

**Desludging of N Reactor Fuel
Canisters: Analysis, Test,
and Data Requirements**

A. B. Johnson, Jr.

January 1996

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *dlc*

DISCLAIMER

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Sludge and Fixed Corrosion Product Issues for N Reactor Fuel

Summary

The N Reactor fuel is currently stored in canisters in the K East (KE) and K West (KW) Basins. In KE, the canisters have open tops; in KW, the cans have sealed lids, but are vented to release gases.

Corrosion products have formed on exposed uranium metal fuel, on carbon steel basin component surfaces, and on aluminum alloy canister surfaces. Much of the corrosion product is retained on the corroding surfaces; however, large inventories of particulates have been released. Some of the corrosion product particulates form sludge on the basin floors; some particulates are retained within the canisters. The floor sludge inventories are much greater in the KE Basin than in the KW Basin because KE Basin operated longer and its water chemistry was less controlled. Another important factor is the absence of lids on the KE canisters, allowing uranium corrosion products to escape and water-borne species, principally iron oxides, to settle in the canisters. The inventories of corrosion products, including those released as particulates inside the canisters, are only beginning to be characterized for the closed canisters in KW Basin.

The dominant species in the KE floor sludge are oxides of aluminum, iron, and uranium. A large fraction of the aluminum and uranium floor sludge particulates may have been released during a major fuel segregation campaign in the 1980s, when fuel was emptied from 4990 canisters. Handling and jarring of the fuel and aluminum canisters seems likely to have released particulates from the heavily corroded surfaces.

Four candidate methods for dealing with canister sludge emerged in the N Reactor fuel path forward:

- place fuel in multi-canister overpacks (MCOs) without desludging
- drill holes in canisters and drain
- drill holes in canisters and flush with water
- remove sludge and repackage the fuel.

For the first three options, which involve leaving the fuel in existing canisters for transition to dry storage, the impacts of the fixed corrosion products and sludge were recognized as a major

consideration in designing a process to dry the MCOs sufficiently. The concept of desludging was introduced in the Independent Technical Assessment (ITA) that addresses a method to transition N Reactor fuel from wet storage to dry storage. The proposed desludging concept involved drilling holes in the canister bottoms and flushing the canisters from the top with pressurized water; an alternative method would involve placing the fuel canisters inside the MCOs and tipping the MCOs 90°, allowing outflowing water to carry away a fraction of the sludge.

Use of the fourth option above mitigates the drying problem by separating the canister sludge and fixed corrosion products on the aluminum canisters from the fuel. The principal remaining corrosion products are then oxides that remain on the corroding uranium metal and the relatively thin oxide on the Zircaloy cladding. Whether the inventory of particulates clinging to fuel surfaces and retained within corroding fuel elements is negligible would need to be considered.

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

"Canister sludge is particulate matter, with particle sizes less than 1/4 in. (6.25 cm), 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."

Note: The sludge includes settled particles that may form gelatinous or crusted layers.

Characterization of canister sludge and fixed corrosion products is needed to establish moisture inventories and particulate properties that define conditioning parameters and post-conditioning moisture levels. The data also feed back to the required efficiency for desludging if the fuel is not reracked.

Only the KE sand filter backwash pit has been sampled with reasonable rigor. From other floor areas only single samples were taken, rather than to characterize the full range of the floor (i.e., a tube was positioned to sample from a limited floor area).

Basin sludge has been subject to limited quantification and characterization (e.g., composition, particle size, radioactivity, drying characteristics). Characterization of canister sludge has been almost nil. There is limited video photography of a few canisters (some empty, one with partial fuel loads) in KE. Three fuel elements were removed from KW canisters; video inspections provided minimal information about sludge, but sludge characterization was not an objective in this first fuel examination campaign.

Plans to store the N Reactor fuel in the MCOs for a period prior to conditioning imposes additional sludge considerations, namely, that additional 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; particulates 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.

Potential sludge impacts include transport of moisture into the conditioning process, effects of particulates on conditioning operations, and possible presence of uranium hydride and metal particles.

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 as indicated for dry materials:

Non-fuel Sludge A	- 15 kg/MCO
Fuel oxides ^(a) in worst case MCO	- 17.5 kg/MCO
Total Sludge B	- 4 kg/MCO (storage in MCO for 2 y in H ₂ O)
Aluminum (A1) Corrosion Product	- 5 kg/MCO ^(b)

Sludge A is the largest component, which might seem to justify desludging. However, sludge weights alone do not define the moisture inventory nor the efficiency of moisture release at conditioning temperatures. These elements need to be defined in the characterization program for moisture-bearing species that will be placed into the MCOs.

Underwater video inspections of the upper ends of canisters and fuel elements imply that only ~10% of the KE canisters have severely failed fuel, suggesting further that fuel sludge is likely to reside predominantly in relatively few (i.e., ~200) canisters. However, 1546 KE canisters (41% of the total) were judged to have elements with some degree of fuel corrosion. At least 85% of the two-barreled canisters that were examined contained at least one breached element (inner or outer).

(a) Includes fixed oxides and particulates.

(b) A recent assessment (Johnson and Burke, 1995) suggests that this estimate of oxide remaining on the KE aluminum canisters may be low.

Desludging and fixed corrosion product issues would be mitigated if the repackaging option is adopted, (involving replacement of canisters and removal of sludge). Impacts of residual moisture also would be mitigated if venting during preconditioning storage is implemented.

A basis for evaluating the required desludging effectiveness is to specify a maximum acceptable post-conditioning pressure in the MCOs during long-term storage. The target value in the ITA study was 0.3 atm. Whether the final determination is this or a different value, it will guide definition of the maximum acceptable post-conditioning moisture value. This value relates to the efficiency of moisture release at the specified conditioning time-temperature parameters and therefore, relates to the moisture inventory of species that do not fully release moisture during conditioning. Consequently, limiting the inventories of these species facilitates attainment of the target moisture value. Particle mobilities, including effects on gas flows, monitoring devices, and transport of radioactivity, must be known to establish an acceptable sludge inventory in the MCOs.

It is strongly recommended that British, French, and Italian experience with storage and handling of heavily hydrided uranium metal fuels be reviewed to investigate the position that the MCOs have sufficient containment integrity that hydrides and metal particles, even if present in N Reactor fuel, do not pose a pyrophoric risk. The conditioning parameters also relate to reacting uranium hydrides and metal particles. There is not a practical basis to demonstrate that all hydrides and metal particles have fully reacted; also, additional hydrides may form during the period of long-term storage. The foreign experience also includes demonstration of safe handling, shipment, and processing of hydrided uranium fuels. However, it is necessary to substantiate that the foreign experience accounts for safety conditions that apply to long-term storage of N Reactor fuel.

Following are the elements required of a characterization plan to determine whether desludging efficiency is a limiting parameter and, if so, how to effectively reduce the Sludge A inventory:

- Improved estimates of sludge and fixed corrosion product inventories, including all moisture-bearing species that are judged to have significant entrained, adsorbed, or hydrated waters, particularly those that retain moisture during conditioning
- Determination of moisture release characteristics of actual sludge and corrosion products
- Estimation of the post-conditioning moisture inventory, its relation to long-term interim storage criteria, and relation to required desludging criteria

- Determination of sludge characteristics (particle sizes, species, compaction, radioactivity and hydride inventories, etc.)
- Pilot runs on canisters with actual sludge, to investigate desludging efficiency if the Sludge A inventory emerges as a controlling factor in attaining the target moisture level after conditioning or if the MCO particulate burden is estimated to interfere with conditioning operations.

Characterization and engineering schedules need to be coordinated to ensure that availability of key information facilitates timely delivery of an informed design. Current schedules indicate KE fuel and sludge examinations in the June 1996 time frame and further KW fuel and sludge characterizations in the September 1996 time frame.

Data Quality Objectives and sampling plans for floor sludge have been issued. Data Quality Objectives for canister sludge are being developed (review draft scheduled for January 1996).

Contents

Summary	iii
1.0 Introduction	1
1.1 Scope	1
1.2 Background	1
1.3 Sludge Definitions	2
1.4 Sludge Characterizations	4
1.4.1 Floor Sludge Characterization	4
1.4.2 Canister Sludge Characterization	5
2.0 Impacts of Sludge and Fixed Corrosion Products on Transitioning N Reactor Fuel to Dry Storage	7
2.1 Impacts of Sludge Characteristics	7
2.2 Impacts of Fixed Corrosion Products	8
2.3 Relationships of Sludge and Fixed Corrosion Product Inventories	12
2.3.1 Sludge Inventories	14
2.3.2 Estimated Inventory of Sludge A-KE	15
2.3.3 Sludge A in KW Canisters	16
2.3.4 Estimated of the Sludge B Inventory in the MCOs	17
2.3.5 Estimate of Fixed Corrosion Products	17
2.3.6 Water Inventory of Aluminum Oxide Hydrates	18
2.3.7 Drying Efficiency of Moisture-Bearing Species	19
3.0 Significance of Conditioning Parameters	21
4.0 Sludge Removal Processes	25
4.1 Proposed ITA Options for Reducing the Inventory of Sludge A	25
4.2 Path Forward Options for Sludge Management	25
4.3 Considerations in Planning for Desludging	26
5.0 Summary of Needs Addressing Desludging	29
5.1 Summary of Key Insights	29
5.2 Needs Relevant to Definition of an Effective Desludging Process	30
6.0 References	33
Appendix	A.1

1.0 Introduction

1.1 Scope

The scope of Element P-2.2 of the Technology Acquisition Program (SNFP 1995) is to define analysis, test, and data requirements to establish the extent of desludging that can be expected and/or must be achieved prior to stabilization. The scope includes interfaces with the Characterization Program on data requirements and schedule to define drying behavior of the N Reactor fuel after desludging.

