

BASES FOR EXTRAPOLATING MATERIALS DURABILITY IN FUEL STORAGE POOLS

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## BASES FOR EXTRAPOLATING MATERIALS DURABILITY IN FUEL STORAGE POOLS

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### ABSTRACT

A major body of evidence indicates that zirconium alloys have the most consistent and reliable durability in wet storage, justifying projections of safe wet storage greater than 50 y.

Aluminum alloys have the widest range of durabilities in wet storage; systematic control and monitoring of water chemistry have resulted in low corrosion rates for more than two decades on some fuels and components. However, cladding failures have occurred in a few months when important parameters were not controlled.

Stainless steel is extremely durable when stress, metallurgical, and water chemistry factors are controlled. LWR SS cladding has survived for 25 y in wet storage. However, sensitized, stressed SS fuels and components have seriously degraded in fuel storage pools (FSPs) at  $\sim 30^{\circ}\text{C}$ .

Satisfactory durability of fuel assembly and FSP component materials in extended wet storage requires investments in water quality management and surveillance, including chemical and biological factors.

### INTRODUCTION

Numerous types of nuclear fuel and storage facility components have resided in wet storage at DOE facilities much longer than was anticipated. Some fuel types and facility components have been subject to substantial degradation in wet storage. This paper presents bases to extrapolate the durability of aluminum, stainless steel, and zirconium alloy materials in wet storage. The bases include a) quantitative data points obtained on the materials after exposures in spent fuel pools; b) data from laboratory studies on the same materials under

conditions relevant to spent fuel pool environments; c) extrapolation of kinetic data from relevant thermal or chemistry regimes; and d) qualitative or semi-quantitative observations on behavior of the materials in wet storage over extended periods, lending corroboration to the quantitative predictions. The data presented in the paper represent, in part, contributions from the US data base to an International Atomic Energy Agency (IAEA) Coordinated Research Program (CRP) on materials issues in spent fuel storage.

The key aspect of the study is to provide storage facility operators and other decision makers a basis to judge the durability of a given fuel type in wet storage as a prelude to basing other fuel management plans (e.g., dry storage) if wet storage will not be satisfactory through the expected period of interim storage. If perforation of the cladding has occurred or is expected in a predictable time frame, then the type of fuel (e.g., oxide or metal) becomes an important consideration in judging the acceptability of further wet storage.

### ALUMINUM ALLOYS

Aluminum alloys are prominent in wet storage as FSP components (Kustas et al. 1981, IAEA 1982) and as fuel-cladding, principally after service in test and defense reactors (Guenther et al. 1994; Howell et al. 1993; Dirk 1994; IAEA 1992). The current condition of the fuel elements is a composite of effects of fabrication, reactor service, interim storage at reactor and AFR pools, handling, and shipping. Penetration of the cladding releases fission products, fuel particles, and transuranic species to the pool water. If the fuel involves metallic uranium, corrosion products may include uranium hydride, which can become pyrophoric on exposure to air (ITA 1994).

It is important to diagnose current fuel condition in wet storage as a basis to define conditioning that will be required if the fuel is transitioned to dry storage (ITA 1994; Guenther et al. 1994). On the other hand, some FSP operators may have a preference to extend the period of wet storage and need a basis to predict fuel durability under the expected storage conditions.

Compared to Al alloys, no other material exposed in FSPs has been subject to such a wide range of corrosion behaviors. This range must be defined and understood before the durability of specific fuels and components can be predicted with confidence.

To illustrate the range of Al alloy corrosion behaviors, conditions and corrosion data are compared for four FSPs in Table 1.

Conditions in Pool A have resulted in low corrosion rates. However, Pool B, with similar chemistry control, has high Al pitting rates; the role of microbially influenced corrosion (MIC) is being investigated. The Pool C environment resulted in pitting in a short time frame. Pitting rates in Pool D, with higher  $\text{Cl}^-$  and conductivities were no higher than in Pool C. However, nitrate was added to inhibit corrosion. A potentially significant difference between conditions at Pools A and B is that lighting has been minimal at Pool A and bright at Pool B, possibly contributing to the biological activity observed at Pool B.

