

WSRC-TR-95-0347 (U)

ACCEPTANCE CRITERIA FOR INTERIM DRY STORAGE OF ALUMINUM-ALLOY CLAD SPENT NUCLEAR FUELS (U)

R. L. Sindelar, H. B. Peacock, Jr., P. S. Lam,
N. C. Iyer, and M. R. Louthan, Jr.

Savannah River Technology Center
Applied Science and Engineering Technology Department
Materials Technology Section

Publication Date: March 1996

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ADC &
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Date: 3/21/96

Patent Status

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**Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808**

This document was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.

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DOCUMENT: WSRC-TR-95-0347

TITLE: ACCEPTANCE CRITERIA FOR INTERIM DRY STORAGE OF ALUMINUM-ALLOY CLAD SPENT NUCLEAR FUELS (U)

TASK: WSRC-RP-94-360, Rev. 1 PLAN FOR DEVELOPMENT OF ACCEPTANCE CRITERIA FOR INTERIM DRY STORAGE OF AL-CLAD SPENT NUCLEAR FUEL (U)

APPROVALS

R. L. Sindelar Date: 3/21/96
R. L. Sindelar, Task Leader and Author
Materials Applications & Corrosion Technology Group
MATERIALS TECHNOLOGY SECTION

H. B. Peacock, Jr. Date: 3/21/96
H. B. Peacock, Jr., Task Leader and Author
Materials Applications & Corrosion Technology Group
MATERIALS TECHNOLOGY SECTION

P. S. Lam Date: 3/21/96
P. S. Lam, Author
Materials Applications & Corrosion Technology Group
MATERIALS TECHNOLOGY SECTION

N. C. Iyer Date: 3/21/96
N. C. Iyer, Author and Manager
Materials Applications & Corrosion Technology Group
MATERIALS TECHNOLOGY SECTION

M. R. Louthan, Jr. Date: 3/25/96
M. R. Louthan, Jr., Author
MATERIALS TECHNOLOGY SECTION

J. F. Krupa Date: 3/21/96
J. F. Krupa, Technical Reviewer
STRATEGIC PROGRAMS & PLANNING DEPT.

T. L. Capeletti Date: 3/21/96
T. L. Capeletti, Manager
MATERIALS TECHNOLOGY SECTION

J. R. Murphy Date: 3/21/96
J. R. Murphy, Customer
Spent Fuels Programs
EXCESS FACILITIES & REACTOR FUEL STORAGE DIVISION

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LIST OF ACRONYMS

<u>Acronym</u>	<u>Definition</u>
ANL	Argonne National Laboratory
ANSI/ANS	American National Standards Institute/American Nuclear Society
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
EIS	Environmental Impact Statement
DRR	Domestic Research Reactor
F&OR	Functioning & Operationing Requirements
FRR	Foreign Research Reactor
HE-SNF	Highly Enriched Spent Nuclear Fuel
HFIR	High Flux Isotope Reactor
IMNM	Interim Management of Nuclear Materials
INEL	Idaho National Engineering Laboratory
LANL	Los Alamos National Laboratory
MRS	Monitored Retrievable Storage
MTR	Materials Test Reactor
MTRE	Materials Test Reactor Equivalent
NDE	Non-Destructive Examination
ORNL	Oak Ridge National Laboratory
PEIS	Programmatic Environmental Impact Statement
RBOF	Receiving Basin for Offsite Fuel
RH	Relative Humidity (vapor pressure of H ₂ O/saturation pressure of H ₂ O)
SCC	Stress Corrosion Cracking
SI	Structural Integrity
SNF	Spent Nuclear Fuel
SRS	Savannah River Site
SRTC	Savannah River Technology Center

1.0 SUMMARY

Acceptance criteria are established for aluminum-clad fuels, received from basin storage, for dry storage. Acceptance criteria are defined as the combined set of environmental limits for drying and for storage to avoid excessive degradation of the fuels during a nominal 50-year storage period. The acceptance criteria for aluminum-clad fuels are contained in Tables 1 and 2 below. The technical bases for these acceptance criteria are summarized in this report. Detailed information on the bases is provided in references 1 to 4 and includes results from a laboratory-scale corrosion test program of aluminum cladding alloys and aluminum-uranium fuel.

Acceptable degradation during dry storage is defined by the following set of limits to the changes in fuel condition as received from basin storage:

- 1) General corrosion or pitting corrosion up to 0.003" in depth of the cladding;
- 2) General corrosion or pitting corrosion up to 0.003" in depth of any exposed fuel (core) material;
- 3) Release of the fuel and fission products up to a predetermined limit (yet to be established) from any single fuel assembly in a non-sealed storage system;
- 4) Plastic deformation of fuel elements up to 1" over a fuel assembly length of 3', not to exceed 3/4 of clearance space between fuel assembly and storage grid; and
- 5) No rupture of the cladding due to creep or due to severe embrittlement.

This set of limits to degradation during the drying and storage for a dry storage system would enable post-storage handleability, a full range of ultimate disposal options, criticality safety, and radionuclide confinement by the cladding.

An evaluation of potential degradation mechanisms is performed based on the fuel and cladding materials' response to a broad range of environmental conditions (temperature, humidity, cover gas) relevant to drying and storage. The response is dependent on the type of materials and the fuel condition. Fuel that has been irradiated and has been wet-stored in basins may be in an initially-degraded condition including through-cladding pits. In general, degradation mechanisms during dry storage can lead to a loss in net section (cracking, thinning, or pitting) of the cladding, consumption of fuel, release of the fuel and fission products, and distortion of the fuel. The most limiting degradation mechanism for aluminum-clad fuels is corrosion; the drying and storage limits provided for both sealed and non-sealed storage systems assures that corrosion does not lead to unacceptable conditions. In addition to a limit for free water based on acceptable corrosion of the cladding and fuel materials, buildup of hydrogen gas and pyrophoricity of uranium metal/uranium hydride are issues that limit the water for a sealed dry storage system to ensure safe recovery of the stored fuel. A cladding temperature limit of 200°C ensures that creep or that diffusion, the next most limiting of the degradation mechanisms, do not lead to unacceptable degradation in 50 years of storage.

Tables 1 and 2 contain the acceptance criteria and the maximum degradation predicted at those limits for aluminum-clad spent nuclear fuels with categories 1 and 1A fuel materials and with category 2 fuel materials, respectively. These criteria are developed for two distinct types of dry storage systems: 1) sealed -- systems that provide for a fully-sealed container for the fuel; and 2) non-sealed -- systems that allow ambient air from the storage facility to be in contact with the fuel.

The maximum degradation predicted at the conditions of the acceptance criteria for either of these storage systems is well-within acceptable degradation for dry storage.

Category 1 material is aluminum-uranium (Al-U) alloy fuel. This material is comprised of a microstructure of uranium aluminides in an aluminum matrix and the fuel is metallurgically bonded to the aluminum cladding. The corrosion response of the aluminum-uranium fuel exposed to temperatures up to 200°C and relative humidities up to 100% is similar to that of the aluminum-alloy cladding as both exhibit the formation of a passive oxide layer under humid conditions and do not corrode in dry air.

Category 1A material is the balance of fuels that contain the uranium compounds in the form of oxides or silicides which, like category 1 fuel material, are dispersed in a matrix of aluminum, and that has the fuel bonded to the aluminum cladding. The category 1A fuels are low enrichment fuels and are typically irradiated to high burnups. The corrosion response of the category 1A materials should be similar to the category 1 material, but these fuels were not specifically tested in the corrosion program.

Category 2 materials are uranium metal and any other uranium alloy fuel that is not a stable uranium compound dispersed in a matrix of aluminum. Uranium metal is more susceptible to corrosion than the category 1 and 1A materials since it does not readily form a passive film and can corrode under dry air conditions.

The acceptable conditions for storage and the predicted degradation in dry storage for the category 1A materials (aluminum-uranium silicide and aluminum-uranium oxide fuels) are predicated on the assumption that the corrosion response and release of volatile fission products from these materials are similar to the aluminum-uranium alloy fuels. Corrosion testing of aluminum-uranium silicide and aluminum-uranium oxide fuels is recommended to verify that their corrosion behavior is similar to the aluminum cladding and aluminum-uranium alloy fuel. Technical validation of these criteria using model irradiated materials is also recommended.

Table 1: Acceptance Criteria for Dry Storage of Aluminum-Clad Category 1 and 1A Fuel Matrix Materials for 50-years Storage

Fuel Category	Fuel Condition	Storage System	Stabilization of Fuel Material	Max. Drying Temp. (Limit); Max Free Water in Sealed System (Limit)	Storage Environment Limits	Maximum Degradation Predicted in Dry Storage
CATEGORY 1 (Al-Uranium alloy) and CATEGORY 1A (Al-Uranium Silicide, Al-Uranium Oxide)	Non-breached	Sealed System	None	Up to 250°C for up to 2 hours; 1 ml free water per 0.1 m ² of cladding surface	Non-Reactive Gas, Air, or Vacuum are acceptable; 200°C cladding temperature limit	< ~ 0.3 mil corrosion of cladding; negligible slough-off of oxide product; negligible f.p. release; less than 0.1" local distortion
	Breached	Sealed System	None	Up to 200°C for up to 2 hours; 1 ml free water per 0.1 m ² of cladding surface	Non-Reactive Gas, Air, or Vacuum are acceptable; 200°C cladding temperature limit	< ~ 0.3 mil corrosion of cladding and of exposed fuel; negligible slough-off of oxide products; low f.p. release; less than 0.1" local distortion
	Non-breached	Non-sealed	None	Up to 250°C for up to 2 hours	Flowing ambient air required, 200°C cladding temperature limit	< ~ 0.1 mil corrosion of cladding; negligible slough-off of oxide product; negligible f.p. release; less than 0.1" local distortion
	Breached	Non-sealed	None	Up to 200°C for up to 2 hours	Flowing ambient air required, 200°C cladding temperature limit	< ~ 0.1 mil corrosion of cladding and of exposed fuel; negligible slough-off of oxide product; low f.p. release; less than 0.1" local distortion

Notes to Table 1:

- 1) The fuel conditions include all levels of enrichment and burnup (see note 2 below).
- 2) The fuel materials are assumed to have been cast and hot-worked or to have been produced by powder metallurgy. The spent fuel is assumed to not have internal cracking of the matrix. If the internal cracking is severe (e.g. may be the case for Al-U silicide fuels at high burn-up due to agglomeration of fission gases into gross bubbles), the prediction of low release of volatile fission products from breached fuel may not be valid due to the communication with large regions of the fuel meat.

