KINETIC AND THERMODYNAMIC BASES TO RESOLVE ISSUES REGARDING CONDITIONING OF URANIUM METAL FUELS

A. B. Johnson
R. G. Ballinger
K. A. Simpson

December 1994

DISCLAIMER

MASTER

DISCLAIMER

Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.

KINETIC AND THERMODYNAMIC BASES TO RESOLVE ISSUES REGARDING CONDITIONING OF URANIUM METAL FUELS

R. G. Ballinger
MIT
77 Massachusetts Ave
Cambridge, MA 02139
(617) 253-5118

A. B. Johnson, Jr.
Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington 99352
(509) 376-3761

K. A. Simpson
Honeysuckle Cottage
Pidenham Chase
Gwent NP67JW
United Kingdom
(44) 291-689-423

ABSTRACT

Numerous uranium - bearing fuels are corroding in fuel storage pools in several countries. At facilities where reprocessing is no longer available, dry storage is being evaluated to preclude aqueous corrosion that is ongoing. It is essential that thermodynamic and kinetic factors are accounted for in transitions of corroding uranium-bearing fuels to dry storage. This paper addresses a process that has been proposed to move Hanford N-Reactor fuel from wet storage to dry storage.

I. INTRODUCTION

Numerous defense, power, and test reactor fuel assemblies have uranium-bearing metal fuels. Several fuel storage pools (FSPs) include fuels with failed cladding, exposing the uranium metal fuels to aqueous corrosion.[1-3] The metal fuels corrode at FSP temperatures, leading to the following considerations:

- fission product and transuranic release to the pool water

- generation of corrosion products, including oxides, hydrides, and hydrates

- safe handling of fuels with uranium hydride inventories

- requirements for conditioning corroded uranium metal fuels for transitioning from wet to dry storage.

The issues outlined above were addressed to analyze the current condition and transition to dry storage of corroding Zircaloy-clad N-Reactor fuel.[1] Engineering aspects of the N-Reactor fuel dry storage transition are summarized in another paper at this conference.[4] This paper deals with the kinetic and thermodynamic aspects.

Cases of pyrophoric behavior have been reported when corroded uranium metal fuels have been exposed to air, due to ignition of uranium hydrides.[5] It is therefore important to identify and implement fuel handling and conditioning regimes that avoid conditions that cause accelerated reactions of corroded metal fuels. Dry storage is being considered for corroded uranium fuels.[1,3] Until now no corroded uranium metal fuel has been moved from wet storage to long-term interim dry storage. This paper and the broader study[1] propose a process to move the metal fuel safely from wet to dry storage.

II. THE RANGE OF URANIUM METAL FUELS

Uranium metal fuels are clad with Magnox (Mg alloy), Al alloys, stainless steel, and Zircaloy. The range of uranium-bearing fuels includes uranium metal (with small concentrations of added elements), uranium alloys (e.g., U-10% Mo), and cermets (e.g., UAl_x particles, generally in an Al alloy matrix). Some metal fuels have been exposed to aqueous corrosion, either where the cladding was penetrated by corrosion (Magnox, aluminum alloys), or by mechanical damage during discharge from the reactor (Zircaloy-clad N-Reactor fuel).

This paper focuses on aqueous corrosion of uranium metal fuels, but references behavior of the alloys and cermets.

