WSRC-MS-96-0669

CONF-970332--11

Corrosion Surveillance in Spent Fuel Storage Pools (U)

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A document prepared for CORROSION NACEXPO/97 ANNUAL CONFERENCE & EXPOSITION at New Orleans, LA, USA from 3/9/97 - 3/14/97.

DOE Contract No. DE-AC09-89SR18035

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CORROSION SURVEILLANCE IN SPENT FUEL STORAGE POOLS

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ABSTRACT

In mid-1991, corrosion of aluminum-clad spent nuclear fuel was observed in the light-water filled basins at the Savannah River site. A corrosion surveillance program was initiated in the P, K, and L-Reactor basins and in the Receiving Basin for Offsite Fuels (RBOF). This program verified the aggressive nature of the pitting corrosion and provided recommendations for changes in basin operations to permit extended longer term interim storage.

The changes were implemented during 1994-1996 and have resulted in significantly improved basin water quality with conductivity in the 1-3 µS/cm range. Under these improved conditions, no new pitting has been observed over the last three years. This paper describes the corrosion surveillance program at SRS and what has been learned about the corrosion of aluminum-clad in spent fuel storage pools.

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

INTRODUCTION

Storage of aluminum-clad spent nuclear fuel at the Savannah River Site (SRS) has been very successful over the forty-three years of plant operations. Each of the operating reactors had a 3.5-4.0 million gallon, light water filled and concrete lined fuel storage basin for fuel to cool prior shipment to the Separations area for processing for the desired nuclear isotopes. Storage times for these fuels generally never exceeded 9-18 months and corrosion of the fuel was rarely an issue. In late 1989, processing was suspended at SRS and other Department of Energy sites by the U. S. non-proliferation policy and irradiated nuclear fuel and target materials were caught in the nuclear pipeline with no place to go. At SRS, reactor operations were suspended, and efforts concentrated on shutting down the reactors permanently, or placing them in some state of standby. During this time, conditions in the reactor basins began to deteriote slowly without notice as other higher priority work continued.

By 1990, the aggressive conditions were beginning to be recognized in the K-Reactor basin as aluminum components were removed from the reactor and stored in the basin for several months before shipment to the Savannah River Technology Center (SRTC) for examination and analysis. Pitting was observed through the 50-mil aluminum wall thickness of the components and the need for a corrosion surveillance program was immediately established. This paper describes the storage of spent nuclear fuel at the Savannah River Site, the corrosion surveillance program that has been put in place, and the improvements that have been made in equipment and basin operations since 1993 which have led to no new pitting corrosion on the aluminum clad materials.

SPENT FUEL STORAGE AT SRS

Reactor Basins.

The P, K, and L-reactor basins at SRS were originally designed for one-pass through water from the Savannah River to cool the fuel. In the 1960's these basins were modified and equipped with portable mixed-bed deionizers, primarily for control of radioactivity in the water. These deionizers were not used continuously, but their use had some beneficial control of the water chemistry and conductivity. During the 1970's and early 1980's, water conductivity was maintained routinely in the 60-70 μS/cm range. Corrosion was never really an issue because of the relatively good water quality and the short storage times. There was some evidence of pitting corrosion on tritium targets during the late 1970's, but this was attributed primarily to materials and fabrication concerns. Some steps were taken to lowering the chloride specifications from 25 ppm to 5 ppm. With initiation of corrective actions, there were no new corrosion problems reported in the during the 1980's.

Over 200 MTHM of aluminum-clad fuel and target materials are stored in the basins at SRS.[1] For the Savannah River production materials, the core materials are primarily depleted uranium metal or uranium-aluminum alloys. These materials are generally protected by a 30-mil aluminum alloy cladding. The target material is usually 1100 aluminum clad and the fuel is a high temperature 8001 aluminum clad alloy, containing nickel and iron in small quantities. Some components, and much of the research reactor fuel which is also stored at SRS, is clad with 6061 or 6063 aluminum alloy. After irradiation in the reactor, the materials develop a high temperature protective Boehmite aluminum oxide coating on the clad. This coating, however, is usually scratched or damaged when removed from the ribbed housing tubes before going into basin storage. The aluminum fuel tubes are placed on stainless steel hangers in Vertical Tube Storage (VTS) and the target slugs are stored in 304L slug buckets.

When the aggressive conditions were first noticed in the K-Reactor basin, immediate attention was initiated to improve the storage environment. K-Reactor was in the process of being overhauled with the implementation of new safety and seismic modifications and this reactor was to be the one reactor to continue production operations at SRS. After re-start of this reactor, and a few months of low power irradiation, the fuel charge was to be removed and stored in the K-basin storage pool for several months while a new cooling water system was tied into the reactor. Plans were to re-start the reactor again using this fuel. The K-basin then became the priority for cleanup because the fuel could not be re-used if the cladding were to be breached by pitting corrosion.

The water chemistry of the K-basin during the 1992 time frame when corrosion was first notice had chlorides in the 6-9 ppm range and the water conductivity was about

180 µS/cm. Up to that point, deionizers were only used periodically. Once they were depleted, which was often within days, they had to be placed on a flat bed truck and transported to another location for regeneration. This process could often take weeks to complete, so continuous deionization was almost out of the question, especially with multiple basins to deionize. Nevertheless, a campaign of intense deionization was begun in the K-basin and the conductivity was lowered to about 102 µS/cm. However, with only limited deionizer operations over the next nine months the conductivity increased to 120-130 µS/cm.

The L-Reactor which was initially a part of the overhaul of the reactors onsite, was shut down permanently in 1992. The fuel storage basin was left open with a full inventory of fuel which had been caught in the pipeline and was waiting to be sent to Separations for processing. Most of the manpower which had been assigned to this reactor was moved to the K-Reactor re-start effort and the doors were essentially closed in both L and P-reactors. During fuel inspections in the L-basin, significant corrosion product was noted on the Mark 31A target slugs which were being stored in 304L stainless steel buckets on the floor of the basin. In addition, the floor of the basin was lined in this storage area with large stainless steel plates serving to enlarge the cathodic area and increase the strength of the galvanic couplingbetween the fuel and the storage system. The Cs-137 content of the basin water was monitored on a daily basin and in mid-1992, the cesium release began to trend upward indicating breach of cladding and radionuclide release to the basin water. Conductivity of L-basin ranged between 90-120 during 1987-1991, but increased rapidly during late 1991 to a peak of about of 160 µS/cm. With intense deionization, the conductivity of reached as low as 95µS/cm in early 1994, rising back to 110 µS/cm a few months later when deionization availability diminished.

