

Experiments for Evaluation of Corrosion to Develop Storage Criteria for Interim Dry Storage of AL

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EXPERIMENTS FOR EVALUATION OF CORROSION TO DEVELOP STORAGE CRITERIA FOR INTERIM DRY STORAGE OF ALUMINUM-ALLOY CLAD SPENT NUCLEAR FUEL

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ABSTRACT

The technical bases for specification of limits to environmental exposure conditions to avoid excessive degradation are being developed for storage criteria for dry storage of highly-enriched, aluminum-clad spent nuclear fuels owned by the U. S. Department of Energy. Corrosion of the aluminum cladding is a limiting degradation mechanism (occurs at lowest temperature) for aluminum exposed to an environment containing water vapor. Attendant radiation fields of the fuels can lead to production of nitric acid in the presence of air and water vapor and would exacerbate the corrosion of aluminum by lowering the pH of the water solution.

Laboratory-scale specimens are being exposed to various conditions inside an autoclave facility to measure the corrosion of the fuel matrix and cladding materials through weight change measurements and metallurgical analysis. In addition, electrochemical corrosion tests are being performed to supplement the autoclave testing by measuring differences in the general corrosion and pitting corrosion behavior of the aluminum cladding alloys and the aluminum-uranium fuel materials in water solutions.

Results of initial test runs exposing corrosion coupons of aluminum 1100 and 6061 to a temperature of $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$ at 100% relative humidity for up to 540 hours show the formation of a hydrated aluminum oxide film with a corresponding loss of average metal thickness up to 0.03 mils. Extrapolation of the general corrosion of aluminum to a target storage period of 50 years, using linear and power law models fit to the data, shows a loss of about 16 mils and 2 mils, respectively. Subsequent tests will include various conditions to allow modeling of a range of temperature and humidity conditions to identify the maximum conditions that do not produce excessive corrosion of the fuels.

I. INTRODUCTION

A fundamental requirement for dry storage of commercial spent nuclear fuels is to prevent gross rupture of the cladding during storage and handling [1], ensuring a measure of confinement against release of fuel and fission products. This requirement has been recommended for dry storage of fuels owned by the U. S. Department of Energy [2] and can be restated as the need to avoid excessive degradation of the cladding so as to maintain confinement. This requirement is achieved through acceptance criteria. Acceptance criteria for dry storage of highly-enriched, aluminum-clad spent nuclear fuels are defined by the combined set of drying criteria and storage criteria, even for those fuels containing minor cladding pits. For example, standards to dry the fuels to remove free water and to subsequently store the fuels at conditions within the limits of these criteria would avoid excessive degradation to assure post-storage handleability, a full range of ultimate disposal options, criticality safety, and provide for maintaining confinement by the fuel/clad system. Fuels with major cladding defects may require separate canning to provide for primary confinement.

The development of acceptance criteria for highly-enriched, aluminum-clad spent nuclear fuels is being performed at the Savannah River Technology Center. This program includes analytical and experimental investigation of the potential for excessive degradation of aluminum-clad fuels under a range of environmental exposure conditions. Degradation of the cladding involves mechanisms that can cause a loss in net section, distortion, or a loss of fuel and fission products through the cladding. A target interim storage of 50 years is assumed for purposes of evaluating all the potential mechanisms that can cause degradation including corrosion, creep, hydrogen blistering, radiation embrittlement, and diffusion of the fuel and fission products through the cladding. In general, these

mechanisms are a function of storage parameters as follows:

Degradation mechanism = f [temperature, time, relative humidity, moisture pH and impurities, and cover gas].

Corrosion of the cladding and fuel matrix materials is the most limiting degradation mechanism (occurs at the lowest storage temperatures) for aluminum exposed to high humidity during dry storage. This condition could occur through insufficient drying prior to a storage scenario involving sealed canisters, or through direct exposure to atmospheric conditions by design or through a breach of the sealed storage system. Maintaining fully-sealed storage in a system initially containing a limited supply of corrosive agents such as moisture could only lead to a limited degree of corrosion.

