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**MATERIALS ISSUES IN INTERIM STORAGE AND DIRECT DISPOSAL
OF ALUMINUM CLAD SPENT NUCLEAR FUEL**

by

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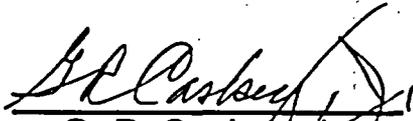
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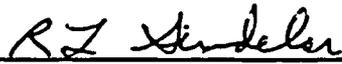
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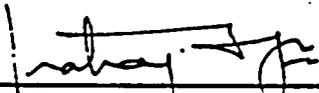
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SUMMARY

This report reviews the material properties and behavior of aluminum based fuels and aluminum cladding alloys as technical background for development of acceptance criteria and specification of environmental conditions for dry storage of aluminum clad spent nuclear fuel (SNF). A preliminary assessment has been made of material properties and environmental conditions as they affect the safe storage of aluminum clad SNF over long time periods. Topics that require further evaluation have been identified.

Direct disposal of highly enriched aluminum clad spent nuclear fuel (HE-SNF) in a geologic repository is an alternative to chemical treatment of the fuel, but a waste form and repository for final disposition of these fuels have not been selected. Consequently, interim dry storage in a monitored retrievable storage (MRS) facility will probably be needed for many decades. Both final disposal and interim storage require that the HE-SNF remain critically safe (continually meet the minimum required sub critical safety margin of $\Delta k_{\text{eff}} = 0.05$ for federal repositories) and that fission product release be prevented. During interim storage 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. Storage conditions and facilities for interim dry storage of Zircaloy clad uranium oxide fuels from light water reactors (LWR) have been developed and have been operated successfully in several countries including the United States. However, acceptance criteria have not been defined and facility designs have not been demonstrated for interim dry storage of aluminum clad spent nuclear fuel.

In order to assure cladding integrity and maintain fuel element dimensions for up to 100 years, the maximum temperature for interim storage of aluminum clad SNF should be held below 150°C. The ductility of irradiated 1100 and 6061 aluminum reduces to less than 1% between 150 and 200°C making the cladding susceptible to failure. Other limitations on the temperature and atmosphere for interim dry storage of aluminum based fuels are:

- Any protection afforded by the oxide films on aluminum is degraded above ~ 120°C because of initiation of dehydration, shrinking, and structural changes in the oxide film.
- Cesium and uranium can diffuse through a 0.030-inch thick aluminum cladding within 100 years at temperatures above 200°C.
- Corrosion of uranium may continue in the presence of any moisture with concurrent swelling and fragmentation of the uranium for temperatures above ~80°C. Encapsulation of fuel elements with breached cladding is desirable to avoid further damage.

- Reaction of aluminum with moist air at temperatures above -250°C forms blisters that could split the cladding.

Direct disposal of aluminum clad spent fuel in a geologic repository requires further evaluation of the following potential problems:

- Compatibility of possible nuclear poisons with the fuel and cladding materials.
- Selective leaching of possible nuclear poisons, fission products, or fissile isotopes from spent fuel.
- Analysis of the mechanical stability of aluminum base fuels taking into account irradiation effects and annealing during long time storage at elevated temperatures.
- Analysis of the effects of radiolytic decomposition products on corrosion of aluminum, uranium, uranium alloys, and aluminum-uranium alloys.
- Consequences of microstructural instability and phase changes during prolonged exposure at moderate temperatures.

INTRODUCTION

Direct disposal of highly enriched aluminum clad spent nuclear fuel (HE-SNF) in a geologic repository is an alternative to chemical treatment of the fuel, but a waste form and repository for final disposition of these fuels have not been selected. Consequently, interim dry storage in a monitored retrievable storage (MRS) facility will probably be needed for many decades. Both final disposal and interim storage require that the HE-SNF remain critically safe (continually meet the minimum required sub critical safety margin of $\Delta k_{\text{eff}} = 0.05$ for federal repositories) and that fission product release be prevented. For interim storage 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. Storage conditions have been developed for interim dry storage of Zircaloy clad uranium oxide fuels from light water reactors (LWR). Facilities for dry storage of these fuels have been operated successfully in several countries including the United States. However, acceptance criteria have not been defined and facility designs have not been demonstrated for interim dry storage of aluminum clad spent nuclear fuel.

A preliminary assessment has been made of material properties and environmental conditions as they affect the safe storage of aluminum clad SNF over long time periods. Topics that require further evaluation have been identified. Properties of aluminum based fuels and cladding alloys were reviewed to provide technical background for development of acceptance criteria and conditions for dry storage of

aluminum clad SNF. The background data and conclusions are applicable to any aluminum clad SNF from research reactors within the United States (USRR), from foreign research reactors (FRR), and for interim dry storage of Savannah River Site (SRS) spent fuel if needed. The review applies to both interim dry storage and direct disposal in a geologic repository.

