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TECHNOLOGY STATUS IN SUPPORT OF REFINED TECHNICAL
BASELINE FOR THE SNF PROJECT

ENGINEERING CHANGE NOTICE

Page 1 of 3

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7. Abstract

The Spent Nuclear Fuel Project (SNFP) has undertaken technology acquisition activities focussed on supporting the technical basis for the removal of the N Reactor fuel from the K Basins to an interim storage facility. The purpose of these technology acquisition activities has been to identify technology issues impacting design or safety approval, to establish the strategy for obtaining the necessary information through either existing project activities, or the assignment of new work. A set of specific path options has been identified for each major action proposed for placing the N Reactor fuel into a "stabilized" form for interim storage as part of this refined technical basis. This report summarizes the status of technology information acquisition as it relates to key decisions impacting the selection of specific path options. The following specific categories were chosen to characterize and partition the technology information status: hydride issues and ignition, corrosion, hydrogen generation, drying and conditioning, thermal performance, criticality and materials accountability, canister/fuel particulate behavior, and MCO integrity. This report represents a preliminary assessment of the technology information supporting the SNFP. As our understanding of the N Reactor fuel performance develops the technology information supporting the SNFP will be updated and documented in later revisions to this report.

Revision 1 represents the incorporation of peer review comments into the original document. The substantive evolution in our understanding of the technical status for the SNFP (except section 3) since July 1995 have not been incorporated into this revision.

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TECHNOLOGY STATUS IN SUPPORT OF REFINED
TECHNICAL BASELINE FOR THE
SPENT NUCLEAR FUEL PROJECT

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TECHNOLOGY STATUS IN SUPPORT OF REFINED
TECHNICAL BASELINE FOR THE
SPENT NUCLEAR FUEL PROJECT

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TECHNOLOGY STATUS IN SUPPORT OF REFINED TECHNICAL BASELINE FOR THE SPENT NUCLEAR FUEL PROJECT

1.0 INTRODUCTION

The Spent Nuclear Fuel Project (SNFP) has undertaken technology acquisition activities focussed on supporting the technical basis for the removal of the N Reactor fuel from the K Basins to an interim storage facility. The purpose of these technology acquisition activities has been to identify technology issues impacting design or safety approval, to establish the strategy for obtaining the necessary information through either existing project activities, or the assignment of new work. In the case of new work, the technology acquisition activities have focussed on defining and executing specific tasks to resolve specific technology issues.

A formal process was employed to identify an initial set of technology issues relating to the SNFP. This process utilized a team of technical experts to review the Independent Technical Assessment (ITA) proposed path^[1] and identify technology data needs required to support the major actions proposed for placing the N Reactor fuel into a "stabilized" form for interim storage. The team reviewed the proposed process steps and for each major process step identified technical information required to support safety assurance and process definition. New work tasks were identified and analyses initiated to provide these technology information needs. This process and the specific tasks were documented in the SNFP Technology Acquisition Plan (TAP)^[2].

The SNFP has now undertaken a reevaluation of their path forward^[3] per the Department of Energy (DOE) direction. A set of specific path options has been identified for each major action proposed for placing the N Reactor fuel into a "stabilized" form for interim storage as part of this refined technical basis. These specific path options are depicted graphically in Figure 1.1.

The identification of technology needs for the SNFP has thus far been focussed on informational needs required to support key near-term project decisions. The following key decisions form the focus for this technology report: should the Multi-Canister Overpack (MCO) loaded with N Reactor fuel be shipped or staged wet or dry; should the MCO be vented; should some desludging be performed, and if so, at what stage in the process; and should drying/conditioning of the fuel be performed. The primary source for this technology information has been the results from the tasks initially identified within the TAP^[2]. A second source for this technology information has been specific studies initiated by the SNFP design team.

This report will summarize the status of technology information acquisition as it relates to these key decisions. In reviewing the issues generated in the TAP process and from consideration of the refined path options several issues were found to overlap the major actions identified in the ITA proposed path^[1] and refined path options. For example the potential for fuel ignition was a primary safety concern for shipping, stabilization and conditioning, and the storage activities. In reviewing the issues identified

Figure 1.1 Schematic Depicting Specific Path Options Under Consideration as Part of the Refined Technical Baseline.

in the development of the TAP, the following specific categories were chosen to characterize and partition the technology issues: hydride issues and ignition, corrosion, hydrogen generation, drying and conditioning, thermal performance, criticality and materials accountability, canister/fuel particulate behavior, and MCO integrity. This report has organized the technology information status into these specific categories.

This report represents a preliminary assessment of the technology information supporting the SNFP. Several key assumptions have been utilized to estimate N Reactor fuel performance for the various path forward options under consideration. In some cases these assumptions have a high degree of uncertainty. For example, the estimate for the available surface area for corrosion reactions is based upon 204 "badly damaged canisters." The number of damaged canisters may be significantly higher based on operations reports. This estimate for the number of canisters is currently under re-evaluation because of its implications to the corrosion rate and related hydrogen gas generation. As our understanding of the N Reactor fuel performance develops the technology information supporting the SNF project will be updated and documented in later revisions to this report.

2.0 HYDRIDE ISSUES AND IGNITION

The investigation into the potential for fuel pyrophoric (runaway oxidation) events has yielded not only the expected understanding of safety issues but also has yielded spinoff results from "ignition theory" which will be explained in this section.

Ignition theory is applicable to the SNF path forward in two basic ways. First, it allows broad quantification of the relative safety benefit of any handling or processing option, because the relative change in the ignition temperature may be calculated for a given fuel composition and configuration. Second, it allows design and optimization of any process involving a change in either the amount or physical location of metal or hydride. As a concrete example, ignition theory has been used to scope feasible conditioning process temperature, pressures, and flow rate combinations. It has also allowed a succinct statement of the decision logic regarding fuel conditioning.

It is important to realize that the quantitative application of ignition theory to the SNFP depends upon an accurate understanding of the N Reactor fuel characteristics. Since the present knowledge of the N Reactor fuel characteristics is very limited, the use of these calculations is focussed on providing design guidance and perhaps assessing the nominal susceptibility of the N Reactor fuel to ignition for the path forward processes under consideration.

2.1 BACKGROUND

2.1.1 Basic Elements of Ignition Theory

Fuel pyrophoricity is a key concern which motivates the study of metallic fuel oxidation and accident potential. A framework for quantifying this issue, ignition theory, is presented in a historical context including the current state of the art and its validation.

Fuel is always potentially chemically reactive when it remains a metal, yet the conditions for its reactivity may be quantified and appropriately addressed in facility design. Natural or engineered phenomena may be shown to prevent fuel oxidation for rational designs, and limit fuel oxidation for hypothetical accidents.

The McGillivray, et al., kinetic rate law for the reaction of unirradiated uranium in moist air^[4] is:

$$w'' = \frac{0.4195 p e^{-6432/T}}{1 + 2.48 \cdot 10^{-7} p e^{5236/T}} + 10.95 e^{-8077/T} \quad (2.1)$$

where w'' is the corrosion rate in kg of O_2 per m^2 per second,

p is partial pressure of steam in kPa, and

T is temperature in Kelvin.

The first term in the expression is the steam oxidation rate contribution and the second term is that of oxygen in air. The corresponding heats of reaction are 1.67×10^7 J/kg for steam and 3.4×10^7 J/kg for oxygen. The McGillivray correlation is based on dry data from 40–350°C and data with water vapor present from 50–200°C, and is believed valid for lower temperatures and vapor compositions up to 100 kPa.

Ignition theory is a framework which combines the chemical reaction kinetic rate law for uranium metal (and possibly hydride) with heat and mass transfer laws for a geometry and scenario of interest in order to judge the potential for runaway fuel oxidation. For the purposes of this discussion, the ignition temperature is defined as the highest stable ambient temperature. As an example, a MCO with a bottom failure and open top valve would allow circulation of air for fuel oxidation. Decay power of the fuel material within a MCO would imply a higher fuel temperature than the ambient environment in which the MCO sits. As the ambient temperature is hypothetically slowly raised, the fuel quasi-steady temperature increases faster because the oxidation rate increases exponentially with temperature. Eventually, heat production cannot be removed by conduction, radiation, and convection losses, and runaway oxidation, i.e., a pyrophoric event, occurs. Assuming no mass transfer limitation, ignition theory can predict the ambient air temperature at which runaway oxidation would occur for a fixed fuel configuration and heat transfer resistance if sufficient air were available during an accident.

Equivalently, ignition theory can predict the necessary fuel configuration or heat transfer resistance for runaway oxidation given a fixed ambient temperature. Both such applications of ignition theory are important for dry storage. In the first case, ignition theory can tell us if no reasonable ambient temperature could cause fuel ignition; this would be a safe configuration. In the second case, ignition theory can tell us the impact of fuel character and storage facility design on the potential for ignition.

The four key elements for application of ignition theory to spent nuclear fuel are quantification of: (1) fuel oxidation kinetics; (2) thermal properties such as thermal conductivity for mixtures of fuel physical and chemical forms; (3) heat balance equation and heat transfer mechanisms and resistances for specific configurations; and (4) mass transfer limitations, if any, for specific configurations.

Ignition theory is best exemplified by the stationary theory of thermal explosions pioneered by Frank-Kamenetskii^[5]. For simple geometries, the theory elegantly summarizes the ignition criterion through the critical value of a single parameter, known as the Frank-Kamenetskii parameter, which contains Arrhenius rate law constants, the heat of reaction, and the thermal conductivity of the medium. The theory has been experimentally verified for many substances, and analytically extended for more complex situations, by many investigators, and this approach to thermal ignition is now found in combustion textbooks.

The four key elements of application of ignition theory were recently assembled for spent nuclear fuel application by Fauske & Associates in 1994^[6] to address the potential for ignition of fuel at the K Basins following hypothetical loss of basin water. The first key element, fuel oxidation kinetics, was provided by McGillivray, et al.^[4], with the published rate law for uranium oxidation in moist air. The correlation of McGillivray, et al., is cast in terms of the power per unit area generated by chemical reactions as a function of temperature and relative humidity in Figure 2.1. For reference, a steam pressure of 2 kPa is typical of Hanford on a pleasant day of 25°C. Experimental validation of the theory also relies upon the second element, a physical property correlation for uranium particle bed thermal conductivity^[7], which was unavailable to researchers who had conducted early uranium ignition experiments.

2.1.2 Validation Status

Ignition experiments were conducted by a number of researchers^[8-11], and the most pertinent to SNF application were those of Tetenbaum, et al.^[11]. Tetenbaum placed metal powder charges in stainless steel crucibles of varying diameter and measured the ignition temperature for various bed depths, Figure 2.2. The chosen values of independent parameters (bed depth, bed diameter, and particle size) were such that the particle size effect was more pronounced than the other effects. Using the McGillivray kinetic rate law^[4] and the Kobayashi correlation^[7], Epstein^[6] was able to explain Tetenbaum's results with no resort to adjustable parameters except recommended published values. This is exemplified in Figure 2.3.

Figure 2.1 Uranium Metal Oxidation Energy Flux (W/m^2)
Correlation⁽⁴⁾.

Figure 2.2 Ignition Apparatus Used in Reference 6.

Figure 2.3 Crucible Wall Ignition Temperature Versus Uranium Powder Height in Different Diameter Crucibles - Ignition Theory Compared with Experimental Data ^[6].

Another important recent development is that the kinetics of uranium hydride are now understood to be for practical purposes identical to those of the metal; this has been suspected from the data of Hartmann, et al.^[8], and recently confirmed by communication with Sandia National Laboratory.

The point of this historical perspective is twofold. First, a reliable ignition theory interpretation of experiments and Hanford experiences has only recently become possible. Given the necessary kinetic and physical property data, experiments with unirradiated uranium metal can be quantified and predicted by ignition theory, and experiences with less well-defined parameters can be satisfactorily explained. Second, the theory may be extended to new situations in order to make predictions of the potential for fuel ignition in a variety of circumstances pertinent to the SNF path forward.

2.1.3 Uncertainties

Reaction kinetics of irradiated N Reactor fuel will differ somewhat from that of unirradiated uranium. Fuel swelling is anticipated to increase the kinetic rate of reaction. Fortunately, swelling of N Reactor fuel elements is expected to be relatively limited and the impact on kinetics is likewise expected, though not yet proven, to be small as well. The influence of irradiation may be quantified by either fuel fragment ignition experiments and/or by more complex experiments to determine the oxidation kinetic rate law.

Steady-state ignition theory may be applied to support potential for pyrophoric reactions for each packaging, shipping, and storage option. However, the extent of fuel damage and the corresponding amount of potentially reactive surface area is unknown, and the impact of irradiation on the kinetic rate of reaction is also not yet quantified. Ignition theory should thus be applied with conservatively large surface area and reaction rate inputs, rendering its results conservative. Fortunately, reasonable scenarios involve inherent air supply limitations that limit the potentially achievable rate of fuel oxidation.

2.2 MAJOR TECHNICAL ISSUES

There exists a potential for oxidation of fuel during dry storage, by design or by accident depending upon the storage and processing options chosen. Runaway oxidation, also known as ignition or a fuel fire, is a safety concern. Spontaneous fuel fires have been effectively hypothesized within ignition theory. Simply, a spontaneous fire, or a runaway oxidation, will occur when the specific area (surface area per unit volume) available for oxidation is large so that the chemical reaction power is large relative to the heat losses for a given fuel configuration. Conditioning, by oxidizing away small fuel particles and hydrides, reduces the specific area of the fuel and consequently can render it nearly impossible to ignite for anticipated storage conditions.

Technical issues for fuel hydride and ignition are:

1. The actual amount of hydride present in fuel, since this impacts the potential for ignition in the current fuel condition.

2. The actual extent of fuel damage, since this impacts the available surface area for chemical reaction beyond that attributable to hydrides. If fuel is relatively undamaged, there is little real safety gain from any passivation process. If fuel is relatively damaged, passivation is difficult to accomplish because of the temperature and time requirements to eliminate large quantities of fuel fragments. If damaged and undamaged fuel are sorted using adequate criteria prior to packaging, then subsequent actions are easier to design.
3. The potential for a evolution of hydride during long-term storage options.
4. Availability of oxygen during accident scenarios. If scenarios implying unrestricted availability of oxygen are deemed sufficiently probable, then the product of a conditioning process and the integrity of storage are important issues. However, it may be deemed improbable to achieve the multiple, large failures required for such availability.

Clearly the first two issues listed above can only be addressed by characterization of the fuel. However, the logical implications of the extent of hydriding and fuel damage have been directly addressed by a number of Technology Acquisition Program reports thus far^[12-15], and these developments are summarized below.

The issue of long-term hydride formation potential for either closed or open systems has not been adequately addressed to date, although the hydrogen concentrations in the absence of reactions with fuel are trivial to derive.

Availability of oxygen is an integral part of accident assessments and is discussed below.

2.3 TECHNOLOGY STATUS

Great progress has been made in understanding the implications of hydrides and fuel damage on shipping, staging, storage, and conditioning processes, although fuel characterization data are required to definitively apply the methods developed to date. The methods and their contribution to decision logic are summarized here.

2.3.1 Rate Limit Issues

Rate limit issues are well-understood and have good experimental pedigree.

When a single failure allows air ingress into an MCO, gas exchange between the MCO interior and exterior is accomplished by density-driven countercurrent flow of gases through the opening. If the failure is oriented for horizontal flow (the failure opening lies in a vertical plane), then warm gas from the MCO interior flows out through the upper half of the opening, and cooler air flows into the MCO through the lower half. If the failure is oriented for vertical flow (the failure opening lies in a horizontal plane), then the two gas streams interact in a complicated pattern without the well-

defined stratification of the horizontal flow case. Countercurrent gas flow rate data from Fauske & Associates, Inc., are presented in Figure 2.4 in terms of a normalized volumetric flow rate versus the length to diameter ratio of the opening. When the correlation is used in the low length to diameter limit, the mass flow rate through a 1 inch diameter opening of an MCO is given in Figure 2.5 for various MCO internal temperatures and hydrogen concentrations.

Suppose that an MCO with fuel heated to a steady temperature of 100°C by its own decay power during shipping was subjected to an accident with sudden shearing of a single 1 inch vent line. Using Figure 2.5, the air ingress rate to the MCO would lead to an oxidation power of about 75 Watts. This oxidation power (presuming adequate reactive area) is less than a typical decay power value of 300 watts in an MCO; actually this value for decay power would lead to a lower steady-state temperature and lower air ingress rate. In this example, clearly the natural rate limitation of gas exchange prevents a pyrophoric reaction.

2.3.2 Application to Wet and Dry Shipment and Staging

Wet shipment causes no ignition concern for realistic fuel reaction rate assumptions. From both Tyfield and the Reactor Handbook, the corrosion rate of uranium in water at 100°C is about 30 g U/m²/hr, which translates to a power of 21 W/m². (Note aqueous corrosion appears faster than corrosion in humid air, since according to Figure 2.1, at 100°C, the reaction heat flux from McGillivray with high steam pressure is roughly 1 W/m².) The corrosion power is about 50,000 times lower than the critical heat flux (CHF) for saturated water pool boiling from an upward facing surface of about 1.4 MW/m², a conservative lower bound heat removal rate for fuel in an MCO. Thus, even if the corroding area and the corrosion rate were both two orders of magnitude larger, the reaction power could be removed by water. It should be borne in mind however that such heat removal rates would require venting capability of a MCO. Thus, while ignition is not a problem, heat removal from the MCO should be addressed.

While ignition of wet fuel has been dismissed, if water drainage during an accident has to be considered, the problem becomes identical to dry shipment or staging. A first-cut MCO water loss example problem is presented here to demonstrate evolution of the fuel shipping accident methods. The representation of the MCO for this example is crude and results are not intended to be used for design purposes. However, the example clearly shows that MCO accident simulation is feasible with incremental changes to current models.

A five-tier MCO was modeled with a single well-mixed gas space and four representative fuel rod groups with different effective heat transfer resistances (inner rods convect to the gas and radiate to the next outermost rods, the outermost rods radiate to the MCO wall, etc., as illustrated in Figure 2.6. Also, the gas compartment communicates with the environment through two 2.54 cm (1 in.) vent holes at the MCO top, the assumed failure. Decay power and oxidation energy are deposited in the fuel, nodes 1 through 4 in Figure 2.6 and the shipping cask radiates and convects to the environment. This crude transient ignition model has since been improved but serves to illustrate capabilities.

Figure 2.4 Counter-Current Flow Rate, Q_{cc} (m^3/s), Data Versus Length to Diameter (L/D) as a Function of Density Difference Ratio $\Delta\rho/\rho$.

Figure 2.5 Counter-Current Gas Flow Rate (kg/s) through a 2.54 cm (1 in.) Diameter Vent for Various MCO Hydrogen Fractions in Air.

Figure 2.6 Simplified Nodalization for First-Cut MCO Shipping Accident Analysis. Nodes 1-4 are Fuel; Nodes 5-7 are the Canister, MCO, and Cask Walls, Respectively.

Complete MCO drainage is assumed at the beginning of the calculation, and the MCO is filled with air at 25°C with a steam pressure of 3 kPa (23 torr). An initial hydride mass present on the fuel was conservatively estimated as 20% of the corrosion product on 10% of the fuel surface area corroded to a depth of 1 mm, for a total mass of 16 kg. Hydrides were assumed to have large surface area and burn at an arbitrary, high rate, so their consumption is effectively determined by the calculated air exchange rate with the environment. Note that the "hydride" considered here could equally well be fuel fragments with high surface area.

Results are exemplified by the temperature history of Figure 2.7. The initial hydride (assumed at the surface) is consumed over a period of 600,000 seconds, or about 170 hours, and its burning rate is determined solely by the availability of oxygen and steam in this example. Maximum temperatures are attained in roughly 40 hours, during hydride burning, but these temperatures are not much above steady state temperatures after complete hydride consumption.

Results of this example problem are in part driven by assumptions and in part a consequence of the MCO steady state temperature distribution and the corresponding kinetic rate law. If the mass of hydride or fuel fragments assumed to burn rapidly was larger, then the steady maximum temperatures would still be the same for the same limiting gas exchange rate. If larger failures were postulated, then the gas exchange rate would be larger than in this example, and temperatures during hydride or fuel fragment oxidation would be higher. For cases with large failure areas, greater care must be paid to the real initial hydride and fragment particle size distribution. Cases with small failures are insensitive to MCO physical or chemical form.

A simple hand calculation technique^[13] agrees well with the computer code prediction of no ignition. This is because the controlling heat transfer resistances are air conduction inside the MCO, in a gap between the MCO and either an external vault tube or shipping cask, and finally from the outer container surface; these resistances are trivial to estimate. The calculation indicates that reaction power will equal decay power at a fuel temperature of about 410 K for a damp MCO, while the reaction power is about 15% of decay power at that temperature when Hanford ambient air enters. At a steady storage temperature of 120°C (about 390 K) the reaction power is about 20% of decay power in a damp case and it is about 5% of decay power in an ambient air case. The dry reaction power is negligible for all reasonable storage temperatures. Note the reaction power values could be higher if the exposed area of damaged fuel is greater than the nominal area.

2.3.3 Application to Conditioning Process

The Independent Technical Assessment (ITA) conditioning process^[11] includes three phases at elevated temperature: Dehydration to remove chemically bound water, dehydriding to decompose uranium hydride, and passivation to oxidize remaining metallic surfaces. Conditioning takes place inside a MCO holding ten fuel canisters of fourteen fuel assemblies each, as illustrated in Figures 2.8 and 2.9. Table 2.1 provides some MCO design and conditioning process parameters. The process history in Figure 2.10 indicates the temperature and gas composition for each of the three phases.

Figure 2.7 Transient Temperature History for Example MCO Shipping Accident.

Figure 2.8 Independent Technical Assessment MCO Concept Cross-Section View.

Figure 2.9 Independent Technical Assessment MCO Concept Elevation View.

Table 2.1 ITA Multi-Canister Overpack Container Design Parameters

Specifications:	
Overall Length	445.26 cm (173.50 in.)
Diameter (O.D.)	60.96 cm (24.00 in.)
Diameter (I.D.)	59.06 cm (23.25 in.)
Free Volume	0.817 m ³ (28.86 cu ft)
MCO Weight (includes internals)	1604 kg (3,536 lbs)
MCO Weight + SNF	4898 kg (10,800 lbs)
Weight (MCO + SNF + Water)	5782 kg (12,750 lbs)
Maximum Temperature	427°C (800°F)
Design Pressure	1034 kPa (150 psi)
Operating Conditions:	
Drying	0.4 kPa @ 100°C (3 Torr)
Decomposition	0.4 kPa @ 300°C (3 Torr)
Passivation	810 kPa @ 250°C (8 atms)
	0.4 kPa @ 200°C (3 Torr)

Figure 2.10 Independent Technical Assessment Baseline Conditioning Process.

A key motivation of the ITA process was minimization of the potential for fuel pyrophoric events. Hydride decomposition and metal surface passivation directly contribute to this goal; the dehydration step reduces long-term radiolytic gas generation which contributes to MCO pressurization and makes hydrogen available for potential hydriding.

As mentioned above, the ignition theory effort has allowed analysis of the conditioning process. Details of the analysis^[15] will be omitted here for brevity, but important ideas will be summarized.

2.3.3.1 Ignition Theory Interpretation of Conditioning. A well-known observation and a prediction of ignition theory is that massive uranium pieces require high ambient temperatures for ignition, while particulate and powders may ignite at relatively low ambient temperature. Thus, for low values of the surface area to volume ratio, A/V , the ignition temperature is high, and it decreases with increasing A/V . When the ignition temperature is plotted as a function of the logarithm of A/V , a nearly linear curve sloping from the upper left to lower right in the plane results as shown in Figure 2.11.

Note that the oxidation rate depends upon the metal temperature, which is higher than the ambient temperature due to the heat of reaction (and decay power if any). If the metal is within an air-filled container, oxidation may still occur, and the total power produced must be removed from the container to the ambient. Since the heat transfer resistance is greater than in the absence of the container, for a given ambient temperature, it follows that the metal temperature, and hence, the oxidation power will be higher for fuel in a container compared to fuel outside a container. Therefore, for a given A/V of the metal, a larger heat transfer resistance to the ambient implies a lower ignition temperature--ignition of the fuel in a container will occur for a lower ambient temperature than for the same fuel out of the container.

The relationship between the ignition temperature and A/V may thus be quantified for any fixed heat transfer resistance. The key to ignition theory is quantification of the appropriate heat transfer resistance in such cases. Final application of ignition theory thus depends upon knowledge of A/V .