Aluminum cladding alloys generally form a protective surface barrier at atmospheric conditions, with a rapidly forming surface oxide film; however, hydrated aluminum oxide films are less protective than films formed in dry air and therefore continued corrosion of the aluminum cladding, especially at high temperature, high humidity conditions is possible. In addition, spent fuel will have an attendant radiation field and, in the presence of moist air, HNO_3 will be generated, lowering the pH of the water solution of the humidity, and thereby increasing the aluminum corrosion rate. A loss of 10% of the average cladding thickness during storage of 50 years is one example of an acceptable degraded condition for storage; therefore, general corrosion should be predicted to not exceed this level during dry storage.

Many fuels irradiated in foreign and domestic research reactors are of the Materials Test Reactor design and are aluminum-uranium fuels (up to 30 wt% U) clad in alloys of or similar to aluminum 1100, 6061, and 5052. Fuel elements that have been stored in basins with corrosive chemistries may have been subjected to pitting corrosion conditions. Information on the corrosion response at high temperatures (100 to 200°C) under high relative humidity conditions (up to 100%) with neutral to acidic moisture conditions is needed to identify the limiting storage conditions. Corrosion testing is being performed and models are being developed to predict the general corrosion and pitting corrosion of these aluminum cladding and aluminum-uranium fuel matrix materials under these conditions. The corrosion testing program and initial test results are summarized in this paper.

II. ATMOSPHERIC CORROSION OF ALUMINUM ALLOYS

A. Aluminum Oxide/Hydroxide Surface Film Growth in Dry and Humid Air

Aluminum is thermodynamically active in environments containing oxygen and/or water vapor, leading to the formation of oxide and hydrated oxide films

[3]. The formation of a passive film generally provides a high resistance to corrosion. If local breakdown in the film occurs without re-passivation, pitting corrosion can develop.

In air environments, an oxide film forms rapidly and grows to a limiting thickness of few tens of nanometers below 200°C; the growth rate of the film increases with temperature [3]. The initial layer of the film is amorphous Al_2O_3 and subsequent layers are most likely hydrated to various degrees. The components include Boehmite, Bayerite, Akdalaite, and Tucanite [4].

Hydrated aluminum oxides are not as protective as Al_2O_3 and the growth of the film is greatly increased in moist air with an increase in the growth rate with relative humidity [5] for a threshold relative humidity of greater than approximately 50% [5, 6]. The growth rates of the hydrated aluminum oxide films have been modeled with a logarithmic growth law and an inverse logarithmic growth law [5, 7]. Aluminum alloys that contain magnesium, (e.g. 5000- and 6000-series aluminum), will have MgO in the film in an amount proportionally larger than the percentage of Mg in the alloy; the resistance to corrosion decreases with an increase of MgO in the film [3]. Atmospheric impurities can also cause an increase in the corrosion of aluminum alloys [8].

In water environments or as a result of exposure to water at moderate temperatures ($\leq 100^\circ\text{C}$) during reactor operation, the film on the aluminum cladding alloys of spent nuclear fuels is a hydrated aluminum oxide that grows to a greater limiting thickness than in air [3]. Below approximately 75°C, Bayerite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is the predominant oxide. Initially, Gibbsite (alpha alumina trihydrate) is formed before a phase change to Bayerite (beta alumina trihydrate) [9]. Above 75°C, Boehmite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is cited the predominant oxide [9]. Films formed on aluminum-clad assemblies during heavy water reactor operation at water temperatures less than 100°C contained deuterated Gibbsite, Bayerite, and Boehmite [10]. These deuterated aluminum oxides had spalled off the fuel cladding during reactor operation. Pre-treatment of the fuel assemblies to form a film of Boehmite, which is more resistant to spallation than Gibbsite or Bayerite, reduced spallation [10].