Emergence of a concept to rerack the fuel would preclude major concerns about sludge because both the canister sludge and the fixed corrosion products on the aluminum canisters would be separated from the fuel elements before the fuel is loaded into the MCOs. This report provides a perspective on the sludge and aluminum corrosion product issues and inventories.

1.2 Background

Desludging is a concept that was proposed in the Independent Technical Assessment (ITA) study (ITA I, ITA II 1994). The concept involves removing sludge from the fuel storage canisters before they are transported from the K Basin areas. It was intended to be conducted on a "best efforts" basis and was not expected to result in removal of all sludge. Subsequent to publication of the ITA report, a concept has emerged that involves storing the MCOs containing the N Reactor fuel, either in water or in an inert gas, for an interim period prior to conditioning. Corrosion during this period will generate additional corrosion product and associated particulates. Estimates of corrosion product generated in the wet storage option (wet staging) during preconditioning interim storage address effects of temperature and time (Ballinger 1994; Beary^(a)). If the fuel were partially dried and stored in inert gas prior to conditioning, the Sludge B inventory would be minimized.

The sludge inventory that would enter the conditioning process therefore includes residual particulates left after desludging and particulates generated in preconditioning storage. Corrosion

(a) Beary, M.M. 1995. "Preliminary Basis for Assessing Gas Release and Fuel Corrosion in an MCO During Wet-Fuel Storage." Letter report submitted under Contract 188694 -A-13, Work Assignment 14, Pacific Northwest Laboratory, Richland Washington

and associated particulate generated after the conditioning process relate to post-conditioning criteria for fuel degradation.

Characterizing inventories of particulates generated in the basins and in preconditioning storage would be important to guide decisions regarding the desludging operations and the impacts of particulates that are not removed during desludging or that are generated after desludging.

The key concerns regarding the particulate inventories that remain in the MCOs center on 1) moisture inventories associated with the particulates, effectiveness of moisture removal during conditioning, and impacts of the moisture during storage; 2) impacts of particulates on transport of radioactivity, plugging of lines and sensors, and blockage of gas flows during conditioning; and 3) possible presence of pyrophoric hydrides and metal particles.

Even in preconditioning storage, the particulate inventories and associated moisture inventories may be important, particularly if damp or nominal dry storage is selected for interim storage. The considerations are pressure increase and further corrosion/hydrating from radiolytic species generated from the moisture inventory; corrosion processes also generate hydrogen that can contribute to pressure increases and formation of hydrides (Beary^(a))

A definition of sludge, proposed below, is confined to corrosion products on fuel and canister surfaces that have been released as particulates. However, fixed corrosion products also contain moisture, adsorbed, entrained, or as specific hydrates. These moisture inventories must also be considered in specifying characterization operations.

The purpose of this assessment is to identify characterization that will facilitate a realistic approach to understand and deal with the particulate inventories, at the same time, acknowledging the need to understand impacts of nonparticulate oxide species, i.e., corrosion films on fuel and canister surfaces.

1.3 Sludge Definitions

The first order is to reach consensus on what is meant by the term "sludge" as it applies to the transition of N Reactor fuel from wet to dry storage. The definition in Webster that comes closest to the conventional concept of sludge is "a muddy or slushy mass, deposit, or sediment."

(a) Beary, M.M. 1995. "Preliminary Basis for Assessing Gas Release and Fuel Corrosion in an MCO During Wet-Fuel Storage", Letter report submitted under Contract 188694 -A-13, Work Assignment 14, Pacific Northwest Laboratory, Richland Washington.

This definition seems reasonably descriptive of the sludge in the bottom of the pools, and relates to the working definition of basin sludge.^(a) However, the definition cited in the footnote encompasses both basin sludge and canister sludge. Because the compositions and impacts of basin and canister sludges differ, it seems appropriate to apply separate definitions.

- Canister sludge is particulate matter, with particle sizes less than 1/4 in. (6.25 mm),^(b) that settles to the bottom of the 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. Note: it does include settled particles that may form gelatinous or crusted layers over time.
- Basin sludge (also referred to as floor sludge) is particulate matter, with particle sizes less than 1/4 in., that for the most part has settled to the bottom of basins and pits; particles that are suspended in water but are subject to settling are included in the definition. Note: the settled particles may form gelatinous or crusted layers over time.
- Because "Basin Sludge" has sometimes been interpreted to include both floor and canister sludges, the term "Floor Sludge" will be used in this report to identify what is defined above as "Basin Sludge."

The Canister Sludge definition also applies when the N Reactor fuel and canister materials are corroding while stored in a gaseous environment, but the emphasis is on particulate matter, that may not settle to the bottom of the canisters.

Data Quality Objectives (WHC 1995a) and sampling and analysis plans for floor sludge (WHC 1995b) have been issued. Floor sludge sampling and analyses were conducted in CY 1995. Data compilations are expected to be issued during the first quarter of FY 1996. Data Quality Objectives for canister sludge are being developed.

(a) A working definition of sludge appears in Baker 1995: "Basin sludge or sediment is particulate matter that for the most part has settled to the bottom of basins, pits, and spent fuel storage canisters." Particles 1/4 in. or smaller are regarded as sludge.

(b) Selecting "less than 1/4 in." has the practical basis that sludge comprises particles not held on a screen of 1/4 in. mesh. The basis for designation of 1/4 in. arises from a determination that particles <1/2 in. will not present a criticality risk; the size was reduced to <1/4 in. for conservatism.

1.4 Sludge Characterizations

Characterizations of canister and basin sludge are underway. Floor sludge characterization has been ongoing for more than two years. These characterizations were prompted by the need to investigate criticality concerns and to determine what the path-forward options are for the sludge, based on concentrations of transuranic (TRU) and pyrophoric species, i.e., metal fines and possible uranium hydride. Characterizations have focused principally on floor sludge in the KE Basin, where sludge inventories are an order of magnitude greater than in the KW Basin (Baker 1995). Canister sludge characterization is in its early stages. The status of the characterizations is briefly addressed in this section.

1.4.1 Floor Sludge Characterization

Baker (1995) summarizes some results from floor sludge characterization, including sludge compositions, particle sizes, radioisotope content, and volumes in KE Basin. The floor sludge compositions and characteristics almost certainly differ from the values for canister sludge. However, they are of some interest because substantive characterizations are not available for canister sludge.

1.4.1.1 Floor Sludge Compositions

Baker lists compositions of floor sludge samples taken from different locations in the KE Basin. The major species are oxides of iron (Fe), uranium (U), and aluminum (Al), generally in that order.

1.4.1.2 Floor Sludge Drying Analysis

Specimens of floor sludge were subjected to thermo-gravimetric analysis. Information regarding the drying tests is based on discussions with Mark A. Meier and Bruce E. Hey of Westinghouse Hanford Company, June 1995. Sample sizes were 20 mg; up to 50% of the specimen weight was released in heating from 25° to 99°C. The weight loss is presumed to represent release of free moisture. The first test was conducted to a maximum temperature of 1000°C. Subsequent tests were terminated at 600°C because drying appeared to be complete at that temperature.

In the first test, 12% weight loss occurred between 100° and 1000°C.

Because the dominant species in the canister sludge are likely to be the same as in the floor sludge, the drying data cited above are of some interest, in lieu of specific data for canister

sludge. The ratios of the dominant sludge species will vary between floor and canister sludges, and, in fact, from canister to canister, depending on canister material and degree of fuel degradation. If all major oxide species are represented, then a maximum drying temperature should be definable. However, if sludge particulates are largely separated from the fuel in a reracking campaign, then drying characteristics of species that remain attached to the fuel (principally uranium oxides) will be the principal drying consideration.

1.4.2 Canister Sludge Characterization

The same species found in floor sludge are expected to dominate the compositions of canister sludge. However, the ratios will vary, depending on the degree of fuel degradation in a given canister. In stainless steel (SS) canisters, the inventory of aluminum oxides is expected to be low. In canisters where fuel corrosion is minimal or absent, iron oxides will likely dominate the sludge composition. The expected dominating Sludge A inventories can be generalized into four categories, based on canister type and whether failed fuel resides in a given canister:

1. SS canisters, unfailed fuel - principally Fe oxides
2. SS canisters, failed fuel - Fe and U oxides
3. Al canisters, unfailed fuel - Fe and Al oxides
4. Al canisters, failed fuel - Al, Fe, and U oxides.

Sludge A in KW canisters will not include iron oxides and may include very little aluminum oxide.