Intact N Reactor fuel has an A/V approximately equal to 220 m^{-1} . Spherical particulate of diameter d has an A/V given by $6/d$, so 1 cm particles have $A/V = 600 \text{ m}^{-1}$. Perfectly intact fuel has no exposed metal surfaces, and thus, has A/V equal to zero for chemical reactions, but many fuel elements are at least partially failed and have A/V between zero and 220 m^{-1} . Fuel that is fragmented may have A/V larger than 220. On the other hand, corrosion during wet storage may have converted some fuel fragments to oxide, and oxidized fuel particulate has A/V equal to zero for the purposes of this discussion.

All exposed surfaces oxidize at the same rate per unit area as illustrated in Figure 2.12. If the reacting surface area is constant, then all exposed surfaces oxidize at the same speed, i.e., an oxidation front penetrates the surfaces at the same rate. Thus, after a given period of oxidation time, all surfaces would be oxidized to the same depth, and all particles of this size or smaller would be completely oxidized, while massive pieces would simply have oxide coatings (which may slough off). The conditioning process can thus oxidize small fuel fragments which are the contributors to high A/V and cause the ignition temperature to be low, leaving behind pieces with larger A/V and a higher ignition temperature.

Figure 2.11 Ignition Temperature Versus Log (A/V) Qualitative Variation for a Fixed Heat Transfer Resistance.

- Ideal Case, 220 m^{-1}
- ⊙ Fuel After Conditioning (Oxidation Process)
- Fuel in Existing Condition (Fragments and Possibly Hydride)

Figure 2.12 Qualitative Oxidation of Metal Pieces for Various Sizes at the Same Temperature.

Suppose a canister contains fuel which is partly damaged and partly fragmented. Keeping in mind that intact fuel does not contribute to A/V for reactions, in this case, A/V could equal 220 but is probably less than 600. In this state, for a given heat transfer resistance to the ambient, the fuel has some initial ignition temperature. The lowest possible A/V for this fuel can be achieved by completely oxidizing the fragments of high A/V, so that the only remaining reactive surfaces are on the damaged fuel rods.

Note that so long as there is metal in damaged elements, A/V is greater than zero, and there is the potential for oxidation. The lowest possible A/V corresponds to the highest achievable ignition temperature. This represents the ideal case of perfect conditioning. In practice, all fragments may not be completely oxidized, so a lower final ignition temperature than the ideal ignition temperature will be achieved, as shown in Figure 2.12.

The conditioning process may now be understood as a process that increases the ignition temperature of the fuel from its initial value to a value approaching an ideal maximum value. The ignition temperature increases as the A/V of the fuel decreases during conditioning.

2.3.3.2 Conditioning Process Safety Impact. Does the conditioning process lead to an increase in safety? In a sense, this is true because the A/V of fuel is guaranteed to decrease so long as there are fragments or hydride fines to be oxidized. However, the fuel initially has some ignition temperature, and even after conditioning it has some (higher) ignition temperature. The real question is how these ignition temperatures relate to the fuel storage environment.

For the sake of clarity, the ignition temperature now under discussion is the ambient temperature in a storage vault or outside a shipping cask. The fuel is understood to be at some (higher) steady-state temperature within the MCO, which in turn is inside the vault tube or cask. Since there is no air normally inside the MCO, the ignition temperature is hypothetical, and depends upon the introduction of air. If air is introduced into a MCO stored at an ambient temperature below the ignition temperature, then oxidation of the fuel can still occur, but a runaway situation cannot. The value added by the conditioning process is measured by the safety margin provided with respect to the ignition temperature as explained in detail below. Since the present planning would have the MCO contain an inert gas, ignition of the fuel should only be considered under credible accident conditions.

If the ignition temperature after conditioning is higher than a reasonable ambient temperature, then introduction of air into a MCO under an accident scenario cannot lead to ignition. The fuel is therefore stored inherently safely with respect to potential fuel burning. If the ignition temperature before conditioning is also higher than a reasonable ambient temperature, as shown in Figure 2.13, then this fuel may be stored safely, too, with respect to potential fuel burning, and conditioning is not required.

If the ignition temperature after conditioning is less than a reasonable ambient value, as shown in Figure 2.14, then the fuel is not inherently safe against potential accidents leading to air ingress, and conditioning by itself does not mitigate the safety concern. However, fuel burning will require an abundant supply of air, which presupposes multiple, massive failures of each barrier to allow a closed-loop, chimney-type flow path.

Figure 2.13 Possible Vault Temperature Less Than Both Pre- and Post-Conditioning Ignition Temperatures.

$T_{\text{vault}} < T_{\text{ignition}}$ Before Conditioning
Unconditioned Fuel Can Not Ignite
Conditioning Is Not Necessary

Figure 2.14 Possible Vault Temperature Greater Than Both Pre- and Post-Conditioning Ignition Temperatures.

$T_{\text{vault}} > T_{\text{ignition}}$ after Conditioning

Fuel Could Ignite

Conditioning Does Not Improve Safety

A reasonable storage design may render multiple barrier failures at multiple elevations incredible, and therefore, the fuel would be inherently stored safely against runaway reactions by virtue of limitations on the oxidant supply. The need for conditioning may be mitigated when the design has such characteristics. Prediction of inherent limitations of oxygen supply is prominent in previous fuel shipping accident analyses^[12-14].

There is only one case in which conditioning changes the safety conclusion, as illustrated in Figure 2.15. The initial ignition temperature is below a reasonable ambient temperature, and the ignition temperature after conditioning is above a reasonable ambient temperature, so that fuel may potentially ignite before conditioning but not after conditioning. In order to judge whether this situation exists, we must have a good understanding of the fuel characteristics both before and after conditioning.

2.3.3.3 Analysis of Conditioning. The conditioning process as envisioned by the ITA involved a combination of process gas flow through a fuel canister and pressure cycling or "breathing" of process gas to force the gas into perhaps otherwise inaccessible, occluded regions. Fundamental variables available for process control are the average operating or inlet gas temperature, T , the total gas flow rate W (the sum of an inert carrier gas flow rate and the oxygen flow rate), and the oxygen concentration, C . A parameter fundamental to the process but beyond process controls is the A/V of the fuel; more precisely the parameter is the distributed value of $A/V(x)$ along the length x of a given canister. Clearly a combination of T , W , and C must be selected which is insensitive to A/V and which meets requirements of the conditioning process.

The conditioning process is required to:

1. Change the A/V of the fuel from its initial value to a value close to the ideal A/V discussed above,
2. Occur within a reasonable period of time, say within 24 hours,
3. Be robust in the sense that it is relatively insensitive to the initial A/V of the fuel,
4. Be controllable in the sense that reasonable imprecision in selection of T , W , and C will still result in changing the A/V in a reasonable time period, and
5. Be safe such that reasonable off-normal variation in either T , W , or C will not cause undesirable consequences.

Calculations^[15] readily show the impact of assumptions of fuel character on the selection of conditioning process parameters. These calculations cannot be repeated here, but the key results are:

1. The most significant assumption is the depth to which fuel must be passivated. This is because once the depth is chosen, the tradeoff between time and temperature may be derived.

Figure 2.15 Possible Vault Temperature Between Pre- and Post-Conditioning Ignition Temperatures.

$$T_{\text{before}} < T_{\text{vault}} < T_{\text{ignition}}$$

Ignition was possible before Conditioning
But Not Possible After Conditioning
Conditioning Improves Safety

2. To remove fuel particulate of modest to high A/V, say particles less than about 1 mm in size, requires either higher temperatures or longer process times than per the ITA process. Note that particulate does appear to passivate (exhibit quadratic rate behavior) when mostly oxidized.
3. Removal of very thin (about 10 micron) layers is achievable for process times and temperatures in the ITA design range.
4. Given the chosen temperature, the next most significant assumption is the reactive surface area. This is because the reactive area and temperature determines the total reaction power, and this power must be removed by the process gas stream.
5. To remove fuel particulate of modest to high A/V, again about 1 mm size particles, requires process gas flow rates well beyond those envisioned by the ITA and which imply quite significant MCO design changes to channel the flow separately to each fuel canister. Also the gas pressure for such a process must be about 10 atmospheres. Necessary MCO design options are either fuel reracking, baffling at each elevation, or separate orificing for each canister.
6. To remove thin hydride layers, reasonable flow rates are achievable, but the flow rates are still significant due to flow split issues, and replacement of canister bottoms by screens to permit throughflow would be required. A high pressure process is still desirable.
7. A pressure cycling or breathing process is simply not possible unless the process temperature lies within the ITA design range. Pressure cycling may not work well for fuel with variations in damaged state.
8. A passivation process may be monitored by checking the exit gas temperature from each canister. The temperature increase will indicate the reactive surface area in the canister.
9. Reactions will not stop until all exposed decladded metal is consumed, so the canister exit temperature is not an indication of the success of conditioning for damaged fuel.
10. If the canister exit temperature is observed to first increase and later to decrease, this can only imply that fuel in the canister has limited damage and the canister contained a limited number of fuel fragments with reactive metal or hydride.
11. The process gas oxygen content may be (and must be) selected to limit local reactions of damaged regions, and judicious choice of this value would permit inference of a highly damaged region in a canister.
12. The implication of a highly damaged region in a canister is that downstream fuel cannot be easily passivated, since the damaged region scavenges oxygen.

13. Fuel conditioning at temperatures sufficient to remove particulate is difficult to control if there are multiple damaged regions in a single canister for the two reasons mentioned above. Fuel conditioning by breathing is difficult to control for the same reasons.

2.3.5 Vacuum Drying

The issue here is whether the ignition temperature of the fuel as-is, i.e., without conditioning, is above the storage temperature. Also, the oxygen limit as a natural way of preventing a pyrophoric reaction should be credited. Calculations with and without the oxygen limit have been made with MCO models improved beyond the one discussed in Section 2.3.2. The results to date suggest that ignition is difficult to achieve, i.e. rather large surface to volume ratios of the fuel would be required. Hence, we recover the basic question of fuel character as an essential input to these evaluations.

2.4 IMPLICATIONS TO KEY DECISIONS

2.4.1 Fuel Shipping and Staging

From the point of view of potential runaway reactions, there is little significant difference between wet or dry shipping or staging, but there are other safety implications due to corrosion rate uncertainties.

Concerning runaway reactions, all accidents tend to look the same because loss of water is essential for runaway, and because an abundant supply of air to oxidize the fuel is required. Since abundant supply of air is strictly a severe accident issue, fuel pyrophoricity should not be a driving concern with respect to this choice.

2.4.2 Vacuum Drying

Vacuum drying at relatively low temperatures to remove evaporable water is an attractive option if conditioning is not chosen. The logic for choosing conditioning is given in Section 2.4.3. One reason vacuum drying is of use is simply that it might limit the amount of hydride that could be generated during long-term closed MCO storage to that producible by radiolysis. If rudimentary precautions are taken during fuel handling at the end of closed storage, then vacuum drying is not of great benefit because of the oxygen limitations discussed above. If open MCO storage is considered (see Section 2.4.4) then vacuum drying is pointless.

Vacuum drying at high temperature to remove chemically bound water is attractive only if the conditions are first met for removal of evaporable water. This implies a significant concern over long-term buildup of radiolysis gases in a closed MCO or the long-term buildup of hydrides in fuel. Again, from the point of view of fuel pyrophoricity, this process will not provide a great safety benefit if oxygen supply limitations are considered.

It should be emphasized that the purpose of removal of evaporable and chemically bound water in reducing the extent of pressure buildup due to radiolysis is a separate issue from that of potential chemical reactions. From the point of view of pressure buildup only, removal of this water is sensible for a closed MCO but not for a vented MCO.

2.4.3 Fuel Conditioning

In view of the ignition theory interpretation of conditioning from Section 2.3.4, conditioning is worthwhile from a safety perspective under the following circumstances:

1. It can be demonstrated that reasonable ambient temperatures, for some, but not necessarily all routine and off-normal circumstances, lie above the pre-conditioning ignition temperature and below the post-conditioning ignition temperature; and
2. Design or licensing limitations force consideration of unlimited availability of air to oxidize the fuel under off-normal circumstances;
3. The frequency of unlimited air ingress accidents during conditioning, when the fuel is at elevated temperature and therefore may succumb to rapid oxidation given available air, is negligible, or alternatively the consequences may be shown to be negligible; and
4. Conditioning increases the ignition temperature significantly.

Conversely, conditioning is not worthwhile when:

1. The ignition temperature (meaning the ambient temperature that leads to ignition of the fuel in the MCO, which will be at higher temperature than the ambient temperature) after conditioning cannot be demonstrated to lie below reasonable ambient temperatures, i.e., fuel after conditioning cannot be demonstrated inherently safe with respect to runaway reactions; or
2. The ignition temperature before conditioning can be demonstrated to lie above reasonable ambient temperatures; or
3. By design the frequency of unlimited air availability to the fuel, regardless of the ignition temperature, is very low.

To conclude, conditioning always provides some benefit, and the key question is whether the benefit is worthwhile for reasonable scenarios. If conditioning makes an impact for some scenarios, then it is potentially worthwhile.

Given that conditioning is worthwhile, it is also clear from the detailed analysis of conditioning that:

1. Conditioning of fuel fragments with sizes on the order of about 1 mm requires either long process durations, which may not be logistically acceptable, or high process temperatures, resulting

in a process which is difficult to control. Multi-canister overpack design also becomes difficult because of flow control requirements.

2. Alternatively, conditioning of fuel with very thin (10 micron or so) layers containing hydride or metal fines may be accomplished within reasonable time frames and temperatures. The problem is that a substantial fraction of K Basin fuel has some damage.
3. Given these facts, sorting of fuel into relatively undamaged and damaged MCO groups is sensible.

2.4.4 Open System Alternative

Difficult questions raised above concerning the viability and feasibility of the conditioning process and MCO design implications naturally lead to consideration of alternatives.

Since the fundamental impact of conditioning is to increase the ignition temperature of fuel (through conversion of surface uranium hydrides to uranium oxide and the addition of increased uranium oxide layers to exposed fuel surfaces), and since fuel burning can only be maintained given a large supply of oxidant (air), a viable alternative to prevention of burn propagation is simply limitation of oxidant supply. Engineered barriers and storage of the fuel in inert gas can achieve this goal for routine circumstances.

The important question is whether the engineered barriers have sufficient reliability to limit the supply of oxidant under off-normal circumstances. An abundant supply of air is only achievable for very large single failures of both a MCO and its surrounding enclosure (a vault tube or transport cask) that allow great countercurrent gas exchange flow, or for small but multiple failures of both the MCO and its surrounding enclosure at different elevations so as to allow for recirculating density-driven flow via a chimney effect. An exception to the multiple failure rule occurs briefly during operations in which the MCO is moved into its transport cask or between the cask and vault tube, etc.

Consider, for example, the ITA standard MCO with a 1 inch diameter vent, not sealed, but instead open through a set of HEPA filters to the atmosphere. The natural breathing rate of the system is about 0.5% per day for typical Hanford barometric pressure variations. There is about 1 cubic meter of free space in a baseline design MCO, so 0.5% of it would be replaced daily, and the potential reaction rate would be governed by the oxygen exchange rate of about 0.001 kg/day. A peak supply rate of water vapor would be about 1/10 the molar supply rate of oxygen, or about 3×10^{-5} kg/day of oxygen (O_2) equivalent.

If the steady MCO storage temperature were about 100°C, and if 2000 kPa water vapor pressure were used in the kinetic rate law, then the chemical reaction power would be a negligible 10 W per MCO, and the equivalent consumption rate of O_2 would be about 3×10^{-7} kg/s or 0.025 kg/day. Thus, the breathing rate of 0.001 kg/day would limit the oxidation rate. (Note that for fairly intact fuel, with limited reactive area, the kinetic rate law could control reactions at a lower overall rate.) If the air were fairly dry, as would be the case in winter, the chemical reaction power would be only about 0.5 W per MCO and the equivalent consumption rate of O_2 would be only slightly

greater than the breathing supply rate. In effect, the breathing rate determines the oxidation rate in a MCO for MCO temperatures above about 60°C.

Since the oxidation rate can be no larger than the breathing rate, 0.001 kg/day oxygen translates to 2.7 kg uranium metal per year in a MCO, which is a small fraction of the total mass of about 3 metric tons. Since the steady storage temperature would decline with time, the reaction would in fact be kinetically controlled under dry conditions near the end of storage. At the end of forty years, about 100 kg uranium per MCO would be reacted, or less than 0.3% of the fuel. The smallest fuel fragments would be passively conditioned during long term barometric breathing.

2.4.5 Rational Alternatives Without Information

In the absence of fuel characterization, rational decisions may nonetheless be made.

One rational decision is to sort fuel at the basin into relatively damaged and undamaged MCO groups, and to store this fuel dry (after gravity draining) with vents or periodic purging. This is rational because we cannot a priori determine the safety gain due to any process, but we do know a priori that unlimited air ingress into a MCO is a highly unlikely severe accident.

Another rational decision is to store fuel closed after vacuum drying to remove sources of radiolytic gas generation. The hot vacuum process would be finished with a single oxygen injection phase to expose fuel to air at higher temperature than it should otherwise encounter. This is rational for the same reason that unlimited air ingress is unlikely, but we also know a priori that some passivation may be helpful. However, it is only rational if we must accept a closed MCO.

Another rational decision is to sort the fuel into relatively damaged and undamaged MCO groups and condition per the ITA process for the relatively undamaged fuel and per a much longer or higher temperature duration process for the damaged fuel, per the tradeoffs discussed by Plys^[15]. This is a risk-averse position which is higher in cost than the two alternatives. This position may be rational where schedule requires a fast decision or limits time available to gather more information.

2.5 UNCERTAINTIES AND REQUIRED INFORMATION

Uncertainties may be clearly identified with the major technical issues described above. Simply put, a clear evaluation of the potential for fuel pyrophoric events is only possible with some knowledge of the fuel character; hence fuel characterization must proceed to identify the extent of hydriding, if any, to identify the extent of damage and existence of decladded and therefore reactive metal surfaces, and to confirm knowledge of the reaction rate for irradiated N Reactor fuel in moist air and water.

As the thermal modeling described in Section 6 evolves, updated and refined boundary conditions for ignition theory will be incorporated into the analyses.

In the absence of this information, rational decisions may nonetheless be made. Several alternatives have been suggested in Section 2.4 from the point of view of potential pyrophoric events.

3.0 CHEMICAL CORROSION

3.1 TECHNICAL ISSUES

Uranium metal is highly reactive and is known to react corrosively in the presence of water and oxygen. Reaction with water results in the formation of a UO_{2+x} /hydride scale and liberates hydrogen in an anoxic environment, or water in an oxygenated environment. Reaction with oxygen creates a UO_{2+x} scale

These reactions are of interest for a number of reasons:

- The exothermic chemical reaction energy can heat the system and accelerate the chemical reaction.
- Hydrides found in the scale can potentially react rapidly with oxygen.
- Hydrogen gas from this reaction can pressurize containers and represents a flammability or explosion hazard.

For all of these reasons, uranium metal is difficult to process and store.

Many principal investigators have measured the reactivity of uranium metal with both oxygen and water. Unfortunately, their results are widely scattered. This scatter results from the fact that the inherent reactivity of uranium metal differs by one or more orders of magnitude depending upon the purity of the metal, the effects of radiation upon the metal, and the strain left as a result of metal forming operations. In addition to the variations in inherent reactivity, the overall reaction rates are surface area controlled. The true surface area is usually quite different from the geometric surface area unless the metal has been polished to a fine finish.

Thermal modeling is required to assure process safety. The chemical reaction heat is an important portion of the total energy releasable from the system. This thermal modeling has been frustrated because of the many uncertainties in predicting the inherent reactivity of spent N Reactor fuel, and the exposed surface area. Order-of-magnitude calculations can be performed quite easily, but the results are not always acceptable. Experimental characterization of the spent N Reactor fuel and its chemical reactivity is needed to refine the output from corrosion models.

3.2 CURRENT TECHNICAL STATUS

3.2.1 Chemical Reactions of Uranium

3.2.1.1 Reactions of Uranium Metal with Water (Oxygen Free). The primary reaction of uranium metal with water is:

For water vapor concentrations varying from 0 to 20% Relative Humidity (RH) the theoretical hydrogen yield is greater than 99%. Under condensation conditions, an interstitial mixture of UO_{2+x} and uranium hydride (UH_3) is formed. The absolute amounts of hydride found varied from 2 to 9wt% according to experimental conditions^[16].

Fixation of some of the hydrogen as uranium hydride, creates a hydrogen gas deficiency from that predicted by equation 3.1. This deficiency varies from 1 to 13% according to the water vapor pressure. The uranium hydride thus formed is embedded in the uranium oxide and has been shown through isotopic experiments to be non-reactive with water vapor over the course of several hundred hours^[16].

In a separate experiment with pure uranium hydride, reaction with water eliminated 15-20% of the hydride within 2 weeks. This information is similar to kinetic data presented by Sandia experts on the reaction of uranium hydrides with water and we may conclude that a heavy layer of oxide on the surface of hydride particles retards the water reaction.

All of these facts suggests that uranium hydride produced by water corrosion is well occluded by oxides and that the hydride will survive for relatively long times.

3.2.1.2 Reactions of Uranium Metal with Water (Oxygenated). In the presence of oxygen (>1000 ppm) and for 2-90%RH, the following reactions are observed:

isotopic studies show that the oxygen combined with the uranium originates in the water molecule, and that the hydrogen from the water is transferred to the oxygen gas molecules thereby regenerating water^[16]. No significant quantities of uranium hydride, nor hydrogen gas are produced in the presence of oxygen.

Under condensation conditions, some yellow UO_3 is also observed.

3.2.1.3 Reaction of Uranium Metal with Hydrogen. Unirradiated uranium metal dissociates molecular hydrogen and dissolves the monatomic hydrogen. The equilibrium monatomic hydrogen concentration is < 1 ppm within the interior. This hydrogen concentration is not high enough to precipitate uranium hydride within the interior.

Near the surface, the energy required to precipitate uranium hydride is not so large, and such precipitation occurs at or within the first micron of the surface. An overall equation can be written:

3.2.1.4 Reactions of Uranium Metal with Oxygen. Uranium metal has been readily demonstrated to form the +4 oxidation state as in the reaction:

The +6 state is found from the reaction:

Uranium is capable of forming a +5 oxidation state with fluorine however the corresponding oxygen compound, U_2O_5 is not known. Intermediate compounds are found such as:

These intermediate compounds are not proof of a U(V) oxidation state, since they could be equally represented as combinations of the +4 and +6 states.

3.2.1.5 Hydration of Uranium Trioxide. Uranium trioxide (UO_3) is typically found in small amounts in sludge that originates in oxygenated conditions. It can hydrate to form the mono and dihydrates as in:

Since all of the above reactions are possible, a study of the corrosion chemistry of uranium is one of assigning reaction rates and in understanding those factors that influence those rates.

3.2.2 Uranium Reaction Rates

Condon^[17] developed a model for the reaction of uranium metal with water. His model correlated quite well with Ritchie's corrosion rate data^[18] in both the oxic and anoxic environment.

Condon's model assumes the rate controlling step for aqueous corrosion is the precipitation of hydride within the first micron of the uranium surface. No more than 3% of the metal need be converted to hydride to effectively break up the metal surface and allow penetration of oxygen and water within that surface. Condon's model shows that the independent parameters are the hydrogen solubility within the metal, and the effective hydrogen diffusivity. The linear front velocity is given by Condon as:

$$V_s = (k \cdot C_o / U_s) \cdot \text{Sqrt}[D / a \cdot k \cdot U] \quad (3.11)$$

where:

- V_s = Reaction front velocity in m/sec
- k = hydriding rate constant
- C_o = hydrogen concentration in metal
- U_s = Uranium metal mole fraction in broken metal at interface
- U = Uranium metal mole fraction in unbroken metal at interface
- D = effective hydrogen diffusivity coefficient in uranium metal
- a = number of hydrogen atoms in 1 molecule of hydride

The movement of this reaction front establishes the corrosion rate of the metal. The broken metal between the surface and the reaction front is rapidly converted to oxide and hydride by reaction with water and oxygen.

3.2.2.1 Variables Affecting Rate Constants

Diffusion Coefficient- The rate for movement of hydrogen within the uranium metal directly affects the reaction front velocity. This rate of movement is affected by anything that affects the metal lattice including metal purity, radiation damage, metal temperature, etc.