In acidic solutions with pH values less than approximately 4, the aluminum oxide film will dissolve and aluminum will corrode [3, 11]. This behavior depends on the acid; aluminum will not corrode in concentrated nitric acid at pH values less than 1 [3].

B. Pitting Development

Pitting of aluminum alloys can occur under both atmospheric and water storage [4, 8]. Chlorides and sulfates promote pitting under atmospheric conditions [8]. The growth in depth goes as $(\text{time})^{1/3}$ in water; whereas an

initial high rate of corrosion followed by a constant rate is cited as typical in atmospheric corrosion [3].

III. CORROSION TESTING PROGRAM

The corrosion testing program for dry storage of spent aluminum clad fuel at the Savannah River Technology Center involves the generation of data to determine the corrosion response of the fuel cladding and matrix materials to humidity, humidity water chemistry and pH level, temperature, time, and cover gas. Specimens for these tests include standard flat plate corrosion coupons and fuel tube specimens containing pits of various diameters and depths drilled into the cladding. Initial tests have been performed with coupon specimens of cladding alloys of aluminum 1100 and 6061. No data from the pitted specimens is presently available.

In addition, electrochemical corrosion tests in water solutions are being performed to supplement the autoclave corrosion testing. These tests include linear polarization and cyclic polarization tests of aluminum cladding alloys and aluminum-uranium fuel matrix material, and static potential tests of pitted fuel tube specimens to investigate galvanic couple and pitting morphology effects on the open circuit potential. Initial tests have included linear polarization runs on aluminum 8001 and on extruded aluminum-10% uranium alloy.

IV. AUTOCLAVE TEST FACILITY PROCEDURE AND INITIAL CORROSION TESTS

The high temperature corrosion tests are conducted with a 3.8 liter autoclave which is heated electrically by a three-zone furnace. The autoclave was retrofitted with a pressure transducer to measure the absolute pressure and a Vaisla™ temperature/humidity probe to measure the temperature and relative humidity inside the chamber. A standard pressure gage and an external thermocouple down in a well near the center of the autoclave chamber are used as backups. A computer-controlled data acquisition system records pressure, temperature, and humidity conditions at user-specified intervals.

Three initial runs in the autoclave facility were conducted with corrosion coupon specimens at a target condition of 150°C, 100% relative humidity. The time to reach the 150°C temperature was about 1 hour. After reaching the setpoint, the controller was maintained within $\pm 5^\circ\text{C}$ of 150°C throughout the test.

The specimens in these runs were aluminum 1100 and 6061, 2" x 1" with a thickness of 1/16" and with a 600 grit finish. Figure 1 is a low magnification micrograph of a specimen of aluminum 6061 prior to exposure. The metal compositions of a specimen of each alloy were determined by x-ray fluorescence and are given in Table 1.

The specimens were hung near the center of the autoclave vessel on aluminum 1100 hangers. The hangers

were attached to a Teflon spacer that was bolted to the top of the autoclave. The Teflon insulated the specimens and hangers from the stainless steel vessel to eliminate the galvanic couple. Up to 5 specimens were placed on each hanger with ceramic spacers to maintain separation of the specimens when loading the autoclave. At specified intervals, the autoclave was turned off and the specimens were removed and placed in a desiccator. After vacuum drying for 1 hour, they were weighed on a five-place analytical balance to obtain weight gain information. The specimens were weighed three times and an average weight gain was determined. The balance was calibrated before each set of weighings using standard weights. Additional specimens of aluminum 1100 and 6061 were added to the autoclave for the second and third runs.

The original oxide coating was not removed before the tests, but each specimen was thoroughly cleaned with acetone to remove surface contaminants. The specimens were handled with plastic-tip tweezers throughout the runs. Low-magnification photomicrographs were made of the oxidized surfaces. Figure 2 shows a specimen of aluminum 6061 following 540 hours of exposure.

