Corrosion Minimization For Research Reactor Fuel

Eric Shaber
Gerard Hofman, ANL

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INL

Idaho National Laboratory

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Idaho National Laboratory
Reduced Enrichment Research Test Reactor Program
Idaho Falls, Idaho 83415

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1.   Introduction

Existing university research reactors are being converted to use low-enriched uranium fue to eliminate the use of highly-enriched uranium. These conversions require increases in fuel loading that will result in the use of elements with more fuel plates, resulting in a net decrease in the water annulus between fuel plates.

The proposed decrease in the water annulus raises questions about the requirements and stability of the surface hydroxide on the aluminum fuel cladding and the potential for runaway corrosion resulting in fuel over-temperature incidents. The Nuclear Regulatory Commission (NRC), as regulator for these university reactors, must ensure that proposed fuel modifications will not result in any increased risk or hazard to the reactor operators or the public.

This document reviews the characteristics and behavior of aluminum hydroxides, analyzes the drivers for fuel plate corrosion, reviews relevant historical incidents, and provides recommendations on fuel design, surface treatment, and reactor operational practices to avoid corrosion issues.

2.   Aluminum Surface Treatments

2.1   Hydroxides

2.1.1   Formation

At temperatures below 400°C in air or water, aluminum will form one of several hydroxides on exposed surfaces. When the temperature of formation is below ~77°C, the end product will be a tri-hydroxide with the structure of Gibbsite (hydrargillite) [γ-Al(OH)$_3$], if the pH is lower than ~5.8 or higher than ~9; Bayerite [α-Al(OH)$_3$], if the pH is between ~5.8 and ~9; or Nordstandite [Al(OH)$_3$], often considered a mixture of the other forms. When the temperature is above ~77°C and below ~102°C, a pseudoboehmite structure is formed, which may age to other hydroxide forms or retain its pseudoboehmite structure. Between ~102°C and ~400°C and at pressures below ~20 MPa (2900 psi), crystalline boehmite [γ-AlOOH] will form[i].

The technical understanding of how aluminum hydroxides form has improved greatly over the last 50 years. In water, these hydroxides are now known to form from precipitation and aging of gelatinous compounds of low crystal order and up to five moles of water per mole of oxide. Formation in water and from dilute acidic solutions is particularly important for understanding and predicting reactor fuel behavior.

The primary ionic species formed is [Al(H$_2$O)$_6$]$^{3+}$, which provides the building block for octahedral chain molecules or hexagonal ring polynuclear complexes. Deprotonation and condensation reactions form a gelatinous boehmite that is the chemical precursor to both the tri-hydroxide and mono-hydroxide crystalline structures [Wefers 1987] (see Figure 1). Octahedral chain molecules, polynuclear complexes and the gelatinous boehmite structures need to be avoided within operating reactor nuclear fuel because their low-density structures are capable of blocking the annulus between fuel plates. Avoiding these

chemical complexes in reactor service is achieved by preparing the fuel with the most appropriate hydroxide surface prior to usage and preventing the dissolution of that hydroxide during operation.
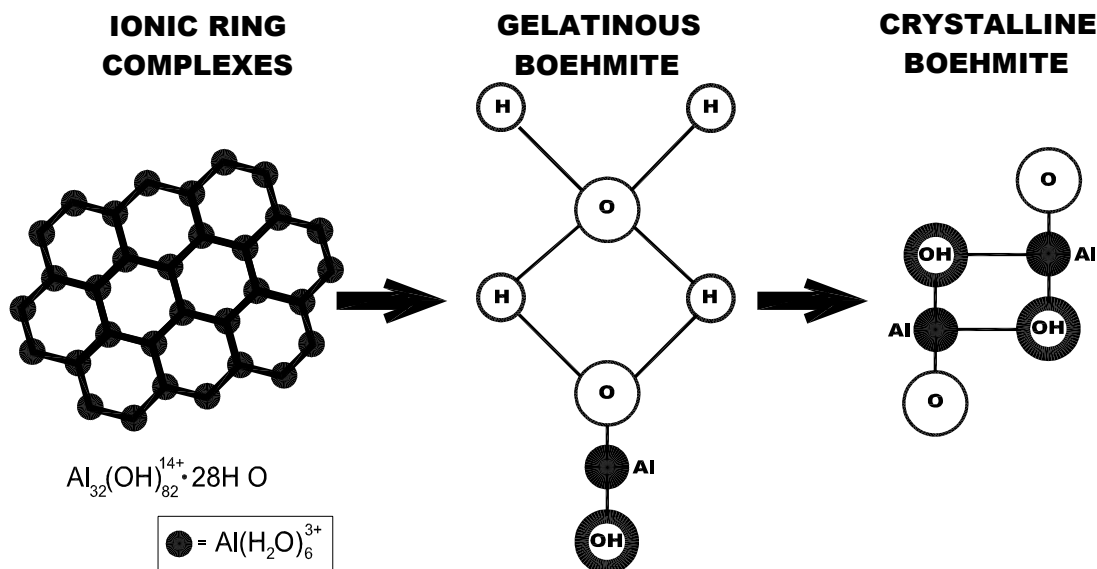
IONIC RING COMPLEXES

