AUG 28 1998

Sta 37   22

ENGINEERING DATA TRANSMITTAL

1. EDT **624550**

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Numatec Hanford Corporation Sludge Treatment Project	4. Related EDT No.: NA
5. Proj./Prog./Dept./Div.: Spent Nuclear Fuel Project	6. Design Authority/ Design Agent/Cog. Engr.: A. G. Westra	7. Purchase Order No.: NA
8. Originator Remarks: For approval and release.		9. Equip./Component No.: NA
		10. System/Bldg./Facility: NA
11. Receiver Remarks: 11A. Design Baseline Document? [ ] Yes [X] No		12. Major Assm. Dwg. No.: NA
		13. Permit/Permit Application No.: NA
		14. Required Response Date: NA

15.	DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted		Approval Desig- nator	Reason for Trans- mittal	Origi- nator Dispo- sition	Receiv- er Dispo- sition
1	HNF-3096		0	K Basin Sludge Dissolution Engineering Study		N/A	1,2	1	

16.		KEY	
Approval Designator (F)	Reason for Transmittal (G)		Disposition (H) & (I)
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 4. Review 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)		1. Approved 4. Reviewed no/comment 2. Approved w/comment 5. Reviewed w/comment 3. Disapproved w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION
(See Approval Designator for required signatures)

(G) Rea- son	(H) Disp.	(J) Name (K) Signature (L) Date (M) MSIN	(G) Rea- son	(H) Disp.	(J) Name (K) Signature (L) Date (M) MSIN
		Design Authority	1		A. G. Westra A.G.Westra 8/5/98
		Design Agent			
1	1	Cog.Eng.T. A. Flament			
1	1	Cog. Mgr.W. W. Rutherford 8/11/98			
		QA			
		Safety			
		Env.			

18. A. G. Westra A.G.Westra 8/11/98 Signature of EDT Originator Date	19. W.W.Rutherford 8/11/98 Authorized Representative Date for Receiving Organization	20. W. W. Rutherford 8/11/98 Design Authority/ Date Cognizant Manager	21. DOE APPROVAL (if required) Ctrl. No. [] Approved [] Approved w/comments [] Disapproved w/comments

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K BASIN SLUDGE DISSOLUTION ENGINEERING STUDY

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Numatec Hanford Corporation, Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-96RL13200

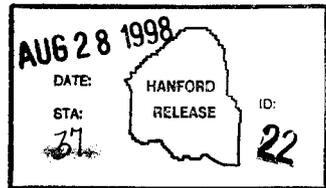Key Words: Sludge, K Basin, dissolution, engineering study

Abstract: This engineering study is an investigation of available technology related to dissolution of K Basin sludge in nitric acid. The conclusions of this study along with laboratory and hot cell tests with sludge samples will provide the basis for conceptual design of a sludge dissolver.

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AUG 2 8 1998

DATE: HANFORD
STA: RELEASE   ID:
                      22

Release Approval   Date   8-28-98   Release Stamp

Approved for Public Release

A-6400-073 (01/97) GEF321

K BASIN SLUDGE DISSOLUTION ENGINEERING STUDY

HNF-3096
Rev. 0

August 1998

1.0   INTRODUCTION

1.1   Purpose

The purpose of this engineering study is to investigate the available technology related to dissolution of the K Basin sludge in nitric acid.   The conclusion of this study along with laboratory and hot cell tests with actual sludge samples will provide the basis for beginning conceptual design of the sludge dissolver.

1.2   Background

The K Basin sludge contains uranium oxides, fragments of metallic U, and some U hydride as well as ferric oxyhydroxide, aluminum oxides and hydroxides, windblown sand that infiltrated the basin enclosure, ion exchange resin, and miscellaneous materials.

The decision has been made to dispose of this sludge separate from the fuel elements stored in the basins.   The sludge will be conditioned so that it meets Tank Waste Remediation System waste acceptance criteria and can be sent to one of the underground storage tanks.   Sludge conditioning will be done by dissolving the fuel constituents in nitric acid, separating the insoluble material, adding neutron absorbers for criticality safety, and then reacting the solution with caustic to co-precipitate the uranium and plutonium.

There will be five distinct feed streams to the sludge conditioning process - two from the K East (KE) Basin and three from the K West (KW) Basin.   The composition of the floor and pit sludges which contain more iron oxides and sand than uranium is much different than the canister sludges which are composed of mostly uranium oxides.   The sludge conditioning equipment will be designed to process all of the sludge streams, but some of the operating parameters will be adjusted as necessary to handle the different sludge stream compositions.   The volume of chemical additions and the amount of undissolved solids will be much different for floor and pit sludge than for canister sludge.

Dissolution of uranium metal and uranium dioxide has been studied quite thoroughly and much information is available.   Both uranium metal and uranium dioxide have been dissolved on a large scale in nuclear fuel reprocessing plants in Europe, Japan, and the USA. Ash and sludge containing uranium compounds also have been dissolved in reprocessing or plutonium scrap recovery plants, but only a limited amount of information is available on how the ferric oxyhydroxide, aluminum compounds and silicates in the sand will behave during nitric acid dissolution.   Laboratory work with simulants and hot cell work with actual K Basin sludge is in progress to obtain data in these areas.

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1.3 Scope

This study will address the effects of temperature, agitation, particle size, nitrate concentration, and nitrous acid concentration on uranium dissolution. Dissolution of iron, aluminum, and silica compounds in the sludge will also be discussed. Most of the organic ion exchange resin in the sludge will be removed upstream from the dissolver, but a small amount will remain with the sludge so it also will be addressed in this document.

Dissolving the uranium in the K Basin sludge is similar in ways to the dissolution of uranium metal and uranium oxide powders in fuel reprocessing plants, but there are also some important differences.

The amount of the uranium in the fuel that is charged to a dissolver during fuel reprocessing is generally well known and the uranium is generally in only one form (metal, metal alloy, UO_2). The K Basin sludge is not homogenous so there will be considerably more uncertainty about the amount of uranium and plutonium in the feed stream to the dissolver than is generally the case for fuel reprocessing plants. The uranium in the K Basin sludge is present in several forms. It is predominantly uranium oxides, but uranium metal and uranium hydride are also present. The uranium metal fragments will dissolve much slower than the uranium oxide and hydride.

The U concentration in the sludge dissolver will be much lower than in most fuel reprocessing dissolvers. The sludge will be transferred from the basins to the sludge conditioning system as a 12 wt% slurry containing uranium at concentrations in the range of 25 - 110g U/l. The uranium concentration will be further diluted when it is mixed with acid in the dissolver.

The scope of this study includes recommending dissolver operating parameters. Parameters that must be decided include:

• Pressure

• Temperature

• Mode of operation (batch, continuous, semi-batch)

• Nitric acid addition schedule (all initially, in increments, continuously)

• Nitric acid concentration profile in the dissolver

• Sludge addition schedule (all initially, in increments, continuously)

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- Dissolution cycle time (assuming a batch process)

The scope also includes making some preliminary decisions on the basic dissolver design such as:

- Method of agitation

- Criticality prevention

- Vessel configuration

- Materials of construction

- Methods for heating and cooling

1.4 Sludge Dissolution Requirements

The process for dissolving K Basin sludge must meet the safety and operating requirements listed below:

- The dissolver operation must ensure an adequate margin of sub criticality

- The uranium oxides and hydride in the sludge must be dissolved at a slow enough rate that the reaction can be controlled

- The concentration of hydrogen gas must be maintained below the flammability limit

- Precipitation of gelatinous solids formed by the dissolution and precipitation of silicates must be minimized

- The uranium metal must be dissolved fast enough that cycle time is not excessive

- The amount of undissolved FeOOH, TRU, and fission products must be minimized in the undissolved solids

- The amount of excess acid should be minimized

- The dissolver design should accommodate mechanical agitation if possible

A critically safe geometry is the best way to meet the first requirement. However, mass limits and other administrative controls are also acceptable methods for ensuring criticality safety. They are less costly and allow more operating flexibility.

The small particle size of the oxidized uranium in the sludge provides a large surface area for reaction. The dissolution process must insure that the reaction rate can be controlled when the small uranium particles are dissolving.

The third requirement deals with a gelatinous precipitate that has formed during some hot cell sludge dissolution tests. If a gelatinous precipitate forms during sludge processing, it could cause problems for both solution and solids transfer as well as for solids/liquids separation.

The uranium metal fragments in the sludge will dissolve much slower than the uranium oxides and hydride so the uranium metal dissolution rate is the predominant factor for determining dissolver cycle time. The dissolver cycle time will directly impact the total time required to process the sludge so there is a big incentive to minimize the cycle time. The cycle time should not exceed 24 hrs in the worst case and preferably will be considerably less.

Since part of the Pu is expected to be tied up with the FeOOH in the sludge, minimizing the undissolved FeOOH should minimize the residual TRU in the undissolved solids. The undissolved solids must be made non-TRU prior to disposal to Environmental Remediation Disposal Facility (ERDF) so if most of the FeOOH and TRU are dissolved in the dissolver it will simplify downstream treatment of the sludge to remove TRU.

The excess acid left at the end of sludge dissolution will be neutralized with NaOH so minimizing the excess acid will minimize the amount of NaOH required and the amount of waste that is transferred to underground waste storage. However, minimizing the waste volume is a lower priority than the other requirements listed.

Mechanical agitation has been used to control the particle size of gelatinous precipitates and make them easier to handle. Since gelatinous precipitates are expected to be a problem when processing some sludges, the dissolver design should accommodate mechanical agitation, if it is compatible with other requirements.

2.0 DISSOLUTION CHEMISTRY

The exact mechanism involved in dissolution of the uranium in the sludge depends on many factors. The sludge contains fragments of metallic uranium and some uranium hydride in addition to several uranium oxides (mostly UO_2 and U_3O_7). A small amount uranium of hydrate ($UO_4 \cdot 4H_2O$) is also present (Pearce et. al., 1998).

