TRANSITIONING METALLIC URANIUM SPENT NUCLEAR FUEL FROM WET TO DRY STORAGE

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ABSTRACT

Approximately 80% (by weight) of the U.S. Department of Energy's inventory of spent nuclear fuel is currently stored in two water-filled concrete basins a few hundred meters from the banks of the Columbia River, at the Hanford Site near Richland, Washington. The fuel is Zircaloy-clad metallic uranium, discharged from the N-Reactor in 1990 and earlier. Some of this fuel was damaged when discharged from the reactor and has subsequently corroded during its years of wet storage. The radioactive fission products released to the basins by corrosion pose a threat to the Columbia River ecosystem. The basins were never intended for long-term storage of spent nuclear fuel; they were built more than 50 years ago, do not meet modern seismic standards, and are well beyond their design life. Stakeholder and regulator concerns have prompted DOE to assign a high priority to moving the spent fuel out of the K Basins and away from the river

Since late 1994, DOE and its contractors have been engaged in a project to move the spent N Reactor fuel into interim dry storage at a new facility under construction at the Hanford Site, about 15km from the river. This paper presents an overview of the process to be used in transitioning the damaged – and chemically reactive – metallic uranium spent nuclear fuel from wet to dry storage. It addresses some of the more difficult technical challenges associated with the process, and how the project is dealing with those challenges.

INTRODUCTION and BACKGROUND

N-Reactor Operations

Nuclear reactors operated from 1944 to 1990 at the U.S. Department of Energy's Hanford Site in Eastern Washington to produce weapons-grade plutonium. One of these reactors - the N-Reactor, which was also used to generate electricity on the commercial grid - continued to operate from 1972 until 1983, a period when fuel reprocessing at Hanford's Plutonium and Uranium Extraction (PUREX) Facility was suspended because of safety and other concerns. With fuel processing suspended, spent fuel accumulated to a point that exceeded the capacity of the N-Reactor storage basin, requiring utilization of the basins at the shutdown K-Reactors[a] for additional storage. Reprocessing resumed from 1983 until 1989, but approximately 2,100 metric tons of Zircaloy-clad, metallic uranium spent nuclear fuel remained in the K Basins when PUREX was permanently shut down in 1990. There is also a small amount (~ 3.4 metric tons) of aluminum-clad metallic uranium spent fuel stored in the K Basins.

Some of the spent fuel was damaged when discharged from the N-Reactor. The damage is primarily to the cladding and occurred as a result of collisions among the fuel assemblies when they dropped into the discharge chute. (The system had not been designed for careful fuel handling because of anticipated reprocessing shortly after discharge). Subsequent corrosion of the exposed uranium metal has produced about 50 m^3 of radioactive sludge in the KE Basin, where the spent fuel is stored in open-topped containers, and a much smaller amount (~ 4 m^3) in the KW Basin where the fuel containers are sealed.

The K-Basins

The K Basins are large (~ 4.9 million liter) enclosed pools built in the early 1950's to temporarily store the discharged fuel from the K Reactors prior to reprocessing. The basins and their enclosures do not meet modern standards (e.g., seismic requirements, confinement, etc.) and they are located within about 420 meters of the Columbia River. Therefore, the spent fuel, radioactive corrosion products (sludge) and contaminated water in them represent a significant environmental threat.

