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Document Approval Sheet

Document No.
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Title
The Corrosion of Aluminum-Clad Spent Nuclear Fuel in Wet Basin Storage

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2. Title The Corrosion of Aluminum-Clad Spent Nuclear Fuel in Wet Basin Storage (U)

3. Product/Report Description

☐ a. Report *(Complete all that apply)*

(1) ☐ Print ☐ Nonprint *(specify)* ____

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C. Contact *(Person knowledgeable of content)*

Name J. P. Howell
Phone 5-3567
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Organization MTS/AS&T

PART 2 *(DOE/DOE Contractors complete/or as instructed by DOE contracting officer)*

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2. Funding Office(s) *(NOTE: Essential data)* DOE-SR

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B. Released by
(Name) Jeanne Sellers
(Signature) Pat Dominey for
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(Date) 4-9-96

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WSRC-MS-96-0141
MSD-STI-96-0353

February 22, 1996

Ms. W. F. Perrin, Technical Information Officer
U. S. Department of Energy
Savannah River Operations Office
Aiken, SC 29801

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W. F. Perrin
W. F. Perrin, Technical Information Officer
DOE-SR

4/3/96
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The Corrosion of Aluminum-Clad Spent Nuclear Fuel in Wet Basin Storage (U)

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A document prepared for ANS TOPICAL MEETING ON DOE SPENT NUCLEAR FUEL AND FISSILE MATERIAL MANAGEMENT at Reno from 06/16/96 - 06/20/96.

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WSRC-MS-96-0141

THE CORROSION OF ALUMINUM-CLAD SPENT NUCLEAR FUEL IN WET BASIN STORAGE

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ABSTRACT

Large quantities of Defense related spent nuclear fuels are being stored in water basins around the United States. Under the non-proliferation policy, there has been no processing since the late 1980's and these fuels are caught in the pipeline awaiting stabilization or other disposition. At the Savannah River Site, over 200 metric tons of aluminum clad fuel are being stored in four water filled basins. Some of this fuel has experienced visible pitting corrosion. An intensive effort is underway at SRS to understand the corrosion problems and to improve the basin storage conditions for extended storage requirements. Significant improvements have been accomplished during 1993-1996.

This paper presents a discussion of the fundamentals of aluminum alloy corrosion as it pertains to the wet storage of spent nuclear fuel. It examines the effects of variables on corrosion in the storage environment and presents the results of corrosion surveillance testing activities at SRS, as well as discussions of fuel storage basins at other production sites of the Department of Energy.

I. INTRODUCTION

Under the non-proliferation policy for nuclear materials, the United States Department of Energy DOE) began to halt processing of nuclear materials for Defense at its production sites during the late 1980's. At this point, about 2800 metric tons of spent nuclear fuel (SNF) was caught in the nuclear pipeline, awaiting processing, while stored in the light-water filled basins.[1] At the Westinghouse Savannah River Site (SRS) where most of the 200 metric tons of stored fuel is aluminum clad, processing in the F-Canyon facilities has been suspended since late 1989. Similar extended storage scenarios exist at the Westinghouse Hanford Site, the Lockheed Idaho Technologies Co., Oak Ridge National Laboratory, and other spent fuel storage sites in the DOE production complex. Significant corrosion problems exist with the spent aluminum-clad fuel at some of the sites, while minimum problems exist in other basins.[2,3]

The fundamentals of aluminum alloy corrosion as they pertain to the wet storage of spent nuclear fuel are examined in this paper. The effects of variables on corrosion in the storage environment are discussed and the results of corrosion surveillance testing activities at storage basins at DOE production sites are presented.

II. CORROSION FUNDAMENTALS

A. Oxide Films on Aluminum

Aluminum is one of the most thermodynamically reactive metals. Aluminum owes its excellent corrosion resistance in most environments to the protective barrier oxide film formed and strongly bonded to its surface. This film of aluminum oxide is relatively inert and tends to resist further oxidation. The film can be dissolved in the presence of some chemicals and this can lead to dissolution of the metal. When the film is damaged under conditions that normal self healing does not occur, localized corrosion in the form of pitting or intergrannular attack can occur.[5] The oxide film formed on aluminum at temperatures above about 70^0 C, typical of irradiation conditions, is predominately the more protective Boehmite ($Al_2O_3 \cdot H_2O$), however, some films show both Bayerite ($Al_2O_3 \cdot 3H_2O$) and Boehmite crystalline electron diffraction patterns.