To date sludge samples have not been obtained from KE or KW canisters. Some sludge was observed when fuel elements were removed from KW canisters, but only small amounts were collected, which do not allow for drying tests. Oxide film thicknesses and characteristics of oxide films on aluminum canisters also have not been quantified. As indicated in the previous section, reracking will preclude most of the particulate species and all of fixed corrosion products in the Al canisters.

Sludge volumes in open KE canisters have been estimated during an underwater video campaign, but only for a few empty or nearly empty canisters (Baker 1995). Therefore, the estimates do not include sludge from corroding uranium fuel. The estimated sludge volumes are applied later in this assessment, but the basis cannot be regarded as definitive.

The canister sludge estimate is based on the measured cesium-137 release rate to the KE Basin water (Beary^(a)). The release rate is used to calculate the uranium metal corrosion rate, based on the indication that the cesium-137 release fraction is near 1 (Tyfield 1988). The current cesium-137 release is applied to calculate uranium corrosion product generation in the 204 worst case canisters (Pitner 1995). The value is corrected to 35°C to estimate corrosion product generation for the worst case fuel during wet staging, after removal from the K Basins, but prior to conditioning. This represents a worst case, because dry staging in inert gas would be expected to generate far less corrosion product and resulting particulates.

The uranium corrosion estimates indicate total corrosion only. There is currently no basis to assess how much of the corrosion product falls from the corroding area and becomes particulate. Photographic and visual inspection clearly indicates rather voluminous corrosion products on corroding areas of KE fuel. There is also no basis to estimate how much oxide will remain on the fuel after desludging and fuel handling operations. Whether the massive corrosion products revert to particulates does not seem important to drying characteristics, but is relevant in assessing the impacts of particulates in drying and conditioning operations.

Sludge A estimates reflect a lack of definitive data that are important to establish bases to guide the design of drying and conditioning; to define desludging criteria and the impacts of particulates; and to predict fuel degradation during long-term interim storage if sludge were to be retained in the canisters and placed into the MCOs. In the fuel reracking mode, the principal remaining issue is the amount of corrosion product retained on the corroding uranium metal fuel and the fraction of that corrosion product that spalls to become particulates inside the MCOs.

(a) Beary, M.M. 1995. "Preliminary Basis for Assessing Gas Release and Fuel corrosion in an MCO During Wet-Fuel Storage." Letter report submitted under Contract 188694-A-13, Work Assignment 14, Pacific Northwest Laboratory, Richland, Washington.

2.0 IMPACTS OF SLUDGE AND FIXED CORROSION PRODUCTS ON TRANSITIONING N REACTOR FUEL TO DRY STORAGE

Confining the definition of sludge to detached particulates does not address moisture inventories associated with corrosion products that remain fixed to fuel element and canister surfaces. Sludge and fixed corrosion products will be treated separately in this section.

2.1 Impacts of Sludge Characteristics

The central considerations for the transition from wet to dry storage, as they relate to sludge, are

- that the moisture inventories on species inside the MCOs are reduced to acceptable levels
- that the mobility and distribution of particulates do not interfere with processing, including transporting radioactivity, plugging lines and sensors, and impeding flow of gases throughout the MCOs during conditioning
- that the particulate impacts on heat transfer are understood and accounted for
- that the possible presence of potentially pyrophoric species, i.e., particles containing hydrides or metal, is accounted for in fuel management procedures.

The target residual moisture level after conditioning, designated in the ITA process, was defined by limiting the pressure increase inside the MCOs to 0.3 atm (ITA vol. II, 1994), based on restricting fuel degradation during long-term interim storage. However, the MCO design pressure, 10 atm, allows for much higher moisture inventories without MCO rupture.

Establishing the target steady state pressure during long-term interim dry storage depends on

- 1) the acceptable level of additional fuel degradation from corrosion and hydriding, and
- 2) the acceptability of resulting hydrogen/oxygen gas mixtures inside the MCOs relative to

flammable mixtures and the occurrence of an ignition source. Owczarski et al.^(a) analyzed corrosion, hydriding, and gas buildups in post-conditioning storage. Gas generation in long-term interim storage can be accommodated if venting of the canisters is practical. Venting is being considered for the canisters containing fuel debris from the TMI Unit 2 core.

Pressure increases in dry storage containers were addressed in a study of aluminum-clad fuel storage (Tamura, et al. 1994). Sources of pressure buildup comprised container water content, chemical reactions by the container atmosphere, chemical reactions between container and fuel materials, and release of fission product gases. Pressure buildup due to radiolytic gases was identified as the dominant source. Pressure increases over a dry storage period of 50 y were calculated for different amounts of water. Pressures at the end of the storage period were 50 to 300 psia, corresponding to water volumes in the container between 1% and 8% (free volume, 77 liters, 200°C storage temperature). Pressure from release of fission product gases was calculated to be 2 psia. Flammability of gases in the containers was recommended for further investigation.

Management of particulates in the ITA conditioning system includes provisions for a HEPA filter and a HEPA/charcoal filter in the exit side of the gas handling system (ITA II 1994). The propensity for plugged gas lines, monitoring equipment, etc., needs to be anticipated and perhaps investigated, but can be mitigated by design features. Blockage of gas flows during conditioning also will need to be anticipated, based on characterization of the inventories and degree to which the sludge solidifies.

2.2 Impacts of Fixed Corrosion Products

Limiting the sludge definition to particulates prompts a need to consider corrosion films that remain on fuel and canister surfaces; the key concern is to understand the inventory of moisture species in terms of how effectively they will be expelled in the conditioning process. If the fixed oxides spall in the conditioning process, they will contribute to the particulate burden. The inventory of components with oxide films appears in Table 1 (ITA II, App. G, 1994). The moisture inventories and drying characteristics for these species need to be understood to ensure that the residual moisture target after conditioning can be achieved.

(a) Owczarski, P.C., et al. 1995. "Technical Bases for Assessing Fuel and Sludge Behavior and Gas Release in an MCO During Dry Fuel Storage." Letter report submitted under Contract 188694-A-A2, Task P-3, Pacific Northwest Laboratory, Richland, Washington.

TABLE 1
N Fuel and Storage Canister Materials;
Implications for Conditioning for Dry Storage

Component	Material	Estimated Condition	Features with Implications for Conditioning
Fuel Cladding	Zircaloy-2 ^(a)	<ul style="list-style-type: none"> Some breached due to mechanical damage during reactor discharge Some intact (est. 50 - 75%) 	<ul style="list-style-type: none"> Zircaloy surfaces readily dried Exposed interior surfaces will have bound H₂O
Fuel Crud	Principally iron oxides	Thin layer	Minor source of adsorbed water and particulates
Uranium Fuel	U metal ^(b)	<ul style="list-style-type: none"> Large fraction contained in intact Zircaloy cladding. Many areas exposed to water at cladding breaches; corrosion products: UO₂ and UH₃, some U metal fragments and particles 	<ul style="list-style-type: none"> UO₂ source of bound H₂O UH₃ can be pyrophoric if exposed to air Conditioning designed to decompose hydrides
Sludge	Uranium and canister corrosion products (e.g. U, UO ₂ , possibly UH ₃ , passivated in UO ₂ , UO ₃ ·xH ₂ O, Al ₂ O ₃ ·xH ₂ O, Fe ₂ O ₃ ·xH ₂ O sand, concrete, dirt)	Small particles, as a layer in the bottom of canisters and adhering to fuel and canister surfaces, possible gelatinous and/or crusting layers	<ul style="list-style-type: none"> May delay escape of moisture Adsorbed water removed at 300°C Waters of hydration may be difficult to remove completely
Canister	Stainless Steel	Evidence of minor corrosion	<ul style="list-style-type: none"> Sturdy vessel for placing fuel inside MCOs Minor source of H₂O and particulates
Canister	Al Alloys ^c	Advanced stages of pitting corrosion in K East; lesser corrosion in K West	<ul style="list-style-type: none"> Mechanical integrity to be confirmed Possible major source of H₂O and particulates

^(a) Nominal composition: Zr-1.5Sn-0.15Fe-0.1Cr-0.05Ni; also, Zr Braze, Be-5%
^(b) Nominal composition: U, 700-900 ppm Al, 300-400 ppm Fe, 365-735 ppm C, 100 ppm Si
^(c) Alloys: 5086 and 6061

HT High-temperature

A prominent case is corrosion product adhering to the corroding fuel; visual examinations indicate that much of the corrosion product currently remains on fuel surfaces. It is not clear how much of the attached oxide will be removed from the fuel when it is desludged, but to expect complete removal does not seem justified without special measures, e.g., high-pressure water jets and/or brushing. These measures also may not be fully effective, particularly for oxides that are occluded under the cladding, but these oxides may represent a relatively small inventory.

It is not clear from the Pourbaix diagram for uranium (Ballinger et al. 1994) whether UO_3 hydrates will form in pool water with dissolved oxygen in the range of 8 ppm O_2 (25°C value) to 14 ppm (10°C value). However, a study of uranium oxide fuel exposed to pool water (~25°C) at a cladding defect for 21 y developed a thin (estimated $< 1 \mu\text{m}$) layer of $\text{UO}_3 \cdot x\text{H}_2\text{O}$ (Wasywich and Frost, 1992). This suggests that formation of UO_3 hydrates on the N Reactor fuel UO_2 corrosion products may be minimal, but needs to be established by characterization.