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2.1 Uranium Dissolution

Several reactions have been proposed for the dissolution of UO_2 in HNO_3. There is quite broad agreement on the following two:

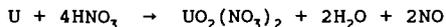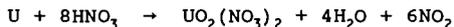$$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO_2$$

$$3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 4H_2O + 2NO$$
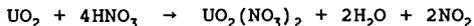
The first equation is dominant at higher acid concentrations (> 8 $\underline{M}$) and the second at lower concentrations (<8 $\underline{M}$).

Not much information is available on the dissolution of U_3O_7 in HNO_3. However, like the UO_2, it is expected to dissolve quickly even in dilute HNO_3 due to the small particle size. The average particle size for the uranium oxides in the sludge is 10 microns.

There have also been several reactions proposed for U metal dissolution in HNO_3.

$$U + 8HNO_3 \rightarrow UO_2(NO_3)_2 + 4H_2O + 6NO_2$$

$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO$$

The first equation is dominant at higher acid concentrations (>8 $\underline{M}$) and the second at lower acid concentrations (<8 $\underline{M}$). The reflux of nitric acid from a condenser will reduce the consumption of HNO_3 from that shown in the above equations. The Reactor Handbook (Blanco and Watson, 1961) reports that the introduction of air into the off-gas system and the use of a downdraft condenser can reduce the consumption of nitric acid to 2.5 - 3.0 moles HNO_3 per mole U when dissolving uranium metal. A similar reduction in acid consumption can be expected when dissolving UO_2.

In practice, nitric acid recovery probably will not be that good. The headend flowsheet for the Plutonium-Uranium Extraction Plant (PUREX) (Allen, et. al., 1985) used a value of 3.8 moles HNO_3 consumed per mole of U metal or UO_3 that was dissolved. This included reflux from the downdraft condenser.

Uranium hydride readily reduces 6 $\underline{M}$ or concentrated nitric acid to NO_2 (Katz, 1951). The following reaction can be written for the dissolution of UH_3 in nitric acid if the HNO_3 is reduced to NO_2.

$$UH_3 + 11HNO_3 \rightarrow UO_2(NO_3)_2 + 9NO_2 + 7H_2O$$
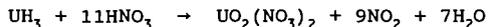
If the HNO_3 is reduced to NO which would be the case for more dilute acid, then the following reaction applies:

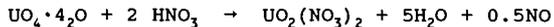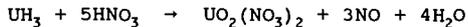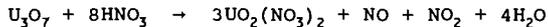$$UH_3 + 5HNO_3 \rightarrow UO_2(NO_3)_2 + 3NO + 4H_2O$$
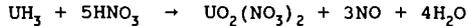
Swanson gave the following reaction for UH_3 dissolution in nitric acid (Swanson, 1985).

$$UH_3 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO + 1.5H_2$$
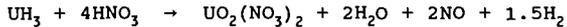
This reaction would only be expected to occur at low acid concentrations. It should be noted that the last reaction above produces hydrogen gas as well as NO. If hot cell dissolution tests indicate that hydrogen is present in the dissolver off gas system, it will need to be monitored and diluted as necessary to ensure that the concentration remains below the flammability limit. Hydrogen generation is not expected to be a problem.

The following reactions are believed to best represent the uranium dissolution reactions that will occur during sludge dissolution.

$$U + 3.8HNO_3 + 0.15O_2 \rightarrow UO_2(NO_3)_2 + 1.9H_2O + 1.8NO$$

$$UO_2 + 3.8HNO_3 + 0.05O_2 \rightarrow UO_2(NO_3)_2 + 1.9H_2O + 1.8NO_2$$

$$U_3O_7 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + NO + NO_2 + 4H_2O$$

$$UH_3 + 5HNO_3 \rightarrow UO_2(NO_3)_2 + 3NO + 4H_2O$$

$$UO_4 \cdot 4_2O + 2\ HNO_3 \rightarrow UO_2(NO_3)_2 + 5H_2O + 0.5NO$$
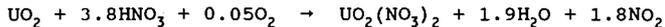
The first two equations were used for the PUREX flowsheet and account for HNO_3 reflux from a downdraft condenser.

2.2 Plutonium and Americium Dissolution

The plutonium and americium present in the sludge will dissolve readily in HNO_3 as long as they are not tied up with the FeOOH which may not completely dissolve.

2.3 Iron Dissolution

Ferric oxyhydroxide which is present in the K Basin sludge due to the corrosion of steel structures is expected to dissolve according to the following equation:

$$FeOOH + 3HNO_3 \rightarrow Fe(NO_3)_3 + 2H_2O$$
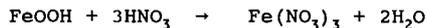
The reaction rate of FeOOH is slower than the reaction rate of uranium oxide. However, in Pacific Northwest National Laboratory (PNNL) tests (Carlson, et. al. 1998a, Carlson, et. al. 1998b), more than 99% of the FeOOH was reported to dissolve after digesting in 6 $\underline{M}$ HNO_3 for 6 hours at boiling temperature.

2.4 Aluminum & Silica Compounds

The Al(OH)$_3$ that is present in the canister/wash sludge due to oxidation of the aluminum canisters will dissolve readily in HNO$_3$ according to the following equation:

$$Al(OH)_3 + 3HNO_3 \rightarrow Al(NO_3)_3 + 3H_2O$$
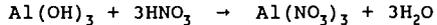
Alumina is also present in the sludge in the form of aluminum silicates that are part of the wind blown sand that has infiltrated the basin enclosures and settled to the bottom of the basins. The alumina will dissolve as follows:

$$Al_2O_3 + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2O$$

The silica (SiO$_2$) present in the sludge from sand intrusion and spalling of the basin concrete has a very low solubility in nitric acid and will constitute the majority of the undissolved solids.

The sand also contains aluminum and silicates in the form of clays and these are partially soluble in nitric acid. A gelatinous precipitate has been observed in hot cell dissolution tests of K Basin canister sludge in 10 $\underline{M}$ HNO$_3$ at both 60°C and 90°C. The amount of precipitate formed increases with temperature and acid concentration. A similar precipitate formed when Hanford blow sand from the 100-K Area was exposed to 10 $\underline{M}$ HNO$_3$.

The main concern with gel formation is that it will prevent efficient separation and washing of the undissolved solids downstream from the dissolver. Efficient separation and washing of the solids are a critical part of making the solids non TRU and reducing the polychlorinated bi-phenyl concentration in the dissolved sludge to less than 0.5 ppb.

Anorthite (CaAlSi$_2$O$_8$) has been identified along with SiO$_2$ as a crystalline phase in the undissolved solids in the samples in which the precipitate formed. Anorthite is identified as a "gelatinizing silicate, i.e. silicates that dissolve with extensive dissolution of silica" (Terry, 1983a). When this type of silicate dissolves, a silica gel may form due to the ready polymerization of silica in aqueous solutions.

Manipulating process conditions to ensure that the silica precipitates in a form that can be filtered rather than forming a gel is the key to processing materials that contain soluble silicates. One way to help form a filterable precipitate is to use a strong acid at or near its boiling point (Terry, 1983b).

2.5   Fission Product Dissolution

The long-lived fission products that are still present in the
K Basin sludge include Cs-137, Sr-90, and their daughter
products, Kr-85, and I-129.   The Cs-137, Ba-137, Sr-90, and Y-90
will completely dissolve in the nitric acid in the dissolver.
The radioactive gases Kr-85 and I-129 remaining in the uranium
metal fragments will be released as the metal dissolves and will
leave the dissolver with the off gas.

2.6   Ion Exchange Resins

Organic ion exchange beads have been found during wet sieving of
KE floor, canister and Weasel Pit sludge.   The ion exchange
modules in both KE and KW Basins have used a Purolite mixed bed
organic resin since 1986.   Most of the ion exchange resin present
in the sludge will be removed upstream from the dissolver, but
the separation will not be complete so a small amount of the
resin will remain in the sludge when it is transferred to the
dissolver.   Laboratory studies by PNNL indicate that the Purolite
mixed bed resin will not dissolve in boiling 10 $\underline{M}$ nitric acid and
will retain most of its functionality (Pool, et al, 1998).   When
contacted with nitric acid in the dissolver, the Cs on the resin
will be displaced by Pu (Bredt, et al, 1998).   The Pu loaded
resin will leave the dissolver as part of the undissolved solids.
The Pu on the ion exchange resin will make the resin beads exceed
the TRU threshold of 100 nCi/gm by a wide margin.   However, if
the resin is a small enough fraction of the undissolved solids,
then the bulk undissolved solids can still be made non TRU.

Nitrated ion exchange resin which has been loaded with Pu and
allowed to dry without water washing is very reactive.   Residual
undissolved solids should not be allowed to dry out in the sludge
dissolver, especially if they have not been washed with water to
remove nitric acid.

2.7   Zeolite

A zeolite believed to be Zeolon 900 is also present in KE Basin
sludge.   Laboratory tests performed by PNNL indicate that heating
Zeolon 900 in hot HNO_3 will remove greater than 90% of the Cs
from the zeolite (Pool, 1998).   In the tests, 1 g samples of
Zeolon 900 were loaded with nonradioactive cesium and strontium,
mixed with 10 ml of 10 $\underline{M}$ HNO_3 and heated to 90°C for 6 hrs.   Some
of the tests included the addition of 0.5g FeOOH to the samples
prior to heating, since FeOOH is present in the basin sludge and
Fe(III) has been reported to reduce the amount of Cs and Sr that
will load onto Zeolon 900.   In the samples without FeOOH, 94.6%
of the Cs was removed compared to 91.9% removal in the samples
containing FeOOH.

The report on these tests included calculations which indicated that the above Cs removal efficiencies were adequate to make the Cs concentration in the undissolved solids 25-75% less than ERDF acceptance criteria. The average nitric acid concentration in the sludge dissolver will probably be closer to 6 $\underline{M}$ than the 10 $\underline{M}$ used in the tests which may decrease the Cs removal efficiency. However even if the Cs removal efficiency in the plant dissolver is an order of magnitude less than measured in the laboratory, it would be adequate for the undissolved solids to meet ERDF acceptance criteria.