While water chemistry is the most important single factor in aluminum durability, other factors must be considered when they apply:

- alloy composition, particularly in more aggressive water conditions (Howell and Zapp 1994)
- characteristics of corrosion films that formed on fuel elements during reactor service; if formed below  $-80^\circ\text{C}$  the films will comprise principally the trihydrate  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; if formed above  $80^\circ\text{C}$ , the monohydrate will be the principal species; unless damaged, both films will suppress further oxidation in fuel storage pools; however, some scratching and even mechanical distortions can be expected as fuel elements and components are handled, which can result in pit initiation sites, particularly in aggressive waters (Howell and Zapp 1994)

- galvanic and crevice factors - in purer pools, these factors will generally be minimal; in aggressive pool chemistries galvanic factors have been evident, between different Al alloys (Howell et al. 1993) and between Al alloys and stainless steels (Howell et al. 1993; Dirk 1994) and carbon steels (Dirk 1994).
- microbiological effects - can develop, even in pools with high water purities (e.g., pool B); the ultraviolet treatment equipment was out of service for more than one year; severe pitting of unirradiated Al alloy specimens has been observed (up to 2.5 mm in one year); algae films were observed and MIC is suspected, though not fully confirmed; there are plans to inspect fuel element surfaces to determine whether the attack is suppressed by radiation.

Prediction of the durability of aluminum fuels and components must acknowledge the broad range represented quantitatively in Figure 1, and represented qualitatively by the following observations:

- Al-clad fuel elements that have survived up to 24 y in wet storage (IAEA 1992)
- Aluminum-alloy racks and other components that continue to function after up to 30 y of service in fuel storage pools (Kustas et al. 1981; Pool A; IAEA 1982; Howell and Zapp 1994)
- Al alloy components that have degraded rapidly in aggressive water chemistries or in high-purity waters where MIC is suspected (Howell et al. 1993; Dirk 1994)

The water chemistries that promote rapid degradation of Al alloys are not fully understood. Howell and Zapp (1994) identify several interacting factors that promote corrosion of Al alloys in FSPs. An IAEA study now underway will include a summary of water chemistry factors that influence aluminum corrosion under wet storage conditions.

In summary, it is evident that optimum management of aluminum alloys in FSP environments can result in satisfactory durability of irradiated fuel cladding and functionality of pool components for more than two decades. The ultimate limits of aluminum alloy durability have not been established, but extrapolations from Figure 1 and continuing

**TABLE 1.** Comparison of Conditions and Al Alloy Corrosion in Four FSPs

	Pool A	Pool B	Pool C	Pool D
Conductivity $\mu\text{S/cm}$	$\sim 1 \times 10^{-6}$	$\sim 1 \times 10^{-6}$	170-190	630
Chloride, ppm	<0.1	<0.01	6-20	760 $\rightarrow$ 50
pH	6.7 - 7.8	5.5 typ	5.5 - 8.5	7.8 - 8.4
other	$\text{NO}_3^-$ , $\text{SO}_4^{=}$ , ppb levels	MIC?	<17 ppm $\text{NO}_3^-$ <14 ppm $\text{SO}_4^{=}$	$\text{NO}_3^-/\text{Cl}^- \approx 3/1$
Al Corrosion Behavior:				
Pitting:	0.25 mm/16 y	0.3 mm/y	0.75 mm/45 to 180d <sup>(a)</sup>	0.44 mm/y
Uniform:	0.25 mm/16 y	$2.5 \times 10^{-4}$ mm/y	low	low
References	Howell and Zapp 1994 Kustas et al. 1981	Dirk 1994	Howell et al. 1993	Dirk 1994

(a) Alloy-dependent 8001 > 1100 and 6063

functionality of SFP components suggest that wet storage can be extended to more than 30 y if pool operating parameters are systematically controlled.

In contrast, when requisite water quality is not maintained and MIC is not controlled, pitting corrosion can penetrate Al alloys in a few months.

Basis for Predicting Zirconium Alloy Corrosion in Fuel Storage Pools (FSPs)

Because zirconium alloys comprise the cladding for the large inventory of power reactor fuel, they have been the subject of several durability studies (Johnson 1977; IAEA 1982, 1988, 1992; Peehs and Fleisch 1986). The inventories of fuel with zirconium alloy cladding includes Zircaloy-clad LWR and CANDU power reactor fuels, East European Zr-1Nb power reactor fuel, Zircaloy-clad defense reactor fuel, and other Zircaloy-clad uranium-bearing fuel.

Zirconium alloy durability studies under FSP conditions are represented in Figure 2. These investigations have involved detailed metallurgical examinations to determine whether periods of wet storage have produced detectable degradation of the fuel cladding.

The conclusion from observations represented in Figure 2 is that there is no evidence that any zirconium alloy fuel cladding has degraded detectably in wet storage over periods up to 35 y and including several million fuel rods. Sequential photographs also have confirmed that holes in cladding that developed during reactor service do not change size or shape (observations up to eight years) while exposed to pool water (Peehs and Fleisch 1986; Johnson et al. 1982). Oxide fuel pellets exposed at the cladding defects also are stable over long periods.

