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**Corrosion  
Wet Spent**

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**Corrosion of Aluminum-Clad Alloys in Wet Spent Fuel  
Storage**

by

James P. Howell

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# Corrosion of Aluminum-Clad Alloys in Wet Spent Fuel Storage

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## Summary

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 processing 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 significant 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 1993-1995, but the ultimate solution is to remove the fuel from the basins and to process it to a more stable form using existing and proven technology.

This report 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 other fuel storage basins within the Department of Energy production sites.

## Introduction

Aluminum alloys have been used as cladding materials for nuclear fuel and targets because of their low-cross-section, enabling the conservation of neutrons. In addition, corrosion of aluminum, such as grade 1100, in high purity waters is excellent up to temperatures of about 100<sup>0</sup> C. With the addition of nickel and iron as alloying constituents, corrosion resistance of some alloys such as 8001 grade aluminum is good up to as high as 300<sup>0</sup> C in thermal reactor operations. Water quality plays a key role in this corrosion and is closely controlled in high temperature reactor operations.

After irradiation in a reactor, the aluminum-clad fuel and target assemblies are stored during the cooling process in large, water-filled basins while awaiting processing to achieve the desired nuclear isotopes. At a typical Department of Energy (DOE) production site in the U.S. such as the Savannah River Site (SRS), fuel storage times have ranged from 6-18 months during normal operations. Most of the storage basins contain high quality deionized water. Continuous deionization of the water often using mixed-bed resins removes corrosion causing impurities and maintains water conductivity usually below 10  $\mu$ S/cm. At SRS, only the Receiving Basin for Offsite Fuels (RBOF) was designed for continuous deionization. The P, K, and L-Reactor basins use portable deionizers to remove radionuclides from the water and make improvements in the water quality. Over the years of operations at these basins, the prime protection against corrosion has been to minimize the interim storage time while awaiting processing. During the relative short storage times at low temperatures during normal operations, corrosion was never a real problem, but nevertheless, has been a periodic concern. At these basins, efforts were made to keep the water quality within desired chemistry specifications, but in some cases, these specifications were not sufficient to maintain the fuel free of corrosion. In the past, the spent fuel was usually processed before the corrosion presented problems.

Under the non-proliferation policy for nuclear materials, the 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 was caught in the pipeline, awaiting processing, while stored in the light-water filled basins.<sup>1</sup> At Savannah River

where most of the 200 metric tons of stored fuel is aluminum clad, processing in the F-Canyon facilities has not taken place since late 1989. Aluminum clad fuel stored in stainless steel slug buckets, as well as fuel and target materials stored on stainless steel hangers have been immersed in SRS reactor basins for over 7 years. Similar storage scenarios exist at the Hanford Site, the Idaho Nuclear Co., Oak Ridge National Laboratory, and other spent fuel storage sites. Significant corrosion problems exist with the spent aluminum-clad fuel at some of the sites, while minimum problems exist in other basins.<sup>2,3,4</sup> Figure 1 and Figure 2 show examples of the corrosion aluminum clad spent fuel stored in deionized water where water quality is aggressive to the aluminum.

The factors promoting the corrosion of aluminum are complex. In many cases, they operate synergistically and are not well understood. This report presents a discussion of the fundamentals on aluminum alloy corrosion. It presents the most important corrosion mechanisms and the effects of variables in the storage environment on these mechanisms as pertaining specifically to aluminum-clad spent nuclear fuel in wet basin storage.

## Oxide Films on Aluminum

Aluminum is one of the most thermodynamically reactive metals. Among the structural materials, only beryllium and magnesium are more reactive. 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 intergranular attack can occur.<sup>5</sup> A discussion of these films formed in high purity water is appropriate to any discussion on the corrosion behavior of aluminum-clad spent nuclear materials.

The formation of protective oxide films on aluminum at moderate temperatures occur in three distinct stages.<sup>6</sup> These stages are a function of time and temperatures. On immersion into water at temperatures below about 80<sup>0</sup> C, the existing amorphous barrier oxide film on aluminum thickens with the formation of the crystalline hydrated aluminum oxide phase, Boehmite ( $Al_2O_3 \cdot H_2O$ ). Continued immersion, ranging from hours to days, results in the formation of the crystalline phase called Bayerite ( $Al_2O_3 \cdot 3H_2O$ ). These films were confirmed to have been formed in a layered fashion by mechanically removing the Bayerite outside layer and identifying the film beneath to be Boehmite using electron diffraction.

At temperatures of about 70<sup>0</sup> C, the films are predominately Boehmite, however, some films show both Bayerite and Boehmite crystalline electron diffraction patterns. At temperatures of 80<sup>0</sup> C and higher, the oxide films formed are usually Boehmite and are tightly adherent. The thickness of the oxide films formed at these temperatures is generally parabolic in nature, increasing with temperature and leveling off with time. The main difference in the oxide film formed by oxidation and that formed by corrosion products is that in oxidation the surface film forms compactly on the metal surface and exerts a protective influence, whereas, the oxide in corrosion is loose and flocculent produced at a distance from the metal-environment interface and is non-protective.

Reactors at Savannah River Site are heavy water moderated and operate at water temperatures slightly below 100<sup>0</sup> C. The moderator water is high purity with impurity concentrations in the part-per-billion range. Metal oxide interface temperatures can get higher than 250<sup>0</sup> C on aluminum-clad fuels and greater than 100<sup>0</sup> C on target materials.

Oxide films formed on the irradiated aluminum-clad nuclear fuels at these temperatures are predominately Boehmite. Maximum film thickness is generally limited to 2-3 mils, before spallation occurs in the reactor because of thermal and other stresses in the oxide. Films of Bayerite, Boehmite, and Gibbsite ( $\alpha$   $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) have all been found on SRS fuel and with spallation have contributed to turbidity in the moderator.

## Thermodynamic and Kinetic Fundamentals

An understanding of certain fundamentals is necessary to be able to prevent corrosion or to be able to interpret corrosion phenomena. Thermodynamic principles can be applied to determine which processes can occur and how strong the tendency is for these changes to take place. Kinetic laws then describe the rates of the reactions. In aqueous solutions and because of the ionic conductivity of this environment, corrosion is due to electrochemical reactions. It is strongly affected by such factors as metal electrode potential and acidity of the solutions.<sup>7</sup>

Thermodynamic factors determine under what conditions the chemical reactions are at an electrochemical equilibrium, and if there is a departure from equilibrium, in what directions the reactions can proceed and the strength of the driving force. The kinetic laws of the reactions are fundamentally related to the activation energies of the electrode processes, mass transport and the basic properties of the metal/environment interface.

Corrosion of aluminum is almost always electrochemical in nature. It occurs when two or more electrochemical reactions take place on the metal surface. As a result, some of the elements of the metal or alloy change from a metallic state to a nonmetallic state. The products of corrosion may be dissolved species or solid corrosion products. In both cases, the energy of the system is lowered as the metal converts to a lower energy form. The change in energy is the driving force for the corrosion process.

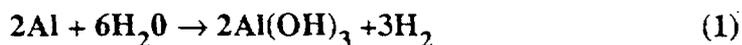
One of the most important steps in the science of electrochemical corrosion has been the development of the Pourbaix diagram showing the thermodynamic conditions as a function of metal (electrode) potential and hydrogen ions. These potential versus pH diagrams graphically express the thermodynamic relationships in metal/water systems and show the regions of thermodynamic stability of the various phases that can exist in the system.

The conditions for the thermodynamic stability of the oxide film on aluminum is shown by the Pourbaix diagram in Figure 3. In this case, the aluminum has a Bayerite film ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) at 25°C. The diagram shows that aluminum is passive (protected by its oxide film) in the pH range of about 4 to 8.5. These limits can vary with temperature, form of oxide present, and with the presence of substances that can form soluble complexes or insoluble salts with aluminum. A similar diagram exists for the Boehmite film.

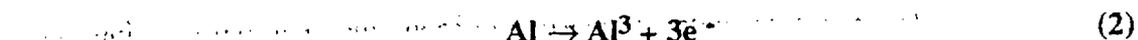
Beyond the limits of its passive range, aluminum corrodes in aqueous solutions because its oxides are soluble in many acids and bases. There are instances when it does not corrode outside the passive range. These can occur when the oxide film is not soluble or the film is maintained by the oxidizing nature of the solution. The Pourbaix diagram for aluminum and other oxides and the details of the aluminum-water system are explain in Pourbaix's "Atlas of Electrochemical Equilibria,"<sup>8</sup>

From an engineering standpoint, the major interest is in the kinetics or rate of corrosion. Corroding systems are not in equilibrium, and therefore thermodynamic calculations

cannot be applied. The aqueous corrosion of aluminum is an electrochemical reaction. 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.<sup>9</sup>



The oxidation (anodic) reaction is given by:



The reduction (cathodic) reaction is given by:



The corrosion process has been written as two separate reactions occurring at two separate sites on the same surface. The two sites are known as the anode, or metal dissolution sites and the cathode, or the site of the accompanying reduction reaction. 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 the corrosion to occur.

The kinetics of the corrosion process caused by these chemical reactions are influenced by the products of anodic and cathodic reactions. The cathodic reaction, and with it the overall corrosion process, would slow down if the hydrogen product were not removed by evolution as gas or some reaction involving oxygen. This slowing down is called cathodic polarization. Similarly, a concentration of ions in the immediate vicinity of the anodic metal, called anodic polarization can cause a slowing down of the reaction. Thus, polarization occurring at the cathode and the anode determine the corrosion rate of most electrochemical cells.

As electrons are liberated by the anodic reaction and consumed by the cathodic reaction, corrosion can be expressed by terms of an electrochemical current. If the current is measurable, it can be taken as the rate of the corrosion process. The current, known as  $I_{\text{corr}}$ , and the amount of metal corroded are related by Faraday's law:

$$I_{\text{corr}}t = nFw/M \quad (4)$$

where  $I_{\text{corr}}$  is expressed in amps;  $t$  is the time in seconds for which the current has flowed;  $nF$  is the number of coulombs (C) to convert 1 mol of metal to corrosion product, where  $n$  is the number of electrons involved in the reaction, and  $F$  is the Faraday constant (96480 C/mol);  $M$  is the molecular weight of the metal in grams; and  $w$  is the mass of the corroded metal in grams. General corrosion rates of a metal, and thus the speed at which these chemical reactions take place, can be measured in the laboratory using

electrochemical testing techniques such as linear polarization and applying the results to equation 4.

## Mechanisms of Corrosion

### General Corrosion

In general, the corrosion behavior of aluminum in high purity water is good. If it is corroded by water the attack usually takes the form of pitting. There is no significant general corrosion or gradual thinning as may occur with steel.<sup>10</sup>

General corrosion has not been a problem in the storage of aluminum clad alloys at many of the basins in the U.S. as long as the protective oxide already 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.<sup>7</sup> The slight reaction that occurs initially in water ceases quickly after the formation of the protective film of equilibrium thickness. After this initial conditioning period the amount of metal dissolved by the water is minimal. General corrosion on aluminum in high purity water is minimized at a pH level of about pH 5.5. Basins, with unlined concrete walls can be attacked by acidic levels of less than pH 7. Therefore, a compromise may sometimes be necessary between the lowest pH necessary to minimize general corrosion of the aluminum clad and protection of unlined or coated basin concrete walls. For a stainless steel lined basins, the variation of high purity water pH levels over the broad range of 4.5-8.5 has provided a regime in which general corrosion of aluminum alloys has not been a problem.

At SRS fuel is unloaded from the reactors and is placed into the 3.5-4.0 million gallon, light-water filled basins for storage during the interim cooling phase prior to processing. Basin operations limit the maximum water temperature to 40<sup>0</sup> C. Heat exchangers are available for cooling, if required. Currently, with the existing inventory of fuel, the basin water temperature at SRS remains between 20<sup>0</sup>-30<sup>0</sup> C, depending on the season of the year. As long as the protective oxide coating on aluminum remains intact, general corrosion of aluminum alloys is not generally a problem at the relatively low temperatures of basin storage. Because of the heat load generated by some fuels, some basins are equipped with heat exchangers which are used to maintain temperatures at low specified levels to minimize corrosion.

For aluminum in high purity water, oxide growth, or film thickness is parabolic with time at a given water temperature. The structure of the oxide has been previously discussed. At temperatures up to about 100<sup>0</sup> C, a number of studies on oxide film growth on aluminum alloys have been reviewed by Thomas and Ondrejcin.<sup>11</sup> Figure 4 provides a graphical representations of the resulting film growth for a number of temperatures up to about 5 years exposure. This data covers a range of basin storage temperatures around the world. The thickness of an oxide coating on an aluminum surface can play a role in the initiation of localized corrosion.