Fuel Description

N-Reactor fuel assemblies consist of two concentric tubes of uranium metal, co-extruded into Zircaloy-2 cladding. There are two basic types of fuel assembly, differentiated by their uranium enrichment [1]. Mark IV assemblies have a pre-irradiation enrichment of 0.947% U-235 in both the inner and outer elements, and an average uranium weight of 22.7 kg. They were fabricated in lengths of 44, 59, 62 or 66 cm. Mark 1A assemblies have a pre-irradiation enrichment of 1.25% U-235 in the outer element and 0.947% in the inner element; their average uranium weight is 16.3 kg and their length is 38, 50, or 53 cm. Roughly two-thirds of the total K Basin inventory is Mark IV fuel, the remainder being primarily Mark 1A. Fig. 1 shows a typical unirradiated Mark IV fuel assembly.
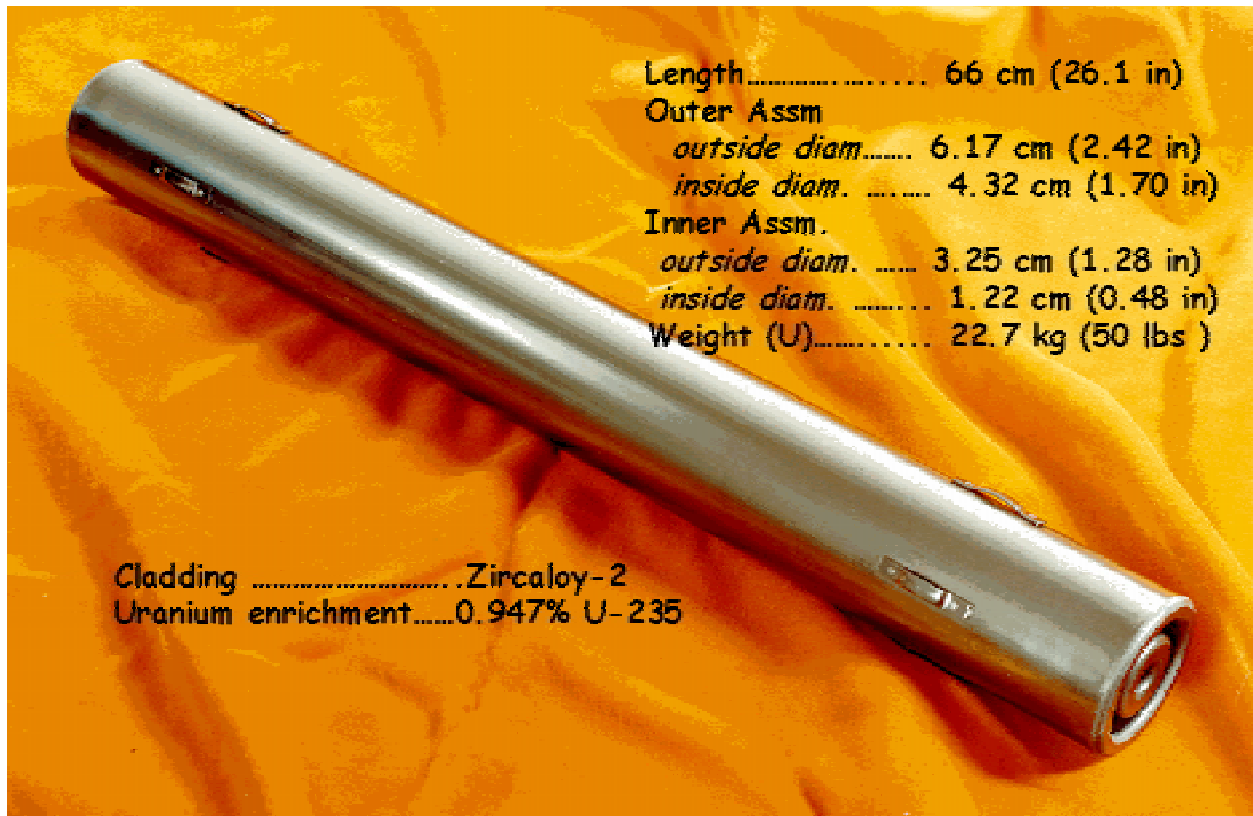

Figure 1. Typical N Reactor Mark IV fuel assembly

In total, about 2,100 metric tons of N Reactor spent nuclear fuel – or approximately 105,000 assemblies – is stored in the K basins. About half of this total is in KE, in 3,700 double-barreled aluminum or stainless steel canisters, each containing 14 fuel assemblies. The remainder is in 3,800 similar canisters in KW.

There is, however, a significant difference in the storage configurations in the two basins. The spent fuel in KE – the first of the two basins to be restored to service - is stored in open-topped canisters (some even have perforated bottoms), such that the fuel is in direct communication with the basin water that provides shielding and cooling. In contrast, the canisters in KW are mechanically sealed and a corrosion inhibitor (potassium nitrite) was added to the water in the canisters prior to sealing them. Fig. 2 shows some of the storage canisters in each of the basins.
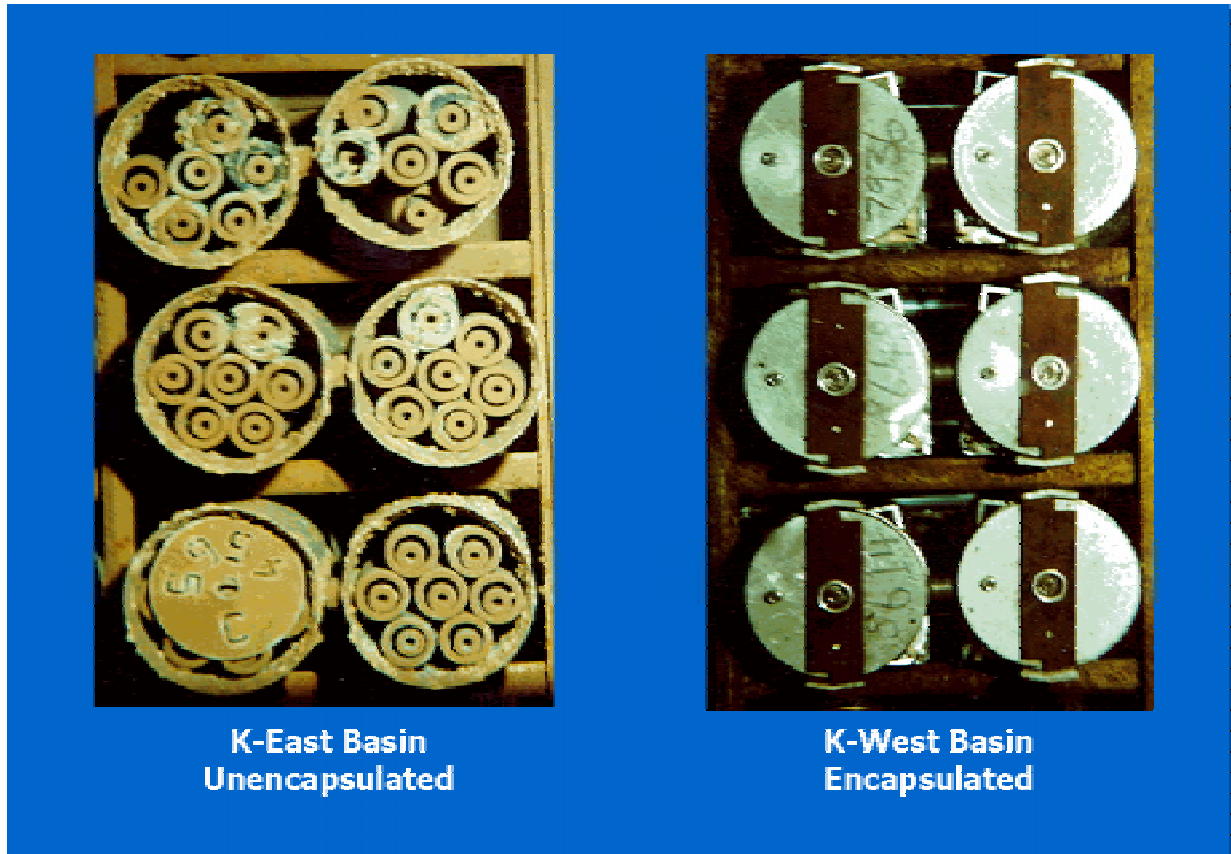