Commercial Zircaloy-clad power reactor fuel is routinely dried by vacuum techniques, augmented by substantial decay heat (Creer et al. 1986; McKinnon and Deloach 1993). Analyses of storage cask cover gases during post-drying storage sometimes show detectable hydrogen, but at concentrations $< 1 \text{ vol.}\%$ (McKinnon and Deloach 1993). Commercial boiling water reactor (BWR) rods with cladding defects that developed during reactor service were subjected to drying tests (Kohli et al. 1985). Moisture was recovered from the water-logged rods a) by evacuation at a maximum temperature of 130°C for approximately 1 h; b) by outgassing at 325°C; most of the residual water appeared to be released within three hours at 325°C, but outgassing essentially ceased only after heating for ~1000 h.

Tenacious corrosion products on canister surfaces have moisture inventories that factor into conditioning considerations. The canister types and numbers in each basin are summarized in Table 2. Corrosion films on the stainless steel canisters are extremely thin ($< 1 \mu\text{m}$) (Johnson & Burke 1995), but will have some amounts of adsorbed and possibly hydrated moisture. More important are moisture inventories on the Al alloy canisters. The canisters in the KE Basin have thick oxide films that are evident even in visual observation from the pool deck (Johnson and Burke 1995). Oxides on Al alloy canisters were characterized at an earlier stage (Richardson 1980). Thick oxide tubercles were evident, associated with pits having depths up to 41 mils (1 mm). At basin temperatures, the trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is the expected corrosion product. Conditions for expelling adsorbed moisture from the porous oxides also must be characterized. Thermal behavior of the hydrates on aluminum oxides has been published (Alwitt 1976) (see Section 2.3.6).

TABLE 2
Fuel and Canister Inventories - K East and K West Basins

	K-East	K-West
Fuel Inventories:		
Fuel Elements	50,603	52,960
MTU	1,150	950
Canister Types:		
Mark 0 - Aluminum	500	0
Mark I - Aluminum	900	800
Mark I SS	1400	1000
Mark II SS	900	2000

Note: The KE campaign began in 1975 and was completed 1981; Mark 0 canisters have open-screened bottoms, backed by a metal plate with drilled holes. Lids on KW canisters include both Al and SS, not always matched to like canister material.

Corrosion studies using coupons have been conducted in both K basins. Results of the corrosion surveillance suggest that oxide films are thinner on the KW Al alloy canisters. The attraction of eliminating the Al alloy canisters, particularly those in the KE Basin, should be weighed in considering arguments for repackaging the fuel.

Crud layers that formed on fuel element surfaces and zirconium oxide films are relatively thin; consequently, they are expected to have minimal moisture inventories. In drying campaigns involving commercial power reactor fuel, zirconium oxide films and crud layers have been dried sufficiently, but with thermal assistance from substantial decay heats.

In summary, considerations for drying conditions must go beyond species defined as "sludge" to include oxide species that are attached to fuel and canisters. Replacement of the aluminum canisters would exclude a major fraction of the moisture-bearing oxide films that otherwise will burden the conditioning process. In fact, the aluminum canisters in the KE Basin will account for the largest non-fuel moisture inventory. However, drying studies on aluminum corrosion products suggest that a major fraction of the moisture will be removed at 300°C (Alwitt 1976), the maximum conditioning temperature recommended in the ITA study (ITA II,

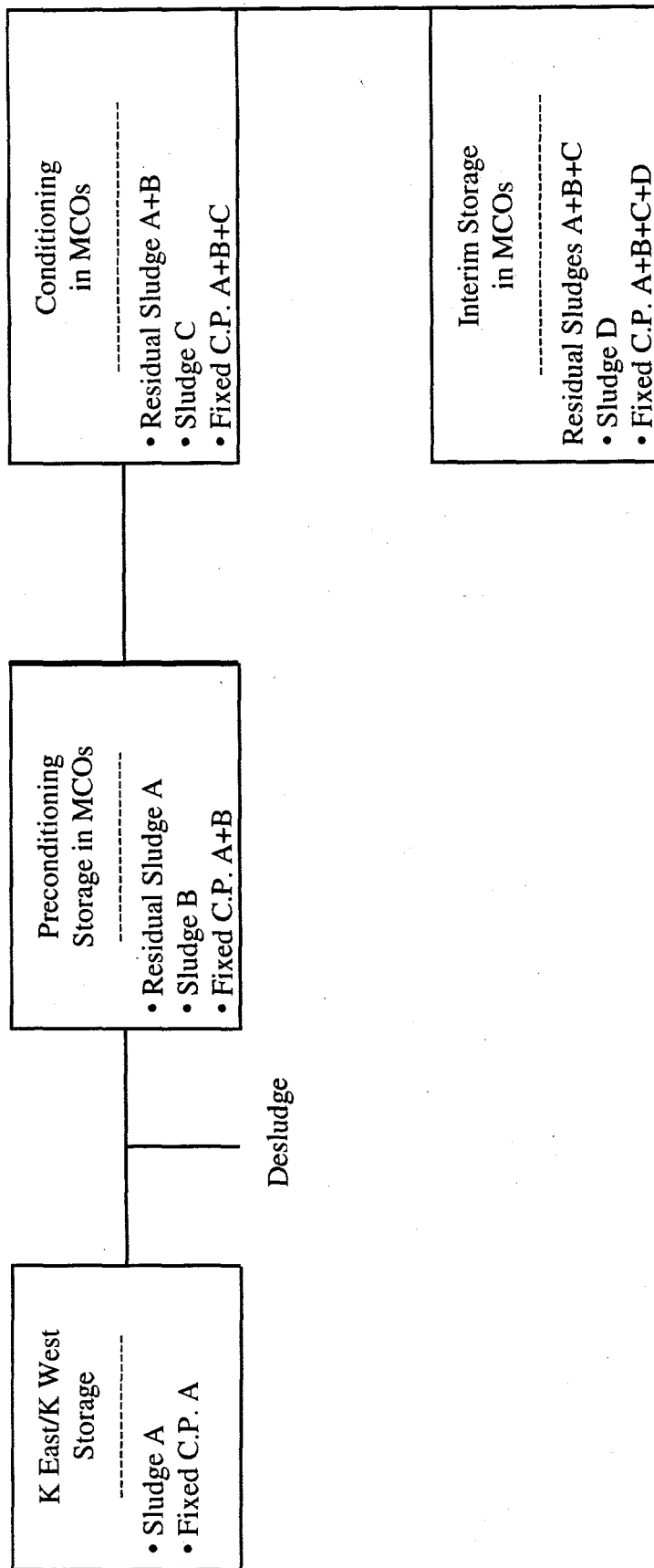
App. G, 1994). Release of mobile nonparticulate radioactive species (e.g., krypton-85, hydrogen-3) by corrosion in preconditioning storage has been addressed in another study^(a).

2.3 Relationships of Sludge And Fixed Corrosion Product Inventories

Sludge has generally been regarded in terms of particulate material that has developed while the N Reactor fuel has corroded in the K basins. Here we consider other sources of particulate matter while the N Reactor fuels are transitioned to dry storage and also during the period of long-term interim storage. Fixed (tenacious) corrosion products that have formed during storage in the K Basins also will be augmented during the period of preconditioning storage, during conditioning, and during long-term interim storage. The inventories are identified in Figure 1 and are defined in Section 2.3.1.

It is beyond the scope of this assessment to quantify all moisture elements identified in Figure 1. The elements that drive desludging requirements are those in the third box.

(a) Owczarski, P.C., et al., 1995. "Technical Bases for Assessing Fuel and Sludge Behavior and Gas Release in an MCO During Dry Fuel Storage." Letter report submitted under Contract 188694-A-A2, Task P-3, Pacific Northwest Laboratory, Richland Washington.



C.P. Corrosion Product
MCO Multi-Canister Overpack

Figure 1. Relation of Sludge and Fixed Corrosion Product Inventories to Stages in Transition of N Reactor Fuel to Dry Storage.

2.3.1 Sludge Inventories

Sludge inventories are likely to change throughout the preconditioning period and even during conditioning. It seems useful to distinguish the following elements of the sludge inventory.

Sludge A is loose particles that will have accumulated in the KE and KW canisters prior to placement into MCOs, including particles loosely adhering to canister and fuel element surfaces, but that have deposited inside the canisters; iron oxides from corroding storage racks and other species generated outside the canisters may be significant sources of moisture and mobile particulates.

Sludge B is particles generated by corrosion after the canisters are placed in the MCOs but prior to conditioning; the corrosion environment that generates Sludge B has not been decided but could be 1) an aqueous phase inside the MCOs; 2) a moist inert gas in contact with dewatered but undried fuel; 3) inert gas in contact with partially dried fuel. Ballinger (1994) and Beary^(a) estimated fuel corrosion and gas evolution during wet-fuel staging; all uranium corrosion product generated was assumed to revert to sludge. The Sludge B inventory will depend on the temperature range and period the fuel is stored prior to conditioning, in addition to the environmental conditions.