Interim dry storage of aluminum based SNF is assumed to follow the general scheme adopted for LWR-SNF. The SNF would be examined, stabilized if needed, placed in a canister, basket, or capsule, and then stored in a cask, vault, or dry well. Evaluation of material properties that govern prolonged (50-100 year) dry storage of aluminum clad SNF is guided by prior work on dry storage of LWR-SNF by Pacific Northwest Laboratory (PNL) and Idaho National Engineering Laboratory (INEL) and by development of waste forms for high level waste (HLW) at the Savannah River Technology Center (SRTC) and Lawrence Livermore National Laboratory (LLNL) .

BACKGROUND

The United States Department of Energy "owns" a wide variety of spent nuclear fuel residing in reactors or storage pools within the United States and overseas [1]. A portion of this inventory is aluminum clad fuel that contains high enriched uranium. The aluminum clad fuels from offsite that are stored in Receiving Basin for Offsite Fuel (RBOF) and the SRS reactor fuels are representative of this type of spent fuel.

OFFSITE SPENT FUEL AT SRS

SRS has acquired a wide variety of spent fuel from research and other reactors located within the United States and foreign countries. The core and cladding materials currently stored in RBOF are listed in Table 1 which is a summary of a presentation to the Defense Nuclear Facilities Safety Board [2]. Fuels clad with stainless steel, high temperature alloys, or zirconium alloys are classed as "nonprocessable" at present and would require installation of equipment for the mechanical or electrochemical penetration of the cladding [3].

Table 1

Off-Site Spent Fuel Stored in RBOF

<u>Fuel Material*</u>	<u>Cladding Alloy</u>
UO ₂ (LE/D)	1100 Al
UO ₂ - ThO ₂ (LE/HE)	6061 Al
UC (LE)	1050 Al
UO ₂ - PuO ₂ (LE/D)	990 Al
UO ₂ (LE/HE)	Type 304**
UO ₂ - ZrO ₂ - CaO (HE)	Type 316**
U-Zr	Type 348**
UO ₂ - BeO (HE)	Hastelloy-X**
UO ₂ - PuO ₂ (HE)	Nichrome**
PuO ₂	Zirconium**
Al-U	Zircaloy-2**
U ₃ Si ₂	Zircaloy-4**
Thorium	
Uranium	

* D = depleted. LE = low enriched. HE = high enriched.

** Fuel clad with these alloys are currently nonprocessable at SRS.

The aluminum clad fuels were received from research reactors in the United States, Japan, and Taiwan over a period of several decades. A variety of burnups, cooling times, heat generation rates, dimensions, and shapes are represented among these fuels. In addition to the SNF listed above, other SNF may be returning to the US during the next decade from FRR. These fuels are aluminum clad also and are primarily the types listed in Table 2. SRS is a potential site for interim dry storage of all aluminum clad fuels that are under DOE control.

TABLE 2

Foreign Research Reactor Spent Fuel

<u>Fuel Material</u>	<u>Cladding Alloy</u>
Aluminum-Uranium Alloy	1100 Aluminum
Uranium Oxide	6061 Aluminum
UAl-Si	(?) Aluminum
Uranium Silicide	6061 Aluminum
Uranium Metal	6061 Aluminum
	(?) Aluminum

SRS SPENT FUEL

The reactor disassembly basins were designed and intended only for temporary storage of irradiated fuel and targets from the Savannah River Site (SRS) reactors pending processing by the Separations Department. At present, uncertainties in the processing schedules may require interim storage of fuel that is now in P, K, and L basins until chemical processing resumes. Continued storage of irradiated components now in the reactor basins is undesirable unless the ongoing pitting corrosion of the aluminum claddings can be mitigated by improving and controlling the purity of the basin water. In addition, encapsulation of corroded fuel

would be required if basin storage were to be continued indefinitely. Welds on the Mark 31 target slugs are potentially more vulnerable to corrosion than the wrought cladding and may become the sites for leaks because of manufacturing defects or handling damage that are acceptable in the short term but which may eventually fail after prolonged (>twenty year) storage under water.

The current operating plans for SRS include processing of all irradiated aluminum-uranium fuel tubes (Mark 16B, 22, 60B), aluminum-lithium targets (Mark 16B) and uranium targets (Mark 31) 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 31 fuel and targets. Zircaloy clad driver tubes of zirconium-uranium alloy from the Heavy Water Components Test Reactor (HWCTR) are also stored in RBOF along with Zircaloy clad uranium oxide test assemblies that were irradiated in the HWCTR during the early 1960's. The Zircaloy clad assemblies are currently classed as "nonprocessable" along with other off-site fuel stored in RBOF. At present there are no plans to process the HWCTR fuel. The types of SRS fuel and targets currently stored in reactor disassembly basins and canyons and the HWCTR fuel in RBOF are identified in Table 3 [2].