The humidity was obtained by putting about 150 cc of atmospheric condensate inside the vessel during set-up for each run. Condensate was used because it contained impurities expected in the atmosphere near the Savannah River Site. After each run, a sample of the remaining water inside the vessel was chemically analyzed to determine if the aluminum oxide had sloughed from the surface of the specimens during the run. Table 2 shows the aluminum content of the initial water sample and of the samples after each separate run of 68, 208, and 540 hours. The pH of the condensate at the beginning of the runs was an average of 6.8 and the conductivity was an average of 0.052 μmhos .

Relative humidity is defined as a ratio of the vapor pressure to the saturation vapor pressure at the test temperature. As a check on the data from the Vaisla™ temperature/humidity probe, the humidity inside the autoclave can be calculated from the temperature and pressure data using

$$\text{RH} = (1/P_s)(100P_t + K[T + 273]) \quad (1)$$

where P_s is the saturation vapor pressure (psia) at temperature T (degrees centigrade) and P_t is the total pressure (psia) inside the autoclave. The value of the constant K is determined from room temperature conditions and represents air remaining inside the autoclave before it is sealed. The value of the constant K is given by

$$K = (\text{RH}_r \times P_s - 1470)/(T_r + 273) \quad (2)$$

where RH_r is the relative humidity of the room air (percent) and P_s is the saturation pressure (psia) at room temperature T_r (degrees centigrade). For the runs at 150°C, 100% RH, the value of K is zero because the autoclave was

vented to the atmosphere at 100°C to remove most of the inside air.

V. TEST RESULTS - AND INITIAL CONCLUSIONS

A. Models for Aluminum Corrosion

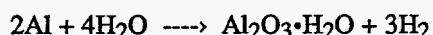
A comparison of the results of the aluminum concentration in the remaining water after each run given in Table 2 indicates that no aluminum oxide sloughed from the surface of the specimens.

Weight gain represents the oxidation of aluminum to produce Boehmite. Weight gain data from for each specimen is plotted on log-log coordinates and is shown in Figure 3. A power law model was fit to the data using linear regression analysis with a least-squares fit and is shown by the dashed line. The weight gain relationship is thus calculated to be

$$w = 210.87 \times t^{0.67} \quad (3)$$

where w is the weight gained (due to oxygen and hydrogen incorporated in the hydrated oxide) in micrograms per dm^2 and t is the time in hours. Also shown on the figure is the data of Godard [4] for aluminum exposed to 100% RH at room temperature. The corrosion rate increases with temperature and the weight gained at 150°C is significantly greater than at room temperature.

Aluminum corrodes in the presence of moisture at high temperatures and Boehmite is presumed to be the sole product formed at temperatures greater than 75°C according to the following reaction



The amount of aluminum consumed from the surface may be calculated by multiplying the specimen weight gain by the ratio of the molecular weight of aluminum atoms present in the Boehmite layer to the molecular weight of the added oxygen and hydrogen atoms. A log-log plot of the metal loss data vs. exposure time in hours is shown in Figure 4. Both linear and power law models for corrosion are fitted to the metal loss data and are shown on the figure. The linear equation obtained from linear regression, least-squares analysis is

$$m = 3.8 \times 10^{-5} \times t \quad (4)$$

and the power law equation is

$$m = 2.5 \times 10^{-4} \times t^{0.67} \quad (5)$$

where m is the average aluminum loss from the metal surface in mils and t is time in hours.

Optical characterization of the specimens before and after the autoclave runs shows two separate effects which

can be seen by a comparison of the low magnification optical micrographs in Figures 1 and 2. First, the initial 600 grit finish is "dulled" by the hydrated aluminum oxide film. Second, crevice corrosion is apparent where the ceramic spacer contacted the specimen during the tests. Qualitatively, the degree of the crevice corrosion varied from specimen to specimen. The authors acknowledge that this crevice corrosion, conditions for which were not controlled in these tests, most likely contributed to the variability in the specimen weight gain data. However, this same phenomena would potentially occur in crevices of fuel assemblies stored under similar conditions.