Sludge C is particles generated during the conditioning process; the Sludge C inventory is generated over a short period, but at elevated temperatures, up to 300°C in the ITA process. During the early stages, at lower temperatures, the moisture levels will be substantial; in the later stages, moisture levels will be low and corrosion will be minimal. The significance of particles generated in conditioning relates to transport of the particles and possible impacts on plugging of lines and sensors, etc., which is likely to be minimal, compared with the effects of residual Sludges A and B. Sludge C also contributes to the inventory of particulates that must be dealt with if the MCOs are opened during or at the end of the interim storage period.

Sludge D is particulates generated during long-term interim storage; estimates were made by Owczarski et. al.;^(b) the inventory relates to criteria for limiting post-conditioning fuel degradation.

(a) Beary, M.M. 1995. "Preliminary Basis for Assessing Gas Release and Fuel corrosion in an MCO During Wet-Fuel Storage." Letter report submitted under Contract 188694-A-13, Work Assignment 14, Pacific Northwest Laboratory, Richland, Washington.

(b) Owczarski, P.C., et al., 1995. "Technical Bases for Assessing Fuel and Sludge Behavior and Gas Release in an MCO During Dry Fuel Storage." Letter report submitted under Contract 188694-A-A2, Task P-3, Pacific Northwest Laboratory, Richland Washington.

Note that the current assumption is that desludging would be conducted at the K Area, prior to shipment; additional desludging prior to conditioning is not currently assumed.

The current concept for desludging addresses only Sludge A. However, estimates of the Sludge A and Sludge B inventories are needed to establish that desludging, to remove a fraction of Sludge A, will result in a justifiable reduction of the moisture inventory that will be transported into the conditioning facility. The following sections address estimates of elements of the sludge inventory for cases where there is some basis for evaluation.

2.3.2 Estimated Inventory of Sludge A-KE (Sludge A in K East Canisters)

Because no characterization data are available for canister sludge, estimates of non-fuel and fuel sludge have been attempted. Recall that sludge species are expected to vary according to four categories indicated in Section 1.4.2 (iron oxides are expected to deposit into all KE canisters).

2.3.2.1 Estimate of Non-Fuel Sludge A-KE

One input to Sludge A has been estimated for KE canisters (Baker 1995), involving sludge in empty or nearly empty canisters. However, the estimate is based on sludge depth measurements rather than quantitative assessment. It does not account for fuel sludge.

The estimated Sludge A-KE volume (without accounting for fuel sludge) in all KE canisters is 7.5 m^3 . The specific gravities of this sludge are reported to be in the range 1.13 to 1.54 g/cc, weighted toward the higher value. Taking the higher (conservative) value, the estimated weight of non-fuel Sludge A-KE is calculated based on Baker 1995:

$$7.5 \text{ m}^3 \times 10^6 \text{ cc/m}^3 \times 1.5 \text{ g/cc} \times 0.5 \text{ (fraction of solids)} = 5.6 \times 10^6 \text{ g}$$

The weight of non-fuel Sludge A per MCO ^(a) for the inventory of KE fuel (1150 MTU) is:

$$5,600 \text{ kg}/385 \text{ MCO} = 15 \text{ kg/MCO}$$

(a) The basis for the calculation is an MCO containing 10 canisters (20 barrels), with a total fuel weight of 3 MTU.

2.3.2.2 Estimate of Fuel Sludge in Worst Case KE Canisters

The fuel sludge input to Sludge A is estimated for 204 KE canisters, identified by Pitner (1995) to have the worst-case corroding fuel. The basis for the calculation is the cesium-137 release rate in KE (Beary^(a)). The mean value for the corrosion rate estimated from cesium-137 release is 2.5 g U/d; the extreme value (95% confidence) is 4.8 g U/d. In the Sludge A estimate, the mean value is applied because a large fraction of the corrosion period is expected to have occurred as the corroding area was expanding. The maximum residence of N Reactor fuel in wet storage is 23 y; the mean value is ~17 y. Applying the mean value for uranium corrosion in the 204 worst case canisters:

$$\begin{aligned}\text{U metal consumed} &= 17 \text{ y} \times 365 \text{ d/y} \times 2.5 \text{ g U/d} = 15512 \text{ g U/MCO} \cdot \text{d} = 15.5 \text{ kg U/MCO} \\ \text{UO}_2/\text{U (amu ratio)} &= 270/238 = 1.13\end{aligned}$$

$$\text{UO}_2 = 1.13 \times 15.5 = 17.5 \text{ kg UO}_2/\text{MCO}$$

The uranium metal oxides include fixed corrosion products and particulates. There is currently no basis for estimating the relative amounts of each.

2.3.2.3 Total Estimated Sludge A-KE in Worst Case MCO

The worst case MCO would contain one canister with worst case fuel in an aluminum alloy canister. Based on the above estimates, total Sludge A is obtained by combining the two inputs calculated above:

$$\text{Total Sludge A/ Worst MCO} = 15 + 17.5 = 32.5 \text{ kg/MCO} \approx 35 \text{ kg/MCO}$$

The first studies of Sludge A in KE canisters are scheduled for June 1996. However, it is not practical to launch a statistically based assessment of the Sludge A inventory, with the possible caveat of a repackaging campaign, which would largely eliminate Sludge A.

(a) Beary, M.M. 1995. "Preliminary Basis for Assessing Gas Release and Fuel corrosion in an MCO During Wet-Fuel Storage." Letter report submitted under Contract 188694-A-13, Work Assignment 14, Pacific Northwest Laboratory, Richland, Washington.

2.3.3 Sludge A in KW Canisters

There currently is no substantive estimate for Sludge A in KW canisters; however, data from recent inspections of three canisters and associated fuel will provide a limited perspective. Further inspections are scheduled in September 1996.

2.3.4 Estimates of the Sludge B Inventory in the MCO

The source of Sludge B will be corrosion occurring during preconditioning storage after the fuel is placed in the MCOs and is removed from the K Area. Three candidate environments inside the MCOs are being considered: 1) water, 2) wet fuel (water drained), and 3) fuel with some level of drying. Environments 2 and 3 would involve inert cover gases. As previously indicated, Beary has estimated Sludge B for cases involving wet staging.^(a)

Assuming water as the medium in the MCOs during preconditioning storage, Ballinger (1994) calculated the Sludge B inventory. Based on a target of 35°C for the maximum MCO water temperature, Ballinger calculated sludge generation of ~3 Kg/MCO (8 canisters per MCO) in 2 y. Ballinger assumed only UO₂ sludge generation and full release of all corrosion product.

To estimate Sludge B for wet staging, the value derived by Beary for uranium metal corrosion, based on cesium-137 is used. In this case, the extreme value, 4.8 g U/d at 10°C, is used because the corrosion areas are now mature. Assuming a staging period of 3 y, the following uranium metal consumption is calculated:

$$3y \times 365d/y \times 4.8 \text{ g U/d} = 5 \text{ kg/MCO}$$

Correcting from 10° to 35°C, a factor of 10 is applied, based on guidance from Beary^(a) and converting U metal to UO₂:

$$5 \text{ kg U/MCO} \times 10 \text{ (temp. corr.)} \times 1.13 \text{ (UO}_2 \text{ corr.)} \approx 55 \text{ kg/MCO}$$

As with Sludge A, the U metal corrosion product is assumed to be particulate.

If dry staging is selected, involving moist or partially dried fuel in inert atmospheres, the total U metal corrosion is expected to be much lower than in the wet staging case.

(a) Beary, M.M. 1995. "Preliminary Basis for Assessing Gas Release and Fuel corrosion in an MCO During Wet-Fuel Storage." Letter report submitted under Contract 188694-A-13, Work Assignment 14, Pacific Northwest Laboratory, Richland, Washington.

2.3.5 Estimate of Fixed Corrosion Products

The next consideration is the inventory of fixed corrosion products. The largest component is expected to be oxides on the aluminum alloy KE canisters. Corrosion surveillance on the canisters identified oxide tubercles over pits with depths up to 41 mils (Richardson 1980). Thick oxides associated with the pits are estimated to cover ~25% of the canister surfaces. Considering oxides on aluminum canister ID, OD, and bottom surfaces (assumes that the screen area offsets the holes in the bottom plate), the area per canister (two barrels) is 19,000 sq cm. The total area of the 1400 aluminum alloy canisters in KE is 3×10^7 sq cm. A rough estimate of the fixed corrosion products on the KE aluminum alloy canisters was derived from the following bases:

- assume that 1/4 of the canister area has thick oxides associated with pitted areas; assume that the average oxide thickness in these areas is 30 mils (0.030 in., 0.075 cm)
- assume that the remaining 3/4 of the surface has oxides with thicknesses of 2 mils (0.002 in., 0.005 cm).

Using the total KE aluminum canister surface area and the oxide thicknesses, the total oxide volume is $\sim 10^6$ cc. The specific gravity of the oxide trihydrate is 2.4 g/cc, but making allowance for porosity, a value of 2.2 g/cc was used, resulting in a total oxide weight of $\sim 2,000$ kg. The aluminum corrosion product weight per MCO is

$$2,000 \text{ kg}/385 \text{ MCOs} = 5 \text{ kg/MCO}$$

If the Al alloy canisters are not uniformly distributed in the MCOs, then upward adjustments will be needed to account for MCOs that have more than the average number of aluminum alloy canisters; the average number for KE fuel is $1400 \text{ Al cans}/385 \text{ MCOs} = 3.6 \text{ Al cans/MCO}$

2.3.6 Water Inventory of Aluminum Oxide Hydrates

The water inventories in a MCO will be the sum of the following:

- free water, e.g., pooled water on the bottom of an MCO with no sludge bed
- entrained water, contained within a bed of sludge particulates
- adsorbed water, held by physical adsorption or chemisorption on sludge and fixed corrosion product surfaces
- waters of hydration, involving chemically bound waters.