Table 3
SRS Spent Fuel and Targets in Reactor Basins, Canyons, and RBOF

<u>Designation</u>	<u>Core</u>	<u>Cladding</u>	<u>Location</u>	<u>Condition</u>
Mark 16B	Al-U	8001 Al	P,K,L	Pitted
	Al-U	8001 Al	RBOF	No evidence of corrosion
Mark 22	Al-U	8001 Al	P,K	Pitted
Mark 60B	Al-U	8001 Al	K	Pitted
Mark 31	U	1100 Al	L, F-Canyon	Pitted
		1100 Al	RBOF	No evidence of corrosion
Mark 42	PuO ₂	Al	P	Pitted
Mark 18A	Pu(?)	Al	RBOF	Unknown
HWCTR	Zr-U	Zr	RBOF	No evidence of corrosion
HWCTR	U Oxide	Zr	RBOF	No evidence of corrosion
HWCTR	U	Zr	RBOF	No evidence of corrosion

METALLURGICAL CHARACTERISTICS

Technology has been developed for prolonged dry storage of Zircaloy clad spent fuel to meet the needs of the light water reactor industry [4]. However, methods for final disposal in a geologic repository have not been established for either Zircaloy or aluminum clad SNF. Both interim storage and final disposition of aluminum clad fuel require additional analysis because the material characteristics that affect the storage life and safety of the aluminum based fuels differ from those of Zircaloy clad

uranium oxide fuel. In addition, much of the fuel contains high enriched uranium which heightens criticality concerns as relocation and concentration of the fissile isotopes could lead to a criticality incident.

Durability and leaching have been identified as general characteristics of concern for evaluation of the metallurgical condition of spent fuel and the specification of conditions for safe storage. The term durability embraces chemical stability, mechanical integrity, radiation stability, and thermal stability of the fuel form. Leaching refers to the transport of hazardous substances such as fission products and fissile isotopes from within the fuel to the immediate surroundings. If disposal of spent fuel were to include incorporation of a neutron poison into the fuel form, selective leaching of the poison would need to be addressed. In the case of metallic fuels and cladding, leaching would occur by diffusion of substances through the cladding or by release of radionuclides concurrent with reaction between exposed fuel and a corrosive atmosphere.

DURABILITY

Durability is the most important metallurgical characteristic of spent fuel that affects design of storage facilities and prescription of storage conditions. The first defense against release of fission products or fissile isotopes to the environment is the cladding which must be protected from corrosion and mechanical damage. In the case of aluminum clad fuel, durability becomes a question of eliminating or minimizing galvanic, crevice, and pitting corrosion, avoiding mechanical damage, and limiting storage temperatures based on the mechanical properties, corrosion, diffusion, and oxidation behavior of the aluminum.

Chemical Stability

Evaluation of the chemical stability of aluminum clad fuels must consider several possible environments such as, inert gas, non-reactive gas, moist air, ground and surface waters, and compounds added as isotopic diluents or neutron poisons to prevent criticality.

Aluminum Corrosion

Spent fuel and targets in the reactor basins are stored in river or well water which has been filtered, is slowly circulating and is deionized from time to time. Waters in the P, K and L reactor disassembly basins are corrosive to aluminum as indicated by the high conductivity and chloride concentrations listed in Table 4 even at the low basin water temperatures of 25-30°C [5,6,7]. Analysis of RBOF water is included as an example of low conductivity water with minimum potential for corrosion of aluminum. Pitting of aluminum clad has not been observed on fuel stored for 3800 days in RBOF. However, the time to initiate pitting in water of this quality and pit growth rates are unknown. Continued corrosion of aluminum cladding, uranium,

and aluminum-uranium alloy with concurrent release of fission products are major concerns for prolonged underwater storage of spent fuel and targets in the reactor basins.

Table 4
Typical Analyses of Basin Water

Parameter	P	K	L	RBOF
Conductivity, $\mu\text{S}/\text{cm}$	142	127	138	1-3
pH	7.1	6.8	6.3	6.3-7.8
Chloride, ppm	?	6	18	< 0.01
Turbidity, NTU	<0.5	0.8	<0.5	0-1

Pitting, galvanic, and crevice corrosion are the principal modes of attack of aluminum and aluminum alloys in fresh water [8,9]. Temperature, chloride anion concentration, the presence of oxygen, and the grade of aluminum are major factors affecting the corrosion rates of aluminum cladding. The pH of the water has little affect between pH 5 and 10 in oxygenated solutions of constant chloride concentration. For example, 8001 aluminum 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 [5]. As seen in recent examinations of spent fuel and experimental coupons of aluminum in the reactor basins, pitting to depths sufficient to penetrate the 1100 and 8001 aluminum cladding can occur within a month or two [6]. 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 fresh aluminum [6]. In these cases, a fluffy corrosion product forms [7]. In many cases, there is evidence that galvanic coupling of the aluminum to stainless steel hangers and stainless steel storage buckets has been a significant factor in initiating the corrosion [7]. 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 relatively high conductivity as found in the reactor basins.