### Galvanic Corrosion

Galvanic corrosion occurs when a metal or alloy is electrically coupled to another metal, usually dissimilar, in the same electrolyte. In the case spent nuclear fuel storage, galvanic corrosion is evident throughout the basins. It is clearly visible, as shown in Figure 5, at SRS where the fuel hangers are 304 stainless steel and the fuel assembly is aluminum clad. Notice the aluminum oxide forming at the point of contact with the stainless steel

for the uninsulated case. When a polymeric insulation was placed at the contact point there was little oxide formed. There was, however, oxide formed on the fuel tube at a joint between two different aluminum alloys. The excessive oxide on this fuel tube is likely due to the absence of the high temperature, protective oxide coating which is present on the uninsulated irradiated fuel, but absent on the dummy, unirradiated assembly used for testing. The electrolyte, in this case, is the basin water and the conductivity of the water plays a key role in the flow of electrons and the corrosion of the metal.

There are three essential components necessary for galvanic corrosion.<sup>7</sup> These are: (1) Metals have different surface potentials, (2) A common electrolyte, (3) A common electrical path. 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. The accelerated corrosion resulting from galvanic corrosion is affected by:

- Potential difference between the metal
- Nature of the environment
- Polarization behavior of the metals
- Geometric relationship of the component metals

The potential differences between dissimilar metals causes electron flow between them when electrically coupled in the conductive solution or basin water.<sup>7</sup> The direction of flow depends on which metal is the more active. The more active metal becomes anodic and the more noble metal becomes cathodic. Whether a metal is the more active anode or more noble cathode can often be determined by the use of a galvanic series. This series is an arrangement or ranking of metals or alloys according to their potentials as measured in a specific environment. Often, the separation between the two metals in the galvanic series gives an indication of the magnitude of corrosion.

Environmental factors affect the metal potential.<sup>7</sup> Corrosion product films and other changes in surface composition can affect the value for a particular metal. A galvanic series for seawater, which can be found in most handbooks, is broadly applicable in other natural waters.

Other factors affect galvanic corrosion. Some of these are area ratios, distance between electrically connected materials, and geometric shapes. Galvanic corrosion of the anodic metal usually takes the form of general or localized corrosion, depending on the configuration of the couple, the nature of the protective films involved, and the nature of the metals.

Aluminum and its alloys occupy active positions in the galvanic series and as such, are highly susceptible to failure by galvanic attack.<sup>7</sup> In chloride-bearing solutions, aluminum alloys are susceptible to galvanically induced localized corrosion, especially in dissimilar metal crevices. Severe attack is often seen when the aluminum alloys are coupled with more noble metals. Galvanic corrosion behavior of stainless steels is difficult to predict because of the influence of passivity of the protective oxide film. In general, it is more noble than the aluminum in the galvanic series and depending on the environment and other factors may promote corrosion of the aluminum. At SRS, some of the fuel tubes are fabricated from different aluminum alloys joined together by a weld or mechanical bonding operation. Galvanic effects promoting corrosion between the two alloys have been noted in basin corrosion tests and storage operations.<sup>12</sup> In addition, underwater

photographs of bundled 1100 aluminum alloy fuel tubes in contact with 6061 aluminum alloy spent fuel storage racks have shown the tubes to remain free of corrosion while the storage racks appear to be corroding sacrificially.

Galvanic corrosion of spent nuclear fuels in the basins is active and can be greatly reduced by lowering the basin water conductivity. At low levels of conductivity in the range of 1-3  $\mu\text{S}/\text{cm}$ , the galvanic effect should be minimized. Basin deionization will remove the corrosion causing anions and cations from the water and will lower its conductivity or ability for electron flow between the dissimilar metals.

### Crevice Corrosion

Crevice corrosion of aluminum alloys is highly localized corrosion occurring on faying surfaces upon entry of water into a crevice.<sup>5</sup> It was initially thought to be caused by differential aeration in the liquid in the crevice. The oxygen deep in the crevice is depleted, but the mouth of the crevice is exposed to more oxygen establishing a local corrosion cell. Later work has shown a more 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 many 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. At SRS, the slug bucket storage used for the storage of aluminum-clad Mark 31A target slugs provides an environment which easily supports crevice corrosion. In this situation, the stacking of slugs combined with the sludge and corrosion product accumulation within the bucket form many possibilities for crevice promoted corrosion.

Crevice corrosion can be avoided by eliminating the crevices wherever possible. Welding is used at joints instead of riveting or bolted joints and designs of equipment and joints are used which minimize crevices.

### Intergranular Attack (IGA)

Intergranular attack or intergranular (intercrystalline) corrosion is selective attack of grain boundaries or closely adjacent regions without much attack of the grains themselves.<sup>4</sup> The mechanism is electrochemical and depends on the presence of local cells at the grain boundaries. The corrosion is caused by potential differences between the grain boundary region and the adjacent grain bodies. The local cells can be caused by second-phase precipitates at the grain boundaries.

This form of corrosion does not occur in aluminum alloys which do not have grain boundary precipitates or in those in which the precipitate has the same potential as the matrix.<sup>5</sup> Such alloys as 1100, 3003, 3004, 5083, 5086, 5154, 5056, 5456 are not generally subjected to IGA. The alloys like Al-Zn-Mg-Cu 7075, Al-Cu 2014, 2017, and 2024 are very susceptible. The Al-Mg-Si alloys like 6061 and 6063 are not very susceptible. Underlined alloys represent specific alloys used as fuel and target cladding materials. The 1100 or the 6000 series which are not susceptible or very mildly susceptible to intergranular corrosion. Intergranular corrosion has not been a major issue in the corrosion of the spent fuel in water storage.

## Stress Corrosion Cracking (SCC)

When certain metal alloys are exposed to a corrosive environment while being subjected to an appreciable, continuously maintained, tensile stress, rapid failure can occur as a result of stress corrosion.<sup>5</sup> This failure is known as stress-corrosion cracking, and is characterized by the brittle nature of the failure in a material that might otherwise be ductile. The cracks propagate in a direction perpendicular to the applied stress. Stresses must be tensile ; compressive stresses have no effect. In most cases the tensile stresses have to be near the yield stress of the metal to cause stress-corrosion cracking.

Cases of SCC in aluminum alloys have generally been limited to such alloys as Al-Zn-Mg-Cu (7075) and Al-Cu (2024) and a few others. The high purity alloys such as 1099, 1100, and 1200 are not subjected to SCC under any conditions. Neither are the Al-Mn alloys (3003, 3004), or the Al-Si alloys (4043). The Al-Mg-Si alloys (6063, 6351, 6061) are not susceptible unless given abnormal heat treatment.<sup>5</sup> The underlined alloys represent specific alloys used as nuclear fuel and target cladding materials.

Stress corrosion cracking has not played a major role in the corrosion of the fuel stored in the basins aluminum as most of the alloys used for cladding materials are pure aluminum, 1100, or 6061-6063, and are not subjected to SCC.

## Pitting Corrosion

### Fundamentals

Pitting 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 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. This enlargement of the surface area of a pit is usually small in comparison with its increase in depth and volume.<sup>13</sup> Pitting requires the presence of an electrolyte and in the case of most storage basins, deionized water serves this purpose. While many pits are hemispherical or conical, the shape varies greatly. The shape of the cavity at the metal surface tends to be round, but the pit walls tend to be very irregular. Typical pits occurring in aluminum-clad alloys are shown in Figure 6. 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. In structures, the occurrence of pitting is not always detrimental since the amount of metal removed is usually small, and the rate of penetration decreases with time, in most cases. On the other hand, under special conditions, the rate of pitting can be quite rapid (e.g., 5000 mpy).<sup>14</sup> When this occurs, it can be one of the most destructive forms of corrosion. The most common undesirable result of pitting corrosion is perforation of the metal. In the case of stored aluminum clad spent nuclear fuel, pitting 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. Build-up of this activity in the basin water can ultimately lead to high radiation levels and exposure to personal working around the basins.

As discussed in the section on General Corrosion, pitting has also been shown to proceed by an electrochemical mechanism. 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. Electrical current flows through the liquid medium

from the local anode( the site of metal removal ) to the adjacent local cathode. Pitting may also be caused by current entering a solution from the metal surface due to an external cause, such as an impressed emf or galvanic corrosion produced by contact with a dissimilar metal.

In the life cycle of a pit, there are four possible stages: initiation, propagation, termination, and reinitiation.<sup>17</sup> In the initiation stage, a metal local cell can be caused by an abnormal anodic site surrounded by a normal surface which can act as an inadvertent cathode or by an abnormal cathodic site surrounded by a normal surface which, therefore, acts as an inadvertent anode. It is believed, that at the time of initiation, the local cell currents are very low. The slow movement of water over the surface (8 ft/sec) has been shown to prevent corrosion that occurred in stationary water.<sup>14</sup> Movement of the water prevented the development of differential activity at the local cathodes and anodes.

Pitting of aluminum can be described as an autocatalytic process. The functioning of local cells in an electrolyte produces changes at local anode and cathode sites which increase the potential between them and therefore, the activity of pits. The corrosion processes within a pit produce conditions which are both stimulating and necessary for the continuing activity of the pit. In a situation where a 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. These processes stimulate the dissolution of most metals.

For initiation of pitting, Evans<sup>15</sup> has suggested that for a metal devoid of pits and immersed in a chloride containing electrolyte, if the rate of metal dissolution is high at one point, for any reason, the chloride ions will migrate to this point. Since chloride stimulates metal dissolution, this change tends to produce conditions that are favorable to further rapid dissolution at this point. Dissolution may be high, locally, because of a surface scratch, defects, or random variations in the electrolyte. For the aluminum clad fuel at SRS, scratches are plentiful on the surface of the clad. Gravity plays a role on pitting, as the concentrated solutions are necessary for continued activity and pits are most stable on flat, horizontal surfaces growing in the direction of gravity where the solutions are more easily contained. In addition, pits are generally initiated on the upper flat surfaces of specimens where chloride ions are more easily contained than on vertical surfaces.

The propagation stage of pitting proceeds by local cell action reinforced by the difference in acidity between the cathode and the anode.<sup>14</sup> As the pit cavity grows, it begins to accumulate a cap or crust of insoluble corrosion product which restricts the flow of oxygen supply to the pit. This causes the generation of stronger cell currents. As the pit deepens the active cathode, which could have been activated by copper or iron deposition (heavy metal ions often present in basin water), tends to move down into the pit, which has become self contained and independent of the original cause of initiation. It is believed that local cell current flowing to the adjacent surrounding area provides some measure of cathodic protection and this causes pits to grow deeper rather than laterally around the mouth of the pit.

In the termination stage of pitting, some pits cease to grow after reaching appreciable depths, probably because the current has been depressed by an increase of the internal

resistance of the local cell or by polarization of either the cathode or the anode or both. Other pits with strong currents terminate only when the pits become dry. The internal resistance of the local cell may also increase when there is buildup of corrosion product in the pit cavity.

In the reinitiation stage, when a completely dried pitted surface is returned to its original environment and rewetted, some of the pits will reinitiate and others will remain inactive.<sup>14</sup> It is suggested that the ones that reinitiate are in the presence of a active cathodic area at the surface or near the inside mouth of the pit. This restarts the action that caused initiation of pitting in the first place. Other possibilities for reinitiation include an imperfect protective film at the base of the pit or the development of differential aeration cells.

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:<sup>16</sup>

$$d = Kt^{1/3} \quad (5)$$

where  $d$  = maximum pit depth,  $t$  = time, and  $K$  = constant, depending on the particular alloy and the water conditions ( composition, temperature, velocity, etc.). The depth of pits on sections of water pipe were measured at various time intervals and the maximum pit depths for a future time were calculated using the cube-root law. Actual pit depth measurements verified the validity and accuracy of the equation. From the equation, one can see that doubling the wall thickness can increase the time for perforation by a factor of eight.

### Pitting Corrosion of Aluminum Clad Fuel in U.S. Basins

#### **Savannah River Site Storage**

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. Normal storage times for these fuel have been between 6-18 months. During the period of 1974-1977, there were four distinct cases of clad-penetrating corrosion in the K-Area disassembly basin. In these cases, tritium and fission product release to the basin were detected by analysis of the basin water within one to three months after the assemblies were discharged from the reactor and stored in the basin.<sup>17</sup>

Subsequent inspection of the target and fuel tubes revealed extensive corrosion and penetration of the aluminum clad.<sup>17</sup> The investigation revealed a number of factors believed responsible for the corrosion. Among these factors were poor cladding material, excessive iron and chloride ions in the water, galvanic couples, and scratches in the oxide coating. Changes such as reducing chloride ions from 25 ppm to 5 ppm were instituted. The galvanic couple caused by the stainless steel hanger in contact with the aluminum clad fuel was not removed because of the high costs involved in the change-out of the hanger system. The pH of the basin water was raised slightly to  $7.3 \pm 0.6$  to reduce the solubility of heavy metal ions in the water. After the new changes were initiated in 1978,

there were no reported specific incidents involving corrosion of fuel in the basins during the early 1980's.