Notes to Table 1 (CONT'D):

- 3) No significant reactions between the container and the fuels are assumed. For example, stainless steel coupled to aluminum would not lead to significant corrosion at the specified storage conditions. Nuclear poisons, if used, are also assumed to be compatible with the fuels.
- 4) The free water limit for the sealed system is based on limiting the predicted corrosion of the cladding and exposed fuel to well within acceptable degradation. The free water limit may be further reduced to limit the hydrogen gas buildup in a sealed container to below the flammability limit in air to ensure safe retrieval.
- 5) For sealed storage, the predicted general corrosion is based on the aluminum oxidation reaction to completion with the free water limit and with the waters of hydration of an initial cladding film of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ with a 50 μm thickness. For non-sealed storage, the predicted general corrosion is based on an assumed continuous growth of aluminum oxide under air at 100% relative humidity at room temperature.
- 6) A rinse step in high quality water (low Cl^- (< 1 ppm), low SO_4^{2-} (< 1 ppm), neutral pH, and low (< ~ 50 $\mu\text{S}/\text{cm}$ conductivity) is recommended for fuels received from basins and to be stored in a non-sealed system to reduce potential for pitting corrosion to occur. The container should be thoroughly cleaned to not be a source for pickup of impurities.
- 7) Except as impacted by the fuel and radionuclide release limits (yet to be established), no limits are placed on the extent of exposed fuel in the breached condition since the predicted corrosion behavior is well-within the limits of acceptable degradation for both sealed and non-sealed systems. Breached fuel that would not meet the release limits at a temperature of 200°C would require a fully-sealed barrier (e.g. canister) since the acceptable condition for radionuclide confinement by the fuel/clad system would be violated. Non-sealed storage at temperatures less than 200°C would be acceptable however if the release limits would not be exceeded at the storage temperature.
- 8) The Al-Uranium Silicide and Al-Uranium Oxide fuels have not been tested in the corrosion program (ref. 3) but are assumed to be resistant to corrosion in dry air (up to 200°C at relative humidities up to 20%). If not corrosion resistant, these fuel materials would be restricted to category 2 conditions for storage. Confirmatory tests are necessary to verify that these fuels are not excessively corrosive in dry air at high temperatures (up to 200°C) or at low temperatures (~ 25°C) with high (~ 100%) relative humidity.

Table 2: Acceptance Criteria for Dry Storage of Aluminum-Clad Category 2 Fuel Matrix Materials

Fuel Category	Fuel Condition	Storage System	Stabilization of Fuel Material	Max. Drying Temp. (Limit); Max. Free Water in Sealed System (Limit)	Storage Environment Limits	Maximum Degradation Predicted in Dry Storage
CATEGORY 2 (U metal)	Non-breached	Sealed System	None	Up to 250°C for up to 2 hours; 1 ml per 0.1 m ² of cladding surface	Non-Reactive Gas, Air, or Vacuum acceptable; 200°C cladding temperature limit	< ~ 0.3 mil corrosion of cladding; negligible slough-off of oxide product; less than 0.1" local distortion
	Breached	Sealed System	May be needed to reduce pyrophoricity. Potential for pyrophoricity is dependent on the free water limit	Up to 200°C for up to 2 hours; 1 ml per 0.1 m ² of cladding surface. Dry under non-reactive gas only	Non-Reactive Gas or Vacuum acceptable; 200°C cladding temperature limit	Corrosion of fuel is based on drying water limit TBD; less than 0.1" local distortion
	Non-breached	Non-sealed	None	Up to 250°C for up to 2 hours	Flowing ambient air required; 200°C cladding temperature limit	< ~ 0.1 mil corrosion of cladding; negligible slough-off of oxide product; less than 0.1" local distortion
	Breached	Non-sealed	*	*	*	*

Notes to Table 2:

- 1) The fuel conditions include all levels of enrichment and burnup (see note 2 below).
- 2) A stabilization step for fuel elements with breached cladding may be needed to remove the potential for pyrophoricity of UH₃.
- 3) No significant reactions between the container and the fuels are assumed. For example, stainless steel coupled to aluminum would not lead to significant corrosion at the specified storage conditions. Nuclear poisons, if used, are also assumed to be compatible with the fuels.
- 4) The free water limit for the sealed system is based on limiting the predicted corrosion of the cladding and exposed fuel to well within acceptable degradation. The free water limit may be further reduced to limit the hydrogen gas buildup in a sealed container to below the flammability limit in air and to avoid UH₃ buildup to ensure safe retrieval.
- 5) For sealed storage, the predicted general corrosion is based on the aluminum oxidation reaction to completion with the free water limit and with the waters of hydration of an initial cladding film of Al₂O₃·H₂O with a 50 μm thickness. For non-sealed storage, the predicted general corrosion is based on an assumed reaction growth of aluminum oxide under air at 100% relative humidity at room temperature.
- 6) A rinse step in high quality water (low Cl⁻, low SO₄²⁻, neutral pH, and low (< ~ 50 μS/cm) conductivity) prior to storage in a non-sealed system is necessary for non-breached fuels received from basins in order to reduce potential for pitting corrosion to occur. The container should be thoroughly cleaned to not be a source for pickup of impurities.

Notes to Table 2 (CONT'D):

- 7) Category 2 fuels do not tend to form a passive, corrosion resistant barrier under high temperature (up to 200°C) dry air (< 20% relative humidity) conditions. Criteria for a non-sealed system for breached category 2 fuels have not been developed and these fuels would have to be stored in a sealed container unless stabilized against degradation in the air and temperature environment. Stabilization of this fuel against gross corrosion and release of radionuclides at high temperatures ($\approx 200^\circ\text{C}$) in air might not be feasible, but stabilization for storage in air at low temperatures ($\ll 200^\circ\text{C}$) might be feasible.
- 8) No limits are placed on the extent of exposed fuel in the breached condition for sealed storage. In this case, it is noted that a confinement barrier (e.g. sealed canister) would be needed in the sealed storage system. Limits on the extent of exposed fuel for non-sealed storage is dependent on the performance of stabilized fuel (see 7 above) in meeting radionuclide release limits (yet to be established).

2.0 INTRODUCTION

2.1 Background

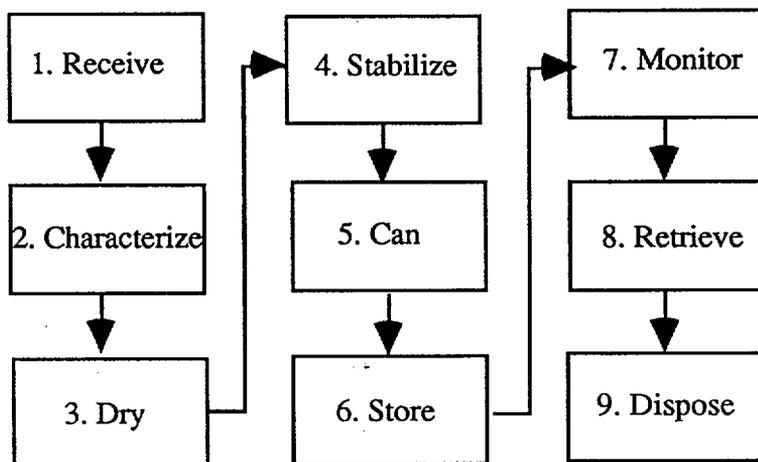
The United States Department of Energy "owns" a wide variety of spent nuclear fuel (SNF) presently in domestic and foreign research reactors or in their basin pools [5]. A portion of this inventory is aluminum-clad fuel, some of which contains highly-enriched uranium. Under the regionalization concept of the Programmatic SNF-EIS [6], the Savannah River Site (SRS) is to receive all the aluminum-clad fuels for handling and storage until ultimate disposal.

Direct disposal of highly enriched aluminum clad spent nuclear fuel (HE-SNF) in a geologic repository or other technologies to be developed are alternatives to chemical processing of these fuels into conventional waste forms for ultimate disposal. Decisions for ultimate disposal have not been made and, if a new technology is selected, the acceptable waste form and packaging needs to be developed and the repository needs to be selected. Consequently, interim storage will probably be needed for several decades. Dry storage in a monitored retrievable storage (MRS) facility and extended basin (wet) storage are the two alternatives for interim storage.

Technology has been developed for interim dry storage of Zircaloy-clad, uranium oxide fuels from light water reactors (LWR) [7] and requirements in national standards [8] and the Code of Federal Regulations [9] have been established to govern their dry storage. The technologies and conditions for storage of these fuels are not applicable to aluminum-clad fuel because of differences in the material characteristics that affect the storage life. Requirements for interim dry storage of aluminum-clad fuels [10] are being drafted. These requirements would specify that fuel and fission product release be limited and that the HE-SNF maintain criticality safety. Therefore, steps must be taken to preserve the integrity of the fuel, prevent damage during handling, stabilize already damaged fuel, and possibly encapsulate or isolate damaged fuel.

The overall sequence of general steps for a dry storage system is shown in Figure 1 below. Several steps may involve substeps. For example, step 2 (characterization) may involve the substeps of measuring heat output and of performing non-destructive examination (NDE) of the fuels on a sampling basis to verify that the fuels are in the appropriate condition for storage.

Some of the steps or the substeps may be optional and not necessary to maintain the integrity of the fuels in a dry storage system. As an example, a storage system that uses a non-sealed configuration in the design would not need canning of the fuel if: i) the fuel cladding is not breached or ii) if the breached fuel has been adequately stabilized for the storage environment or iii) if materials analyses demonstrate that exposure of fuel material not stabilized does not result in excessive degradation. Severely degraded fuel that is not readily handleable prior to dry storage should be canned. The SNF dry storage facility would provide for sealed or in non-sealed canisters stored in casks, vaults, or drywells, etc.

Figure 1: Steps for the Dry Storage System for Aluminum-Clad SNF

As part of the Research & Development activities needed to develop an engineered dry storage system for aluminum-clad fuels, the Acceptance Criteria (AC) program [11] was developed. The acceptance criteria for dry storage of aluminum-clad fuels are defined as the combined set of environmental limits for drying and storage and are dependent on the initial condition of the cladding. Non-breached fuels are those without any cracks or other thru-cladding pits/penetrations. Therefore, breached cladding would have fuel matrix material exposed to some extent to the environment. The drying criteria specify the acceptable quantity of water (free water by weight with an assumption of waters of hydration on existing oxide films) and the acceptable maximum temperature for drying. The storage criteria are the temperature/humidity/cover gas conditions to avoid degradation outside of the acceptable limits. The acceptance criteria are developed to enable post-storage handleability, a full range of ultimate disposal options, criticality safety, and confinement by the fuel/clad system. This report contains the acceptance criteria for a dry storage system for aluminum-clad fuels. Additional requirements for dry storage and specifications for a dry storage facility are outside the scope of the AC program.