All instances of rapid corrosion in the reactor basins are associated with water of high conductivity, > 100 $\mu\text{S}/\text{cm}$ (micro-Siemens per centimeter), Table 4. In contrast, aluminum clad fuel elements have been stored in water of low conductivity (~ 1 $\mu\text{S}/\text{cm}$) in RBOF for over ten years with no evidence of pitting or galvanic attack and for up to twenty years at other installations [10]. Corrosion control for underwater storage can be achieved when the conductivity is low (~ 1 $\mu\text{S}/\text{cm}$) and concentrations of harmful impurities such as iron, copper, and mercury, as well as chloride and sulfate anions are well below ~1 ppm (parts per million).

During dry storage of aluminum, temperature becomes the principal factor affecting the corrosion rate and the nature of the oxide film. The oxide films present on the aluminum cladding when the fuel goes into reactor service consist of a thin (1-2 nm) protective barrier layer and a thicker (5-10 nm) more permeable outer layer [9,11,12]. Upon exposure to the hot water (heavy water moderator in the SRS

reactors) during reactor operation, the oxide thickens. The nature and thickness of the film depend upon the film temperature regardless of the initial thickness [9,11,12]. Beta-alumina-trihydrate (bayerite) forms when water temperatures are below 80°C and decomposes to either alpha-alumina-monohydrate (boehmite) or gamma-alumina when heated in air to between 120 and 250°C [9]. Boehmite forms when water temperatures are above 80°C and decomposes to gamma-alumina at 200 to 500°C [9]. In both cases, the film shrinks when dehydrated and may crack, thus exposing new surface to oxidation.

The 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 [9,11,12]. Final thickness is, however, a function of the relative humidity [9,11,12]. Furthermore, oxidation of aluminum in moist air can cause blister formation and would degrade the integrity of the cladding if the temperature were above ~ 250°C [13-18]. 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 [14]. 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 [16]. Blister formation during oxidation in humid air will depend on several factors: relative humidity and the area of freshly exposed aluminum determine the extent of the water-aluminum reaction and the quantity of hydrogen formed; temperature determines the solubility and diffusivity of hydrogen in aluminum; irradiation fluence and temperature establish the yield strength of the aluminum cladding. Blistering would not be expected during dry storage provided the relative humidity were low and 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 or cask. 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.

Uranium Corrosion

Uranium fuel is represented in the SNF from domestic and FRR, Table 2 and 3. In addition, depleted uranium had been irradiated in Mark 31 target slugs at SRS to generate plutonium at SRS. Corrosion of the uranium cores would occur if the cladding and bond layers of the target slugs were breached, releasing uranium, transuranic radionuclides, and fission products [19-26]. Uranium is anodic to the aluminum cladding and would corrode preferentially at cladding penetrations. Hyperstoichiometric uranium dioxide (UO_{2+x}) is the principal product of uranium corrosion in aerated water [19-21]. 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 [19-21]. A portion (~12%) of the hydrogen gas is adsorbed in the UO_2 and the remainder escapes during corrosion. At temperatures below $\sim 80^\circ\text{C}$, the film of UO_2 that forms is initially protective and further reaction is delayed for a period of time that depends upon the temperature, impurities in the water, and the condition of the uranium. Eventually, the film breaks down and corrosion proceeds more rapidly. The delay time and reaction rates are temperature dependent. In tests at 50°C , the delay before onset of rapid corrosion varied from zero to 859 hours [21]. For temperatures over $\sim 80^\circ\text{C}$, corrosion proceeds rapidly from the start with no evidence of an initial protective stage [21]. All experiments have confirmed that the presence of oxygen in the water suppresses the corrosion reaction [19-21].

The volume increase attending corrosion of uranium will generate 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 [23]. In the case of the Mark 31 slugs, iron and silicon additions of 175 ppm (by weight) are made to the uranium to control grain size and dimensional stability of the target slugs during irradiation [26]. These alloy additions should have no influence on the corrosion rate of the uranium in water or air. The uranium core and aluminum cladding are bonded through an intermediate layer of electroplated nickel [26]. Irradiation induced swelling is less than 1% and is attributed solely to accumulation of solid transmutation products for the temperatures and burnups attained during SRS irradiation [26]. Fission gases form $0.1 \mu\text{m}$ 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 [23].