Hydrogen Concentration - The hydrogen concentration in uranium metal is generally in the part per billion range and is affected by the metal purity, external hydrogen pressure, oxygen poisoning, internal reaction equilibria, metal temperature, etc. It is known that impurities such as aluminum decrease the hydrogen solubility in uranium metal and also decrease the corrosion rate. If the metal surface is oxygen poisoned, the hydrogen activity is in equilibrium with uranium hydride. Increasing the external water or hydrogen pressure does not increase the corrosion rate significantly because of the slow transfer rate of hydrogen through the oxygen poisoned surface. If the surface is not oxygen poisoned, the internal hydrogen concentration does increase proportionately as a function of the external water or hydrogen pressure and the corrosion rate rises proportionately. In the oxygen poisoned case, the presence of other metal oxides can control the hydrogen concentration by such reactions as:

Temperature - Temperature directly affects the hydrogen diffusivity and concentration in the metal, and also plays an important part in chemical reactivity.

At higher temperatures, the maximum energy increases and the proportion of atoms or molecules within the group having higher energies increases. Therefore, the reaction rate increases exponentially with temperature. This is expressed mathematically by the Nernst equation:

$$\text{rate} = A_0 \text{Exp}[-E/RT] \quad (3.13)$$

Where all factors affecting the rate except the activation energy and the temperature are expressed by A_0 (commonly called the frequency factor), E is the activation energy, R is the gas constant and T is the absolute temperature.

Strain - As mentioned above, radiation damage affects both the hydrogen diffusivity and the hydrogen concentration within the metal. Tyfield^[19] showed that radiation induced swelling increases the reactivity of uranium metal by a factor $(1+V_i/V_o)$, where V_i is the fuel volume after swelling and V_o is the original fuel volume. For N Reactor fuel, the mean reactivity increase due to radiation swelling may be about 1.5 times the reactivity of unirradiated fuel. Corrosion processes can also induce strains affecting rate constants.

3.2.2.2 Gas-Solid Reactions (Moist Air). McGillivray^[4] modeled the rates of reaction for mixtures of oxygen and water by assuming the water reaction rate was proportional to the fraction of the oxide surface that was covered by water in a langmuirian absorption pattern. He then adds the oxygen reaction rate obtained from dry air to obtain the total corrosion rate. This approach is foundationally wrong since both the bulk water and oxygen reactions are affected and controlled by the movement of the hydriding reaction front as stated above. McGillivray's results also do not agree with the bulk of the published uranium corrosion data.

In moist air, the reaction is oxygen poisoned, and the reaction rate is essentially nonresponsive to either oxygen or water pressures. Both the water and the oxygen reactions release the same exothermic energy since hydrogen is oxidized back to water. From a thermal modeling viewpoint, it is unnecessary to differentiate between the oxygen and the water reaction.

3.2.2.3 Liquid-Solid Reactions. Since it is known that at equilibrium, the activity of a liquid and its saturated vapor are equal, one can predict that the solubility of hydrogen within the uranium metal will be the same in the presence of either saturated vapor or liquid water. Baker^[16] predicted this behavior and Tyfield^[19] found an activation energy for the uranium-liquid water reaction that is experimentally equivalent to Ritchie's vapor phase activation energy. Tyfield also correlated the effect of variations in aluminum content, and for the swelling effect due to irradiation.

3.2.2.4 Summary of Reaction Rate Constants. Equations for calculating the reaction rate constants under a variety of conditions are given in Table 3.1.

Table 3.1 Uranium Corrosion Rates

Purity % Al	N Fuel Exposure MWD	H ₂ O MT	O ₂ %	Rate Constant Equation mg U/cm ² /hr
0.1	0	2-75% RH	0	$1/((5.72507 \times 10^{-6}) \times \text{Exp}[6945.14/T]/P^3) - ((3.09671 \times 10^{-6}) \times \text{Exp}[6945.14/T]/P^2) + ((4.32118 \times 10^{-7}) \times \text{Exp}[6945.14/T]/P)$ (Cooper regression of Ritchie data 1966 ^[18])
0.1	0	100% RH	0	$K = (3.2 \times 10^8) \times \text{EXP}[-14283/RT]$ (ref. Ritchie ^[18])
0.06	0	aq.	0	(5 K) (ref. Tyfield ^[19])
0.1	8000	aq.	0	(1.5 K) (ref. Tyfield ^[19])

R = gas constant (1.987 cal/mol/K)

T = temperature in K

P = pressure in kPa

Some of the equations from Table 3.1 are plotted in Figures 3.1 and 3.2 to allow their ready visualization.

3.3 NEAR-TERM TECHNICAL ISSUE RESOLUTION

3.3.1 Heat Transfer Modeling

Heat transfer modeling must sum the radiolytic heat energy, the chemical heat energy, and the solar heat energy to obtain the total heat generation rate. This must be balanced against the system heat dissipation rate to establish; 1) that the processes reach an equilibrium condition and 2) to obtain estimates of the equilibrium process temperatures. To do this, one must have appropriate data for the hydrogen diffusivities, hydrogen concentrations, process temperatures, and reactive surface areas.

3.3.2 Desludging

Desludging can reduce process complexity, reduce process times, and improve safety. The presence of sludge increases the amount of free water in the MCO due to capillary action. For one typical case, it was estimated that 15 liters of free water could be retained in sludge after draining the MCO. This extra free water lengthened the warm vacuum drying time from 11 hours to several days.

Sludge also is a principal source of chemically bound water. It is estimated that 95% of the chemically bound water within a MCO is contained within the canister sludge. Oxides retain volatiles through the conditioning process equal to approximately 1 wt%^[20]. It is believed these volatiles are either chemically bound water or hydroxides attached to the oxide surfaces. Sludges are therefore believed to be the principal source of hydrogen within the MCO during long term storage.

It is recommended that sludge be removed as quickly as possible to expedite the handling and storage of fuel, and so that it may be conditioned by a more suitable high temperature process.

3.3.3 Application to Vacuum Drying

3.3.3.1 Warm Vacuum Drying. When a roughing vacuum of approximately 1 kPa is applied to a warm (50°C) MCO, a low temperature, low pressure steam atmosphere is created that drives oxygen out of the MCO by a steam distillation process. The reaction rates of this water vapor with the uranium surface can be modeled using Ritchie's equations for an oxygen free environment and at reduced pressure in Table 3.1.

3.3.3.2 Hot Vacuum Drying. Hot vacuum drying is designed to remove all of the free water, and almost all of the chemically bound water, by a combination of low vapor pressures and temperatures. The reaction rate of water and oxygen with unirradiated uranium metal during hot vacuum drying can be predicted and modeled also.

Figure 3.1 Uranium Corrosion Rates with Water (Oxygen Free).

Figure 3.2 Uranium Corrosion Rates at 100% RH with Oxygen.

3.3.4 Application to Wet and Dry Shipment and Staging

No information has been developed that clearly eliminates either wet or dry processes from consideration. The final choice will be made after considering cost, schedule and safety implications.

3.3.4.1 Wet Shipment and Staging. Corrosion and hydrogen generation rates can be modeled for the wet shipment and staging processes. Preliminary heat transfer modeling results indicate that wet shipments can be safely made for the vast majority of fuel elements. The high radiolytic heat, highly corrosive elements can be segregated and shipped in actively cooled shipping casks.

3.3.4.2 Dry Shipment and Staging. Warm vacuum drying will remove the free water from the canisters, and will allow the safe shipment and staging of the MCO's. The chemically bound water will not have time to radiolyze and become a problem over storage time less than several months.

3.4 IMPLICATIONS TO KEY DECISIONS

3.4.1 Desludging

Desludging is highly recommended at the earliest opportunity since almost all of the significant process and safety problems are associated with sludge. It is believed that desludging is essential to safe long term storage of spent fuel, since otherwise it is believed that a significant potential exist for the creation of fresh uranium hydride after the conditioning process.

3.4.2 Wet Vs. Dry Shipping and Staging

Warm vacuum drying is recommended at the pool to eliminate all free water from the MCO. This should be achievable and decreases hazards from uncontrolled water reactions thereafter.

3.4.3 Hot Vacuum Drying Vs. ITA Process

Hot vacuum drying is recommended over the ITA process, since it is simpler and quicker to run, and also has significant safety advantages.

3.5 UNCERTAINTIES AND REQUIRED INFORMATION

The principal uncertainties are the lack of precise knowledge of the reactivity and exposed uranium surface area of the spent N fuel assemblies.

Parameters affecting fuel chemical reactivity are:

- Hydrogen diffusivity
- Hydrogen solubility in the metal

- Irradiation induced microbubbles within the metal that result in:
 - 1) Increased uranium metal surface area
 - 2) reservoirs containing uranium hydride
- Corrosion Induced Surface Area Expansion - Pitting and intergranular corrosion can potentially increase the exposed surface area.
- Chemical contaminants within the fuel, such as aluminum, iron, etc.

Estimates are available for the exposed uranium surface area of the entire K-East pool; however, the exposed surface area of individual assemblies are not known.

From Pitner's camera survey^[21], some estimates of the exposed surface area have been made for individual assemblies; however these estimates are not considered extremely accurate, since the corrosion can extend below the cladding, and since only one end of each assembly is visible.

4.0 HYDROGEN GENERATION

4.1 TECHNICAL ISSUES

Water corrosion of uranium metal (see Section 3.0) and radiolysis of water produce hydrogen in a MCO. For every mole of uranium consumed, approximately 2 moles of hydrogen gas are produced^[19]:

Radiolytic decomposition of water results in formation of hydrogen and oxygen gas, in a 2:1 molar ratio.

There are several interrelated concerns associated with gas generation within a MCO. The rates at which gases are evolved under various conditions must be calculated to determine the potential for MCO over-pressurization during transportation (wet or dry), during staging (wet or dry), and during long-term storage. The potential for generating combustible mixtures of gases during dry transportation, staging, and long-term storage must also be considered. These technical issues will drive the functional requirements for the MCO, staging facility, stabilization facility, and the long-term dry storage facility.

Failure of a MCO could result from gas generation and pressurization or a deflagration. Gas generated pressure in a MCO would increase the over-pressure generated by deflagration. The residual moisture-causing pressure failure of a MCO is different than the residual moisture produced flammable gas that fails the MCO in a deflagration.

4.2 TECHNOLOGY STATUS

4.2.1 Gas Generation During Wet Transportation/Staging

Gas generation during wet transportation and staging will result from both uranium corrosion and radiolysis of water. Technology Acquisition Plan Task P-1, "Fuel Corrosion and Gas Evolution During Retrieval, Transportation, and Wet-Fuel Staging"^[22] developed the preliminary basis for estimating gas evolution rates during wet transportation and wet staging.

Although theoretical rates for aqueous uranium corrosion are available in the literature, these values are based on surface area of exposed uranium, which is unknown for the spent nuclear fuel. Instead, the uranium corrosion rate in the K Basin pool at 10°C was estimated using release rate data on Cs-137, which is released into the pool as the fuel corrodes. Trend graphs were analyzed to determine the distribution of Cs-137 concentration in the KE-Basin water and the mean ion exchange efficiency. It was assumed that the 204 poor-rated canisters^[21] were the source of all corrosion and all corresponding Cs-137 release to the water. Using SCAT database information, the Cs-137 to uranium ratio was determined for the 204 poor-rated canisters.

Using these data, the distribution of expected corrosion rates for the KE Basin fuel was estimated. The resulting distribution has a mean corrosion rate for the entire KE-Basin of 0.52 kg U/day, with a 5th percentile value of 0.24 kg U/day and a 95th percentile value of 0.98 kg U/day. This represents a mean of 2.5 g U/day for one of the 204 poor-rated canisters. The corresponding mean hydrogen evolution rate from this canister, assuming none of the hydrogen is retained by the fuel and the corrosion product UO_2/UO_3 in the ratio given in the above equation.

$$\begin{aligned}\text{The mean } H_2 \text{ generation rates} &= (2.5/238) \times (21/10) \times (0.08205 \times 283.16) \\ &= 0.513 \text{ liters } H_2/\text{canister/day, and}\end{aligned}$$

$$\begin{aligned}\text{the 95th percentile hydrogen rates} &= (4.8/2.5) \times 0.513 \\ &= 0.98 \text{ liters } H_2/\text{canister/day.}\end{aligned}$$

These hydrogen generation rates can be adjusted for different temperatures by:

$$\text{rate } (T_2) = \text{rate } (T_1) \times (\text{Exp}[-13800/(R \cdot T_2)] / \text{Exp}[-13800/(R \cdot T_1)]). \quad (4.2)$$

The corrosion and gas evolution rates at higher transportation or staging temperatures can be obtained by simplifying the above equation to obtain a temperature correction factor:

$$\ln CF = \frac{-13,800}{RT} + 24.5387 \quad (4.3)$$

where

CF is the temperature correction factor,

R is the gas constant (1.987 cal/mol/K), and

T is the temperature in Kelvin.

This equation is based on the activation energy of Ritchie^[18], which is valid over the temperature range of 20-100°C. However, Tyfield^[19] reports a similar activation energy over the range of 70-150°C. Therefore, the temperature correction expression is valid up to 150°C.

Task P-1 also developed a heterogeneous model to estimate gas generation from water radiolysis within a MCO. Radiolytic gas generation has been estimated at 0.34 L/day of hydrogen and oxygen combined. This estimate is expected to be independent of temperature over the temperature range of interest to wet transportation and staging.

Based on these assumptions, the total gas generation rate from a single MCO due to both corrosion and radiolysis is estimated to be on the order of 0.57 - 1.24 L/day at 10°C. This rate will rise roughly exponentially with temperature. This range of gas generation rates is based on an 8-canister MCO holding only one poor-rated canister of fuel.

The information on generation of gases from radiolysis and aqueous corrosion at 10°C can be combined with information on expected temperatures within flooded MCOs of various packing configurations during wet transportation and wet staging to calculate gas generation rates during wet transportation and wet staging for the various MCO packing configurations. These gas generation rates can be converted to pressure build-ups within the MCO to determine if the MCO could be shipped in any flooded configuration without venting. Venting is assumed to be required for wet staging of any duration, but gas generation rates will be calculated for the wet staging option once temperature information is available.

4.2.2 Reactive Uranium Surface Areas

The reactive uranium surface area per double barrel canister can be estimated from the estimated corrosion rates:

for a mean corrosion rate of 2.5 g U/canister/day, the

canister surface area = $(2500 \text{ mg}/24)/(3.2 \times 10^8) \times \text{Exp}[-13800/R \times 283.16] = 1.46 \text{ m}^2$

for the 95th percentile corrosion rate of 4.8 g U/canister/day

the double barrel canister uranium surface area = 2.81 m^2

4.2.3 Dry Transportation/Staging

Pressure build-up within a MCO due to corrosion and radiolysis during dry transportation and staging is currently being estimated. It is anticipated that this work will determine the acceptable levels of moisture

remaining after in-basin vacuum drying for various lengths of dry transportation and staging times. The basis of the acceptable residual moisture criteria will encompass gas generation, possible combustible mixture formation, and the potential for thermal runaway conditions due to the exothermic heat given off by uranium corrosion and the acceleration of uranium corrosion rates with increasing temperature.

Results of the initial, simple, adiabatic model with all moisture reacting with fuel in a single canister show that 4.9 kg of residual moisture would result in a pressure build-up of 1 mPa (150 psig) within the MCO. About 5.4 kg of residual water would raise the temperature within a canister to the melting point of uranium. These initial estimates will be refined to consider the rates at which the corrosion reaction will occur and the effects of heat transfer.

4.2.4 Long-Term Dry Storage

Technology Acquisition Plan Task P-3, "Technical Bases for Assessing Fuel and Sludge Behavior and Gas Release in a MCO During Dry Fuel Storage," [24] assessed the gas evolution and fuel behavior expected during long term dry storage. During long-term dry storage, radiolysis of any residual, chemically bound water in a sludge matrix is expected to be the main source of gas generation. To make a preliminary assessment of the possible changes within a MCO during long term storage without actual data, an attempt was made to make reasonable estimates of the amounts of sludge possibly present, the amounts of residual water remaining in the sludge after the ITA stabilization process^[1], and the expected radiolysis rates. Consumption of radiolysis gases through further attack on the uranium was ignored.

Modest gas generation rates were found for most input assumptions. However, several cases with specific sludge levels, water content levels, and G value assumptions produced flammable stoichiometric mixtures of $2H_2$ and O_2 in the MCO helium atmosphere. The pressure pulse due to deflagration of a mixture of 13.9% of $2H_2 + O_2$ in helium was estimated to be about 5 atm. However, the worst case analyzed resulted in 46.2% H_2 and a pressure pulse of about 36 atm.

As part of this task, a modifiable spreadsheet has been created which calculates gas pressure and composition within a MCO as a function of design and operating parameters, storage time, and the nature of the remaining sludge deposits. It is anticipated that the model will be rerun as better information becomes available.

4.3 IMPLICATIONS TO KEY DECISIONS

4.3.1 Desludging/Canister Preparation

The degree of desludging and canister preparation performed will affect the extent of moisture removal obtained during any in-basin, pre-staging, or stabilization process. The amount of residual moisture is directly tied to gas generation rates during dry transportation, dry staging, and long term dry storage. The extent of desludging needed to maintain gas generation at acceptable rates is a function of drying temperature, sludge drying characteristics, and residual moisture criteria. Residual moisture criteria

are being estimated for various transportation and staging times, but sludge drying characteristics, as a function of drying temperature, vacuum, and sludge configuration, must be understood before desludging criteria to prevent gas generation concerns can be set.

4.3.2 In-Basin Processing

The acceptable levels of residual moisture remaining after vacuum drying to prevent gas generation concerns during dry transportation and/or staging are currently being developed. The level of drying which needs to be achieved by in-basin processing, as a function of transportation and/or staging times, to prevent over-pressurization and fuel melting will be determined. The simplest model has shown about 4.9 kg of moisture would generate 1 mPa (150) psig of pressure within the MCO; better modeling is in progress.

4.3.3 Transportation

Work in progress will calculate gas formation rates during wet and dry transportation. The ability to ship wet without venting will be determined. Gas formation during dry transportation will depend on the amount of residual moisture remaining after vacuum drying. Therefore, the ability to ship dry without venting will depend on the extent of moisture removal achieved by desludging and vacuum drying, which is currently unknown.

4.3.4 Staging

It is assumed that wet staging will require some type of venting system. Gas generation rates are currently being calculated for wet staging based on the temperatures expected during wet staging. Residual moisture levels within a MCO which would allow for sealed dry staging are being estimated. The number of uncertainties involved with estimating gas generation rates during dry staging (amount of sludge and fixed corrosion products, drying characteristics of the products, etc.) may drive the CSB to monitoring MCOs, even if venting is expected to be unnecessary.

4.3.5 Stabilization

Stabilization affects the condition of the MCO contents (fuel, sludge, fixed corrosion products, moisture) entering long term dry storage. Gas generation rates during dry storage have been modeled based on the ITA stabilization process and various design and process input variables. For the ITA stabilization process, it was determined that canisters with low amounts of residual sludge can tolerate higher water levels without over-pressurization. For large quantities of residual sludge, even the low estimate of residual water may be problematic. Several combinations of model inputs were identified which result in combustible mixtures. This model could be used to put functional requirements on the products of the stabilization process, at least in terms of gas generation limitations. Functional requirements for stabilization based on hydride formation concerns may need to be developed separately.

4.4 UNCERTAINTIES

4.4.1 Gas Generation During Wet Transportation and Staging

There are uncertainties surrounding the estimated gas evolution rates due to uranium corrosion and due to radiolysis during wet transportation and staging.

Estimates of gas evolution rates from uranium corrosion involved assuming a value for the split fraction of solubilized Cs-137 that is adsorbed by the ion exchange module. The remaining fraction is absorbed on the sludge and basin walls. This split fraction was assumed to be 75% to the ion exchange module, in the absence of any analytical data.

The 204 canisters with poor-rated fuel include 53 canisters that contain more than one poor-rated fuel assembly. These canisters are rated very bad because more than one severely deteriorating (poor-rated) fuel is contained in the canisters. A further examination of the Pitner videotapes and database will show the number of poor fuel elements in these very bad canisters. A better apportioning of the corrosion between poor and very bad canisters might refine the present estimate. Corrosion, and associated gas generation, is currently assumed to be equal throughout the 204 poor-rated canisters.

The uranium dissolution rate in the K East pool was estimated^[22] to be 500 grams per day. This dissolution rate is associated with a total exposed uranium surface area. There is no absolute way to distribute that surface area to individual fuel elements or groups of elements in canisters, even though such a distribution is needed to estimate fuel reactivity in individual MCOs.

The first method used for surface area distribution was to use the results of a camera survey showing visible corrosion at the tops of the fuel elements. On this basis, all of the exposed uranium surface area was assigned to 204 "bad" canisters out of the 3,660 total canisters in the K East pool.

Temperature correction for the uranium corrosion reaction rate is based on experimental data using uranium samples, rather than uranium-zirconium couples similar to the spent nuclear fuel elements found in KE Basin. There is significant scatter in the temperature correction data found in the literature for oxygen-depleted aqueous uranium corrosion^[23].

Improvement in the calculation of gas generation by radiolysis is also possible. The presence of sludge in a MCO will result in alpha and beta irradiation of the water in the sludge, which will cause additional water radiolysis in excess of that caused by gamma irradiation. The alpha and beta irradiation of the water by sludge has been ignored in the current estimates. Estimation of these effects requires knowledge of the extent of sludge remaining after canister preparation.

If wet transportation and/or wet staging are chosen, a more accurate determination of gas evolution rates due to radiolysis is possible using the computer code RADIOL^[23]. The code was developed to determine radiolysis in light water reactor cores and more accurately models the potential side reactions. Using the improved absorbed dose calculated in under Task P-1, RADIOL could be used to obtain a better estimate the gas generated in a MCO

due to radiolysis. The basis for the radiolysis calculations could also be updated to reflect a MCO with 10 canisters, rather than the 8 canister basis used in Task P-1. However, the amount of refinement in the radiolysis estimate which could be achieved may not be worthwhile, in light of the minimal contribution of radiolysis to gas evolution rates in the flooded condition, compared to the contribution from uranium corrosion.

In light of the above uncertainties, if the gas evolution rate estimates based on the K Basin corrosion rate estimate become necessary information or a limiting criteria for either the MCO or safety analysis, then the above assumptions should be verified experimentally.

4.4.2 Gas Generation During Long-Term Dry Storage

The existing model to calculate gas generation rates during long-term dry storage is built on numerous assumptions, most of which can be easily changed. However, the current model does not consider consumption of hydrogen or oxygen by further oxidation or hydriding of uranium during the long term storage period. While consumption of radiolysis gases by further uranium corrosion may help prevent potential pressure build-up or combustible mixture formation during long term storage, additional uranium hydride may form during long term storage which may present a separate hazard.

Other uncertainties in the existing model focus on the characteristics of residual sludge. The model requires assumptions on the quantity, composition, drying characteristics, and G values of the sludge. Until additional sludge characterization data becomes available, assumptions on the characteristics of the sludge must be made to calculate gas generation rates.

Again, if the gas generation estimates based on the KE Basin corrosion rate become necessary information or a limiting criteria for MCO design or safety analysis, then the uncertainties discussed in this section should be reduced through experimental data.

4.5 PROPOSED FUTURE WORK

4.5.1 "Dry" Path Forward

The residual moisture criteria for vacuum drying prior to dry transportation and staging must be used to develop a process or processes which can attain the required criteria. The possibility of using simulated sludge to initially investigate the capability of various vacuum drying processes should be considered. Uranium oxide material formed through calcination might be stored in an autoclave for a period of time to create material more closely approximating the uranium sludge formed by aqueous corrosion in K Basin. Drying curves could be obtained with sludge layers of varying thickness to estimate amounts of residual moisture per pound of sludge remaining after vacuum drying at various temperatures. This information should then be used to drive acceptance criteria for desludging.

A method for determining the amount of residual moisture remaining after vacuum drying needs to be developed. This is required to verify that in-basin processing meets the established criteria for each MCO processed.

4.5.2 Long-Term Dry Storage

Residual moisture criteria must be developed for the stabilization process to prevent gas generation concerns. The potential for, and danger of, additional hydride formation during long-term storage from hydrogen gas generated by radiolysis should be investigated. A method for measuring residual moisture following conditioning or stabilization must be developed to verify the acceptability for long term storage of each MCO after the stabilization process.

The existing model should be revised to account for consumption of hydrogen and oxygen due to reaction with uranium during long term dry storage. While gas consumption will only help prevent over-pressurization or combustible mixture formation, the extent of further hydriding needs to be addressed.

The model for gas generation during long term dry storage should be rerun as better information becomes available. The model should also be extended to cover a 100-year, long-term dry storage period.