The use of poisons is not envisioned for the interim dry storage system. If poisons are used in the dry storage system due to other requirements (e.g., criticality protection), they must be fully compatible with the fuels and storage containers.

Two distinct types of storage systems are envisioned: a "sealed system" would store fuel assemblies in fully-sealed containers and a "non-sealed" system would store assemblies in non-sealed containers or holders open to the environment of the facility. If a sealed system is used, the seal must be of adequate design to last the duration of the storage period (e.g. 50 years) or allowances (e.g., cost) must be made for resealing. The need for sealed storage in a dry storage facility will be driven by the requirements for confinement barriers including the acceptable level of radionuclide release from a confinement barrier and the number of barriers. The fuel/clad system provides one such confinement barrier with the release of radionuclides limited by the criteria for acceptable degradation.

2.2 Scope of Aluminum-Clad Fuels Covered by the Acceptance Criteria

The data and conclusions are applicable to aluminum clad SNF from research reactors within the United States (DRR), from foreign research reactors (FRR), and for interim dry storage of spent fuel and targets from the Savannah River Site (SRS) production reactors.

For aluminum-clad fuel, the predominant research reactor fuel design and fuel material is the Materials Test Reactor (MTR) design and Al-U alloy fuel [5].

2.2.1 Aluminum-Alloy Clad SNF from Domestic and Foreign Research Reactors

SRS currently stores a wide variety of spent fuel from research and other reactors located within the United States and foreign countries. The aluminum clad fuels were received from research reactors in the United States, Japan, and Taiwan over a period of several decades. In addition to this fuel presently stored in the Receiving Basin for Off-site Fuel (RBOF), other aluminum-clad SNF from DRR and FRR will be returning to SRS. The fuel and cladding materials for these fuels are the types listed in Table 3. A variety of burnups, cooling times, heat generation rates, dimensions, and shapes are represented among these fuels. The dimensions and inventory of this fuel are listed in Table 4.

Table 3: Foreign Research Reactor Spent Nuclear Fuel Materials [5]

Fuel Material	Cladding Alloy Equivalents - (see ref. 3)
Aluminum-Uranium Alloy ¹	1100 Aluminum
Aluminum-Uranium Oxide ¹	6061 Aluminum
Aluminum-Uranium Silicide ¹	5052 Aluminum
Uranium Metal	

¹These fuels are characterized by particles of UAl_x , UO_x , and USi_x , respectively, dispersed in an aluminum matrix and can be produced by casting methods or powder metallurgy methods. The term "dispersoid fuels" is applied to describe these fuels although the term historically has been restricted to those fuels produced by powder metallurgy methods only.

Table 4: DRR and FRR Aluminum-Clad SNF Dimensions and Inventory [5]

Fuel Type	Representative Reactor	Dimensions (mm)	U-235 fissile mass (gms)	Quantity IDSF (number of assemblies)
MTR				
a) high power	ORPHEE	80.5Hx80.5Wx	400-840	10,930
b) low power	IRR-1	778L	80-300	4542
Tubes	BR2	82.8Dx970L	400	4610
Involutes	RHF	406Dx965L	8500	110
Pins	NRU	63Dx3352L	491	440

2.2.2 SRS Aluminum-Alloy Clad SNF and Targets

The Savannah River Site (SRS) reactor disassembly basins were designed and intended only for temporary storage of irradiated fuel and targets from the SRS production reactors to allow cooling prior to transportation for reprocessing at site facilities. At present, fuels in P, K, and L basins are being stored pending a decision on processing and/or storage options following the issuance of the IMNM-EIS [12]. Dry storage is an alternative for interim storage of these materials until ultimate disposition. Other options include extended storage of these fuels and storage of the FRR and DRR fuels in the reactor basins. Basin storage would require controlled "good" water quality to prevent pitting corrosion and mitigate existing conditions of pitting. Encapsulation of severely corroded fuel in the basins may also be an option to ensure handleability and avoid exceeding radionuclide release limits for the basins if reactor basin storage were to be extended.

The inventory of SRS fuel and targets include irradiated aluminum-uranium fuel tubes (Mark 16B, 22, 60B), aluminum-lithium targets (Mark 16B) and uranium targets (Mark 31A) which are currently stored in the reactor disassembly basins and separations canyons. In addition to these components, RBOF contains some Mark 16, Mark 18A, and Mark 31A fuel and target components. The types of aluminum-clad SRS fuel and target components currently stored in reactor disassembly basins and canyons are identified in Table 5.

Table 5: SRS Spent Fuel and Targets in Reactor Basins, Canyons, and RBOF

Designation	Core	Cladding	Location	Condition
Mark 16B	Al-U alloy	8001 Al	P,K,L	Some Pitted
	Al-U alloy	8001 Al	RBOF	No evidence of corrosion
Mark 22	Al-U alloy	8001 Al	P,K	Some Pitted
Mark 60B	Al-U alloy	8001 Al	K	Some Pitted
Mark 31A	U	1100 Al	L, F-Canyon	Some Pitted
		1100 Al	RBOF	No evidence of corrosion
Mark 42	Al-PuO ₂	Al	P	Some Pitted
Mark 18A	Al-U alloy	Al	RBOF	Unknown

2.3 Report Objective and Organization

This report establishes acceptance criteria for the dry storage of aluminum-clad fuels so as to avoid excessive degradation of the fuels during a nominal 50-year storage period. Acceptable degradation, that is, the set of limits to degradation that may occur during the dry storage period, is also defined. The full reports containing the degradation evaluation and corrosion program results and conclusions to date are provided in references 1 to 4.

A summary of the technical bases for the predicting degradation is provided in Section 3 of this report. Section 4 applies these results and conclusions to develop the acceptance criteria that ensure degradation is within defined acceptable conditions. Section 4 also lists recommendations for additional corrosion testing and verification and validation activities.

This report may be revised upon completion of the corrosion testing program (see reference 3 and section 4.3 of this report).

3.0 SUMMARY OF DEGRADATION OF AL-CLAD FUEL IN STORAGE

The aluminum-clad fuel to be put in dry storage includes fuel irradiated in nuclear reactors and stored in basins with various water qualities. The fuel is in various levels of initially-degraded conditions. The degradation of aluminum-clad SNF under drying and storage is dependent on the initial condition of the fuel and on the conditions of drying and storage. Section 3.1 provides a summary overview of corrosion of the fuel in water storage. Section 3.2 summarizes the degradation evaluation [1] and the results to-date of the corrosion testing program for simulated dry storage conditions [3].

3.1 Spent Aluminum-Clad Fuel in Basin Storage - Summary of Corrosion Behavior

Aluminum-clad spent nuclear fuels have been used successfully in research and production reactors in light and heavy waters for over 40 years. The irradiation and subsequent storage in water basins has caused changes to the fuels including a degree of consumption of the cladding. The initial condition of the fuels (e.g. breached or non-breached claddings) impacts the dry storage criteria. An assessment of the initial condition of the fuels, including a summary of the materials' behavior in water storage, is given in this section.

A comprehensive summary of the technology base characterizing the performance of aluminum-clad fuels in reactors was assembled by ANL, SRTC, INEL, and ORNL [13] personnel. The post-irradiation microstructural condition of these fuels shows that the low enrichment fuels run to high burnups (e.g. Al-U silicide fuel) contain a microstructure of large bubbles in the dispersoids with possibly some internal microcracking of the aluminum matrix; the microstructure of high enrichment Al-U alloy fuels contains only relatively small bubbles.

The claddings of spent fuels are consumed to some extent during irradiation by growth of passive hydrated oxide films. Films, up to approximately 50 μm in thickness, of predominantly Boehmite develop [14, 15] when the fuel cladding at high temperatures (up to 200°C) under heat flux conditions is exposed to coolant water during reactor operation.

Pitting, through breakdown of the passive films on the claddings, is of primary concern for fuels in basin storage. Information on mechanisms of corrosion of aluminum in basin waters along with the observed degradation of aluminum-clad fuels during storage in the basins of domestic research and production reactors has been recently compiled [16].

3.1.1 Aluminum Corrosion in Water

Comprehensive reviews of corrosion of aluminum in water are given in references 17 and 18. Temperature, chloride anion concentration, the presence of oxygen, and the grade of aluminum are major factors affecting the corrosion of aluminum. Films of hydrated oxides form and are stable at pH levels between approximately 4 and 10 with little effect of pH in oxygenated solutions of constant chloride concentration. At temperatures below approximately 80°C, beta alumina trihydrate or Bayerite ($\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is the predominant oxide while above approximately 80°C, alpha alumina monohydrate or Boehmite ($\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is the predominant oxide.

The formation of aluminum oxides on the cladding of SRS fuels during reactor operation is detailed in reference 15. This work shows that hydrated oxides are formed in heavy water as in water, except that the waters of hydration are deuterium oxide, D_2O . The films grow in thickness with a growth in oxide crystal size when exposed to the high temperature water. Particles that spalled and caused moderator turbidity were observed at a size ranging from less than 1 μm to about 3 μm [15]. Other work

characterizing the overall thickness of oxide films on several selected MTR elements following irradiation also identified Boehmite at thicknesses up to about 50 μm [14]. A Boehmite thickness of 50 μm corresponds to consumption of the aluminum cladding of 0.0011 inches.

The growth of films on aluminum immersed in water are generally expressed in a logarithmic format [19, 20]. The weight gain, oxide thickness, or metal consumed can be expressed in the following general model [1]:

$$\Delta W, \text{ oxide thickness, metal loss} = A \ln(1 + B(\text{time})) \quad (1)$$

where A and B are parameters dependent on temperature, water quality, alloy type, etc. Pitting, galvanic, and crevice corrosion are the principal corrosion modes for aluminum and aluminum alloys in fresh water [17, 18] under certain ("aggressive") water quality conditions. The distribution of pits initiated in an aluminum alloy is reported to follow an extreme value statistical distribution [21]. Typically, only the deepest 1 to 2% of the pits continue to grow and they grow by the following kinetic expression [17, 18, 21]:

$$\text{Maximum Pit Depth} = A \text{time}^n \quad (2)$$

where n is reported as equal to 1/3 [21] and where A is a parameter dependent on water quality, alloy type, etc [1].