The observations of cladding stability are consistent with extrapolation of Zircaloy oxidation kinetics. Even at 100°C, extrapolation of post-transition rates (consistent with oxide films on the majority of fuel rods) predict oxide thickness increases of < 1 mg/dm<sup>2</sup> (< 0.07  $\mu\text{m}$ ) in 100 y, based on a kinetic expression developed by Hillner (1977).

Assessment of localized cladding failure mechanisms also has not revealed potential degradation that is likely to cause failures over several decades in wet storage (Johnson 1977, Peehs and Fleisch 1986).

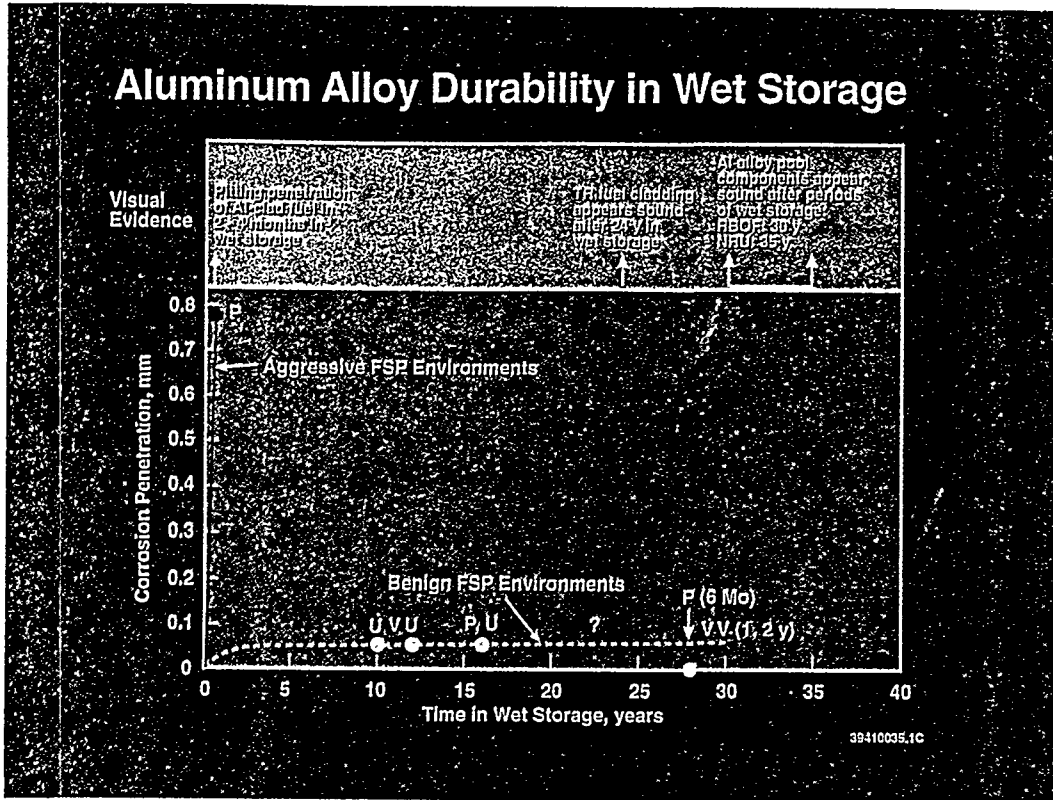


Figure 1. Range of Aluminum Alloy Corrosion and Durability in Fuel Storage Pools.