GELATINOUS BOEHMITE

CRYSTALLINE BOEHMITE

$Al_{32}(OH)_{82}^{14+} \cdot 28H_2O$

$\bullet = Al(H_2O)_6^{3+}$

Figure 1. Precipitation and aging of Al hydroxide to boehmite

2.1.2 Characteristics

2.1.2.1 Region of Stability. Aluminum hydroxides are amphoteric but relatively stable over a specific range of pH, primarily because of passivation due to the positive charge on the hydroxide surface provided by the Al^{3+} ion. The tri-hydroxide forms have a wider range of chemical stability (pH of ~ 4.0 – 8.5) but do not provide exceptional corrosion resistance within the region of passivation. Crystalline boehmite (mono-hydroxide) has a narrower passivation range (pH of ~ 4.7 – 6.2) but better water corrosion resistance within its range of stability. Boehmite treatments are commonly applied to improve the corrosion resistance of anodized aluminum components by "sealing" them in boiling water. Crystalline boehmite is routinely applied to Advanced Test Reactor fuel assemblies prior to their usage by treating them with deionized water in a high-temperature autoclave.

2.1.2.2 Effect of Anions. Acidic anions, especially carbonate and sulfate have been shown to adversely affect the aging of aluminu gels to achieve stable crystalline compounds. Chloride and nitrate are also undesirable but somewhat less damaging. Carbonate appears to have the strongest retarding effect. Conversely, removal of acidic anions from the chemical system helps accelerate the aging process. Because of these interactions, it is important that water supplies and water treatment systems prevent contamination with CO_2, carbonic acid, oxalic acid, or sulfuric acid.

2.2   Anodizing

Anodizing is an electrolytic method of depositing nearly pure Al_2O_3 on an aluminum surface. The metal is used as the anode in an electrolytic cell in an acidic electrolyte with a current applied to drive the chemical reaction with oxygen. Two basic types of anodizing treatments are in common use: those

designed to provide a non-porous barrier oxide film, and those that generate a thick but porous structurally favorable coating. Porous anodic oxides are not discussed further as they could not perform the desired function. Barrier layer anodizing, however, could be used as an aluminum surface treatment. It could provide significant advantages over hydroxide coatings in that a very stable, fully crystalline alumina is generated.

Barrier layer anodizing involves an electrolyte of either ammonium tartrate or boric acid[ii] and an operating voltage of typically 200 – 300V to generate an Al_2O_3 layer of up to 0.2 μm thickness. The layer formed is relatively pure Al_2O_3 but it will contain up to one percent of the acidic ion used in its formation. Boric acid electrolytes would be unacceptable for nuclear fuel. Although technically attractive, this approach to pretreatment does not have an existing experience base for use with nuclear fuel and would require testing for qualification before it could be seriously considered as a pre-treatment approach.

3.   Aluminum Fuel Corrosion

Corrosion is essentially an electrochemical process that may be enhanced by mechanical interactions or stresses on the components involved. Since aluminum is protected by a "corrosion" product, the term corrosion used here is defined as uncontrolled or unexpected hydroxide growth or change. Corrosion rates may be altered significantly (either positively or negatively) as a result of combinations of dissimilar metals or the application of electric currents.   Conversely, corrosion can generally be minimized by maintaining water purity and preventing interactions with dissimilar materials in the reactor. The corrosion issues experienced with aluminum research reactor fuels are radiolysis and localized corrosion.

3.1   Radiolysis

Neutron radiolysis is currently thought to cause breakdown of water molecules in the reactor coolant by ionization of the water to yield H_2O^+, radical-cations, fast electrons, and electronically excited water molecules. The fast electrons rapidly thermalize and are solvated by interaction with neighboring water molecules to form what is chemically an anion of the hydrogen radical. This anion is the strongest known reducing species with a reduction potential of –2.9V at a pH of 7. As a result, the anion rapidly grabs oxygen (from the water or from the aluminum hydroxide surface) to form O_2^- that is a strong oxidizing agent and the precursor for formation of H_2O_2. The H_2O^+ ions also decompose rapidly to form the OH^- radical that may recombine as H_2O, H_2O_2, or HO_2.   Radiolysis reactions are typically at a maximum near the surface of active fuel plates. The first few atom layers of water molecules next to the surface are affected both because of their proximity to the fission reaction and because of the nearly nonexistent flow rate of the water at the surface of the fuel. Radiolysis reactions cannot be avoided on nuclear fuel cladding surfaces. The radiolysis reaction, however, may either accelerate corrosion by facilitating the cathodic process or reduce the corrosion by anodic passivation[iii].

3.2   Localized Corrosion

Localized corrosion may occur in locations where water stagnates or is allowed to concentrate through evaporation such that its oxygen potential decreases and its ionic activity and acidity can increase beyond the hydroxide passivation range allowing the aluminum and/or its hydroxides to be attacked or dissolved. Localized corrosion includes pitting, galvanic, filiform, and crevice corrosive attack and often more than one specific mechanism is involved with corrosion issues. Although bulk reactor core water is normally quite clean, water that stagnates in corners, crevices, connector boxes, (or water that pools in such locations when the core is drained) may tend to increase in conductivity to the point that it becomes an effective electrolyte, allowing the corrosion mechanism to kick in.