Figure 2. Comparison of storage conditions in KE and KW basins.

Fuel Condition

Visual surveys [2,3] of more than 90% of the spent fuel assemblies in the KE basin revealed that about half of the canisters contain undamaged fuel, and the remaining half contain assemblies with varying amounts of damage, ranging from minor cladding ruptures to gross failure with substantial swelling or fuel voiding. About 4% of the spent fuel in KE is estimated to be in the latter condition, including some assemblies that have broken into two or more pieces. To assess the condition of fuel in KW, some of the sealed canisters in that basin were opened and the spent fuel visually examined [4]. Based on this small but statistically significant sample, the KW fuel is judged to be in no better condition than that in KE, despite the corrosion inhibited storage. The damaged fuel assemblies in both basins generally have some portion of their uranium metal surface exposed.

In the course of the visual examinations, it was noted that all fuel assemblies exhibit a thin coating of a light gray material, and some assemblies also have black or reddish-orange coatings on some portions of their surfaces. Analyses of these coatings [5,6,7] revealed that they are principally oxides or hydrated

oxides of uranium or iron, including uranium peroxide ($UO_4 \cdot 2H_2O$), studtite ($UO_4 \cdot 4H_2O$), metastudtite ($UO_4 \cdot 2H_2O$), uranium oxide (UO_2, U_3O_8 and UO_3), hematite (Fe_2O_3) and goethite ($FeOOH$). In KW only, some assemblies from aluminum canisters also exhibited a translucent white substance on portions of their surface. This substance was subsequently identified as aluminum hydroxide ($Al(OH)_3$). Obviously, some of these substances contain water. As discussed later in this paper, the elimination of the residual free water, via vacuum drying, is an important step in preparation for sealed dry storage. Some reduction in the amount of bound water will also occur during drying, but the safety basis for the process does not take credit for it.

OVERVIEW OF THE SNF PROJECT

Selecting the Path Forward

Alternatives for dealing with the K Basin fuels were studied, beginning in 1995, and an Environmental Impact Statement (EIS) [8] was prepared. The EIS identified dry storage, calcination and processing as fuel treatment options, and it also addressed disposition of the sludge, water and debris in the K Basins. A Record of Decision [9] in March 1996 selected the preferred alternative: dry storage in a new facility to be built at Hanford, away from the river. Since that time, DOE and its contractors have been engaged in the project to move the spent N-Reactor fuel into interim dry storage and to dispose of the sludge, debris and water in the K Basins.

As it has evolved, this selected path forward involves the transfer of the fuel from its existing canisters into specially designed pressure vessels, called "Multi-Canister Overpacks" (or MCOs), each holding the equivalent of about 20 fuel canisters. Prior to placement of fuel into the MCOs, the bulk of the sludge is removed via a fuel cleaning process. Broken pieces of fuel are placed in scrap baskets and also loaded into the MCOs. The loaded MCOs are transported to an adjacent facility where they are sealed and dried, via an elevated temperature drying process called "cold vacuum drying" or (CVD). From there, the loaded MCOs are transported approximately 15 km to the dry storage facility, a new building called the Canister Storage Building (or CSB)[b], designed for extended term (nominally 40-year) passive storage of the fuel. After the fuel has been removed, a separate project effort will complete the basin cleanup, including the collection and removal the residual sludge, the empty fuel canisters, and residual contamination.