B. Kinetics

From an engineering standpoint, a major interest is in the kinetics or rate of corrosion of systems. Corroding systems are not in equilibrium, and therefore thermodynamic calculations cannot be applied. For metal corrosion to occur, an oxidation reaction (generally a metal dissolution or oxide formation) and a cathodic reduction (such as proton or oxygen reduction) proceeds simultaneously. In most normal water environments, the overall reaction for aluminum corrosion is reaction with water to form aluminum hydroxide and hydrogen which has very low solubility in water and precipitates into Bayerite or Boehmite, depending on the temperature of the water.[5]

$$2Al + 6H_20 \rightarrow 2Al(OH)_3 + 3H_2 \qquad (1)$$

In the electrochemical reaction, the positive charged ions leave the surface of the anode into the electrolyte solution leaving electrons behind to flow through the metal to the cathode. At the cathode, the electrons are consumed by the hydrogen ions at the surface and hydrogen gas is liberated. The oxidation and deterioration of the anode surface causes corrosion to occur.

C. Corrosion Mechanisms

In the wet storage of aluminum-clad spent nuclear fuel, a number of corrosion mechanisms potentially play a role. Some appear more prevalent in basin storage than others. The general corrosion behavior of aluminum in high purity water is extremely good. There is no significant general corrosion or gradual thinning of aluminum as may occur with steel.[6] General corrosion has not surfaced as a problem in the storage of aluminum clad alloys at basins in the U.S. as long as the protective oxide on the aluminum remains intact. As a general rule, the protective oxide film is very stable in aqueous solutions in the pH range of 4.0 to 8.5.

Galvanic corrosion occurs throughout most fuel storage basins. It occurs when a metal or alloy is electrically coupled to another metal, usually dissimilar, in the same electrolyte. 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. The driving force for the corrosion or current flow is the potential developed between the dissimilar metals.

Galvanic corrosion of spent nuclear fuels in most basins can be greatly reduced by removing the couple and by lowering the basin water conductivity. At low levels of conductivity in the range of 1-3 μS/cm, the galvanic effect is minimized. Basin deionization removes the corrosion causing anions and cations from the water and increases the resistance to current flow.

Crevice corrosion of aluminum alloys is highly localized corrosion occurring on closely fitted surfaces upon entry of water into the crevice.[4] Recent work has shown a complex mechanism exists in which chloride ions are drawn into the crevice as metal dissolution occurs and acidic conditions exist. Metals like aluminum which depend on oxide films or passive layers for corrosion resistance are particularly susceptible to crevice corrosion. Crevices exist in may locations in the storage basins where nuclear fuel is supported by hanger and storage racks. These locations provide the environment for localized corrosion to occur because of the stagnant areas and differential oxygen cells that can be set up.

Pitting corrosion of the aluminum clad fuel and target materials in wet basin storage is the primary mechanism of corrosion in the U.S. and other basins around the world. 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 extremely small areas while the remaining surface is relatively unaffected. The pits usually start at small points on the surface and enlarge with time. Pitting requires the presence of an electrolyte and in the case of most storage basins, less than optimum deionized water serves this purpose.

Pitting is most common in metals that are covered with an adherent surface film. The pits tend to develop at defects or flaws in the surface film and at sites of mechanical damage where it is unable to repair itself. Pitting of spent fuel can be extremely undesirable as perforation of the clad material allows the release of uranium, plutonium, cesium-137, and other radionuclide activity to the basins as the core corrodes. Build-up of this activity in the basin water can ultimately lead to high radiation levels and exposure to personal working around the basins.

The rate of penetration of pits in aluminum has been shown to decrease rapidly with time. Aziz and Godard found in test samples and in the field that the pitting rate curve follows a cube-root law given by:[7]

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

where d = maximum pit depth, t = time, and K = constant, depending on the particular alloy and the water conditions (composition, temperature, velocity, etc.).