Although about 50% of the Al and 75% of the Fe in the Zeolon 900 were removed by the nitric acid digestion, the crystal structure was not changed. The measured weight loss from the Zeolon 900 varied from 2-13%.

3.0 DISSOLUTION KINETICS

Many factors can affect the reaction rate of U metal and uranium oxides in nitric acid. These include temperature, total nitrate concentration, nitrous acid concentration, stirring rate, and particle surface area (CEA-TR-2216, 1986). Each of the above factors will be discussed in the following sections. The dissolution rate of UO_2 is also reported to be enhanced by the presence of Fe^{+3} (Taylor, 1963).

3.1   Effect of Temperature on Uranium Dissolution

The dissolution rate of both uranium metal and uranium oxide increases with increasing temperature as would be expected. Arrhenius plots of UO_2 dissolution data (Taylor, et. el., 1963) show that the dissolution rate triples for every 15°C increase in temperature up to a temperature of about 65°C for 14 $\underline{M}$ HNO_3 acid and up to about 95°C for 2 $\underline{M}$ HNO_3. At that point, there is a break point and the slope of the dissolution rate increases at a slower rate in relation to the temperature. This effect is less pronounced at 1-2 $\underline{M}$ HNO_3 than at 8-12 $\underline{M}$. The dissolution rate decreases between 95°C and the boiling temperature. This has been attributed to the decomposition of nitrous acid as the temperature approaches boiling.

The temperature also affects the uranium reaction mechanism which affects the composition of the off gas. Higher temperatures favor the formation of NO_2 while lower temperatures favor the formation of NO.

3.2   Effect of Nitric Acid Concentration

The dissolution rate of uranium increases with increasing HNO_3 concentration. Taylor, et. al., 1963, reported the UO_2 dissolution rate was proportional to the nitric acid concentration raised to the 2.3-3.3 power while Uriarte and Rainey, 1965, reported that it was proportional to the nitric

acid concentration raised to the 2.03-2.12 power. Ikeda, et. al., 1995, reported the dissolution rate was proportional to the total nitrate concentration raised to the 2.3 power.

Blaine, 1960, found that uranium metal dissolution was proportional to the total nitrate concentration raised to the 2.7 power. Swanson, 1985, reported that uranium metal dissolution was proportional to the total nitrate concentration raised to the 2.6 power.

The nitric acid concentration not only affects the reaction rate, it also affects the reaction mechanism and the composition of the dissolver off gas stream. Low acid concentrations favor the formation of NO while higher concentrations favor the formation of NO_2.

3.3   Effect of Nitrous Acid Concentration

Nitrous acid is formed during uranium dissolution and catalyzes the dissolution of additional uranium making it an autocatalytic reaction. The nitrous acid present during uranium dissolution will be a balance between what is being formed and what is lost by decomposition and volatilization. During HNO_3 dissolution of UO_2, nitrous acid is formed and decomposes by the following reactions:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$
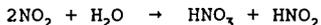
Higher temperatures favor the decomposition of HNO_2 by the second reaction which results in a lower reaction rate than would otherwise be expected. The formation of HNO_2 becomes extremely low at boiling temperature.

Nitrous acid decomposes more rapidly at higher nitric acid concentrations than at lower concentrations. The induction period at the beginning of uranium dissolution has been attributed to the buildup of nitrous acid in the solution. The dissolution reaction is slow until nitrous acid has build up and then suddenly takes off due to the autocatalytic action of nitrous acid. Swanson conducted dissolution tests in which hydrazine was added to prevent the buildup of nitrous acid (Swanson, et.al., 1985). The dissolution rate was very low compared to a similar test in which no hydrazine was added. Swanson also tracked the nitrous acid concentration during dissolution experiments and found that initially there was a close correlation between nitrous acid concentration and the concentration of dissolved uranium. However, the nitrous acid concentration soon did not increase as rapidly as the uranium concentration.

3.4 Stirring Rate

The UO_2 dissolution rate will decrease with an increase in
stirring rate up to a stirring speed somewhere in the range of
300-600 rpm. Several researchers have examined the effect of the
reactor stirring rate on the rate of uranium dissolution. Taylor
(Taylor, et. el., 1963) reported that the dissolution rate of UO_2
pellets decreased with an increase in stirring speed up to rate
of about 600 rpm. The dissolution rate at 600 rpm was typically
a factor of 4 less than the dissolution rate in an unstirred
vessel. Bubbling oxygen through the solution decreased the
reaction rate to about the same extent as mechanical stirring.
The rate at which the oxygen was bubbled through the solution was
not reported.

Shabbir and Robbins, 1969, reported that the reaction rate
decreased with an increase in stirring rate up to a stirring
speed of 400 rpm. This has been attributed to changes in the
nitrous acid concentration at the particle surface. The nitrous
acid concentration at the surface is highest in an unstirred
solution and decreases with an increase in stirring speed. The
stirring disperses the nitrous acid that is formed during
reaction. As the nitrous acid is dispersed away from the
reaction surface, it reduces the effective concentration at that
point which reduces the reaction rate.

Although their work was done with UO_2 pellets, the same principal
can be applied to UO_2 powder and small fragments of U metal.

Others have reported 300 rpm (Ikeda, et. al., 1995) and 500 rpm
(Inoue, 1986) as the minimum stirring speed at which the
dissolution rate of UO_2 powder was independent of the stirring.
The wide range reported for the minimum stirring speed may be due
to the design and/or configuration of the stirrers in the test
equipment. Since stirrer design and configuration also affect
agitation, laboratory data on stirring speeds can not be applied
to a plant scale dissolver.

3.5 Particle Size

The effect of particle size on dissolution rate is directly
related to the surface area. For a given mass of material, the
surface area available for reaction increases as the particle
size decreases. The average particle size of the UO_2 in the
sludge is about 10 microns which means that initially there will
be a very large surface area for reaction. After the reaction
starts, the surface area will decrease as particles dissolve from
the outside toward the center and then completely go into
solution.

3.6   Uranium Oxide and Uranium Metal Reaction Rates

The uranium oxides in the K Basin sludge will dissolve quickly in
nitric acid due to the small particle size and large surface
area.   The U metal fragments will dissolve much slower.   Only
sludge that will pass through a screen with $\frac{1}{4}$ in. (6.4 mm)
openings will be transferred to the sludge conditioning system.
Larger particles will be stabilized with the spent fuel elements.
Most of the uranium in the basin sludges is in the form of
uranium oxides, although the fuel wash sludge is estimated to
contain 40 wt% U metal fragments.   The uranium oxides in the
sludge are a mixture of mostly UO_2 and U_3O_7, but some U_4O_9 and
other U compounds have also been identified in sludge samples.

Early studies on UO_2 dissolution rates were done with UO_2 pellets
to develop a process for reprocessing commercial nuclear fuel by
the shear/leach method (Taylor, et. al., 1963; Uriarte and
Rainey, 1965).   Some early studies of UO_2 powder dissolution were
reported by Shabbir and Robins at the University of New South
Wales (Shabbir and Robins, 1969).

More recently, researchers in Japan have been doing dissolution
studies with UO_2 powders to develop a process for reprocessing
nuclear fuel using a rolling straightener to declad the fuel
resulting in pulverized UO_2 pellets.

The data reported by Taylor, et al, show dissolution rates of
0.5-20 $mg/cm^2/min$ for 2-14 $\underline{M}$ nitric acid concentrations at 95°C.
Uriarte reported that at boiling temperature, the dissolution
rates are in the range of 0.9-60 $mg/cm^2/min$ for 2-15.6 $\underline{M}$ HNO_3
concentrations.

Several laboratory studies on the dissolution rates of UO_2
powders have been done in Japan at the Kashiwa Laboratory,
Institute of Research and Innovation and by the Naka Energy
Research Center, Mitsubishi Materials Corp (Ikeda, 1995;
Nishimura, 1995).   Their data show reaction rates in the range of
0.35-2.9 $mg/cm^2/min$ for 4-10 $\underline{M}$ total nitrate concentrations at a
dissolution temperature of 80°C.   This is a little lower than the
rates reported by Taylor, et. al. and Uriarte and Rainey, but the
tests were done in a stirred system which can be expected to
reduce the reaction rate.

Based on their UO_2 powder dissolution tests, these researchers
derived the following rate equation (Ikeda, et.al., 1995):

$$\phi = (2.2 \times 10^4 e^{-79500/RT} + 0.46 e^{-36800/RT} [HNO_2]) [HNO_3^-]_T^{2.3}$$

where ϕ is the dissolution rate in units of $mol/cm^2/min$, R is the
gas constant, and T is the absolute temperature.   The dissolution
tests were done using UO_2 powders in three different particle
size ranges (90-150 microns, 300-355 microns, and
850-1000 microns).   The value of ϕ was found to be independent of

the particle size. The above rate equation is useful because it includes both the temperature and total nitrate concentration so it can easily be used to calculate UO_3 dissolution rates for changes in both temperature and nitrate concentration.

Dissolution tests of UO_2 powders with particle sizes in the range of 2-10 microns are also reported in the literature (Inoue, 1986). Dissolution rate curves from these tests show that 100% of the UO_2 powder in this size range could be dissolved in 5 minutes in 2 $\underline{M}$ HNO_3 at 95°C. In 1 $\underline{M}$ HNO_3 at 95°C, it took 15 minutes to dissolve 100% of the UO_2 powder. The conditions that were used for this test are close to the conditions anticipated for K Basin sludge dissolution. The average UO_2 particle size in the sludge is about 10 microns compared to about 5 microns for the powder used in the test. The results of these tests indicate that the uranium oxide in the sludge will dissolve very quickly even in 1-2 $\underline{M}$ HNO_3.