III. URANIUM CORROSION REACTIONS AND PRODUCTS

Aqueous corrosion of uranium metal is represented in the stability diagram (Figure 1) at 25°C.[6] The leading reactions and corresponding free energies of reaction at 25°C appear below:
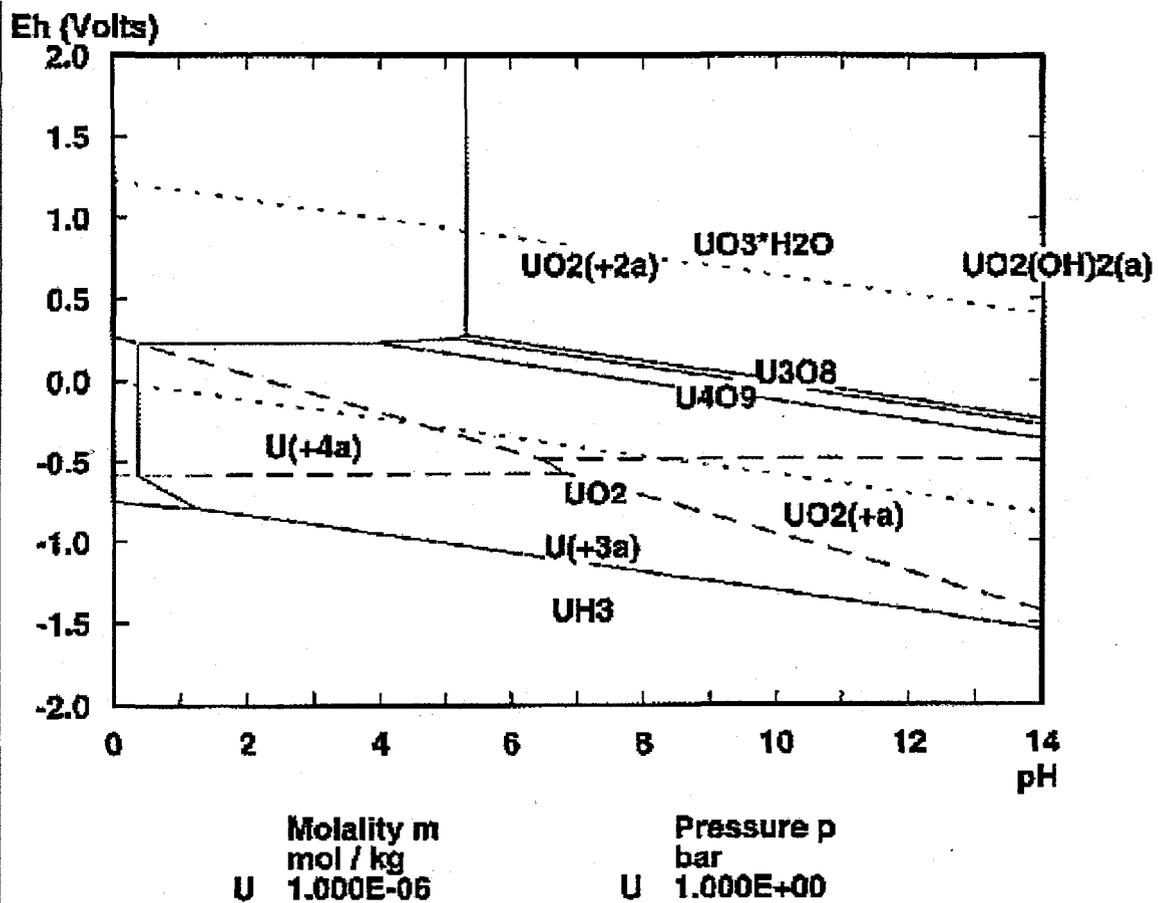
FIGURE 1 Stability Diagram

	ΔG, kcal/mole at 25°C	
$U + 2H_2O \rightarrow UO_2 + 2H_2$	-133.3	(1)
$2U + 3H_{2(g)} \rightarrow 2UH_3$	-34.8	(2)
$2UH_3 + 4H_2O \rightarrow 2UO_2 + 7H_{2(g)}$	-231.8	(3)
$2UH_3 + 2O_{2(g)} \rightarrow 2UO_2 + 3H_{2(g)}$	-229.3	(4)
$UO_2 + 2H_2O + 0.5O_{2(g)} \rightarrow UO_3 \cdot H_2O + H_2$	-31.6	(5)
$UO_2 + 2H_2O \rightarrow UO_3 \cdot H_2O + H_{2(g)}$	+25.0	(6)

Thermodynamics favor reactions 1 through 5 in the FSP temperature range. Reactions 1 and 2 denote formation of oxide and hydride corrosion products. However, reactions 3 and 4 indicate that the hydride is unstable in the presence of water and oxygen. Therefore hydrides survive in the corroding fuel only at locations in the metal or oxide where they are occluded. Spent fuel pool waters are saturated with oxygen (e.g., ~ 8 ppm O_2 at ambient temperatures). In oxygenated systems the hydride is generally in the range of 1 to 10% of the corrosion product. When corroding uranium is exposed in hydrogenated environments the hydride fraction increases.