The P-Reactor basin at SRS has spent fuel stored in it, but none of this aluminum clad fuel is stored on stainless steel hangers. The fuel is stored in Horizontal Tube Storage (HTS) in aluminum bundles and aluminum racks. Even though the conductivity of the water has been as high as 150 µS/cm, the basin appears not to have the significant corrosion problems of the other two reactor basins. Little deionization was carried out this basin until the conductivity increase to 165 µS/cm and some pitting was detected on corrosion coupons. Cesium 137 activity remained fairly constant in this basin at 150-200 dpm/ml. A strategic decision was made in 1994 to close P-basin and consolidate the spent nuclear fuel being stored there into the K-basin. This consolidation has been underway during 1996 and will be completed later in the year.

With three reactor basins full of aluminum-clad fuel and target materials and visible indications of corrosion product on the fuel, significant steps were taken to mitigate the corrosion problems and improve the storage environment for the spent nuclear fuel. In 1992-1993, the moratorium on processing the inventory of fuel in the basin was in full effect and there was no indication of the fuel being removed in the near future. The objective of the basin cleanup activitieswas to slow the existing corrosion process on the fuel, if possible, and to minimize any new corrosion on the protective aluminum clad.

Receiving Basin for Offsite Fuels (RBOF)

The RBOF basin at SRS is a 450,000 gallon wet storage facility designed for and dedicated to the receipt, storage, and conditioning of spent nuclear fuel from offsite reactors.[2] This basin is located away from the reactor sites in the H-Area of the site near the chemical separations facilities. This arrangement was convenient when there was processing of materials underway at the Site with the close proximity of the H and F-Canyon facilities nearby.

The nuclear materials being stored in the RBOF facility are both domestic and foreign experimental research reactor fuels. Currently most of the materials are from domestic sources, but the Department of Energy (DOE) has made a commitment to bring back SNF from foreign research reactors in Europe, South America, and other locations around the world. This fuel was provided to these countries in the 1950's as part of an Atoms for Peace program. Foreign shipments to SRS have been initiated over the last two years. The RBOF basin is approaching about 90% capacity. More than 18,000 fuel assemblies are expected to be received from these sources over the next 10-15 years. Once RBOF reaches capacity, the fuel storage for these foreign research reactor fuels will be take place in the L-basin which has been renovated and equipped with new aluminum storage racks and a new permanent mixed-bed deionizer to meet this increased storage demand.

Corrosion on spent nuclear fuel in the RBOF basin has never been an issue over the 34 years of operation. The primary mode of operation over these year has been to run the mixed-bed deionizer continuously from 5-7 days per week maintaining the water chemistry to low parts-per-billion (ppb) range for impurities such as chloride. The conductivity of the water is maintained in the low range of from 1-3 μS/cm. In addition, much of the fuel is stored in aluminum cans on aluminum storage racks. There is cesium-137 activity in the basin coming from failed foreign fuel whose cladding was breached when shipped to SRS over the years. Most of this fuel was canned prior to what was expected to be short, interim storage in the basin before processing in the SRS Canyons. This longer storage has seen some leakage of the overpacked cans resulting in radionuclide release to the basin water. This radioactivity is removed and carefully controlled by the continuous deionization process and has negligible impact on safety anf health of operating personnel.

CORROSION SURVEILLANCE PROGRAMS

With visible corrosion on Mk-16, Mk-22, and Mk-31A fuel and target assemblies being stored in the L and K-basins at SRS and the known pitting on the USH components, the need to establish a corrosion surveillance program became paramount in mid-1991. The program was initiated with a few small coupons of 1100, 6063, and 8001 aluminum alloy immersed in L-basin. After exposure for 42 days, these coupons were removed and the 8001 aluminum was found to have 30-mil pits. Based on this finding a more extensive surveillance program was put in place in the K-basin initially and then expanded to include all the active storage basins on site.

Component Immersion Tests

In late-1991, corrosion testing switched to the K-Reactor basin to determine the aggressiveness of the basin water and its ability to store the K-Reactor fuel charge while completing tie in to the new cooling water tower. A surveillance program was designed to develop quantitative data on pitting from corrosion coupons manufactured from actual fuel components and to develop an understanding of the corrosion mechanisms at work in the basins. The ultimate objective was to be able to make recommendations to guide and direct the basin cleanup activities to mitigate the degradation of the fuel stored in the basins. The continuation of the surveillance program as the cleanup activities proceed serves as a measure of the success of the cleanup.

The corrosion surveillance coupons for this program were fabricated from actual nuclear components. Six-inch long cylindrical tubes were cut from unirradiated fuel and target tubes of the SRS Mark 22 fuel assembly.[3] The target material is irradiated to produce tritium for the Nations Defense system. The tube-ends contained no uranium. The tubes were pre-oxidized at temperatures about 95° C in deionized water to give a Boehmite phase of aluminum oxide of about 1 micron in thickness on the surface of the tubes. The 1100 outer tube and the 8001 aluminum alloy clad inner 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 as shown in Figure 1. 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 to pitting 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.

The Component Immersion Tests were started in the P and L-Disassembly basins in September 1993 and in RBOF in April 1994 and are continuing into 1997. 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 have been withdrawn at various time intervals during 1994-1996 and evaluated for pitting corrosion. The results of these analyses are also shown in Table 1. No pitting corrosion has been found on coupons withdrawn from K-Basin after 17.5 months of exposure through August 1995 as opposed to through-clad penetration in as little as 45 days in 1992. As seen in the table, no pitting of any kind has been seen on surveillance coupons removed from the RBOF basin up to 24 months exposure Specimens removed from L-basin in August 1995 after 23 months exposure showed no pitting. 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. Coupons withdrawn from P-basin after 23.5 months showed no pitting. These coupons had seen the same environment as the 11 months exposure coupons, but were free of pits. This might be explained by the lack of defects in the protective oxide coating of these two test coupons as compared to one of the two coupons in the previous withdrawal. This kind of pitting behavior is a demonstration of the random and unpredictable behavior of the pitting corrosion process.