Localized corrosion is always exacerbated by galvanic interaction where dissimilar metals are in electrical contact and the electrical potential difference between the materials helps strip the positive charge from the anode and drive the corrosion reaction. Probably the most common situation with aluminum-clad fuels is contact with stainless steel components or reactor hardware. The difference in electro-negativity between the two metals promotes current flow leading to Al corrosion. The galvanic coupling of aluminum and stainless steel has been an especially difficult issue for spent fuel in water basins.

3.3   Protective Oxides and Reformation

Most fuel cladding materials are active metals (Al, Zr, Mg, Cr, or Ni) where the cladding metal is protected from water corrosion by a stable passive surface compound containing oxygen. Radiolytic decomposition of surface oxides or hydroxides tend to be countered by reformation reactions that rebuild the surface protective layer. Therefore, the measurable effects of radiolysis may be very small if the cladding material rebuilds a structurally equivalent passive surface layer in rapid response to the radiolytic reactions taking place. This happens with Zr alloy commercial nuclear fuel cladding where core conditions are quite similar to the autoclave pre-filming conditions initially used to form the protective oxide. The Zr will continually re-form surface oxides damaged or lost during reactor operation.

Although similar in principle, the re-formation of Al hydroxides is subject to the thermal limitations involved with specific Al hydroxides as matched with the reactor operating parameters. For example, the ATR reactor uses Al fuel protected with an autoclaved crystalline boehmite surface. Although the core water average temperature is only about 68°C the surface temperature of the fuel is considerably higher and is sufficient to form at least a pseudoboehmite structure when/if the hydroxide is damaged by radiolysis.

For research reactor operations, where the average core water outlet temperature is around 38°C, the hydroxide resulting from reformation reactions would be difficult to predict without detailed data on the surface temperature and heat flux history for the fuel involved[iv].

3.4   Case Histories of Interest

3.4.1   ETR Cycles 108 – 109 B/C

3.4.1.1   Incident. An incident occurred with the Engineering Test Reactor at Idaho with operating cycle 108. Maintenance work had been performed prior to startup and on startup the water was turbid. Some ion exchange resin had gotten into the primary water boosting the Cl content. The pH of the primary water was reduced using CO_2 with the intent of obtaining a pH of 5.0 but extra CO_2 was added as the initial additions did not appear to have the desired effect on the bulk water pH. After beginning operations in this mode, a fuel failure indication resulted in reactor shutdown. Investigation showed that a fuel plate had buckled from overheating resulting in cladding failure.

3.4.1.2   Analysis. Significant effort was expended trying to determine the exact cause of this incident[v]. Unfortunately, the incident occurred before the chemistry of aluminum hydroxide was thoroughly understood. Although the details cannot be stated at this point with certainty, the following summary technical sequence is thought to be a good explanation of what happened:

1. Turbidity in the water was aluminum hydroxide particulate and colloids mixed up from the maintenance activities.

2. Attempts to reduce the pH using CO_2 did not work as expected because the carbonate ion was attaching itself to the aluminum hydroxides in the water and on the surfaces of the fuel.

3. As the pH at the aluminum surfaces went lower, large quantities of the hydroxide went into solution.

4. When reactor operation started, the coolant began heating and the Al in solution began the deprotonization/condensation sequence to re-precipitate as the ionic compound $[Al(H_2O)_6]^{3+}$ at the hottest location in the core: the fuel surface. The carbonate present, however, prevented normal aging of the hydroxide.

5. The formation of polynuclear rings/gel chain molecules and gelatinous boehmite at the fuel surface caused a rapid increase in "hydroxide" thickness that blocked water flow and prevented heat transfer.

6. The fuel overheated and buckled causing cladding failure.

During the next cycle at ETR, (109 A) the pH was tightly controlled at exactly 5.0 but carbonate ion was still present. The historical account of this cycle states:

> *Beginning with cycle 109, the corrosion product film was a "soft", "tacky", "spongy", material in varying degrees and appeared to be soluble, with some position dependence.*

This historical account is a very good description of gelatinous boehmite that was not able to age to its crystalline form as a result of the carbonate present in the system.

For the next cycle at ETR, (109 B/C) the pH was increased back to ~5.5 and the filterable solids containing much of the carbonate had been effectively removed from the water by filtration. As a result, the fuel surface hydroxides aged back to their original condition and the entire system returned to normal. **Iowa State UTR – 10 Fuel Plate Corrosion**

Figure 2: Three Dummy fuel plates after exposure

3.4.2.1 Incident. A relevant and more recent event of unexpected fuel plate corrosion occurred with UTR – 10 fuel plates at the Iowa State University reactor in the early 1990's. These fuel plates were low enriched uranium fuels designed to replace highly enriched plates used previously. Because of the low enrichment, additional fuel plates were required in each element which resulted in a reduction of the water annulus between fuel plates. The fuel plate surfaces were not pre-treated before being placed into service. The fuel plates were made using 6061aluminum in an "O" temper condition. Shortly after initial loading in August 1991, unexpected "staining" and corrosion was noted on the fuel plates. The corrosion was more severe and dissimilar to that noted on the fuels used previously. In an attempt to correct the issue, the core water was changed out in November 1991.