Pitting corrosion of aluminum claddings has been observed in SRS and other domestic basins [16]. SRS alloys experience has shown that 8001 aluminum alloy pits more rapidly than either 1100 or 6061 aluminum in basin water at 20-30°C although it is more corrosion resistant at reactor operating temperatures, > 100°C [16]. As seen in recent examinations of spent fuel and experimental coupons of aluminum alloys in the reactor basins, pitting rates have been sufficient to penetrate the 1100 and 8001 aluminum claddings (0.030" thick) within a month or two [16]. In some cases, the corrosion is associated with mechanical damage where ribs on the housing or fuel tubes have abraded the normally protective oxide film and exposed a fresh aluminum surface [16]. In these cases, a fluffy corrosion product forms containing $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and, if the cladding is breached, oxides of the fuel and fission products. Results from basin storage have shown that galvanic coupling of the aluminum to stainless steel hangers and stainless steel storage buckets can be a significant factor in initiating the corrosion [16]. SRS studies of fuels in basin storage indicates a strong correlation between the incidence of pitting and the lack of an initial thick protective layer of Boehmite. Crevice corrosion is possible where ribs on fuel elements contact the surface of the another fuel element in nested fuel assemblies stored in water of high conductivity.

All instances of rapid (pitting) corrosion in the SRS reactor basins are associated with high conductivity water, > 100 $\mu\text{S}/\text{cm}$ (micro-Siemens per centimeter) [16]. In contrast, aluminum clad fuel elements have been stored in low conductivity water ($\sim 1\mu\text{S}/\text{cm}$) for over ten years in RBOF, for more than seven years at the HFIR pool at ORNL, and for approximately ten years at the 666 Basin at INEL with no evidence of pitting or galvanic attack. These storage conditions are characterized by low conductivity ($\sim 1\mu\text{S}/\text{cm}$) water and low concentrations (below ~ 1 ppm) of harmful impurities such chloride anions [16].

3.1.2 Uranium Corrosion in Water

The films formed during corrosion of uranium is less cohesive and more porous (less protective) than the films formed on aluminum. Hyperstoichiometric uranium dioxide (UO_{2+x}) is the principal product of uranium corrosion in aerated water [22-24]. There is some evidence that uranium hydride (UH_3) also forms at the oxide-metal interface. The UH_3 can react further to form UO_2 and hydrogen gas, a reaction that proceeds slowly at room temperature [22-24]. At temperatures below approximately $80^\circ C$, the film of UO_2 that forms is initially protective and further reaction is delayed for a period of time depending on the temperature, impurities in the water, and the condition of the uranium. Eventually, the film breaks down and corrosion proceeds more rapidly. The reaction rates are temperature dependent. In tests at $50^\circ C$, the delay before onset of rapid corrosion varied from zero to 859 hours [24]. At temperatures above approximately $80^\circ C$, corrosion proceeds rapidly from the start with no evidence of an initial protective stage [24]. All experiments have confirmed that the presence of oxygen in the water suppresses the corrosion reaction [22-24].

The volume increase associated with corrosion of uranium will generate compressive stresses in the uranium oxide film. The films eventually spall exposing fresh metal to further oxidation. Corrosion rates are enhanced by internal porosity formed during irradiation of uranium because of the additional surface area that would be exposed to any water if the cladding were breached [25]. In the case of the Savannah River Site Mark 31 slugs, iron and silicon additions of 175 ppm (by weight) were made to the uranium to control grain size and dimensional stability of the target slugs during irradiation [26]. Irradiation induced swelling is consequently less than 1% and is attributed solely to accumulation of solid transmutation products for the temperatures and burnups attained during SRS irradiation [26]. These alloy additions should have no significant influence on the corrosion rate of the uranium in water or air. Fission gases form $0.1 \mu m$ diameter bubbles and account for volume increases of less than one percent. Because no gross porosity forms during irradiation, no enhancement of the corrosion rate is expected such as has been observed in the case of Magnox fuel in Britain [25].

The uranium core and aluminum cladding were bonded through an intermediate layer of electroplated nickel in the production of SRS target slugs [26]. Uranium is cathodic to aluminum and, at cladding penetrations, would corrode preferentially by forming UH_3 [27]. The UH_3 product would subsequently oxidize upon contact with the water to form UO_2 . In zircaloy clad fuels, uranium is anodic to the cladding and UO_2 would be formed directly if the cladding would be breached.

3.1.3 Aluminum-Uranium Alloy Corrosion in Water

The fuel cores in most research reactor assemblies and in the Savannah River Site Mark 16B, Mark 22, and Mark 60B elements are aluminum-uranium alloys formed by casting or powder metallurgy methods. The cores are a mixture of 10 to 50 volume % UAl_x particles, where x is 3 or 4, within a matrix of commercial purity 1100 aluminum.

During corrosion in water at $290^\circ C$ for 60 days, corrosion rates in 15 and 53 wt % uranium alloys were 9.4 and 5.3 mg/square decimeter/day (mdd), respectively [28]. These rates are about twice those of 8001 aluminum alloy at the same temperature. Intergranular attack has been observed at 350° at the ends of cast alloys that contain 6 to 15 wt % uranium [29]. At room temperature, linear polarization measurements show the 8001 aluminum and aluminum-10% uranium have approximately the same corrosion rate of 0.17 mils per year (mpy) in SRS reactor disassembly basin water at room temperature [30].

As discussed above, hydrated oxides of aluminum, are the expected corrosion products of the aluminum matrix in basin water. Corrosion of the UAl_x particles in water is assumed to form U_3O_8 or U_4O_9 and possibly a thin film of Al_2O_3 (formed by oxidation of UAl_x in air [31]) or one of the

hydrated aluminum oxides, Bayerite or Boehmite. In addition, hydrogen gas would be evolved and possibly uranium hydride would be formed. Particles of UAl_x in an aluminum matrix would be expected to cause a galvanic couple with the aluminum acting as the large anode. This would tend to promote a passive film of Bayerite or Boehmite on the aluminum. Evidence for this behavior has been reported under saturated water vapor at 200°C [3].

3.1.4 Radionuclide Release by Leaching and by Corrosion

A cladding breach would expose the core to release of radionuclides into the basin water by leaching. Corrosion of the fuel would be expected to cause a much greater release rate of radionuclides in the corrosion products compared to the leaching release rate. Fission product release rates could be estimated from corrosion rates and the concentrations of radionuclides present in the spent fuel. The amount released would depend on the storage temperature, storage time, and depth of corrosion.

Radiochemical monitoring of SRS basins is performed to ensure releases are within specified limits and has been used to estimate consumption of corroding fuel and target materials.

3.2 Aluminum-Clad Fuel in Dry Storage

Degradation mechanisms that can potentially affect the integrity of aluminum-clad spent nuclear fuels (SNF) were evaluated for a range of storage environments as technical background for development of acceptance criteria for dry storage for a 50-year period [1-3].

Degradation mechanisms which could cause the following degradation modes were evaluated:

- a loss in net section of cladding through cracking, pitting, or general thinning;
- embrittlement of the cladding;
- distortion (slumping) of the fuel;
- diffusion of fuel or fission products through the cladding; and
- diffusion of volatile fission products through the fuel matrix (in fuel that may have breached cladding)

for the following potential environments of dry storage:

- temperature (room temperature up to maximum feasible);
- cover gas (air, vacuum, or non-reactive (nitrogen or helium)); and
- humidity (0 to 100% relative humidity, defined as the partial vapor pressure of water divided by its saturation pressure at temperature).

Evaluation of all degradation mechanisms under potential dry storage environments is summarized in section 3.2.1 below. Evaluation of corrosion, the primary degradation mechanism, and the results to-date of the corrosion test program are summarized in section 3.2.2 below.

3.2.1 Evaluation Degradation Mechanisms - Summary of Results

The potential for degradation of aluminum cladding alloys and fuel matrix materials under a wide range of potential environments pertinent to dry storage has been evaluated [1]. Table 6 below contains a listing of the degradation modes and mechanisms which could potentially effect the fuels in various dry storage environments. The environmental conditions at which the degradation mechanisms would be sufficiently active to degrade the integrity of the bonded aluminum clad/aluminum-based fuel matrix fuels to the extent that the fuel/cladding system confinement and dimensional stability are effected are identified.

Degradation of the spent fuel aluminum cladding alloys is not strongly dependent on alloy type except for corrosion at various environmental conditions. The corrosion response of the fuel matrix materials is strongly dependent on alloy type and for breached fuel, must be considered.

Table 6 - Summary of Potential Degradation Modes & Mechanisms During Drying and Storing Aluminum-Clad Spent Nuclear Fuels

DEGRADATION MODE & MECHANISM	PREDICTED DEGRADATION AT ENVIRONMENTAL CONDITIONS
<p>General Thinning of Cladding by General Corrosion (growth of hydrated aluminum oxide films and consumption of aluminum)</p>	<p>General corrosion (thinning) and pitting can occur at all temperatures for all cladding alloys under air storage with water vapor or under water vapor alone. The growth of a passive hydrated oxide film with concurrent metal consumption can be modeled with a mechanistically-based, phenomenological model given by a power law with metal loss = $Ae^{(-Q_n/RT)}t^n$, where Q is the activation energy. In general, A and n are dependent on alloy type, relative humidity, and water chemistry of the humidity. Departure from parabolic behavior (e.g. parabolic corrosion or even breakaway corrosion) may occur depending on the alloy.</p> <p>The high magnesium alloys (e.g. Al 5052) exhibit a higher corrosion rate than the low magnesium alloys (e.g. Al 1100).</p> <p>Above an effective threshold relative humidity (RH) of approximately 20%, general corrosion of aluminum cladding alloys increases with temperature and with relative humidity.</p> <p>The attendant gamma radiation field of spent fuels can cause the production of NO_x gases in air. If water vapor is additionally present HNO₃ can be formed. General corrosion is significantly increased by exposure to these vapors. No other significant effect on corrosion due to the radiation field or the irradiated microstructure of the cladding alloys is predicted.</p> <p>General corrosion effectively stops in the absence of water vapor in air and would stop if corrodant species are consumed in a closed system. Hydrogen gas is produced in the corrosion reaction with water.</p> <p>The corrosion response of dispersoid fuel materials (Al-U, Al-U oxide, and Al-U silicide) should be similar to the aluminum cladding alloys in that the aluminum matrix oxidizes and forms a passive oxide layer which is adherent to the metal. The dispersoids promote formation of the aluminum matrix oxide (passive film) since they act as the cathode with the aluminum matrix as the anode in a microgalvanic cell. Uranium metal fuel does not passivate and corrodes readily under dry or moist air conditions.</p>