III. PITTING CORROSION IN U.S. BASINS

A. Savannah River Site

Storage of aluminum clad fuel and target assemblies in the reactor disassembly basins at the Savannah River Site has been successful over the forty-plus years of plant operations. Pitting corrosion of spent fuel stored in the water-filled basins while awaiting processing has, however, been a periodic concern during several time periods over the history of plant operations.

Evidence of new aggressiveness of the basin water was found in 1989-1990 when 6063 aluminum sleeve housings, which surround the fuel in the reactor, were stored in the K-basin for 25-70 days while awaiting shipment back to the lab for metallurgical analysis. Upon examination, sixteen of twenty-four specimens showed evidence of pitting corrosion and seven pits had penetrated the 0.050-inch wall. Based on these findings, an immersion test program was implemented in the reactor basins at SRS in mid-1991.

1. Corrosion Surveillance Program. Coupons for the Component Immersion Tests were cut from actual unirradiated fuel and target tubes of the SRS Mark 22 fuel assembly and pre-oxidized to give a one micron thickness of Boehmite oxide. The 1100 and 8001 aluminum alloy clad tubes were nested together on a corrosion rack and immersed in the basins. Initial testing was conducting in the K-Basin during 1992. After various exposure times up to one year, specimens were removed from the basin and evaluated metallurgically in the laboratory. The results of these evaluations are shown in Table 1. Pitting exceeding the 30- mil cladding thickness was observed in the 8001 alloy in 45 days. These corrosion surveillance tests demonstrated the aggressive nature of the K-Basin water during 1992.

With the recognition of the aggressive nature of the basin water, a Basin Management Team was formed and new basin cleanup activities were implemented.[8] The corrosion surveillance tests were expanded to include all active basins onsite during 1993-1995. With more continuous deionization in L and K-basins over the next two years, no new initiation of pitting corrosion has been observed as is shown in Table 1. With limited deionizer availability, P-Basin received little water treatment over this time period and some pitting was observed after 11 months exposure.

The water chemistry of the basins was analyzed during the interval of testing from 1992-1995. When the K-Basin was extremely aggressive in 1992, the conductivity of the water was 178 µS/cm. Impurities like chloride were in the 6-9 ppm range. During 1994-1995, the conductivity of K and L-Basins ranged between 100-135 µS/cm. Chlorides in K-Basin were about 6 ppm and L-Basin ranged between 11-18 ppm with no pitting corrosion evident on the coupon specimens. Conductivity of P-Basin when pitting was observed was 165 µS/cm with chlorides at about 10 ppm. After deionization, the conductivity was lowered to 128 µS/cm and no further pitting has been observed.

B. Receiving Basin for Offsite Fuel

The RBOF facility at SRS is the primary storage basin for domestic and foreign research reactor spent fuel from the U.S. and other parts of the world. SRS is expected to received over 18,000 aluminum-clad assemblies for storage in RBOF and L-Reactor basins during the next 10-15 years. A mixed-bed deionizer is operated at RBOF for about 5 days a week to minimize the corrosion of the fuel elements, fuel racks, and underwater equipment and to remove radioactive ions from the water. The purification system maintains the conductivity of the water between 1-3 µS/cm and impurities in the parts-per-billion (ppb) range. Under these low conductivity conditions, there is no visible evidence of corrosion on the aluminum canisters which house most of the fuel or on the 6061 aluminum alloy storage racks which have been in the basin for 30 years.

The oldest aluminum-clad fuel in the RBOF basin is from the French Nereide Reactor. This fuel has been stored in the basin for 12.5 years and was removed from it's canister and inspected originally in 1993 and again in 1994 after 10.5 and 11.5 years exposure to the RBOF water conditions. There were no visible signs of corrosion on this fuel or the canister. There is some evidence of corrosion of uranium metal fuel whose clad was failed at the reactor site prior to storage in the RBOF facility. Component Immersion Test specimens withdrawn from this basin after 16 months exposure show no evidence of pitting on the aluminum alloys. The RBOF basin has a long history of successful storage of spent nuclear fuel.