The sludge contains uranium metal fragments as well as uranium oxides, so U metal reaction rates were also investigated. The uranium metal fragments will dissolve much slower than the uranium oxides due to the lower surface area to weight ratio. Uranium metal particles up to 6 mm (0.25 in) in diameter may be present in the sludge. In dissolution tests of pieces of N reactor fuel, a dissolution rate of 100 mg $U/hr-cm^2$ in 3 $\underline{M}$ HNO_3 at 97-98°C was reported (Swanson, 1985). The reaction rate was 270 mg $U/hr-cm^2$ in 5 $\underline{M}$ HNO_3 at 97-98°C.

Swanson derived the following rate equation for dissolution of uranium metal:

$$\text{Dissolution rate} = k([HNO_3] + 2[U])^{2.6}$$

where $k = 4.6$ at 103°C and the rate units are mg $U/hr-cm^2$. Since uranyl nitrate contains 2 moles of nitrate for every mole of uranium, the term in parenthesis is equal to the total nitrate in solution. This is quite consistent with the results reported by others (Blaine, 1960). Blaine reported the following equation for dissolving uranium metal in boiling nitric acid.

$$\text{Penetration rate} = 0.03[NO_3^-{}_{Tot}]^{2.7} \text{ mils/hr}$$

When this is converted to the same units as Swanson's equation, it becomes:

$$\text{Dissolution rate} = 1.5[NO_3^-{}_{Tot}]^{2.7} \text{ mg } U/hr-cm^2$$

When Swanson's equation is converted to a linear dissolution rate and applied to a 6 mm particle of U metal in HNO_3 at 103 C, the time required for total dissolution would be 71 hr in 3 $\underline{M}$ HNO_3 and 22 hr in 5 $\underline{M}$ HNO_3.

4.0 DISSOLUTION SAFETY

The following safety requirements that were listed earlier in this document will be addressed in this section:

• The dissolver operation must ensure an adequate margin of sub criticality

• The uranium oxides and hydride in the sludge must be dissolved at a slow enough rate that the reaction can be controlled

• The concentration of hydrogen gas must be maintained below the flammability limit

4.1 Criticality Safety

Either engineered controls, administrative controls, or a combination of the two can be used to insure criticality safety in the sludge dissolver. Engineered controls are preferred because they are harder to change and are less susceptible to human error. However, engineered controls are often costly and require vessel configurations that restrict volume and/or mixing. Engineered controls that could be used include geometry and fixed nuclear poisons. Administrative controls that could be used include mass limits, concentration limits, and soluble nuclear poisons.

Prior to dissolution of the sludge, concentration limits and soluble nuclear poisons are of limited value since in the event of an agitator failure the sludge would settle to the bottom of the vessel. This would concentrate all the fissile material in a layer which would probably violate the concentration limit unless it is very low. The soluble nuclear poison would remain distributed throughout the solution so only the portion of it present in the interstitial liquid in the sludge layer would provide any poisoning effect. The poison concentration would need to be high enough to be effective in the settled sludge, or one contingency would be lost if the agitator failed or was inadvertently shut off.

The dissolver configurations that can be considered are limited if the dissolver is going to have a critically safe geometry. If a mass limit is imposed on the dissolver for criticality control, then the dissolver configuration will be determined by other factors such as mixing, heat transfer, and ease of solids removal. An analysis of mass limits for criticality control, soluble nuclear poisons, and geometrically safe configurations are discussed below. For this analysis, it was assumed that a dissolver volume of 700 gals will be required.

4.1.1 Critically Safe Geometry - No Mass Limit

Preliminary calculations show that an annular dissolver with an 18 in. annulus and 20 in. inside diameter would have a critically safe geometry. A solution depth of 6 ft would be required to hold 700 gals in this configuration. An annular dissolver has some drawbacks in that mechanical agitators cannot be readily used and transfer of undissolved solids out of the annulus would be considerably more difficult than in a cylindrical or slab tank.

It is assumed that without mass limits, criticality considerations will limit a slab dissolver to a width of 20 in. Two 20 in wide x 4 ft long slab dissolvers with a 7 ft solution depth will provide 700 gals of capacity. One 20 in wide x 8 ft long slab dissolver with a 7 ft solution depth would provide the same capacity. A slab dissolver has some of the same drawbacks as an annular dissolver. At least two mechanical agitators would be required for agitation and possibly two lines would be required for solids removal.

It is assumed that without mass limits, criticality considerations will limit a cylindrical dissolver to a diameter of 20 in. For a batch process, six 20 in. diameter cylindrical dissolvers with a solution depth of 7 ft would be required to obtain a capacity of 700 gals. Operating six cylindrical dissolvers even if they are interconnected is considered impractical. If a cylindrical shape is going to be used, then either a larger diameter vessel with mass limits on the amount of fissile material, or a much lower processing rate will be needed.

4.1.2 Fissile Material Mass Limit - Unfavorable Geometry

The minimum critical mass for various uranium enrichments can be found in HNF-SD-SNF-CSER-006, Rev 1, (Kessler, 1998). The minimum critical masses for 1.0% and 1.25% enriched uranium with no burnup are 2000 kgs and 612 kgs, respectively. During irradiation in the reactor, U-235 is burned up and Pu-239 is formed, but irradiation of the fuel will not increase the total reactivity of the fuel above its reactivity prior to irradiation. Since the KE Basin has only been used to store 0.95% enriched fuel, the 2000 kg minimum critical mass would apply to sludge from that basin. The KW Basin has stored 1.25% enriched fuel so the 612 kg minimum critical mass would apply to KW sludge.

Assuming that the dissolver mass limit is set at 1/3 of the critical mass, then the uranium mass limits would be 612 kgs for sludge from the KE and 204 kgs for sludge from the KW Basin. Since there is a wide range of uranium concentrations in the sludge, no credit could be taken for the other components of the sludge. In other words, the batch size limit would be based on the assumption that the sludge is 100% uranium.

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Preliminary batch sizes of 300 kg sludge (dry basis) when processing floor/pit sludge and 160 kg sludge (dry basis) when processing canister/wash sludge have been proposed. A 612 kg U mass limit for KE Basin sludge is a factor of four more than the total solids anticipated to be in a batch of KE canister sludge and a factor of 2.2 more than anticipated in a batch of KE floor sludge. A 204 kg U mass limit for KW canister sludge is a factor of 1.27 more than the total solids anticipated for a batch of KW canister sludge.

The above analysis is based on conservative assumptions and criticality calculations should allow at least a small increase in the mass limits.

One of the problems with using mass limits for criticality control in the sludge dissolver is that at least a small amount of undissolved solids will remain as a heel in the bottom of the dissolver after the majority of undissolved solids are transferred out. The uncertainty associated with the fissile material in the dissolver heel would have to be included in the mass limit. The uncertainty would increase with each subsequent batch of sludge processed through the dissolver.

The amount of uranium in each sludge batch that is transferred into the dissolver will need to be closely controlled to insure that the mass limit is not exceeded. The uranium in each batch can be controlled in the following ways:

1)   Use assay instrumentation to measure the fissile material in the lag storage tank and dissolver.

2)   Control both the wt% solids in the batch and the batch volume to limit the amount of uranium that is transferred into the lag storage tank and from there into the dissolver.

The assay instrument will need to provide a real time or close to real time indication of the total fissile material in the lag storage tank. The uncertainty associated with the measurement will have to be subtracted from the allowable mass limit as required when using a nondestructive assay for criticality control. An instrument meeting the above requirements is not commercially available, but contacts with vendors indicate one could be custom built. A study of assay methods for K Basin sludge retrieval was completed when the plan for sludge disposition was to send it directly to the waste tanks without processing (Wootan, 1995). The conclusion was that the differential dieaway, or pulsed active neutron, technique was the most promising. The study was done assuming a more dilute solution than will used for sludge processing. The conclusion was reached that the technique did not have a low enough detection limit and would have to be coupled with another technique since it did not differentiate between total fissile and Pu. The Pu concentration in the sludge processing stream is

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high enough to be above the detection limit of this type of
instrument and the total fissile value will be adequate for
controlling the mass limit during sludge processing.

Limiting the wt% solids and the batch size to ensure compliance
with the mass limit will require measuring both the volume and
weight of each sludge batch. The sludge will be transferred from
the basins to the sludge processing facility in batches as a
12 wt% slurry. Prior to transfer, the sludge will be staged in
the sludge loadout bin located underwater in the fuel storage
basin. The loadout bin will be operated as a flooded collection
tank with excess water leaving through a screen. The amount of
sludge added to the loadout bin will be determined using load
cells. A sludge/water mixture will be pumped into the bin until
load cells indicate that enough sludge has been transferred to
obtain a 12 wt% slurry. The batch volume transferred out of the
sludge loadout bin can be controlled by using the load cells on
the loadout bin to determine the mass transferred out and using
level instrumentation on the transport container to measure the
volume. The loadout bin will be sized to hold only one batch of
sludge.

The amount of uranium in a batch could be controlled using load
cells and level instrumentation on the lag storage vessel. Load
cells on the lag storage tank would be more accurate for
controlling the sludge batch than load cells on the underwater
loadout bin since they would be measuring weight in air instead
of weight in water. Both weight and volume limits would be
required to ensure that the mass limit was not exceeded. The
weight, volume, and density of the sludge batch would be
monitored as each batch was transferred into the lag storage
tank. The volume limit would be based on the density of a
solution containing 120 g/l solids. If the density indicated
that the sludge contained more than 120 g/l solids, the volume
limit for the tank would be lowered to ensure that the mass limit
was not exceeded.

At a solids concentration of 120 g/l (Slurry SpG = 1.109 for
KW canister wash sludge), a batch volume of 1333 liters would be
allowed. If the solids concentration increased to 140 g/l, the
slurry SpG would go up to 1.127 and the batch volume limit would
be 1142 liters. For 160 g/l solids, the SpG would be 1.146 and
the batch volume limit 1000 liters.

The sludge will be transferred from the lag storage tank to the
dissolver in batches so if the batch size in the lag storage
vessel is controlled at less than the mass limit, the mass limit
will not be exceeded in the dissolver as long as the heel in the
dissolver is not greater than the difference between the batch
size and the mass limit. The uncertainty associated with the
fissile material in the dissolver heel will have to be included
in the mass limit. The uncertainty will increase with each
subsequent batch of sludge processed through the dissolver.