In an attempt to determine the cause of the corrosion, dummy plates of exactly the same material and fabrication history were placed in the core in March 1992. The plates were removed and inspected after each 20 hours in reactor core water. For inspection, the plates were removed from their holder, cleaned

with ALCONOX, rinsed, dried, and photographed. Corrosion was noted almost immediately and the corrosion continued to develop with time. Corrosion was found to be most severe around the stainless steel pins used to hold the samples in the core (See Figure 2). However, other spotty corroded areas were noted and locations were found where the corroded material [analyzed as α-Al(OH)$_3$] had apparently separated from the base metal. In all, the dummy samples were in the core for about 6.5 years, exposed to reactor water for 234 hours, and experienced 318 wet – dry cycles.

An initial analysis of the dummy fuel plate corrosion was performed by Hofman in 1993[vi] that indicated that nothing was in the water that would account for the corrosion. It concluded that:

- That the overall corrosion was bayerite formation from prolonged exposure of wet fuel plates in ambient air.

- That pitting corrosion was taking place underneath the bayerite crust, likely due to pollutants entering the core from the air when the core water was drained. (Ca and Cl were suspected, and precipitates of a calcium compound (possibly CaCO$_3$) were found on the pitted surface.) (The authors guessed that the source of the calcium was concrete sawing dust from building construction in progress adjacent to the reactor building.)

Additional analysis of the Iowa State dummy test coupons was performed by Shaber in 1999 to determine the usability/disposition of the fuels from the reactor[vii]. This analysis concluded that the fuel was usable and that the pitting reached a maximum depth of only 18 μm (0.0007 in) which was less cladding loss than would result from acid or caustic cleaning and re-treatment of the fuel surfaces.

3.4.2.2 Analysis. *A*lthough insufficient information is available on this corrosion situation to fully define exactly why the fuel staining corrosion occurred, a lot is known about the incident and the dummy test materials. The analysis [Hofman 1993] stated that the water chemical analysis found no obvious impurities or deviation from acceptable values for pH and electrical conductivity, but this was not the core water involved when the fuel corrosion occurred initially. A tangible hypothesis is that the original staining corrosion was a direct result of poor core water quality during the first few days in operation when the fuel bayerite layer was actively growing in thickness from a few nanometers to approximately 0.5 μm. Without detailed information on the water quality of the core water in use at the time, detailed understanding of the corrosion product will not occur short of performing post irradiation examination of the fuel plates.

The dummy fuel corrosion test had design problems. The corrosion around the pins holding the dummy plates in place was obviously accelerated by galvanic interaction. It is postulated that normal cracks and fissures in the surface hydroxide, with assistance from the galvanic couple and chloride ion allowed localized crevice corrosion to occur resulting in the dark blisters noted in Figure 2. Crevice corrosive attack would promote the localized spalling of the hydroxide noted by Hofman. The cleaning of the samples every 20 hours used ALCONOX cleaner with a pH of 9.5 that contained 7 – 13% sodium carbonate. The cleaning solution would have been effective in removing part of the hydroxide each time it was used and would have left residual
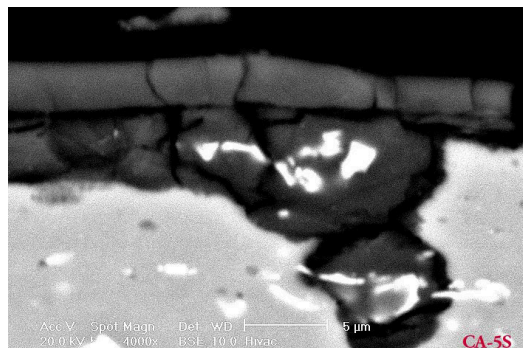

Figure 3: Hydroxide pit surrounding Mg-Si-Fe particles

carbonate that would prevent full aging and passivation of the surface; therefore, the corrosion would continue with a new dose of carbonate every 20 hours.

The presence of $CaCO_3$ was suspected on the dummy fuel. If it was not present in the core water, it could have come from pre-existing water spots on the dummy samples, from sample cleaning solutions, or external sources as presumed by Hofman. Only carbonate from the core water, however, would have actually affected the fuel and not just the dummy plates.

The pitting noted in the Hofman analysis is not expected to be from external contaminants, but alloying elements in the dummy fuel cladding. This type of micropitting is normal in 6061-O Al that has been treated to form a surface hydroxide[viii]. The pitting occurs at every location where the hydroxide surrounds a second phase particle in the aluminum that was in contact with the surface during hydroxide formation. These second phase particles (typically Mg – Si – Fe) are large particles because of the fully annealed condition of the 6061 Al involved. Because the hydroxide grows and surrounds the surface connected particles, they would tend to be removed with the hydroxide when it spalls leaving the pitted surface noted in Hofman's analysis. In the second analysis [Shaber 1999] the pitting was confirmed to be due to hydroxide surrounding surface-connected second phase particles (see Figure 3).

3.4.3   RERTR Program Cladding Corrosion by Coolant

As described in detail in the preceding sections, a general feature in water-cooled reactors is the formation of corrosion products on the fuel cladding surface. The primary detrimental property of aluminum hydroxide is its low thermal conductivity, approximately one tenth that of the A1 cladding. It is a thermal barrier to the heat flow from the cladding to the water and causes the cladding and fuel meat temperature to increase. Corrosion does not present operational problems for typical low and medium power research reactors using fuels without pretreatment. As shown in Fig. 4 for fuel plates irradiated in the 30-MW Oak Ridge Research Reactor, the corrosion layers are uniform, adherent, and about 20 μm thick, for two Al-Mg cladding alloys used by European manufactures and the standard Al6061 alloy used in the US.