C. Idaho National Engineering Laboratory (INEL)

The Lockheed Idaho Technologies Company operates the Idaho Chemical Processing Plant (ICPP) CPP-603 and CPP-666 water storage basins at the Idaho National Engineering Laboratory. The CPP-603 has operated since 1951 and the CPP-666 began operation in 1984.[9] As processing of this fuel ended in April 1992, the mission has changed to long term storage until a final disposition is defined and implemented.[3]

The fuel matrices currently being stored in these basins include uranium oxide, hydride, carbide, and alloy fuels. These fuels are clad with aluminum, zirconium, and stainless steel. Galvanic couples of carbon steel-aluminum, carbon steel-stainless steel, and stainless steel-aluminum are present in the basins.

The CPP-603 Basin is a 1.5 million gallon, unlined concrete basin. From the treatment for algae with sodium hypochlorite over the years, concentrations of chloride in the basin reached 800 ppm by 1976. This accelerated the corrosion of many materials in the basin. Using a reverse osmosis system and low chloride makeup water, this has been reduced to about 50 ppm. The pH is maintained in the range of 5-8.5 and the conductivity in 1994 was above 600 µS/cm. Nitrate is added to the basin water to reduce the corrosive effects of chloride, keeping a nitrate to chloride ratio between 3:1 and 5:1. In 1994, this nitrate to chloride ratio was 3.26:1.

Periodic visual examinations, including underwater video inspections, are made of fuel and basin components. Four different materials have been evaluated in these inspections; stainless steel, zirconium alloys, carbon steel, and aluminum. No appreciable corrosion has been detected on the zirconium and stainless steel alloys. Carbon steel, used only in the handling equipment, has corroded extensively and is being replaced with stainless steel. Aluminum has shown preferential attack in the form of pitting and crevice corrosion.

In the corrosion surveillance program, stainless steel and aluminum corrosion coupons have been immersed in the basin and evaluated semi-annually over the past 10-13 years. The welded stainless steel plate has shown no attack after 13 years of exposure. Expanded metal mesh and woven metal mesh aluminum coupons have been used to duplicate screens used on aluminum racks in the basin. The coupons have been inspected every 6 months and in 1994 had about 10.6 years of exposure. The aluminum has shown a general attack of 1.5 mpy with preferential attack in the form of pitting and crevice corrosion. A representative sample of each type of fuel stored in the CPP-603 basin is inspected for corrosion every 18 months. The initial inspections were performed with underwater lights and binoculars through 20 feet of water. Zirconium-clad fuel stored in stainless steel cans showed no visible attack. Aluminum cans showed moderate to heavy oxide buildup indicating pitting attack on the aluminum.

The CPP-666 Basin, located at the Chemical Processing Plant, is the most modern fuel storage facility in the DOE Complex.[9] It was built in 1984 and consist of six stainless steel lined storage pools with aluminum and stainless steel storage racks in 3.5 million gallons of recirculated, deionized water. The deionizer system consists of : (1) stainless steel filters with backwash capability, (2) stainless steel vessels containing cation and anion exchange resins, (3) chillers with stainless steel-wetted parts, and (4) quartz tubes in ultraviolet (UV) sterilizers.

The water treatment system maintains a high quality storage environment for all cladding materials, especially aluminum. The pH is typically in the range of 5.2-6.0, a chloride content of about 0.05 ppm, and a water conductivity of less than 2 µS/cm.[9] Aluminum and stainless steel corrosion coupons representing the storage racks are stored in the basin and monitored periodically by visual examination and ultrasonic inspection. Periodic inspections of the stainless steel liner have shown that both the base metal and the liner welds are sound with no indications of corrosion. A thin film of algae has been found on the surface, apparently forming when the ultraviolet lights were out of service for two years.

The stainless steel coupons removed from the basin after 8 years of exposure showed no localized corrosion and a low general corrosion rate of 0.13 mpy. Some pitting was seen on the dummy aluminum cans immersed in the basin after 7 years of exposure. None of the typical white corrosion product was seen on the aluminum, but the pitting perforated the can allowing water to get inside. Subsequent ultrasonic inspection confirmed this pitting which is suspected to be the result of microbiologically influenced corrosion (MIC).[3] It is assumed from the observation on the corrosion coupons that all stainless steel and zirconium type fuels in the CPP-666 basin are in good condition.