The products from reaction of uranium with air are UO_2 , UH_3 , and U_3O_8 at higher temperatures and are the same as for the reaction of uranium with water [19,22,24,25]. Extensive studies of uranium oxidation have shown that reaction rates depend upon relative humidity and temperature, are suppressed by oxygen, but are not affected by the presence of nitrogen, hydrogen, and carbon dioxide [22,25]. At temperatures up to 100°C , uranium reacts with air forming a yellow tarnish film of UO_2 which converts to a blackish UO_2 after several days exposure under normal humidity [21]. Up to 200°C the oxide formed is UO_2 . U_3O_8 is the oxidation product above 275°C . The thin tarnish film of UO_2 is mildly protective, whereas the blackish UO_2 and U_3O_8 are not [21].

Aluminum-Uranium Alloy Corrosion

The fuel cores in most research reactor assemblies and in the 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 percent UAl_x

particles, where x is 3 or 4, within a matrix of commercial purity 1100 aluminum. During corrosion in water at 290°C for 60 days, corrosion rates in 15 and 53 wt % uranium alloys were 9.4 and 5.3 mils/square decimeter/day (mdd), respectively [27]. These rates are about twice those of 8001 aluminum at the same temperature. Intergranular attack has been observed at 350° at the ends of cast alloys that contain 6 to 15 wt% uranium [27].

Bayerite or boehmite are the expected corrosion products of the aluminum as discussed above. Corrosion of the UAl_x particles is assumed to form U_3O_8 and possibly a thin film of Al_2O_3 , the products which are formed by oxidation of UAl_x in air [28], or one of the hydrated oxides, bayerite or boehmite. In addition, hydrogen gas or uranium hydride would be formed. Corrosion of the aluminum matrix and the UAl_x particles would release actinides and fission products to the water or air.

Mechanical Integrity

Two general modes of mechanical failure of SNF are possible that could lead to release or redistribution of fission products or fissile material are excessive distortion and fracture of the cladding. Distortion of the fuel could interfere with cooling and lead to overheating and possibly failure. Assessment of these or other modes of mechanical failure must take into account the stresses arising during storage and the mechanical properties of the alloys which may slowly change depending upon the temperature during dry storage. Sources of stress include: thermal stress from differential thermal expansion of dissimilar alloys; weight of the assemblies; swelling from gases trapped within the fuel; volume increases from oxidation of fuel; phase changes within the core or at the clad-core interface. Mechanical damage could also occur during handling of the fuel into and out of storage and could lead to fission product or fissile material release.

Neutron irradiation affects the mechanical properties of aluminum alloys in several ways: formation of dislocation loops; void formation; transmutation produced silicon; gas bubble formation from helium and hydrogen formed by (n,p) and (n,α) reactions. Thermal neutron transmutation of aluminum produces approximately 1900 atom parts per million (appm) silicon in 1100 aluminum for a thermal neutron fluence of 10^{22} n/cm² [29]. The added silicon is present as microscopic silicon particles, or Mg_2Si if sufficient magnesium is present. For a fast fluence ($E > 0.1$ MeV) of 10^{22} n/cm², about 5 appm and 25 appm, respectively, of hydrogen and helium are produced in aluminum [29].

The temperature limit to avoid failure of irradiated 1100 aluminum cladding is between 150 and 200°C. Between 150 and 200°C, tensile ductility drops below 5% and 1% for total and uniform strain, respectively, and the fracture mode changes from ductile failure to intergranular fracture [29]. The ductility loss in non-irradiated aluminum is associated with grain boundary sliding and growth of grain boundary cavities, deformation mechanisms that occur within the temperature range for

recovery [30]. The intergranular fracture is promoted by slow strain rates and the presence of helium which stabilizes grain boundary cavities. For non-irradiated 1100 aluminum, thermal annealing of the tensile yield strength can occur as low as 100°C and complete annealing of cold work takes place in five hours at 250°C [31]. Stress rupture of 1100 aluminum can occur in about 10^7 hours at a stress of 1.5 ksi at 200°C and in less than 10^7 hours at a stress of 4.4 ksi at 100°C [30]. During prolonged dry storage the properties of irradiated 1100 aluminum are expected to gradually change toward the non-irradiated properties for storage temperatures as low as 100-150°C except for the small strengthening afforded by silicon that is generated by transmutation during irradiation. Further analysis is needed to determine if the stresses in the various fuel assemblies are sufficient to cause distortion or failure and thus contribute to the development of temperature limits to maintain structural integrity of each type of fuel.

Property changes of 6061 aluminum during irradiation are similar to those for 1100 aluminum and depend on the initial temper [32-33]. Ductility is reduced especially at test temperature of around 200°C [32]. Uniform tensile elongation reduces to below 1% for the -T6- temper at 150°C but remains above 4% for the -0- temper at fluences of above 10^{22} n/cm² (thermal) [33]. Although severe ductility losses occurred, no intergranular fracture was seen [32]. Because 6061 aluminum is stronger than 1100 aluminum and is further strengthened by irradiation, fuel elements based on 6061 aluminum would resist distortion and fracture to higher temperatures under larger stresses. The yield strengths of irradiated 6061 approach those of non-irradiated 6061 at test temperatures above 200°C [32].