5.0 VACUUM DRYING AND CONDITIONING

5.1 BACKGROUND

The ITA conditioning process^[1] included three phases at elevated temperature: Dehydration to remove chemically bound water, dehydriding to decompose uranium hydride, and passivation to oxidize remaining metallic surfaces. A key motivation of the ITA process was minimization of the potential for fuel pyrophoric events. Hydride decomposition and metal surface passivation directly contribute to this goal; the dehydration step reduces long-term radiolytic gas generation which contributes to MCO pressurization and makes hydrogen available for potential hydriding. The vacuum drying process envisioned here would be accomplished at a low temperature of approximately 50°C. The purpose of the vacuum drying process is to remove the maximum amount of free water that is practicable. The vacuum drying process may proceed the shipment of the MCO, containing fuel, from the K Basins. The vacuum drying process may also be a precursor process to MCO staging at the Canister Storage Building (CSB).

Both the ITA conditioning process and the current path options would dry and condition the N Reactor fuel within the MCO. The current design option for the MCO and the ITA conditioning process practices are discussed in Section 2.0. Section 2.0 also covers the implications of N Reactor fuel conditioning. Section 5.0 will focus on vacuum drying.

5.2 KEY TECHNICAL ISSUES

One issue has been identified for vacuuming drying the MCO:

Gas will be generated within the MCO by radiolysis and corrosion processes, resulting in an undesirable increase in internal pressure and increase in hydrogen concentration presenting a potential explosive condition.

5.3 TECHNOLOGY STATUS

5.3.1 Vacuum Drying System Configuration

A depiction of the proposed vacuum system is shown in Figure 5.1. This system is based upon the concept provided in the ITA concept^[1]. There are a few changes from the baseline ITA concept: 1) the gas recycle system (for passivation) has been replaced with a simple flow through purge system, 2) a vacuum purge controller has been added to control vacuum system pressure, 3) a non-diffracting pressure reducer for the Residual Gas Analyzer (RGA) has been added, 4) a vacuum pump exhaust filter has been added, and 5) pressure gauges to monitor the level of vacuum have been added.

The purge controller will throttle the vacuum pump such that the pressure inside the MCO will be maintained at 5 Torr (1×10^{-2} atm.) or more. If the vacuum pressure inside the MCO is dominated by water vapor then at pressure greater than 5 Torr the water in the MCO will not freeze as the equilibrium vapor pressure of water at 0°C is 4.56 Torr. The purge flow will also prevent oil from back streaming into the MCO from the vacuum pump. The ultimate pressure capability of typical dual stage vacuum pumps is 1×10^{-3} Torr (1×10^{-5} atm.). If the gas inside the MCO is not dominated by water vapor, possibly due to chemical reactions, then the vacuum pressure could be controlled by the vacuum pump inlet valve. The valve could be partially closed reducing the pumping speed of the pump.

The non-diffracting pressure reducer will allow the representative sampling of the gas stream by the RGA. If a simple capillary tube were used as a pressure reducer, then the lower molecular weight gasses would be sampled at a higher rate than the higher molecular weight gasses. The pressure reducer for the RGA is a special purpose capillary system that will bypass a small percentage of the total gas flow. The RGA must operate at a pressure of 1×10^{-5} Torr (1×10^{-7} atm.) or lower. This will be achieved by a small capacity turbo molecular vacuum pump package as noted in Figure 5.1.

The exhaust filter will coalesce oil vapor from the pump before it reaches the tritium getters and HEPA filters and thus prevent the fouling of the latter components.

A moderate size vacuum system is envisioned requiring a vacuum pump utilizing a 5-10 HP motor per MCO. Commercially available vacuum systems are capable of achieving the required vacuum pressures and should be utilized.

The vacuum pressure gauges contemplated for this system are of a conventional type that will measure the system pressure from 0.1 torr to 1 atm. This range is usually monitored by a number of sensors optimized for a set pressure range. The instrumentation controller will automatically select the proper sensor for readout depending on the pressure in the vacuum system. Capacitance manometers are recommended for this application as they more rugged than the other types of vacuum pressure sensors.

For the system depicted in Figure 5.1, a number of different types of vacuum pumps can be utilized. Dual stage rotary vane, rotary piston pump, roots pump package or water seal ring pump can be utilized. These pumps are representative of the types of vacuum pumps that are commercially available.

Figure 5.1 Proposed Vacuum System for N Reactor Fuel Drying.

These pumps also are representative of the different vacuum pump technologies that are available and cover a wide range of pumping speeds (capacity). A pump capacity on the order of 50 to 70 liters per second was calculated to be acceptable for the vacuum drying process⁽²⁵⁾.

5.3.2 Vacuum System Thermal Analysis Results

Pumpdown times to remove water are moderate to long depending on nature of sludge and damaged spent fuel. Thermal analysis study results⁽²⁶⁾ are listed in Table 5.1. Figures 5.2 through 5.6 present the transient results of the thermal analyses for the five cases listed in Table 5.1. (Note: The oscillations in the evaporation rate noted on the figures is an artifact of the numerical techniques utilized. A refined numerical algorithm will be utilized in future analysis.)

The assumptions for the results in Table 5.1 are presented as follows:

Canister and MCO Load Assumptions:

- Analysis assumes that MCO will contain at most one "bad" canister and nine canisters with fuel elements in pristine condition
- "Bad" canister assumed to be one of following:
 - High radiolytic decay heat of 4.82 watts per element and maximum probable corrosion heat of 10 times average value (i.e., 522 watts/canister at 90°C).
 - Two fuel elements with loose end caps and two fuel elements with split cladding per canister barrels. Damage affects outer element only:
 - Loose end caps = 2 inches of fuel gone; split cladding = 1/3 of fuel gone. Worst case assumption is that all the fuel is gone. Relatively large cracks assumed - no choked flow.
 - One sludge filled canister barrel with other barrel containing fuel in pristine condition.

Radiolytic and Chemical Reaction Source Terms:

- Upper/lower bounds for radiolytic and chemical reaction source terms required for maximum temperatures and worst case times for passive dewatering and drying process respectively.
- Radiolytic decay heats (Table 5.2).

Table 5.1 Vacuum Drying Times for Various Canisters Conditions

Case No.	Heat Source	Annulus Heating	Amount of Water, Liters	Vacuum Drying Time ^[5] Hours	Transient Response
1	Probable Max/Min.	No	14.02 ⁽¹⁾	100+/100+	Fig. 5.2
2	Probable Max/Min.	Yes	14.02 ⁽¹⁾	16/16	Fig. 5.3
3	8 Split/Loose End Cap Elements	Yes	15.65 ⁽²⁾	40/60	Fig. 5.4
4	8 Split/Loose End Cap Elements	Yes	15.65 ⁽³⁾	64/100+	Fig. 5.5
5	8 Split/Loose End Cap Elements	Yes	17.52 ⁽⁴⁾	100+/100+	Fig. 5.6

- 1) All water is free water, i.e., not chemically bound or bound in sludge.
- 2) 14.02 liters of free water in MCO and 1.63 liters contained in failed fuel elements.
- 3) 14.02 liters of free water and 1.63 liters in contained as sludge in failed fuel elements.
- 4) 14.02 liters of free water, 1.22 liters in contained as sludge in failed fuel elements and 2.45 liters in sludge contained in bottom of canisters.
- 5) Times are for the maximum probable heat load and minimum heat load respectively.

Figure 5.2 Passive Vacuum Drying of MCO and Fuel Elements. Comparison Between Maximum and Minimum Heat Dissipation Scenarios.

Figure 5.3 Vacuum Drying of MCO and Fuel Elements with Annulus Heating.
Comparison Between Maximum and Minimum Heat
Dissipation Scenarios.

Figure 5.4 Vacuum Drying of MCO and Damaged Fuel Elements with Annulus Heating; Damage Modeled as "Free" Water. Comparison Between Maximum and Minimum Heat Dissipation Scenarios.
(Four Elements with Split Cladding and Four Elements with Loose End Caps.)

Figure 5.5 Vacuum Drying of MCO and Damaged Fuel Elements with Annulus Heating. Comparison of Water Fill Versus Sludge Fill of Fuel Elements. (Four Elements with Split Cladding and Four Elements with Loose End Caps.)

Figure 5.6 Vacuum Drying of MCO and Sludge Filled Canister with Annulus Heating. 10 cm (4 in.) of Sludge in One Canister with Damaged Fuel Elements. (Four Elements with Split Cladding and Four Elements with Loose End Caps.)

Table 5.2 Radiolytic Heat Source Term

Fuel	Watts Per Element	Watts Per Canister	# Canisters Per MCO
Extreme Peak	4.82	67.5	1
Probable Maximum	3.375	47.3	10
Average	1.59	22.3	10
Minimum	0.53	7.4	10

- Chemical reaction heats:
 - Low value assumed to be 0 watts per canister.
 - Average value assumed to be 2.529845×10^6 J/kg of Uranium reacted for reaction in water or steam
- Combined Radiolytic and Chemical Reaction Heat:
 - Maximum Heat Load: One (1) canister with 67.48 watts of radiolytic heat and a peaking factor of 10 on the computed average corrosion heat, plus nine (9) canisters with 47.3 watts of radiolytic heat and no corrosion heat.
 - Probable Max. Heat Load: Ten (10) canisters with 47.3 watts of radiolytic heat and the computed average corrosion heat (i.e., PF=1).
 - Average Heat Load: Ten (10) canisters with 22.3 watts of radiolytic heat and no corrosion heat.
 - Minimum Heat Load: Ten (10) canisters with 7.4 watts of radiolytic heat and no corrosion heat. Moisture Retention Following Draining:
- Assume a 0.004 inch water film on vertical surfaces:
 - MCO sidewalls @ 0.81 liters (12,367 sq. inches)
 - Canister sidewalls @ 1.95 liters (29,677 sq. inches)
 - Separator plates @ 0.46 liters (6,125 sq. inches)
 - Fuel elements @ 4.46 liters (68,040 sq. inches)
- Water retention on horizontal surfaces:
 - MCO bottom @ 4.33 liters (assumes 1.25 inch depth)
 - Canister gas traps @ 0.35 liters (0.10 inch sludge depth)
 - Canister sludge @ 1.70 liters (0.10 inch sludge depth)
- Water retention in failed fuel elements:
 - 1.64 liters of water was assumed within the elements (total)

- Water retention in sludge contained within the canisters (total):
 - 1.70 liters of water was assumed within the canisters (total)

Conclusions from the Vacuum Drying Thermal Analysis^[24]:

- Passive heating for drying feasible only for average or above decay heat generation and with pristine fuel conditions.
- Pre-heating of MCO water prior to de-watering will aid drying process, but only marginally due to low thermal mass of fuel elements.
- Heating of cask/MCO annulus with 50°C water in tandem with evacuation of MCO provides the most efficient removal of retained moisture following MCO drain down.
- Since each pound of water remaining in MCO following draining requires about 293 watt-hours of thermal energy to remove, design features should be incorporated to maximize mechanical moisture removal.

5.3.3 Vacuum Drying System Gas Velocities Results

Gas flow velocities for a moderate size pump are acceptable for the proposed 2.5 cm (1 in.) nominal diameter process line penetrating the MCO top shield. Flow Mach numbers of 0.3 have been calculated for the 2.5 cm (1 in.) vacuum line and 0.08 if the line were increased to a nominal 5.0 cm (2 in.)^[25].

5.3.4 Vacuum Drying System Issues

The effects of water vapor expansion as it exits the MCO into the larger diameter vacuum line should be investigated. This condition may require that the vacuum lines be trace heated to prevent ice formation inside the vacuum line.

The chemical reaction potential and products of reaction inside the MCO during vacuum drying should be investigated. If the water vapor reacts to form hydrogen then the pumping speed of the vacuum pump could be substantially reduced.

Process monitoring by total pressures sensor and RGA are commercially available. The RGAs are recommended for the vacuum drying process, these sensors will sample the vacuum system process stream and determine the partial pressures of the gases in the process stream. Gasses with in the range of 1 to 300 AMUs can be measured down to the ppm level. A RGA has been installed at the 241-SY-101 tank in the 200 Area to monitor the hydrogen concentration of the tank, it has operated for over two years. The operability of a RGA in the field should be investigated based upon the 241-SY-101 experience.

Condensate and vacuum gas streams will contain radioactive materials. The condensate will be processed in closed piping system, transferred to a holding tank during vacuum drying and then returned to the basin. The radiological control and shielding aspect of this should be investigated.

The vacuum system exhaust gas will have to be filtered and gettered to remove contaminated particulates and condensable/getterable gasses, inert non-condensable gases will be vented to the atmosphere through a monitored HVAC stack. The radiological control and shielding aspect of this should be investigated.

The performance and operability of the vacuum system should be verified at the selected vendor's shop prior to installation at the conditioning/drying facility. A prototypic MCO with dummy fuel elements should be included as part of the vendors test setup. Vacuum systems of the type envisioned can be operated continuously for up to two years with only a short downtime for annual maintenance.

5.4 IMPLICATIONS TO KEY DECISIONS

Desludged and/or desludged/reracked MCO shipping with warm vacuum drying at K Basin is practicable. The warm vacuum drying at the K Basin with as-is condition fuel or with appreciable quantity of damaged fuel appears to be impracticable due to the excessive time to dry. Also sludge will tend to be entrained in the vacuum system, it will foul the water condenser surfaces and load up the HEPA filters. Therefore, desludging of spent fuel prior to drying is recommended.

5.5 UNCERTAINTIES

The risks and or uncertainties associated with the vacuum drying process are:

- Rapid chemical reaction of the fuel during vacuum drying due to process instability.
- Loss of vacuum and air inrush into MCO during drying.
- Inability to dry the MCO in a timely manner.
- Inability to measure the water concentration the MCO. Water concentration is inferred by the amount of water vapor that is measured in the vacuum system exhaust stream.
- Processing of inert non-condensable fission gases will be problematic for any approach, whether at the K Basins or at a new conditioning facility in the 200 Area. Inert non-condensable fission gases will be vented to the atmosphere, a controlled rate of release is feasible if required.
- Differentiation between "damaged" and "undamaged" fuel as it relates to the need for "conditioning" to meet safety requirements.

5.6 PROPOSED FUTURE WORK

1. After the design of the MCO and fuel packaging is finalized, the total surface area, sludge content and resulting water content of the MCO including all items inside the MCO should be estimated.
2. Prototype testing of vacuum drying spent fuel elements with various damage, corrosion and sludge conditions should be performed to check whether the process requirements are satisfied. The information obtained will be used to redesign the vacuum drying process.
3. The performance characteristics of the HEPA filters and the getter system should be investigated. The information obtained will be used to redesign the vacuum drying process.
4. The requirements for inert non-condensable fission gases release should be determined. The information obtained will be used to redesign the vacuum drying process.
5. One type of pump that was not evaluated was the water sealed rotary vane pump. This pump should be investigated in the future as it could potentially eliminate the need for the HEPA filter at the pump inlet. This is due to the fact that water will form the vacuum seal at the rotating vane instead of oil as in a conventional pump. The seal water can be filtered and reprocessed. The seal water replaces the HEPA filter as the contamination control mechanism.
6. The issue involved with the uncertainty in differentiating "damaged" from "undamaged" fuel and the need to develop criteria for this differentiation based on the safety consequences needs to be resolved in relationship to the degree of "conditioning" undertaken on the fuel.

6.0 THERMAL PERFORMANCE

6.1 BACKGROUND

The purpose of this section is to document the development of the initial thermal models and preliminary performance assessment of the MCO and how the results of the thermal analyses can provide technical support in defining and resolving path forward issues for the SNFP.

Peak temperatures, radial and axial temperature profiles, and component temperature histories will be calculated for a variety of steady and transient conditions, including a range of ambient temperatures, MCO decay heat loads, multiple chemical reactions involving uranium metal, as well as simulations of various K Basin operations and processes. The effects of buoyancy driven internal convection flows within the MCO will be accounted for, as well as the effects of external solar insolation for those analyses involving shipping casks.

6.1.1 Status of Thermal Modeling

Steady state and transient finite element thermal models of a shipping cask, MCO, Fuel Encapsulation Canister (FEC), and seven fuel assemblies (FA) have been developed using the FIDAP computer code, which has been validated and verified for use at Hanford^[27]. Figures 6.1 and 6.2 present the overall geometry and the quarter symmetric geometry that was actually modeled, respectively. The thermal model developed from Figure 6.2 represents a two dimensional quarter symmetric radial cross section of MCO containing a FEC and seven fuel assemblies each consisting of a outer annular ring and inner annular ring. The quarter symmetry allows for the expansion of the model to half or full symmetry at a later date.

The radial model as presented by Figure 6.2 was originally developed as part of a series of coupled energy, momentum and mass transport models of the MCO and shipping cask and reflects the additional nodding required to resolve the expected flow fields. However, for the purposes of this report the above model was run in the thermal mode only, which solves only the conservation of energy equation. A second thermal-hydraulic and mass transport model representative of the axial configuration of a cask containing a MCO is currently in development and will be used to quantify the extent of the internal natural circulation patterns, mass transfer, potential hot spots, and the extent and duration of surface chemical reactions under various operating and off-normal scenarios.

Together the above thermal-hydraulic models will provide a mechanism that will help determine the range of temperatures and heat up rates associated with each of the proposed path forward options and engineering alternatives; such as wet versus dry shipping, hot versus cold vacuum drying scenarios, dense packing, as well as providing an analytical base for performing the required safety analyses.

6.1.2 Modeling Description and Methodology

The thermal model as described above incorporates heat sources from both nuclear decay heat and chemical reactions. The nuclear decay heat is applied as an volumetric heat source; whereas, the heat of reaction resulting from the surface chemical reactions is applied as a surface heat flux at the surface of the uranium metal.

Currently only two surface reactions involving reactions between water, water vapor, and oxygen with uranium metal are modeled, as shown in the following equations.

Figure 6.1 Overall MCO Radial Geometry Used in FIDAP Computer Code.

Figure 6.2 MCO Quarter Symmetric Radial Geometry Modeled into FIDAP
Computer Code.

The heat of reactions shown above were chosen to bound the heats of reaction from other potential reactions with Uranium

The two dimensional radial modeling approach was to treat each of the seven fuel assemblies separately, each with an inner and outer fuel element, within a Fuel Encapsulation Canister (FEC), within a MCO, within a shipping cask. This was done to maximize the thermal resistance and, hence, the maximum temperatures. As shown in Figure 6.2, three of the seven fuel assemblies were assumed to be orientated along a 45 degree line relative to the center point and external surface of the shipping cask. Again this was done to maximize the thermal resistance. The remaining four fuel assemblies were located two above and two below the 45 degree line. The natural configuration of the seven fuel assemblies within an FEC is that of a hexagon.

Packing configurations other than seven complete fuel assemblies have not yet been investigated. It is possible that packing alternatives involving more than seven inner or less than seven outer fuel elements will have to be investigated. Other alternatives currently being discussed involve removing the fuel assemblies from the existing FECs and packing up to 140 fuel elements at one level. This would significantly increase both the decay heat and surface area available for reactions and must be thoroughly analyzed prior to committing to this alternative. Other packing options involve fuel debris and sludge.

All three modes of heat transfer are used; conductive, convective, and radiative. Radiative heat transfer is particularly noteworthy, since it involves a series of highly detailed but automated view-factor calculations involving a series of full or partially obstructing surfaces.

The thermophysical properties for density, specific heat, thermal conductivity, and emissivities were obtained for the various materials from a series of handbooks; such as the Nuclear Systems Material Handbook (NSMH)^[28], ASME steam tables, and various engineering texts and references manuals^[29-32].

Estimates of the convective heat transfer coefficients were made from well known empirical treatments for natural circulation from vertical flat or cylindrical surfaces. The assumption is that the shipping cask and MCO remain in a vertical position is critical during shipping.

6.1.3 Nuclear Decay Heat and Chemical Reactions

As discussed above, both nuclear decay and heat from chemical reactions were accounted for within the thermal model. The estimated nominal decay heat load is 221 watts per MCO^[33] or approximately 1.58 watts per fuel assembly. Decay heat is estimated to range from an extreme value of 4.82 Watts per fuel assembly to a minimum value of 0.53 watts per fuel assembly. Additional calculations utilizing the estimated maximum and minimum nuclear decay heats as well as asymmetrical distributions will be performed as necessary to support the engineered methods being developed for the removal of spent nuclear fuel and sludge from the K Basins.

The chemical reactions proceed at different rates depending on the individual reaction, activation energy, temperature, the amount and form of reactant media involved; such as water, moist air, and for low pressure conditions the partial pressures of water vapor and oxygen. The heat of

reaction for those cases involving water or water vapor was assumed to be 155 kcal/gram-mole uranium metal. For those cases involving reactions with oxygen a heat of reaction of 284.8 kcal/gram-mole uranium metal was assumed.

The rate of reaction of a particular reaction is usually presented in terms of milligrams (mg) of uranium (U) or oxygen (O₂) reacted per cm² per hour and is highly dependent on the surface area available for reactions, temperature of the fuel, and amount of reactants (i.e., water, water vapor or uranium metal) to drive the reactions. The functional form of the above reactions are usually expressed in terms of a generalized Arrhenius Rate Law as shown by Equation 6.3, where the temperature dependence is usually treated as an exponential function. In addition, most Arrhenius Rate based chemical reactions are mass limited or depend on the near surface concentration of the reactant.

An Arrhenius type of reaction was modeled with FIDAP. FIDAP supports reactions based on both chemical kinetic-controlled models, such as the Arrhenius Law, where the reaction rate is determined from chemical kinetic considerations or mixing-controlled reactions where the mixing action of a turbulent velocity field determines the rate of reaction. Both mass fraction and molar concentration forms for the Arrhenius type reaction models are supported. Simple one-step, competing, controlling, and multi-step chemical models are also supported. The mass fraction form of an Arrhenius reaction is shown by the following equation;

$$R_{\alpha l}^{mass} = K_{\alpha l}^{mass} (T + T_{Ref})^{B_l} \exp\left[\frac{E_l}{(T + T_{Ref})}\right] \prod_{j=1}^N C_j^{n_{jl}} \quad (6.3)$$

where,

- $R_{\alpha l}^{mass}$ = Reaction rate for species α in reaction 1 (kg/m³-sec)
- $K_{\alpha l}^{mass}$ = Reaction rate constant for species α in reaction 1 (kg/m³-sec-°K^B). Where, °K^B is dependent on the temperature power discussed below.
- B_l = Temperature power in reaction 1. (Set to zero for the subject analyses. Hence, the unit term °K^B reduces to 1 and can be dropped from the reaction rate constant.)
- E_l = Activation energy for reaction 1 divided by Universal Gas Constant (K)
- n_{jl} = Power index of reacting species j in reaction 1.
- N = Number of reacting species in reaction 1 ($N \leq 15$)
- T_{ref} = Reference temperature (K). Where $(T + T_{ref})$ is an absolute temperature. If the analyses are already based on an absolute temperature scale (i.e., R or K), then T_{ref} can be set to zero.
- C_j = Mass fraction of species j . Subject to the constraint

$$\sum_{j=1}^N C_j = 1.0 \quad (6.4)$$

Similarly, the energy produced by the reactions is shown by the following equation:

$$q_t = \sum_{\alpha=1}^N H_{\alpha} R_{\alpha t}^{mass} \quad (6.5)$$

where,

q_t = Heat of reaction for reaction 1 (J/m³-s)
 H_{α} = Enthalpy of formation for reaction 1 (J/Kg) and, $R_{\alpha t}^{mass}$ is previously defined.

Since the reaction rate constant and activation energy are physical constants dependent on the reaction, the only mechanisms for reducing the rate of reaction are reducing the system temperature and/or reducing the relative mass fractions associated with the reactants.

For multiple surface based reactions the general form of the Arrhenius based rate remains, but subject to the following surface (boundary) constraints, including the rate at which mass can be transported to the reacting surface.

$$-\rho \alpha_i \frac{\partial C_i}{\partial n} + C_i S = S_i; \quad i = 1, \dots, n_s \quad (6.6)$$

Together with the normal velocity condition

$$\rho \vec{U} \cdot \vec{N} = S \quad (6.7)$$

and,

$$S = \sum_{i=1}^N S_i; \quad N = n_s + 1 \quad (6.8)$$

where,

ρ = Density of reacting media (Kg/M³)
 α_i = Mass diffusivity of species i (M²/S)
 C_i = Mass Fraction of species i (dimensionless)
 S_i = Surface reaction term (Kg/M²-S)
 $\vec{U} \cdot \vec{N}$ = Velocity (m/s) normal to surface
 S = Sum of all reaction terms including any reaction term for the carrier gas
 n_s = Number of reacting species.