Table 1 CONT'D - Summary of Potential Degradation Modes & Mechanisms During Drying and Storing Aluminum-Clad Spent Nuclear Fuels

<p>Pitting by Self-Pitting Corrosion (local breakdown of passive film by aggressive ions)</p> <p>Pitting by Galvanically-Coupled Pitting Corrosion (clad/fuel galvanic corrosion cell in exposed fuel)</p>	<p>Self-pitting of aluminum can occur at all temperatures under conditions of moist air or in non-reactive gas with water vapor if aggressive impurity species such as chlorides or sulphates are present in the water or on the surface of the aluminum.</p> <p>The distribution of self-pits in aluminum is characterized by extreme value statistics. The growth of the pits of maximum depth has been modeled phenomenologically by pit depth = At^n. In general, A and n are parameters dependent on alloy type, relative humidity, and water chemistry of the humidity. The exponent n has been reported equal to 1/3.</p> <p>A pit breach in the aluminum cladding allows communication to the fuel and could set up galvanic corrosion under water film conditions (i.e. with humidity). The potential for significant galvanic corrosion for the aluminum-clad fuels are dependent on the fuel material, fuel design (e.g. bonded clad/matrix), and water quality. Dispersoid fuels (Al-U, Al-U oxide, and Al-U silicide) should not be subject to galvanically-coupled pitting unless the water vapor is aggressive. Uranium is cathodic to aluminum and can corrode by reactions producing UH_3 followed by the production of UO_2. No effective passivation occurs and the uranium metal with matrix materials other than aluminum-uranium are more reactive to (air and/or water vapor) environments and bonded designs provide only limited communication between the environment and the fuel matrix if an opening in the cladding exists.</p> <p>A surface film (adsorbed) of water is required for pitting corrosion and therefore pitting can not occur in the absence of water vapor for any clad or coupled clad/fuel material.</p>
<p>Cracking of Cladding by Stress Corrosion Cracking</p>	<p>SCC can not occur in these alloys under saturated vapor conditions because the degree of alloying of the claddings is too low (material is not susceptible), and there is no sustained stress condition.</p>
<p>Cracking of Cladding by Hydrogen Blistering</p>	<p>Corrosion of aluminum with humidity above approximately 275°C can form blisters (aggressive corrosion condition) that can split cladding</p>
<p>Embrittlement and Cracking by Radiation Embrittlement</p>	<p>The aluminum cladding is embrittled following exposure to fast ($E_n > 0.1$ MeV) neutron fluence levels above 1×10^{19} n/cm², a condition typical for the spent fuels -- this may impact the pre-storage handleability by avoiding deformation of the fuel. The ductility of irradiated 1100 and 6061 aluminum reduces to less than 1% between 150 and 200°C making the cladding susceptible to failure.</p> <p>Upon exposure to high temperatures (200 to 250°C), the radiation damage anneals out, leading to a reduction of strength with a recovery of ductility.</p>

**Table 1 CONT'D - Summary of Potential Degradation Modes & Mechanisms
During Drying and Storing Aluminum-Clad Spent Nuclear Fuels**

Distortion of Fuel by Creep	Distortion of the fuel under self weight becomes significant (measurable) within 50 years at temperatures above approximately 200°C. For the Materials Test Reactor fuel design, distortion of 0.1" would occur in storage at 200°C for 50 years.
Diffusion of fuel/fission products through cladding	Fission products (cesium) and fuel (uranium) can diffuse through a 0.030" thick aluminum cladding within 50 years at temperatures above 250°C. Subsequent corrosion of the cladding would contain these species in the corrosion product.
Diffusion of volatile fission products through fuel matrix	Fission product krypton can migrate through the fuel matrix but would not lead to significant release from the fuel matrix of exposed fuel unless the fuel is either: 1) at high temperatures (> 200°C); 2) greatly cracked; or 3) the area of exposed fuel is large.
Pyrophoricity of Fuel	Pyrophoricity of aluminum alloy fuel is very unlikely. Bare uranium metal or uranium hydride, UH ₃ , are pyrophoric under certain conditions. The UH ₃ would be produced if U metal is directly exposed to H ₂ or is exposed to H ₂ O producing UO ₂ and H ₂ with occlusion of additional water.

3.2.2 Dry Storage Corrosion - Summary of Results

Environments relevant to dry storage, specifically those containing oxygen or water vapor, can consume fuel and cladding materials in corrosion reactions. The following evaluation of corrosion of aluminum cladding and fuel materials under vapor space corrosion is summarized from references 1 and 3.

3.2.2.1 Aluminum Corrosion in Water Vapor in Air or in Non-Reactive Gas

The initial oxidation rate of a freshly exposed aluminum surface in air is mainly a function of temperature and is not significantly affected by the relative humidity or the presence of hydrogen gas [18, 32, 33]. The continued growth of the hydrated oxide film is a function of the relative humidity [18, 32, 33]. Aluminum does not corrode in dry air but rather forms an oxide barrier or adherent protective film of amorphous Al₂O₃ which resists further oxidation upon growth to a "limiting thickness" [34].

Oxidation of aluminum in moist air can cause blister formation and would degrade the integrity of the cladding if the temperature was above ~ 250°C [35-40]. Hydrogen is a product of the reaction between aluminum and water vapor. At elevated temperatures some hydrogen dissolves into the aluminum, diffuses into the metal, becomes trapped and accumulates at internal boundaries, eventually forming gas pockets or blisters [36]. Blisters have been observed following oxidation of fresh surfaces in moist air at temperatures as low as 275°C and are readily formed at higher temperatures [38]. Blister formation during oxidation in humid air will depend on several factors. The relative humidity determines the extent of the water-aluminum reaction and the quantity of hydrogen formed; the temperature determines the solubility and diffusivity of hydrogen in aluminum; and the irradiation fluence and temperature establish the yield strength of the aluminum cladding. Blistering of aluminum would not be expected during dry storage provided the relative humidity were low (< 20%) or the temperature remained below ~250°C.

Storage of aluminum clad spent fuel in an inert or non-reactive gas does not preclude the possibility of blister formation at temperatures above 250°C. Moisture will be present because the aluminum oxide films formed during corrosion in water will dehydrate during storage releasing moisture inside the canister. In a sealed container, this moisture would react with freshly exposed aluminum surfaces and be a source for hydrogen gas. Radiolysis of water would also produce some hydrogen gas as well as oxygen and hydrogen peroxide.

The corrosion test program [3] in progress provides data to develop corrosion models to allow prediction of corrosion (up to 50+ years) of the aluminum alloy claddings and the fuel materials over a temperature range from room temperature to 200°C at relative humidities from 20 to 100% under water vapor or water vapor plus air conditions. Aluminum forms a passive film that, at low RH (<~ 20%), effectively stops [3]. At high RH, hydrated oxide would keep on growing with an increase in growth rate with temperature in accordance with a Arrhenius relation.

For aluminum cladding alloys that tend to form a coherent, passive film, a mechanistically-based, phenomenological model is [1, 3]:

$$\Delta w, \text{ oxide thickness, metal loss} = Ae^{\left(\frac{-Qn}{RT}\right)} \text{time}^n \quad (3)$$

where Δw is the weight gain of a specimen which is related to the average oxide thickness on the specimen and to the metal consumed in the corrosion reaction. The parameter A is a function of alloy composition, cover gas, water vapor composition, and RH. The activation energy Q is a function of alloy composition and n is a function of both alloy composition and water vapor composition. A marked departure from parabolic behavior is being observed for the Al 5052 alloy following growth of a Boehmite film to several μm . A post-parabolic, linear regime of film growth is therefore anticipated for at least some of the cladding materials.

Self-pitting in aluminum occurs with breakdown of the passive film. Breakdown is promoted by Cl^- and SO_4^- ions in air environments [41]. In water environments, the pitting distribution has been characterized by extreme value statistics where only the deepest pits grow with time [21]. Although no statistical study on aluminum pitting under atmospheric conditions has been reported in the literature, it is postulated that the maximum pit depth can be expressed as [1]:

$$\text{Maximum Pit Depth} = K \text{time}^{1/3} \quad (4)$$

where K is a function of alloy composition, water vapor composition, and RH. Note that if the clad is "thin enough" and the growth rate is high enough, through-clad growth of pits would occur and cause a new condition, that is, a galvanically-coupled pit (e.g. Al and U couple). In this case, the extreme value distribution characterizing self-pitting in the aluminum cladding would not be valid and the above model for the maximum pit depth would not be valid.

In a sealed environment, corrosion would decrease due to the consumption of the corrodant species, effectively stopping at some threshold of water vapor for aluminum and water and oxygen for fuel materials. For helium-cover-gas storage in a sealed system, there would initially be some water vapor even in a closed system. Under air and water vapor conditions, nitric acid would be produced when the radiolysis product, NO_2 contacts H_2O [1, 3]. Simulation of this condition by exposing aluminum cladding alloys to nitric acid solution vapors has shown greatly accelerated corrosion rates over those from water vapor alone [3].

3.2.2.2 Al-U Alloy Corrosion in Water Vapor in Air or in Non-Reactive Gas

Tests of corrosion of aluminum-uranium alloys have been performed in the corrosion test program [3] and show the corrosion of the material to be similar to the aluminum claddings. Tube specimens of aluminum 8001 clad, Al-18%U and Al-33%U alloys containing machined pits were exposed to 150°C at relative humidities of 20, 50, 80, and 100% and to 200°C at a relative humidity of 100%. A black oxide film, adherent to the fuel substrate formed on regions of fuel exposed to the environment. The oxide appeared to form a passive film that did not appear to be effected by the coupled clad/fuel configuration. The X-ray diffraction results show the oxide to be a combination of Boehmite and U₄O₉ and UAl₄ particles. The metallographic results of the tube specimens exposed to 100% RH show that the thickness of the oxide over the fuel material to be approximately one to four times as that formed on the adjacent 8001 aluminum cladding. No oxide films were apparent on either the cladding or exposed fuel of the tube specimens exposed to 20% RH.

Additional tests were run with coupons of Al-10%U exposed to 200°C at 100% relative humidity [3]. This material was in a heavily-worked condition with regions of small (average size < 1 μm) aluminides. The corrosion of this material in this form was observed to be much greater than the Al-U in the fuel tube specimens which had been extruded. Mild hydrogen blistering was observed following exposure to 200°C, 100% relative humidity of the heavily-worked sheet material for a one week period whereas no blistering was observed in the Al-18%U and Al-33%U materials in the extruded tube specimens.