Table 1 shows a collection of corrosion layer thickness data obtained during the RERTR fuel test programs carried out in various research reactors. The appearance of the corrosion layers is very similar to those shown in Figure 4. No evidence of pitting has been observed, and where x-ray diffraction was performed the corrosion was found to consist of a mixture of Bayerite and Boehmite. There appears to be no discernable difference in the corrosion behavior of the solution hardening Al-Mg alloys (AlMg2, Ag2Ne, etc. which are comparable to the 5000 type alloys) and the dispersion hardening alloys (SAV 1 and 6061).   All cladding alloys were, because of the hot

AG5NE
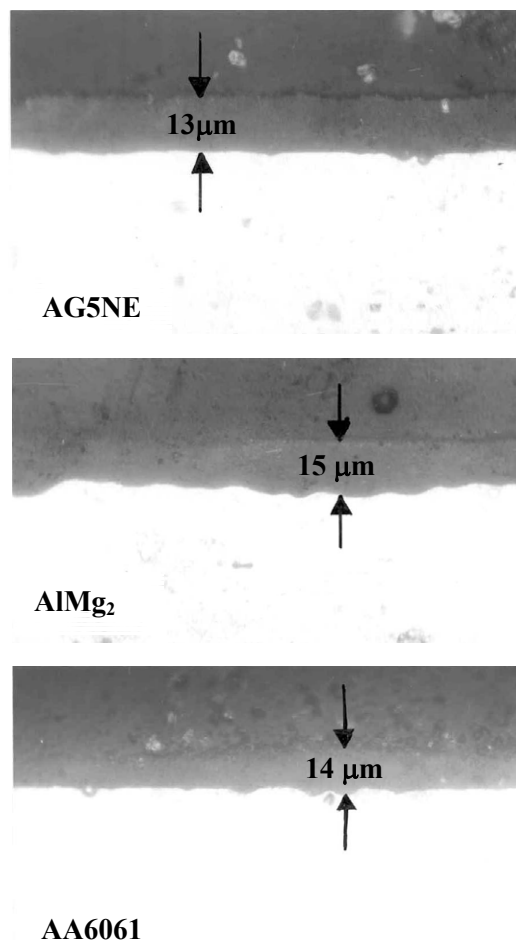
AlMg$_2$

AA6061

Figure 4: Boehmite layers on various Al cladding alloys irradiated in ORR for ~300d, pH 5.5 - 6.5

rolling and blister anneal procedures, in a fully annealed condition with, depending on the finishing fabrication step, a small (~10%) amount of cold work. None of the reactors employ pH reduction by coolant acidification, nor do they pre-film the cladding.

We may conclude from this experience that in reactor corrosion is not a fuel performance issue in any of these varied reactors if, as is the case for all listed in Table 1, coolant water purity is maintained by de-ionization, within a narrow pH range and at low conductivity values.

At heat fluxes typical of the reactors in Table 1, the cladding temperature is only modestly increased by the presence of the corrosion product. However, for higher power density reactors such as the ATR, corrosion was recognized early as a potential performance issue. The ATR (and SRS production reactors) have been operated quite successfully by pre-treating the fuel cladding with a very thin, highly crystalline layer of boehmite. This layer minimizes the temperature differential across the hydroxide layer, eliminates spalling, and helps preclude significant additional hydroxide growth during irradiation.

Table 1: Corrosion layer thicknesses on irradiated Al-Clad dispersion fuels used without pre-filming with aluminum hydroxide

Reactor	Alloy	Thickness (μm)	Water pH	Coolant outlet Temp. (ºC)	Surface Heat flux (W cm^{-2})
ORR	AlMg2	24	5-6.3	53	120
	AG3NE	20			
	6061	24			
HFR	AG5NE	45	6.70	55	120
RGAS	AlMg2	40	6.5-7.0	54	60
NRU	6102	35	5.5-6.5	70	250
JMTR	AlMg2	20	5.5-6.0	45	100
IVV-2M	AlMg2	25	6	40	70
	SAV-1				
RA3	6061	12	5.0-6.2	35	40
OSIRIS	AG2NE	35	6	47	130