D. Westinghouse Hanford Company (WHC)

Defense program fuels irradiated in the Hanford N-Reactor and the Single Pass reactor are currently stored in the K-East and K-West basins at Hanford.[2] Over 2000 MTHM of enriched uranium metal co-extruded into Zircaloy-2 cladding is stored in the two basins. This represents about 80% of the spent nuclear fuels inventory in the DOE complex. K-East and K-West basins were originally used to provide temporary storage for spent fuel from the K-Reactor complex prior to shipment to the chemical processing plants at Hanford. The basins operated in a feed and bleed, once through mode, using river water without a water purification system from 1954 until 1971 when the K-Reactors were shut down.

Beginning in 1973, the KE basin was reactivated and significantly modified to store N-Reactor fuel.[2] The concrete basin surfaces were not cleaned or coated. The basin was initially filled with filtered river water and makeup water was filtered water. Various algaecides and chlorine were used to control bacteria growth. The original water treatment system in the basin consisted of the primary recirculation loop with two cartridge filters and a heat exchanger. The poor quality water that resulted from this initial setup was characterized by high conductivity, high chloride concentrations, high corrosion rates and extremely high radionuclide concentrations and dose rates. A high percentage of the N-Reactor fuel was breached during the unloading operation and when shipped to the basin for cooling. The fuel was stored in open top aluminum cans with the uranium metal exposed directly to the basin water. Corrosion of the uranium occurred immediately, releasing the radioactivity to the basin at a high rate. The leach rate for radioactivity from the damaged fuel into the basin water is about 1.2 Ci/day at 50 ^{0}F and 3.5 Ci/day at 70 ^{0}F.

Fuel shipments began in mid-1975 and within a few months, KE basin radionuclides began increasing at a high rate. This prompted major modifications to the system to install three ion exchange columns and a sand filter in 1978. The heat exchangers were replaced with a water cooled system by 1983. This allowed the basin to be maintained at a constant low temperature which was found to be extremely important. They found that radionuclide release rate was three times higher in the summer than in the winter due to higher water temperatures.

Preparations begin for activating K-West basin in 1979. This basin was completely drained, its concrete surfaces sand blasted, primed and painted with an epoxy paint, and filled with demineralized water. The ion columns and later, the ion exchange modules were filled with mixed bed ion exchange resin which maintained the water conductivity in the 1-2 µS/cm range. Initially, the water treatment system was similar to KE, but the basins were converted to ion exchange, mixed bed resins and the columns were changed to modules by 1984.

Fuel is encapsulated in aluminum and stainless steel canisters in KW basin. The canisters contain the spent fuel in deionized water with 500 ppm of potassium nitrate added as an inhibitor. The leach rate of activity in KW is small compared to KE, but there is some leakage from the sealed canisters. This rate is about 0.03 Ci/day of Cs-137. The water treatment systems in both KE and KW are doing a good job of keeping the water purified and at low conductivity. KE, despite its uncoated walls and sludge, is currently maintaining conductivity in the 3-5 µS/cm range and KW is deionizing the water to a low level of 1-2 µS/cm.[2]

A corrosion monitoring program was implemented in 1980 to determine the uniform corrosion rates of the major materials in the basin environment. Corrosion coupons included 1018 carbon steel, 2410 copper-nickel alloy, 5086 aluminum and 6061 aluminum alloys . After storage times from several weeks to several years, the samples were removed from the basins and analyses made to determine corrosion rates. The corrosion rate data has been reported in internal documents over the years as uniform corrosion in mils/year. For the aluminum alloys, severe pitting corrosion occurred, resulting in high corrosion rates in KW and KE in the early 1980's. This corrosion was believed to be caused by the use of a chlorine base algaecide which attacked the copper-nickel heat exchanger tubes, dissolving the copper into the basin water. Copper is a known promoter of pitting corrosion of aluminum. A similar high corrosion rate occurred on the copper-nickel surveillance specimens in the basins during that time period. Low corrosion rates in the order of 0.01-0.02 mpy have been seen over the past ten years at the low conductivity levels achieved by the mixed bed deionizers. Most of the severe corrosion damage appears to have been done during the early 1980 time frame.