New evidence of the 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.<sup>21</sup> Upon examination, sixteen of twenty-four specimens showed evidence of pitting corrosion and seven pits had penetrated the 0.050-inch wall. In order to confirm this pitting, new corrosion coupons cut from housings were placed in the basin. No pitting corrosion was found after 14 days, but specimens removed after 93 days showed pitting through the wall. Based on these findings, an immersion test program was implemented in the reactor basins at SRS in mid-1991.

The initial reactor basin corrosion tests were conducted in L-Disassembly basin using one-inch wide by two inch long corrosion coupons.<sup>17</sup> The coupons were made from 6063, 1100, and 8001 aluminum alloys. After 42 days exposure to the basin water conditions, the 8001 aluminum alloy showed formations of white, nodular corrosion product on the surface. Further microscopic analysis indicated that pits were formed in this alloy on the order of 30 mils deep (the thickness of cladding on the fuel tube).

#### **Component Immersion Test**

In late 1991, corrosion testing switched from the L-Basin to the K-Disassembly Basin.<sup>17</sup> At that time, seismic and safety upgrades were being made to the K-Reactor in preparation for reactor re-start. Plans were to re-start the reactor and run for several months, before discharging the fuel for storage in the basin while installing a new above ground cooling tower. Surveillance tests were initiated in the K-Basin to determine whether the stored fuel would be able to be used again when the reactor was to be re-started after the cooling tower installation.

Six-inch long cylindrical tubes were cut from actual unirradiated fuel and target tubes of the SRS Mark 22 fuel assembly.<sup>18</sup> This assembly is irradiated to produce tritium. The tube-ends contained no uranium. The tubes were pre-oxidized at temperatures greater than 95 °C in deionized water to give a Boehmite oxide of about 1 micron in thickness. The 1100 and 8001 aluminum alloy clad tubes were nested together on a corrosion rack to simulate an assembly stored in the basin. The racks consisted of three rows of nested coupons with two coupons on each row. The aluminum alloy racks were immersed in the basin at a depth of 3-6 feet below the surface of the water. After various exposure times, one row of two coupons was withdrawn from the water and this row was replaced with two fresh coupons. The two nested coupons were photographed and analyzed in the laboratory. Metallography was done on the pits to determine the maximum pit depths for each exposure time. The results of the 5 different exposure times for these nested tube end components during 1992 are shown in Table 1. The aggressive nature of the K-basin water during 1992 was verified by the short 45 day time period required to develop a pit 53 mils deep in the 8001 aluminum alloy cladding. (This exceeds the 30 mil fuel cladding thickness). The 8001 fuel tube cladding appeared to be more susceptible than the 1100 aluminum alloy target tube cladding. An exposure time of about 6 months was required to develop a similar depth pit in the 1100 alloy.

In addition to the Component Immersion Tests conducted in the K-Basin during 1992, additional small 1-inch x 2-inch x 1/16 inch thick coupons of 8001 alloy were placed in RBOF and in K-Basin for surveillance tests. These coupons were withdrawn on a schedule from 15 days up to one year. These K-Basin coupons developed pits of about 30 mils in 15 days exposure. Pitting exceeded the thickness of the sample in 60 days (60

mils). Samples removed from the RBOF facility showed no corrosion for any withdrawal periods through 1 year. The coupons withdrawn at one year were visually inspected in September 1993 and no evidence of corrosion was found. These were re-immersed immediately and then inspected again after two years of exposure in September 1994 with no signs of pitting corrosion evident.

With the aggressive nature of the water in K-Basin having been demonstrated by the pitting corrosion of the samples 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.<sup>18</sup> 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. The effort initially started in the K-Basin with extensive deionization of the basin water. Using the portable mixed-bed deionizers, the conductivity and impurity concentration of the water was slowly lowered. The deionizer mixed-bed resin would deplete within a few days of operation and would have to be taken to the regeneration facility before the deionizers could be operated again. The deionization schedule was not continuous, but consisted of several days of operation, followed by 2-3 weeks of no deionization while the deionizers were being regenerated.

Component Immersion Tests using the tube ends were started in the P and L-Disassembly basins in September 1993 and are continuing into 1995. In addition, these tests were re-started in the K-Basin so that a comparison of the aggressiveness of the water in 1992 could be made with the 1994-1995 time period after cleanup activities were initiated and underway. Coupons were withdrawn at various time intervals during 1994 and 1995 and evaluated for pitting corrosion. The results of these analyses are shown in Table 1. No pitting corrosion was found on coupons withdrawn from K-Basin after the first 6 months of exposure in the 1994 withdrawal as opposed to through-clad penetration in as little as 45 days in 1992. Figure 7 shows a relative comparison of the test specimens after exposure for 1992 and 1994. An additional withdrawal from K-Basin at 13 months showed no pitting corrosion. Likewise, specimens exposed in the L-Basin through 11 months have shown no pitting corrosion. Specimens removed from P-Basin through 8 months showed no pitting, however, after 11 months exposure, two pits were found in the 8001 aluminum-clad alloy. The deepest pit was 35 mils which exceeds the cladding thickness for this fuel.

The K-Basin water chemistry and conductivity during the Component Immersion surveillance tests are shown in Table 2. The conductivity was relatively high at immersion of the coupons in the 1992 tests. At 178  $\mu\text{S}/\text{cm}$ , this level is significantly greater than the 1-3  $\mu\text{S}/\text{cm}$  range of the Receiving Basin-for Off-site Fuels (RBOF) at SRS where aluminum clad Foreign Research Reactor (FRR) fuel is currently being stored without corrosion. Other known pitting causing impurities like chloride are in the 6-9 ppm range which is 1000X higher than the RBOF facility. For the tests conducted during 1994-1995, the conductivity in K-Basin was reduced to about 135  $\mu\text{S}/\text{cm}$  through deionization. Later during the year, the conductivity began to slowly rise again due to lack of deionizer availability. Other parameters such as chloride ion concentration varied very little from the earlier tests. In L-Basin, where extensive deionization occurred during early 1994, the conductivity reached a level of 96  $\mu\text{S}/\text{cm}$  and the chloride content of the basin was lowered from 18 to 11 ppm. At these lower conductivity levels, no pitting corrosion has been seen in the K and L basins up through the 13 month exposure. In P-Basin, where pitting corrosion was seen for the first time at the 11 month withdrawal from the basin, the conductivity of the basin at the time of specimen removal was about 165  $\mu\text{S}/\text{cm}$  and rising. This basin has had no deionization for over two years and no

water circulation for an extended time. Plans call for fuel removal from this basin in the near future for consolidation and storage in L or K-Basin. With limited deionizer availability, emphasis on basin cleanup activities have revolved around the L and K basins.

A series of laboratory corrosion tests were conducted during 1993-1994 to examine the effects of basin water conductivity on the pitting corrosion of the aluminum alloys.<sup>18</sup> Using the same nested tube-ends as used in the basin tests and using water from the K-Basin, immersion tests were conducted in 8-liter polyethylene mini-basins. The conductivity of the basin water at the time of testing had been reduced to about 130  $\mu\text{S}/\text{cm}$  by concentrated deionization. This was about 50  $\mu\text{S}/\text{cm}$  below the 180  $\mu\text{S}/\text{cm}$  level at which K-Basin water caused extensive pitting corrosion of the 8001 aluminum alloy in 45 day exposure tests. Using deionized water to dilute the basin water and reduce the conductivity, tests were conducted at 130, 47, 13, and 3  $\mu\text{S}/\text{cm}$ . These tests did not duplicate the actual basin conditions as no sludge or galvanic couples were used. Under these laboratory conditions and with a maximum water conductivity of about 130  $\mu\text{S}/\text{cm}$ , no pitting corrosion has occurred through the first 24 months of exposure. After 4 1/2 months with no corrosion product visible, one of the test tubes was scratched to break the protective oxide coating. Potential measurements were made and the corrosion potential was lowered, but the surface repassivated and no corrosion was evident during the remaining 14 month exposure period.

To determine the effect of a 304L stainless/aluminum galvanic couple of the corrosion process, tests were conducted in deionized water at 3  $\mu\text{S}/\text{cm}$  and in K-Basin water at 130  $\mu\text{S}/\text{cm}$  with a 304L band clamped around the outer 1100 aluminum alloy tube. Within one month, white oxide product began to form on the basin water coupon and by seven months the outer aluminum tube was heavily pitted as seen in Figure 8. For the galvanic couple sample in deionized water at 3  $\mu\text{S}/\text{cm}$ , only a small ring of loose, white corrosion product was found adjacent to the stainless steel band.<sup>12</sup>

Corrosion of the fuel and target material in the SRS basins appears to have been reduced significantly over the two year aggressive basin cleanup campaign currently underway. The pitting corrosion of these aluminum-clad materials is believed to be caused by a number of factors which operate both independently and synergistically. Among those factors believed to promote this corrosion are:

- High basin water conductivity (180  $\mu\text{S}/\text{cm}$ ).
- Aggressive ions (20 ppm  $\text{Cl}^-$ )
- Sludge (contains Fe, Cl, Etc., in 10X water concentrations).
- Galvanic couple between stainless steel bucket and aluminum.
- Galvanic couple between aluminum and uranium.
- Scratches and imperfections in protective oxide coating on the cladding.
- Relatively stagnant water.
- Microbiological Influenced Corrosion (MIC) has not been found at SRS, but is believed to be playing a role in the Idaho basin.

Deionization of the water resulting in a lowering of the conductivity and impurity concentration is believed to be primarily responsible for the improvement in fuel storage performance. A quantitative measure of this improvement will be discussed in a later section of this report dealing with water chemistry and the Pitting Rate Index (PRI).

## **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.<sup>19</sup> A total of 55 different fuels are currently stored at ICPP. 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.<sup>3</sup>

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. The corrosion resistance of the barrier material is a primary concern in the integrity of the fuel in storage. This barrier material is either the fuel cladding or the can material if the fuel is stored in a container in the basin. Containment materials are either stainless steel or aluminum. Some carbon steel has been used as buckets and in the original monorail and hanger construction in the older, CPP-603 basin. Galvanic couples of carbon steel-aluminum, carbon steel-stainless steel, and stainless steel-aluminum are present in the basin.

### **CPP-603 Basin**

Originally, like SRS, water flowed through the 1.5 million gallon, unlined CPP-603 concrete basin and was disposed of on site. In 1966, this was changed to a recirculating system. About the same time a basin algae growth problem was treated by several algaecides, including sodium hypochlorite, chlorine, and iodine. By 1976, the concentrations of chloride reached a level of 800 ppm which accelerated the corrosion of many materials in the basin.<sup>20</sup>

In late 1976, a reverse osmosis (RO) system was installed to remove the chloride from the water and has operated periodically over the years.<sup>19</sup> This, along with the use of low chloride make-up water and transfers out of basin water to the process equipment waste evaporator, have reduced the chloride level to about 50 ppm. The pH is maintained in the range of 5-8.5 (8.1 in 1994) and the conductivity in 1994 was about 637  $\mu\text{S}/\text{cm}$ . 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.

An inspection program has been in place in CPP-603 to evaluate the fuel and storage equipment condition.<sup>3</sup> Periodic visual, including underwater video, inspections, are made of the concrete structure, the monorail, hangers, buckets and cans, and some of the fuel. 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. The amount of attack is dependent on exposure time in the basin water.

The corrosion in CPP-603 is increased where the galvanic couples exist (aluminum in contact with zirconium or stainless steel).<sup>3</sup> The less noble aluminum becomes the anode and is corroded preferentially to the more noble stainless steel or zirconium, which serves as the cathode in the reaction. Ceramic insulators between the two different alloys are being used to electrically isolate them.

Failure of the carbon steel hooks on a double trunion hanger in 1992 led to an increased inspection of existing hangers for the monorail system used in the basin for fuel movements. The failure occurred near a carbon steel to stainless steel weld and was attributed to general corrosion of the carbon steel.

Stainless steel and aluminum corrosion coupons have been immersed in the basin and evaluated semi-annually over the past 10-13 years.<sup>3</sup> 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.<sup>21</sup> 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. Later inspections were done with underwater camera systems. With these systems in place, Space Nuclear Power (SNAP) fuel elements were stored in aluminum cans. A camera inspection revealed that galvanic corrosion had occurred on the aluminum can at the contact between the can and the stainless steel storage bucket. There was heavy buildup of aluminum oxide corrosion product and pitting corrosion penetrated the can wall exposing the fuel pins to the water.