The thermodynamic data suggest that the $UO_3 \cdot XH_2O$ hydrate forms at elevated oxygen levels (Reaction 5), but does not form by reaction 6. Whether some hydrate forms in the oxygen saturated pool water will be determined in fuel characterizations, but formations seems doubtful from inspection of the stability diagram, which suggests that higher oxidant levels are required, consistent with equation 5. A UO_2 hydrate also is not indicated. However, hydrated corrosion products on Al alloy canisters are stable at FSP conditions.[7] The N-Reactor fuel is stored in Al alloy and stainless steel canisters.

The fuel compound UAl_x also has favorable thermodynamics for aqueous corrosion at SFP conditions (25°C):[6]

$$UAl_2 + 4H_2O \rightarrow 1/2UH_3 + Al_2O_3 + 1/2UO_2$$

$$\Delta G = -259.8 \text{ kcal/mole}$$

Formation of both the hydride and oxides is indicated. The fuel particles are dispersed in an Al alloy matrix, so it is doubtful that local hydride concentrations are sufficient to cause ignitions if exposed to air.

The reaction characteristics of uranium alloys are referenced under Alloy Composition.

IV. KINETICS OF URANIUM METAL CORROSION

Favorable thermodynamics do not assure significant rates of reaction. However, kinetics indicate that reactions 1 through 4 proceed at significant rates, and buildups of radioactive species in SFPs where the corroding fuels reside provide convincing evidence of uranium metal corrosion in the range 10 to 30°C.[1-3] In fact, systematic assurement of ^{137}Cs inventories provide rough estimates of the uranium corrosion rates in FSPs.[1] The release rates of ^{137}Cs also

have been utilized in laboratory studies to measure corrosion kinetics of irradiated uranium metal.

A. Uranium Metal Corrosion Data

Figure 2 is a compilation, developed for the ITA assessment of uranium corrosion rates in water vapor and liquid water. What becomes readily apparent is that corrosion rates are about two orders of magnitude lower in environments where oxygen is present, presumably including oxygen - saturated pool waters. Metallic uranium fuels exposed in moist gaseous atmospheres that include hydrogen have been subject to advanced fuel degeneration.[5,8] Uranium metal aqueous corrosion is reported to be similar in water at 25°C and in moist gases at 100% relative humidity at 100°C.[9]

B. Temperature Effects

There is some disagreement regarding the activation energy for aqueous uranium corrosion, with values in the range of 12 to 27 kcal/mole.[10] A decrease in pool temperature in the Hanford K-East pool from 20°C to 10°C resulted in a decrease in ^{137}Cs release rates of a factor of three,[11] which agrees with other observers. However, temperature reduction is only an interim measure. The calculated uranium corrosion rate at 10°C is ~ 100 g/d in the K-East pool (data from B. Emory, Westinghouse Hanford Company). Rates of release of fission products and corrosion product buildups suggest that actions are justified to remove the fuels from active aqueous corrosion.

C. Alloy Composition

Corrosion rates between uranium metal and its most resistant fuel alloys vary markedly.[12] For example U-10 Mo corrodes ~three orders of magnitude slower in water vapor than does unalloyed uranium at 75°C.[12] Corrosion data comparisons for cermets (i.e., UAl_x) are less definitive, but the intermetallic particles are contained in a metal matrix, usually an Al alloy, so their exposure to water is largely controlled by the Al matrix corrosion. Uniform corrosion of Al alloys is generally low at FSP temperatures.[13]