The average water chemistry and conductivity of the basins during the Component Immersion surveillance tests are also shown in Table 1. These parameters varied during the exposure period because of deionization, or in some cases, lack of deionization. The conductivity was relatively high at immersion of the coupons in the 1992 tests in K-basin.. At 178 µS/cm, this conductivity level is significantly greater than the 1-3 µS/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 µS/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 µS/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 µS/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.

Disassembly Basin Corrosion Monitoring Program

In March 1993, a Plant surveillance program was initiated to monitor the corrosion of the fuel in the basins. The program consisted of a monthly walkdown of the three reactor fuel storage basins with visual observations on selected target slugs and fuel assemblies in (HTS), Vertical Tube Storage (VTS), and in the Machine Basin (MB). Still color photography recorded the appearance of each component selected for observation and a databook of baseline observations was established A detailed analysis and interpretation of the observations was done initially and the walkdown and photography was carried out on a monthly basis. As changes in the basin were occurring so slowly, the frequency was later changed to every 4 months. Figure 2 is a picture of a bucket of 18 Mark 31A uranium metal target slugs stored underwater for about 6 years in L-basin. The voluminous and extensive corrosion product was analyzed and found to consist of aluminum oxide, oxides of uranium and plutonium, cesium-137, and other fission products indicating that the cladding was breach and corrosion was proceeding slowly into the core region. Changes were difficult to detect on a monthly basis, but with comparisons of photographs taken a year apart, additional corrosion product was evident. Slow changes occurred as evidenced by color changes in the uranium oxides, but no dramatic and significant changes have occurred in the slugs since the time observations were initiated.

Aluminum-clad Mark 16 and Mark 22 fuel tubes are stored on stainless steel hangers in both K and L-basins. Figure 3 is an underwater surveillance photograph in K-basin showing the aluminum oxide corrosion nodules lined up in the scratches on the outer fuel tubes. These deep scratches were apparently deep enough to penetrate the protective oxide coating when the tubes were discharged from the Universal Sleeve Housings (USH). The corrosion product was analyzed on some tubes and found to contain Gibbsite and Bayerite, two aluminum oxides, and uranium-containing deposits, along with cesium-137. Evidence of these radionuclides indicates that pitting had penetrated the aluminum cladding. Corrosion of the UAl_4 core is slower than the uranium metal and similar to the rate of corrosion of aluminum. There was never any obvious or significant changes in the amount of oxide visible on these vertically hanging fuel tubes between inspections. Mark 22 fuel tubes were also stored horizontally in the HTS area of the basins in aluminum bundles. In this situation, unlike the fuel stored on stainless steel hangers, surveillance photos and underwater video revealed no pitting corrosion on the fuel tubes. The 6061 storage racks, however, which have been in the basin water for over 35 years were heavily corroded as seen in Figure 4. The racks may have been undergoing some sacrificial corrosion, offering protection to the fuel tubes.

The surveillance monitoring program is currently still active even though there is some movement of materials in the basins. All fuels are being moved from the P-basin to the K-basin. This consolidation will enable the P-basin to be shut down and the L and K-basins, along with RBOF, to be used for continued interim storage of fuel. In addition, the Mark 31A target slugs are scheduled for processing, along with the Mark 22's and Mark 16's, during 1996-1997.

Factors Affecting the Corrosion of Aluminum Clad Fuels

A detailed discussion of the environmental factors affecting aluminum corrosion was provided in reference 4. 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 which is the predominant mechanism in the SRS basins. This pitting corrosion 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.[5]

Based on the corrosion surveillance tests, the laboratory electrochemical corrosion tests, and a comprehensive review of the literature conducted between 1992-1996, a number of factors have been shown to promote corrosion of the aluminum clad in the wet storage pool. Among those factors which are thought to be the most important are:

- High basin water conductivity (180 μS/cm).
- Aggressive ions (20 ppm 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.

The galvanic couple between the stainless steel and the aluminum alloys appears to lower the pitting potential of the fuel and plays a bigger role than originally suspected. Almost all of the pitting originates at scratches and imperfections in the protective oxide coating. The relatively high water conductivity permits the flow of electrons from the metal enabling the electrochemical corrosion process to proceed. Extensive deionization of the water resulting in a lowering of the conductivity and aggressive impurity concentrations is believed to be primarily responsible for the improvement in fuel storage performance between 1994-1996. We have seen no pitting in these basins since the water conductivity as been below about 125 μS/cm. Figure 5 shows a relative comparison of the corrosion product on the surface of surveillance samples in 1992 versus lack of corrosion product on K-basin sample withdrawn in 1995.

CORROSION OF URANIUM METAL AND URANIUM-ALUMINUM ALLOY FUELS

Corrosion of Mark 31A Target Slugs

Most of the fuel and target materials stored in the SRS basins are clad with aluminum alloys, but the active core of the fuel is uranium metal or a uranium-aluminum alloy, UAl_4. Once the 30 mil-cladding (some foreign fuels have 15 mil clad) is breached, the active core material is exposed to water. The Mark 31A target slugs stored in the SRS basins have an 1100 aluminum alloy cladding and a uranium metal core. When the cladding was breached during the first two years of storage, the corrosion continued into the uranium metal core material producing voluminous uranium oxide corrosion product as seen in Figure 2.

Metallography was done on a corroded Mark 31A slug removed from the basin in 1995 and the results published in reference 6. An excellent description of classical corrosion of uranium clad is provided by the work done in the late 1950's and was reviewed in this report. In general, for aluminum clad fuel, once the clad has been penetrated by pitting corrosion, the compounds formed by the nickel bonding layer between the aluminum and the uranium may become slightly anodic to the aluminum and result in undercutting of the cladding by galvanic corrosion when exposed to the basin water. When uranium is metallurgically bonded to aluminum by 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:

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

The corrosion can be divided into two stages: an initiation stage, corresponding to the induction period observed in the corrosion of bare 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 microstructure of the corroded uranium metal Mk 31A fuel is shown in Figure 6. As can be seen, corrosion appears to be proceeding by intergrannular attack with whole grains apparently dropping out of the structure. The metallography confirmed that pitting depths into the aluminum core varied, with the deepest pit found to be only about 0.12 inches (3.05 mm) after about 5 years exposure. Less than 2% of the aluminum cladding was found to be breached resulting in less than 5% of the uranium surface area being affected by corrosion. The overall integrity of the slug remained intact.