IV. ENVIRONMENTAL FACTORS

The corrosion of aluminum alloys in high purity water is complex and many of the factors responsible for this corrosion are interrelated. When corrosion does occur by water, it generally takes the form of pitting, and is associated with the breakdown of the protective oxide coating. The number of pits formed and their rate of penetration depend on the water composition and the conditions of service.[6] Pitting that normally would occur in stagnant waters can often be prevented by water in constant motion.

A. Influence of Water Composition

In general, a soft water is less aggressive toward the pitting corrosion of aluminum than a hard water. Hardness of the water is due to calcium carbonate ($CaCO_3$) and other ions like sulfates and chlorides present in the water. The major factors believed to influence the pitting of aluminum alloys are: conductivity, pH, bicarbonate, chloride, sulfate, and oxygen content.[4] Because of the inter-relationship of the composition and service factors, it is difficult to predict the influence of the water on aluminum from a table of water composition alone. A number of studies have found that corrosion of aluminum was accelerated by combinations of salts of copper, chlorides, and bicarbonates, over the single impurities.[10] In cases where two of the three constituents were present, there was little corrosion, but with the three species were present, nodular corrosion occurred.

The conductivity of basin water is one of the most important parameters in corrosion control. As most of the corrosion processes associated with the aluminum fuels in the storage basins are electrochemical, the nature of the electrolyte, or basin water, plays a key role in the flow of electrical current and electrons in the process. The amount of metal removal 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 and is much less corrosive than impure or natural waters. Natural lake waters in some areas like Lake Ontario, Canada have a typical conductivity of about 270 µS/cm . On the other extreme, seawater conductivity runs about 40,000 µS/cm.

Storage basins around the U.S. which are storing aluminum-clad spent nuclear without reportable corrosion problems are operating deionization equipment continuously and maintaining a conductivity level of typically less than 5 µS/cm. Storage times for aluminum-clad alloys up to 25 years without corrosion at these low conductivity levels have been reported at some of these basins.

For the larger fuel storage basins in the DOE complex, the ones which are not experiencing corrosion problems are operating deionizers continuously and achieving conductivity levels routinely between 1-3 μS/cm. The RBOF facility at SRS operates at 1-3 μS/cm. At the Idaho CPP-666 basin, the deionization system routinely maintains the basin water at about 1-2 μS/cm. At the Westinghouse Hanford Company K-East and K-West basins, each basin currently uses mixed-bed resin ion exchange technology for continuous deionization. K-East basin, with its bare, uncoated concrete walls is now operating at 3-5 μS/cm, down from the typical 250 μS/cm of the mid-1970 to 1980's before the ion exchange columns or mix-bed resins were used. K-West is currently operating at 1-2 μS/cm.

Aluminum is passive and protected by its oxide film in the pH range of about 4 to 8.5. For pitting, the pitting potential of aluminum in chloride solutions, like iron and steel, has been found to be relatively independent in the pH range of 4-9.[11] Godard indicated some evidence that a deviation from neutrality (pH 7) on both acid and alkaline sides increased the rate of pitting in natural fresh waters.[4]

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 extent by the ability of impurity ions to penetrate the oxide film to attack the aluminum metal. Sverpa found that the penetrating power of anions in decreasing sequence to be chloride, bromide, iodide, fluoride, sulfate, nitrate, and phosphate.[12]

For aluminum, pitting corrosion is most commonly produced by halide ions, of which chloride (Cl^-) is the one most 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 metal dissolution. Chlorides from the bulk electrolyte solution migrate into pits and crevices causing more rapidly dissolution at that point. Pitting occurs in the presence of oxygen because the metal is readily polarized to its pitting potential.[13] In the absence of oxygen, aluminum will not corrode by pitting because the metal is not polarized to its pitting potential. In general, aluminum will not pit in aerated solutions of most non-halide solutions because its pitting potential is much more noble (cathodic) than in halide solutions.