D. Water Chemistries

Systematic studies of water chemistry effects on uranium metal corrosion in SFP conditions are largely lacking. Uranium metal fuel corrosion is ongoing in both low conductivity[1] and high conductivity waters.[2] The Hanford N-Reactor fuel provides conditions of special interest. One pool contains corroding fuel in open canisters
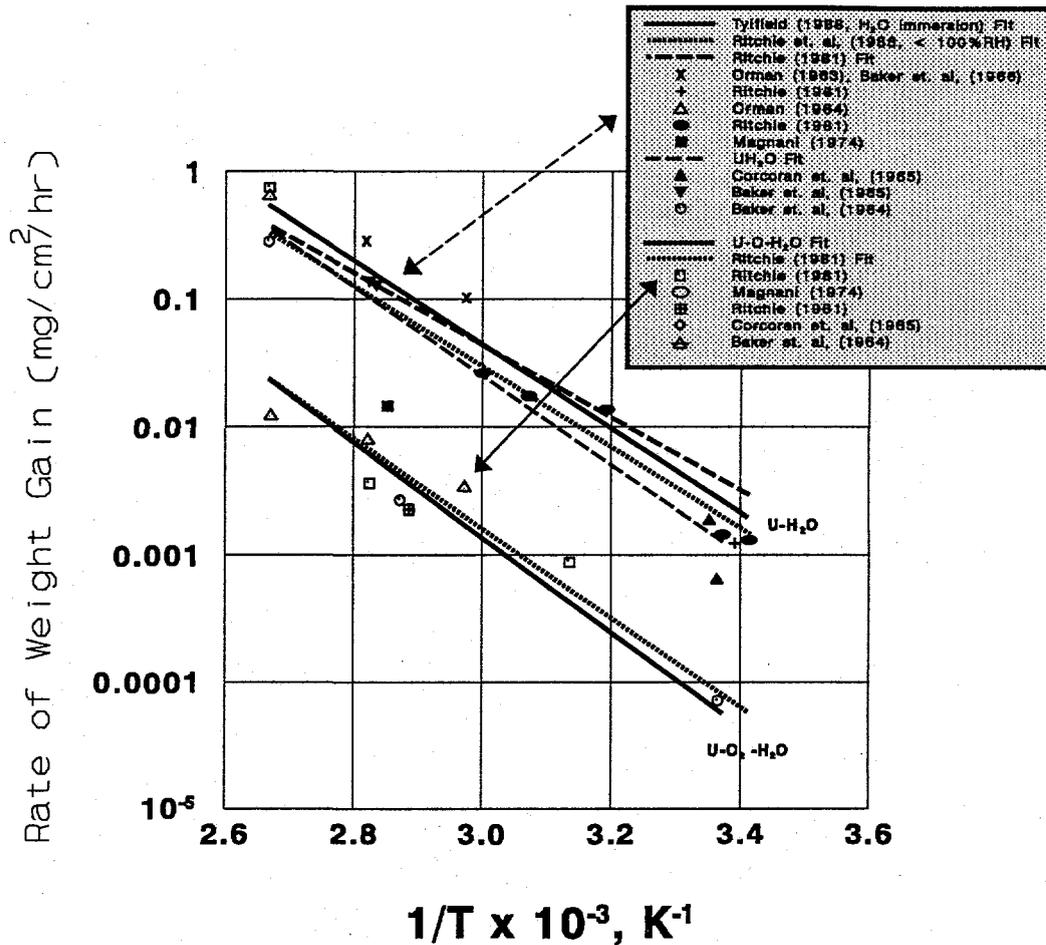
FIGURE 2 Kinetics

(oxygen-saturated water) at relatively low conductivities (10 μS/cm). The other pool contains corroding fuel in closed canisters; however, the canister water was dosed with potassium nitrite (studies by B. Emory, Westinghouse Hanford Company, indicated that the nitrite inhibits uranium corrosion). Whether the nitrite has been effective or whether corrosion has generated a hydrogen-rich environment in the canisters are subjects of speculation that will be resolved when the canisters are sampled.

V. PYROPHORICITY

Corroded uranium metal is widely regarded as pyrophoric. Indeed, numerous case histories have been cited (e.g. Ref. 5). The more flagrant cases involve damaged fuel stored in cans under water in cover gases (nitrogen or argon). Some cans leak, allowing water to corrode the exposed uranium, generating a moist hydrogen atmosphere

that favors buildup of hydrides. When the hydrided elements are exposed to air, ignition events have occurred in some cases; they were extinguished by argon blanketing or with a fire blanket. Porosity generated in Magnox fuel of higher burnups promotes corrosion and hydride formation, but some events have occurred with corroded unirradiated uranium.