The subject thermal analyses assume unlimited reactants and zero mass flow resistance. This effectively sets the multiplicative summation term for the species mass fractions in Equation 6.3 to 1.0, sets the concentration gradients for each species in Equation 6.5 to zero, and assumes the transportation of unlimited reactants to the reacting surface.

A user subroutine to limit the chemical reactions based on total energy equivalent to a given mass of reactant has recently been written and incorporated into the FIDAP model and has been used to determine the peak fuel temperatures as a result of chemical reactions for various amounts of residual water.

In addition, the chemical reactions are assumed to be not limited by the buildup of a oxide layer, the difference in the relative rates at which water vapor can be produced versus the rate at which water vapor can be transported to the reacting surfaces, or hydrogen blanketing near the reacting surfaces. (Hydrogen is produced by the water or water vapor reactions with uranium metal and is assumed to be expelled from the reaction surface. This hydrogen is concentrated near the surface and effectively reduces the mass flux of the water or water vapor transported towards the reacting surface; hence, the term hydrogen blanketing.) Refinements in these areas will be incorporated into the thermal-hydraulic models at a later date.

The rate at which the reaction proceeds determines the production rate of hydrogen. The presence of hydrogen may or may not have implications for the vacuum system, but must be investigated as part of the design of the vacuum system (see Section 5.0).

Uncertainties in the nuclear decay (distribution and magnitude), reaction rates, and material properties, especially emissivities and the thermal conductivity of gases at low pressures will have a major affect on the thermal results. Calculations will be performed investigating the ranges of uncertainties.

6.1.4 Thermal Performance Factors

To prevent runaway chemical reactions, temperatures must be maintained less than the "threshold" temperature limit. Temperature control involves maintaining an energy balance where the energy gains to the system equal the energy losses from the system. If the energy gains exceed the losses the system temperatures will increase until the energy losses increase to balance the system. If the energy gains far exceed the capability of the system to reject energy the temperature will continue to increase. The mechanisms for temperature control must be based on analytical studies that qualify the design and/or sets process operating limits necessary to prevent a runaway chemical reactions.

Besides nuclear decay heat and chemical reactions, solar insolation (incident surface heat flux) corresponding to the latitude of Hanford was treated as an energy gain. Energy losses from the system involve heat transfer from the outer surface of the shipping cask to ambient conditions via convective and radiative heat transfer mechanisms. Clearly the correct treatment of the system boundary energy gain and loss mechanisms are very important. The energy gain from nuclear decay heat was considered constant for these analyses. The energy gain from chemical reactions can be limited by

limiting the amount of reactants such as water or oxygen remaining after any process such as draining, vacuum drying, or purging by an inert gas. However, the rate of energy gain from chemical reactions is dependent on the Arrhenius Rate Law (Equation 6.3).

Convective losses from the cask surface involve a combination of both forced convection from wind affects and natural circulation losses due to axial temperature differences. This is further complicated by the cylindrical curved outer surface of the shipping cask, which under forced convection result in increased losses from the "upwind" side and reduced losses on the "downwind" side. The standard methodology usually employed in this situation is to ignore the effects of forced convection and take credit only for natural circulation.

The convective heat transfer coefficients and, hence, energy transfer, are dependent on material properties, which are temperature dependent, as well as the temperature difference between the surface of the shipping cask and the ambient atmospheric temperature. Numerous correlations have been developed for a variety of geometrical configurations. Heat transfer coefficients for vertical plates or vertical cylindrical surfaces are some of the best known correlations and represent a small uncertainty to the energy balance.

Energy transfer between the interior surfaces and the MCO to shipping cask gap involve a combination of all three modes of heat transfer; conduction, convection, and radiation. Under low pressure conditions it is expected that the convective heat transfer mechanism within the MCO will be significantly reduced. Thermal radiation and conduction will remain. However, the thermal conductivity of gases and gas mixtures under low pressure conditions is not well known and represents another source of materials based uncertainties that will have a significant impact of the thermal performance of the proposed system.

Radiative losses from the cask surface depend on the surface area of the shipping cask, the difference between the temperature of the cask surface to the fourth power and the ambient temperature to the fourth power, and the emissivity of the cask's surface. Emissivities for most materials as a function of temperature are rather sparse. Usually a single value at some temperature and surface condition (i.e., polished, pitted, oxidized, etc.) is quoted. The lack of emissivity data represent a significant uncertainty in the energy removal capabilities of the above system. One option to remove the uncertainties associated with the emissivities and solar insolation would be to specify a that the outer surface of the shipping cask would be painted with a material such UNIFLEX or Aztec 100 white paint, which have known low solar absorptivity values ranging from approximately 0.15 to 0.18 and a relatively high normal emissivity value of 0.85.

Clearly, an unacceptable thermal performance will result given a worst case rack-up of the various combinations of ambient conditions, decay heats, and material property uncertainties.

6.1.5 Modeling of "Hot and Cold Spots"

The potential effects of degraded, badly damaged, or missing cladding or fuel on the thermal performance of the MCO can be easily accommodated and modeled. The impact of "hot or cold spots" can be investigated with FIDAP as described within the following paragraphs.

The thermal analyses discussed with Section 6.0 incorporate heat sources from both nuclear decay heat and chemical reactions. The conservation of energy equation as programmed within FIDAP, assumes that the total volumetric heat generation term H (J/m^3-s) is a combination of several factors, as shown within the following equation:

$$H = q_s + q_d + q_r + q_j + q_p \quad (6.1)$$

where, q_s = the total heat generation rate due to the applied sources or sinks per unit volume,

q_d = the total heat generation due to viscous dissipation,

q_r = the total heat generation due to chemical reactions,

q_j = the total heat generation rate due to electrical (Joule) heating, and

q_p = the total heat generation rate due to participating media radiation.

Not all of the above terms are used for each analysis. The user has complete control over the number of heat generation terms and the degree of detail used.

Each of the above terms is based on the total (i.e., cumulative) heat generation rates as determined from user entries for groups of elements, individual elements, or individual nodes. It must be emphasized that the above terms are cumulative. Localized "hot spots" can be accommodated by the application multiple positive heat generation source terms to individual nodes within an element or an element within a group of elements, etc. Localized "cold spots" can be accommodated by the application of negative (i.e., sinks) volumetric heat generation rates or the non-application of additional source terms.

The nuclear decay heat values for each individual fuel element within the MCO model are usually applied as constant volumetric heat sources (i.e., SOURCE) (J/m^3-s) separate from heat sources produced by chemical reactions. This allows the potential for modeling a distribution of decay heats, subject to symmetry considerations, independent of the chemical reactions. The decay heat values can be applied on a global elemental, individual element, and nodal basis. The user has complete control to specify heat generation values down to the nodal level. If necessary, a user supplied subroutine can be compiled and linked with the main program to return volumetric heat generation values for a set of nodal points at a specified time.

The chemical reaction heat sources can be applied several different manners, as follows:

1. Direct application of a surface chemical reaction source term, q_r (REACTION), where the local reaction rate is determined subject to chemical kinetic considerations utilizing local conditions (i.e., temperatures and mass concentrations).
2. Applied at the outer surface of the cladding as a heat flux (BCFLUX), which may or may not be subject to a user supplied subroutine using an iterative process and local conditions to determine the local chemical reaction rate and, hence, applied heat flux.
3. Applied as a separate volumetric heat source (SOURCE) deposited within the four thin rings of cladding surrounding the fuel elements, subject to a user supplied subroutine and local conditions.

Finally, both hot and cold spots can be modeled by changing the thermo-physical properties of the elements that may be associated with degraded fuel or the absence of fuel. Thermo-physical property sets (i.e., density, specific heat, thermal conductivity, emissivity) representative of degraded or reacted fuel and/or cladding can be applied on an individual elemental basis. The absence of fuel can be modeled by changing the subject fuel elements to some other material, such as water, air or helium. Some iteration with the geometrical setup, subject to symmetry considerations, may be necessary to accommodate irregular degraded fuel.

6.2 TECHNICAL ISSUES

Three major issues will effect thermal performance. These are, 1) fully defining the multiple and competing chemical reactions that will occur between water, water vapor, oxygen and uranium, 2) determining the reaction surface area associated with corroded or breached fuel assemblies, and 3) quantifying the difference between the relative rates of water vapor production and rate at which mass can be transferred to the reacting surface. The above issues must be thoroughly investigated and understood such that conditions within the MCO can be maintained to prevent chemical reactions from occurring to such an extent that a temperature excursion will occur, possibly compromising the mechanical integrity of the fuel encapsulation canisters, MCO, and shipping cask.

Secondary issues involve the uncertainties associated with various material properties; especially, thermal conductivity of various gases under low pressure conditions, the effective thermal conductivity of porous, corroded and/or declad fuel, and the emissivities of materials (including corroded fuel) as a function of temperature.

6.3 TECHNOLOGY STATUS

Preliminary thermal analyses have been performed for the shipping case where 1) the MCO is filled with water, and 2) the MCO has been drained and is filled with water vapor at low pressures. These preliminary calculations have assumed that fuel that has been stored under water for years will have corroded and the effective surface area available to support reactions may be

much greater than the original fuel surface area. Therefore, the subject analyses were performed assuming a reactive surface areas of one and ten times those estimated in Section 4.2 of this report. These analyses also assumed unlimited chemical reactants and zero mass transport resistance to the reacting surfaces.

Preliminary results indicate that water is the best thermal coupling media available. Relative to air, temperatures in a water filled environment are more uniformly distributed within the MCO and the thermal gradients within the MCO and FEC are reduced. However, a water filled MCO represents a nearly unlimited source of reactants that could maintain fuel corrosion of metallic uranium fuel for many years to come, as well as a potential source of groundwater contamination should a MCO leak occur. In addition, the presence of water provides for a potential accident scenario where the water is lost and the fuel begins to heat up with residual water vapor and oxygen available as reactants.

An air filled environment results in higher temperatures and more pronounced temperature gradients. The increase in peak temperature for a air versus water filled MCO under identical steady state conditions with nuclear decay heat only is about 20 K. This at first glance appears to be an insignificant amount. However, under conditions with chemical reactions and solar insolation the additional twenty degrees causes the rate of chemical reactions to increase nearly a factor of four and provides a means for accelerating the chemical reactions above those encountered during the water based analyses.

The results from a series of preliminary thermal analyses indicate that cases where the available reactive surface is ten times the estimated reactive surface area may lead to runaway chemical reactions. These analyses assumed both a shipping cask containing a liquid water or water vapor filled MCO under worst case ambient and solar heating conditions. The analysis was a transient that subjected the shipping cask up to thirty days of solar insolation cycles. Time history plots of the temperatures for various internal nodes show a classical exponential rise in temperature when the chemical reactions runaway. For the water filled MCO, fuel temperatures were predicted to increase with time to the boiling point of water. (The present analyses do not effectively model temperatures beyond water boiling at this time.) For the MCO with water vapor the fuel temperatures continue to increase.

It must be emphasized that these are preliminary calculations that were performed as part of model development and refinement and are not expected to be representative of the results that may be obtained from the final model.

6.4 IMPLICATIONS TO KEY DECISIONS

The preliminary thermal analyses performed to date do not yet provide definitive information which precludes any of the current path options. Material properties, definition of the multiple and competing chemical reactions, and reactive surface area uncertainties presently overwhelm these early thermal analyses making definitive statements difficult.

6.5 UNCERTAINTIES

The following conclusions with respect to uncertainties are based the preliminary thermal analyses discussed in Section 6.3:

- 1) Large and significant uncertainties exist in the individual fuel assembly decay heats, potential chemical reactions, reaction rates assumed for the chemical reactions, reaction surface areas, and material properties, particularly with regards to the thermal conductivity of gases under low pressures and emissivities as a function of temperature and surface conditions.
- 2) Large reactive surface area will lead to runaway chemical reactions given a threshold temperature and sufficient reactants.
- 3) Runaway chemical reactions can be achieved by increasing the nuclear decay heat, chemical heat, and external solar heat loads, as well as decreasing the external surface heat rejection capabilities of the shipping cask or increasing the gap resistance between the MCO and shipping cask.
- 4) Combinations of increased surface areas, decay heat loads, and material properties can lead to runaway chemical reactions.
- 5) Worst-case combinations of uncertainties will lead to unacceptable thermal performance.
- 6) Zero mass transfer resistance is overly conservative and does reflect the differences between the relative rates of water vapor production and transport to the reacting surface.

6.6 FUTURE WORK

The following recommendations are based the results of the preliminary results discussed above:

- 1) Continue to investigate the effects of uncertainties on the thermal performance of the shipping and MCO. It is expected that the thermal performance of the shipping cask and MCO will be most sensitive to those items that have the greatest uncertainty.
- 2) Develop a project consensus on what constitutes a best estimate (i.e., design basis) versus worst-case condition (i.e., safety basis).
- 3) Complete the development of the coupled thermal-hydraulic axial model. This model is necessary to resolve issues associated with mass transport, natural circulation flows, and surface reactions under low pressures with residual water. This model will also form the basis for additional analyses concerning the stacking of multiple MCOs within the CSB. The proposed axial model will include node specified chemical reaction heat sources. The resulting temperature profile can be used as input and/or iterated with the ignition theory analyses discussed in Section 2.0.

- 4) Develop a matrix of design basis thermal/hydraulic analyses that are required to support each step in the SNF path forward process; initial loading (possible dense packing), vacuum drying and helium purging, shipping, and long term canister storage.

7.0 CRITICALITY AND MATERIALS ACCOUNTABILITY

7.1 BACKGROUND

Both nuclear criticality of N Reactor fuel and plutonium accountability are well studied issues. Over the last 25 years, a large number of criticality analyses have been completed pertaining to low-enriched uranium metallic fuel elements, sludges, and solutions.

Although the ^{235}U enrichment is low, 0.72 - 1.25 wt%, ^{235}U critical masses can be assembled under proper conditions of moderation and reflection. These masses can be very large and decrease in size as enrichments increase. There is one distinct advantage associated with low-enriched uranium. Unmoderated systems containing less than 6 wt% ^{235}U cannot be made critical. Therefore, any operations involving dry fuel in a dry MCO have no criticality problems as long as accidental moderation is precluded. Therefore, the criticality analysis effort needs to concentrate on baseline concepts that involve fuel elements in water, fuel fragments in water, and moderated sludges.

Fuel burnup in the reactor tends to decrease reactivity. Actual subcritical measurement with N Reactor fuel indicated that for exposures corresponding to fuels-grade plutonium, the difference in critical mass between exposed and unexposed fuel was a factor of 2. For weapons-grade plutonium, the value would be less but still significant. Another important consideration for criticality analyses is that less than 1 wt% ^{235}U homogeneously distributed in water cannot be made critical. Therefore, any sludges or sediments in the basin, canisters, or MCO consisting of homogeneous uranium concentrations with an effective uranium enrichment less than 1 wt% ^{235}U would not be a criticality concern. Any such sludge included in water surrounding fuel tends to reduce the reactivity compared to fuel in plain water. This presumes that uranium to plutonium ratios are maintained and there is no preferential concentration of plutonium.

Plutonium production is well understood and verified extensively with chemical analyses. Therefore, the total inventory sent to the K Basins should be well known from fuel production data, irradiation histories, exposure distributions in the core, and confirmatory chemical analyses from PUREX. The accountability issue will be in terms of how much plutonium has been lost from the fuel due to corrosion or hydrating, how much fuel is in the sludge, the sediments, and the basin water, and how much has been removed by filtering systems. Weighing of assemblies, canisters, baskets before they are placed in the MCO or counting the number of elements in the compacted loading may be required to get a better estimate of how much plutonium was removed from the fuel due to corrosion and hydrating.

7.1.1 Technology Assessment Purpose

7.1.1.1 Identify Nuclear Criticality Issues Impacting Design or Safety Approval. Nuclear criticality safety plays an important role in the design of the MCO, the process steps considered necessary to place the fissionable material in dry storage, and the safety evaluations associated with the prolonged storage.

Criticality mass values for fuel, fragments of fuel, and sludge will contribute to the determination of an acceptable size for the MCO^[33]. Because the MCO contains more than one critical mass, safety analyses requirements will impose constraints on the integrity of the container. With ten canisters of MKIV fuel, the MCO would contain 3356 kg of low-enriched uranium and for ten canisters of MKIA, the uranium content would be 2371 kg of low-enriched uranium. For repacked fuel, the MCO could contain 6472 kg of MKIV fuel (5 tiers, 54 elements per tier) and 4877 kg MKIA (6 tiers, 48 elements per tier). Criticality for low-enriched uranium is highly moderation-dependent; removal and subsequent exclusion of water from the MCO contribute to enhanced criticality safety margins. Therefore, the sooner water can be removed from the MCO, the sooner enhanced nuclear criticality safety margins can be achieved.

Safety approval from a nuclear criticality standpoint requires compliance with the double contingency criterion and the establishment of a defensible safety limit. Compliance with double contingency requirements is provided by geometry controls, use of special neutron absorbers, and moderation control. Concentration control can be applied to load the MCO with different enrichment fuel and accounting for fuel burnup will contribute to enhanced subcritical margins.

For N Reactor fuel, the nuclear criticality safety limit has been established at $k_{eff} = 0.98$ ^[34]. For the low enrichment of uranium in question, this safety limit provides the equivalent protection to that at a $k_{eff} = 0.95$ value for higher enriched fuel such as power reactor fuel. Imposing a $k_{eff} = 0.95$ value on N Reactor fuel would substantially increase excessive conservatism. Figure 7.1 shows the behavior of mass required to reach certain k_{eff} values for different fuel enrichments. With the computer codes used for N Reactor fuel analyses, measured minimum critical masses can be calculated to better than 10%. For MKIV mass corresponding to a $k_{eff} = 0.98$ would require 60% mass addition for criticality while a mass corresponding to a $k_{eff} = 0.95$ would require a 289% mass addition to reach critical. Commercial fuel is handled with a 30 - 40% mass addition to reach critical.

7.1.1.2 Establish Strategy to Acquire Necessary Information. The strategy employed consisted in familiarization with the extensive documentation available on N Reactor fuel nuclear criticality safety evaluations and performing essential calculations to resolve specific issues. Both earlier documentation and documentation generated within the last 5 years were considered^[35-40]. The analyses employed state-of-the-art computer techniques including the MCNP Monte Carlo code^[41-42] and the WIMS-E reactor physics/criticality analysis code^[43]. Analyses were benchmarked to available experimental data. Typical agreement with the WIMS-E code and MCNP are shown in the above mentioned references. Results of the analyses are contained in Appendix A.

Figure 7.1. Mass Required for K_{eff} Commercial Versus N Reactor Fuel.

7.1.1.3 Define Technology Acquisition Tasks. No new technologies are needed to support implementation of criticality control. The necessary nuclear criticality information to assure safety margins was based on prior documented criticality safety analyses and new computations. Actual subcritical measurements of MCO loadings could be desirable but are currently not within the scope or schedule of the project. Detailed calculations with validated models will be employed to acquire the necessary information for determining subcritical margins. Key experimental data used for establishing the margins need to be documented according to latest requirements. Analyses supporting design options have to be prepared to satisfy independent review and public release criteria. Application of any fixed neutron absorbers will require establishment of a means of periodically verifying their integrity.

7.1.2 Process Utilization to Identify Issues

The path forward process steps were evaluated in light of nuclear criticality safety. Conceptual dimensions of the MCO and proposed process steps were discussed in detail with a number of criticality experts. The most reactive situations were identified. Accidents were considered and calculations were performed assessing the subcritical margins. Results from the original design calculations were input to the design process. Iterations between the designers and criticality safety analysts will result in resolution of items of concern.

7.1.2.1 Technology Issues Overlap Major Activities. There are no special technology issues imposed by criticality on other activities. Any steps and processes that reduce the presence of moderation will enhance subcritical margins. Any processes that would preferentially segregate uranium and plutonium during desludging or stabilization would be of concern. Basic criticality control is premised on the fact that the uranium to plutonium ratio remains fixed, without that assumption criticality safety would have to be reevaluated. Furthermore, it is assumed that during any vacuum drying operation, no oils in significant quantities can backflow into a MCO. N Reactor fuel moderated by hydrocarbons would be more reactive than systems moderated by water. Packing of MCO in the basin and all processing and handling operations with MCO have to be performed such that interactions between MCOs are minimized and a MCO drop would result in no uncontrolled fuel accumulations. Wet shipment of MCO and subsequent staging require special safety evaluations. Attention needs to be paid to stabilization efforts so that the process does not tend to concentrate plutonium relative to uranium. The extent of fuel hydration needs to be assessed and the impact on criticality safety, especially in interim storage, needs to be evaluated.

7.2 MAJOR TECHNICAL ISSUES

7.2.1 Plutonium Inventory

An accurate determination of the plutonium inventory by measurement may be difficult. The amount of plutonium produced by N Reactor and placed into the basins is well known. The amount loaded into a MCO can be determined by weighing or counting of elements. The quantity contained in sludge, suspended or in solution in the basin water, and the amount removed by filtration systems is not well defined. Some sampling or nondestructive assay may be required to reduce uncertainties in these estimates. If canister sluicing is

considered, the weight before and after this process may provide some insight on how much fuel has corroded and ended up as sludge. The weight of plutonium placed into a MCO can be derived from individual canister weights. If the compacted storage is used, a count of fuel elements can be made. Canisters containing fragments would have to be weighed before they are loaded into MCOs and some additional characterization of canister with fuel fragments will likely be required. Plutonium content of sludge will require assessing the volume of sludge in the basin and the density of heavy metal in the sludge. Some sampling of sludge may be needed to arrive at the density values. Plutonium content of the water is expected to be small based on past analyses but additional measurements may be desirable. Plutonium removal by filtering systems will require some estimates.

7.2.2 Definition of Safety Margin

Nuclear criticality safety implementation is dependent on the safety limit considered for the activities. Historically, N Reactor fuel has been produced, handled, stored, and processed using a safety limit of $k_{eff} = 0.98$ ^[34,44]. For the very low enriched uranium in question (maximum 1.25 wt% ²³⁵U), this safety limit provides adequate protection, see Figure 7.1. For higher enrichments such as used in commercial power reactors (up to 4.00 wt% ²³⁵U) a more suitable safety limit may be $k_{eff} = 0.95$. For the N Reactor and tubular low-enriched uranium metal fuel, hundreds of critical mass measurements exist for computer methods validation. The codes used in the analyses replicate closely related experimental data very well. Imposing a safety limit of $k_{eff} = 0.95$ on N Reactor fuel for the path forward would have significant design impacts and would impose conservations far in excess of what is required in the commercial industry. The load per MCO would have to be reduced or neutron absorbers would have to be incorporated in a large number of MCOs.

For a $k_{eff} = 0.98$, the MCO would be a favorable geometry for MKIV assemblies and MKIV fuel fragments, see Table 7.1. This means that the MCO geometry provides sufficient constraint to assure subcriticality when the inside containers are destroyed and all fuel slumps to the bottom into an optimum lattice arrangement. For the MKIA fuel or its fuel fragments, the $k_{eff} = 0.98$ would not be exceeded during an accident if sufficient neutron absorbers and geometric constraints are built into the MCO.

7.2.3 Criticality

Criticality of the fissionable material during the path forward approach can be controlled to meet the double contingency criterion. In other words, no single accident shall elevate the neutron multiplication constant of the fissionable material systems beyond a $k_{eff} = 0.98$. The subcritical limit of 0.98 allows for uncertainties in the calculations and the experimental data.

To maintain adequate subcriticality requires controls on mass, geometry, spacing, concentration, and the use of special neutron absorbers.

There are a series of basic facts and assumptions concerning nuclear criticality safety that will be relied on.

Table 7.1. K-effective = 0.98 and Critical Masses and Dimensions for MKIV and MKIA Fuel.