Verification that a heel is not building up in the dissolver will also be required to avoid continued reductions in the batch size. The heel verification could be done by inspections, dissolution with concentrated acid, or gamma monitoring of the lower part of the dissolver.

4.1.3 Soluble Nuclear Poison

As mentioned earlier, a soluble nuclear poison would lose much of its effectiveness in the sludge dissolver if the agitator fails and the fissile materials in the sludge settle to the bottom of the dissolver. However, if used along with mass limits, a soluble nuclear poison will provide a second contingency. Boric acid, gadolinium nitrate, and cadmium nitrate have been used as soluble nuclear poisons. If a soluble nuclear poison is used for criticality safety in the sludge dissolver, it would be preferable to add it to the sludge batch as far upstream as possible. It should be added upstream of the first vessel that does not have a critically safe configuration, or added to that vessel before it receives a batch of sludge. The soluble nuclear poison will need to be included in laboratory or hot cell sludge dissolution tests to ensure that it does not have a negative effect on sludge dissolution.

4.1.4 Criticality Safety Conclusions

The conclusion reached from the above analysis is that mass limits can be used for criticality control in the sludge dissolver using either an assay instrument or load cells and level instrumentation to control the amount of fissile material in each batch. Using an assay instrument is the preferred method. However, an instrument that would work in this application is not commercially available and building a custom one is expected to be very costly. If it is not feasible or cost effective to build an assay instrument, then load cells and level instrumentation could be used.

The uncertainty associated with the fissile material in the dissolver heel will need to be included in the mass limit. The uncertainty will increase with each subsequent batch processed unless the size of the heel is verified. Visual inspections or a gamma detector will be used to verify that a heel is not building up in the dissolver.

A soluble nuclear poison should be used along with the batch controls to provide a second contingency.

The use of mass limits and a soluble nuclear poison will allow the use of a single cylindrical dissolver vessel which will facilitate mechanical agitation.

Additional studies will be done in the early phases of conceptual design to further define and evaluate the use of mass limits and soluble nuclear poison for criticality control. The use of geometrically safe vessels for criticality control will be reconsidered at this time.

4.2 Reaction Control

The sludge dissolution process must be designed to ensure that the dissolution reactions in the dissolver can be controlled. The rate at which heat is generated by the exothermic dissolution reactions must not exceed the rate at which heat can be removed from the dissolver. Heat can be removed by cooling coils and also by boil off if the dissolver is at boiling temperature. The reaction must not become so vigorous that foam and dissolver solution are entrained into the off-gas system or that dissolver vacuum is lost. The dissolver must be designed with adequate head space to allow foam to dissipate before it enters the off gas system.

Runaway reactions were encountered on two occasions during PNNL hot cell studies in the 1980's involving the dissolution of oxidized N Reactor fuel elements (Swanson, 1988). The studies were done to support operation of the PUREX dissolvers when processing fuels grade N Reactor fuel which had been stored under water for over 10 years. Many of the fuel elements had been damaged during reactor discharge and sorting operations. The damaged cladding exposed uranium metal to the basin water and allowed it to oxidize.

Some of the oxidized uranium in the hot cell studies was due to water reaction with the fuel elements while in the fuel storage basins and the remainder was formed during the hot cell test when potassium hydroxide (KOH) was used to convert the uranium fluoride compounds formed during cladding removal to uranium oxides.

The first runaway reaction occurred during a PUREX headend flowsheet simulation run. During this simulation run, a water reacted fuel element section had fallen apart during the decladding step and a large portion of the uranium had reacted with the ammonium fluoride decladding solution. The UF_4 solids were subsequently metathesized with KOH to form $UO_2 \cdot 2H_2O$. The runaway reaction occurred during dissolution of the broken fuel element and uranium oxide in a solution of 6 $\underline{M}$ HNO_3 and 0.6 $\underline{M}$ aluminum nitrate (ANN). Prior to adding acid, the cooling coil for the reaction vessel was turned on because a vigorous reaction was expected. Within seconds of the addition of the HNO_3 to the reaction vessel, the foam level rose to approximately equal the solution volume and would have overflowed the vessel if the reaction had not been quenched with water. The heat of reaction raised the solution temperature to 60°C in spite of the cooling coil being on.

The second runaway reaction occurred during dissolution of a fuel element that had gone through the decladding step and then was held in a water rinse for an extended period. The dissolution conditions were the same as those in the first runaway reaction. In this case, no visible reaction occurred until several minutes after the ANN and HNO_3 were added. Then the foam level rose very rapidly and water was added to quench the reaction. The reaction became so vigorous that solution spewed out of the dissolver vessel. After about a minute the foaming subsided about as fast as it had built up.

The results of these studies indicated that the oxidized N Reactor fuel initially reacts very rapidly in a solution of 6.6 $\underline{M}$ HNO_3 and 0.6 $\underline{M}$ ANN and may produce runaway reactions. When a more dilute solution of 3 $\underline{M}$ HNO_3 and 0.3 $\underline{M}$ ANN was used in a later test, the oxidized uranium was dissolved under controlled conditions.

As discussed earlier, low operating temperature, low nitric acid concentration, low nitrous acid concentration and a well stirred vessel will tend to slow the reaction rate, while the opposite conditions will increase the reaction rate.

The reaction rate also can be controlled by limiting the surface area available for reaction. For the sludge processing dissolver, this means limiting the amount of undissolved uranium that is present in the dissolver at any given time. This could be done by using a small enough batch size that the reaction heat can be removed adequately even if all of the uranium reacts in a very short time, or by adding the sludge in increments with adequate time in between to allow the fast reacting uranium particles to dissolve before more sludge is added.

The average particle size of the sludge is about 10 microns which means that there will be a large surface area for reaction. Reaction control will be especially critical as the dissolution is initiated. After the reaction starts the surface area will decrease as particles become smaller and then completely go into solution.

The following alternatives for dealing with the initial rapid reaction rate were evaluated:

(a) Use dilute nitric acid to control the reaction rate. Transfer a full sludge batch into the dissolver, heat the dissolver to boiling temperature, and then continuously add nitric acid to maintain the acid concentration in the 1-2 $\underline{M}$ range.

(b) Limit the amount of unreacted uranium that is present in the dissolver. This would be done by calculating the amount of acid that will be required and adding it to the dissolver first. Then transfer the sludge into the dissolver at a

slow enough rate that the reaction is spread out over a period of several hours.

(c)   Use dilute acid <u>and</u> control the amount of unreacted uranium that is present in the dissolver. Part of the water used to transfer the sludge could be transferred to the dissolver after allowing the sludge to settle in the lag storage tank. Nitric acid would be added to this to make a 1-2 $\underline{M}$ solution. The solution would be heated to boiling and then both sludge and acid would be added to the dissolver continuously over a period of several hours.

Calculations were done to determine the reaction rate and maximum heat generation rate for the alternatives for two bounding case sludge streams. The two types of sludge used in the calculations are not typical sludge from the basins but represent the worst cases for reactivity and heat generation. The first sludge was assumed to be 100% UO_2 with a particle size of 10 microns. This represents a worst case for reaction rate. Samples show that the floor and pit sludges generally are mostly iron oxide and sand and contain less than 20 wt% uranium.

The other sludge chosen for these calculations consists of 100% uranium metal fragments in the size range of 250 microns to 6 mm in diameter. This represents canister wash sludge from the dropout drums and is the worst case for heat of reaction. An average particle size of 1 mm was assumed for this sludge when performing calculations.

4.2.1   Evaluation of Alternative (a)

In this alternative, the full sludge batch would be transferred into the dissolver before the start of dissolution. Then enough acid would be added to make a 1-3 $\underline{M}$ solution and the dissolver would be heated to boiling temperature. The acid concentration would be monitored with a conductivity probe and as the sludge dissolved in the acid, more acid would be added as necessary to maintain the concentration at 1-3 $\underline{M}$. Cooling water to the cooling coil would be adjusted as necessary to remove the heat generated by the reaction. The dissolver temperature, dissolver vacuum, and NO_x concentration in the off-gas would be used to monitor the reaction. After the reaction rate slowed down as indicated by the rate of NO_x evolution, acid consumption, and temperature, the cooling water flow would be reduced and heat turned on as necessary to maintain the temperature at boiling.

If these parameters indicated an excessive reaction rate, the cooling water flow to the dissolver would be increased to slow the reaction. If this measure was not adequate, quench water would be added to slow or stop the reaction.

Calculations were done to determine the reaction rate and maximum heat generation rate for this alternative for three batch sizes and two types of sludge. Batch sizes chosen were 160, 200 and 250 kg of uranium on a dry basis.

The calculations for the 100% UO_2 sludge were made based on the following reaction which is dominant at lower acid concentrations.

$$3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 4H_2O + 2NO$$
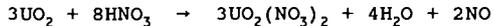
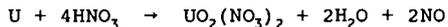The heat of reaction for this reaction is -25.4 kcal/mole U.

The following reaction rate equation was used (Ikeda, et.al., 1995):

$$\phi = (2.2 \times 10^4 e^{-79500/RT} + 0.46 e^{-36800/RT}[HNO_2])[HNO_3^-]_T^{2.3}$$

where ϕ is in units of $mol/cm^2/min$, R is the gas constant, and T is the absolute temperature. At boiling temperature and low nitric acid concentrations, the nitrous acid concentration would be very low so that term was neglected in the reaction rate equation. The nitric acid concentration was used for the total nitrate concentration which would be the case at the start of batch dissolution.

The calculations for the 100% U metal sludge were based on the following reaction which is dominant when dissolving uranium metal at low acid concentrations.

$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO$$

The heat of reaction for this reaction is -238 kcal/mole U.

The following rate equation was used for dissolution of uranium metal (Swanson, 1985):

$$\text{Dissolution rate} = k([HNO_3] + 2[U])^{2.6}$$

where $k = 4.6$ at 103°C and the rate units are mg $U/hr\text{-}cm^2$.