The current condition of spent Advanced Test Reactor (ATR) fuel stored in the CPP-603 basin is not clearly known. Video inspections have shown that visible surfaces have corrosion product, but the overall integrity of the fuel cladding is generally unknown<sup>21</sup>. Their study has concluded that the aluminum cladding of a typical ATR fuel element is pitted and thinned by corrosion, especially in those locations on the fuel plates that operate at the highest temperature in the reactor.

### **CPP-666 Basin**

This basin, located at the Chemical Processing Plant is the most modern fuel storage facility in the DOE Complex.<sup>19</sup> 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  $\mu$ S/cm.<sup>19</sup> 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 thought to be the result of microbiologically influenced corrosion (MIC).<sup>3</sup>

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.<sup>3</sup> Although MIC is under investigation for the aluminum materials, it is possible that the high radiation fields associated with the actual fuel would kill the micro-organisms. LITCO is conducting a joint program with the Center for Biofilm Center at Montana State University on effects of MIC corrosion on aluminum alloys and methods to mitigate this corrosion. Details on this investigation are discuss in a separate section of this report.

### **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.<sup>2</sup> 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 basin 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.<sup>2</sup> 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 algacides 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 cartridge filters were intended to remove particles and provide water clarity. The heat exchanger was intended to remove decay heat from the fuel and to control basin temperature. 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 °F and 3.5 Ci/day at 70 °F.

Fuel shipments began in mid-1975 and within a few months, KE basin radionuclides began increasing at a high rate.<sup>2</sup> This prompted major modifications to the system to install three ion exchange columns and a sand filter in 1978. Initially, the ion exchange columns with Zeolon 900 resin were operated a few days a week, but later were operated continuously to bring radionuclide concentrations under control. The heat exchangers were replaced with water cooled Freon 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. The KE basin currently has a considerable amount of sludge on the basin floor.

Preparations begin for activating K-West basin in 1979.<sup>2</sup> 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  $\mu\text{S}/\text{cm}$  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.<sup>2</sup> The canisters contain the spent fuel in deionized water with 500 ppm of potassium nitrate added as an inhibitor. Hanford has never quantified what the inhibitor does for the metallic uranium, but feel that it slows corrosion. 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. Unlike KE basin, there is little sludge on the basin floors.

The water treatment systems in both KE and KW are doing a reasonable 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  $\mu\text{S}/\text{cm}$  range and KW is deionizing the water to a low level of 1-2  $\mu\text{S}/\text{cm}$ .<sup>2</sup>

A corrosion monitoring program was implemented in 1980 to determine the uniform corrosion rates of the major materials in the basin environment.<sup>2</sup> 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.<sup>5</sup> 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. Detailed results of these programs will be published by WHC/PNL in the near future.

→ Env. in  
basins  
Controlled  
or parms  
(T, C, etc.)  
recorded  
?

### Oak Ridge National Laboratory High Flux Isotope Reactor (HFIR)

During normal operations, spent fuel elements from the HFIR have been stored in the HFIR storage pool for about two years before shipment to SRS for processing.<sup>4</sup> For the first 25 years of operation this procedure worked very well. In recent years with no processing at SRS, some fuel elements have been stored in the HFIR basin for more than 7 years.

The fuel elements for the HFIR Reactor have a nominal thickness of  $10 \pm 2$  mils of 6061 aluminum over a fuel matrix of  $\text{U}_3\text{O}_8\text{-Al}$ .<sup>4</sup> The cladding may be thinned during the reactor cycle by as much as 2 mils, leaving the possibility of a minimum cladding thickness of 6 mils at some spots when the fuel elements are transferred to the water basin.

The HFIR pool is lined with stainless steel and a side stream of water is continuously deionized.<sup>6</sup> The conductivity is usually kept at lower than 1  $\mu\text{S}/\text{cm}$ , but at times has been as low as 0.5  $\mu\text{S}/\text{cm}$ . At this level of water quality there has not been any evidence of cladding failure in the pool as of 1994. Examination of 6061 aluminum side plates of the elements underwater also revealed no damaging corrosion or obvious pitting.

After about two years in the basin, the temperature has cooled to the point that there is no convective flow and the water is essentially stagnant in the channels of the fuel.<sup>6</sup> Several fuel elements were back lighted to see if nodular corrosion, characteristic of pitting, were evident in the channels. Some debris did exist, but signs of pitting were not evident. There was some evidence of aluminum oxide present, but whether it came from a surface in the same channel or was transferred from some other place, could not be determined.

During an extended HFIR shutdown, starting in 1986, some target rods from the reactor were stored in the pool for over 3 years, before being returned to the reactor for an additional 4 cycles of irradiation.<sup>4</sup> The target rods were clad with 8001 aluminum and were surrounded by 6061 aluminum shrouds. Video inspection on all visible surfaces showed no discernible corrosion. Fine scratches, probably from handling instruments, could clearly be seen, but no corrosion was seen to originate at these scratches.

### Microbiologically Influenced Corrosion (MIC)

MIC can be defined as corrosion initiated or accelerated by microorganisms. MIC is also known as biological corrosion, microbial corrosion, microbiologically induced corrosion and biocorrosion.

Natural waters, and even potable waters, contain a variety of bacteria. When aluminum or any metal is immersed in natural water, two processes occur simultaneously. Corrosion of the metal starts immediately and a biofilm begins to form. A biofilm is a microbial mass composed of aquatic bacteria, algae and other microorganisms.<sup>22</sup> The metabolic processes of the microorganisms are sustained by chemical reactions energized by nutrients obtained from the surrounding environment. These processes can influence the corrosion behavior of materials by introducing or enhancing heterogeneity at the metal surface by :

- Destroying the protective oxide film on the metal surface.
- Producing a localized acid environment.
- Creating corrosive deposits.
- Altering anodic and cathodic reactions, dependent on the environment and organisms.

The bacteria themselves don't cause the corrosion, but create the environment which enables one of the standard corrosion mechanisms to be accelerated on the metal.<sup>22</sup> It is generally localized in nature and, unlike some of the other corrosion processes, may not have extensive corrosion products associated with it. For this reason, it is often easy to overlook. Nuclear power plants can be particularly susceptible to MIC as a result of their design and operation. Stagnant flow occurring with the redundant systems associated with nuclear facilities establishes ideal conditions for MIC to occur.

Biocides are chemical compounds which kill or reduce the number of organisms. Chlorine and bromine are classified as oxidizers.<sup>22</sup> The hypochlorites, like sodium or calcium hypochlorite is an effective treatment of bacteria in some cases, but for aluminum fuel, the addition of any chloride into a fuel storage basin is extremely dangerous because of the potential to promote severe pitting corrosion. The problems

associated with corrosion of aluminum and steel in the Idaho CPP-603 basin was caused by excessive use of hypochlorite leading to chloride levels of about 800 ppm. Idaho now uses ultraviolet lights on the inlet water stream to control algae and bacteria in this basin.

In the Idaho CPP-666 basin, the water quality is among the best of all the nuclear fuel storage basins. With a low chloride concentration and low conductivity, corrosion of the aluminum-clad fuels stored in that basin has not been a problem. However, during a liner inspection in 1992, there was some corrosion noticed on aluminum coupons stored in the basin. These coupons were found to have a biofilm covering the pit initiation. In 1993 dummy aluminum cans were found to have indications of pit initiation and later of actual can perforations. LITCO has done ultrasonic mapping of the pits sites on these cans and confirmed that penetrations have occurred through the can walls. The pits contained no corrosion product and cannot be seen visually with the eye a few feet away.

Based on indications of Microbially Influenced Corrosion, LITCO established a program with Montana State University (MSU) and the National Science Foundation Center for Biofilm Engineering to study the MIC on aluminum alloys. Using a dual compartment corrosion monitor (DCCM) and deionized make-up water from the CPP-666 basin, a series of electrochemical experiments were carried out under the direction of Dr. Gill G. Geesey at Montana State University and William J. Dirk at LITCO. With test alloys of 1100 and 6061 aluminum and 304 and 308 stainless steel immersed in sterile and non-sterile water, combinations of these alloys were coupled together and galvanic current measurements made. From these measurements, a contribution from microorganisms to the corrosion process could be determined.

For the aluminum alloys, a dramatic shift of corrosion potential occurred in the biotic potential on the 21st day of testing when the alloys were exposed to the microorganisms in the pool makeup water. The maximum biotic contribution to the corrosion current occurred after day 21 and remained constant at  $5.1 \mu\text{A}/\text{cm}^2$  for 6061 aluminum specimens and about  $6.0 \mu\text{A}/\text{cm}^2$  for the 1100 alloy.

Similar measurements for the 304 and 308 stainless steel alloys yield a corrosion current of  $1.9 \mu\text{A}/\text{cm}^2$  and  $2.35 \mu\text{A}/\text{cm}^2$  respectively. In contrast to the more negative shift in corrosion potentials seen on the aluminum alloys, the corrosion potential for the stainless steel alloys shifted to a more positive value or in the passive direction. This is consistent with the theory that bacterial attachment and biofilm formation causes an ennoblement to the corrosion potential of stainless steel.<sup>23</sup> Examinations of the surface of the stainless steels showed that the biofilm was more evenly distributed over the surface.

At the end of 60 days, the 6061 and 1100 aluminum specimens were examined by SEM and the surfaces contained a mixture of bacteria and corrosion products. The numerically dominant microorganisms on the surface of both alloys were rod-shaped bacteria approximately  $0.2\text{-}0.5 \mu\text{m}$  in length and a large, filamentous microorganism,  $0.5\text{-}0.7 \mu\text{m}$  in width and up to  $10 \mu\text{m}$  in length. The corrosion product from the metal and the biofilm from the various microorganisms together formed the surface deposit on the alloys. The bacteria formed a patchy distribution across the surface of the two aluminum alloys.

Thus, from the Montana State study on the aluminum and stainless steel alloys immersed in makeup water from the CP-666 basin, the microorganisms were shown to contribute to the galvanic corrosion potentials and current of these alloys. The 1100 alloy which is typically of many aluminum-clad, spent fuels was found to be the most susceptible to MIC. The susceptibility decreased in the order:

### Al 1100 > Al 6061 > SS 308 > SS304

The study showed that a solution of deionized water with low ionic strength and organic carbon content, when replenished periodically, can support the establishment of a microbial biofilm, derived from microorganisms that occur naturally in that water. This biofilm contributes to a corrosion current density higher in each alloy than seen in similar tests in sterile water with no biofilm.

Future efforts in this study will look at the effects of biocides in the mitigation of the MIC corrosion on aluminum/stainless steel in CPP-666 basin makeup water. Currently, ozone is being investigated. Initial experiments show that the corrosion current drops immediately after the injection of ozone into the water. This indicates a kill of bacteria. A determination of appropriate quantities of biocide and frequencies of injection is critical to the success of the investigation.

## Environmental Factors Affecting Corrosion of Aluminum Alloys

The corrosion of aluminum alloys in high purity water is complex and many of the factors responsible for this corrosion are interrelated. In high purity, deionized water which is used in most of the U.S. basins storing aluminum-clad spent nuclear fuel, general thinning of the clad caused by general corrosion is minimal. The fuel enters the basin with, in some cases, several mils of high temperature formed protective oxide coating. 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.<sup>13</sup> Pitting that normally would occur in stagnant waters can often be prevented by water in constant motion. This section contains a discussion of some of the most important factors affecting the corrosion of aluminum alloys as related to the water chemistry and service environment.

### 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 ( $\text{CaCO}_3$ ) and other ions like sulfates and chlorides present in the water. A  $\text{CaCO}_3$  content of about 1-60 ppm is considered soft and over 60 ppm is classified as hard with over 181 ppm, very hard.

The major factors believed to influence the pitting of aluminum alloys are: conductivity, pH, bicarbonate, chloride, sulfate, and oxygen content.<sup>4</sup> 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 been conducted in synthetic waters containing several metal and salt ions alone and in combinations.<sup>24,25,26</sup> They found that corrosion of aluminum was accelerated by combinations of salts of copper, chlorides, and bicarbonates, over the single impurities. In cases where two of the three constituents were present, there was little corrosion, but with the three species were present, nodular corrosion occurred.

