimum corrosion for times exceeding 25 years in water with a conductivity near 1 µS/cm and ppb quantities of impurities.

References

1. J. P. Howell, "Corrosion of Aluminum Alloys in a Reactor Disassembly Basin," NACE Corrosion/93, paper No. 609, (Houston, Texas : National Association of Corrosion Engineers, 1993).
2. J. P. Howell, "Durability of Aluminum-Clad Spent Nuclear Fuels in Wet Basin Storage" NACE Corrosion/96, paper No. 128, (Houston, Texas: National Association of Corrosion Engineers, 1996).
3. J. P. Howell and S. D. Burke, "The Corrosion of Aluminum-Clad Spent Nuclear Fuel in Wet Basin Storage," Proceedings of the American Nuclear Society Embedded Topical Meeting on DOE Spent Nuclear Fuel & Fissile Material Management, (Reno, Nevada, June 1996): p. 49-56.
4. J. P. Howell, "Corrosion Surveillance in Spent Fuel Storage Pools," NACE Corrosion/97, paper 107, (Houston, Texas: National Association of Corrosion Engineers, 1997).
5. S. D. Burke and J. P. Howell, "The Impact of Prolonged Wet Storage of DOE Reactor Irradiated Nuclear Materials at the Savannah River Site," Proceedings of the Topical Meeting on DOE Spent Nuclear Fuel-Challenges and Initiatives, "(Salt Lake City, Utah, December 1994): p. 118-124.
6. H. P. Godard, "The Corrosion of Light Metals," John Wiley & Sons, Inc., New York, 1967, p.3.
7. F. C. Porter and S. E. Hadden, J. Applied Chemistry, Vol. 3, (1953): p. 385-409.
8. D. E. Davies, J. Applied Chemistry, Vol. 9, (December 1959): p. 651-660.
9. L. C. Rowe and M. S. Walker, Corrosion, Vol. 17, (1961): p. 105-108.
10. H. P. Godard, Materials Performance, Vol. 18, (May 1979): p. 21-27.
11. Z. Szlarska-Smialowska, Pitting Corrosion of Metals, (Housston, Texas: National Association of Corrosion Engineers, 1986).
12. O. Swerpa, Werk. And Korr., Vol. 9, (1958): p. 533.
13. J. E. Draley, U. S. AtomicEnergy Commission T.I.D. 7587, (1960): p. 165.
14. P. M. Aziz and H. P. Godard, Journal of Industrial and Engineering Chemistry, 44, 8, (August 1952): p. 1791-95.
15. D. Z. Nelson and J. P. Howell, "Metallography of Pitted Aluminum-Clad, Depleted Uranium Fuel," NACE Corrosion/95, paper No. 430, (Houston, Texas: National Association of Corrosion Engineers, 1995).
16. H. B. Peacock, R. L. Sindelar, P. S. Lam, and T. H. Murphy, "Experiments for Evaluation of Corrosion to Develop Storage Criteria for Interim Dry Storage of Aluminum-Alloy Clad Spent Nuclear Fuel," Proceedings of The Topical Meeting on DOE Spent Nuclear Fuel-Challenges and Initiatives, (Salt Lake City, Utah, December 1994): p. 76-82.
17. P. Brooks and R. L. Sindelar, "Characterization of FRR SNF in Basin and Dry Storage Systems," Proceedings of the Third Topical Meeting on DOE Spent Fuel and Fissile Materials Management, (Charleston SC, September 1998): p. 542-549.
18. J. P. Howell, "Corrosion Surveillance for Research Reactor Spent Nuclear Fuel in Wet Basin Storage," NACE Corrosion/99, paper No. 462, (Houston, Texas: National Association of Corrosion Engineers, 1999).