Hydrides develop as spurs in the metal and as a layer at the metal/oxide interface. In general the corrosion product oxides are not protective, but there is evidence that oxide layers can passivate the hydrides.[14]

It is essential to understand how to avoid conditions that promote significant ignition events when corroded uranium fuels are handled and are conditioned for transitioning to dry storage. Important considerations were utilized in designing the ITA process:

- ignitions have never been observed while the corroded fuel is submerged in water

- ignitions are precluded when the fuel is removed from water to an inert environment or is processed in a vacuum.

- hydrides formed during corrosion react with water or oxygen except where occluded; therefore sudden exposure of the corroded uranium to air would result in immediate ignition only if an accompanying event (e.g., mechanical damage) exposed the occluded hydride.

The key safety consideration is to preclude contact of corroded uranium metal fuel with large inventories of air or oxygen.

VI. PROPOSED CONDITIONING CYCLE

The conditioning cycle proposed for the N-Reactor fuel is indicated in Figure 3.[1] It includes the following steps:

- Dewatering and Drying; during the drying cycle at 300°C, most water absorbed on the uranium oxide and waters of hydration from $Al_2O_3 \cdot XH_2O$ are expected to be expelled (to be confirmed by treatment of actual corrosion products). Some UH_3 will thermally decompose, generating uranium metal particles.

- Passivation: metal particles and other exposed metal, if any, will be passivated in a controlled oxidation process, with argon + 2% O_2, designed to provide sufficient oxidation, but to quickly blanket accelerated reactions with argon.

- Inerting with a Cover Gas: The fuel will be seal welded in a Multicanister Overpack (MCO),[1-4] using technology that is licensed and has become routine for dry storage of commercial fuels. One option would involve sealing MCOs inside a MultiPurpose Cask (MPC) of a type designed for repositories, providing double containment. A vault storage option also is being considered.[1]

While the details are beyond the scope of this paper, the conditioning processes were selected, based on kinetic and thermodynamic considerations.[1]

VII. CONCLUSIONS

1. Numerous uranium-bearing fuels are corroding is FSPs, generating oxide and hydride corrosion products and releasing radioactive species to pool waters.

2. The uranium hydrides can become pyrophoric if exposed to air, but not when submerged in water or processed in inert gases or a vacuum.

3. Thermodynamic and kinetic parameters were utilized to design a process for transitioning corroded uranium metal fuel from wet storage to dry storage.

REFERENCES

1. Dry Storage of N Reactor Fuel Independent Technical Assessment, Vols I and II, MAC Technical Services Company, Richland, Washington (1994).

2. J. P. Howell, P. E. Zapp, and D. Z. Nelson, "Corrosion of Aluminum Alloys in a Reactor Disassembly Basin," Corrosion 93, Paper No. 709, National Association of Corrosion Engineers, Houston, Texas (1993).

3. R. J. Guenther, et al., "Basis for Assessing the Movement of Spent Nuclear Fuels from Wet Storage to Dry Storage at the Idaho Chemical Processing Plant," PNL-SA-24585, Pacific Northwest Laboratory, Richland Washington (1994). Proceedings of the Symposium "DOE Spent Nuclear Fuel Challenger and Initiatives," Salt Lake City, Utah. December 13-16, 1994.

4. T. L. Bradley, Application of Commercial Nuclear Dry Spent Fuel Storage Technology to the Dry Storage of N Reactor Fuel at the U.S. DOE Hanford Site Proceedings of the Symposium "DOE Spent Nuclear Fuel Challenges and Initiatives," Salt Lake City, Utah. December 13-16, 1994.

5. D. Fisher, and S. Knight, B30 Bottled Fuel Opening Study AEA-D&W -0566, AEA, Windscale, Cumbria, England (1993).

6. Outokumpu Research Oy, OutoKumpu HSC Chemistry for Windows, Version 1.10, Finland (1993).

7. R. S. Alwitt, "The Aluminum - Water System" Chapter 3, in Oxides and Oxide Films, Vol. 4, J. W. Diggle and A. K. Vijh (eds) Marcel Dekker, Inc., New York (1976).

8. F. J. Bindon, "Dry Store Water Leakage at Wylfa Power Station," The Nuclear Engineer, Vol. 33, No. 2, pp. 44-47 (1992).