In addition to moving the K Basins spent nuclear fuel away from the Columbia River to redress the threat it poses to that environment, another DOE objective was to reduce the cost of storing the spent fuel until it can be disposed of in the geologic repository. Maintaining the two K Basins costs about $100,000 per day. To minimize costs of operating the new dry storage facility, a design objective was that it be unmanned or minimally manned after the dried spent fuel is transferred there. An existing building design from a terminated project was adapted for the purpose. Since the building was not designed to deal with hydrogen and its related safety concerns, allowing continuous venting of the MCOs to eliminate pressure buildup was rejected. Vented Multi-Canister Overpacks (MCOs) would require essentially continuous monitoring of the storage building and storage tubes to ensure that the hydrogen evolved from reactions in the container did not reach dangerous concentrations. The personnel and equipment required would be expensive, and the monitoring would be necessary over the entire projected interim storage period of 40 years. Thus, to support the objective of low maintenance cost, the MCOs containing the dried fuel will be sealed and will not be equipped with over pressure protection. This completely eliminates the concern for hydrogen safety in the building or the storage tubes by also removing the possibility of leaking relief devices.

More detail on the MCO, the drying process and the CSB is provided in the following sections.

The Multi-Canister Overpack (MCO)

The MCO has been described in detail elsewhere [10]. In summary, it is a cylindrical vessel 64 cm in diameter and 4.16 m long, made of 1.3 cm-thick 304L stainless steel with a bottom cap of 304L stainless steel 5.1 cm thick and a stainless-steel shield plug, ~30 cm thick, inserted at the top. The MCO has a design pressure of 3.2 MPa (450 psig) and is being built to Section III, Subsection NB, of the American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code*. Each MCO will receive an ASME "N" stamp. The design is deliberately robust to provide real (rather than calculational) margin in its pressure handling capability.

Fuel Drying at the CVD Facility

The process to be used to remove the water from the N Reactor spent fuel is conceptually similar to that used for commercial spent nuclear fuel. After the fuel and scrap baskets are placed into the MCO, the shield plug will be installed and mechanically sealed and locked in place. Then the MCO, filled with about 5.5 metric tons of spent fuel and about 700 kg of water, will be lifted in its cask and placed on its transporter. It will then be taken to the nearby CVD facility where, still in its cask and on its transporter, it will be connected to the vacuum drying equipment and heated to about 50 $^\circ$C by circulating hot water in the annulus between the MCO and its cask. After heating to the drying temperature, the bulk water will be pumped out and the vacuum drying process will begin. After drying is complete, as determined by a pressure rebound test, the MCO will be backfilled with helium, the process ports will be sealed and the integrity of the mechanical seal on the shield plug verified by test.

It is not practical to remove all water. At the completion of the drying process, water may remain in any or all of three forms:
- *Residual free water*, that remains in capillaries or inaccessible pockets
- *Chemically bound water*, in the form of hydrates of various oxides that may have been present on the surface of the spent fuel
- *Chemisorbed water*, present on all surfaces that were wet (a small quantity unless the surface area is huge).

The forces binding chemisorbed water to the surface are very strong, so that very high temperature is required to release it. Hydrated oxides release their water when the temperature is sufficiently high; in some cases very high temperature is required. Thus, in any practical situation, all chemisorbed water and some chemically bound water in the form of hydrated oxides in entrained sludge will remain. In the safety analyses for the vacuum drying process, all of the waters of hydration are assumed to remain in the MCO after vacuum drying at the relatively low temperature of 50 $^\circ$C. Some will, in fact, dehydrate at this temperature. No more than 0.2 L of free water is expected to remain in the MCO at the completion of the drying process [11].

Drying of N Reactor fuel is further complicated by two factors. First, the fuel is relatively old and cold; i.e., it is from 10 to 25 years post-irradiation and has an average decay power of less than about 1.4 W/assembly. Thus, a container of 277 such assemblies (typical of a loaded MCO) would generate about

400W of decay power. Second, as discussed previously, some of the assemblies have damaged cladding, such that uranium metal is exposed. Uranium metal is chemically unstable with respect to its oxides and will therefore tend to react with air, water or water vapor. These reactions are sufficiently exothermic (see the Appendix) so that if heat is not rejected at a sufficient rate during the drying process, when water

or water vapor is present in the absence of air, the temperature of the fuel will increase. This temperature increase will, in turn, cause the reaction to proceed more rapidly, resulting in an autocatalytic reaction.

Long term dry storage in the CSB

The sealed MCO in its mechanically-sealed shipping cask is transported from the CVD to the CSB, where a cover cap is welded on the top. The seal welded and inerted MCO is then placed into one of the storage tubes in the Canister Storage Building.