B. Linear Polarization Tests

Linear polarization tests were performed with aluminum 8001 and extruded aluminum-10% uranium alloy in reactor basin water at room temperature at an initial average pH of 6.7. The corrosion rate for 8001 was calculated to be 0.175 ± 0.129 mpy at an open circuit potential of -0.422 ± 0.028 volts; the rate for the aluminum-uranium alloy was 0.171 ± 0.088 mpy at an open circuit potential of -0.814 ± 0.159 volts. Although the uniform corrosion rates for these alloys are similar, the open circuit potentials indicate that the aluminum-uranium alloy would be anodic to the 8001, if coupled. Additional electrochemical tests are being performed to investigate potential galvanic couple effects in the aluminum cladding/aluminum-uranium fuel matrix system.

C. Conclusions

The strategy in the development of the storage criteria is to develop models to cover the range of environmental storage conditions and identify those conditions at which the extent of degradation after 50 years meets the maximum acceptable degraded condition (to be defined). Storage of fuels at conditions within the criteria would avoid stringent treatments and controls that may be required to ensure that no degradation occurred during storage and would thereby provide a lower cost system.

A sealed storage system, providing a second confinement barrier, may be used for dry storage. Therefore, the maximum extent of degradation (e.g., corrosion) would be dependent on the initial amount of corrodant species in the fuel storage system prior to sealing. The development of models based on unlimited supplies of corrodant species provides defense-in-depth in the event the fuels would be exposed to vault atmospheric conditions. In the absence of corrosion, other mechanisms (e.g. creep) would limit the maximum temperature of storage.

Extrapolation of corrosion data in the present tests to 50 years indicates that after continuous exposure to 100% vapor, about 16 mils is corroded using the linear model and about 2 mils is corroded using the power law model. For a fuel with an initial cladding thickness of 30 mils, the power law fit shows the storage condition to be acceptable

whereas the linear law fit does not. Additional exposure of the specimens is being performed to generate data to gain confidence in applying the power law model for aluminum metal loss over extrapolated times at these conditions. Future autoclave corrosion tests in the near-term will include conditions with pH levels reduced by nitric acid and conditions with reduced relative humidity levels. Models covering a range of environments will be developed and criteria for dry storage will be specified. In addition, tests are being planned to validate dry storage criteria using irradiated aluminum-clad, uranium metal matrix fuels.

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TABLE 1
Aluminum Alloy Composition, Wt%

Alloy	Si	Fe	Cu	Mn	Cr	Zn	Ti	Mg	Al
6061	0.613	0.497	0.300	0.031	0.228	0.024	0.012	1.019	97.236
1100	0.104	0.521	0.128	0.005	0.007	0.009	0.007	0.012	99.179

TABLE 2
Aluminum Content of Water Samples

Time(hrs)	0	68	208	540
PPM	<0.029	<0.010	<0.010	<0.020

These data indicate that no aluminum oxide sloughed from the surface during corrosion testing.