Uranium Metal Corrosion Based on Cesium-137 Measurements

A novel approached was used to estimate the corrosion rate of the Mark 31A slugs in L-basin. Daily measurements of the cesium release to the basin water were made during regular intervals of 2-3 weeks when the mixed-bed deionizers were not operating. During this time, the rise in activity in the basin was found to be relatively constant over the last few years at about 2 dpm/ml/day. Knowing the amount of cesium produced per slug pair during the irradiation processes, the amount of cesium necessary to produce the 2 dpm/ml/day was calculated to be about 0.0001 grams/day coming from the total inventory of Mark 31A slugs or about 2×10^{-8} gms/day/slug pair.

Assuming that the cesium-137 goes into solution as the uranium metal corrodes one can then say that the ratios of corrosion rate of Cs-137/ corrosion rate of uranium equals the weight Cs-137/ weight of U per slug pair. Solving for the corrosion rate of uranium from all other parameters which are known, the rate was determined to be about 0.0027 grams/day /slug pair. Knowing the total weight of uranium in a slug pair, the time to dissolve was calculated to be greater than 10,000 years assuming the corrosion rate were to remain constant over that time period. This low corrosion rate exists because only about 2% of the aluminum clad was breached, the remaining core protected, and the pitting penetrated only a short depth into the core.

Corrosion of the Uranium-Aluminum Alloy Fuels

The Mark 22 fuels used in the SRS reactors contained two concentric aluminum-clad fuel tubes using an enriched uranium-alloy core This alloy core consisted primarily of particles of UAl_3 and UAl_4 embedded in an aluminum alloy matrix. The nominal distance between larger particles is generally in the range between 1.5 to 45μm (0.06-1.8 mil). Figure 7 is the microstructure of a typical extruded, 18% enrichment UAl_4 in an aluminum alloy matrix. Notice that the particles are broken up after the extrusion process. Corrosion of this alloy based on SRTC preliminary electrochemical laboratory tests was found to be similar to an aluminum alloy itself. The corrosion rate of 8001 aluminum was measured at about 0.175 mpy compared to 0.171 mpy for the UAl_4 alloy. It is expected that the release of cesium from this type fuel would be much slower than that from uranium metal.

In a recent visit to the Institute for Nuclear Energy Research in Sao Paulo, Brazil, a team of engineers from SRS inspected the spent nuclear fuel stored in the storage basin of the IEA-R1 research reactor. The purpose of this inspection was to characterize this enriched aluminum-clad U-Al fuel for suitability of shipment back to the United States for storage in the RBOF or L-basin fuel storage pools. Some of this MTR type fuel had visible nodular corrosion product on the fuel plates. Fuel cladding was a 15-mil, 6061 aluminum alloy. Using an underwater video probe/camcorder system, close-up inspection revealed that every nodule of corrosion product of any size had pits beneath it, most of which, were clearly judged to have breached the clad. In some cases when the nodules were removed, the hydrogen generated from the corrosion process of the uranium and aluminum bubbled from the pit for several minutes. In addition, there was some evidence of subsurface corrosion when the pit tunneled parallel to the surface of the plate and the hydrogen remained trapped in the tunnel, resulting in a raised, blister-like area on the outer surface of the fuel plate. Almost two thirds of the fuel assemblies had some penetrations of the cladding.

The unique aspect of the corrosion of this fuel was the extremely low level of radioactivity release, even when corrosion nodules were removed exposing the open pit to the water environment. Even on the most highly corroded U-Al fuel, the release of Cs-137 an other fission products was so low that it was extremely difficult to detect. Measurements of this activity were made using gamma ray spectroscopy and found to be about 0.32 pCi/ml/hr for a water volume to MTR assembly ratio of approximately 7.1 gal./assembly. This is well within the interim criteria for Cs release of 35.9 pCi/ml/hr established for the SRS basin. This low level of activity could effectively be managed by the water deionization systems with minimum concerns to the safety and health of the operating personnel. Some of this breached fuel may still have to be canned in order to be shipped back to the United States.

IMPROVEMENTS TO SPENT FUEL STORAGE AT SRS

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.[7] 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. The results of deionization are seen in Table 1 where K-basin conductivity reached as low as about 125 µS/cm by early 1995.

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

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

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

As part of the cleanup activities in the reactor basins, a Disassembly Basin Upgrade (DBU) Project was initiated in 1994. This project initially was to include three new permanent deionizers for the P, K, and L-basins, sludge removal from the basins, and new aluminum storage racks for L and K-basins. During the design phase for the deionizers, a decision was made to close down the P-basin and move the fuel stored there into the other two basins. This resulted in a significant cost savings with the elimination of the new deionizer for P-basin.

The new DBU deionizer system began operating in both L and K-Areas on June 3, 1996. The new systems are designed to operate continuously at a flowrate of approximately 200 gpm through four vessels which are connected in series. The first two vessels contain 50 cubic feet of mix-bed resin, the third vessel holds 70 cubic feet of cation resin, and the final vessel contains 50 cubic feet of anion resin. With continuous deionization by the new DBU system, the conductivity and chemistry of the L and K-basins continues to improve as seen in Table 2. After two months of use, the conductivity of L-basin was lowered from 3.5 µS/cm to 1.5 µS/cm and in K-basin from 8.5 to 2.5 µS/cm. The anions and cations in the water were all lowered to less than the detection limit of 0.1 ppm (100 ppb). These levels are comparable to the RBOF basin which has been routinely been kept at a level of 1 µS/cm or lower since continuous seven day a week deionization program was put into place. At five day a week deionization, the level was maintained at 1-3 µS/cm.

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

New 6061 aluminum storage racks were installed in the L-basin in 1995-1996 as a part of the basin upgrades and to prepare this basin for the receipt of the Foreign Research Reactor fuel. This basin will store the fuel coming from off site. In addition, old storage racks in the Machine Basin of both L and K-basins were replaced after about 40 years of use during SRS production operations.