The CSB is designed for long-term, passive storage of the MCOs containing N-Reactor fuel, and it has additional space for future storage of other (not yet determined) material. The building configuration includes three very similar below-grade bays, each capable of containing 220 vertical steel storage tubes of a size that will accommodate the diameter of an MCO. Only one bay is so equipped at present. One of the bays has sufficient capacity to store all of fuel from the K Basins. Each tube can store two MCOs, one above the other, accessible at its top via a shielded plug in the 1.5 m-thick concrete operating deck. MCOs are loaded into the tubes through the upper access ports, from the grade-level operating deck. The MCOs are handled in the building by means of a large, remotely controlled, shielded transfer crane called the MCO Handling Machine (MHM).

Once the MCOs are placed into their storage tubes, surveillance and maintenance requirements are minimal. The fuel is fully contained and isolated from the surrounding air, and the MCOs are cooled by natural convection in the building.

TECHNICAL CHALLENGES

Challenges, in summary

As with any large and complex technical project, there are many technical challenges that, if not adequately handled, can threaten the technical or programmatic success of the effort. For this paper, the author has selected five challenges that are key to the viability of this project and that have proven particularly important to its successful execution. These are:
1) Adequately characterizing the fuel and the sludge, so that their behavior could be confidently predicted
2) Developing a safe process for heating and sufficiently drying the damaged metallic uranium fuel
3) Ensuring that over pressurizing the MCO is not credible
4) Ensuring that hydrogen generated in the MCO will not reach the flammability limit any time over the interim storage period
5) Maintaining the spent fuel in a criticality-safe configuration at all times.

Each of these will be addressed below.

Characterization

The term characterization refers to the collection of technical information about the materials in storage in the K Basins needed to support engineering, design and safety analysis of the Project's facilities, systems and equipment. The objective is to ensure that, to the maximum degree practical, the path forward is founded on real – not just hypothetical – information to reduce the potential for unpleasant surprises when fuel removal begins. The difficulty is that the quantity of spent fuel in storage is huge, and that sampling and testing it is time consuming and expensive. Therefore, achieving a timely, cost effective and meaningful characterization program required a balance among competing considerations.

In the case of the K Basins Spent Nuclear Fuel Project there are two general categories of materials of interest to the safety case and to the design of the process: the spent fuel and the particulate matter (sludge) associated with it. Information about these materials was obtained in the form of tests and measurements on samples of the materials, combined with *in-situ* observations and examinations and the use of literature data.   Technical information of particular importance to the Project included

- the reaction rate of irradiated N Reactor fuel with water vapor (in an oxygen-free environment),
- the surface area of exposed uranium that could be in an MCO,
- the composition of the sludge in the basin and in the fuel storage canisters (since some sludge could be entrained with the spent fuel).

A major issue in this characterization effort was the question of statistical significance. As described above, there are ~105,000 spent fuel assemblies varying in condition from like-new to nearly completely corroded. The physical properties of the assemblies themselves vary from point to point. If a 10 g sample is a reasonable size on which to perform tests and measurements, there are potentially ~ 2×10^8 such samples of spent fuel that could, in principle, be obtained. Similarly, there are an estimated 54 m^3 of sludge in the two basins. There is no reason to assume that the sludge composition is homogeneous. Thus, if a 1/4-L sample of sludge is a reasonable test sample size, there are at least 2.2×10^5 potential sludge samples. Even if a variance of a factor of two or three on the mean is satisfactory in the test results, a very large number of samples would be required to determine a parameter within a reasonable confidence interval. Since each radioactive sample costs hundreds of thousands of dollars to obtain, package, ship and test, and since the process takes months for each sample, large numbers of tests were clearly impractical[c].

The only practical resolution of this problem was to recognize and accommodate the mathematical realities of the situation. That is, accept the fact that it is not realistically possible to obtain and test enough samples to provide a high degree of certainty or precision (based on sampling alone) on any of the parameters of interest. Instead, the approach taken was as follows:

- For design purposes, determine values for key parameters based not solely on characterization tests, but on all the information available, including literature data, information from comparable work elsewhere, measurements and tests, computer analyses and expert judgment.
- For each of the key parameters, select a value for safety analyses large[d] enough that it would be extremely unlikely (if not incredible) to exceed it, but not so large that extraordinary measures would be required to deal with it in the design. In other words, establish conservative limits but not excessively so. Use overview by outside subject matter experts to validate the values so obtained.

In applying these adequately conservative values, additional margin is then provided in the form of ruggedly designed equipment and systems, such as the MCO.

Safely Vacuum Drying Damaged Uranium Spent Fuel

The crux of this issue is whether or not it is possible for a rapid oxidation reaction to occur in the MCO during the drying process, causing a rapid increase in the temperature of the fuel and, possibly, ignition of the fuel. A rapid reaction is potentially possible because:

- The reaction of uranium with either water or water vapor is exothermic (see the Appendix)
- The reaction will continue until or the water vapor or all the uranium is consumed (see the Appendix)
- The reaction rate increases with increasing temperature (as a general rule the rate of a chemical reaction, k, depends on temperature according to the Arrhenius Law: $k = A \exp(-C/T)$, where A and C are constants for a given set of reactants and T is the temperature in degrees Kelvin. For uranium in the temperature range of interest, the reaction rate approximately doubles for every 10-degree Kelvin increase in temperature).