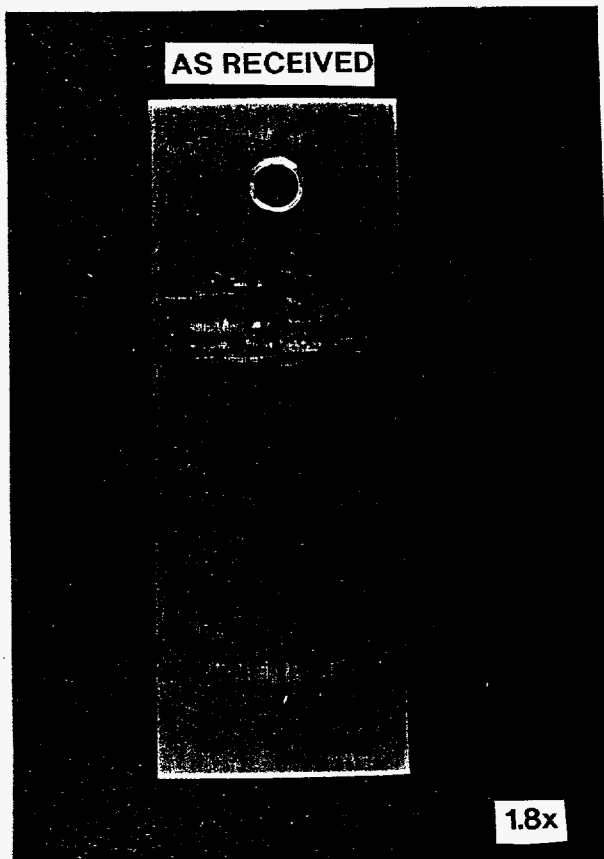


FIGURE 1 AL 6061/#111 BACK

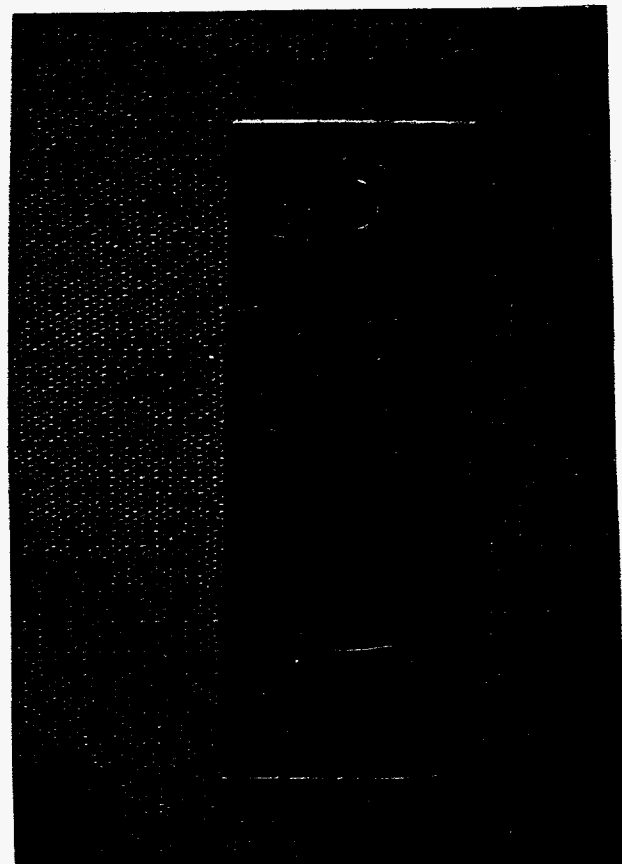


FIGURE 2 AL 6061/#111 8/24/94

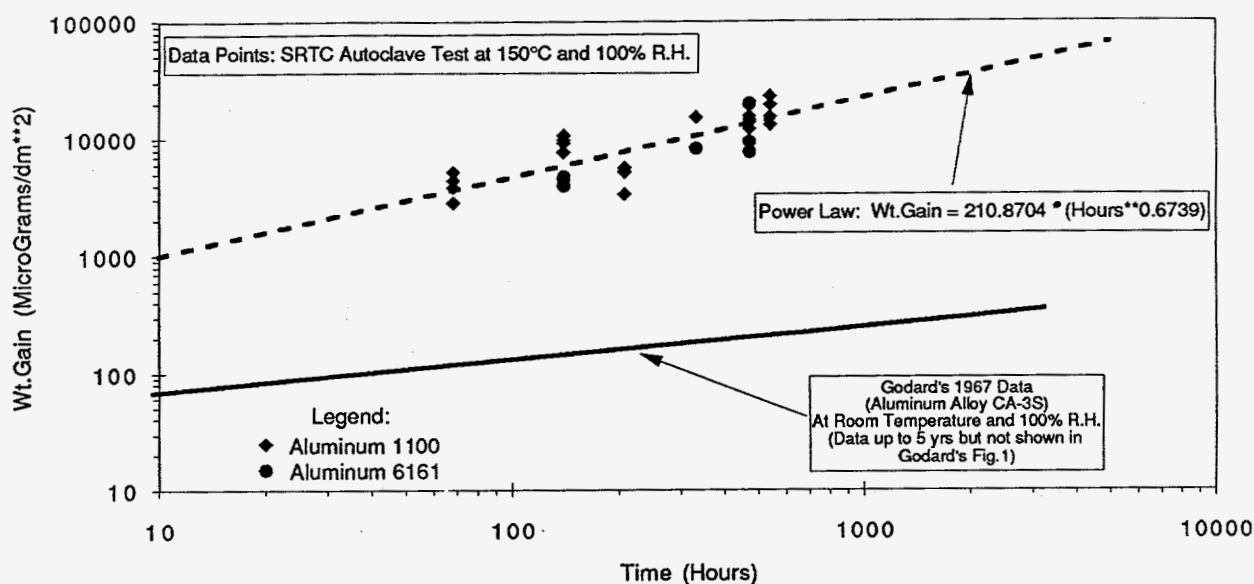