An example of the efficacy of pre-filming is shown in Figure 5 for the RERTR tests performed in ATR. Test plates in RERTR-1 and 2 were not pre-filmed and experienced severe corrosion-erosion and occasional pitting whereas the pre-filmed RERTR-3, 4 and 5 test plates[a] showed uniform adherent and thin boehmite layers over the clearly visible fuel regions.
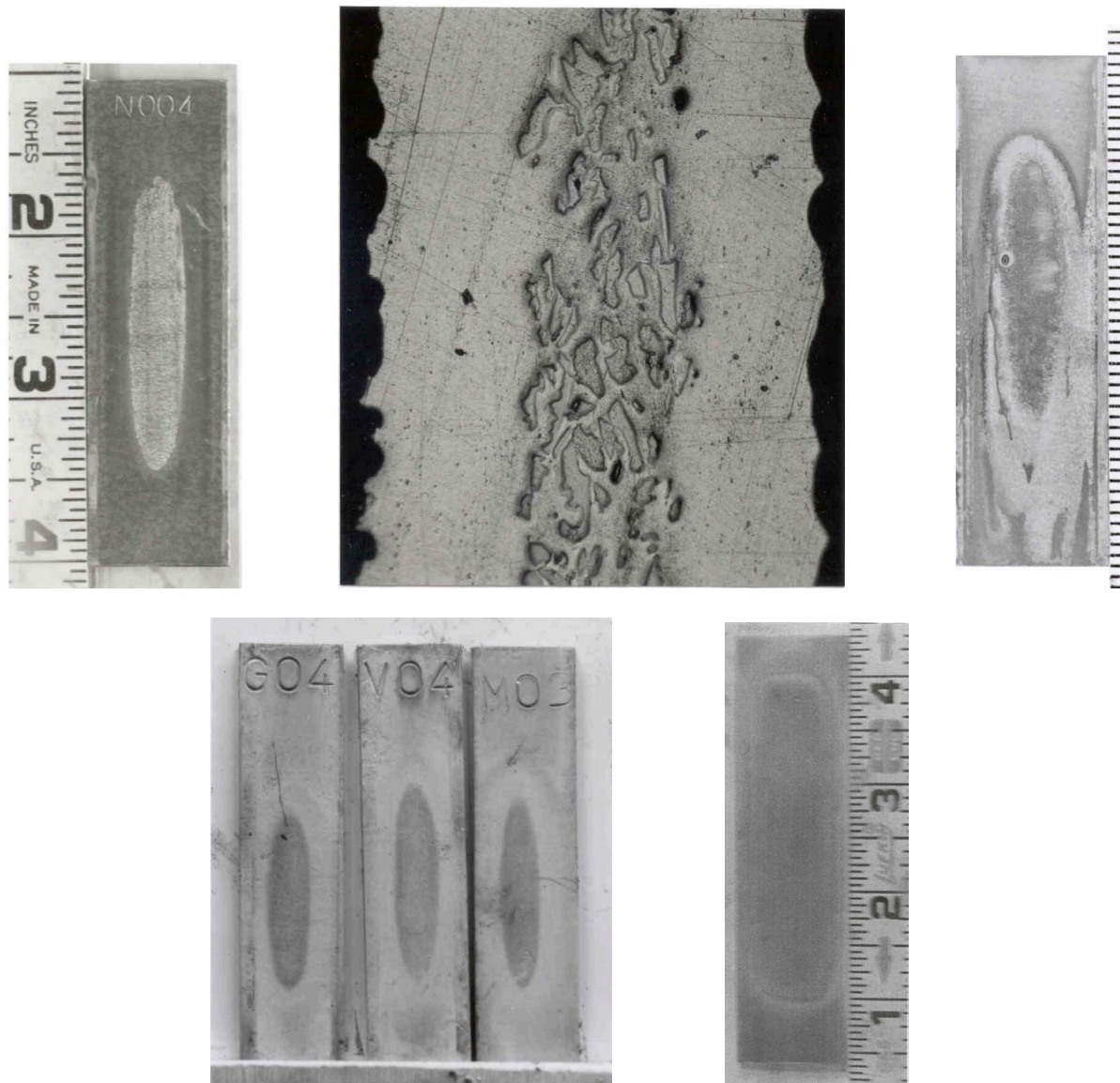

Figure 5: Aluminum cladding corrosion, upper: untreated RERTR-2; lower: Prefilmed RERTR-3 and 4.

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[a] Prefilming performed at 180°C for 48 hours at pH of 5.0.

4. Fuel Design Considerations

4.1 Cladding Alloy

Aluminum is the cladding material of choice for research reactor plate fuels because of its neutron transparency, high thermal conductivity, oxide/hydroxide stability in water, availability, and cost. Although there is no doubt that aluminum should be the cladding material, the specific alloy and the finished condition should be considered carefully. Early fuel development efforts utilized the 1100 alloy (99% pure aluminum) with great success. This evolved to use of "AlCLAD" in which the 1100 alloy was roll-bonded to 6061 alloy to improve strength and welding compatibility with end boxes/hardware and match thermal expansion coefficients, and then to exclusive use of 6061 alloy in the fuel cladding. These two alloys became the standards in the nuclear industry for fuel cladding as their operating database grew.

Other than historical precedent, however, the use of 6061 for fuel cladding may not be the best choice. In practice it is impractical to take the 6061fuel cladding back to its T6 (heat treated and precipitation aged) condition as part of the fuel fabrication process. The annealed alloying compounds provide no beneficial effect in the alloy and those in contact with the cladding surface cause the micro-pitting [Shaber 1998] discussed previously.

If historical precedent were ignored, the optimum technical solution to prevent micro-pitting would be to change alloys. If cladding mechanical strength is not a significant issue and welding is not required, pure aluminum (AA1070 alloy[b]) should be considered for fuel cladding. If additional strength is required without weldability, 5000 series alloys should be considered to match or increase the strength of the AA6061 in the "O" temper, eliminate the undesirable addition of Cu, and remove the Si that is not serving its intended purpose.