9. S. Orman, Oxidation of Uranium in Water and Water Vapor, Report 025/64, Atomic Weapons Research Establishment (1964).

10. T. Kondo, F. H. Beck, and M. G. Fontana, "A Gas Chromatographic Study of the Kinetics of Uranium Oxidation," Corrosion Vol. 30, pp. 330-339 (1974).

11. S. P. Burke, "Corrosion Briefing to Fuels Substeam," Westinghouse Hanford Company, Richland Washington (1993).

12. L. J. Weirick, "Corrosion of Uranium Alloys" in Metals Handbook Ninth Edition, Vol. 13 Corrosion, ASM International, Metals Park, Ohio, p. 815 (1987).

13. A. B. Johnson, Jr., "Basis for Extrapolating Materials Durability in Wet Storage," PNL-SA-2416, Proceedings of the Symposium "DOE Spent Nuclear Fuel Challenger and Initiatives," Salt Lake City, Utah. December 13-16, 1994.

14. J. T. Waber, "Aqueous Corrosion of Uranium and Its Alloys," AEC-EURATOM Conference on Aqueous Corrosion of Reactor Materials, TID-7587 (1960).
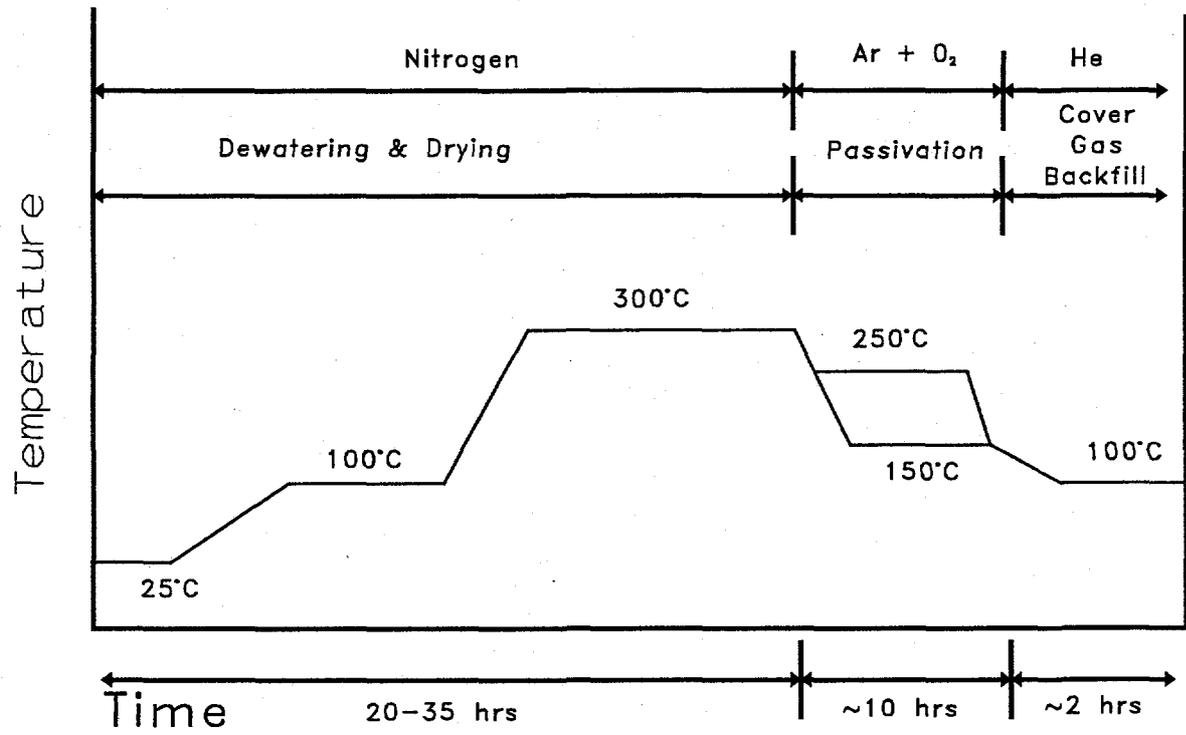
FIGURE 3 Conditioning