Figure 3. Corrosion of Al-Cladding Alloys Under Air-Water Vapor and Water Vapor Conditions

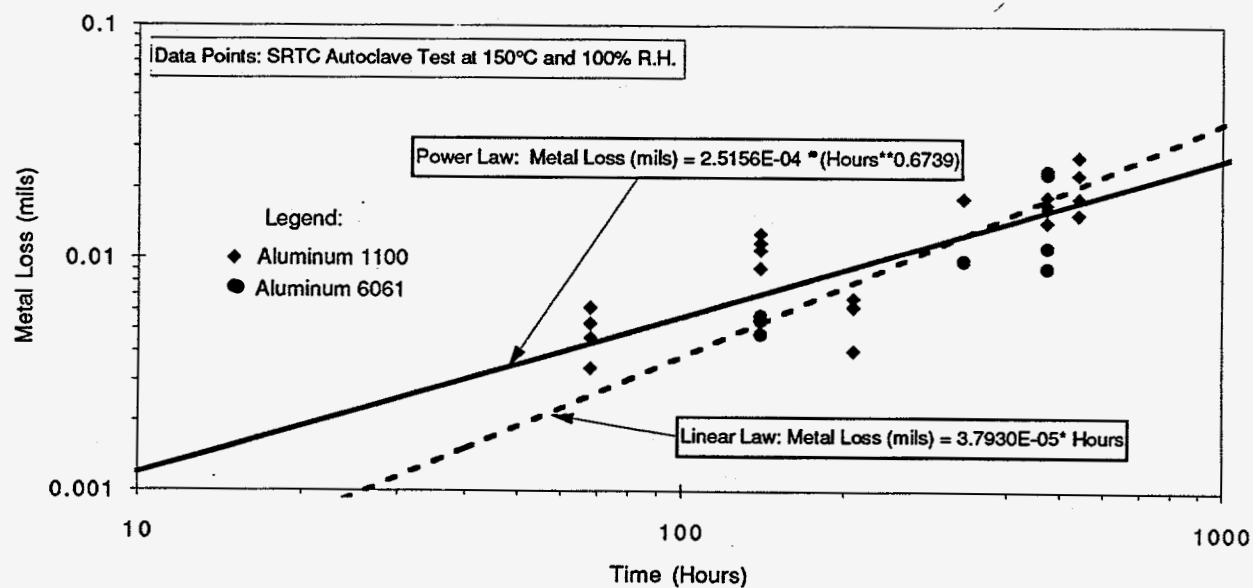


Figure 4. Aluminum Cladding Thickness Consumed by Corrosion Under Air-Water Vapor and Water Vapor Conditions