Aluminides were observed in the oxide film and they did not appear to be attacked in the oxidation of the aluminum matrix. This is expected since the aluminides should be cathodic to the aluminum matrix and the effect of this microgalvanic couple would be to enhance the formation of the aluminum hydrated oxide layer which was observed [3].

3.2.2.3 Uranium Corrosion in Water Vapor in Air or in Non-Reactive Gas

Corrosion of unirradiated uranium has been measured and a model has been developed to calculate the rate of uranium oxidation at any temperature/water vapor pressure combination in the range 0 to 350°C and 0 to 101.3 kPa (760 Torr) [42, 43]. The kinetic equation is:

$$w = \frac{0.4195pe^{\left(\frac{-6432}{T}\right)}}{1 + 2.48 \times 10^{-7}pe^{\left(\frac{52236}{T}\right)}} + 10.95e^{\left(\frac{-8077}{T}\right)} \quad (5)$$

where w is the corrosion rate in kg of O₂ per m² per second, p is the partial pressure of steam in kPa, and T is the temperature in K. The first term in the expression is the steam oxidation rate contribution and the second term is the dry air oxidation rate contribution. This kinetic equation shows that uranium corrodes linearly in time and therefore does not form a passivating film to effectively "slow down" the rate of corrosion with time.

The products from reaction of uranium with air are UO₂, U₄O₉, U₃O₇, and U₃O₈ at higher temperatures and are the same as for the reaction of uranium with water [22, 44-46]. Extensive studies of uranium oxidation have shown that reaction rates depend upon relative humidity and temperature, and are suppressed by oxygen, but are not affected by the presence of nitrogen, hydrogen, and carbon dioxide [44, 45]. At temperatures up to 100°C, uranium reacts with air forming a yellow tarnish film of UO₂ which converts to a blackish UO₂ after several days exposure under normal humidity [24]. Up to

200°C the oxide formed is UO_2 . U_3O_8 is the oxidation product above 275°C and is the stable oxide. The thin tarnish film of UO_2 is mildly protective, whereas the blackish UO_2 and U_3O_8 are not [24].

4.0 ACCEPTANCE CRITERIA

Ensuring no degradation of the aluminum-clad fuels during interim dry storage would be economically prohibitive and would require the highest levels of drying and stabilization, absolutely sealed containers with adequate cooling, and sensitive monitoring throughout the storage period to ensure no leaks in the storage container. Therefore, allowances for degradation must be made in an engineered dry storage system to achieve a reasonable, cost-effective design of this system including staging and storage facilities. Fuels retrieved from basin storage would be handled and transported to a staging facility for drying and other substeps before placement into a dry storage facility.

Limits to acceptable degradation during the drying and the storage period are needed to enable post-storage handleability, a full range of ultimate disposal options, criticality safety, and radionuclide confinement by the fuel/clad system.

Normal handling of the fuel does not impose significant loadings above self weight. Fuel assemblies have a minimum cladding thickness (MTR fuel) of 0.010" covering fuel of 0.050" thick and contained within support side plates. A loss of 0.003" of each aluminum surface during dry storage would not impact the integrity of the fuel assembly during normal handling. Similarly, a loss of 0.003" from fuel exposed through a pit or even a larger breach would not impact the fuel integrity.

A limit to the amount of plastic deformation is needed for handleability to ensure that the fuel is removable from the storage container, and is needed to ensure no significant reconfiguration of the fuel by slumping which may impact criticality safety.

A set of release limits is needed to provide a level of primary confinement as characterized by release of fuel and radionuclides from the fuel/clad system. These limits are not specified in this report. It is assumed that any corrosion of the fuel material is not confined by the cladding. That is, no credit is taken for the adherency of oxide films on the fuel. This is conservative, especially for fuels that are dispersed in an aluminum matrix (i.e. dispersoid fuels). These materials would have an adherent oxide layer on the aluminum approximating the characteristics of the aluminum hydrated oxides. Credit is taken, however, for the passivation and resistance to corrosion of the dispersoid fuels in predicting its corrosion response. For example, corrosion of the dispersoid fuel materials in dry air (< 20% relative humidity) is not significant at all temperatures below 200°C since these fuels should behave similarly to aluminum in their corrosion response¹. Uranium metal however is not resistant to corrosion in dry air (does not readily passivate) and corrosion at a linear rate predict by equation (5) above would be used for fuel exposed to the environment.

¹Only the Al-U alloy fuel is being presently tested in the corrosion program. The results to-date [3] show that low humidity (~ 20% relative humidity) air is a threshold for corrosion of aluminum cladding alloys and for extruded Al-U at 18 and 33% U at dry storage temperatures (~ 150°C). Testing of Al-U oxide and Al-U silicide dispersoid fuels is recommended to verify the assumed similarity in corrosion behavior to Al-U alloy dispersoid fuel.

Summarizing the above discussion, acceptable degradation during dry storage includes the following set of changes to the fuel condition during dry storage as received from basin storage:

- 1) General corrosion or pitting corrosion up to 0.003" in depth of the cladding;
- 2) General corrosion or pitting corrosion up to 0.003" in depth of any exposed fuel (core) material;
- 3) Release of the fuel and fission products up to a predetermined limit from any single fuel assembly in a non-sealed storage system;
- 4) Plastic deformation of fuel elements up to 1" over a length of fuel assembly length of 3', not to exceed 3/4 of clearance space between fuel assembly and storage grid; and
- 5) No rupture of the cladding due to creep or due to severe embrittlement.

Maintaining changes to the fuels' condition within acceptable degradation is consistent with the requirements for dry storage of commercial spent nuclear fuel given in Title 10 of the U.S. Code of Federal Regulations, Part 72, paragraph h, which allow no large breach of the cladding during storage and subsequent handling.

Acceptance criteria are developed to ensure that the aluminum-clad fuels are within this acceptable degradation for a period of 50 years. Two distinct storage systems are considered: 1) sealed (with drying, provides limited contact with corrodant species) and 2) non-sealed (allows ambient air to contact fuel) in both a breached and non-breached condition yielding four sets of acceptance criteria each for both the Category 1 & 1A fuels and the Category 2 fuels (defined below). The drying criteria, stabilization need, and storage criteria for the sealed and non-sealed systems are discussed in sections 4.1 and 4.2, respectively. These criteria are based on the engineering analyses and laboratory-scale testing provided in references 1 to 4.

The aluminum-clad fuels to be dry-stored are categorized by fuel material response to environments. Category 1 material is aluminum-uranium (Al-U) alloy fuel. This material is comprised of a microstructure of uranium aluminides dispersed in an aluminum matrix and the fuel is metallurgically bonded to the aluminum cladding. The corrosion response of the aluminum-uranium fuel exposed to temperatures up to 200°C and relative humidities up to 100% is similar to that of the aluminum-alloy cladding as both exhibit the formation of a passive oxide layer under humid conditions and do not corrode in dry air.

Category 1A material is the balance of fuels that contain the uranium compounds in the form of oxides or silicides which, like category 1 fuel material, are dispersed in a matrix of aluminum, and that have the fuel bonded to the aluminum cladding. The category 1A fuels are typically low enrichment, fuels and are typically run to high burnups. The corrosion response of the category 1A materials should be similar to the category 1 material, but these fuels were not specifically tested in the corrosion program [3].

Category 2 materials are uranium metal and any other uranium alloy fuel that is not uranium compound dispersed in a matrix of aluminum. Uranium metal is more susceptible to corrosion than the category 1 and 1A materials since it does not readily form a passive film and can corrode under dry air conditions.

The initial conditions of aluminum-clad fuels that have been stored in basins include assemblies with pitting in the cladding due to localized corrosion. The physical examination of fuels to ensure

no thru-clad pitting (i.e., breached vs. non-breached) would be difficult and may involve the development of advanced NDE techniques. For this reason, it is assumed that fuels contain through-clad pits at the onset of visual detectability, assumed to be one 1/32" diameter pit per 1 square inch of cladding area. This is an assumed breach of approximately 0.1% of the cladding. Breaches at and below this level should not be subject to excessive release of volatile fission products; however, this assumption needs to be demonstrated. Category 1 fuels are not subject to excessive degradation in dry air whereas category 2 fuel would be susceptible to corrosion in air especially at high temperatures. Damaged fuel that is not readily handleable from basin storage should be canned for dry storage.

The acceptance criteria are formulated from an upper bound prediction of degradation corresponding to the limits for drying and storage environmental conditions. No uncertainty analysis has been performed in the predicted degradation. The difference between the predicted degradation at the conditions of the acceptance criteria and the acceptable degradation provides a pad to account for the combined uncertainties.

Dry storage of aluminum-clad fuels in foreign dry storage facilities [47] is being successfully achieved as the degradation is apparently within acceptable bounds as defined in this report. The storage is at low storage temperatures, estimated to be less than 50°C; the other conditions of storage are also within the acceptance criteria specified in this report. The possible exception is that the criterion for flowing air for a non-sealed storage configuration may not be met in the non-sealed storage system used in Canada.

4.1 Sealed System

A sealed storage system is one in which a fully-sealed container enclosing one or more fuel assemblies is placed within a dry storage facility. The approach to avoid excessive degradation in a sealed system is to dry the contents to a level of free water (remaining in the container to-be-sealed) such that if all water is fully consumed by corrosion of the fuel, that: 1) the conditions of acceptable degradation are not exceeded; 2) the production of hydrogen does not pose a threat to post-storage retrieval due to build-up of hydrogen to levels that could result in a deflagration event; and 3) the production of hydrogen does not pose a threat to post-storage retrieval due to production of pyrophoric substances. The temperature (upper) limit is based on the most limiting non-corrosion degradation mechanism.

4.1.1 Drying Criteria

The total amount of waters available for corrosion are from three basic sources. These are: 1) free water (which includes water in pits in the cladding, crevices, etc.); 2) waters of hydration on existing oxide; and 3) adsorbed waters on oxide and on aluminum. The amount of adsorbed water on the surface of a metal varies with the relative humidity and the temperature. Volpe [48] determined that at 20°C, the amount of absorbed water is approximately 20 monolayers at 100% relative humidity. This is much less than the water of hydration in a 50 µm Boehmite film, assumed to be the initial condition of the cladding, and is therefore negligible.