## Conductivity

As most of the corrosion processes going on 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 pitting, or general 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. The low corrosivity of high-purity water is primarily due to its high electrical resistance (low conductivity).<sup>13</sup>

The electrical resistivity of the water is defined as :

$$R \text{ (specific resistivity)} = \frac{1}{C \text{ (specific conductivity)}} \quad (6)$$

The specific resistivity unit is ohm-cm and conductivity is given by 1/ohm-cm or mho/cm. A smaller popular unit is micro mhos/cm or :

$$\text{ohm-cm} = \frac{1,000,000}{\mu\text{mhos/cm}}$$

In International Units, 1  $\mu\text{mho/cm}$  = 1 $\mu\text{S/cm}$  where S is the unit Siemen.

Extremely pure water is produced by deionization for atomic energy purposes. Some of this water has a conductivity less than 1  $\mu\text{S/cm}$ . Type I reagent-grade water can be produced by deionization, distillation, reverse osmosis, or combinations of these techniques to a conductivity level of less than 0.1  $\mu\text{S/cm}$ . Natural lake waters in some areas like Lake Ontario, Canada have a typical conductivity of about 270  $\mu\text{S/cm}$ . On the other extreme, seawater conductivity runs about 40,000  $\mu\text{S/cm}$ .<sup>27</sup>

Storage basins around the U.S. which are storing aluminum-clad spent nuclear without reportable corrosion problems are typically operating deionization equipment continuously and maintaining a conductivity level of typically less than 10  $\mu\text{S/cm}$ . Storage times for aluminum-clad alloys up to 25 years without corrosion at these low conductivity levels have been reported.<sup>4</sup>

At Brookhaven National Laboratory, the aluminum fuel elements are stored in a canal (pool) and subjected to continuous by-pass demineralization. The conductivity is maintained at about 0.5  $\mu\text{S/cm}$  and when it reaches 1  $\mu\text{S/cm}$ , the resins are regenerated. Fuel elements have been stored continuously in the canal without any evidence of cladding breaches. At Oak Ridge, the conductivity is routinely maintained at 1  $\mu\text{S/cm}$ , but at times has been as low as 0.5  $\mu\text{S/cm}$  and again, no evidence of corrosion in fuel stored for 8 years. Georgia Institute of Technology has reported successful storage of 1100 clad aluminum fuel stored in their pool for over 25 years in continuously deionized water at typically 1  $\mu\text{S/cm}$  or better.

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  $\mu\text{S/cm}$ . At the Idaho CPP-666 basin, the deionization system routinely maintains the basin water at about 1-2  $\mu\text{S/cm}$ . They have a current operating limit of less than 10  $\mu\text{S/cm}$  and take immediate action in determining if chloride ion increase is causing the anomalous increase in conductivity when the

operating limit is reached. 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  $\mu\text{S}/\text{cm}$ , down from the typical 250  $\mu\text{S}/\text{cm}$  of the mid-1970 to 1980's before the ion exchange columns or mix-bed resins were used. Severe corrosion problems have been encountered in this basin in the early years, because a relatively high percentage of the zirconium clad, depleted uranium fuel elements were breached during the unloading process from the N-Reactor before shipment to the basin for storage. This basin was initially filled with only filtered water and had significant quantities of algacides and chlorine added for control of biological growth. The K-West basin was completely drained in 1979, primed and painted with an epoxy paint, and filled with demineralized water. The ion exchange modules use a mixed-bed resin and maintain this basin at a conductivity of 1-2  $\mu\text{S}/\text{cm}$ . The fuel in this basin is stored in sealed aluminum and stainless steel canisters. The condition of the fuel is unknown, however, there is some known leakage of Cs-137 activity from these canisters to the basin water.

The RBOF basin at Savannah River operates a mixed-bed deionizer deionizer for about 5 days a week, except over the week-ends, 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  $\mu\text{S}/\text{cm}$ . 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 over 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 the fuel or the canister.

As can be seen from the surveys of the best basins in the United States, conductivity of the basin water plays a very key role in minimizing the corrosion of aluminum alloys. Basins with a conductivity in the low 1-3  $\mu\text{S}/\text{cm}$  levels support the storage of aluminum clad alloys with little or no pitting corrosion. In achieving these low levels of anion and cation concentrations, other corrosion inducing impurities like the chloride ion are also generally reduced to low levels in the ppb range where they make the water significantly less aggressive.

In the SRS reactor basins, corrosion was a significant problem in the K-Basin during 1992 when the conductivity was approaching 180  $\mu\text{S}/\text{cm}$ . In this same basin during 1994, there has been no visible pitting corrosion for the first 13 months of exposure at a conductivity ranging from 120  $\mu\text{S}/\text{cm}$  to 147  $\mu\text{S}/\text{cm}$ . In P-Basin we saw no pitting corrosion after 8 months at a conductivity of 145  $\mu\text{S}/\text{cm}$ , but saw pitting corrosion after 11 months with the conductivity at 165  $\mu\text{S}/\text{cm}$ . From this data, some may try to deduce that as long as you keep the conductivity below about 150  $\mu\text{S}/\text{cm}$  one will get no corrosion. However, these test coupons had no 304L/aluminum galvanic couple which exists on much of the fuel in the various basins. This couple has been shown to significantly reduce the pitting potential of the uncoupled aluminum. In addition, the time to initiate pitting of the aluminum may be longer than the 11-13 months of the latest round of testing. Figure 8 shows the results of laboratory testing using a galvanic couple in deionized water at 130  $\mu\text{S}/\text{cm}$  versus the same set-up in water at 3  $\mu\text{S}/\text{cm}$ . In just a few months, the couple in water at 130  $\mu\text{S}/\text{cm}$  showed extensive pitting over the outer surface, whereas the coupled specimen in very pure, low conductivity water showed only a small white ring of oxide product adjacent to the stainless steel. Samples in 130  $\mu\text{S}/\text{cm}$  deionized water without the stainless steel couple showed no corrosion over the 24 month testing period.

While coupon data from the SRS basins indicate that corrosion performance has improved with the cleanup of the basins, there is no solid evidence that lowering the conductivity to 100  $\mu\text{S}/\text{cm}$  will be adequate for 10-20 years of continued storage of aluminum alloys. Engineering judgment based on available information indicates that a level of about 50  $\mu\text{S}/\text{cm}$  may be adequate for a few years, but there is no field storage data or coupon test data available for 25 year test exposures at this level to determine whether this level of purity will protect aluminum from pitting corrosion for this long term storage period. There is evidence based on a number of deionized storage basins around the world that aluminum-clad spent nuclear fuel can be stored successfully in basins with conductivities of less than 10  $\mu\text{S}/\text{cm}$  and generally in the 1-3  $\mu\text{S}/\text{cm}$  range for times exceeding 25 years without breaching the cladding alloys. Basin deionization systems should be designed and operated to achieve these low conductivity levels to ensure successful long term storage of aluminum alloys spent nuclear fuels.

### Effect of pH

Aluminum is passive and protected by its oxide film in the pH range of about 4 to 8.5. The limits of this range 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. This is shown in Figure 3. The oxide coating is soluble at pH values below 4 and above 8.5. General corrosion in distilled water at 60  $^{\circ}\text{C}$  has been shown minimum at pH 4 rising slightly in the passive range and faster between pH 9 and 10. For pitting, which is the predominant mechanism of corrosion with aluminum alloys in water, 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.<sup>28</sup> 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.<sup>5</sup>

The corrosion rate often depends more 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 acetic acid at a pH of 3, but is corroded rapidly by hydrochloric or phosphoric acid at a pH of 4. On the alkaline side, aluminum is resistant to ammonium hydroxide at pH 13, but is rapidly corroded by sodium hydroxide at pH of 11. The probable reason for this specific behavior lies in the composition of the corrosion product, and their tendency to form protective films on the surface of the aluminum.<sup>7</sup>

### 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 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.<sup>29</sup>

For aluminum, pitting corrosion is most commonly produced by halide ions, of which chloride ( $\text{Cl}^-$ ) 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.<sup>7</sup> 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. Sverpa<sup>29</sup> found that increasing the chloride content from 0 to 50 ppm in water containing 116 ppm bicarbonate increased the number of pits, but not the depth. With 0.1 copper the effect was much greater. With 10 ppm chloride and 116 ppm bicarbonate at pH 8.0, very little attack occurred, while at pH 8.0 with 50 ppm chloride and 232 ppm bicarbonate, 4 mil pits occurred. At a lower pH of 6.4 corrosion occurred with only 20 ppm chloride and 116 ppm bicarbonate.

What is known, however, is that high chloride contents like the 800 ppm in the Idaho CPP-603 basin that occurred during 1976 with the additions of chloride bearing algaeicides like sodium hypochlorate, cause severe corrosion to the fuels in the basin. Basins like those at SRS have had limits of 20-25 ppm Cl<sup>-</sup> 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<sup>-</sup> and the CP-666 basin at Idaho operates at about 50 ppb.

## Copper

Heavy metal ions such as copper and mercury are very aggressive toward the pitting corrosion of aluminum alloys.<sup>5</sup> 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. These levels are considered the threshold for initiation of pitting on aluminum. A specific value is not normally proposed because the pitting tendency also depends on a number of other factors: concentrations of other ions, particularly chloride, bicarbonate, and calcium; pH of the water, the aluminum alloy, and whether the pits are open or occluded.<sup>7</sup> The influence of copper is less at a pH of 8.0 than at 6.4 because of the lower solubility of copper in the water at the higher pH level. Based on two case histories, Godard believes that about 0.10 ppm in distilled water is sufficient to cause pitting of aluminum.<sup>5</sup> Ions of copper and mercury are usually low in the storage basins where analytical data is available. However, some of these basins have heat exchangers with copper tubes and copper thermocouples or mercury thermometers are sometimes used in measuring water temperature. The RBOF basin has a limit of 0.01 ppm for copper in the basin water and usually operates at about 2 ppb. In the early 1980's, an algaeicide added to the basin water at Hanford's K-E basin resulted in dissolution of the copper from the heat exchanger tubes causing nodular pitting corrosion on the aluminum canisters containing the spent fuel.

## Bicarbonate

An important factor in determining the aggressiveness of the water toward the pitting corrosion of aluminum is the hardness or softness of the water as measured by the carbonate content.<sup>5</sup> In an unlined concrete basin where there is likely calcium carbonate continuously leaching into the water, there is some buildup of carbonate hardness. In addition, there is generally large surface areas associated with the basins where atmospheric carbon dioxide can react with the surface water to form the bicarbonate ion,  $\text{HCO}_3^-$ . The bicarbonate ion alone at concentrations up to 300-400 ppm has been shown not to cause pitting, but in combinations with chloride and copper, calcium carbonate ions led to intensive pitting.<sup>25,26,29</sup> Sverepa found that at low bicarbonate 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 adhered firmly to the pits.

Continuous deionization of the storage basin water softens the water as it removes the calcium bicarbonate and other ions contributing to the hardness. Godard, however, found that zeolite-soften, deionized water had the same pitting behavior in aluminum as the parent water.<sup>5</sup>

## Sulfates

Studies by Draley have shown that the presence of sulfate at 50 °C and 70 °C reduce the corrosion rate of aluminum.<sup>30</sup> Rowe and Walker<sup>26</sup> 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.<sup>5</sup> He concluded that the pitting corrosion, i.e., pitting density and pitting rate, is influenced by the film thickness.<sup>31</sup> 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.<sup>41</sup>

## Oxygen

Surface waters and storage pools at SRS are normally saturated with oxygen so that oxygen is not a variable in many of the corrosion problems associated with wet stored fuel. Godard has shown that complete elimination of oxygen from Kingston tap water markedly reduced the corrosion of aluminum.<sup>5</sup> Rowe and Walker reported that in a water containing copper, bicarbonate, and chloride, the exclusion of air reduced the amount of corrosion to only one-third of that when saturated with oxygen.<sup>26</sup> Measurements of the oxygen content of L-Basin water at SRS at 15 °C found the dissolved oxygen to be constant with depth in the basin and saturated at 10.9 ppm.

## Temperature

Mears and Brown studied the influence of temperature on pitting of aluminum alloys in chloride solutions.<sup>33</sup> They found that as the temperature rose, both the density and the probability of pitting increased, while the pitting rate or average depth of pits decreased. Godard<sup>5</sup> studied the influence of temperature on the pitting of AA-1100 alloy by surveys of pit density and maximum pit depth in tap water at temperatures up to 70 °C. It was

found that the pitting rate temperature-temperature curve for some pits had a maximum at about 40 °C. The rate of pitting at this point was 5 times as great as at 25 °C.

An increase in temperature affects pitting rates by: (1) reducing the solubility of oxygen in the solution, and (2) by stimulating the initiation of pitting, which in turn reduces the pitting rate. Most basin operations seek to maintain low basin temperatures. Much of the fuel in the US basin has been in the basins for several years and the radioactive decay heat is diminishing. Maintaining low temperatures in the basins is extremely important in the corrosion of the uranium metal cores as has been seen during temperature excursions at the Hanford basins.