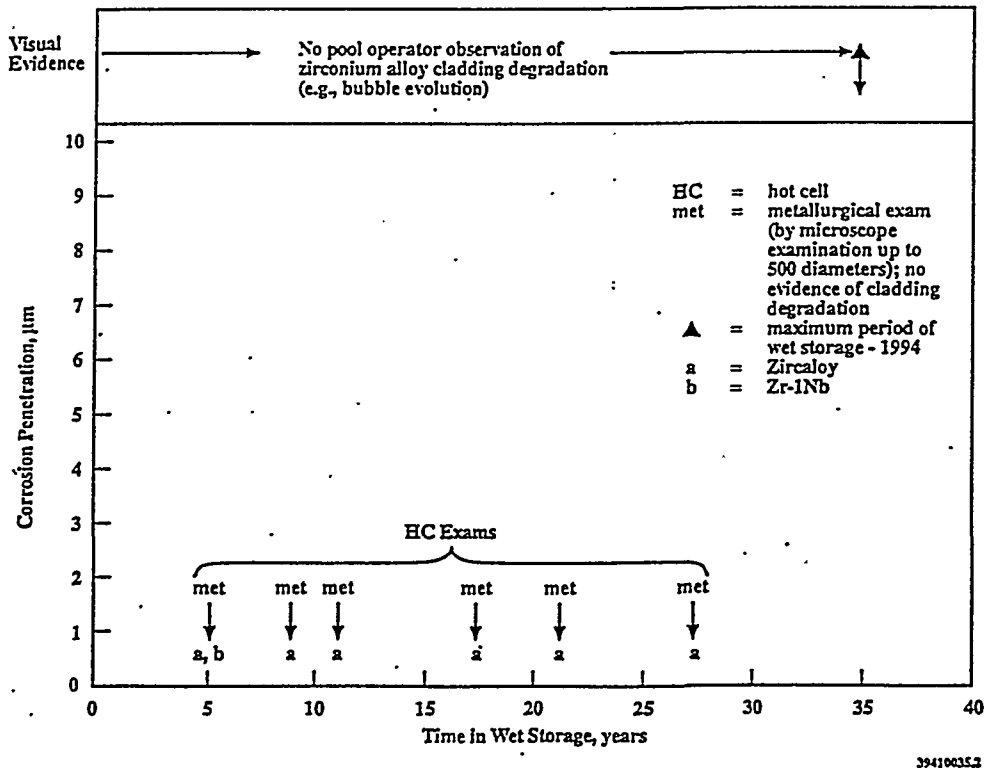


Figure 2. Examinations and Observations to Evaluate Zirconium Alloy Cladding Durability in Wet Storage.

Results of the specific examinations summarized above are consistent with observations by pool operators that represent less quantitative but much more broadly-based evidence that zirconium alloy fuel is not degrading after wet storage periods up to more than three decades. Visual evidence of cladding degradation includes absence of bubble evolution. The LWR fuel has gas plenums and internal gas pressures that would evolve gases if cladding failures occurred in wet storage. Some older Zircaloy-clad fuel has been shipped (e.g., from the former Nuclear Fuel Services plant, West Valley, New York) to PWR and BWR reactors that utilized the fuel, providing opportunities for visual inspections with video cameras.

Zircaloy-clad defense reactor fuel has been subject to substantial corrosion of metallic uranium that was exposed by mechanical damage of the Zircaloy cladding upon reactor discharge (US DOE 1993). However, this phenomenon does not reflect negatively on the extended durability of zirconium alloys in wet storage. Some Zircaloy-clad fuel resided in the relatively aggressive conditions in Pool D, Table 1, for approximately two decades. Visual inspections do not indicate evidence of detectable degradation, which is consistent with the generally excellent corrosion resistance of zirconium alloys in a wide range of aqueous solutions (Schemel 1977).

In summary, specific examinations and pool operator observations provide a basis for continued confidence that fuel clad with zirconium alloys can be safely stored in FSPs for time frames exceeding 50 y.

#### Basis for Predicting Stainless Steel Corrosion in Fuel Storage Pools

Stainless steel (SS) pool components are prominent in most FSPs, including fuel storage racks, pool liners, piping, heat exchangers, and fuel handling equipment. Several types of stainless-steel-clad spent fuels also reside in FSPs, including the following: LWR, Advanced Gas Reactor, and test reactor types. Detailed analysis of the behavior of the various types in wet storage is beyond the scope of this paper, but is being addressed in an IAEA coordinated research program. Several fuel examinations have been conducted to investigate fuel behavior in wet storage (Johnson et al. 1980; Langstaff et al. 1982; IAEA 1982). There was no evidence of storage-induced degradation on LWR fuel cladding after wet storage for periods up to five years. Pool operator observations also have not indicated evidence of

cladding failures (e.g., gas bubble evolutions) in storage periods up to 25 y.

Fuels with stainless steel cladding that have had service in liquid metal and gas-cooled reactors operate in temperature regimes where sensitization can occur. Therefore, they are susceptible to accelerated intergranular attack in wet storage (e.g., Long & Michelson 1964).

Several sections from SS spent fuel pool components were examined by metallography after periods of wet storage up to 15 y (Kustas et al. 1981). Most of the SS components were free of detectable oxidation, pitting, or intergranular attack, including at welds. However, spent fuel pool piping at some PWR FSPs failed in weld heat-affected zones, promoted by sensitization and high stress levels (e.g., Kustas et al. 1981; Jones et al. 1981).

Stainless steel components exposed in pool D (aggressive environment) have not shown accelerated corrosion (Dirk 1994).

An analysis of 304L SS behavior in a wet storage environment at 20°C, 2 ppm Cl<sup>-</sup> led to predictions that localized corrosion would not be significant in extended exposures (Johnson et al. 1994). Uniform corrosion (based on data at 105°C) was estimated to be  $\sim 3 \times 10^{-4}$  mm/y. The data suggested that SS alloys that are not susceptible to intergranular attack, e.g., at sensitized welds, will have satisfactory durability in benign wet storage environments over storage periods much longer than those currently foreseen.

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