However, it must be emphasized that AA6061 has been used quite successfully as a fuel cladding material for many years reactor service, even in the most demanding of reactor conditions. Although micropitting is undesirable, it has not been a fuel performance issue. Therefore, AA6061 must be considered a fully acceptable cladding material.

4.2 Hydroxide Pre-Treatment

As a design consideration, the hydroxides of aluminum have a much lower thermal conductivity than the base metal. Therefore, the hydroxide surface layer on aluminum fuel plates must be limited in thickness to prevent fuel overheating. It is also essential that the hydroxide thickness be relatively consistent to prevent the formation of localized hot spots or areas that abnormally stress the fuel plate and can warp a fuel element to the extent that the water annulus is reduced or eliminated.

Historical practice with Advanced Test Reactor fuel that is supported by thermal modeling data and many years of successful operating history places the maximum allowable hydroxide thickness on the surface of fuel cladding at 0.00135" or 34 μm for ATR reactor conditions[ix]. The ATR fuel hydroxide application process, is specified[x] to require application of hydroxide within the thickness range of 1.5 – 7.6 μm (0.00006 – 0.0003 in), and the actual average thickness resulting from the current process is 1.92 μm

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[b] Alloy 1070 is designated rather than 1100 because the 1100 alloy has evolved over the last 40 years to become more of a general purpose "trash" alloy. Alloy 1070 is 99.7% pure aluminum and will provide better, more consistent performance than 1100.

(0.000076") [Shaber 1998]. This layer thickness is still much more than is actually needed to protect the aluminum surface from water corrosion[xi,c].

Research reactor fuels have historically not been treated or coated prior to usage. Normal air exposure of the fuel prior to usage, starting from a chemically cleaned surface would be expected to result in a tri-hydroxide of only 2 – 10 nm in thickness. When inserted in the reactor core water and heated, the hydroxide will grow. In pure water, the hydroxide growth should reach a limiting thickness (typically < 0.5 μm) within a few days. At the limiting thickness, the hydroxide should remain stable. Neutron radiation will adversely affect the growth of the hydroxide layer. Tests have shown that hydroxides grown under irradiation grow much thicker and are less resistant to chemical attack than hydroxides grown outside the radiation field[xii]. Abnormal water pH, high conductivity, or retarding anions may also radically change the limiting thickness or prevent the hydroxide from ever reaching a limiting thickness. Historical situations like the Iowa State fuel corrosion incident show that normal development of the surface layer does not always occur as expected. The surface hydroxide may vary widely in thickness and stability if it was formed while the reactor was in operation or at locations where the surface came into contact with unwanted chemical species (packaging materials, fingerprints, oils, sulfur rich exhaust fumes, high levels of CO_2, or other anion sources) that adversely affect the normal aging and passivation of the hydroxide.

A process for application of an effective hydroxide pretreatment (0.2 – 0.5 μm thick boehmite) for research reactor fuel would have the following parameters:

- Temperature – 185 ± 8°C

- pH – 5.6 – 6.0

- Time – 8.0 hours

- Pressure – 130 ± 30 psig

- Preheat time - ~ 4 hours

5.   Fuel & Reactor Operation "Best Practices"

5.1   Reactor Core Water

5.1.1   Purity

The ASTM provides a standard specification for reagent waters (ASTM D 1193 – 99) that provide a reasonable yardstick for evaluating water quality. The specification defines four types of waters as shown in Figure 6. Maintaining type 1 water quality in a reactor core would be highly desirable but is probably not feasible. Type IV water is not acceptable because of the potential dirt (Si and organic carbon) and the wide band of possible pH. Type II and Type III water should be acceptable although tighter control over organic carbon than allowed in Type III water is preferred when aluminum fuel is involved. These water

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[c] Development testing to finalize the ATR boehmite application process showed that within the normal passivation band for boehmite (pH ~ 4.7 –6.2), the maximum hydroxide thickness that could be achieved was ~ 0.6 μm in deionized water at 185°C at 0.9 MPa for 18 hours. To achieve the specified hydroxide thickness the treatment water pH was raised above the normal passivation range to increase the hydroxide thickness.

purity considerations are also consistent with IAEA guidance for corrosion protection of aluminum-clad fuel in water[xiii].

5.1.2   Control of pH

Some confusing technical data is present in the literature on the best pH of primary water in contact with aluminum nuclear fuel. The majority of the data available indicates that the minimum corrosion rates will occur by being centered within the passivation region for the hydroxide fuel surfaces involved. Another set of data, however, effectively ignores passivation and sets the optimum pH at the equilibrium between the AlO_2^- ion and the Al^{3+} ion in solution that occurs at a pH of 5.07[d].   Other data indicates that this equilibrium pH tends to drop to below 5.0 with increases in temperature above 90°C[xiv].