## 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.<sup>32</sup> Using 67 natural waters where analyses were available and AA3003 aluminum alloy, tests were conducted to determine the maximum pit depth as a function of exposure time. From the data, an analysis of the time required to develop a 40 mil pit was extrapolated.

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:

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

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

A pitting rate index of less than 25 weeks is indicative of aggressive water. The bicarbonate content is not included as it was found that inclusion did not increase the standard error of the equation. This equation is not mathematically valid at a pH of 7 and begins to break down as one approaches pH 7 from greater or lower values. This abnormality is a fundamental result of the format used to express PRI. Additional work is needed to refine this relationship. The authors have indicated that the agreement of this relationship to performance was only fair, but nothing has been found in the literature in the past 25 years that does a better job of providing a relative comparison of the aggressiveness of basin water on the corrosion of aluminum alloys in long term storage.

With values from analysis of water quality at SRS basins shown in Table (4), the pitting rate equation was used to determine the relative aggressiveness of the storage basins at SRS as the water chemistry of the basins varies. The pitting rate index was calculated based on the analyses of water samples taken from the basins. Comparisons of the maximum pitting depths of the component immersion test samples removed from these basins at various times between 1992-1995 provides some benchmarks for the equation. Using the basin conditions for K-Reactor on December 3, 1991, when the conductivity was 178  $\mu\text{S}/\text{cm}$ , the pitting rate index was calculated to be about 35 weeks. During this 1992 time period, the 8001 aluminum alloy clad pitting to a depth of 53 mils in about 11 weeks and the more corrosion resistant 1100 alloy took about 26 weeks to pit to a depth of 58 mils. Using the median value of 130  $\mu\text{S}/\text{cm}$  in April 1994, the pitting rate index for K-Basin was calculated to be 68 weeks or twice the 1992 index. No pitting of the

aluminum alloys has been seen in 56 weeks of exposure in K-Basin. This indicates that water conditions were improved significantly by the deionization and basin cleanup activities during 1993 -1995.

The pitting rate index for L-Basin, which reached a lower conductivity level of 102  $\mu\text{S}/\text{cm}$  in 1994 was found to be 117 weeks, which was about twice as good as the other two basins. This improvement in the water quality in L-Basin is attributed to the campaign to lower the conductivity by sludge removal and more continuous operations of deionizers in that basin during 1994. The improvement in initiation of no new pitting corrosion is seen in Figure 10 which shows the lack of corrosion product on the corrosion test specimens in the L and K-basins after 11 and 13 months, respectively. All basins, except P-Basin received concentrated deionization during the 1993-1994 time frame. After several years of no deionization in P-Basin and with conductivity increasing in that basin, pitting corrosion is starting on the corrosion surveillance test samples. Efforts are underway to resume deionization and reduce the aggressiveness of the basin water. From all indications, the cleanup campaign to improve storage conditions in the SRS basins has made positive process.

Similar calculations for the pitting rate index in P-Basin in 1994, using the median value of conductivity of 149  $\mu\text{S}/\text{cm}$  yields a PRI of 64 weeks and likewise no pitting was seen on samples removed from P-Basin after 8 months. By February 1995, the conductivity in P-Basin reached 170  $\mu\text{S}/\text{cm}$ . The PRI for basin conditions in early 1995 was calculated to be 50.5. Component immersion test specimens removed from the basin after 11 months exposure under these condition showed two, 35 mil deep pits compared to no pitting after the 8 month exposure at lower conductivity.

The effects of extremely low conductivity and low impurity concentrations of the RBOF basin at SRS on the pitting rate index are seen in Table (4). Using the low range of conductivity at 1  $\mu\text{S}/\text{cm}$ , the PRI was calculated to be over 10 years. We have inspected fuel which has been stored in this basin almost 12 years and see no signs of corrosion.

The pitting rate equation thus predicts when basin water is aggressive to pitting corrosion of aluminum and predicts when aluminum alloys can be stored in a given purity water for extended time periods. Godard indicates that it is more accurate for aggressive waters than non-aggressive waters. It appears to be a reasonable indicator for relative comparisons of basins and for following the cleanup and deionization activities of a given basin. It does not predict with great accuracy the exact timing to pit 40 mil pits in deionized waters of fuel storage basin.

## Uranium Corrosion

An excellent description of classical corrosion of uranium clad is provided by the work done in the late 1950's.<sup>34</sup> For aluminum clad fuel, once the clad has been penetrated by pitting corrosion, the compounds formed by the nickel bonding layer 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 an intermediate material like nickel, it corrodes somewhat more rapidly than bare uranium, but the increase in rate is more than offset by the restricted area of attack. The corrosion of uranium in water can be expressed by the reaction:



The corrosion can be divided into two stages: an initiation stage, corresponding to the induction period observed in the corrosion of bare aluminum, 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 hydride attack is generally more rapid than the direct attack by water.

The formation of uranium hydride in water is governed by the corrosion reaction given by equation 9 which uses the hydrogen generated by the corrosion reaction of equation 8.



As long as there is oxygen present, which is generally the case in an open pool, it will quickly react with the hydride to produce more  $UO_2$  and  $H_2O$  by the reaction:



Thus, for spent fuel storage in an open pool, the reaction given by equation 10 tends to minimize the inventory of available hydride and the risks of pyrophoricity. Only hydrides which are occluded will remain, either under passivating films or in crevices where oxygen and water can not penetrate in sufficient quantities to react with the hydrides after they are formed.

In a closed container where oxygen can be depleted by the corrosion process, the risk for pyrophoricity increases as from the air, a cover gas composed primarily of nitrogen remains along with the uranium hydride.<sup>35</sup> A uranium fire occurred at Oak Ridge when a bottle with uranium foil was sealed with air containing moisture. The water vapor and oxygen were totally consumed by the corrosion process, leaving only U,  $UO_2$ ,  $UH_3$ , and a reduced pressure cover gas containing nitrogen. When the bottle was opened, air rushed in due to the reduced pressure. The hydride reacted immediately with the oxygen, releasing enough heat to cause the uranium to reach its ignition point and burn.

C.W.E. Addison, of British Nuclear Fuels, has discussed the storage and corrosion of spent metal fuel based on the United Kingdom experience.<sup>36</sup> The majority of English

stored fuel from power reactors is metallic uranium clad with a magnesium aluminum alloy known as Magnox. After irradiation in a reactor, the Magnox fuel is discharged into a pond located at the power generation station. After a short time, it is transferred wet to BNFL Sellafield, England, where the fuel is transferred into a holding pond to await processing. After storage in water ponds for times often exceeding 140 days allowed for Iodine<sup>131</sup> decay, pitting of the Magnox clad has resulted in exposure of the uranium metal to water. The result of this exposure to water is that when corrosion occurs, with it comes the formation of uranium hydride, in some circumstances.

The corrosion product contains a proportion of UH<sub>3</sub> which equilibrates between 2-9%, assuming free access to water and oxygen. In a closed system, the reaction proceeds until virtually all the oxygen has been consumed, after which the corrosion rate increases significantly. In the absence of oxygen, the proportion of UH<sub>3</sub> in the UO<sub>2</sub>/UH<sub>3</sub> corrosion deposit can increase up to about 50% by weight. These conditions which are necessary for excessive hydride formation are categorized as "special environments". They can occur under the following circumstances:

- (a) In elements with cladding perforations allowing limited access,
- (b) Where porous uranium has been exposed to water,
- (c) Combinations of (a) and (b)
- (d) In dry bottled fuel where the bottles have suffered small leaks,
- (e) In closed environments where the oxygen has been consumed.

Addison states that considerable caution must be exercised when handling and processing metallic fuel which might have become hydrided under the special circumstances described above. But, he says that "it is generally considered that corrosion of non-swollen uranium with free access to water and oxygen, although producing some hydride, does not represent a significant pyrophoric risk". This is true because of the dilution of hydride by the UO<sub>2</sub> in the corrosion product, and the presence of a large thermal mass in the uranium slug, prevents significant temperature increases.

The potential for pyrophoric reactions on the aluminum-clad Mark 31A slugs stored in the SRS basins has been assessed by M.R. Louthan. He provided the technical basis to conclude that the exposure of these corroded slugs to air during removal from the basin or in a loss water accident would not result in spontaneous combustion of the uranium slugs. Based on his evaluation of the literature and SRS experience, Louthan concluded that the corrosion products were hydrated oxides of aluminum and uranium and were not pyrophoric, and pyrophoric particles of UO<sub>2</sub> and/or UH<sub>3</sub> would not be expected.

The formation and retention of uranium hydride on the slugs would require that water be excluded from the hydride containing area. This exclusion might develop as the hydrogen release by the corrosion process became trapped between the aluminum cladding and the uranium core. But, for this to occur:

- (a) the uranium core must corrode while the more anodic aluminum cladding retains shape,
- (b) the hydrogen pressure inside the cavity must be sufficient to exclude water from the cavity, and
- (c) the vapor pressure of water in the hydrogen environment must be low enough to preclude reaction with the uranium hydride.

Condition (a) can be satisfied because uranium corrosion might be enhanced by contact with the aluminum clad even though the contact forces the uranium to be cathodic and the

aluminum anodic. The uranium corrosion can be enhanced because the uranium interacts with hydrogen ions discharged at the cathode. The uranium ions formed by this interaction in the water are converted to  $UO_2$ .

Condition (b) is difficult to establish because the reaction of uranium with hydrogen would reduce the pressure inside the cavity and tend to draw the water into the corroded area. The water would then react with the hydride to form uranium oxide or a complex hydrated oxide.

In regard to condition (3), the hydrogen environment which develops inside the postulated cavity will have a hydrogen-water interface. Under equilibrium conditions, the hydrogen gas will be saturated with moisture. This moisture will react with uranium hydride to form uranium oxides and remove the potentially pyrophoric material.

The question of whether the Mark 31A aluminum clad, depleted uranium slugs stored in the L-Disassembly at SRS could have spontaneous hydride ignition on removal from the basin and exposure to air was addressed and tested in 1994. Two unirradiated Mark 31A slugs were removed from the stainless steel storage buckets and sent to the SRTC metallography labs for analysis.<sup>37</sup> The slugs were removed from the water environment and exposed to the air around the basins as well as being handled, shipped ten miles across SRS, and analyzed without incidence over a several month time period. These slugs showed visible corrosion product in the stainless steel storage buckets and evidence that the corrosion had penetrated the aluminum clad, exposing the uranium core. An earlier analysis of this corrosion product on irradiated slugs showed that aluminum oxide, the minerals becquerelite (calcium uranyl hydroxide hydrate), and compreignacite (potassium uranium oxide hydrate) were present. No evidence of hydride formation was evident. Identification of becquerelite and compreignacite by x-ray diffraction indicates these, or other similar compounds, were present. A discussion in the literature supports the presence of these compounds in the samples.<sup>38</sup> It states that corrosion of uranium metal in water in an oxidizing environment always produces a variety of minerals such as the two discussed above. Furthermore, the phase diagram for the uranium-water system shows that  $UO_3 \cdot 2H_2O$  and uranates are the thermodynamically stable uranium forms in an oxidizing system at neutral pH which are the conditions found in the water basins at SRS.

The inner and outer Mark 31A target slugs are shown in Figure 9. Note that the inner slug is free of pitting and that the pits in the outer slug appear to originate in scratches and imperfections in the cladding. Metallography on one of the slugs removed from the basin confirmed that pitting depths through the clad and into the uranium core varied, with the deepest pit found to be about 0.12 inches. Less than 2% of the aluminum cladding was found to be breached. This resulted in about 5% of the uranium surface area of the slug being affected by corrosion. Figure 10 shows typical cross sections of pitting found on this aluminum clad uranium material after about 6 years in water storage. **The overall integrity of the slug remained intact as seen in Figure 11.**

## Conclusions

The key to long term storage of aluminum clad spent nuclear fuels in wet basins at SRS and around the world is water quality. Experience has shown that successful storage without significant corrosion for times exceeding about 25 years can be accomplished by control of variables affecting water quality and good engineering design. Although complex and not always well understood, a number of factors responsible for corrosion

are believed to operate both independently and synergistically. Among those factors believed to promote this corrosion in SRS basins are:

- High basin water conductivity (180  $\mu\text{S}/\text{cm}$ ).
- Aggressive ions (20 ppm  $\text{Cl}^-$ )
- Sludge (contains Fe, Cl, Etc., in 10X water concentrations).
- Galvanic couple between stainless steel bucket and aluminum.
- Galvanic couple between aluminum and uranium.
- Scratches and imperfections in protective oxide coating on the cladding
- Relatively stagnant water.
- Microbiological Influenced Corrosion (MIC) has not been found at SRS, but is believed to be playing a role in the Idaho basin.