Table 1
Component Immersion Test Results
1992-2000

1992									
Basin	**Date**	**Exposure (Days)**	**Maximum Pit Depth (Mils)**	**Pit Density ($Pits/cm^2$)**	**Avg. Cl ppm**	**NO_3**	**SO_4**	**pH**	**Avg. Conductivy (µS/cm)**
K	7-92	45	1100 8001 2 53	1100 8001 0.125 .01	8	20	15	7.5	175
K	6-92	75	13 45	0.125 .01					
K	3-92	107	23 39	0.125 .01					
K	6-92	182	58 27	0.125 .01					

K	12-92	365	100 57	0.125 .05					
1993-2000									
K	3-94	65	No Pitting						
K	7-94	181							
K	2-95	403			6	18	9	7.3	125
K	8-95	590							
K K	8-97 2-99	1091 1240	 No Pitting		<0.1	<0.1	<0.1	7.25 6.9	2.5 3.5
L	11-93	61	No Pitting						
L	3-94	127							
L	7-94	241							
L	2-95	336			14	20	2	6.6	102
L	8-95	340							
L L	8-97 2-99	1114 1240	 No Pitting		<0.1	<0.1	<0.1	6.6 6.5	1.8 1.0
P	11-93	61	No Pitting						
P	3-94	127							
P	7-94	241							
P P	2-95 9-95	336 715	35 mil Pits in 8001 No Pitting		10	9	18	7.5	160
RBOF RBOF	9-97 3-99	1222 1290	No Pitting No Pitting		0.1			6.19 6.5	1.18 1.0
RBOF	8-95	480	No Pitting		0.2	1.5	0.5	7.4	1
RBOF	4-96	723	No Pitting						