The uranium metal fragments will dissolve much slower than the uranium oxides due to the lower surface area to weight ratio. Uranium metal particles up to 6 mm (0.25 in.) in diameter may be present in the sludge. In dissolution tests of pieces of N Reactor fuel, Swanson reported dissolution rates of 75 and 100 mg $U/hr\text{-}cm^2$ in 3 $\underline{M}$ HNO_3 at boiling and 97-98°C, respectively. The reaction rate was 270 mg $U/hr\text{-}cm^2$ in 5 $\underline{M}$ HNO_3 at 97-98°C.

The results of the reaction rate and heat generation calculations for the three batch sizes and two sludge types are shown in Table 4.1. The heat generation rates at 2 and 3 $\underline{M}$ HNO_3 are so high that it would be difficult to remove the heat fast enough

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without an over size off gas line and condenser. The cooling
water probably would have to be turned on before the reaction
started in order to get a quick enough response to control the
reaction. This would make it nearly impossible to operate close
to boiling temperature.

Computer modeling calculations by SGN (Nevers and Flament, 1998)
for batch dissolution of 160 kg of UO_2 powder in 1-2 $\underline{M}$ HNO_3
showed heat generation rates between 33 and 68 KW. Those
calculations included a 1 and 2 hr heat up times rather than the
instantaneous rate assumed when calculating the values in
Table 4.1. The gradual heat up would result in a slower reaction
rate and a lower maximum heat generation rate. The 1-2 hr heat
up time better simulates how a batch dissolver would operate.

Table 4.1 Initial Reaction Rates and Heat Generation for Batch
Addition of Sludge to the Dissolver

Sludge Type	Batch Size kg U	2 $\underline{M}$ HNO_3		3 $\underline{M}$ HNO_3	
		Rxn Rate mol/min	Heat Gen KW	Rxn Rate mol/min	Heat Gen KW
Floor/Pit	160	74.1	132	190	336
Floor/Pit	200	93.4	165	237	420
Floor/Pit	250	116.8	207	297	525
Dropout Drum	160	0.99	16.4	2.83	47
Dropout Drum	200	1.24	20.6	3.55	59
Dropout Drum	250	1.55	25.7	4.44	74

Dissolver control would most likely be difficult using this
alternative due to the rather high heat generation rate. The
rapid reaction rate at the beginning of the dissolution period
would result in a high concentration of NO_x in the dissolver off
gas for a short period of time. This would be followed by a very
low concentration of NO_x generated during the rest of the
dissolver cycle. If this alternative were implemented, the NO_x
absorber in the dissolver off-gas system would need to be
designed to handle the large peak of NO_x which would make it much
larger than necessary for handling the NO_x concentration during
the rest of the dissolver cycle.

The advantage of this alternative is that the entire sludge batch could be transferred into the dissolver at one time which would make it easier to keep the solids suspended than when metering in the sludge stream at a slow rate. If the velocity in the line is not adequate to keep the solids suspended, they will settle out and plug the line. Maintaining adequate velocity in a line to keep the solids suspended is easier at a higher transfer rate.

4.2.2 Evaluation of Alternative (b)

For this alternative, all the nitric acid needed to dissolve a batch would be added to the dissolver before transferring in any sludge. The acid would be heated to boiling temperature and then the sludge would be slowly fed to the dissolver over a period of hours. The small sludge particles would dissolve almost immediately after coming in contact with the boiling nitric acid. This would result in a slow steady reaction over the course of the sludge addition. The sludge addition rate could be slowed down or stopped if the reaction became too vigorous. After all of the sludge batch was transferred into the dissolver, the dissolver would be held at boiling temperature long enough period to dissolve most of the U metal and iron oxide in the sludge.

The uranium reaction rate and heat generation rate were calculated for three sludge feed rates and two types of sludge. The feed rates selected were 2, 4, and 6 liters/min at a uranium concentration of 120 g/l. This corresponds to 14.4, 28.8, and 43.2 kg/hr. The two types of sludge are the same as those described in the previous section. The heat generation rates were calculated assuming all the uranium dissolved immediately when it contacted the nitric acid in the dissolver. This is a conservative assumption for the dropout drum sludge which contains uranium metal particles up to 6 mm in diameter. The results of the reaction rate and heat generation calculations for this alternative are shown in Table 4.2.

Table 4.2 Reaction Rates and Heat Generation for Continuous
         Sludge Feed

Sludge Type	Sludge Feed Rate, l/min	Reaction Rate mol U/min	Heat Generation, KW
Floor/Pit	2	1.01	1.8
Floor/Pit	4	2.02	3.8
Floor/Pit	6	3.03	5.4
Dropout Drum	2	1.01	17
Dropout Drum	4	2.02	33
Dropout Drum	6	3.03	50

The heat generation rates for the floor/pit sludge are less than
10 KW for all of the flowrates analyzed. The heat generation
rates for the dropout drum sludge are considerably higher than
for the floor/pit sludge. The reason for this is the higher heat
of reaction for dissolving U metal in nitric acid
(-238 Kcal/mole) compared to dissolving UO_2 (-24.4 Kcal/mole).

Computer modeling calculations by SGN (Nevers and Flament, 1998)
at feed rates of 20 and 40 kg/hr for 10 micron UO_2 particles
indicated a heat generation rate of 1.8 - 6.2 KW which is
consistent with the values in Table 4.2. The values in Table 4.2
for dropout drum sludge are bounding numbers since the 6 mm
diameter U metal pieces will not dissolve quickly unless the acid
concentration is around 12 $\underline{M}$ (Nevers and Flament, 1998).

4.2.3 Evaluation of Alternative (c)

This alternative is similar to alternative (b) except part of the
water in the lag storage vessel would be transferred to the
dissolver ahead of the sludge and used to dilute the initial
nitric acid concentration in the dissolver.

The dissolver would be operated as follows. The agitation in the
lag storage vessel would be shut down and the solids allowed to
settle. Then one third of the water in the tank would be
transferred to the dissolver. Enough acid would be added to the
dissolver to make a 6 $\underline{M}$ acid solution and the dissolver would be
heated to boiling temperature. Then the agitation in the lag
storage vessel sludge would be restarted to suspend the sludge
and the sludge would be fed to the dissolver continuously over a
8 hr period. The acid concentration in the dissolver would be
monitored and more acid added as necessary to maintain the
concentration above 1 $\underline{M}$. The heat to the dissolver and water

flow to the cooling coils would be adjusted as necessary to control the temperature. After all of the sludge batch was transferred into the dissolver, the dissolver would be held at boiling temperature for a long enough period to dissolve most of the U metal and FeOOH in the sludge.

The reaction rates and heat generation for this alternative are bounded by the values in Table 4.2 since the initial nitric acid concentration in the dissolver would be lower.

Removing a third of the water from the lag storage vessel would concentrate the sludge by a factor of 1.5. This would make it more difficult to transfer the sludge into the dissolver. Fresh water could be used to dilute the nitric acid to get around this problem. Adding fresh water might increase the waste volume transferred to underground storage. This depends on whether the waste stream will need to be diluted anyway to ensure it can be transferred to the underground tank without plugging the transfer line into the tank.

4.2.4 Reaction Control Conclusion

After evaluating the above alternatives, the conclusion was reached that acid should be added to the dissolver first and then the sludge should be fed to the dissolver continuously over a period of several hours to limit the amount of uranium that is available for reaction. Additional nitric acid can be added to the dissolver continuously during sludge addition to maintain a constant acid concentration. This will give much better control of the reaction than adding all of the sludge to the dissolver initially and then feeding in nitric acid to control the reaction rate.

The dissolver will be easier and safer to operate close to or at boiling temperature than at a lower temperature. At boiling temperature, excess heat generation will increase the boiloff rate rather than increase the temperature. Since reaction rate is a function of temperature, if the temperature can only increase a few degrees before it starts boiling, then there cannot be a big increase in reaction rate due to an increase in temperature. The uranium reaction rate reaches a maximum at 95-100°C and then decreases to boiling temperature as the nitrous acid concentration decreases at this temperature.

Following is a description of the dissolver control scheme as envisioned at this time. This is preliminary and will most likely change as the details of dissolver design and operation are developed.

If the dissolver is operated at 95°C instead of at boiling, an increase in reaction rate can be detected by an increase in temperature. The dissolver temperature and vacuum as well as the NO_x concentration in the offgas will be closely monitored to

ensure that the reaction remains under control. If the
temperature increases from 95°C to 100°C, both sludge addition
and acid addition will be stopped, and the cooling water flow
will be increased. The sludge addition control system will be
interlocked to the dissolver temperature instrument to
automatically stop sludge addition at 105°C, if it has not been
done manually. If the temperature and NO_x concentration continue
to increase after the sludge feed is stopped and the cooling
water increased, water will be added from a drown tank to quench
the reaction. A decrease in dissolver vacuum is an indication
that the dissolver solution is boiling. If this is observed,
water from the drown tank should be used to quench the reaction.

4.3 Hydrogen Gas Generation

The water oxidation of U metal and U hydride produces H_2 which
becomes flammable at concentrations greater than 6 vol% in air.
Most of the uranium in the sludge has already been oxidized while
in the fuel storage basins and released hydrogen there. However,
hydrogen gas generation has been observed in several samples of
sludge from KE Basin canisters indicating that U metal was
present. The fuel wash sludge from the dropout drums is expected
to contain mostly U metal fragments, but may also contain up to
5 wt% UH_3. Many of U metal fragments will have bare metal
surfaces since the washing process can be expected to knock off
most of the uranium oxide that formed during storage in the
basins. The uranium metal will be slowly oxidizing and
generating H_2 during transport to the sludge processing facility
and storage in the lag storage tank.

The H_2 generation rate was calculated for a 160 kg batch of
dropout drum sludge made up of 100% U metal fragments in the size
range of 250 microns to 6 mm. The calculations were done using
the following correlation for uranium metal corrosion in water
from the Spent Nuclear Fuel Project Technical Databook.