Tensile and creep tests on non-irradiated 6061 aluminum show both yield and creep-rupture strengths below 10 ksi at 200°C for a 10,000 hour exposure with lower strengths for longer exposure at lower temperatures [34]. Thermal annealing of cold worked 6061 occurs above 250°C.

Mechanical properties of aluminum uranium fuel alloys are controlled by the base aluminum alloy and the percent uranium. Cast alloys are made from pure aluminum. Dispersion or powder metallurgy alloys normally use 1100 aluminum also but may have an aluminum alloy base such as 6061 or 8001. For the 35 wt % uranium fuel based on 1100 aluminum, irradiated properties approach those of the non-irradiated alloy above 300°C [35].

Further analysis of the stresses that might be encountered during storage is needed to establish the temperature dependence of the mechanical stability of aluminum clad SNF. The analysis should be based on stress analyses for each fuel type, size, shape, and dimension. Other factors to take into account are: irradiation effects and subsequent annealing for the long storage times of interest; the composite nature of the fuel elements; multiaxial stress states such as arise from swelling of the core or blister formation; the volume fraction of UAl_x in the fuel core; the properties of the fuel core; the composition, temper, and irradiation history of the cladding alloy.

Radiation Stability

Radioactive decay of fission products and spontaneous neutron emission from actinides in spent fuel generate a low intensity radiation field. The only process that appears to have a potentially adverse effect the durability of aluminum clad is radiolysis within any surrounding gas or liquid phase. Displacement damage, radiation enhanced diffusion, and radiation induced segregation are unlikely to affect stability of the fuel during 50-100 years of interim storage because neutron fluences are too low to contribute radiation damage or to generate sufficient numbers of excess vacancies or interstitials to enhance diffusion and segregation.

Radiolysis of a gas or liquid in the immediate surroundings of the fuel could affect corrosion by altering reaction kinetics or by generating more reactive species. For example, radiolysis of water generates free radicals, hydrogen, oxygen, and hydrogen peroxide. Nitric acid can be formed by radiolysis of nitrogen in moist air. Analyses of these processes is a necessary task in estimating the time evolution of composition changes in the atmosphere surrounding the fuel as a basis for evaluating the potential for enhanced corrosion of the fuel.

Thermal Stability

In addition to the temperature dependence of the properties, thermodynamic stability of the several material phases becomes an issue when considering dry storage of spent fuel. During storage in water pools, temperatures are maintained well below any limits imposed by the phase stability of the materials or melting of the alloys, Table 4. Data in the table are nominal values which do not take into account changes in composition caused by transmutations during irradiation. For example, silicon formed in 6061 aluminum during a five year irradiation at nominal SRS reactor power levels lowers the melting point a few degrees and modifies mechanical properties slightly. Precipitation of Mg_2Si occurs in 6061 aluminum at $160^{\circ}C$ in 18 hours and at somewhat lower temperatures for longer times [31].

Several processes are possible at elevated temperatures which could affect durability of the fuel:

- dehydration of the oxide films;
- interdiffusion between contiguous phases;
- swelling and blister formation from fission gases, hydrogen, and helium.

Dehydration of Aluminum Oxides

Aluminum oxides films on irradiated fuel, bayerite and boehmite, are not stable in air or inert atmospheres, but will lose water and convert to boehmite or gamma-

alumina, Table 4. The oxides shrink during dehydration and exposed fresh aluminum surfaces are exposed for oxidation or reaction with water vapor.

Table 4
Thermophysical Properties of Materials

<u>Material</u>	<u>Melting Point, °C</u>	<u>Phase Changes</u>
Uranium	1132	$\alpha \Rightarrow \beta$ at 668°C
UO ₂	2878	
U ₂ O ₃	-	
UH ₃	-	
1100Al	643	
6061Al	582	aging at 160°C
α -Al ₂ O ₃ ·H ₂ O (boehmite)		$\alpha \Rightarrow \gamma$ at 200°C
β -Al ₂ O ₃ ·3H ₂ O (bayerite)		$\beta \Rightarrow \alpha$ or γ at 120/250°C
γ -Al ₂ O ₃	2015	

Interdiffusion

Uranium is nickel plated to prevent interdiffusion of uranium and aluminum during cladding with 1100 aluminum and attendant formation of brittle aluminum-uranium intermetallic phases [26]. Further growth of the aluminum-nickel and uranium-nickel intermetallic phases formed during cladding could occur if the storage temperature were high enough. For example, uranium could penetrate a 0.030-inch thick cladding in about 13,000 hours at 200°C [36].