The quality of water at basins at SRS and other facilities around the US that are successfully storing aluminum clad fuel without corrosion has similar characteristics. The water quality in each of these basins has an extremely low conductivity and low chloride ion content. These basins primarily use mix-bed resin deionizers to achieve low conductivity and impurity content in the water storage pools. The conductivity of basins where no corrosion of aluminum is evident is about 200X lower than in basins where pitting corrosion is significant (1-3  $\mu\text{S}/\text{cm}$ ). In addition, aggressive ions like chloride are 1000X lower (20 ppb). This water quality cannot be maintained unless the systems are designed to operate continuously.

From the experience in the SRS basins, the galvanic couples between the stainless steels and the aluminum clad alloy fuels and storage racks play a larger role in the acceleration of the pitting process of the fuel than originally anticipated. Even though the area ratios between the dissimilar metals may not be too unfavorable, the pitting potential of the aluminum fuel assembly may be lowered enough to cause pitting to initiate.

The pitting rate equation discussed in this report, although not precisely accurate, gives a reasonable evaluation of the aggressiveness of the water quality in fuel storage basins. It has been used to monitor the basin water cleanup activities at the SRS and improvements in water chemistry have been verified by corrosion coupon tests. Additional work needs to be done to improve this correlation.

Based on the corrosion surveillance tests at SRS, pitting corrosion has been seen in a few months on aluminum alloys exposed to basin water conductivity levels of 170-180  $\mu\text{S}/\text{cm}$ , but has not been seen within a year's exposure at levels of 100-145  $\mu\text{S}/\text{cm}$ . From the pitting rate equation, we would not expect to see pitting at 100  $\mu\text{S}/\text{cm}$  for more than 2 years. Aluminum clad fuel stored in water at 1-3  $\mu\text{S}/\text{cm}$  appears to be reasonably immune to the initiation of pitting corrosion. Because of the synergistic nature of those factors which promote the pitting corrosion of aluminum clad spent fuel, it is not possible to say, with precision, the highest water conductivity that could be tolerated and still prevent initiation of new pitting corrosion. Good engineering judgment requires that the deionizers be sized to operate to drive the water conductivity to an optimum goal of 1-3  $\mu\text{S}/\text{cm}$  to ensure long term extended storage. Some of the older, concrete lined basins may have difficulty achieving this ultra low level. Based on the performance of deionizers at the Hanford K-East basin, a reasonable goal of 10  $\mu\text{S}/\text{cm}$  may be achievable for basins like those at SRS. At this level of conductivity, along with the corresponding low levels of impurities, corrosion performance for any new fuel stored in these basins will be enhanced and the existing corrosion on old fuel stored in the basins could be slowed. Vendor deionization, underway for about 2 months, at L-React

basin at SRS has achieved a water conductivity level as of September 1995 of less than 30  $\mu\text{S}/\text{cm}$  and dropping.

At SRS and other basins storing Defense related spent nuclear fuel, extensive efforts are underway to improve fuel storage conditions. These efforts should result in extended storage capability. This wet storage, however, cannot be extended infinitely and provisions must be made for other disposition. The ultimate solution for this problem is processing the fuel to a more stable form using standard techniques readily available and utilized at SRS for over 35 years.

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TABLE 1  
Maximum Pit Depths  
Basin Corrosion Tests

1991 - 1992						
Basin	Date	Exposure (Days)	Maximum Pit Depth (Mils)		Pit Density (Pits/cm <sup>2</sup> )	
			1100	8001	1100	8001
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	<del>6-92</del>	<del>182</del>	<del>58</del>	<del>27</del>	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	No Pitting Corrosion			
K	2-95	403	No Pitting Corrosion			
K	8-95	590	No Pitting Corrosion			
L	11-93	61	No Pitting Corrosion			
L	3-94	127	No Pitting Corrosion			
L	7-94	241	No Pitting Corrosion			
L	2-95	336	No Pitting Corrosion			
L	8-95	340	No Pitting Corrosion			
P	11-93	61	No Pitting Corrosion			
P	3-94	127	No Pitting Corrosion			
P	7-94	241	No Pitting Corrosion			
P	2-95	336	35 Mil deep pits in 8001 Aluminum Alloy			
P	9-95	775	No Pitting Corrosion			

TABLE 2  
K-Disassembly Basin Water Conditions

	Dec. 1991 - Dec. 1992			Jan. 1994 - January 1995		
	Immersion (ppm)	Range (ppm)	Median (ppm)	Immersion (ppm)	Range (ppm)	Median (ppm)
Nitrate	17	24-16	20	16	16-19	18
Sulfate	14	22-11	15	11	14-7	9
Chloride	9	9-6	8	7	8-6	6
pH	7.9	8.3-6.7	7.5	7.2	6.5-8	7.3
Conductivity ( $\mu$ S/cm)	178	178-135-147*	175	130	130-120-147*	125

\* Denotes conductivity at immersion, at lowest level, and at end of time period.

TABLE 3  
P and L-Disassembly Basin Water Conditions  
September 1993 - January 1995

	L			P		
	Immersion (ppm)	Range (ppm)	Median (ppm)	Immersion (ppm)	Range (ppm)	Median (ppm)
Nitrate	19	19-26	20	8	7-17	9
Sulfate	1	1-4	2	18	15-21	18
Chloride	18	18-11	14	10	9-11	10
pH	6.6	5.6-7.5	6.6	7.8	8-6.4	7.5
Conductivity ( $\mu\text{S}/\text{cm}$ )	112	112-96-107	102	145	145-164	160

Table (4)  
Pitting Rate Index Parameters

K-Basin 1992	K-Basin 1994	L-Basin 1994	P-Basin 1995	RBOE 1993
$\text{SO}_4 = 22$ ppm	9	2	19	<0.5
$\text{Cl} = 9$	6	14	10	0.215
$\text{NO}_3 = 17$	18	20	9	<1.5
$\text{pH} = 7.9$	7.3	6.6	6.66	7.4
Cond. = 178 $\mu\text{S}/\text{cm}$	125	102	170	1
Cu	<0.05	<0.05	<0.05	<0.05
PRI = 35	68	117	50	568

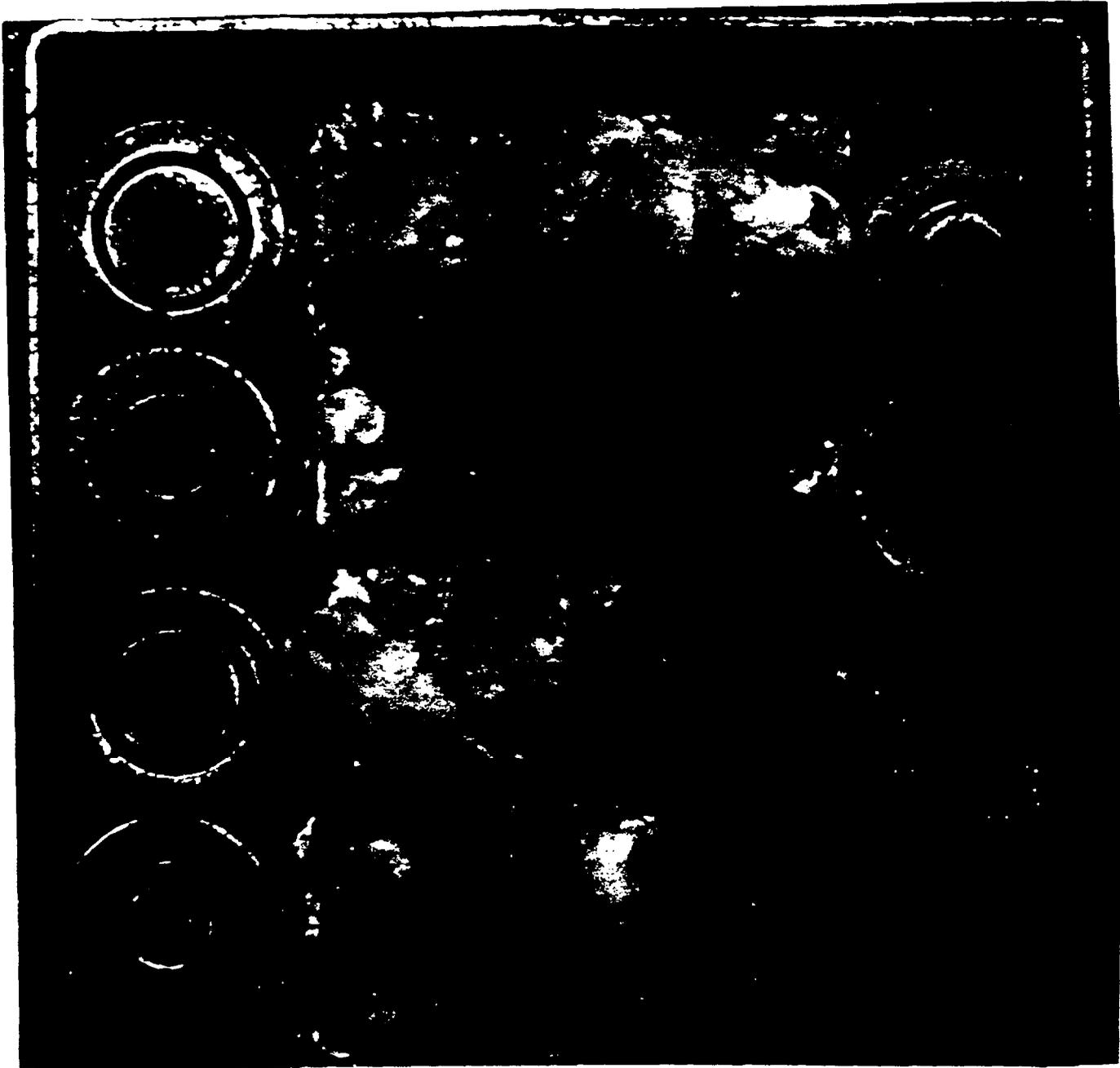


Figure 1. Corrosion of Mark 31A Slugs in L-Disassembly Basin



Figure 2. Mark 22 Fuel in Vertical Tube Storage Basin (4 Months)

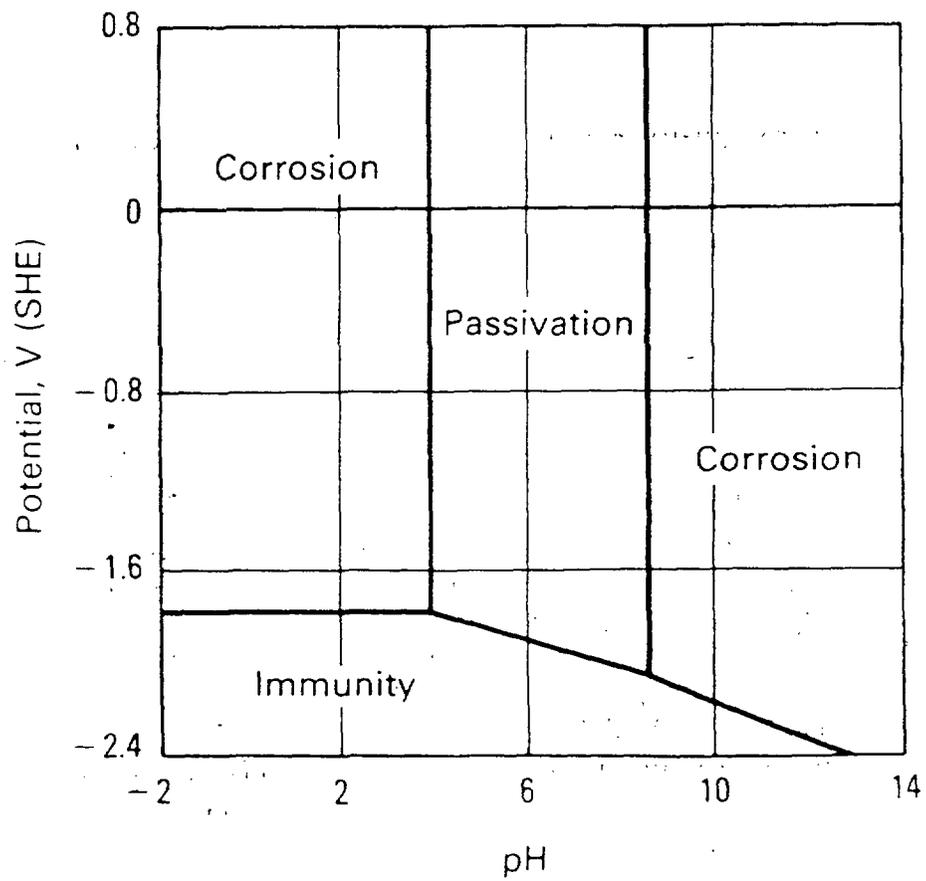


Figure 3. Pourbaix Diagram (From Reference 10)