FOREIGN RESEARCH REACTOR CORROSION SURVEILLANCE PROGRAM

With the refurbishment of the L-Reactor basin to receive a large number of the 18,000 aluminum-clad research reactor assemblies from both domestic and foreign sources over the next 20 years, a more comprehensive corrosion surveillance program was designed to support this extended fuel storage activity. This program was intended initially for L-basin to demonstrate that it could provide a suitable environment for long term interim storage of aluminum alloys after the basin upgrades during 1994-1996. The RBOF basin with its superb water quality over the years of operations and extremely low conductivity has not experienced the pitting corrosion problem seen in the reactor basins in the 1992 -1993, but the new surveillance program was also added in this basin to provide additional data to supplement the existing Component Immersion Program underway in each basin.

The corrosion surveillance program designed to support the receipt of Foreign Research Reactor (FRR) fuels will concentrate on aluminum alloys which are typical of cladding materials of the majority of spent foreign reactor fuel stored in RBOF and expected to be received in the future. Zircaloy and stainless steel clad fuels are likely to go to another storage basin in Idaho. The program includes:

(1) exposure of ASTM type corrosion coupons to the L-Reactor and RBOF water storage environment,

(2) a standard program for monitoring, examination, and evaluation of the coupons,

(3) a monitoring program to assure a uniform assessment of water chemistry,

(4) documentation of the results of these tests.

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

Corrosion Racks and Test Coupons

The corrosion racks are manufactured from an 18 inch long, threaded 304-L stainless steel rod of 0.25 inch diameter. The rod has an eyebolt welded to the top for use in suspending the rack in the basin. The threaded stainless steel rod is covered by a Teflon rod to provide insulation of the corrosion samples from the stainless steel.

The corrosion samples will be 1 1/4 inch circular disks of 1/8 inch thickness with a hole in the center designed to fit over the Teflon rod. Individual samples, or sample pairs, will be separated by Teflon insulators. The coupons will not be pre-oxidized other than the normal air-formed 25 Angstroms thickness which should make them more sensitive to water chemistry changes. The three basic types of corrosion specimens to be tested in the L-basin water environment are:

- Standard alloy circular disk.
- Welded alloy circular disk.
- Galvanic couple alloy circular disk with a 4:1 Area ratio.
- Crevice alloy pairs.

Based on the current inventory in RBOF and the available information for incoming FRR fuel, 1100, 6061 and 5086 aluminum alloys are the primary cladding alloys expected to be stored in the basin. Welded and galvanic samples will concentrate on the 1100 and 6061 alloys. Some 304 stainless samples will be included in galvanic couple tests to represent potential interactions which have typically existed over the years at most storage basins around the world. Multiple samples of each type may be included in the makeup of each corrosion rack for a total of 60 samples per rack.

A total of 20 corrosion racks are available for the FRR surveillance program. A total of 12 racks will be exposed initially in two area of L-basin with 6 racks immersed in RBOF available to support the program currently scheduled to last for twenty years.

Sampling Frequency and Evaluation

The proposed corrosion monitoring program is designed to provide samples after six months, one year, two years, five years, ten years, and twenty years of exposure with duplicate racks will be examined at the end of each exposure period in L-basin. The first three withdrawals up through two years of exposure will provide an early indication of the aggressiveness of the storage environment on the aluminum coupons. These evaluations will help provide information on the effectiveness of basin operations and water quality and provide. directions for improved operations. The second three sampling periods (5,10, 20 years) will provide the continuing data necessary to predict the long term corrosion behavior of the stored fuel. The evaluation of pitting corrosion on the fuel will provide information on the effectiveness of the new deionizers and other basin upgrades which have been implemented in L-basin. After withdrawal from the basin at the specified intervals, the corrosion racks will be allowed to air dry and will be bagged and shipped on the sample truck to the SRTC for evaluation.

Along with metallurgical examination of the specimens, a detailed characterization of the basin water during the exposure period will be obtained from the existing water sampling program underway in the reactor basins. As a minimum, the following water qualities will be monitored:

(a) Conductivity
(b) pH
(c) Temperature
(d) Chloride content
(e) Nitrate content
(f) Nitrite content
(g) Sulfate content
(h) Basin radioactivity

Each of the items will be reported as at least a quarterly number obtained as a single measurement or an average of a number of measurements.

The three racks have been withdrawn from the basins after the initial six months exposure and individual evaluation of the coupon samples is currently underway. The second withdrawal is scheduled for early in 1997.

CONCLUSIONS

The corrosion surveillance program at the Savannah River Site, formally in place since late 1991, has provided a wealth of knowledge about the storage of aluminum-clad spent nuclear fuel. The Component Immersion Tests demonstrated the aggressive nature of the water environment in the very early stages of the program . It showed that pitting corrosion was the dominant mechanism involved and that the most important parameters affecting this corrosion were water conductivity, aggressive ion content, and galvanic coupling between stainless steel and the aluminum cladding. From the understanding developed in the corrosion testing, recommendations were made to clean up the basins, including sludge removal, and significantly improving the water quality. Testing in the RBOF basin demonstrated that when water quality was maintained between 1-3 μS/cm with chloride content in the low parts-per-billion, pitting corrosion was non-existent.

Early recommendations led to shock vendor deionization of the L and K-basins and a large capital project to provide upgrades to the deionization equipment in those basins. In addition, improvements in basin operations in RBOF and all the reactor basins have been implemented with the results being followed closely by the corrosion surveillance program. With these improvements to the L and K-basins no new pitting has observed over the past three years.

The basins at SRS will continue to serve as interim storage for research reactor aluminum-clad fuel from around the world. Some of.the existing fuels in the basins are being processed at this time. The 18,000 new fuel assemblies that are scheduled for storage in ROOF and the L-reactor basin will see a significantly improved water storage environment with the water conductivity of each basin ranging from 1-3 μS/cm and impurities like the chlorides in the low ppb range. These conditions rank among the best in the DOE Complex. With this quality of water in the basins, there should be adequate time to develop new dry storage techniques, or to process the material to a more stable form. Corrosion surveillance will continue to provide a check on the success on the storage of aluminum-clad spent fuel in the basins at SRS and will help to predict its long term response in this interim wet storage environment.

ACKNOWLEDGMENTS

The information contained in this paper was developed during the course of work under Contract No. DE-AC09-89SR19035 with the U. S. Department of Energy. The author would like to than D..Z. Nelson for his assistance in the metallography and photography in carrying out these tests.