	Sphere		Hemisphere		Infinite Cylinder		Infinite Slab	
	kg	cm	kg	cm	kg/m	cm	kg/m ²	cm
$k_{eff} = 0.98$ Masses and Dimensions								
MKIV (0.95 wt% inner and outer)								
Billets - unlimited								
Assemblies	4744	110.5	7780	164.1	3482	81.3	3149	50.0
Outers	3270	105.9	5374	157.5	2499	78.0	2358	48.3
Inners	2798	97.8	4647	146.1	2296	71.6	2339	45.5
Scrap	1951	91.4	3269	136.9	1688	69.9	1763	46.5
Solution - unlimited								
MKIA (0.95 wt% inner, 1.25 wt% outer)								
Billets	8944	115.1	14485	170.2	6353	84.8	5703	50.8
Assemblies	1432	77.0	2464	116.3	1446	57.4	1826	34.8
Outers	845	70.6	1469	107.2	918	52.3	1240	31.0
Inners	2881	98.0	4794	146.3	2308	74.9	2314	44.2
Scrap	532	64.5	941	98.3	621	48.3	864	30.0
Solution	1364	89.9	2303	134.9	1204	65.5	1269	45.2
Critical Masses and Dimensions								
MKIV (0.95 wt% inner and outer)								
Billets - unlimited								
Assemblies	7795	130.3	12569	192.5	4909	96.5	3838	61.0
Outers	5273	124.2	8522	183.9	3476	91.9	2861	58.4
Inners	4220	112.3	6898	166.6	3054	82.6	2783	54.4
Scrap	2886	101.3	4774	151.1	2247	77.0	2124	48.0
Solution - unlimited								
MKIA (0.95 wt% inner, 1.25 wt% outer)								
Billets	14239	134.4	22734	197.9	8755	99.8	6787	60.5
Assemblies	1893	84.6	3211	127.3	1769	61.5	2056	36.8
Outers	1087	77.0	1864	115.8	1103	57.4	1387	34.8
Inners	4315	112.3	7068	166.6	3122	87.1	2729	52.1
Scrap	672	69.6	1172	105.7	740	52.8	967	33.5
Solution	2070	103.4	3434	154.2	1610	75.5	1533	61.7

Note that MKIA billets, scrap, and solution results are based on 1.25 wt% enrichment.

- For very low enriched uranium such as N Reactor fuel, small changes in k_{eff} result in large changes in fissionable material mass or geometry, see Figure 7.2.
- Dry or unmoderated N Reactor fuel in any form cannot be made critical.
- Homogeneous distribution of uranium with an enrichment of less than 1 wt% ^{235}U in uranium or equivalent enrichment cannot be made critical under any conditions of water moderation^[45]. Any contaminants in the sludge will raise the enrichment. For uranyl nitrate systems, the minimum critical enrichment is 2.1 wt% ^{235}U ^[46].
- All handling and processing in the path forward does not perturb the uranium to plutonium ratio in a way that would concentrate plutonium.
- Irradiated fuel is less reactive than unirradiated fuel.
- Fuel fragments are the most reactive configuration for N Reactor fuel.
- Any processing steps that decrease water moderation of the fissionable material in the MCO will enhance nuclear criticality safety margins.
- Perforation of canisters will weaken the canister structure and reduce the likelihood that canisters will stay intact during a drop accident.
- The presence of sludge will decrease the reactivity of a canister below its original loading value.

7.2.4 Use of Special Neutron Absorbers in MCO

For the MKIA fuel and MKIA fuel fragments, the MCO is not a favorable geometry. Criticality control can be established by use of neutron absorbers. Canister loading of a MCO will require the use of special neutron absorber plates. They could be made either of borated steel or stainless steel. If the fuel is repacked, a central tube in the middle of the MCO packing basket would provide criticality control, see Figure 7.3. The tube could be made of special neutron absorbing steel or even stainless steel. The use of fixed neutron absorbers is only important as long as the fissionable material is moderated. Once the source of moderation has been eliminated, the need for fixed neutron absorbers has vanished. If water-filled MCO are stored in the staging area for any extended period of time, such as years, the effectiveness of the neutron absorbers needs to be verified. The safety analysis report should spell out the surveillance requirements.

Figure 7.2. Mass Required for Different K-Effective Values.

Figure 7.3. Alternate Loading Arrangement for MCO Container with Borated or Stainless Steel Insert.

7.2.5 MCO Transportation

Dry MCO transportation will have no nuclear criticality concerns. There will always be more than an adequate margin of subcriticality. Wet transport will necessitate criticality analysis consistent with transport requirements. Interactions between identical shipments as well as the impact of the cask on criticality will need to be considered.

Transportation accidents are premised on the fact that a MCO can survive the prescribed drop test. Should the MCO fail and spill its content into properly moderated and reflected configuration, criticality is possible. Table 7.1 contains the hemispherical masses for optimally arranged fuel with full moderation and reflection for N Reactor fuel.

7.2.6 Fuel Burnup and Subcritical Margins

Because nearly all of the fuel in the basins has experienced burnup, the discharged fuel is less reactive than the charged fuel. Measurements and detailed computer analyses indicate that substantial subcritical margin benefits can be realized by the fuel currently stored in K Reactor basins. In terms of critical mass increases, spent nuclear fuel critical masses can be larger by 20 to 100%, depending on the fuel exposure. A 20% increase could be realized for fuel containing 6 wt% ^{240}Pu while 100% increase was measured for 12 wt% ^{240}Pu . Burnup credits could be used as a tradeoff with the use of fixed neutron absorbers or serve as a special incremental safety margin. Isotopic composition of N Reactor fuel as a function of fuel exposure is a well known quantity, extensively measured and tracked against reprocessing data. Special critical mass experiments were performed for MKIA fuel for green and for fuel irradiated to 12 wt% ^{240}Pu [47-49].

7.2.7 Accountability Monitoring in MCO

Once the MCO are placed in interim storage, it may be necessary to periodically verify the presence of plutonium. Selected MCOs may be interrogated on the outside for spontaneous fission neutrons that would be representative of the presence of plutonium.

7.3 TECHNOLOGY STATUS

7.3.1 Past Criticality Safety Evaluation Reports

Since the inception of N Reactor, nuclear criticality analyses have been prepared covering fuel manufacturing, storage, and post discharge handling. Extensive documentation has been generated over the last 30 years on this topic [33,37,48,52]. Conclusions and results from these analyses are still valid. In the last 5 years, special attention has been focused on fuel storage in the 300 Area and fuel handling in the K Reactor basins. Extensive use of this documentation can be made [33,35-37,39].

7.3.2 Experimental Measurements and Data

There exist a significant amount of experimental data for low-enriched tubular metallic uranium fuel elements [53-55]. Figure 7.4 shows agreement between experimental data and computer calculations for MKIA fuel. Such measurements were mostly performed at Hanford in the 1950's and 1960's.

Figure 7.4. Number of MKIA Assemblies for Critical for Experimental and Calculated Results.

Subsequently, special measurements were performed on both irradiated and unirradiated MKIA fuel elements and special tests were carried out with neutron absorber plates in latticed fuel^[47]. The experimental data have been replicated successfully with computer methods thereby providing the necessary validation for the computer codes^[33,36-39,56], see Figure 7.4. Experimental information on low enrichment homogeneous solutions of uranium in water^[44,45] have been successfully validated with the computer codes in use, thereby extending capabilities to predict criticality of sludges and sediments^[38,54].

7.3.3 Plutonium Inventory Shipped to Basin

There exists extensive detailed records on the plutonium production in N Reactor and subsequently shipped to K Reactor basins. Experimental measurements on special fuel elements as to isotopic content of fuel and feedback from PUREX helped put in place a validated computer-based production table for predicting N Reactor plutonium production. Each discharge key from N Reactor has a well established plutonium content associated with it. Key locations in the K Basins are known. Segregated fuel remaining in the KE Basin has been characterized into specific categories corresponding to ²⁴⁰Pu content. Plutonium-240 content allows determination of total plutonium in such fuel. Extensive sludge sampling in various locations in the KE Basin^[57] has provided some insight into how much plutonium is in sludge and has also supplied knowledge of uranium/plutonium ratios. Similarly, water samples have been analyzed to determine plutonium content in solution.

7.3.4 Preliminary Calculational Criticality Results for Baseline Concepts

Extensive sets of calculations using the WIMS-E and MCNP codes have been performed on what constitutes safe loadings for the MCO and how criticality safety can be implemented using special neutron absorbers and spacing constraints. The results are contained in Appendix A.

The results confirm that the MCO is a favorable geometry for MKIV fuel in any configuration. In other words, no accident other than spilling all the fuel from a MCO into an optimum geometry and water moderator and reflecting it could approach criticality. For MKIA fuel, special neutron absorbers and geometric constraints are needed to assure subcriticality during accidents that maintain the fuel inside the MCO at optimum spacing, full moderation, and no canister materials present. Spill from the MCO into an optimum geometry with concurrent water reflection and moderation is an item of concern.

7.3.5 Conceptual Plutonium Monitoring Ideas

Techniques and experience gained in determining plutonium in Hanford Site waste tanks could be applied to Nondestructive Examination (NDE) applications associated with determining plutonium in canisters or MCOs. Passive counting methods using either neutron detectors, fission track recorders, or neutron activation foils could be applied. Correlation techniques could distinguish between spontaneous fission and alpha,n source neutrons. Active neutron counting using either isotopic or pulsed neutrons could also be applied to determine total fissionable material content.

7.3.6 Refined Calculational Results

The scoping calculations need to be refined and focused on the criticality controls implemented for MCO loadings and material processing. Accident analyses associated with MCO falling over have to be addressed. Calculated results contained in separate documentation need to be collected into one technical basis document.

7.3.7 Subcritical Measurements Documentation Upgrade

Key subcritical measurements on MKIA fuel pertinent for computer code validation and burnup credit assessment have to be collected and updated with all pertinent information into one document. Currently this information is in a number of documents and personal notebooks.

7.3.8 Subcritical Margin Definition

The normal operations and the accident situation subcritical margins have to be defined. The margin will be impacted by the geometry in which the fuel is constrained in an MCO, by the use of special neutron absorbing materials, by any deliberate mixing of MKIV and MKIA fuel in a MCO, and by the estimates of burnup credit. The impact of MCO reflection by water and the cask wall material will be considered in the margins.

7.3.9 Fuel Fragment Criticality Analyses for Special Containers

Fuel fragments placed in a canister or some other container which are subsequently loaded into a MCO will require a criticality assessment. Canisters loaded with scrap have been analyzed in the past and use of such information will be made. Storage criteria for the containers to assure subcriticality before they are loaded in a MCO need to be considered.

7.3.10 Refinement of Measurement Needs for Plutonium Accountability

The NDE measurements as well as any sampling have to be carefully evaluated in terms of the information to be derived from it. The NDE measurements, if they involve passive neutron counting will require time, have to be sufficiently isolated from other neutron generating systems, and a means of discriminating between alpha,n neutrons and spontaneous fission neutrons has to exist. Sources of spontaneous fission neutrons have to be established through detailed depletion calculations. As demonstrated in the KE Basin backwash pit characterization, sampling of sludge for plutonium and other constituents need to be performed with great care.

7.3.11 Finalize Best-Estimate Basin Plutonium Inventory

The production tables used and the method for combining the information with the discharge keys and how to handle heels of discharge keys needs to be reviewed and published in definitive, defensible documentation. Currently there are some differences of opinion in the process for accounting for the fuel plutonium content and how it contributes to total basin inventory.

7.4 IMPLICATIONS TO KEY DECISIONS

- Although the loading of a MCO with fuel either in canisters or in a repack geometry will have different impacts on subcritical margins, criticality control can be implemented through different control approaches to assure subcriticality even under accident situations.
- Removal of water from the MCO will significantly enhance criticality safety.
- Results of analyses indicate that if a MCO can be safely loaded and handled in the basin, it should also be safe for transport. Subcritical margins incorporated in the design of the MCO and fuel containers should account for transport situations.
- Staging and stabilization efforts should not result in the increase of criticality potentials. Calculations have shown that the low-enriched fuel has a negative temperature coefficient. The only item of concern is that the stabilization operation in some manner preferentially concentrates plutonium.
- Sludge processing should not present a criticality problem as long as the effective sludge enrichment is less than 1 wt% ²³⁵U and the existing uranium/plutonium ratio is maintained. Any preferential segregation of plutonium and uranium would require more stringent criticality controls.
- Handling and packing of fuel fragments can be accomplished safely by limiting the mass and container loadings as prescribed by criticality control procedures.
- Once the path forward process has been finalized, subcritical margins for all process steps can be evaluated and criticality safety can be demonstrated utilizing appropriate control concepts.
- Some promising passive NDE methods exist that can be employed to measure neutron backgrounds and from these, in conjunction with calculations and an understanding of N Reactor fuel irradiation, plutonium levels in the fuel can be calculated. Sludge analyses for plutonium may require some NDE methods and selective sampling.

7.5 UNCERTAINTIES AND REQUIRED INFORMATION

- Final design calculations for criticality safety need to be performed with independent approaches to eliminate possible computer code biases.
- Subcritical margins can be calculated with validated computer codes and, if possible, confirmed with experimental measurements. In situ measuring techniques are available that provide a measure of the subcritical neutron multiplication coefficient, k_{eff} . A measurement of the MCO k_{eff} in water would significantly enhance and confirm the safety analyses.

- Plutonium concentration determination in sludge requires very careful chemical and isotopic analyses. Discrepancies and misinterpretations could lead to increased uncertainty in how much plutonium is in sludge.
- Monitoring for plutonium in a MCO in interim storage can be accomplished with passive neutron counting techniques. Care needs to be taken on how to correct for time-dependent phenomena and the discrimination of neutrons due to different source reactions.

8.0 CANISTER/PARTICULATE/FIXED CORROSION PRODUCT BEHAVIOR

8.1 BACKGROUND

Based on recognition that basin sludge and canister sludge differ in composition and impact, the following definition is proposed for canister/fuel particulate:

"Canister/Fuel particulate is particulate matter, with particle sizes less than 6.35 mm (1/4 in.), that settles to the bottom of storage canisters or is attached as loose particles to fuel element or canister surfaces. It does not include corrosion products that are firmly attached to fuel element or canister surfaces."

The key concerns regarding the particulate inventories that remain in the MCOs center on a) moisture inventories associated with the particulates, effectiveness of moisture removal during conditioning, and impacts of the moisture during storage, b) impacts of particulates on transport of radioactivity, plugging of lines and sensors, and blockage of gas flows during conditioning, c) possible presence of pyrophoric hydrides and metal particles, d) particulate effects on heat transfer, and e) impacts in accident scenarios.

Plans to store the N Reactor fuel in the MCOs for a period prior to conditioning imposes additional sludge considerations, viz., that more particulates will be generated during the storage period. The amount will depend on the storage environment inside the MCOs, either water or inert gas. To differentiate the sludge sources, particulates deposited in the fuel canisters during storage in the K Basins are designated Sludge A; generated during preconditioning storage are designated Sludge B. Not included in the sludge definition are fixed corrosion products on fuel element and canister surfaces. Moisture inventories will be associated with both the sludges and the fixed corrosion products. Figure 8.1 summarizes the sequences of operations (assumes desludging at the K Basins), and identifies sludge and fixed corrosion products generated in each stage.

Inventories of Sludges A and B and fixed corrosion products on KE aluminum canisters (expected to represent the largest fixed corrosion product) were estimated to derive an order-of-magnitude perspective on which inventory is likely to dominate. The results are indicated in Table 8.1.

Figure 8.1 Relation of Sludge and Fixed Corrosion Product Inventories to Stages in Transition of N Reactor Fuel to Dry Storage.

C.P. Corrosion Product
MCO Multi-Canister Overpack

Table 8.1 Sludge Estimates

	Avg. Case ¹	Worst Case ²
Total Sludge A -	15 kg/MCO ³	30 kg/MCO
Total Sludge B -	4 kg/MCO (storage in MCO for 2 y in H ₂ O)	55 kg/MCO
Al Corrosion Product -	5 kg/MCO	15 kg/MCO

1. Failed fuel and Al canisters uniformly distributed in MCOs; does not include fuel sludge A.
2. Concentration of severely failed fuel and Al canisters in ~10 MCOs, some Al canisters have open bottoms, expected to allow escape of some sludge (some Al canisters may have closed bottoms); sludge B assumes wet staging at 35°C.
3. Does not include worst-case fuel sludge.

Bases for these sludge estimates are provided in Reference 54. Sludge weights alone do not define the moisture inventory nor the efficiency of moisture release at conditioning temperatures. These are elements that need to be defined in the characterization program. The worst case fuel resides in aluminum alloy canisters; some canisters are known to have open bottoms; some may have closed bottoms.

Underwater inspections^[21] imply that at least 10% of the KE canisters have severely failed fuel, suggesting that fuel sludge is likely to reside predominantly in relatively few canisters, which prompted the worst case estimate.

8.2 MAJOR TECHNICAL ISSUES

8.2.1 Water Contained Within Sludge

Water can be retained in sludge as either "free water" or as chemically bound water. Free water is defined as water that is present within the MCO as a liquid, is not chemically bonded to any substrate material, and exhibits the normal vapor pressure of water. Free water can form pools of water within canisters and within the MCO, and also can cling to any available surface through weak physical bonds (absorbed water).

Free and absorbed water must be removed before the conditioning process by vaporization. It is more difficult to remove free and absorbed water from sludge than from metal surfaces because of the relatively large amount of free water held within the pore structure of the sludge and the poor heat conductivity of sludge.

Chemically bonded water is water that has formed a chemical union with a substrate material, is not a free liquid, and whose vapor pressure is substantially depressed compared to free water. An example of chemically

bonded water is water of hydration. Because of the depressed vapor pressure of chemically bound water, it is difficult to remove through normal drying processes, and the system temperature must typically be raised to 200°C or more to remove it at a rapid rate.

8.2.2 Hydride Contained Within Sludge

The formation of hydrides and oxides by reaction of water with the reactive uranium metal surface was discussed in Section 3 of this report. As soon as the uranium metal saturates with hydrogen, uranium hydride begins forming within the metal near the surface. Only 3% of the metal needs to convert to hydride before the metal lattice structure is distorted and broken due to the pressure from the hydride. The broken metal then allows the free permeation of oxygen and water and the subsequent oxidation of the metal. In the presence of oxygen, only negligible amounts of hydride are formed; however, in an oxygen-free environment, typically 2 to 10% of the metal^[58] is converted to hydride and is occluded in the oxides. These oxides will spall to form sludge, hydride may be exposed and further react with water and oxygen; therefore, hydride inventories in uranium oxide particulates in KE floor sludge are expected to be small, but that needs to be confirmed in floor sludge characterizations. Hydride contents in KW canister sludge also needs to be determined in the ongoing KW fuel characterization investigations." Additional hydride forming in sealed systems cannot be ruled out.

As additional water permeates through the outer scale and reaches this hydride, some additional hydride reaction is anticipated, however, the reaction rates are not known. As the metal surface continues to oxidize, the scale gets thicker and thicker, until finally the outer surface begins to flake off. Below 140°C, the scale tends to flake off as a powder. Above 150°C, the scale tends to separate as laminar sheets and the permeation of oxygen through this scale increases.

8.2.3 Thermal Insulation

The most significant safety concerns involved in processing or storing spent fuel have (as a common element) the concern that the fuel temperature will rise significantly. Since the release of chemical heat energy is exponentially related to the fuel temperature, it is imperative that the fuel temperature remain at or near ambient until all significant water and oxygen sources are removed.

Since sludge has a lower heat conductivity than water, significant quantities of sludge could thermally insulate the fuel elements. This could initiate a spiralling increase in fuel temperature until a runaway chemical reaction occurs.

8.2.4 Retention of Volatiles During Long Term Storage

Plutonium oxides destined for long term vault storage must be heated to 800°C or more to reduce volatiles to less than 1/2 wt% . Plutonium oxides heated in muffle furnaces for 4 hours at 300°C, frequently release gases during long-term storage.

Since sludge is composed principally of uranium oxides, the similarity between these oxide chemistries leads one to suspect that uranium oxides heated to 300°C may still retain significant quantities of volatile materials.

Basin floor sludge samples were thermogravimetrically tested, and 1% volatiles were retained after a 300°C heat treatment.

The chemical form of these volatiles are not known for certain, but it is suspected that they are either waters of hydration or are hydroxide groups attached to the oxide surface.

Radiolysis during long term storage would convert hydrogen on either water or hydroxides to hydrogen gas. It is believed that during long term storage, uranium metal would convert this hydrogen quantitatively to hydride.

Significant quantities of sludge therefore could induce the formation of significant quantities of hydride during long term storage. This hydride is of concern because of it could serve as an ignition source under accident conditions.

8.3 TECHNOLOGY STATUS

8.3.1 Removal of Water from Sludge

Removal of free water from sludge is accomplished by providing the required heat of vaporization. The heat of vaporization of water is a function of the water temperature and a graph of this function is shown in Figure 8.2.

One sees from this graph that the amount of heat required to vaporize water is significant and that more heat is required to vaporize water at ambient temperature than at the normal boiling point.

Providing the required heat of vaporization may prove difficult for free water contained in sludge because of the relatively poor heat conductivity of that sludge. Preliminary heat transfer modeling shows that 15 liters of free water spread over the interior of the MCO as a film will vacuum dry in approximately 11 hours. An additional 15 liters of water contained in sludge will require approximately 3 days to vacuum dry (see Section 5.0).

Chemically Bound Water - Water may be incorporated chemically as waters of hydration, which are distributed uniformly throughout the crystalline structure, or as surface absorbed water. Since the bulk of uranium is converted to UO_2 which does not form hydrates, surface absorbed water will be discussed first.

Within the crystalline phase, uranium metal ions are surrounded by 4 oxygen ions with single bonds connecting each uranium ion to each of the oxygen ions. This configuration allows maximum bonding strength and crystalline density to be achieved. Near the planar surface this spatial symmetry cannot be maintained and considerable distortion of the lattice

Figure 8.2 The Heats of Vaporization of Water at 1 Atm.

occurs, leading to large bond strains. As a result of the bond strain very little energy is required to separate a uranium to oxygen bond leaving a positively charged empty uranium orbital extending out past the planar surface and a negatively charged oxide orbital. Either orbital can absorb a water molecule and subsequent rearrangement leaves 2 hydroxide moieties at the surface as in:

These hydroxide moieties are bonded very strongly to the oxide surface.

To remove them would require the recreation of the highly strained original surface. They are the last hydrogen containing species to be eliminated by high temperature treatment (600-800°C), and the first to reform upon re-exposure to moisture containing air.

Normal water molecules can be surface absorbed also and two types of absorption is noted. The first type is hydrogen bonded and these can be removed at room temperature using a vacuum. The second type is oxygen bonded and can be removed using higher temperatures in the 200 to 300°C range under vacuum or up to 400°C without vacuum. Carbonates can also be chemisorbed and also are removed in the 200-300°C range.

Fuller⁵⁹¹ experimentally observed both hydroxide and water on uranium oxide surfaces through Diffuse Reflectance Infra-red Fourier Transform Spectroscopy.

Waters of hydration differ from surface absorbed water, in that they are uniformly distributed throughout the crystalline phase. The total water content will be much higher with crystals that contain waters of hydration than those with only surface water, since the interior volume of the crystal can be filled with water. Waters of hydration are oxygen bonded and are typically removed by heating to 200-300°C range under vacuum or up to 400°C without vacuum.

Known hydrates of the oxides are $\text{UO}_3 \cdot \text{H}_2\text{O}$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ A&B, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The water vapor partial pressure over these hydrates can be calculated from thermodynamic principles and the vapor pressure graphs are presented in Figure 8.3.

From Figure 8.3, one sees that the water partial pressure over iron oxide reaches one atmosphere at 87°C. Corresponding temperatures for $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, and $\text{UO}_3 \cdot \text{H}_2\text{O}$ are 127°C and 177°C, respectively.

The partial pressure of water vapor reaches 1 atmosphere over $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, & $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ B&A, at 147°C, 200°C, and 210°C, respectively as shown in Figure 8.4.

This shows that upon simple heating to 250°C or more, the bulk waters of hydration should be removed. These same graphs show that under vacuum conditions, at 1 kPa pressure, the waters of hydration can be removed at temperatures ranging from 50 to 100°C less than that required at atmospheric pressure.

Figure 8.3 Water Partial Pressure over Uranium and Iron Oxides.

Figure 8.4 Water Partial Pressure over Aluminum Oxides.

8.3.2 Hydride in the Sludge

The concentration of hydride in the sludge is not a constant since hydride reacts with both water and oxygen. If any hydride is retained, it is important to know the vapor pressure as a function of temperature. This relationship was calculated^[60] from thermodynamic principles and is presented graphically in Figure 8.5.

Figure 8.5 shows that hydrogen can be removed from uranium hydride at 300°C at 1kPa (8 torr) partial pressure. A temperature in excess of 400°C is required to raise the hydrogen partial pressure to 1 atmosphere.

8.4 IMPLICATIONS TO KEY DECISIONS

8.4.1 Application to Canister Preparation

Since the hydroxides at the surface of uranium oxide are not removed during the fuel conditioning process, and since these hydroxides will liberate hydrogen gas from radiolysis during long term storage, it is reasonable to believe that uranium hydride formation may occur during long term storage. The relative importance of hydride formation will be a function of the ratio of sludge to fuel (i.e., the total amount of hydride that will form), and whether these hydrides are acceptable within the safety analysis.