	Type I	Type II	Type III	Type IV
Electrical conductivity, max, µS/cm at 298 K (25°C)	0.056	1.0	0.25	5.0
Electrical resistivity, min, MΩ·cm at 298 K (25°C)	18	1.0	4.0	0.2
pH at 298 K (25°C)	A	A	A	5.0 to 8.0
Total organic carbon (TOC), max, µg/L	50	50	200	no limit
Sodium, max, µg/L	1	5	10	50
Chlorides, max, µg/L	1	5	10	50
Total silica, max, µg/L	3	3	500	no limit

Microbiological contamination—When bacterial levels need to be controlled, reagent grade types should be further classified as follows:

	Type A	Type B	Type C
Maximum heterotrophic bacteria count	10/1000 mL	10/100 mL	100/10 mL
Endotoxin, EU/ml [B]		<0.03	0.25	not applicable

[A] The measurement of pH in Type I, II, and III reagent waters has been eliminated from this specification because these grades of water do not contain constituents in sufficient quantity to significantly alter the pH.
[B] EU = Endotoxin Units.

Figure 6: ASTM D 1193 - 99 Water Types

The ATR reactor core water specification was set at a nominal pH of 5.0 in the 1960's on the basis of rapid heating tests that effectively showed that the minimum fuel corrosion rates occurred at a pH of 5.07[xv]. However, the test data was obtained by using the aluminum sample as the heating element in the test with an applied current flow of up to 10,000 amps. The current flow effectively stripped away the positive charge on the surface hydroxide, thus eliminating the effect of passivation for the data set. That data set indicated that fuel corrosion continued indefinitely at a constant rate. In actual practice, however, the rate is about half of that predicted and then essentially stops because of passivation when the hydroxide layer reaches a limiting thickness.

As a best practice for research reactor fuel, maintenance of core water at the center of the passivation region (a pH of 5.4 – 6.0) is recommended as it provides the most margin for abnormal water conditions without any significant effect on the fuel. Although this is higher than the tightly controlled ATR water system operating at 5.0, it is considered appropriate for the lower temperature and flux levels for research reactor fuel.

5.2   Fuel Treatment

New research reactor fuel elements of current designs with no pre-treatment, will grow a hydroxide surface layer during the first few days in reactor service. Depending on radiation levels, water quality, and fuel surface cleanliness at the time, this hydroxide formation may be entirely normal and acceptable or result in significant corrosion issues.

To obtain the thinnest, most conductive, most protective surface on the fuel and eliminate any potential for startup incidents, fuel surfaces should be pre-treated to achieve a consistent, fully-aged fuel hydroxide surface while the fuel is being manufactured and potential water quality and surface contamination issues

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[d] This equilibrium pH was originally defined in the Pourbaix diagram for the aluminum – water system.

can be tightly controlled. Treatment to achieve a minimum hydroxide layer thickness of 0.3 - 0.5 μm should be entirely sufficient.

If reactor water pH can be adequately controlled within a range of ~5.4 – 6.0, the pre-treatment process should be designed to provide fully aged, crystalline boehmite.

5.3   Reactor Operation

5.3.1   Impacts of Reactor Operating Temperature

Research reactors operating at temperatures from 30 - 40°C are not a threat to the thermal stability of the aluminum cladding or the hydroxide surfaces. Although formation of the tri-hydroxide forms are thermodynamically favored at the lower temperatures, history has shown that further hydration of the crystalline boehmite has not occurred in spent fuel that has been stored at low temperatures for many years[xvi,e].

During reactor operation radiolysis reactions may tend to interact with the surface hydroxide causing a reduction or increases in layer thickness. Any increase will most probably be a deposition of bayerite over the boehmite. This is not problematic at the thicknesses involved (<0.5 μm) as boehmite has the higher density and better bond strength with the base metal. Bi-layered hydroxides are common in aluminum reactor fuel and are not known to cause any significant issues.

5.3.2   Reactor Shutdown Configuration

The issue of whether to drain the water from the reactor core on shutdown or leave the fuel covered is not easily answered from the technical viewpoint. The core is designed to operate with flowing water. If the water quality is very good, water removal may not make any significant difference to the fuel. Draining the core when the water quality is poor (especially high conductivity and low pH) nearly guarantees that contaminants in the water will be able to concentrate on hydroxide fuel surfaces as the water evaporates. These contaminants may allow the initiation of crevice corrosion cells bringing unwanted corrosion issues.   Leaving the water in the core but turning off the pumps is also unacceptable from the corrosion viewpoint as the stagnant water invites both crevice and galvanic corrosion to proceed in susceptible locations.

6.   Summary/Conclusions

Reduction of the thickness of the water annulus between fuel plates should not result in new or higher risks of fuel failure from aluminum corrosion if appropriate fuel plate fabrication and reactor operational practices are employed.

The best practices are summarized as follows:

6.1   Fuel

- Use a qualified, corrosion resistant aluminum or aluminum alloy for fuel cladding (AA6061, AA1070)

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[e] The relative stability of hydroxide forms is theoretically due to the hydrogen to oxygen bond length. This length is less for boehmite than for bayerite or gibbsite; therefore, once formed, the boehmite should be more stable, even at low temperatures.

- Pre-treat the fuel during manufacture to achieve a well-aged crystalline boehmite of about 0.5 μm thick.

6.2   Reactor

6.2.1   Water

- Maintain ASTM D 1193, Type II water quality if possible,

- Never put new fuel in poor quality core water (especially if it has not been pre-treated),

- Maintain the core water at a pH of 5.7 ± 0.3,

- Keep carbonates, sulfates, and chlorides out of the system if possible.

6.2.2   Reactor Shutdowns

- Do not let core water stagnate,

- Do not drain the core when water or air quality is poor.

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