Log K = 7.634 - 3016/T   where T is in degrees Kelvin

The rate constant K is in units of mg wt gained/hr-cm^2 assuming
the uranium corrodes according to the following reaction.

$$U + 2H_2O \rightarrow UO_2 + 2H_2$$

If the mg of oxygen added to the uranium metal is converted to
gm-moles of H_2 released and a temperature of 318 K (45°C) is
plugged into the equation, it becomes

$$K = 8.8E-7 \text{ g-mol } H_2/hr\text{-}cm^2$$

If a conservative particle size of 250 microns is assumed for all
the sludge in a 160 kg batch, the H_2 generation rate calculated
by the above equation is 46 l/hr or 0.77 l/min. An air bleed
rate of 39 l/min (1.4 cfm) would be required to a vessel

containing a batch of this sludge in order to dilute the H_2 in the tank vapor space to less than 2 vol%. This would apply to the sludge transport vessel and the lag storage tank.

Nitric acid dissolution of the uranium oxides and uranium metal fragments in the dissolver will not produce any hydrogen gas. Dissolution of the UH_3 also is not expected to generate any hydrogen at the conditions that will be present in the dissolver.

However, the following reaction for dissolution of UH_3 in nitric acid was found in the literature (Swanson, 1985).

$$UH_3 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO + 1.5H_2$$
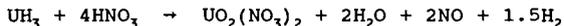
This reaction generates H_2, but the reaction is only expected to take place in dilute nitric acid ($< 1 \underline{M}$).

Calculation were done to determine the H_2 that would be generated assuming all the UH_3 in a sludge batch dissolved according the above reaction. This is a bounding case and would only occur if dilute nitric acid is used in the dissolver. Dissolving a 160 kg batch of sludge containing 5 wt% UH_3 (maximum UH_3 content in any sludge stream) would release 50 moles (1520 liters at 100°C and 1 atm) of H_2 into the dissolver off gas. The U hydride will have a small particle size and can be expected to dissolve quickly in nitric acid. No reaction rate data was found for U hydride in nitric acid. If all of the sludge batch were added to the dissolver at once, mixed with nitric acid, and heated, there would be an initial H_2 spike in the off-gas followed by little if any H_2 released during the rest of the dissolution cycle.

The hydrogen spike in the off-gas can be avoided by feeding the sludge to the dissolver over a period of several hours rather than adding it all initially. If the 160 kg sludge batch is added to the dissolver continuously over an 8 hr period and the uranium hydride dissolved as soon as it contacted the nitric acid, the H_2 generation rate would be 3.2 l/min. An air bleed of 160 l/min (5.7 cfm) would be required to dilute the H_2 below 2 vol%. This is less than the air bleed rate that will be needed to oxidize NO to NO_2 for efficient operation of the NO_x absorber in the dissolver off gas system.

5.0 RECOMMENDED CONCEPT FOR SLUDGE DISSOLUTION

The following process requirements that were listed earlier in this document will be addressed in this section:

- The uranium metal must be dissolved fast enough that cycle time is not excessive.

- The amount of undissolved FeOOH, TRU, and fission products must be minimized in the undissolved solids.

- Precipitation of gelatinous solids formed by the dissolution of silicates and precipitation of silica must be minimized or controlled so that the precipitate an be handled by downstream processing equipment.

- The amount of excess acid should be minimized.

- The dissolver design should accommodate mechanical agitation if possible.

5.1 Batch Size

The K Basis sludge will be transferred from the basins to the sludge processing facility in batches and will also be processed in batches. Many factors must be considered when selecting a batch size for the sludge treatment process. These factors include hazards classification, shielding requirements, criticality concerns, and processing rate. Another question that must be addressed is whether the batch size should be the same for the different sludge streams since the composition of the floor/pit sludges is quite different from the composition of the canister/wash sludge.

Several factors favor a smaller batch size for canister/wash sludge than for floor/pit sludge. The concentrations of U, Pu, and Cs-137 are 4.5 - 5 times higher in canister/wash sludge than in the floor/pit sludge. Therefore, the source term for safety evaluations, the radiation dose rate, and the amount of absorber that must be added for tank farm criticality requirements will be much higher on a per liter basis for canister/wash sludge than for floor/pit sludge. This must be weighed against the simplicity of a common batch size for sludge streams.

The conclusion was reached that a common batch size based on 160 kg of dry solids should be used for all sludge streams. At a solids concentration of 12 wt%, this will make a batch volume of 1215 liters. With a batch size of 160 kg of dry solids, it will take approximately 214 batches to process all the K basin sludge. Assuming a one batch/day processing rate, and 60% operating efficiency, 214 batches can be processed in a 1-year period. This fits in with the commitment to complete sludge processing within a 1-year period following removal of the fuel from the KE and KW Basins.

A batch size of 160 kg dry solids will allow mass limits to be used for criticality control. One third of a minimum critical mass of 1.25% enriched uranium is 204 kg which is a factor of 1.27 times the 160 kg batch size. Even if the conservative assumption is used that a 160 kg batch is composed of 100% uranium, there will still be 44 kg margin between the batch size and an operating limit of 204 kg of uranium.

The neutralized waste will be hauled to the waste tank by truck using a shielded container so it is desirable to keep the batch size from getting too large. With a sludge batch size of 160 kg dry solids, the volume of a batch of neutralized waste from processing KE basin sludge is expected to be about 6500 liters. A waste batch of this size can most likely be hauled in one truck load. If the volume of a batch of waste gets much larger than this, it will probably take two truckloads per batch to haul the waste from the sludge processing facility to the waste tank.

5.2 Uranium Dissolution

As discussed earlier, the dissolution rates for different sludge streams are very different. The uranium oxides and hydride will dissolve quickly in dilute HNO_3 due to their small particle size while the uranium metal fragments from fuel washing and the FeOOH will require more concentrated HNO_3 and/or longer digestion times. The uranium in the floor/pit and settler tank sludges is mostly in the form of uranium oxides with a particle size around 10 microns. Any uranium metal and uranium hydrides in the floor/pit sludges are also expected to have a small particle size. The uranium in these sludges will dissolve quickly even in dilute (1-2 $\underline{M}$) HNO_3.

The fuel wash sludge that will collected in the dropout drums is expected to be mostly uranium metal with a particle size between 250 microns and 6.4 mm for the KE basin and between 500 microns and 6.4 mm for the KW basin. Dissolving the uranium in these sludges will require more concentrated (5-6 $\underline{M}$) HNO_3 to complete dissolution in a reasonable time.

5.2.1 Floor/Pit and Settler Tank Sludges

The finely divided uranium in the floor/pit and settler tank sludges will react very rapidly in boiling nitric acid even at low concentrations. The conclusion reached in the safety section of this document was that the best way to control the reaction is to add the sludge to the dissolver continuously over a period of several hours, thus limiting the amount of uranium that is available to react at any given time. Computer modeling calculations by SGN (Nevers and Flament, 1998) indicate that a minimum HNO_3 concentration of 4.2 $\underline{M}$ at 100°C is required to continuously dissolve the 500 micron uranium metal particles that could be present in the KW settler tank sludge. The maximum heat generation rate at these conditions is 13.4 KW. An acid concentration of 6 $\underline{M}$ was selected for dissolving the floor/pit ans settler tanks sludge since hot cell tests indicate that the TRU concentration in the undissolved solids will be lower using 6 $\underline{M}$ HNO_3 than with 4 $\underline{M}$ HNO_3 (Carlson et al, 1998a, Carlson et al, 1998b).

This following paragraphs describe a recommended process for dissolving the floor/pit and settler tank sludge while

accommodating the conclusions reached in the safety section. These sludge streams should be dissolved as described in the following paragraphs.

A batch of 600 liters of 6 $\underline{M}$ nitric acid solution will be made up in the dissolver. The acid will be agitated and heated to 95°C. Then sludge will be pumped into the dissolver continuously at a rate of 2.5 l/m (20 kg solids/hr). The dissolver temperature and vacuum along with the NO_x concentration in the off gas will be monitored to ensure that the reaction is under control. The Kr-85 and Xe concentration in the off gas will be monitored to track U metal dissolution. The acid concentration will be monitored using a conductivity probe. Additional acid will be added continuously to maintain the acid concentration at approximately 6 $\underline{M}$.

At a feed rate of 2.5 l/min, it will take 8 hrs to transfer the 1215 liter batch of sludge into the dissolver. The dissolver will be held at 95°C for 2 hrs after sludge addition is completed to ensure that essentially all of the uranium is dissolved. Then the dissolver will be cooled to 45°C and the solution will be transferred out of the dissolver. A dissolver vessel with a capacity of 1000 gals (3785 l) and a diameter of 4 ft (122 cm) is recommended for dissolving the sludge as described above. With this configuration, the initial 6 $\underline{M}$ acid makeup in the dissolver would come to a depth of 1.68 ft (51 cm). This is considered adequate to cover the blades of a mechanical agitator. The final solution volume in the dissolver when processing a batch of KE floor sludge would be approximately 550 gals (2080 l) which would come to a solution depth of 7.45 ft (227 cm). This would leave a 3 ft headspace in a 4 ft diameter 1000 gal tank.

A critical component of the sludge dissolution system as described above is the sludge feed system. The feed system must be capable of feeding the sludge into the dissolver at a slow controlled rate without allowing the suspended solids to settle out in the transfer lines.

One possible solution to the above problem is to recirculate the sludge from the lag storage tank to a small head tank located above the dissolver. The recirculation rate would need to be high enough to keep all the solids suspended. The sludge could then be fed from the head tank down a short vertical line into the dissolver. Fluidic pumps also have been successfully used to feed suspended solids at a controlled rate without plugging lines.

Some development work will be needed to ensure that a feed system for continuous sludge addition will work, but this is not an insurmountable problem.