To illustrate the significance of specific moisture inventories, this assessment only addresses the waters of hydration on the aluminum oxides. While the ITA assessment included estimates of moisture inventories, wide variations in literature data dictate that a definitive knowledge of moisture inventories and drying characteristics would need to be based on characterization of the actual species if the fuel were to be conditioned and stored in the MCOs.

The water inventory associated with the aluminum oxide trihydrate is the sum of entrained, adsorbed, and hydrated moisture. The temperature range for conversion of trihydrate to monohydrate depends on the species present, but is reported to be complete at about 200°C (Alwitt 1976). If psuedoboehmite (monohydrate) is formed, it has high surface areas, up to 600 m²/g, increasing the prospect of large inventories of adsorbed waters (the desorption temperature range is not clear). The psuedoboehmite reverts to $\gamma\text{Al}_2\text{O}_3$ below 350°C; boehmite typically dehydrates in the 450 to 600°C range, but if poorly crystallized, it can dehydrate at ~350°C. If one water of hydration persists after conditioning, the estimated inventory is

$$230 \text{ kg H}_2\text{O}/385 \text{ MCOs} = 0.6 \text{ kg H}_2\text{O}/\text{MCO}$$

corresponding to ~0.6 liters of water/MCO. The free volume in an MCO is estimated to be 850 liters. The monohydrate water would generate a pressure of 1.3 atm at 120°C and nearly double that pressure if fully decomposed by radiolysis. If this estimate of only one of the potential residual moisture sources is realistic, it represents nearly an order of magnitude higher pressure than the target pressure of 0.3 atm in the ITA study. This assessment does not address release of adsorbed water on the aluminum corrosion products nor post-conditioning moisture inventories on uranium oxides and other species in the MCOs. It is not the function of this analysis to analyze the moisture inventories in detail, but rather to provide a perspective that indicates the importance of reducing the total moisture to an acceptable target level. That level then guides the desludging campaign at the K Area and the drying conditions in the conditioning cycle.

Note that the aluminum alloy canister moisture inventory is potentially important in preconditioning storage; for example, if prestorage drying does not remove the waters of hydration and if inert gas storage is chosen as the staging storage mode, radiolytic decomposition of the trihydrate, in the limit, could generate pressures in the MCOs of up to ~8 atm.

2.3.7 Drying Efficiency of Moisture-Bearing Species

The moisture inventories represented above are only one element of the drying process during conditioning. The other element is how readily the moisture will be expelled from each moisture-bearing species. The ITA studies (ITA I, II 1994), addressed estimates of moisture release from species assumed to be present in the sludge and on the canisters. However, the

moisture release characteristics of the actual sludge and fixed corrosion products will be needed to establish the drying efficiency during conditioning.

The characterizations need to differentiate the drying efficiencies of the sludge from those of the fixed corrosion products. If canister corrosion films have large moisture inventories that evolve readily in the conditioning temperature regime, they represent a minimal concern. However, it seems important to assess all species that need to be dried and include in drying pilot studies those with moisture inventories that emerge as significant.

3.0 Significance of Conditioning Parameters

Conditioning is proposed to

- reduce the moisture burden to a level that will meet the target steady state pressure in the MCOs
- minimize residual uranium hydrides and uranium metal fines that could become pyrophoric if exposed to air.

Effectiveness in reducing the moisture relates to understanding retained water in the sludge and fixed oxide inventories as the N Reactor fuel enters the conditioning cycle and how efficiently it will be expelled under the design parameters of the conditioning process. The importance of meeting the target degree of dryness is illustrated by French experience, related during discussions with F. Boussard, CEA, Paris, France, August 3, 1994. Three cases involving corroded Magnox fuel (magnesium-clad metallic uranium) were described:

- Case A - Corroded Magnox fuel having exposed uranium metal was placed in a closed canister with a pressure gage; the fuel was in a damp condition; after 2-3 months, the pressure exceeded the limit of the pressure gage, which was 10 atm.
- Case B - Corroded Magnox fuel having exposed uranium metal was conditioned at 430°C and placed in a closed canister with a pressure gage; after 6 months there was almost no pressure increase
- Case C - Corroded Magnox fuel having exposed uranium metal was placed in a vented canister; after several years there was no further evolution of gases.

A British drying process for wetted Magnox fuel was proposed to have a maximum conditioning temperature of 160°C (CEGB/SSEB 1986). The proposed conditioning temperature for the ITA process, 300°C, is intermediate between the French and proposed British temperatures. It is based on literature and other data available when the process was designed. It did not have the benefit of drying data from the actual sludge and fixed corrosion products. The French cases, outlined above, illustrate the importance of sufficient drying. Comparing data from ITA II, App. G with other data reveals that different uranium oxides dry at markedly different thermal conditions. (Olander et al. 1982). It therefore is necessary to define the drying characteristics of actual Sludge A and other significant moisture-bearing species.

Regarding the second aspect of conditioning, minimizing the inventories of uranium hydrides and metal fines, the hydride inventories in the N Reactor fuel have not been characterized. A program is in progress to examine several fuel elements from KE and KW fuel canisters. However, a statistical sampling is not affordable, and therefore knowledge of the inventory will be incomplete. That aspect is mitigated by two circumstances:

- Addisson observed that nonswollen uranium metal fuels corroding in an open pool will form some hydrides, but will not present a pyrophoric risk (Addisson 1994). The reason is that hydrides react with water and with oxygen dissolved in the water. Only occluded hydrides will survive; therefore, the hydride inventories, at least in the N- Reactor fuel stored in the open KE canisters, would be expected to have minimal hydride inventories. That may also be true of fuel stored in the closed KW canisters, if the potassium nitrite inhibitor has been effective. The ongoing characterization study is expected to provide some answers.
- The MCOs are intended to be inerted, sealed with high-integrity welds, and stored in a second containment. The inerting and seal-welding process have been demonstrated for power reactor fuel. The N Reactor fuel will be isolated from air. The importance of that measure is illustrated in the following examples from experience with corroding Magnox fuel.

Two cases will be outlined, although others can be cited:

- Case 1 - Magnox fuel was placed in carbon steel canisters with an air cover gas and was stored in a wet storage facility at Sallugia (Italy) (Alonzo et al. 1993). The cover gas was monitored via plastic hoses attached to each canister. Water leaked into the canisters through the hoses and lid seals, causing severe corrosion of some fuel elements. Observation of hydrogen buildup in the canisters prompted the cover gas to be changed to nitrogen. After 19 y, some fuel elements were essentially fully corroded and undoubtedly hydrided in the moist nitrogen, hydrogen-rich atmospheres. Other elements were judged to be essentially intact, involving fuel in canisters that had not leaked. Staff from British Nuclear Fuels filled the canisters with water; placed the fuel into casks; and shipped them to Sellafield, where the fuel was reprocessed. There was no exposure to air during storage, conditioning with water, and shipping. The hydrided fuel was therefore not subject to pyrophoric events, and the hydride inventories were reduced by reaction with oxygenated water.
- Case 2 - The normal procedure in British and French practice with Magnox fuel has been that when fuel cladding fails in reactor service, the failed elements are placed into canisters with inert cover gases. The canisters are then submerged in the fuel storage pools. Frequently, the cans leak over periods of years, and water attacks the exposed uranium metal. This also generates a moist hydrogen atmosphere that promotes further corrosion and hydride formation. Cans removed to hot cells and exposed to air became pyrophoric

(Fisher and Knight 1993). While in cans, isolated from air, the hydrided fuel did not become pyrophoric.

The relevance of these cases to conditioning of the N Reactor fuel is that it will not be practical to demonstrate that the fuel is completely free of uranium hydrides and particles. Even though the process is designed to attack them when contained and inerted, residual hydride and particles will not have pyrophoric significance unless a credible accident is identified that breaches the containments and exposes the fuel to significant air ingress. Even if all hydrides were known to be destroyed in the conditioning cycle, the formation of additional hydrides from hydrogen evolved by radiolysis cannot be ruled out. Therefore, if the MCOs are to be opened after interim storage, operations must be conducted such that pyrophoric events are precluded.

4.0 Sludge Removal Processes

Desludging involves a process that removes a significant fraction of the sludge from the KE and KW canisters. In the ITA concept, desludging would occur at the K Basins. The current path forward concepts also assume sludge management at the K Basins, with no further provisions for desludging at the storage or conditioning facilities.

4.1 Proposed ITA Options for Reducing the Inventory of Sludge A

In the ITA study, two alternative desludging methods were proposed:

- Option 1: a high efficiency flushing process that would involve drilling holes in the bottoms of canisters, placing a cap on the canister, and flushing with high-pressure water (ITA II 1994).