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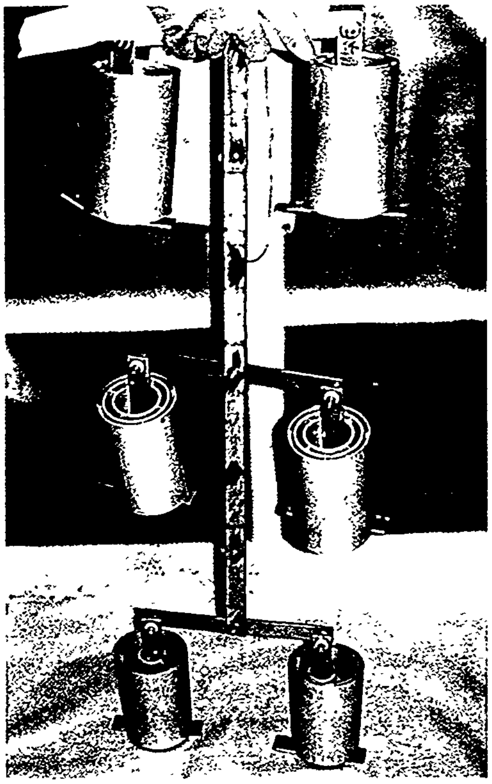
TABLE 1
COMPONENT IMMERSION TEST RESULTS
1992-1996

Basin	Date	Exposure (Days)	Maximum Pit Depth (Mils)		Pit Density (Pits/cm^2)		Avg. Cl ppm	NO_3	SO_4	pH	Avg. Conductivy (µS/cm)
1992											
			1100	8001	1100	8001					
K	7-92	45	2	53	0.125	.01	8	20	15	7.5	175
K	6-92	75	13	45	0.125	.01					
K	3-92	107	23	39	0.125	.01					
K	6-92	182	58	27	0.125	.01					
K	12-92	365	100	57	0.125	.05					
1993-1996											
K	3-94	65	No Pitting								
K	7-94	181									
K	2-95	403					6	18	9	7.3	125
K	8-95	590									
L	11-93	61	No Pitting								
L	3-94	127									
L	7-94	241									
L	2-95	336					14	20	2	6.6	102
L	8-95	340									
P	11-93	61	No Pitting								
P	3-94	127									
P	7-94	241									
P	2-95	336	35 mil Pits in 8001				10	9	18	7.5	160
P	9-95	715	No Pitting								
RBOF	4-94	480	No Pitting				0.2	1.5	0.5	7.4	1
RBOF	4-94	723	No Pitting								

TABLE 2
CHEMISTRY AFTER SHOCK DEIONIZATION AND NEW DEIONIZERS
SEPTEMBER 1996

Basin	Date	Avg. Cl (ppm)	NO_3	SO_4	pH	Avg. Conductivy (μS/cm)
K	9-96	<0.1	<0.1	<0.1	6.9	2.8
L	9-96	<0.1	<0.1	<0.1	6.2	1.2
P	9-96	9	8	4	7.7	85
RBOF	9-96	<0.1	<0.1	<0.1	5.8	0.90



96x03910.01//4"