Swelling

Fission product gases, helium, and hydrogen are formed during irradiation and accumulate at crystal defects, internal boundaries, porosity, and in nanometer size bubbles. Subsequent heating of irradiated metals can cause agglomeration of these gases and lead to swelling and cracking of the metals. Postirradiation heating tests on cast/wrought aluminum-uranium alloys have shown that swelling and blistering do not occur until the temperature exceeds 400°C and that the swelling temperature is independent of uranium content in the range 18 to 25 wt% uranium [35,37]. The swelling/blistering temperature threshold for uranium aluminide fuel plates with 50 vol. percent UAL_x was 440°C, consistent with the data for cast/wrought aluminum-uranium alloy fuel. Fission gas release from UAL_x in fuel based on 6061 aluminum only occurs above 500°C [35].

Swelling of uranium has been demonstrated during post-irradiation annealing at temperatures above 450°C [26]. Swelling and cracking of the fuel are associated with formation of fission gas bubbles and cracks, processes that are aggravated by thermal cycling.

LEACHING

Leaching of radionuclides or hazardous substances from spent fuel could occur by diffusion of the nuclide through the cladding, by active corrosion following breach of the cladding, or by release during corrosion of cladding that contains radionuclides that have diffused into it.

Diffusion

Diffusion of radionuclides through aluminum is not a problem for interim storage times of up to 100 years provided the aluminum temperature does not exceed $\sim 300^{\circ}\text{C}$. The time needed for a radionuclide to diffuse through aluminum cladding 0.030-inch thick was calculated for temperatures between 100 and 600 $^{\circ}\text{C}$. Time periods of interest are the time to breakthrough (T_b) and the time to steady state (T_{ss}) which are given by

$$T_b = 0.06 l^2/D \text{ and}$$
$$T_{ss} = 0.45 l^2/D,$$

where D is the diffusivity (cm^2/sec) and l is the cladding thickness (cm) [38]. The times plotted in Figure 1 were based on published diffusion data for several radionuclides of interest which are representative of actinides, fission products, and uranium, Table 5 [38-44]. Cesium diffusion is more rapid than plutonium, uranium, or xenon diffusion at temperatures up to 200°C . Cesium would penetrate the cladding in about 140 years and attain steady state in about 1000 years at 200°C , Figure 1.

Table 5
Solute Diffusion in Aluminum

Solute	D_0 , cm ² /sec*	Q , kcal/mole	Temp Range, °C	Ref.
Aluminum	2.25	34.5	300 - 650	39
Cesium	6.4×10^{-5}	32.41	460 - 628	40
	2.98×10^{-7}	21	380 - 615	40
	1.28×10^{-9}	9.11	180 - 600	40
	(2.4×10^{-13})		200	41
	(2.8×10^{-11})		300	41
Plutonium	1.1×10^{-9}	12.6	400 - 650	42
Uranium	0.1	28	525 - 625	39
	(12.8×10^{-9})		625	43
	(7.6×10^{-9})		600	43
	(9.1×10^{-9})		600	43
	(6.4×10^{-9})		575	43
	(3.2×10^{-9})		550	43
	(1.7×10^{-9})		525	43
Xenon	(2.8×10^{-13})		200	44
	($\sim 10^{-8}$)		650	44

* Numbers in parentheses are measured diffusivities for the temperatures indicated

Uranium penetrates aluminum more rapidly than the other isotopes at higher temperatures. At 300°C, for example, steady state is reached in about thirty years. However, analysis of uranium diffusion through the aluminum cladding on uranium slugs is complicated by the presence of a nickel plate and the aluminum-nickel and nickel-uranium intermetallic compounds formed during fuel fabrication. These phases act as barriers to uranium diffusion. The diffusivities of uranium in these phases are not known.

Diffusion of plutonium and xenon are unlikely at any expected storage temperature. Plutonium diffuses slowly and does not penetrate the cladding in a 100 year period until temperatures exceeded ~400°C. Xenon is an inert gas and either becomes trapped at internal defects or incorporated into large defect complexes that are essentially immobile at temperatures below 500°C [43]. Xenon diffusivity is reported to be 2.8×10^{-13} at 200°C [44]. These defects only acquire mobility at elevated temperatures and may diffuse along grain boundaries.

The quantities of radionuclides that permeate the cladding can be estimated from permeation formulae for any period of time of interest [38]. The quantity of substance permeating the cladding depends not only on the diffusivity, but also on the of the solubility of the substance in the aluminum, quantities which are temperature dependent. Concentrations of radionuclides within the core would

decrease with time at rates governed by the decay constants of the radionuclides, thus reducing the quantity of material available for diffusion.