If the safety analysis indicates these hydrides are unacceptable, then the sludge must be separated from the fuel at some process point and in a general sense the sooner the better. Removing the sludge in the basin as part of canister preparation would also assist in the initial vacuum drying operation at the pool, since the sludges also retain significant quantities of free water that is difficult to remove with warm vacuum drying.

8.4.2 Application to Vacuum Drying

Figures 8.3, 8.4, and 8.5 give the partial pressures of water and hydrogen over hydrates of uranium oxide, aluminum oxide, iron oxide, and uranium hydride respectively. From these graphs one can see that warm vacuum drying (50°C) in the pool will remove free water, but will not remove chemisorbed water. Hot vacuum drying at 300°C, will remove chemisorbed water but will not remove the hydroxide moieties at the surface.

Figure 8.5 Partial Pressure of Hydrogen over UH_3 .

8.4.3 Application to Wet, Dry, Shipment and Staging

The presence of sludge during wet shipment and staging affects the heat transfer rate from the fuel elements to the environment since large quantities of sludge can effectively eliminate convection of water as a heat transfer mechanism. Heat transfer modeling is not yet complete to quantify this effect, but it can only be deleterious.

Since sludge carries chemisorbed water, the presence of sludge during dry shipment and staging will allow the generation and accumulation of hydrogen gas during dry shipment and staging. The hydrogen generation rate will depend upon the amount of sludge within the MCO and the radiation levels. The total amount of hydrogen generated during dry shipment and storage will depend upon the rate and the total storage time. This case has not been modeled satisfactorily yet, but it is certain that hydrogen generation will not be significant for dry shipments lasting no more than 14 days.

8.4.4 Application to Long Term Storage

As indicated earlier, all free water and chemisorbed water can be removed from sludge by either the hot vacuum treatment at 300°C, or by flowing gas treatments at 400°C. None of these treatments are adequate to remove hydroxide moieties at the surface of the oxides and return these oxides to a highly strained configuration. Treatment at 800°C would remove these hydroxides, but is not possible in the presence of the metallic fuel.

If sludge is not treated separately from the fuel, one should expect hydroxides to carry hydrogen through the stabilization process and be a source of hydrogen gas due to radiolysis during long term storage. The presence of hydrogen gas or the formation of additional uranium hydride during long term storage is a safety concern that has not been thoroughly examined. Such examination should be completed before sludge is treated with fuel and committed to long-term storage.

8.4.5 Application to Decisions between Options

Myriad options are available to the SNFP and almost all can be accomplished with enough money and time. Some represent larger safety risks than others. Thus at the basin we must decide if we are going to remove the free water, if we will remove the sludge, and if we are going to repack the fuel elements into a different configuration to increase the loading density within the MCOs.

If the free water is not removed at the basin, we face a wet shipping and staging scenario. If it is removed, shipping and staging will be dry.

We must decide if we are going to go to remove chemisorbed water or hydrides via hot vacuum drying or through a flowing gas system, and finally whether the MCOs will be vented or sealed during long term-storage.

A common thread runs through almost all of these options and that is that the presence of sludge increases the process time, cost, and risk for each of these options. Sludge is efficient in retaining free water and increases the time required to perform a warm vacuum drying operation.

Sludge increases the hazards during either wet or dry shipment. It raises the fuel temperature during wet shipment, and generates hydrogen gas during dry storage and staging.

Sludge contains both chemisorbed water and hydroxide moieties that on the first part increases the time and cost of water removal during conditioning, and on the second part cannot be removed at the fuel conditioning temperature and increases the ultimate risk during long-term storage.

8.5 UNCERTAINTIES AND REQUIRED INFORMATION

Hydride Concentrations - It has been experimentally determined that freshly formed sludge will contain 2-10% hydride within the UO_2 matrix. Logic would lead one to believe that hydride will continue to decrease in sludge over time and is probably at inconsequential levels in older sludge at this time. No experimental evidence has been found to bolster this opinion. It is recommended that such evidence be determined experimentally upon K Basin canister sludge at the earliest opportunity.

In the relatively unlikely event that significant hydride still exists in the sludge, the reactivity of that hydride must be evaluated for ignition theory applications.

Heat Conductance - If desludging is not accomplished, the heat conductivity of sludge for both the wet and dry case must be evaluated. Heat transfer studies are currently underway to resolve predicting the heating curves for the MCO under various conditions. Thermal insulation of the elements with sludge is one of the variables being studied. Resolution of this issue is expected within 30 days. The heat conductivity will effect the equilibrium storage temperature of the fuel elements which in turn strongly affects their chemical reactivity.

Hydrogen Generation Rates - If sludge is to be kept within sealed containers, and has been low fired rather than high fired to 800°C , it is important to know what the hydrogen generation rates will be from the hydroxide moieties. No experimental evidence has been discovered to aid in hydrogen gas modeling studies from radiolysis of the hydroxide moieties.

9.0 MULTI-CANISTER OVERPACK STRUCTURAL INTEGRITY

9.1 BACKGROUND

The MCO is designed to provide containment for spent nuclear fuel during transportation, wet staging, stabilization, and dry storage. The present MCO design will hold ten canisters; each canister contains 14 fuel rods. A material performance study has recommended that the MCO, a cylindrical pressure vessel, be made of austenitic stainless steel (SS) such as 304L or 316L SS^[60]. The advantages of these materials are good corrosion resistance and sufficient strength at the design temperature and in spent nuclear fuel environments. The MCO made of 304L SS not only has adequate corrosion resistance to prevent wall thinning, pitting, or cracking, but also exhibits

excellent ductility to absorb impact loading to maintain containment boundary without losing water during wet storage or releasing radioactive particulates during stabilization, under normal or accident conditions.

The MCO containing spent nuclear fuel will be stored in the storage tubes in the CSB. Under the present conceptual design this tube is 10.7 m (35 ft) long. The lower end of the storage tube is restrained in the base tube assembly, which is anchored to the vault floor. The outside of the upper end of the tube is welded to one end of a bellows. The other end of the bellows incorporates a flange that will be field-welded to the existing floor plug embedment. Impact limiters (approximately 50.8 cm [20 in.] thick) are lowered into each tube before the MCO is inserted to protect the MCO from impact associated with an accidental drop during unloading.

9.2 KEY TECHNICAL ISSUES

The integrity of the MCO is affected by corrosion and mechanical loading. Pitting corrosion, crevice corrosion, Stress Corrosion Cracking (SCC), microbiological attack, and Hydrogen Embrittlement (HE) are major corrosion mechanisms threaten the MCO integrity. Most pitting is associated with halide ions which exist in sludge and water. Corrosion products from the fuel or the aluminum canisters may deposit in the regions with stagnant solution conditions causing crevice corrosion. Once a crack is initiated (by pitting corrosion, for example), the combined effects of corrosion and stress which may be from hydrogen pressure or residual stresses due to welding or cold work can fail the material by brittle fracture at low stresses; this failure mechanism is called stress-corrosion cracking and is a major concern for MCO integrity. In the spent nuclear fuel, hydrogen is generated by radiolysis and may cause delayed failure through hydrogen embrittlement. For example, the hold bar made of Type 416 stainless steel of a K Basin Mark II canister was found broken in 1991. Investigation found that the cover hold bar failed by environmentally-assisted fracture mechanisms such as SCC and HE^[62]. Also possible is the attack of living organisms from water. Microbiological attack of aluminum has been observed in fuel storage pools. Clearly, the MCO is subjected to very corrosive environments, the first defence for the MCO integrity is to select appropriate materials.

In addition to selecting a good material for construction of the MCO, proper design based on understanding of mechanical loading ensures the integrity of the MCO. Sources of mechanical loading includes pressure, impact, and earthquake.

Gas will be generated within the MCO by radiolysis and corrosion processes, resulting in an undesirable increase in internal pressure (assuming the MCO is not vented). Also, during the stabilization process, the pressure within the MCO may need to increase to improve conditioning efficiency. Therefore, it is important to evaluate the pressure capability of the MCO. The rate and magnitude of this pressure buildup within the MCO depends predominately on the quantity of water within the MCO and the temperature within the MCO. Possible ignition of the fuel and hydrogen within the MCO can also challenge the MCO integrity.

Drying the contents within the MCO is being considered for shipping, staging, and stabilization prior to interim storage. Heat and a vacuum may be used to remove water from the MCO to minimize MCO pressurization. The MCO may therefore be subjected to external pressure and high temperature during the drying process.

The following issues have been identified for staging and storage of the MCO in the CSB. Federal regulations^[63] require that the radioactive material container be evaluated for a free drop through a distance of 9.1 m (30 ft) onto a flat, unyielding, horizontal surface. Therefore, the capability of both MCO and impact limiter to withstand this free drop condition should be evaluated. Also, the capability of the storage tube containing MCO to withstand seismic loading needs to be evaluated.

9.3 TECHNOLOGY STATUS

9.3.1 Allowable Working Pressure

Stresses that exist in the sections of the cylinder maintain the wall of the cylinder in equilibrium against internal pressure. The pressure capability is determined as the maximum pressure that induces the maximum stress allowed by the ASME Section III Code^[64] for each material used to make the pressure vessel. Stress calculations are based on the compatibility of deformation around the juncture where the elements of a cylindrical shell and a flat head meet. Radial displacement and rotation of the meridian tangent at the adjoining edges are estimated in terms of shear (Q), moment (M), and pressure (Figure 9.1). The procedure used for calculating the shear and moment of the maximum stress at the juncture of the cylinder and plate is that given in Reference 65. Stress analysis methods accepted by the ASME Section III Code^[66] are also used to determine the stresses of the MCO. Calculation details are documented in Reference 66.

The stress limit is well defined in the ASME Section III Code for 304L SS. The pressure capability of the MCO is computed as the internal pressure that causes the maximum stress to reach the allowable stress of 115 MPa (16,700 lbf/in²) at 38°C (100°F) for 304L SS. Analysis shows that for the 0.953 cm (0.375 in) wall thickness MCO with 2.54 cm (1.0 in) thick flat plates the allowable working pressure is approximately 1 MPa (150 lbf/in² (gauge))^[67]. The von Mises stress at the shell-plate juncture reaches the yield of the vessel material when the internal pressure increases to 1.7 MPa (250 psi). One way to increase working pressure safely is to increase the thickness of the MCO end plate or shell, although the disadvantage of increasing MCO weight also should be considered.

The capability of the MCO to withstand external pressure at elevated temperatures is checked on the basis of ASME Section VIII Code^[68]. Results show that an MCO with a length of 439.4 cm (173 in), a diameter of 61.0 cm (24 in), and a thickness of 0.953 cm (0.375 in) can withstand an external pressure much higher than an atmosphere, during the vacuum drying process with the structural material at 427°C.

Figure 9.1 Stress Analysis of Cylindrical Vessel.

9.3.2 MCO Free Drop and Impact Limiter

For normal conditions of transport, Subpart F of 10 CFR 71 requires that a 1.2-m (4-ft) free drop of a package with a weight less than 5,000 kg (11,000 lb) be evaluated. Evaluation of the MCO design under normal conditions of transport also includes a determination of the effects of compression and penetration tests on that design.

The CFR also requires that a 9-m (30-ft) hypothetical accident condition free drop be considered for the package. A 12.2-m (40-ft, about 2½ times MCO height) free drop of the MCO against an impact limiter placed in the bottom of the storage tube in the CSB is evaluated. The design of the impact limiter is based on the impact load delivered by the falling MCO. The impact (or dynamic) force resulting from a freely falling body striking a structure is analyzed by assuming that the kinetic energy of the moving body is completely transformed into the internal strain energy of the resisting system (Figure 9.2).

If the MCO with a weight of W falls from a height of h and strikes the impact limiter with a maximum displacement of D , the kinetic energy (KE) can be calculated from the following equation:

$$KE = W (h + D) = \frac{1}{2} F_{\text{dyn}} D = F_{\text{av}} D \quad (9.1)$$

where F_{dyn} is the maximum dynamic force and F_{av} the average force.

Because the limiter takes on the load gradually, the average force (F_{av}) against the limiter is equal to one-half of the maximum dynamic force: F_{av} is the crush load of the absorbing material. Most energy absorbing materials have this type of mechanical property. However, a honeycomb material exhibits a nearly constant crush load during displacement after impact. If the crush load of the limiter is known from the vendor, the maximum displacement (D) of the MCO after striking the limiter can be estimated from Equation 9.1.

The velocity (V_o), acceleration (a) at impact, and the time (t) to reach zero velocity can be estimated. Since $mV_o^2/2 = mgh$, it follows that

$$V_o = \sqrt{2hg}. \quad (9.2)$$

We can calculate the values of acceleration, time to reach zero velocity, and the displacement in terms of time. Also, we can estimate the crush load of the absorber to absorb the whole kinetic energy of the falling weight with a given displacement^[67].

The kinetic energy of the falling MCO is about 5.21×10^5 J (384 kip-ft)^[67], which is too great for a 50.8 cm (20 in) thick impact limiter to absorb, and impact-induced structural deformation is expected. The energy is even greater if the MCO is filled with water. According to 10 CFR 71, the MCO should be evaluated for a free drop in a position that is expected to inflict maximum damage and may adversely affect shielding capability and criticality control. Compliance with the CFR requirements is demonstrated by developmental drop testing. Tests performed under hypothetical accident

Figure 9.2 Analysis of Free Drop.

conditions should demonstrate that the MCO maintains its containment boundaries and remains leak-tight. Under the free-drop tests, there would be no external radiation dose rate exceeding the level required in 10 CFR 71.51 and under the tests the package would be subcritical as required in 10 CFR 71.55.

9.3.3 SEISMIC EFFECT

The structural integrity of the tube is verified by calculating the seismic loads from the natural frequency of the tube, which is changed by liquid content. The liquid in the tube will experience sloshing and rocking oscillations during horizontal seismic excitation. Studies have shown that the natural frequency of the tube increases with increasing liquid level^[69]. Analysis of liquid-to-tank interaction is complicated, but an assumption of a 5 to 10% decrease in sloshing frequency resulting from the presence of items inside the storage tube^[70] does not change seismic acceleration significantly. Seismic loading on the storage tube and MCOs increases because the total weight is increased by water. However, the deflection of the tube center due to lateral seismic motion is found to be insignificant and will not threaten the integrity of the MCO or the storage tube^[67].

9.4 IMPLICATIONS TO KEY DECISIONS

Austenitic stainless steels are satisfactory materials for the MCO. Low carbon stainless steels (304L or 316L SS) are used to minimize sensitization-related problems such as stress-corrosion cracking during welding of the MCO vessel. Because there is a larger knowledge base about Type 304L SS, the MCO is recommended to be made of Type 304L SS, although Type 316L SS is known to have better resistance to pitting corrosion but costs 20-25% more. Both materials are suitable for wet staging and dry storage.

The higher the internal pressure, the higher the stress on the MCO will be. Naturally, there is a stress limit, so there is also a limit on the pressure to which the MCO material can be subjected without failure. The allowable working pressure of the vessel is determined with stress analysis methods. Because of pressure limit low gas generation, venting, or using getters should be considered when making wet/dry decision.

A 12.2 m (40 ft) free drop of the MCO is analyzed to check whether the MCO can withstand the accidental free drop condition as required by Code of Federal Requirement. Since there will be two MCOs and two impact limiters stored in one storage tube in the canister storage building, the impact limiter is unlikely to absorb fully the kinetic energy of the 12.2 m (40 ft) falling MCO. Filling the MCO with water only adds more problems. Free drop testing should be performed to demonstrate that the MCO is adequately designed to maintain its containment boundaries and remain leak-tight under hypothetical accident conditions.

The strength of the storage tube containing two MCOs is adequate to withstand seismic loading. To determine seismic forces, the natural frequency and seismic acceleration of the MCO storage tube are estimated. The calculations meet the strength requirements of the American Institute for Steel Construction^[71] for the tube. If water fills either the MCOs or the storage tube, the weight and natural frequency of the tube assembly will be

different compared to dry conditions. As a result, the seismic acceleration and loads will vary, but the changes are not expected to affect the integrity of the tube and MCO significantly.

In general, a MCO containing no or little water is less susceptible to corrosion and subjected to lower mechanical loads.

9.5 UNCERTAINTIES

The values of the pressure limits determined vary if the support conditions for the end plate change. In some cases the values would decrease substantially as calculated by stress analysis methods accepted by the ASME Section III Code. The large uncertainty in evaluating the pressure capability of the MCO should be taken into account in assessing the risk of high-pressure operating conditions.

Because the impact limiter is unlikely to absorb fully the kinetic energy of the falling MCO, part of the energy is absorbed by the MCO. The extent of the impact-induced deformation is uncertain.

Uncertainties exist during wet staging due to presence of water, sludge and other materials which may impact MCO corrosion.

9.6 PROPOSED FUTURE WORK

1. The design of top and bottom plates for the MCO is being revised. Because the pressure capability of the MCO varies with the structure of the end plates, the pressure limit for the currently designed MCO needs to be reevaluated.
2. After the design of the MCO is finalized, the total weight of the MCO including all items inside the MCO and the total kinetic energy of the 40-ft falling MCO will be estimated. The dimension and crush load capability of the impact limiter will be determined so that the amount of the kinetic energy absorbed by the MCO can be estimated. Free drop testing will be performed to check whether the requirements of Federal Regulations are satisfied. The information obtained will be used to redesign the MCO.
3. Safe storage of the MCO in the storage tube depends on how well do the floor plug and the tube base withstand an earthquake. Therefore, their strength will be qualified seismically.

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PRELIMINARY RESULTS: CRITICALITY ANALYSIS OF MCO CONTAINER

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cc: D. G. Erickson
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KNS-File/LB

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The MCO container is a large over-pack intended to store up to 10 N Reactor fuel storage canisters. Each fuel storage canister consists of two container halves linked together, holding seven N Reactor fuel assemblies each, in a cluster arrangement. There are two canisters in each of the five tiers inside an MCO or 28 fuel assemblies per layer. Figure 1 illustrates an axial cross section of the MCO design.

In the event of fuel damage accompanied by loss of geometry control (such as if the individual fuel storage canisters break apart, allowing fuel debris to accumulate towards the bottom of the MCO container), the accepted practice is to assume debris of uranium to be of optimal size and spacing. Previous calculations have established that the minimum critical cylindrical radius for 0.95 wt% enriched uranium is equal to 36.7 cm for an infinitely long cylinder fully reflected by water. Assuming that the MCO inner radius is 30.48 cm (diameter = 24 inches), it is clear that 0.95 wt% enriched uranium scrap represents no criticality danger, for any amount of material loading within the MCO. Other calculations also have shown that optimally spaced uranium rods are more reactive than tubular fuel components or N Reactor concentric tube assemblies (Schwinkendorf 1995).

The mass-averaged enrichment of N Reactor MKIA fuel is 1.15 wt% ²³⁵U in uranium; the inner element is 0.95 wt% while the outer element is 1.25 wt% enriched. The infinite cylinder minimum critical radius for 1.15 wt% scrap is

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Figure 1. Onsite Transfer Cask

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equal to 26.2 cm, which is less than the MCO inner radius. Table 1 contains the minimum radii for several different enrichments of interest, for both critical and $k_{eff} = 0.98$ ($k_{eff} = 0.98$ has been used extensively for N Reactor fuels as the safety limit).

For N Reactor MKIV fuel, which consists of 0.95 wt% enriched inners and outers, the MCO container inner radius is still less than the infinite cylinder radius required for $k_{eff} = 0.98$, and so MKIV fuel is considered safe in this accident scenario. The WIMS-E lattice transport code (Gubbins 1982) was used to generate two-group cross sections for the fuel debris lattice, while the diffusion code GOLF was used to calculate finite radial dimensions and to include axial neutron leakage using axial bucklings.

The calculated results in Table 1 are valid for infinitely long cylinders of uranium metal scrap, optimally sized and spaced, and fully reflected with water in the radial direction. For cylinders of finite height, the additional neutron leakage requires an increased radius to maintain the same k_{eff} . Figure 2 shows how k_{eff} increases as the height increases for cylinders of two different radii, the critical radius of the infinitely-long cylinder, and the actual inner radius of the MCO container. As expected, the k_{eff} approaches 1.0 as the height approaches infinity (i.e., becomes large as compared to the thermal neutron mean-free-path) when the radius is equal to the infinite cylinder critical radius. This is true by definition of the critical radius of an infinitely long cylinder. However, as the height increases for the actual MCO inner radius, the k_{eff} exceeds 0.98 for uranium metal mass in excess of 1,011 kg. Calculated k_{eff} exceeds 1.0 for a uranium mass greater than 1,763 kg. Therefore, if the MKIA-loaded fuel canisters exceeds two layers, the accident k_{eff} limit of 0.98 would be exceeded. This first curve in Figure 2 is idealistic; it provides a comparison against the infinite cylinder limits established in (Schwinkendorf, 1995). If the 0.375 inch stainless steel liner is included, the additional neutron absorption depresses the k_{eff} curve several mk, to where the system appears as though it has the infinite cylinder critical radius.

Table 1. Minimum Critical and $k_{eff} = 0.98$ Radii for Infinite Cylinders.

Enrichment (wt%)	$k_{eff} = 1.00$	$k_{eff} = 0.98$
0.947	36.7004	32.2526
1.147	26.2204	24.0342
1.247	23.3818	21.6524

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Unfortunately, when the 8 inches of steel were included, representing the cask wall itself, the additional fast neutron reflection caused the k_{eff} to increase rather dramatically, as shown with the highest curve on Figure 2. The MCNP code (Carter 1994) was executed on this same problem (finite fuel debris height with both the stainless steel liner and 8 inch cask wall). Several of these calculated points are included in Figure 2, and are labeled "MCNP model, actual MCO".

The degree of agreement between WIMS-E and MCNP is good, given that there were some differences in the input. For example, the WIMS-E cross section library contains a material simply called "stainless steel", which was used for the scoping studies to represent both the inner stainless steel liner and 8 inches of carbon steel in the container. In the MCNP models, a material composition used previously for Type 304 stainless steel was used. The MCNP code calculated $k_{eff} = 1.01339 \pm 0.0022$ at a debris height of 60 inches, which corresponds to a uranium mass equal to 1,681 kg, or 3.5 levels with MKIA fuel. MCNP calculated $k_{eff} = 0.97691 \pm 0.0028$ at a debris height of 30 inches.

These results for "Actual MCO radius" will change slightly as the assumed inner diameter changes. For a 23.25 inch diameter and a 25.25 inch diameter, which are considered to be the end-points, Figure 3 shows how the k_{eff} results change. The 24.00 inch diameter case is the same as the "Actual MCO with cask" curve in Figure 2.

Figure 2. k_{eff} vs. Debris Height.
 Single MCO Unit, Optimal 1.15 Scrap.

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Figure 3. k_{eff} vs. Debris Height.
 Single MCO Unit, Optimal 1.15 Scrap.

The minimum critical masses for 0.95 wt%, 1.15 wt%, and 1.25 wt% enrichment are contained in Table 2. The first mass column in Table 2 assumes whatever critical radius is required to attain a minimum critical mass for an infinite cylinder containing scrap of the indicated enrichment. The second mass column is constrained by an assumed MCO inner radius of 30.48 cm, and the height was varied to achieve the indicated k_{eff} , for each enrichment.

For intact fuel, the calculated reactivities are significantly less. Intact MKIV fuel is less reactive than is optimally sized and spaced 0.95 wt% scrap. The infinite cylinder $k_{\text{eff}} = 0.98$ radius is greater than the inner radius of the MCO container for 0.95 wt% scrap, and it is greater still for intact MKIV fuel. The infinite cylinder $k_{\text{eff}} = 0.98$ radius for MKIA fuel is also greater than the inner radius of the MCO container, even though this presents a problem for the 1.15 wt% scrap. The minimum infinite cylinder $k_{\text{eff}} = 0.98$ radius for intact MKIA fuel is equal to 30.78 cm. The k_{eff} values for various fissionable material heights (with the radius equal to that of the MCO container, but fully water reflected) are shown in Figure 4, where the previous values for 1.15 wt% scrap are compared to the corresponding results for 1.25 wt% scrap and intact MKIA fuel.

Figure 5 is the same as Figure 4, but with the stainless steel of the MCO cask included between the fissionable material and the water reflector. As before, these curves are several mk higher than with full water reflection alone.

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Table 2. Minimum Critical and $k_{eff} = 0.98$ Masses.