The concept involves placing a canister in a fixture, removing the canister lid in the Canister Preparation Station (CPS), closing the CPS enclosure lid that has been mated with the top of the canister. High pressure water injected through the CPS lid is directed down through the spent fuel. The holes drilled in the bottom of the canister allow water and a fraction of the sludge to escape. The drill run-through for the bottom holes will be restricted to less than 0.03 in., which is the distance the fuel is held above the bottom by the dimpled bottom plate. The operation is monitored, and the drain holes are inspected with a camera attached to the fixture (ITA II, App. E). Appendix E, Attachment 1, indicates where in the flow chart the drilling and desludging takes place.

- Option 2: placing canisters into MCOs and tipping the MCOs to allow water from a lower efficiency flush to drain.

4.2 Path Forward Options for Sludge Management

Four concepts addressing sludge management are being evaluated:

- Concept 1: load canisters without desludging
- Concept 2: drill canisters and drain
- Concept 3: drill bottoms and sides of canisters and flush with water at moderate pressures

- Concept 4: repack the fuel into a hexagonal array of 54 elements in canisters that would be loaded into MCOs, disposing of Sludge A as the fuel is removed from the current canisters.

Current plans are to seal the MCOs for shipment, vent during staging, and condition through small penetrations in the MCOs.

The desludging efficiencies for the candidate processes obviously differ, with Concept 4 having the highest efficiency. If desludging efficiency emerges as an important parameter, based on judgements after drying data for Sludge A are available, that will help to guide the decision regarding desludging effectiveness that is required. Desludging pilot studies involving Concepts 2 and 3 would provide a basis for selection of a process with requisite effectiveness, once a target is established.

The desludging target would be established from drying data that indicate the efficiency of the conditioning process to expel moisture from the MCO contents. That perspective also needs to include drying of non-sludge moisture sources, principally corroded aluminum alloy canisters if they continue into conditioning/storage of the N Reactor fuel.

Moisture inventories inside the MCOs will also be a consideration in preconditioning storage if the environment is inert gas. The French experience illustrates the potential consequences of storing moist fuel; however, the ratio of free volume to corroding fuel area in the French case may be quite different from that in the N Reactor fuel cases.

4.3 Considerations in Planning for Desludging

The most significant perspective involving desludging is the obvious efficacy of sludge removal if Concept 4 is pursued. That concept also affords other potential attractions, including removing corroded aluminum canisters from MCO storage and segregating failed and unfailed N Reactor fuel elements; however, these pluses are being weighed against impacts on K Basin operations and activity levels. Segregation markedly reduces the conditioning burden. If failed and unfailed fuel both go on to dry storage, then including a few early-stage failures that are missed in segregation inspections would not have a significant consequence. However, with storage times of 8 to 23 y, it seems likely that essentially all cladding defects will have become evident.

If Concepts 2 or 3 are pursued, there are also significant considerations that have become evident in campaigns to characterize the fuel inventories, particularly in KE.

The inventory of failed KE fuel has been assessed systematically from video and visual inspections; while the perspectives represent imprecise estimates, they provide valuable insights to fuel condition; the estimates suggest the following distribution of fuel condition (Pitner 1995):

- 51% of the canisters (1824) are rated "good," denoting all elements are basically intact
- 43% of the canisters (1546) are rated "fair," denoting that at least one element has a significant area of exposed fuel
- 4% of the canisters (151) are rated as "poor," denoting that one element is evident that is in advanced stage of degradation
- 1.5% of the canisters (53) are rated as "very bad," denoting that multiple elements are in advanced stages of degradation.

From a desludging standpoint, the data cited above represent a favorable perspective: only a small fraction of the canisters are likely to have large inventories of fuel sludge. If effective desludging concentrated on approximately 10% of the canisters, it seems likely that a dominant fraction of fuel particles would have been eliminated. The data also suggest that fuel-bearing sludges may carry only a small fraction of the total Sludge A moisture inventory. These insights are important in selecting Sludge A samples for characterization. On the other hand, eliminating fuel sludge may be a small factor in moisture reduction, given the amount of moisture associated with the aluminum alloy canisters and the inventory of non-fuel sludge.

The fuel inspections indicated that at least 85% of the two-barreled canisters examined contained at least one breached fuel piece, either an inner or outer element (incipient ruptures excluded).

Another significant consideration is that Mark 0 aluminum canisters in KE have bottoms with screens backed by a plate with drilled holes. The hole diameter is 1 in. (2.5 cm), and there are 21 holes in the bottom plate. Photographs indicate that some sludge masses are retained on the screen; however, a substantial fraction would be expected to escape through the holes; also, water jets or even vigorous movement of the canisters may expel a large fraction of the Sludge A retained on the screen.

5.0 Summary of Needs Addressing Desludging And Fixed Corrosion Product Issues

Key insights are summarized to facilitate understanding of the technical basis needed to resolve issues related to desludging and fixed corrosion products.

5.1 Summary of Key Insights

- Sludge definition: focuses on particulates, the effects of fixed corrosion products must be characterized separately.
- Sludge effects include associated inventories of entrained, adsorbed, and chemically bound moisture; impacts of the particulates on radioactivity transport; possible pyrophoric species; plugging of pipes and sensors, and blockage of gas flows.
- Particulate formation at various stages in fuel management is differentiated as Sludges A, B, C, and D, (corresponding to formation in the K Basins), in preconditioning storage, during conditioning, and in post-conditioning storage.
- Species with moisture inventories that drive desludging requirements comprise

Residual Sludge A^(a) + Sludge B + Fixed C.P. A + B

- The following inventories of particulates and fixed corrosion products have been estimated:
 - Non-fuel Sludge A 15 kg per KE MCO
 - Fuel oxides (worst case) 17.5 kg per MCO
 - Total Sludge B^(b) 4 kg per KE MCO
 - Fixed C.P. on aluminum canisters 5 kg per KE MCO

The weight comparison suggests that there is an incentive to reduce the Sludge A inventory by desludging, but the estimates are very rough and do not account for related moisture amounts and drying behavior of the various species.

- The Sludge B inventory and characteristics will depend on which storage environment is selected; water storage will generate the most sludge and associated moisture.

(a) After desludging at the K Basins.

(b) Assumes that preconditioning staging involves water in MCOs.

- Desludging is currently foreseen to involve operations at the K Area only, with no further desludging prior to conditioning.
- French experience illustrates the importance of sufficiently drying the fuel prior to storage. Damp fuel developed high pressures (> 10 atm) in 2 months because of gas buildup from radiolysis of moisture. Fuel dried at 430°C did not show pressure increases in 6 months.
- It is not practical to ensure that all hydrides and metal particles have reacted during conditioning. However, experience with storage of corroded Magnox fuel demonstrates that isolation of hydrided fuel from air facilitates safe storage for up to 19 years.
- Inspections of the N Reactor fuel in KE suggest that only about 10% of the canisters have severely degraded fuel elements. This suggests that the main inventory of fuel sludge may be localized in relatively few canisters.
- Mark 0 aluminum canisters in KE have openings in the bottoms, with metal screens over a drilled plate. Inspections suggest that some sludge is retained on the screens, but a large fraction is likely to have fallen through the holes. The retained sludge may be largely removed by flushing or vigorous movement of the canisters.
- Four sludge management concepts are identified in the current path forward for N Reactor fuel:
 - placing canisters into MCOs without sludge removal
 - drilling holes in the canisters and draining water and some sludge
 - drilling holes in the canisters and flushing with water to increase sludge removal
 - repackaging the fuel, with associated removal of sludge.

5.2 Needs Relevant to Definition of an Effective Desludging Process

Effective desludging addresses reducing the impacts of moisture, particulate mobility and gas blockage, and potentially pyrophoric species to acceptable regimes.

1. Acceptable sludge inventories in MCOs during conditioning is the primary basis that drives the criteria for desludging. The basis included the need to limit impacts of moisture, mobile particulates, and pyrophoric species. A required action is the final decision regarding the specification (target) for the maximum pressure inside the MCOs during long-term interim storage. The value selected in the ITA study was 0.3 atm.

2. Designation of a maximum MCO pressure establishes a basis to investigate the inventories and water release characteristics of moisture-bearing species that will enter the conditioning process (see Owczarski, et al.^(a)). Options to control the post-conditioning moisture level to an acceptable range include the following:

- limit the inventory of moisture-bearing species that are carried into the conditioning process inside the MCOs
- adjust the conditioning time-temperature parameters, to the extent practical, to achieve the requisite drying.

3. Inventory estimates and moisture release characteristics that need to be investigated include

- Sludge A
- Sludge B
- Fixed corrosion products A and B
- Sludge C and fixed corrosion products C, if they are judged to affect conditioning.

Elements of the sludge and fixed corrosion product characterizations are outlined in the Appendix.

Characterization of the Sludge A-KW inventory has begun on a limited scale. Additional sampling is projected for early in FY 1996. Sampling for characterization of Sludge A-KE is projected for the January/February 1996 time frame. The assessment of the Sludge B inventory and moisture release characteristics can proceed after the decision is made regarding the preconditioning storage conditions inside the MCOs.