FIGURE 1- Component Immersion Tests corrosion rack

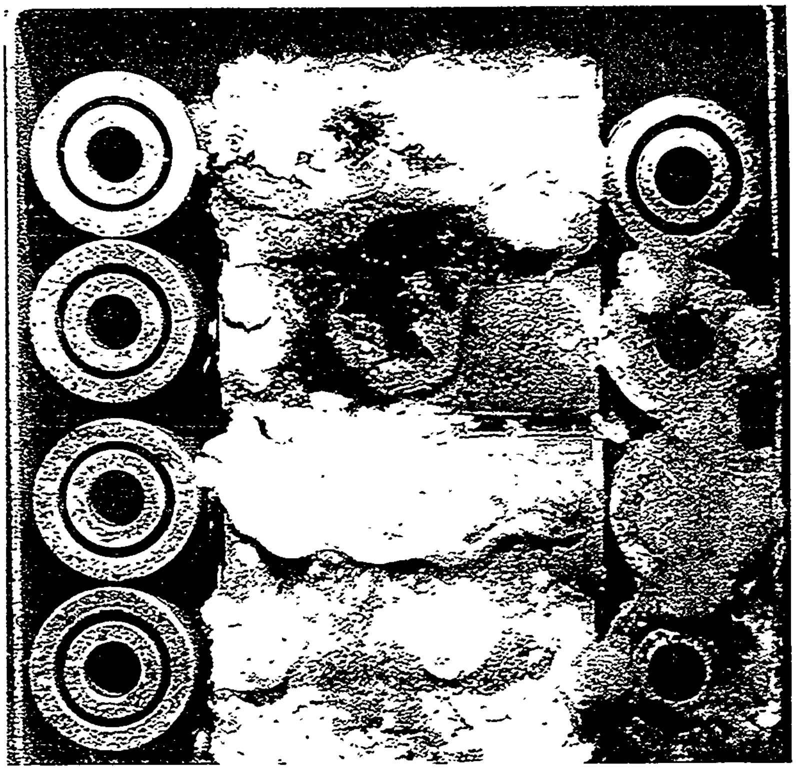


FIGURE 2- Corrosion of Mark 31A target slugs stored in L-basin

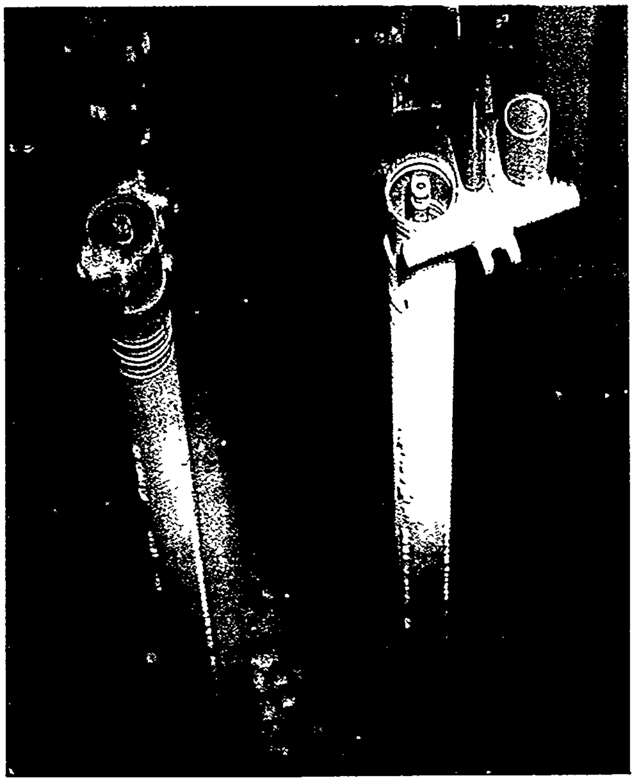
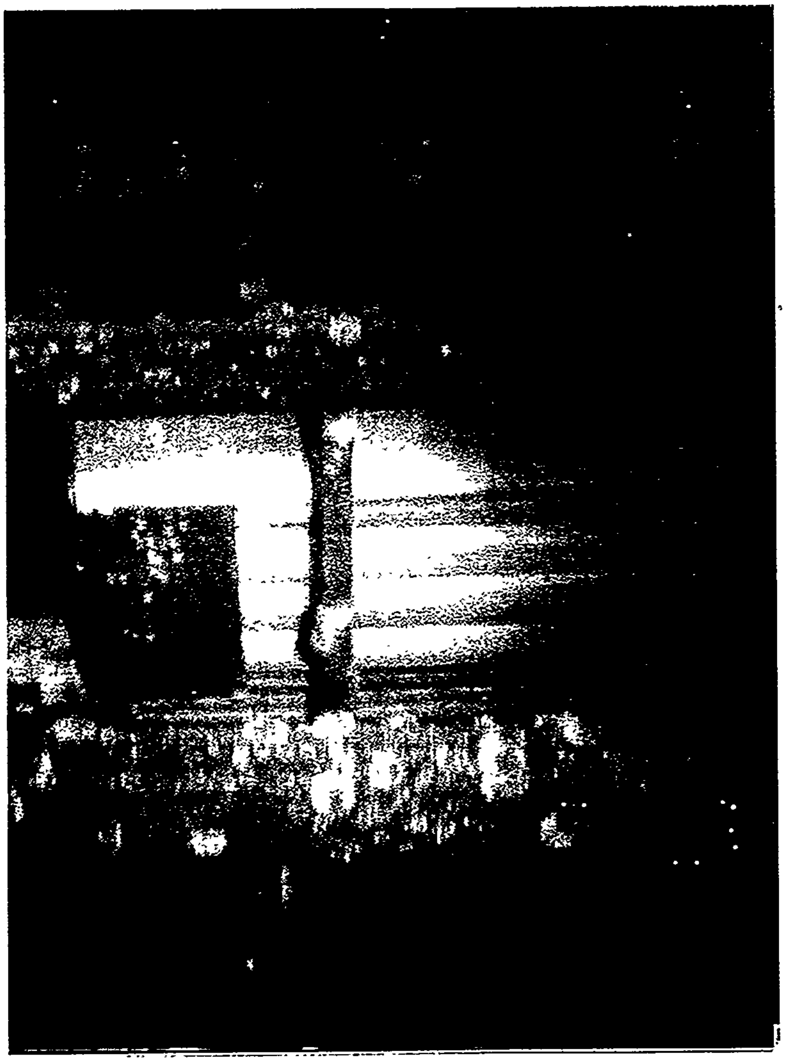
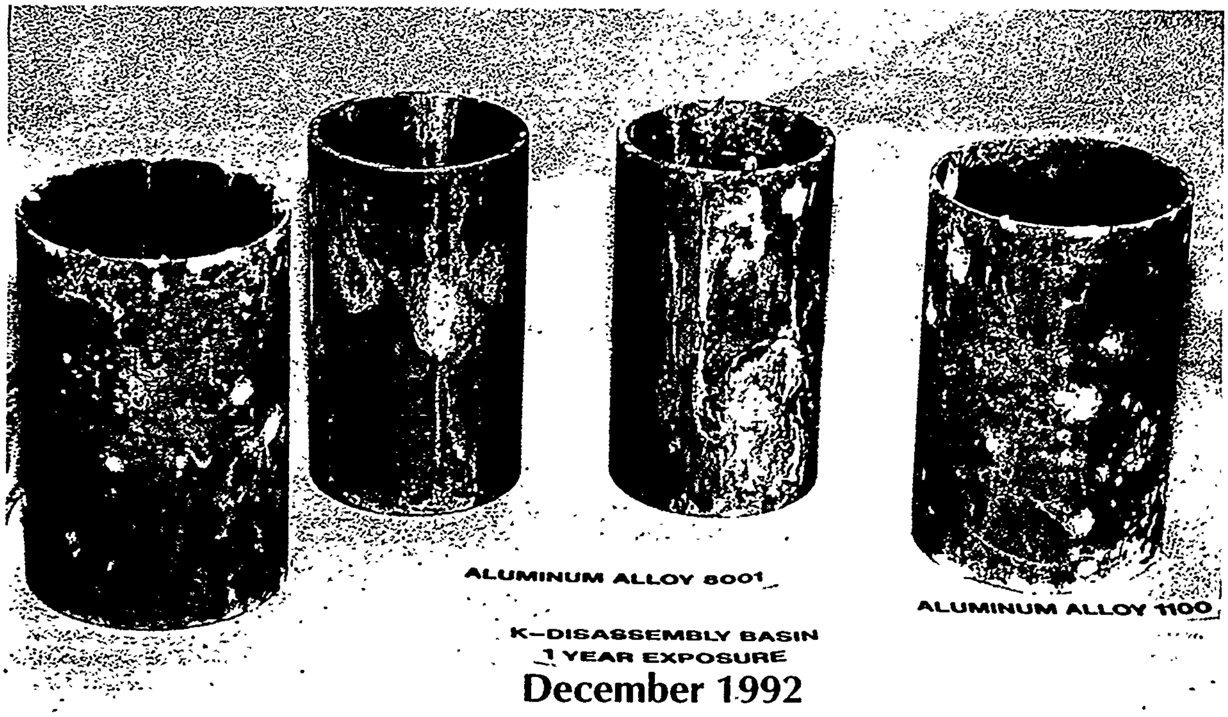