Critical - $k_{eff} = 1.00$				
Enrichment (wt%)	Mass ⁽¹⁾	Radius (cm)	Mass ⁽²⁾	Height
0.947	685.096 kg/ft	38.381	(infinite)	(infinite)
1.147	301.403 kg/ft	28.852	1763. kg	62.9 inch
1.247	225.806 kg/ft	26.442	960. kg	38.4 inch
$k_{eff} = 0.98$				
Enrichment (wt%)	Mass ⁽¹⁾	Radius (cm)	Mass ⁽²⁾	Height
0.947	514.712 kg/ft	34.931	(infinite)	(infinite)
1.147	248.333 kg/ft	26.189	1011. kg	36.1 inch
1.247	189.211 kg/ft	24.205	714. kg	28.6 inch

- (1) Mass per unit length of an infinite cylinder (critical or $k_{eff} < 1.0$)
 (2) Actual mass for a cylinder 30.48 cm in radius (critical or $k_{eff} < 1.0$)

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For fully intact geometry (as depicted in Figure 1), criticality is of no concern. MCNP was used to calculate the k_{eff} of this geometry, if loaded with MKIA assemblies, and the result was $k_{\text{eff}} = 0.66681 \pm 0.00194$. MKIV assemblies would be less reactive than this.

The highest value for k_{eff} (calculated by MCNP) depicted in Figure 2 is 1.020. This value corresponds to 2520 kg of 1.15 wt% enriched scrap, or over eight fully loaded tiers of MKIA canisters; this is well beyond the design load for the MCO. A criticality safety design improvement was analyzed, where a cruciform "control blade" was inserted into the MCO, consisting of 0.25 inch thick borated steel, containing 1 wt% natural boron. The MCNP calculation of this arrangement is highly encouraging, $k_{\text{eff}} = 0.89590 \pm 0.00311$. This calculation illustrates the feasibility of controlling the more reactive scrap configuration in the event that all geometry control is lost inside the MCO while loaded with MKIA fuel. If this change is implemented in the MCO design, final, more detailed MCNP models of the borated steel structure will have to be created and analyzed, but this preliminary result is very promising.

All of these calculations were performed for unirradiated fuel. Fuel burnup credit would provide an additional safety margin. Experimental data exist for MKIA fuel showing the impact of fuel burnup on nuclear criticality safety parameters. Burnup calculations have been performed for both MKIV and MKIA fuel types, using hot operating conditions in the N Reactor lattice.

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Figure 6 shows the reactor lattice k_{∞} for both MKIV and MKIA fuel. The initial drop in reactivity is due to the buildup of equilibrium xenon poisoning. The subsequent behavior of MKIA fuel shows that reactivity decreases monotonically with exposure. MKIV fuel, because of the lower initial enrichment, shows an increase in reactivity due to the buildup of ^{239}Pu . This behavior has been shown in previous analyses using the HAMMER lattice code (Toffer 1975). The minimum spherical critical mass for unirradiated MKIA fuel is 1893 kg. This calculation assumes optimal moderation (hexagonal lattice spacing of 3.1 inch center-to-center) and full water reflection. With burnup equal to 92 days (which corresponds to 6 wt% ^{240}Pu in total plutonium), this minimum critical mass increases to 2419 kg, an increase of 28%. With burnup equal to 162 days (9 wt% ^{240}Pu in total plutonium) this critical mass increases to 2946 kg, an increase of 56% over the unirradiated value. These results are consistent with the earlier cited work, as shown in Figure 11 of the reference. These burnup effects were calculated assuming the isotopic concentrations present at each of the exposure points, but because of its short half-life, ^{135}Xe was eliminated. Figure 7 shows the variation in calculated lattice k_{∞} as the spacing in cold water is varied. Figure 8 shows the corresponding spherical critical mass.

As shown in Figures 7 and 8, taking credit for burnup to 6 wt% ^{240}Pu for MKIA fuel gives approximately 20 mk in reactivity, and a 28 % increase in the minimum critical mass. Figures 9 and 10 illustrate these same results for the less reactive MKIV fuel.

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Figure 9. k -infinity vs. Spacing.
 Cold MKIV Fuel in Water.

Figure 10. Critical Mass vs. Spacing.
 Cold MKIV Fuel in Water.

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The variations in maximum lattice k_{∞} and minimum critical mass (MCM) are plotted as functions of exposure in Figures 11 and 12. In Figure 12, this evolution is plotted as the ratio of the MCM as exposure increases, divided by the MCM with no exposure. Figure 12 may be compared directly with Figure 11 in the Toffler reference. The new and the old figures are in reasonably good agreement, but Figure 12 was not computed for burnups as high as those shown in the Toffler reference. As before, burnup effects were treated by using the isotopics generated with the WIMS-E lattice code, in the hot operating lattice environment of the N Reactor. These isotopics (except for ^{135}Xe , which was effectively set to zero) were then used in a cold water lattice model, where the spacing between fuel assemblies was adjusted to find maximum k_{∞} and MCM. The first points plotted in Figures 11 and 12 are for two days. In Figure 12 the point plotted at zero exposure would be exactly equal to 1.0.

Figures 6 and 11 are different. Figure 6 shows the change in k_{∞} inside the fixed graphite lattice of the N Reactor, using hot operating conditions. These are the k_{∞} values produced by WIMS-E as the burnup calculation proceeds. Figure 11 shows the maximum k_{∞} when the fuel is removed from the reactor, ^{135}Xe is allowed to decay away, and the fuel is immersed and optimally spaced in a light water moderator. The relative shapes of the two curves in Figures 6 and 11 are quite similar.

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Another option under consideration is to unpack the existing N Reactor fuel assemblies from their canisters, and close-pack them into MCO containers with an internal arrangement such as that depicted in Figure 13. MKIV fuel could be stored in this manner without limitation. MKIA fuel may be packed according to the arrangement shown in Figure 14. The cylindrical insert is to be composed of 1 wt% boron stainless steel. MCNP calculations of this geometry have been completed, and are shown in Figures 15 and 16. The lattice spacing of the fuel in this arrangement is 2.8 inches, center-to-center, which is less than the optimal value of 3.1 inches. MKIA fuel, if packed in the arrangement shown in Figure 13, will exceed $k_{eff} = 0.95$ for values of height greater than approximately 50 inches (or two vertical tiers). The removal of the inner ring of six assemblies, together with inclusion of the borated steel insert, reduces k_{eff} dramatically (approximately 100 mk). For a fissionable material height equal to 90 inches, a single calculation was made of k_{eff} without the inner ring of six assemblies, but also without the borated steel insert; this allows for the calculation of the reactivity worth of the insert, which is equal to 44 mk. If the insert is made of the same composition steel as the material in the MCO liner (i.e., without 1 wt% natural boron), the reactivity worth of the insert is reduced, to 23 mk. Therefore, most of the reduction in k_{eff} is due to the removal of the inner ring of six fuel assemblies. Figure 16 repeats the highest curve found in Figure 15, but with the 95% confidence bounds included. Inserting one more MKIA assembly into the center of the cluster was also analyzed; this worth was equal to 6.7 mk.

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Figure 13. Alternate Loading Arrangement for MCO Container.

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Figure 14. Alternate Loading Arrangement for MCO Container with Borated steel insert.

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If the inner ring of six assemblies is removed, the insert should also be included, as this provides geometry control, without which the remaining assemblies might shift to larger, more reactive lattice spacings.

Three final possibilities were analyzed. First, if MKIA assemblies, loaded as shown in Figure 1, were to fragment, the debris would settle to the bottom of each canister. Given the cross sectional area of the canister, and the volume fraction occupied by fuel fragments when at the most reactive configuration for 1.15 wt% rods (rod OD = 0.6 inches, spaced 1.0 inches center-to-center on a hexagonal pitch), this corresponds to a debris height slightly greater than the original fuel (about 25 inches). The k_{eff} of this configuration was equal to 0.75652 ± 0.00186 (increase from 0.66681 for intact MKIA fuel). Second, all calculations involving intact canisters within the MCO assume that the canisters are made of stainless steel. The model that produced the above result was redone, assuming the canister material was aluminum. The k_{eff} increased to 0.80239 ± 0.00180 . This is consistent with previous calculations of the reactivity worth of stainless steel versus aluminum canisters.

Finally, if some type of oil moderator were to intrude into the MCO in the loading concept shown in Figure 13, k_{eff} could increase somewhat. A long carbon chain material (such as $[CH_2]_n$) was assumed to completely replace water as the moderator in one of the MCNP calculations. In the top curve shown in Figure 15, k_{eff} will increase from 0.95639 ± 0.00321 to 0.98103 ± 0.00292 , for a fuel loading height of 60 inches.

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Technology Support Programs

Westinghouse
Hanford CompanyInternal
Memo

From: Process Chemistry Laboratory 12110-PCL93-058
Phone: 3-2529 T6-09
Date: July 14, 1993
Subject: RESULTS OF THERMAL GRAVIMETRIC ANALYSIS ON K-EAST BASIN SLUDGES
AND SUPERNATANT LIQUIDS.

To: M. A. Meier X5-58
C. L. Bennett X0-44

cc: D. B. Bechtold T6-09
J. R. Jewett DL T6-09
BEH File/LB

Four sludge samples and two supernatant liquid samples were submitted to Process Chemistry Laboratory for thermal gravimetric analysis (TGA). The results of those analyses are addressed in this letter.

The preparation of the samples is recorded in controlled laboratory notebook "Process Chemistry Support," WHC-N-341 1. The TGA operation of the samples is recorded in controlled laboratory notebook "Process Chemistry Thermal Analysis," WHC-N-522.

Table 1 lists the samples which were analyzed and their identification numbers. Also listed in Table 1 is a brief comment on the physical description of the samples.

Table 2 lists the highlights of the TGA results for the sludge samples plus two samples containing supernatant liquid from the sludge samples. Two sets of results are listed: initial analysis results and replicate analysis results. Results of the initial analysis for sample S303204 are not listed due to a technical error; listed instead are the first and second replicate analysis results. Figure 1 graphically illustrates the quantities of each component reported in Table 2. (The term "replicate" in this letter means a repeat of the analysis of the sample conducted precisely as the first analysis.)

The first sample to be analyzed using TGA was sludge sample S303201. It was run to 1000°C at 5°/min in order to detect any chemical reactions which it might have undergone at both low and high temperatures. No chemical reactions were detected in the upper temperature range between 600°C and 1000°C. Subsequent samples were not analyzed higher than 600°C.

It was discovered that when the sludge samples were homogenized there always remained a certain amount (5-10 percent) of the sample which would not remain in suspension. This insoluble material would fall out and form a sandy-gritty layer at the bottom of the sample. This "inhomogeneity" of the samples influenced the TGA to a greater or lesser extent based upon the size of the sample being analyzed such that the larger the sample the less the influence and vice versa. The effect of inhomogeneity could be seen by observing differences between sample and replicate thermalgrams.

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Table 1. List of K-East Basin Samples Analyzed by TGA.

Customer ID	Sample ID	Physical Description
SB-75F Sludge Sample	S303201	Before analysis: Thick brick red muddy liquid. Would divide into a clear supernatant liquid on top with thick sludge on the bottom if allowed to settle for a few minutes. Contained some sandy-gritty material. After analysis: Unfused dark powder. Very dry, no tackiness.
SB-74F Sludge Sample	S303202	Same as sludge sample S303201.
SB-73D Sludge Sample	S303203	Same as sludge sample S303201 and S303202.
SB-70B Sludge Sample	S303204	Before analysis: Thin brick red muddy liquid. Similar to the other sludge samples but contained much less sludge component. Also contained some sandy-gritty material. After analysis: Unfused dark powder. Very dry, no tackiness.
SB-75B Supernatant Liq	S303201	Before analysis: Clear colorless liquid. No particulate solids observed: After analysis: No residue.
SB-70C Supernatant Liq	S303204	Observations the same as SB-75B supernatant liquid.

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Table 2. TGA Results of E-East Basin Sludge Samples.

S303201 (SB-75F)	Sample	Replicate	Average
Free Water	49.97	50.16	50.07
Residual Solids	50.03	49.84	49.94
Hydrated Water	6.09	6.08	6.09
Anhydrous Solids	43.94	43.76	43.85
S303203 (SB-73D)	Sample	Replicate	Average
Free Water	72.31	73.19	72.75
Residual Solids	27.69	26.81	27.25
Hydrated Water	4.32	4.21	4.27
Anhydrous Solids	23.37	22.6	22.99
S303202 (SB-74F)	Sample	Replicate	Average
Free Water	46.34	48.38	47.36
Residual Solids	53.66	51.62	52.64
Hydrated Water	6.01	6.04	6.03
Anhydrous Solids	47.65	45.58	46.62
S303204 (SB-70B)	Replicate 1	Replicate 2	Average
Free Water	90.42	88.98	89.7
Residual Solids	9.58	11.02	10.3
Hydrated Water	1.58	1.32	1.45
Anhydrous Solids	8	9.7	8.85
Supernatant Liquids	S303201	S303204	Averages
Free Water	100	100	100
Residual Solids	0	0	0
Hydrated Water	0	0	0
Anhydrous Solids	0	0	0

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Figure 1. K-East Sludge Sample Components.

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Sludge Sample S303201

Sludge Sample S303201 consisted of a thick, reddish colored immiscible solid material under an equal volume of clear, colorless supernatant liquid. The sludge would not easily disperse into the supernatant liquid but had to be homogenized for about two minutes before a fairly representative subsample could be obtained.

Approximately 20 mg of the wet, homogenized sludge was placed in the TGA furnace. In the temperature range of 25°C to 99°C a mass loss of approximately 50% was observed. This mass loss was attributed to the evaporation of free water in the sample.

A second mass loss of approximately 12.2% of the total residual solids was observed in the temperature range of 99°C to 550°C. The thermalgram profile in this temperature region suggested the mass loss was due to the simultaneous decomposition of predominantly ferric hydroxide oxide ($\text{FeO}(\text{OH})$) and small amounts of aluminum hydroxide ($\text{Al}(\text{OH})_3$). A numerical analysis of the results suggested that 92% of the total residual solids was $\text{FeO}(\text{OH})$ (Attachment 1). This would correspond to 46% of the total mass of the sample. The remaining 4% of the sample is believed to be mostly $\text{Al}(\text{OH})_3$.

The results of the replicate analysis deviated from the initial results by less than 1%.

Sludge Sample S303202

Sludge Sample S303202 consisted of a thick, reddish colored immiscible solid material under clear supernatant liquid. Like sludge sample S303201, this sample also had to be homogenized before subsampling.

Approximately 58 mg of the wet, homogenized sludge was placed in the TGA furnace. In the temperature range of 25°C to 139°C a mass loss of approximately 48% was observed. This mass loss was attributed to the evaporation of free water in the sample.

Similar to sludge sample S303201, a second mass loss of approximately 11.7% of the total residual solids was observed in the temperature range of 139°C to 550°C due to the decomposition of ferric hydroxide oxide ($\text{FeO}(\text{OH})$) and small amounts of aluminum hydroxide ($\text{Al}(\text{OH})_3$). A numerical analysis of the results suggests that 94% of the total residual solids was $\text{FeO}(\text{OH})$ (Attachment 1). This would correspond to 48% of the initial mass of the sample. The remaining 4% of the sample is believed to be mostly $\text{Al}(\text{OH})_3$.

The results of the replicate analysis deviated from the initial results by about 2%. The initial results, however, suffered from a slightly off-zeroed balance. The replicate analysis was used to make the above determinations.

Sludge Sample S303203

Sludge Sample S303203 consisted of a thick, reddish colored immiscible solid

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material under a somewhat larger volume of clear supernatant liquid. Again the sludge would not easily disperse into the supernatant liquid but had to be homogenized for about two minutes before a representative subsample could be obtained.

Approximately 24 mg of the wet, homogenized sludge was placed in the TGA furnace. In the temperature range of 25° to 122°C a mass loss of approximately 72% was observed. This mass loss was attributed to the evaporation of free water in the sample.

As in sample S303201, a second mass loss of approximately 15.6% of the total residual solids was observed in the temperature range of 112°C to 550°C indicative of the decomposition of ferric hydroxide oxide ($\text{FeO}(\text{OH})$) and small amounts of aluminum hydroxide ($\text{Al}(\text{OH})_3$). A numerical analysis of the results suggests that 78% of the total residual solids was $\text{FeO}(\text{OH})$ (Attachment 1). This would correspond to 22% of the initial mass of the sample. The remaining 6% of the samples is believed to be mostly $\text{Al}(\text{OH})_3$.

The results of the replicate analysis deviated from the initial results by less than 1%.

Sludge Sample S303204

Sludge Sample S303204 consisted of a thin liquid sample, red brick in color and opaque. This sample contained less solids than all the other sludge samples. But like the other sludge samples, this sample too, had to be homogenized before a fairly representative subsample could be taken.

Approximately 39.2 mg of the wet, homogenized sludge was placed in the TGA furnace. In the temperature range 25°C to 143°C a mass loss of approximately 90% was observed. This mass loss was attributed to the evaporation of free water in the sample.

A second mass loss of approximately 17% of the total residual solids was observed in the temperature range of 143°C to 550°C due to the decomposition of ferric hydroxide oxide ($\text{FeO}(\text{OH})$) and small amounts of aluminum hydroxide ($\text{Al}(\text{OH})_3$) as in the previous samples analyzed. A numerical analysis of the results suggests that 74% of the total residual solids was $\text{FeO}(\text{OH})$ (Attachment 1). This would correspond to 7% of the initial mass of the sample. The remaining 3% is believed to be mostly $\text{Al}(\text{OH})_3$.

The results of the first replicate analysis deviated from the second replicate analysis results by about 2%. Since the sample contained very little residual solids and since there was a certain degree of inhomogeneity to the sample, it is believed that sample inhomogeneity is mostly responsible for the 2% deviation between the replicate analyses.

Supernate samples from S303201 and S303204

Supernate samples from S303201 and S303204 both contained clear, colorless

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liquids. The TGA revealed no detectable solids (dissolved or otherwise) in either sample. No replicate analyses were conducted on these samples.

Attachment 1 describes the numerical method which was used to calculate the amount of $\text{FeO}(\text{OH})$ and $\text{Al}(\text{OH})_3$ present in the residual solids. Thermal gravimetric analysis thermograms are also attached to this letter (Attachment 2).

If you have any questions please call me at 373-2529.

Bruce Hey, Advanced Scientist

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Attachment (2) -----

NUMERICAL METHOD FOR $\text{FeO}(\text{OH})$ AND $\text{Al}(\text{OH})_3$ DETERMINATION.

In all the sludge samples analyzed it was observed that each sample possessed two characteristic weight loss events. The first event was the most pronounced change in weight loss and was attributed to the loss of free water from the sample. The second event was considerably less pronounced but more complex. The shape of the curve suggested that at least two events were happening simultaneously.

It was assumed that $\text{FeO}(\text{OH})$ and $\text{Al}(\text{OH})_3$ were the principle components of the total residual solids and that the concentrations of all other components were negligible. This assumption is based upon 1) the appearance of the sample, 2) the description of the physical layout of the K-east basin configuration, 3) results of polarized light microscopy analyses conducted on the same K east basin sludge samples and 4) the temperature region indicated by the TGA thermalgram which the second weight loss event took place.

Ideally, the percentages of $\text{FeO}(\text{OH})$ and $\text{Al}(\text{OH})_3$ could be derived directly from the TGA thermalgram but in the case of these samples the events took place simultaneously so that direct determination was not possible.

Nevertheless since the values for percent total residual solids and percent total water of hydration were determined from the thermalgram and since two independent equations could be used to describe the events, the percentages of $\text{FeO}(\text{OH})$ and $\text{Al}(\text{OH})_3$ were determined through algebra.

Two linearly independent equations were set up to describe this event. The first equation was simply the sum of the components that equals the %Total Residual Solids (%TRS):

$$\% \text{FeO}(\text{OH}) + \% \text{Al}(\text{OH})_3 = \% \text{TRS}$$

The second equation was the sum of the components that equals the %Total Water of Hydration (%TWH):

$$(0.1014)\% \text{FeO}(\text{OH}) + (0.3464)\% \text{Al}(\text{OH})_3 = \% \text{TWH}$$

where the coefficient 0.1014 is the fraction of water liberated from $\text{FeO}(\text{OH})$ and is derived from the decomposition reaction:

and therefore:

$$0.1014 = \left[\frac{18.0152 \text{ g}}{\text{mol H}_2\text{O}} \right] \left[\frac{\text{H}_2\text{O}}{2\text{FeO}(\text{OH})} \right] \left[\frac{\text{mol FeO}(\text{OH})}{88.8537 \text{ g}} \right]$$

Likewise the coefficient 0.3464 is the fraction of water liberated from $\text{Al}(\text{OH})_3$ and is derived from the decomposition reaction:

and therefore:

$$0.3464 = \left[\frac{18.0152 \text{ g}}{\text{mol H}_2\text{O}} \right] \left[\frac{3 \text{ H}_2\text{O}}{2 \text{ Al(OH)}_3} \right] \left[\frac{\text{mol Al(OH)}_3}{78.0034 \text{ g}} \right]$$

In algebraic terms the equations could be expressed as:

$$x_1 + x_2 = b_1$$

$$0.1014x_1 + 0.3464x_2 = b_2$$

where x_1 and x_2 represent FeO(OH) and Al(OH)_3 respectively and b_1 and b_2 represent %TRS and %TWH respectively.

The application of linear algebra for this system of equations was used to solve for x_1 and x_2 . Table 3 in this appendix lists the constants and solutions to the above system of equations for each of the samples which were analyzed.

Sample	%TRS	%TWH	%FeO(OH)	%Al(OH) ₃
S303201	50.03	6.09	45.88	4.15
S303201 Rep	49.84	6.08	45.65	4.19
S303202	53.66	6.01	51.34	2.32
S303202 Rep	51.62	6.04	48.33	3.29
S303203	27.69	4.32	21.52	6.17
S303203 Rep	26.81	4.21	20.72	6.07
S303204 Rep 1	9.59	1.59	7.07	2.52
S303204 Rep 2	11.03	1.32	10.21	0.82

ATTACHMENT 2 TO 12110-PCL93-058
THERMAL GRAVIMETRIC ANALYSIS THERMALGRAMS

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K BASIN SLUDGE R3889 SB-74F

WT: 60.5297 mg

SCAN RATE: 5.00 deg/min

Cover gas: N₂ 50 cc/min

% WEIGHT

B-12

55.00

50.00

45.00

100.00

150.00

200.00

250.00

300.00

350.00

400.00

450.00

500.00

550.00

600.00

53.45%

FROM: 138.9

TO: 234.21

WT. % CHANGE: 1.86

FROM: 234.21

TO: 315

WT. % CHANGE: 2.95

51.59%

FROM: 315

TO: 599

WT. % CHANGE: 1.04

48.63%

47.59%

Temperature (C)

TG

DEH FILE: R3889.TG (WHC-N-3411)

DATE: 93/06/03 TIME: 11:17

WHC-SD-SNF-TI-014, Rev. 1

DEH FILE: 03889.TG (WHC-N-341)

DATE: 93/06/03 TIME: 13:51

BEH FILE: D3889.TG (WHC-N-3411)

DATE: 09/06/03 TIME: 10:51

Temperature (C)

FILE: R3885.TG

DEH: CHIC-N-341 D

TIME: 18.10

% WEIGHT

K BASIN SLUDGE R3885 SB-73D

WT: 24.1664 mg

SCAN RATE: 5.00 deg/min
Cover gas: N₂ 50 cc/min

TG

Temperature (C)

FILE: R3885.TG

BEH WHC-N-341 D

DATE: 93/06/04 TIME: 05:10

TG

Temperature (C)

DEH (WHC-N-341 1) FILE: D3885.TG

DATE: 93/06/04 TIME: 17.55

TG

Temperature (C)

FILE: D3885.TG

BEH WHC-N-341 1)

DATE: 93/06/04 TIME: 17:55

TG

Temperature (C)

FILE: R3900.TG (WHC-N-341)

BEH

DATE: 93/06/02 TIME: 08.44

BEH FILE: R3900.TG (WMC-N-3911)

DATE: 93/06/02 TIME: 08:44

TG

FILE: D3900.TG (WHC-N-341)

DATE: 93/06/02 TIME: 14:16

K BASIN SLUDGE R3847 DUPLICATE
 Replicate 2
 WT: 39.1935 mg
 SCAN RATE: 5.00 deg/min
 Cover gas: N₂ 50 cc/min

FILE: D3847.TG

DATE: 93/08/04 TIME: 14:56

SECOND DUPLICATE R3847

Replicate 2

WT: 42.5936 mg SCAN RATE: 5.00 deg/min

K BASIN SLUDGE R3847 DUPLICATE

Replicate 1

WT: 39.1935 mg SCAN RATE: 5.00 deg/min
Cover gas: N₂ 50 cc/min

SEN (WHC-N-341 I)

FILE: R3908.TG

DATE: 93/06/07 TIME: 08:19