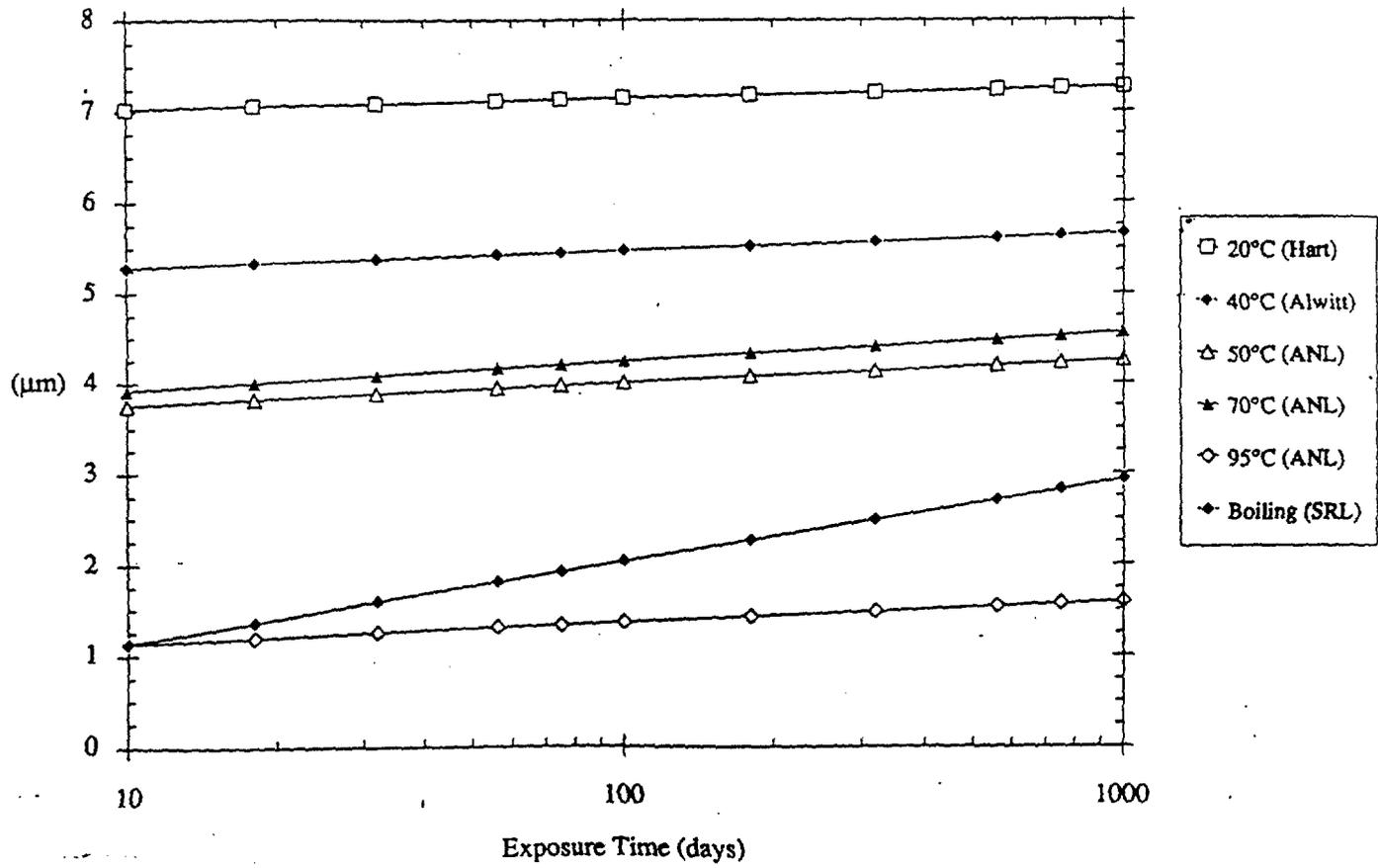


Figure 4. Aluminum Oxide Growth versus Time (From Reference 4)



Figure 5. Aluminum/304L Galvanic Couple in the Basin



25X

**8001 Aluminum Alloy  
45 Mils  
1 Year Exposure**



25X

**1100 Aluminum Alloy  
72 Mils  
1 Year Exposure**

Figure 6. Typical Pitting Corrosion in Aluminum



Figure 7. Comparison of K-Basin Corrosion 1992 versus 1994

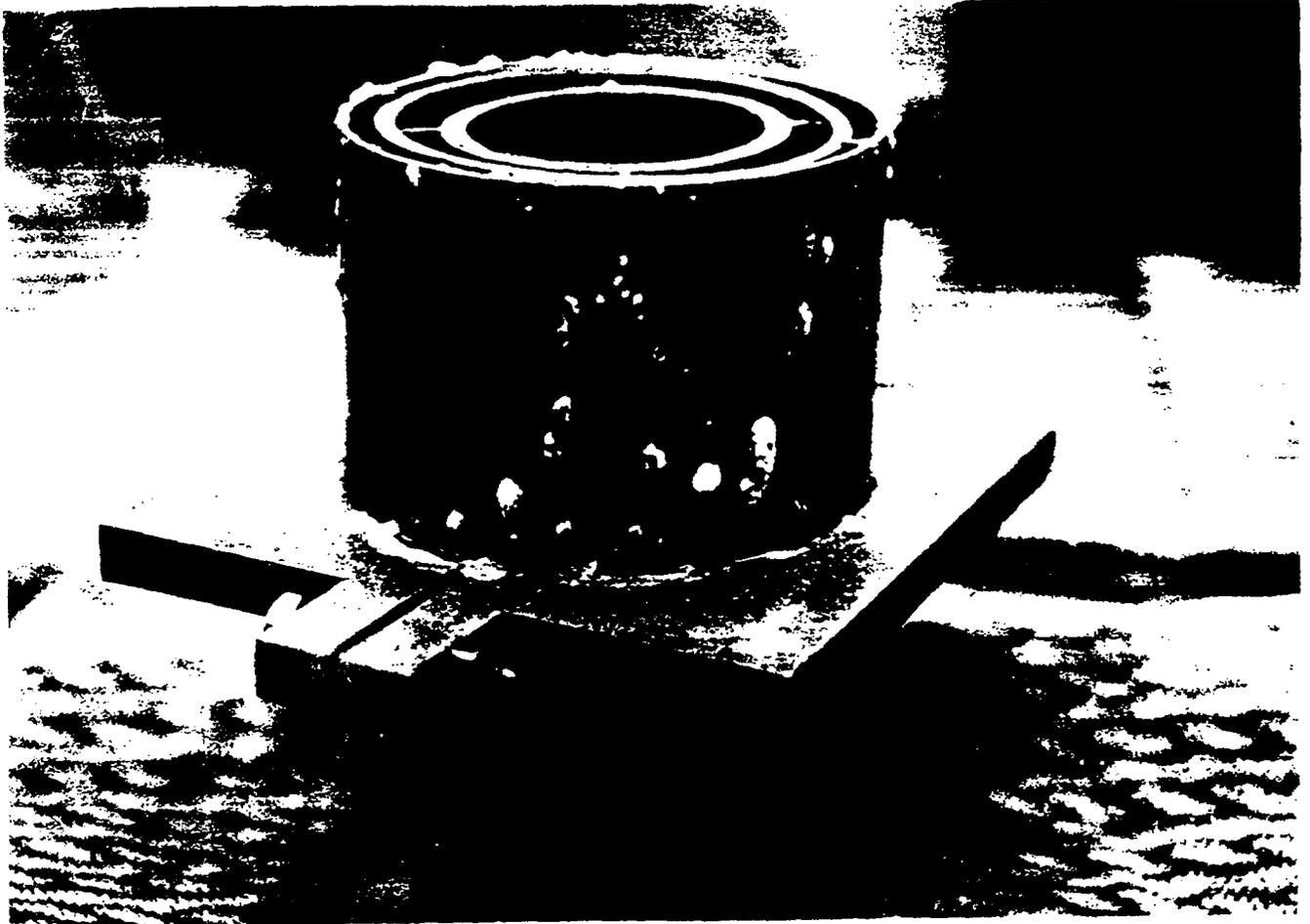


Figure 8. Aluminum/304L Galvanic Couple in Laboratory Testing



Figure 9. Mark 31A as Removed from L-Basin

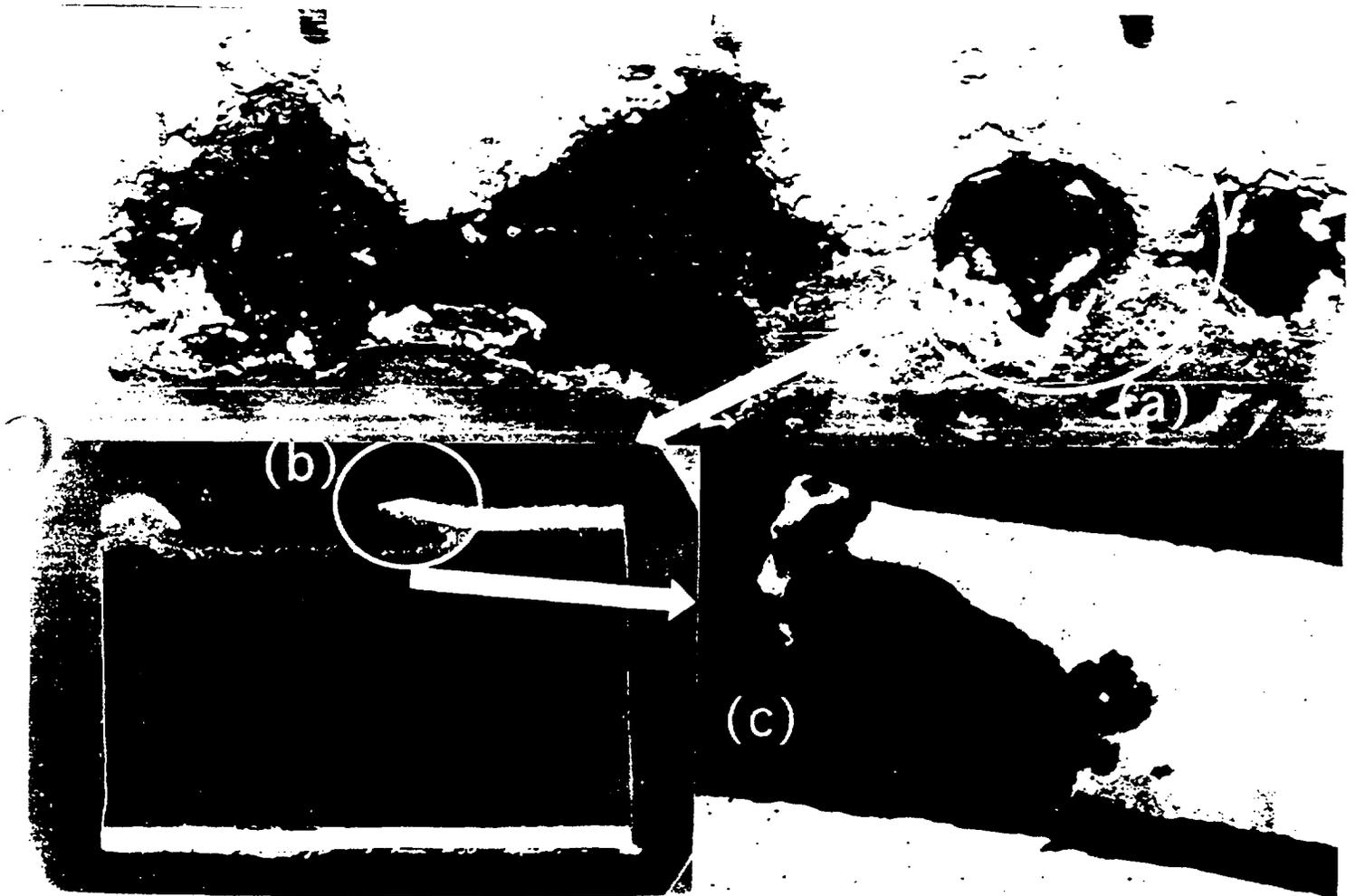


Figure 10. Metallographic Sections of Pitted Aluminum-Clad Uranium Target



Figure 11. Cross Section of Outer Slug Showing Overall Integrity

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