Chloride content of the basin water should be minimized to prevent pitting corrosion . 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. What is known, however, is that high chloride contents like the 800 ppm in the Idaho CPP-603 basin that occurred during 1976, cause severe corrosion to the fuels in the basin. Basins at SRS have had limits of 20-25 ppm Cl^- over the years which have permitted the addition of hypochlorate for algae control, but these levels are not likely to ensure no pitting corrosion over long storage lifetimes with galvanic coupling existing throughout the basins. Basins throughout the DOE Complex that are successfully storing aluminum-clad fuel have chloride contents of less than 1 ppm or in the parts-per-billion range. The RBOF basin at SRS is typically operated at less than 10 ppb Cl^- and the CP-666 basin at Idaho operates at about 50 ppb.

Heavy metal ions such as copper and mercury are very aggressive toward the pitting corrosion of aluminum alloys.[4] The aluminum reduces the ions of copper, mercury, lead, etc., and also the heavy metal ions can plate out on the aluminum and form galvanic cells with the aluminum becoming the anode and the heavy metal a very effective cathode.. The threshold concentration for reduction of the copper ion by aluminum is about 0.02 to 0.05 ppm in neutral and acidic solutions.

Other impurities like sulfate have been shown to play a role in the corrosion of aluminum. Studies by Draley have shown that the presence of sulfate at 50 ^{0}C and 70 ^{0}C reduces the corrosion rate of aluminum.[14] Rowe and Walker[10] found that up to 300 ppm of sulfate alone did not increase the corrosion of aluminum. Godard, however, found that sulfates decreased the oxide film thickness formed as the concentration of sulfates increased. He also had evidence some evidence that the pitting rate increased with the sulfate/chloride ratio.[4] He concluded that the pitting corrosion, i.e., pitting density and pitting rate, is influenced by the film thickness.[15] The thinner the oxide film, the more susceptible the metal is to corrosion. In a later work in developing a pitting rate equation to correlate the variables in the water in time to pit aluminum, Pathak and Godard's data showed that the increase in sulfate concentration reduced the time to form a 40 mil pit in aluminum.[16]

Other parameters such as oxygen content and temperature of the water play a role in the corrosion of aluminum alloys. The SRS basins are saturated with oxygen. Elimination or reduction of oxygen is known to reduce corrosion. Increases in water temperature can increase the density and probability of pitting, but reduce the average depths of pits.[17] Godard found a maximum pitting rate at 40^0 C of 5X that at 25^0C.[5] Much of the fuel in the U.S. basins has been in storage for a number of years and the radioactive decay heat is low and is diminishing.

B. Pitting Rate Corrosion Index

Although the prediction of the corrosivity of natural and other waters from the values of their individual composition has proven to be extremely difficult, Pathak and Godard developed an empirical relationship for predicting the corrosivity of natural fresh waters to aluminum in 1967.[16] The pitting rate index (PRI) is defined as the number of weeks to achieve a maximum pit depth of 40 mils. The equation is shown below:

$$\log \mathrm{PRI} = 2.5 - 0.28 \log(\mathrm{sulfate}) + 0.18 \log(\mathrm{chloride}) - 0.20 \log[(\mathrm{pH} - 7)^2 \times 100] - 0.42 \log(30000/R) - 0.064 \log(\mathrm{copper} \times 10^3)$$

$$\text{where } R = 1/C \text{ (conductivity, } \mu\text{S/cm)} \qquad (3)$$

A pitting rate index of less than 25 weeks is indicative of aggressive water.

From analysis of water quality at SRS basins, the pitting rate equation was used to determine the relative aggressiveness of the storage basins at SRS as the water chemistry of the basins varied during cleanup activities over the 1992-1995 time period.

V. BASIN MANAGEMENT

Significant improvements to the spent fuel storage facilities at SRS have been accomplished since the 1993 DOE vulnerability assessment identified the K and L-reactor basins as requiring increased attention. A Basin Management Team consisting of plant and laboratory personnel were assembled to address the issues.