- As a result heat is generated at an increasing rate, which causes the temperature in the MCO to rise if heat is not lost at the same or a higher rate. This, in turn, causes the reaction rate to increase further
- When the heat of reaction cannot be rejected fast enough, the reaction can in principle "run away"; that is, become autocatalytic.

The heat generation rate in the MCO is proportional to the product of reaction rate per unit area of uranium metal and the total area of exposed metallic uranium in the MCO. The concern that needed to be resolved is whether or not it is credible to have enough exposed uranium surface area on the fuel in an MCO to generate heat faster than it can be dissipated. This involved determining how much surface area is "conservative" enough and the appropriate reaction rate relation to use since, for any given reaction rate, it is always possible to imagine a uranium surface area large enough to cause the reaction to "run away". This is particularly true if the multiplicative factor applied to the reaction rate (to ensure it is conservative) is made large enough. Characterization [12] provided the appropriate reaction rate: measurements performed on samples of the spent fuel showed that the reaction rate in moist helium is the same as that given by the Pearce reaction rate correlation [22a] for oxygen-free water vapor. A multiplicative factor of 22 was used to safely bound the reaction rate in all safety analysis calculations.

Determining how big an area of exposed uranium is credible was more difficult. The most vulnerable area in the MCO is the scrap basket, which will be the topmost of the five baskets in a typical MCO. It is obvious that, for a given basket volume, the smaller the pieces of spent fuel that fill the scrap basket, the greater will be the total exposed uranium surface area. Since scrap is defined as fuel pieces larger than ¼-inch but smaller than 3 inches in size, there is a lot of latitude in (conceptually) filling the scrap basket.

A Monte-Carlo study [13] of the expected exposed fuel area in a scrap basket was performed, using data on typical fuel scrap size and shape from the numerous visual surveys to model the scrap pieces. The study concluded that the exposed uranium area in a scrap basket could range from $1.1m^2$ to $4.5m^2$, depending on the assumed packing density (porosity) of the basket. The most probable value was $1.7m^2$; exceeding $4.5m^2$ is considered extremely unlikely (so long as the minimum size piece was ¼-inch).

Study of the damage surveys also provided a conservative estimate [14] of the exposed uranium area associated with the relatively intact fuel assemblies that will be placed into the fuel baskets. This resulted in a safety limit value of uranium surface area of $0.8m^2$ for a fuel basket and $8.0m^2$ (rounded up) for an MCO containing four fuel baskets and one scrap basket. The safety limit value is $12.0m^2$ for an MCO with three fuel baskets and two scrap baskets (the configuration on which the Safety Analysis Reports are based). For reference, the best-estimate value for the area of exposed uranium in a fuel basket is $0.04m^2$; the best estimate area for a typical MCO with one scrap basket is slightly less than $1.9m^2$.

To accommodate the potentially large heat generation in the limiting area scrap basket, the scrap basket design was modified to provide copper segment dividers. These copper "fins" ensure that during vacuum drying heat is conducted to the MCO wall and out to the water circulating in the cask annulus. Figure 3 shows a prototype scrap basket. Thermal analyses done for the Safety Analysis Report [15], using $12.0 \, m^2$ of exposed uranium metal and a factor of 22 multiplier on the reaction rate, show that there are no credible circumstances in which an autocatalytic reaction can occur.

Figure 3. Mark 1A prototype fuel (L) and scrap baskets. Note the copper segment dividers in the scrap basket, and the large diameter stainless steel center post in both baskets.

Pressure Buildup in an MCO

The principal concern with placing spent nuclear fuel into a sealed MCO is pressurization by gases produced by various processes that can occur in the MCO. The only significant source of gas is water in any form that remains with the fuel after completion of the drying process (see discussion above, in Fuel Drying at the CVD Facility).

Free water or water vapor can react with exposed uranium to form uranium dioxide and hydrogen gas as described in the Appendix. <u>All</u> forms[e] of water can, in principle, undergo radiolysis, producing hydrogen and oxygen gases in the process. It is clear from Eq. (1) of the Appendix that each mole of water present in any form can ultimately produce one mole of hydrogen gas through reaction with exposed uranium. Radiolysis breaks a water molecule into hydrogen and oxygen, producing one mole of hydrogen gas and one-half mole of oxygen gas from each mole of water. It is conservative, then, to say that each mole of water can at most yield 1.5 moles of gas. Since some water vapor will react with uranium and some will undergo radiolysis, each mole of water will actually yield less than 1.5 moles of gas.

Other potential sources of gas in the MCO are fission products (such as krypton or xenon) liberated from the fuel in the corrosion process, helium formed from alpha emitters in the fuel and sludge, and radiolysis of any hydrocarbons that may be present (e.g., residual cutting oil on the MCO surfaces or contaminants in the sludge). Compared to the water that may credibly be in the MCO, it is easy to show that these sources are negligible.