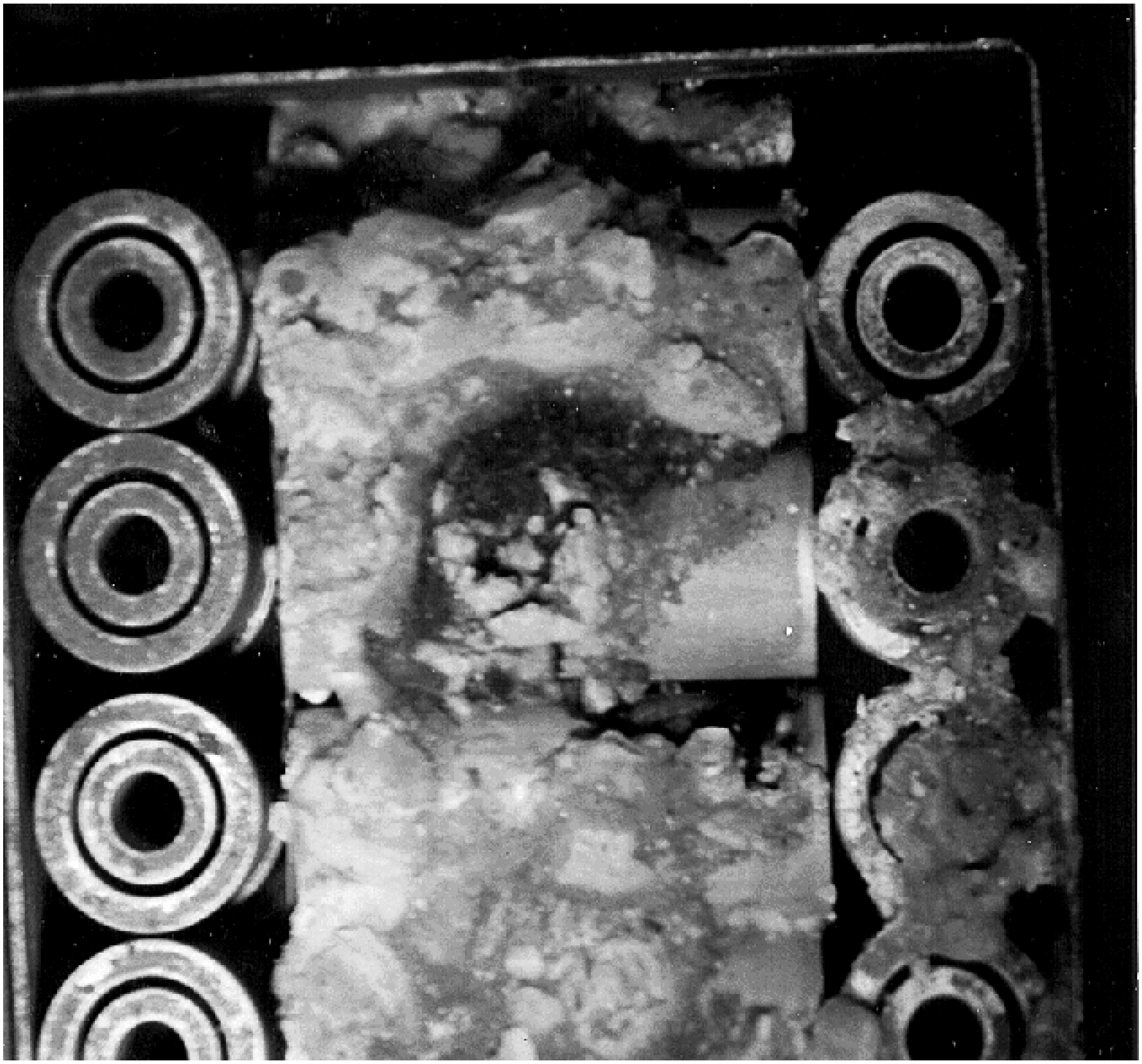

Figure 1. Corrosion products on Mark 31A target slugs stored in L-Reactor basin.

Figure 2. Nodular Corrosion Product on Underwater stored Mk 22 Fuel Assemblies

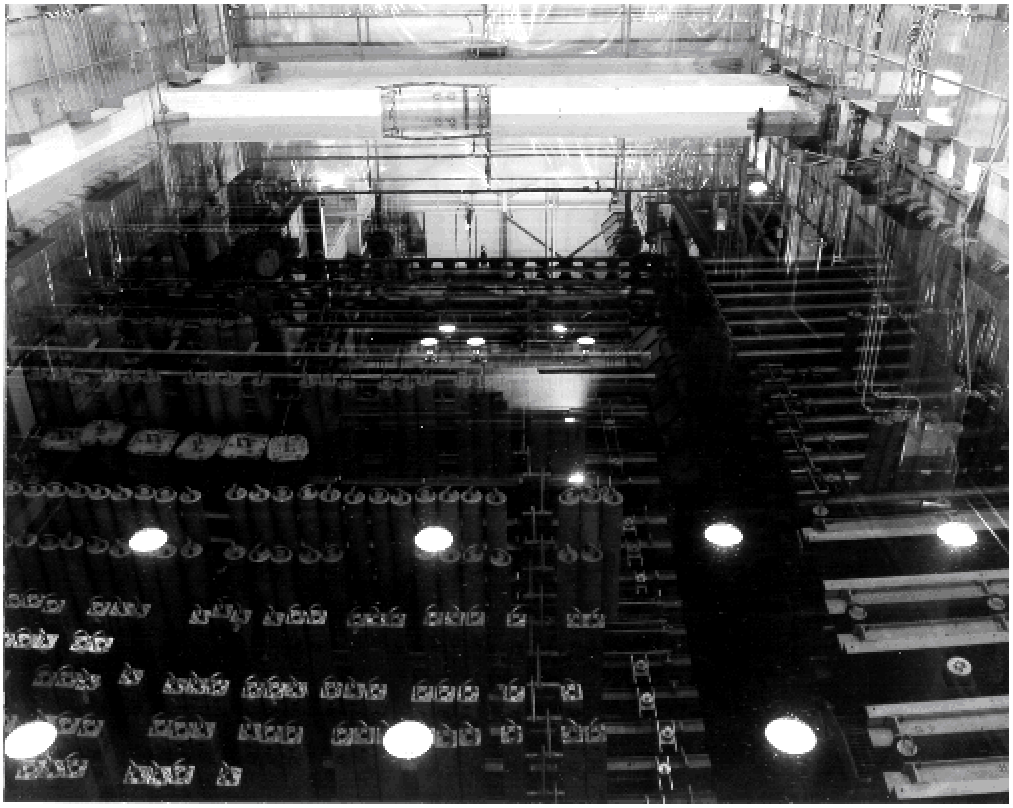

Figure 3. RBOF spent fuel storage basin

Figure 4. Typical Corrosion Surveillance Rack