The inventory of fixed corrosion-Sludge A- K East (FC-A-KE) depends on whether the existing canisters are placed into the MCOs or whether the fuel is repackaged into new canisters. Particularly relevant to the moisture inventory is the decision regarding continued use of heavily corroded KE aluminum canisters. Other fixed corrosion product inventories should be assessed regarding potential impacts during conditioning, particularly regarding contribution to the

(a) Owczarski, P.C., et al. 1995. "Technical Bases for Assessing Fuel and Sludge Behavior and Gas Release in an MCO During Dry Fuel Storage." Letter report submitted under Contract 188694-A-A2, Task P-3, Pacific Northwest Laboratory, Richland, Washington.

associated moisture and moisture release characteristics. The amount of corrosion on the KW aluminum canisters is considered to be substantially less than on KE canisters; however, the amount and moisture content need to be established.

A shortcut to characterize KE aluminum alloy corrosion might proceed by retrieval of an aluminum alloy canister lid, if it is determined to have thick, nodular corrosion areas, prototypic of the canisters.

4. Effectiveness of the candidate desludging methods will need to be investigated if reducing the Sludge A inventory emerges as a priority. Pilot studies using canisters with typical sludge inventories offer the most definitive approach. Attempts to simulate desludging operations with artificial, nonradioactive sludge seem unsatisfactory.

5. While not directly related to desludging, the position regarding possible residual uranium hydrides and metal particulates after conditioning will need to be finalized because there is no practical basis to demonstrate that they have been quantitatively destroyed. French, British, and Italian experience with heavily hydrided metallic uranium fuels should be reviewed to investigate the position that the containment of the MCOs has sufficient integrity to preclude inadvertent exposure to air and that the hydride and metal species inside the MCOs do not constitute a pyrophoric threat. Methods have been demonstrated to deal with hydride inventories if it becomes necessary to open the MCOs at a future time.

6.0 References

- Addisson, C. W. E. 1994. "Storage and Corrosion of Spent Metal Fuel - UK Experience and Capability and its Implications to DOE Spent Nuclear Fuel Management." *Proceedings of American Nuclear Society Meeting. DOE Spent Nuclear Fuel - Challenges and Initiatives*, Salt Lake City, Utah, December 13-16. (Paper not included in proceedings.)
- Alonzo, G., G. A. Hall, F. Pozzi, and M. Raspollini. 1993. "Experience in the Interim Dry Storage of Magnox Fuel Elements in the EUREX Plant." IAEA-TECHDOC-686, International Atomic Energy Agency, Vienna, Austria.
- Alwitt, R. S. 1976. "The Aluminum-Water System." Ch. 3 in *Oxides and Oxide Films, Vol. 4*, J. W. Diggle and A. K. Vijh (eds.). Marcel Dekker, Inc., New York.
- Baker, R. B. 1995. *Summary Status of K Basins Sludge Characteristics*. WHC-SD-SNF-TI-006, Rev. 0, Westinghouse Hanford Company, Richland Washington.
- Ballinger, R. G. 1994. "An Analysis of Corrosion Related Pressure Buildup and Sludge Production During Wet MCO Storage of N Reactor Fuel." Addendum to ITA Assessment, Altran Materials Engineering, Inc., Boston Massachusetts.
- Ballinger, R. G., A. B. Johnson, Jr., and K. A. Simpson. 1994. "Kinetic and Thermodynamic Bases to Resolve Issues Regarding Conditioning of Uranium Metal Fuels." PNL-SA-24458, *Proceedings of American Nuclear Society Meeting. DOE Spent Fuel - Challenges and Initiatives*, Salt Lake City Utah, December 13-16.
- Central Electric Generating Board (CEGB)/South of Scotland Electric Board (SSEB). 1986. *The CEGB/SSEB Response to Recommendations 17 and 18 in the Environmental Committee's Report on Radioactive Waste*. 621.039.7 Central Electric Generating Board, London, England.
- Creer, J. M., R. A. McCann, M. A. McKinnon, J. E. Tanner, E. R. Gilbert, R. L. Goodman, D. H. Schoonen, M. Jensen, C. Mullen, D. Dxiadosz, and E. V. Moore. 1986. *CASTOR-V/21 PWR Spent Fuel Storage Cask Performance Testing and Analysis*. PNL-5917/EPRI NP-4887, Electric Power Research Institute, Palo Alto, California.
- Fisher, D., and S. Knight. 1993. *B30 Bottled Fuel Opening Study*. AEA-D&W-0566, AEA Windscale, Cumbria, United Kingdom.
- Independent Technical Assessment (ITA) I. 1994. *DRY STORAGE OF N REACTOR FUEL - Independent Technical Assessment, Vol. I*. MAC Technical Services Co., Richland Washington..

Independent Technical Assessment (ITA) II. 1994. *DRY STORAGE OF N REACTOR FUEL - Independent Technical Assessment, Vol. II*. MAC Technical Services Co., Richland, Washington.

Johnson, A. B., Jr., and S. P. Burke. 1995. *K Basin Corrosion Program Report*. WHC-EP-0877, Westinghouse Hanford Company, Richland, Washington.

Kohli, R., D. Stahl, V. Pasupathi, A. B. Johnson, Jr., and E. R. Gilbert. 1985. "The Behavior of Breached Boiling Water Reactor Fuel Rods on Long-term Exposure to Air and Argon at 598 K." *Nuclear Technology* 69:186-197.

McKinnon, M. A. And V. A. Deloach. 1993. *Spent Nuclear Fuel Storage - Performance Tests and Demonstrations*. PNL-8451, Pacific Northwest Laboratory, Richland Washington.

Olander, D. R., D. Sherman, and M. Balooch. 1982. "Retention and Release of Water by Sintered Uranium Dioxide." *J. Nucl. Mat.* 107:31-45.

Pitner, A. L. 1995. *KE Basin Underwater Visual Fuel Survey*. WHC-SD-SNF-TI-012, Westinghouse Hanford Co., Richland Washington.

Richardson, C. A. 1980. *Aluminum Fuel Canister Corrosion*. UNI-1430, UNC Nuclear Industries, Richland Washington.

Spent Nuclear Fuel Project (SNFP). 1995. *Spent Nuclear Fuel Project, Technology Acquisition Plan*. Applied Technology Project Office, Westinghouse Hanford Company, Richland Washington.

Tamura, C. A., W. G. Lussie, B. K. Hampton, and R. M. Gale. 1994. "Pressure Buildup in a Dry Storage Container of Spent Nuclear Fuel." *Proceedings of American Nuclear Society Meeting, DOE Spent Nuclear Fuel - Challenges and Initiatives*, Salt Lake City, Utah, December 13-16.

Tyfield, S. P. 1988. "Corrosion of Reactor Grade Uranium in Aqueous Solutions Relevant to Storage and Transport." *Nuclear Energy* 27(2):91-98.

Wasywich, K. M., and C. R. Frost. 1992. "Examination of Used CANDU Fuel Following 27 Years of Storage Underwater." Paper presented at ECDOD 91, Third Conference on Nuclear Fuel Reprocessing and Waste Management, Sendai, Japan, April 14-18, 1991.

Westinghouse Hanford Company (WHC). 1995a. *Data Quality Objectives for K-East Basin Floor and Weasel Pit Sludge Sampling*. WHC-5D-SNF-DQO-005, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Westinghouse Hanford Company (WHC). 1995b. *Sampling and Analysis Plan for Floor Sludge of the 105-K East Basin and Weasel Pit*. WHC-SD-SNF-PLW-005, Westinghouse Hanford Company, Richland, WA.

Appendix

Characterization, Test, And Data Needs

SLUDGE:

Sludge A

- Species and inventories
- Particle size distribution
- Consistency: loose, compact, gelatinous
- Pyrophoric properties
- Radioactivity inventory
- Drying characteristics
- Desludging effectiveness
- Residual Sludge A: amount, condition, distribution
 - Anticipated effects of conditioning
 - Anticipated effects on storage and downstream operations

Sludge B

- Amount generated
- Characteristics (see Sludge A list) if justified
- Anticipated effects on conditioning
 - Anticipated effects on storage and downstream operations

Sludge C

- Amount generated
- Location
- Characteristics
- Anticipated effects on conditioning
- Anticipated effects on storage and downstream operations

Sludge D

- Amount generated
- Species and characteristics
- Anticipated effects on storage and downstream operations

FIXED CORROSION PRODUCTS

- A+B+C+D inventories
- Species
- Drying Characteristics (A+B+C)

Distribution

No. of
Copies

No. of
Copies

OFFSITE

1 Technical Advisory Group

R. G. Ballinger
MIT
Building 24, Room 221
77 Massachusetts Ave.
Cambridge, MA 02139

ONSITE (continued)

20 Pacific Northwest National Laboratory

A. L. Doherty
A. B. Johnson, Jr (10)
P. A. Scott
S. M. Short
Information Release Office, K1-06 (7)

ONSITE

2 DOE Richland Operations Office

P. G. Loscoe
G. D. Trenchard

10 Westinghouse Company

C. J. Alderman
R. B. Baker
B. J. Makenas
L. M. McWethy
C. R. Miska
K. L. Pearce
A. L. Pitner
P. K. Shen
J. P. Schmidt
J. C. Wiborg