Release by Chemical Reaction and Cladding Corrosion

A cladding breach would expose the core to corrosion and radionuclide release. This process is a major concern for water pool storage of aluminum clad spent fuel as there are known cases of breached cladding stored in basins at several reactor sites. Corrosion of aluminum, uranium, and aluminum-uranium alloy in water have been discussed above. Fission product release rates could be estimated from corrosion rates and the concentrations of radionuclide present in the fuel. Selective leaching of nuclear poisons from conditioned fuel assemblies could compromise the criticality safety of the stored fuel. This question can only be addressed after specific poisons are recommended. In dry storage, the likelihood of leaching would be negligible unless there were water intrusion into a canister that contained spent fuel with breached cladding.

Radionuclides may diffuse into the aluminum cladding during storage as discussed above. Any subsequent corrosion of the cladding would release plutonium, uranium, or cesium into the surroundings. The amount released would depend on the storage temperature, storage time, and depth of corrosion.

Radiochemical techniques exist for monitoring of basins and canyons to detect releases caused by breach of cladding or diffusion. A surveillance program for spent fuel storage would include a monitoring system to detect radionuclide release within the storage system, although not necessarily within individual canisters.

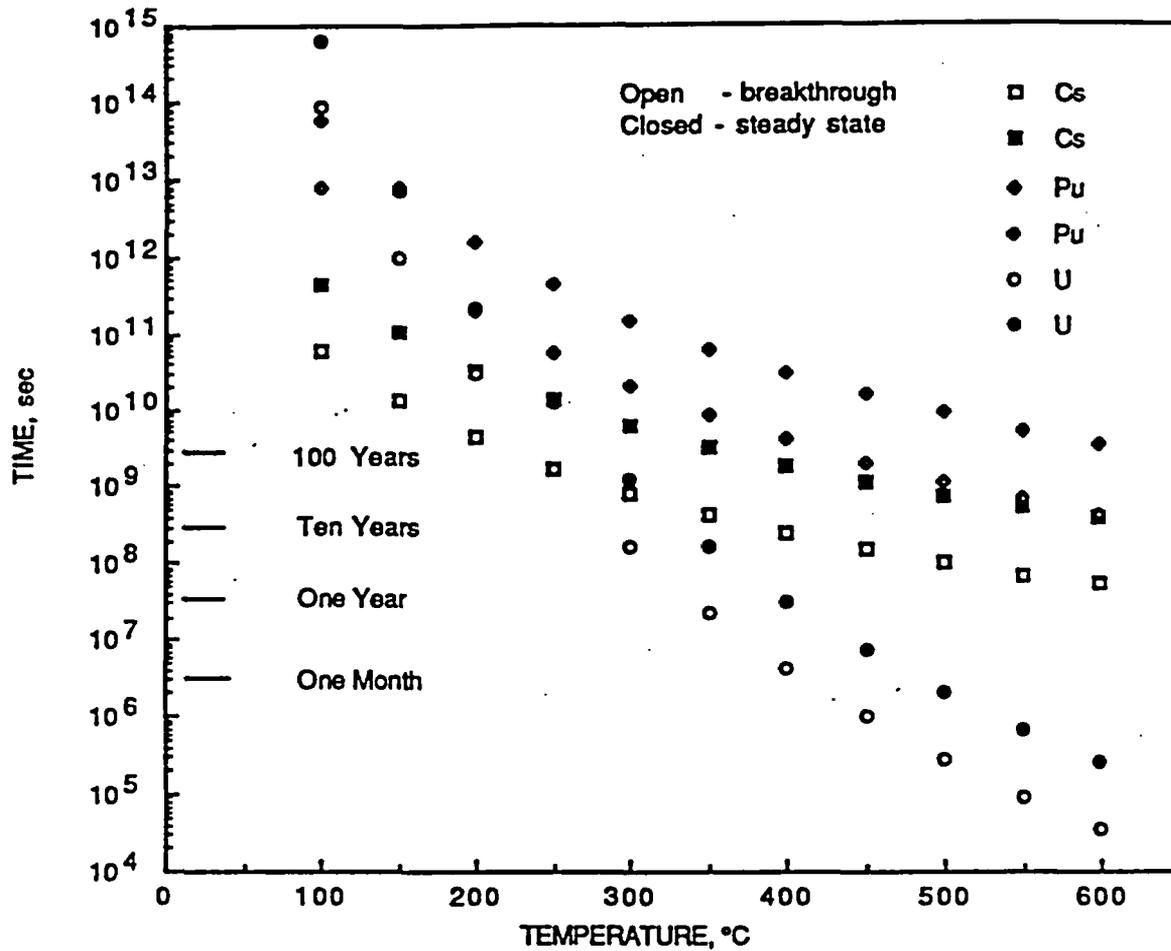
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Radionuclide Diffusion Through Aluminum
(0.030-inch thick cladding)

Figure 1

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