If the total amount of water in the MCO is known – or if a limit on the total amount of water that cannot credibly be exceeded can be determined – the theoretical maximum pressure can be easily calculated from the Ideal Gas Law using the maximum temperature attainable in the MCO and its minimum free volume. From characterization data (including sludge drying tests), visual survey damage estimates and conservative estimates of the amount of damaged fuel and its accompanying water-bearing sludge, the limiting amount of water that could be in an MCO after vacuum drying was determined to be 4.84 kg [16]. This is for an MCO with two scrap baskets and three fuel baskets. For a minimum free volume of 0.5 m^3 in the MCO and a maximum temperature of 103 ^{o}C, this would, at most, produce a pressure in the MCO of 366 psig. Actual calculations, realistically accounting for the reactions and interactions that can occur, yield a limiting value of 143 psig for the safety-case MCO [17]. This is well below the design pressure of 450 psig. The nominal free-volume of an MCO is 0.7 m3, the nominal MCO internal temperature is expected to be 65 ^{o}C, and the pressure in any MCO is not expected to exceed 30 psig over the entire interim storage period (including the ~7 psig of helium added to each MCO).

Hydrogen

Hydrogen generated in the corrosion of the exposed uranium by residual water or water vapor, and from radiolysis of this water, poses a threat of deflagration or detonation if the flammability limit is reached or exceeded. For the H_2-O_2-He mixture in an MCO this limit is taken to be 4% O_2 [18]. Competing with the gas generation processes are reactions of the oxygen and hydrogen with the materials in the MCO. These reaction rates depend on the area of the reacting material and are strongly influenced by temperature.

Uranium has a strong affinity for oxygen and will react with it to form various oxides, depending upon the temperature (and exposure time). At low temperatures the reaction is principally the one given in the Appendix (i.e., Eq. 2) and this reaction will continue as the oxide layer builds up and spalls off, until all the oxygen is consumed. A clean uranium surface also has a strong affinity for hydrogen, but the reaction [19] does not occur in the presence of water or oxygen above a few parts per million, and the reaction rate is decreased for an oxidized uranium surface (as will be the case in an MCO). The reaction of hydrogen with uranium was therefore ignored in the safety-basis analyses. (It should be noted that the reaction of hydrogen with uranium produces uranium hydride, a highly pyrophoric material. Over the interim storage period of ~ 40 years, some hydride formation will certainly occur, reducing the hydrogen inventory - which is good - but creating uranium hydride - which is not so good).

Generally speaking, MCOs with a scrap basket will have a relatively large area of exposed uranium, while those with no scrap basket will have a relatively small uranium area. The former would be expected to effectively react with (i.e., getter) any oxygen produced by radiolysis for any credible fuel decay power , temperature and radiolysis rate. It is less obvious that the no-scrap-basket case will result in maintaining oxygen levels below the 4% limit. A parametric study was performed [20] using a range of fuel and scrap basket uranium areas, for MCOs with no, one or two scrap baskets, and with the limiting high value of water content after CVD. In the case of an MCO with no scrap basket there is no credible combination of MCO decay power, water content, temperature or exposed uranium area that results in oxygen concentrations above 4% after 40 years, given the presence of the helium added after CVD. All MCOs with one or two scrap baskets had appreciably less than 4% oxygen over 40 years for all credible conditions.

Criticality

Uranium-235 is a fissile material and, as such, must be handled carefully to avoid a configuration that could sustain a chain reaction. The amount of U-235 in "green"(i.e., unirradiated) N Reactor fuel is, however, relatively low; as described previously, only the outer element of the Mark IA assemblies contained pre-irradiation enrichments of 1.25% U-235, while all other elements and assemblies had pre-

irradiation enrichments of 0.947% U-235. Assuming all the spent fuel and scrap in an MCO is at its pre-irradiation enrichment, it is not possible to attain criticality even when all the fuel is rubbleized and optimally spaced in cold water [21]. However, under optimum (but essentially incredible) conditions, the value of the effective multiplication factor, k_{eff}, slightly exceeds 0.95 for rubbleized Mark IA green fuel of optimum particle size and optimum water-to-fuel ratio. The value of 0.95 is an administrative limit that cannot be exceeded if the fissile material is to meet Federal transportation requirements. An MCO containing dry N Reactor spent fuel or scrap cannot be made critical under any conditions.

Despite the fact that the criticality calculations are very conservative, and the margin of safety provided by using the 0.95 limit for low-enriched uranium metal fuel is substantially greater than the margin provided by using the same limit for higher enriched commercial fuels on which the limit is based, the fuel and scrap baskets were designed to keep k_{eff} below 0.95 for any condition. The large stainless steel center post shown in Fig. 3 above serves, among other functions, to physically exclude fuel or scrap from the center region of the baskets, thereby reducing k_{eff}.