Drying to a free water level of 9.4 grams per cubic meter of volume of the container (pit) has been suggested by licensing authorities in Germany [49]. The container could hold 2 MTR elements and therefore approximately 1.9 gms water per m² of cladding surface would be available for corrosion.

As a candidate drying criterion in this work, drying to 1 ml free water per 0.1 m² of cladding surface (equivalent to 10 gms/m²) yields approximately 0.0001 inches of uniform aluminum corrosion. Dehydration of the hydrated oxide layers is not readily achievable nor is necessary in drying. The waters of hydration from Boehmite (assumed to be released in storage due to radiolysis) for a film of 50 μm is assumed to be released and to corrode the aluminum cladding to form Al₂O₃. It does not recombine with the original Al₂O₃ left from dehydration of Boehmite. This results in 0.0002 inches of aluminum corrosion. Therefore, the maximum possible uniform consumption of aluminum dried to 1 ml per 0.1 m² of cladding surface in a sealed system is approximately 0.0003 inches which is well below the acceptable 0.003 inches of cladding consumption.

Hydrogen build-up occurs in a closed system according to:



Assuming the reaction goes to completion, 1 ml of H₂O yields 0.042 moles of H₂. A general formula can be derived to relate the volume fraction of free water to the hydrogen pressure for the reaction to completion [4]:

$$\frac{FW}{V} = 292505 \frac{P_{H_2}}{(273.15 + T)} \quad (6)$$

where FW is the free water volume in ml;
V is the volume of the container in m³;
P_{H₂} is the pressure due to H₂ in atmospheres;
and T is the temperature in °C.

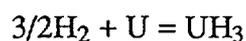
One impact of hydrogen buildup is the potential for an explosion hazard. The explosive range of hydrogen is 4 to 75 percent by volume in air at room temperature. Therefore, the partial pressure of hydrogen must be below 0.59 psia or the ratio of free water (ml) to the volume of the container (m³) must be kept below 39 to ensure that hydrogen at 4 volume percent of a container with air is not produced.

Another impact of hydrogen buildup is the potential for production of UH₃, a compound which is pyrophoric under certain conditions. For category 1 and 1A, dispersoids such as UAl_x are not expected to be reduced by hydrogen atmospheres to produce UH₃; however, oxides of uranium could be if the partial pressure of H₂O is low enough and the partial pressure of H₂ is high enough in an H₂O/H₂ system. However, because aluminum surrounds the oxides in the dispersoid fuel and does not allow direct contact with the fuel particles, this is not expected to result in significant production of UH₃.

For exposed uranium metal (category 2 fuel), H₂ buildup should be limited to avoid significant UH₃ formation. Considering the reactions



and



with the simple assumption that the reactions go to completion results in the formation of 1 mole of UH₃ for each two moles of H₂O consumed.

Figure 2 shows an example case of hydrogen build-up with time in a closed capsule for the assumption of reaction to completion and using corrosion rates corresponding to saturated vapor conditions at 150°C [3].

A limit to the cladding temperature of 250°C for non-breached cladding is imposed as a short term (2 hours) limit under all relative humidity conditions. This limit would avoid excessive creep which may occur under longer term exposure and would avoid the potential for hydrogen blistering. For breached cladding, the temperature should be kept below 200°C since mild hydrogen blistering has been observed in dispersoid fuel exposed to 200°C at 100% RH for 1 week [3].

4.1.2 Stabilization

Considering the potential for existing UH₃ on uranium metal fuels retrieved from basin storage, only uranium metal fuels may need to be stabilized. The INEL has developed a stabilization treatment with the technical bases [51] to convert UH₃ to uranium oxide. As discussed in section 4.1.1, the amount of water enclosed in a sealed canister could be controlled to avoid production of additional UH₃.

4.1.3 Storage Criteria

The results from the capsule tests in the corrosion program [3] show that consumption of the corrodant species will eventually lead to cessation of consumption of the fuel and cladding materials.

Assuming that the oxides on the cladding of as-received fuels would range in thickness from 10 nm to 50,000 nm (50 μm) [14], and that pre-storage drying and handling would not de-hydrate, remove, or otherwise change the oxide, any additional corrosion during the storage could lead to sloughing off of the film. However, films approaching 100 μm with no slough off under vapor conditions have been observed in the corrosion testing program. Given that the maximum estimated increase due to storage in a sealed system at the drying conditions above would be less than 1 μm (0.0003"), the films will remain adhered.

Due to creep and diffusion of fission gases and products as summarized in section 3, 200°C is an upper limit for storage temperature in the sealed storage system.

4.2 Non-sealed System

A non-sealed system is one in which fuel would be in contact with the ambient air in a dry storage facility (e.g. outside air temperature and relative humidity conditions). Since the corrosion of aluminum exposed to ambient air corrodes at a slow rate, even at high humidities (up to 100%) at near room temperatures [50], storage in a non-sealed system is feasible in "non-dirty" atmospheres (those containing low chloride and sulphate compounds). It is not possible to produce high humidities (up to 100%) at high temperatures (up to 200°C) in non-sealed system and therefore cladding materials would not experience the corrosion rates observed in corrosion testing program [3].

The corrosion response of the fuel meat of dispersoid fuels (i.e. the category 1 and 1A fuels) should be approximately the same as aluminum alloys. That is an adherent, protective layer of hydrated aluminum oxide should form and continue to grow under humidity conditions.

Category 2 fuels (uranium metal) do not form protective oxides layers and can still corrode in air at a linear rate, significantly if at high temperatures (see section 3.2.2.3, equation 5). Therefore storage of breached category 2 fuel can only be stored at low temperatures ($\ll 200^\circ\text{C}$) to avoid significant corrosion predicted by equation 5 for a 50-year interval.

4.2.1 Drying Criteria

Pitting of aluminum can occur in "dirty", urban atmospheres that contain chlorides and sulphates [41]. Pitting was observed in a test run of the corrosion testing program when chloride contamination was present. A rinse step in high quality water (low Cl, SO_4 , neutral pH, and low ($< \sim 50 \mu\text{S/cm}$) conductivity) is highly recommended for fuels received from basins and the storage containers for a non-sealed system to reduce potential for pitting corrosion to occur. Therefore there should be no pitting that occurs in non-sealed system although minor, general corrosion would occur (see 4.2.3 below). After the rinse, a general drying should be performed to remove bulk water from crevices of the fuel.

4.2.2 Stabilization

Non-breached fuels of both categories 1 and 1A and category 2 do not require stabilization (against pyrophoricity) treatments. Also, as discussed in section 4.1.1, breached category 1 and 1A fuels would not contain significant levels of uranium hydride and would not require stabilization.

An open system would not provide for the generation of uranium hydrides since no partial pressure of hydrogen could be established. Considering the possibility for existing UH_3 on breached aluminum-clad, uranium metal fuels retrieved from basin storage, stabilization could be performed as a protection against pyrophoricity. The potential for pyrophoricity has been estimated to be low [27].

Pyrophoricity of uranium metal, even at temperatures up to 200°C would not be expected unless the uranium metal were finely divided particulates [52].

4.2.3 Storage Criteria

The results of the corrosion program [3] show that a threshold RH exists below which corrosion stops for the aluminum cladding alloys. Figure 3, reproduced from reference 3 shows the results for aluminum 6061 exposed to various initial relative humidities at 150°C in sealed capsules. The data clearly show the trend that a reduction in the relative humidity leads to less corrosion at a given time and also the demonstration of the threshold of approximately 20%RH needed for corrosion of aluminum to occur. The results to date from the tube specimens of Al-18% and Al-33%U alloy fuel [3] also shows a threshold of approximately 20%RH for corrosion of Al-U alloy, although the results are based on visual observation data only.

Godard [50] investigated experimentally the effects of humidity on the corrosion response of aluminum alloys at room temperature. After 5 years at 100% relative humidity, had a maximum film thickness of $0.3 \mu\text{m}$. A conservative estimate of the growth to 50 years is 10 times this result yielding $3 \mu\text{m}$ of oxide. The data of Godard is shown on Figure 4 along with the high temperature (150 and 200°C), 100% RH data from the corrosion testing program [3]. Extrapolation of this log-log plot is use to estimate the effect of continued corrosion (non-limited-specie system) at the extremes of potential storage temperatures and humidities. Extrapolation of the low temperature trend to 50 years does not result in corrosion which would violate the condition of acceptable corrosion. It is not possible to produce a high humidity condition in an open system. Table 7 lists the RH vs. Temperature for an initial volume of air at 100°F (38°C), 90% RH. For example, if air

inlet to a dry storage facility at 38°C, 90% RH picked up heat as it flowed over the open containers of the fuel, it may exhaust the facility at 100°C but the RH would have fallen to 6.9%, well below the expected threshold for corrosion of aluminum cladding and dispersoid fuels of at least 20%.

Table 7 - RH vs. Temperature for Air Initially at 38°C (100°F), 90% RH.

Temperature (°C)	Relative Humidity (%)
38	90
50	50
100	6.9
150	1.6
200	0.5

Assuming that the oxides on the cladding of as-received fuels would range in thickness from 10 nm to 50,000 nm (50 µm) [14], and that pre-storage drying and handling would not de-hydrate, remove, or otherwise change the oxide, any additional corrosion during the storage could lead to sloughing off of the film. However, films approaching 100 µm with no slough off under vapor conditions have been observed in the corrosion testing program. Given that the maximum estimated increase due to storage in a sealed system at the drying conditions above would be less than 3 µm, the films will remain adhered.

No RH threshold exists for the corrosion of uranium metal (category 2) fuel. When exposed to dry air, breached uranium fuel can be oxidized to UO₂ and subsequently to U₄O₉, U₃O₇, and U₃O₈ and can lead to enlargement of the breach and potential for sloughing off and dispersal of the fuel. Due to this predicted behavior, an acceptable temperature of storage of breached uranium metal fuel would have to be less than 200°C. An acceptable temperature limit for this fuel has not been specified in this report.

In air storage, radiolysis can cause combination of N₂ and O₂ to NO₂ and other N_xO_y gases which leads to the formation of HNO₃, if H₂O present, and increased corrosion over that from water vapor alone (see section 3 above and references 1 and 3). However, at low humidity conditions, the corrosion is still markedly reduced from that at high humidity conditions (see results in reference 3 at 100% and 20% RH with a nitric acid solution). Flowing air is required to sweep N_xO_y gases in a non-sealed system to avoid increased corrosion over that from water vapor alone. Experiments are in progress in the corrosion program to further investigate the effect of gamma radiation in an air/water vapor environment on the corrosion of aluminum cladding alloy materials.