FIGURE 3- Oxide nodules on Mark 22 fuel tubes in K-basin

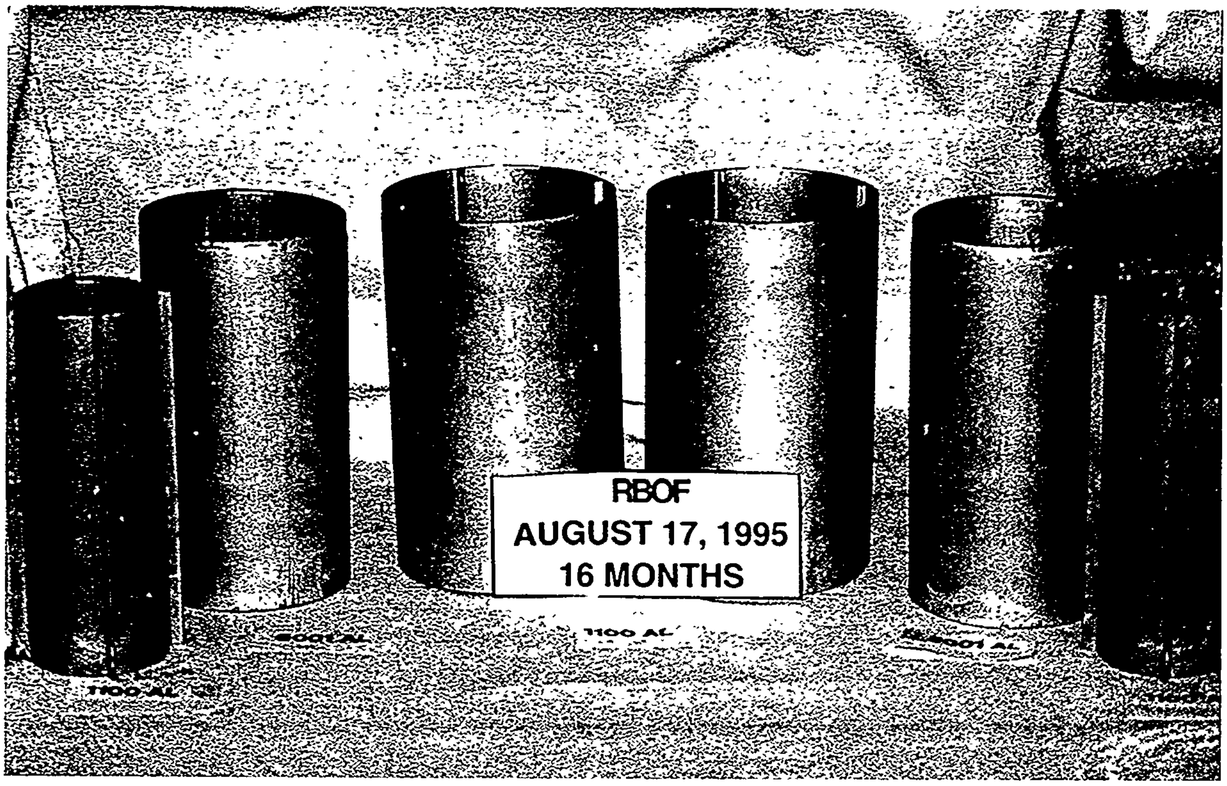


96x03910.04

FIGURE 4- Mark 22 fuel in Horizontal Tube Storage



96x03910.06

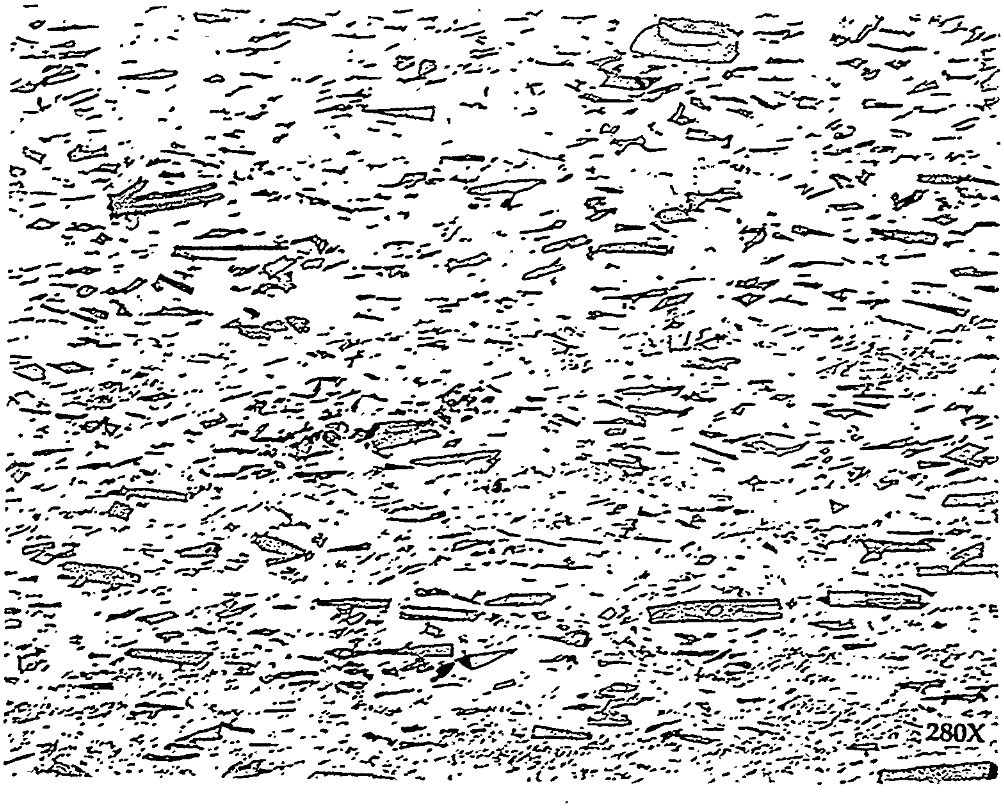


96x03910.05

FIGURE 5- Comparison of corrosion coupons in 1992 versus 1995

96x03910.07

FIGURE 6- Corrosion of uranium metal in deionized basin water



96x03910.08

FIGURE 7- Microstructure of an extrude, 18% enriched UAl_4 alloy

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