SUMMARY AND CONCLUSION

Transitioning the damaged, metallic uranium N Reactor spent fuel from wet to dry storage, in a timely and cost-effective manner, presented several technical challenges. Each of those challenges has been resolved satisfactorily, although not without considerable effort on the part of the contractor and DOE. All required facilities are nearing completion on schedule and testing of the required systems is in progress. Fabrication of the 400 MCOs required has commenced as has manufacture of the ~2,700 fuel and scrap baskets. All facility Final Safety Analysis Reports are nearing completion of their review/comment cycle and will be issued in the near future. Fuel removal from the K West basin is scheduled to begin in November 2000.

APPENDIX: RELEVANT URANIUM PROPERTIES – A BRIEF REVIEW

Numerous measurements of the reaction of uranium in various environments have been conducted in the past 60 or so years, and several excellent reviews of these measurements have been published [22]. The reactions of concern here are those that can occur in water or water vapor, with or without the presence of air (i.e., oxygen). It is well established [23] that the reaction that occurs in water or water vapor is

$$U + 2H_2O \rightarrow UO_2 + 2H_2 \hspace{4cm} \text{Eq. (1)}$$
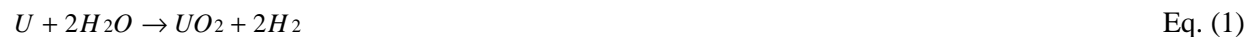
This reaction is exothermic and releases about 515 kJ of heat/mole of uranium reacted at 50 ^{o}C in liquid water, and 600 kJ/mole in water vapor at the same temperature [24]. The reaction is generally not exactly stoichiometric as shown here, but the (small) difference has no relevance to this discussion.

If oxygen is present in the water or water vapor above a few parts per million [25], the production of hydrogen is inhibited and the reaction that occurs is

$$U + O_2 \rightarrow UO_2 \hspace{4.5cm} \text{Eq. (2)}$$

with the release of about 1,085 kJ of heat/mole at 50 ^{o}C. This is the same reaction that occurs in air. Oxygen also reduces [25] the reaction rate by about a factor of 40 at temperatures in the range of interest to us.

In the presence of hydrogen, either from the reaction of Eq. (1) or, say, from radiolysis, uranium can react to form uranium hydride (UH_3) according to

$U + 1.5H_2 \rightarrow UH_3$, accompanied by the release of about 128 kJ of heat/mole at 50 ^{o}C.   Eq. (3)

Uranium hydride is also chemically reactive, and can react vigorously with water or water vapor according to:

$UH_3 + 2H_2O \rightarrow UO_2 + 3.5H_2$, and the production of about 387 kJ of heat/mole at 50 ^{o}C.   Eq. (4)

In air two reactions are possible:

$UH_3 + O_2 \rightarrow UO_2 + 1.5H_2$, with the release of $\sim$ 960kJ of heat/mole at 50 ^{o}C, or   Eq. (5)

$UH_3 + 1.75O_2 \rightarrow UO_2 + 1.5H_2O$, and the release of about 1,380 kJ of heat/mole at 50 ^{o}C.   Eq. (6)

Both uranium metal and uranium hydride are pyrophoric materials; that is, they are capable of spontaneous ignition in the presence of air. This is a consequence of the significant heat produced in their reactions with air - see Eqs. (2), (5), (6) - and is especially a concern when the materials are in a form that has a high specific area (ratio of surface area to mass). Uranium hydride is always formed with high specific area [26] and therefore has a deserved reputation for pyrophoric behavior.

One additional relevant property of uranium metal is its corrosion behavior with time. In water, water vapor or air the corrosion products formed are all less dense than the parent metal [27]. Except for a very thin layer of oxide that is tightly adherent, and reduces the reaction rate compared to that of the "clean" metal by only a small amount, the corrosion product spalls off the reacting surface. For this reason, uranium does not passivate in the usual sense as understood by metallurgists – no protective oxide layer is formed that greatly reduces the corrosion rate. Thus uranium will continue to corrode until either all the reactant or all the uranium is consumed.

FOOTNOTES

[a] The two K-Reactors are co-located near the Columbia River. Each reactor has its own fuel storage basin, identified in this paper (and commonly referred to) as the K-East (KE) and K-West (KW) basins.

[b] The somewhat imprecise terminology reflects the changes in the path forward as the work has progressed. The original plan was to load the spent fuel in its storage canisters into the MCO – hence the labels 'Multi-Canister Overpack' and 'Canister Storage Building'. That concept was changed to improve packing efficiency. Also, it was planned to have two stages of vacuum drying, the first ('cold') stage at 50 ^{o}C and the second ('hot') at ~300 ^{o}C. These were referred to as "cold" and "hot" vacuum drying, respectively. Studies showed the benefit of the hot stage was outweighed by the risk of heating the spent fuel to such a high temperature.

[c] Characterization of the spent fuel and sludge have cost a total of ~ $35 Million.

[d] In some cases, a low value of a parameter could be limiting. In those cases, a sufficiently conservative low value was identified. An example would be the reaction rate of uranium with oxygen where gettering of the oxygen is important to safety.

[e] Radiolysis of tightly chemically-bound water (water of hydration) is probably unlikely. The conservative approach used here is to assume it will occur.

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