Tables 1 and 2 in section 1 of this report summarize the above discussion.

4.3 Recommendations

Laboratory testing in the corrosion program is continuing. Sealed capsules containing water vapor and air are being exposed to environments at the acceptance criteria temperature limit (200°C) including separate runs in a gamma field. In addition, tests to measure the release of volatile fission products and gases from breached fuel (well-characterized as to the extent of breach, fuel microstructure, radionuclide composition, etc.) are being performed to provide a benchmarked estimate of the release at and above the present temperature limit of 200°C. The following recommendations are for additional tasks to ensure the successful storage of aluminum-clad fuel in a full-scale dry storage facility.

- 1) The corrosion response of the aluminum-uranium oxide and aluminum-uranium silicide dispersoid fuels has been assumed to be similar to the aluminum-uranium alloy fuel. Expansion of the corrosion testing program to include these fuels is recommended.
- 2) Validation of dry storage technologies using model irradiated materials is recommended. A plan to use SRS Mark 31A target slugs which are an Al 1100 clad, uranium metal core system has been prepared.
- 3) A demonstration facility prior to design and construction of a full-scale dry storage facility had been previously recommended [53] to validate the acceptance criteria and the heat transfer analytical tools. A reduced scope test with full length spent fuel currently being stored at LANL is an option for a validation and verification activity and may eliminate the need for a full-scale demonstration prior to design and construction of a dry storage facility.

Figure 2: Calculated Hydrogen Build-up in Capsule of Volume 70 ml. Initial volume of water at room temperature of 0.155 ml (0.00861 moles of water), leads to H₂ at a final pressure of 47 psia at 150°C (33 psia at 20°C) from the 0.00646 moles of H₂ produced. The pressure due to the initial water (before corrosion) is 70 psia at 150°C.

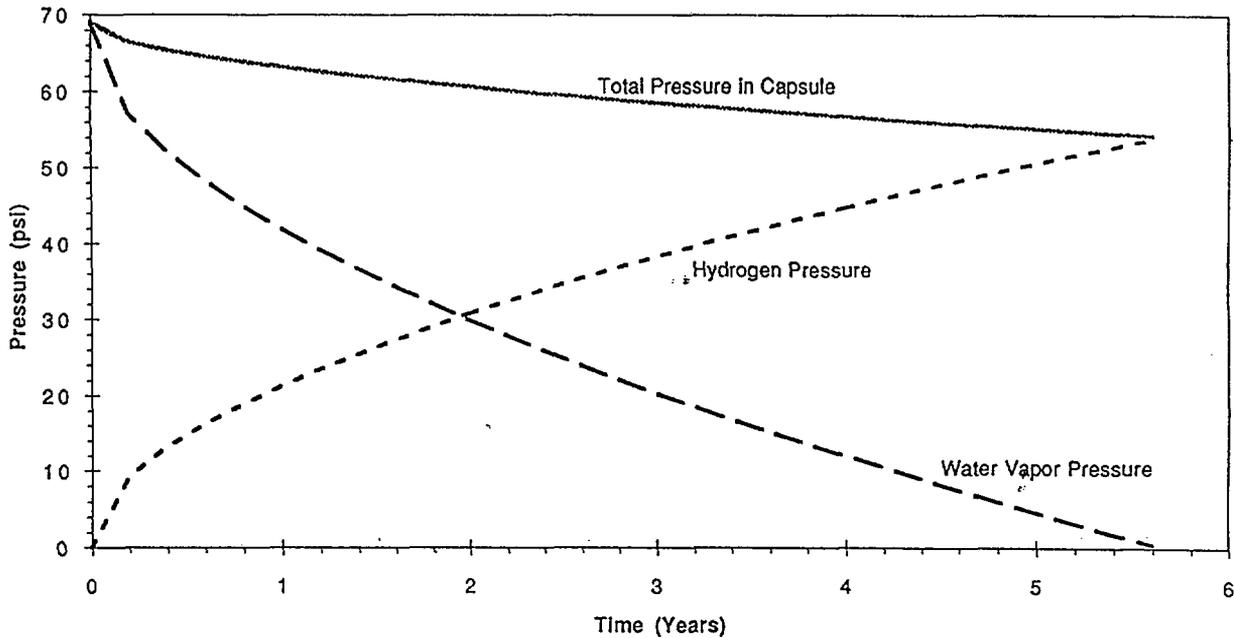


Figure 3: Weight Gain Data for Al 6061 from Capsule Tests [3].

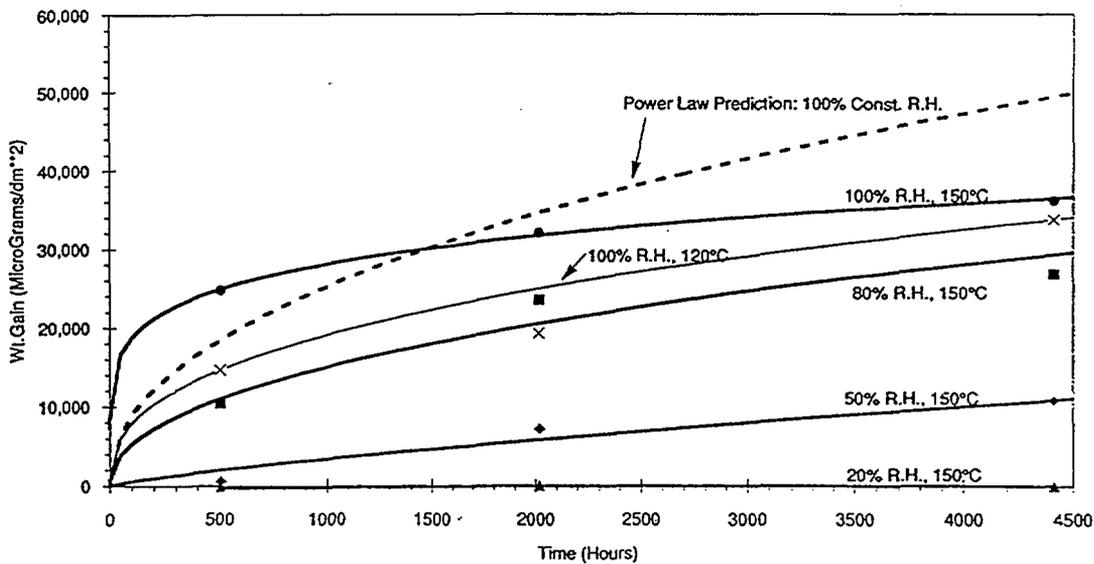
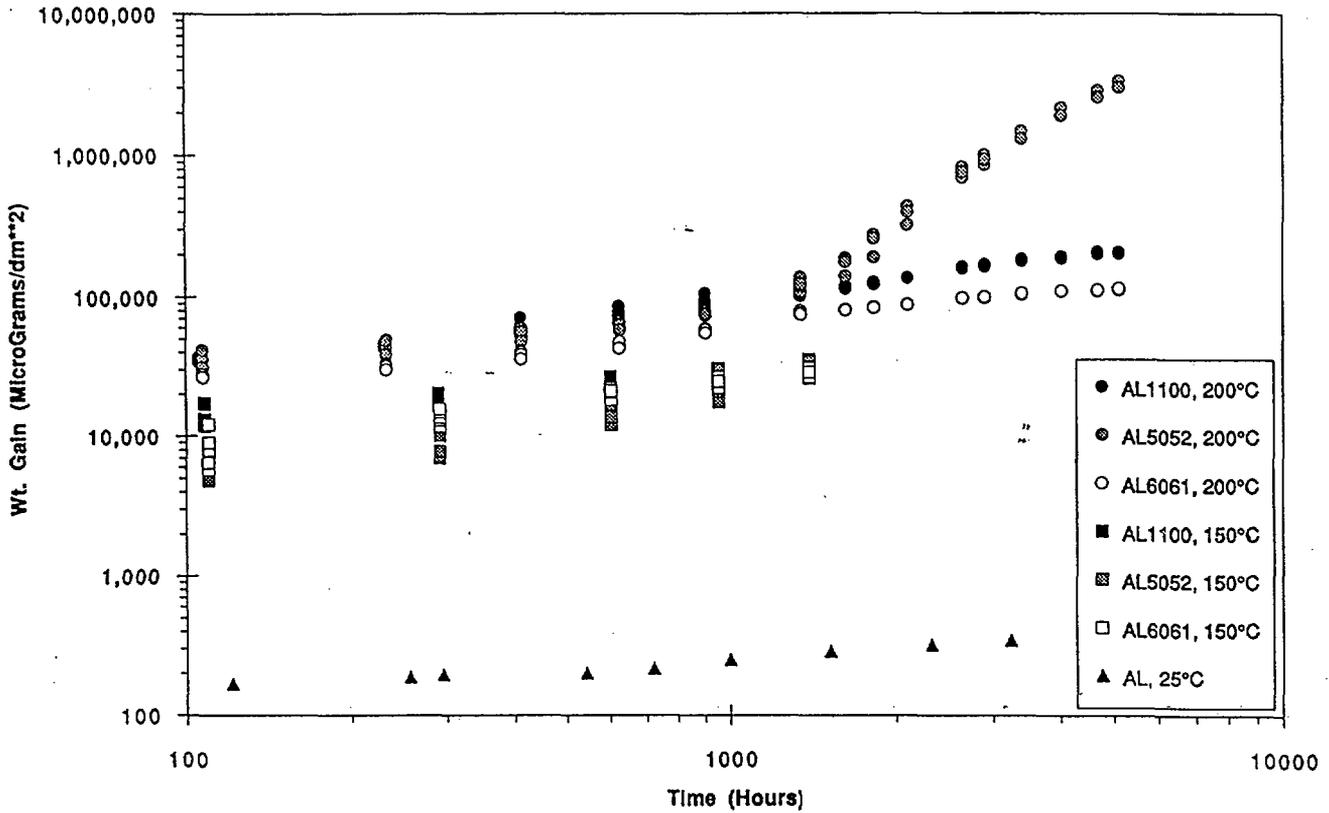


Figure 4: Weight Gain Data Compiled from Aluminum Alloys Exposed to 150 and 200°C from the Autoclave Corrosion Testing Program [3] and to 25°C [50] at 100% Relative Humidity. Note that the aluminum consumed (mils) = $1.193E-6 \times$ wt. gain ($\mu\text{g}/\text{dm}^2$) and the oxide film thickness (nm) = $0.053319 \times$ wt. gain ($\mu\text{g}/\text{dm}^2$) [4].



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