Corrective action plans were developed to improve the storage situation and reduce the perceived vulnerabilities. The plans included safety analysis upgrades to better characterize facility operation risks, a $13 million facilities capital upgrade project, and a number of operational improvements. Much of this work has already been accomplished or will be completed by mid-1996.

Good water quality being recognized as essential for successful storage of SNF, a commercial vendor was contracted to deionized the K and L-basins. Portable mixed-bed resin deionization equipment was operated in conjunction with the existing SRS equipment. In 2.5 months, L-basin conductivity was lowered from 110 µS/cm to less than 10 µS/cm. With new resin in the SRS deionizer, the conductivity has been further reduced to <3 µS/cm. Similar deionization in the K-basin has lowered the conductivity in that basin to well below 10 µS/cm. In addition, the chloride, sulfate, and nitrate concentrations have been significantly reduced. The Cs-137 activity, the only significant fission product potential, has been reduced to levels below 50 dpm/ml. This is well below the 500 dpm/ml administrative limit set for the reactor basins.

The P-basin will continue to be deionized using existing plant equipment until all fuel is transferred to the L and K-basins this year. This will enable P-basin to be closed and save the expenses of upgrading and maintaining this basin.

Additional operational improvements, including sludge vacuuming, corrosion monitoring, water sampling, and installation of new storage racks in the basin are currently underway. New continuous deionizer systems are under construction for both K and L areas and these systems are expected to be on-line during FY-96. With the improvements to the SRS basins, DOE will be able to continue receipt and storage of off-site research reactor fuel when the RBOF basin reaches capacity in mid-1996.

VI. CONCLUSIONS

The key to extended long term storage of aluminum-clad spent nuclear fuel in wet basins at SRS and other sites around the World is high purity water. Aluminum-clad alloys can be stored in high quality, deionized water for times exceeding 25 years without significant corrosion. If the clad is breached by pre-existing corrosion or mechanical damage exposing the core, corrosion of uranium metal fuel will continue even in high purity water.

The factors affecting corrosion of aluminum alloys are complex and not always thoroughly understood. The can operate both independently and synergistically. The parameters believed to be most important in corrosion control are water conductivity, chloride content, and galvanic couplings in the basins. No pitting corrosion is generally observed where conductivity is 1-3 µS/cm and chloride impurity concentrations are in the parts-per-million range.

Maintaining high basin water purity will permit some extended storage, but the ultimate solution to the fuel storage corrosion problems is processing and stabilization of the fuel in the pipeline. There are indications that SRS will be moving in that direction in 1996.

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Table 1. Maximum Pit Depths

Basin	Date	Exposure (Days)	Maximum Pit Depth (Mils)		Pit Density (Pits/cm²)	
			1100	8001	1100	8001
1991 - 1992						
K	7-92	45	2	53	0.125	0.01
K	6-92	75	13	45	0.125	0.01
K	3-92	107	23	39	0.125	0.01
K	6-92	182	58	27	0.125	0.01
K	12-92	365	100	57	0.125	0.05
1993 - 1995						
K	3-94	65	No Pitting Corrosion			
K	7-94	181				
K	2-95	403	No Pitting Corrosion			
K	3-95	525	No Pitting Corrosion			
L	11-93	61	No Pitting Corrosion			
L	3-94	127				
L	7-94	241				
L	2-95	336	No Pitting Corrosion			
L	8-95	690	No Pitting Corrosion			
P	11-93	61	No Pitting Corrosion			
P	3-94	127				
P	7-94	241				
P	2-95	336	35 Mil deep pits in 8001 Aluminum Alloy			
P	8-95	705	No Pitting Corrosion			

Table 2. Pitting Rate Index Parameters

K-Basin	K-Basin	L-Basin	P-Basin	RBOF
1992	1994	1994	1995	1993
SO_4 = 22 ppm	9	2	19	<0.5
Cl = 9	6	14	10	0.215
NO_3=17	18	20	9	<1.5
pH =7.9	7.3	6.6	6.66	7.4
Cond.= 178 µS/cm	125	102	170	1
Cu	<0.05	<0.05	<0.05	<0.05
PRI = 35	68	117	50	568