5.2.2   Canister/Wash Sludge from Dropout Drums

The conclusion reached in the section on reaction control is that the sludge should be added to the dissolver continuously over a period of several hours. If the reaction rate is controlled by feeding the sludge into the dissolver slowly over a period of several hours, then dilute nitric acid is not required for reaction control.

Since the reaction rates for both uranium oxides and uranium metal increase with increasing temperature and HNO_3 concentration, the time required to dissolve the uranium in a batch of sludge can be minimized by operating the dissolver at or near boiling temperature with concentrated HNO_3. The dissolution rate of FeOOH also increases with temperature and HNO_3 concentration. Using concentrated acid will result in excess acid at the end of dissolution which is undesirable because it will increase the amount of caustic needed for neutralization. This in turn will increase the waste volume sent to underground storage. However, completing a dissolver cycle in approximately 20 hrs is a higher priority than minimizing the waste volume that will be sent to the underground waste tank.

If the following reaction rate equation for N Reactor fuel dissolution at 103°C (Swanson et al, 1985)

$$\text{Dissolution rate, mg/hr-cm}^2 = 4.6 \ ([HNO_3] + 2[U])^{2.6}$$

is converted into a linear penetration rate, it becomes

$$\text{Penetration rate, cm/hr} = 2.42E\text{-}4 \ ([HNO_3] + 2[U])^{2.6}$$

Using the above equation, the time required for total dissolution of a 6 mm particle of uranium metal in HNO_3 at 103°C would be 71 hrs 3 $\underline{M}$ HNO_3, 19 hrs in 5 $\underline{M}$ HNO_3, and 12 hrs in 6 $\underline{M}$ HNO_3. These dissolution times are in addition to the time in which sludge is being continuously fed to the dissolver since some of the 6 mm particles may be added right at the end of the continuous feed.

The following alternatives were evaluated for completing dissolution of the U metal fragments after the fast reacting uranium oxides and hydride have dissolved.

(1)   Dissolve the sludge in two cuts. The first cut would dissolve the fast reacting uranium oxides and hydrides in dilute acid and the second cut would dissolve the slower reacting uranium metal fragments and FeOOH in a smaller volume of more concentrated acid.

(2) Dissolve the fast reacting uranium oxides and hydrides in
     dilute acid, then add additional acid to increase the
     concentration in order to reduce the time required to
     dissolve the uranium metal fragments and FeOOH.

(3) Leave a heel of undissolved solids in the dissolver through
     two or three dissolver cycles and then use more concentrated
     acid and a longer digestion time to dissolve as much of the
     heel as possible.

(4) Use more concentrated acid for the entire dissolution cycle.
     The sludge feed rate would control the reaction rate for the
     fast reacting uranium oxides and hydrides.

In alternative (1), a 2 $\underline{M}$ HNO_3 solution would be made up in the
dissolver and heated to 95°C. Then the sludge would be fed into
the dissolver over an 8 hr period. More acid would be added
continuously to maintain the concentration at 1-2 $\underline{M}$. After all
the sludge batch was added to the dissolver and the reaction
slowed down, the dissolver would be cooled and the agitation shut
off to allow the solids to settle. Then half of the solution
would be transferred out of the dissolver and through a
centrifuge to remove suspended solids.

The uranium metal fragments are dense enough that they should all
stay in the dissolver. However, some of the small particles of
FeOOH and silica would be entrained in the solution removed from
the dissolver. These solids would be returned to the dissolver.
Then fresh acid would be added to the dissolver to make a 6 $\underline{M}$
solution. The dissolver would again be heated to boiling and
held there until uranium metal dissolution was complete. This
would take about 12 hrs. The acid concentration would be allowed
to drop to 3 $\underline{M}$ at the end of the second cut to decrease the
amount of caustic needed to neutralize the acid in a subsequent
step.

Alternative (2) is the same as alternative (1) up to the point
that the initial reaction rate slows down. At that point, the
acid concentration in the dissolver would be increased to 6 $\underline{M}$ by
adding fresh acid to the 95°C dissolver solution. Then, the
dissolver would be held at 95°C until dissolution of the uranium
metal was complete which would take about 12 hrs. This
alternative was evaluated by SGN (Nevers and Flament, 1998) at a
temperature of 100°C. The conclusion was that the 6 mm uranium
fragments could be dissolved in a total of 19 hrs by this method.

Alternative (3) would reduce the dissolver cycle time by leaving
a heel of undissolved solids in the dissolver through several
dissolution cycles. It would be the same as alternatives (1) and
(2) up the point that the initial reaction slows down. Then
enough acid would be added to dissolve the remaining soluble
materials and leave an ending concentration of 1 $\underline{M}$ acid. The
dissolver would be held at 95°C until the dissolver acid

concentration and the Kr-85 and Xe concentration in the off gas
indicated that the remaining soluble materials were dissolving
very slowly. At that point, the dissolver would be cooled and
the agitation turned off.

The undissolved solids would be allowed to settle and then the
solution would be transferred out of the dissolver and through
the centrifuge. Since the density of the uranium metal is much
higher than the density of the other sludge components, the
uranium metal fragments would quickly settle to the bottom of the
dissolver when the agitator is shut off. This would allow
solution to be transferred out of the dissolver without much risk
of entraining uranium metal fragments. After two to three
dissolver cycles, a heel cleanout would be done. The solids in
the dissolver would be digested for several days using
concentrated HNO_3. Then the dissolver would be cooled and the
acid and undissolved solids would be transferred out the
dissolver and through the centrifuge.

In alternative (4), 6 $\underline{M}$ HNO_3 would be made up in the dissolver
and heated to 95°C. Then sludge would be continuously added to
the dissovler over an 8 hr period. Acid would be added to
maintain the concentration at approximately 6 $\underline{M}$.

Alternatives (1) and (3) were rejected because they are
complicated and involve additional solids/liquid separations.
Alternatives (2) and (4) are the same except for the acid
concentration during the sludge addition period. Alternative (4)
is considered the best for the following reasons:

(a)   Less water would need to be added when making up the initial
      acid in the dissolver.

(b)   The reaction rate would be more constant since less uranium
      would build up in the dissolver during sludge addition and
      there would be no increase in acid concentration.
      Increasing the acid concentration could cause a sudden
      increase in reaction rate.

The following paragraphs describe the recommended method to
dissolve the canister/wash sludge using Alternative (4).

A batch of 600 liters of 6 $\underline{M}$ nitric acid solution will be made up
in the dissolver. The acid will be agitated and heated to 95°C.
Then sludge will be pumped into the dissolver continuously at a
rate of 2.5 l/m (20 kg solids/hr). The dissolver temperature and
vacuum along with the NO_x concentration in the off gas will be
monitored to ensure that the reaction is under control. The
Kr-85 and Xe concentration in the off gas will be monitored to
track U metal dissolution. The acid concentration will be
monitored using a conductivity probe. Additional acid will be
added continuously to maintain the acid concentration at
approximately 6 $\underline{M}$.

At a feed rate of 2.5 l/min, it will take 8 hrs to transfer the 1215 liter batch of sludge into the dissolver. The dissolver will be held at 95°C for another 12 to 14 hrs after sludge addition is completed to ensure that essentially all of the 6 mm uranium metal particles are dissolved. Since Kr-85 and Xe will be released as long as uranium metal is being dissolved, the Kr-85 and Xe concentration in the off gas will be used to determine when dissolution of uranium metal is complete.

The dissolver configuration described in the previous section could be used to dissolve the canister/wash sludge as described above.

5.3 FeOOH Dissolution

The FeOOH dissolves slower than uranium, but it should nearly all be dissolved after 10 hrs in 6 $\underline{M}$ HNO_3. Hot cell dissolution tests with sludge samples have shown that greater than 99% of the FeOOH is dissolved after boiling for 24 hrs in 6 $\underline{M}$ HNO_3 (Carlson et al, 1998a, Carlson et al, 1998b). Any FeOOH that does not dissolve will be transferred out of the dissolver with the other undissolved solids and will be treated downstream to reduce the TRU and Cs-137 concentration. The TRU concentration must be less than 100 nCi/g and the Cs concentration less than 32 Ci/m^3 to meet the ERDF acceptance criteria.

5.4 Dealing with Potential Gel Formation

The potential for gel formation during the dissolution of some sludge types was described earlier. When processing this sludge, the dissolver must be operated at conditions that minimize silica precipitation as much as possible, or that result information of the type of precipitate that can be handled by downstream processing equipment.

Manipulating process conditions to ensure that the silica precipitates in a form that can be filtered rather than forming a gel is the key to processing materials that contain soluble silicates. One way to help form a filterable precipitate is to use a strong acid at or near its boiling point (Terry, 1983b). The process conditions described in the previous sections (6 $\underline{M}$ HNO_3 at 95°C) will not prevent silica precipitation, but should cause the silica to precipitate in a form that can be filtered and washed.

The dissolver should also be designed to minimize handling problems with any gel that might form. As discussed earlier, at the La Hague reprocessing plant in France, problems with gel formation have been reduced to a manageable level by using a mechanical agitator. The gel formation was encountered while processing incinerator ashes contaminated with Pu. The hydraulic shear of a mechanical agitator apparently prevents the growth of gel particles above a threshold size. The gel particles that

formed when using a mechanical agitator were small enough that they were manageable in the equipment downstream from the dissolver. The cylindrical dissolver described in the previous section will allow the use of a mechanical agitator.

5.5 Recommendations for Dissolver Design

This section describes preliminary design recommendations for the sludge processing dissolver.

5.5.1 Dissolver Configuration

Several different dissolver configurations were discussed in the criticality safety section of this study. The geometrically safe configurations that were evaluated included annular, slab, and multiple barrel dissolvers. These configurations are more costly and complex to build than standard cylindrical vessels. They also would make solids removal more difficult. None of these configurations will allow good mixing with a mechanical agitator which may be needed from a processing standpoint for control of silica gel formation. The conclusion was reached that mass limits along with a nuclear poison should be used for criticality control as described in the safety section of this document.

The dissolver should be a cylindrical vessel with a capacity of 1000 gals (3785 l) and a diameter of 4 ft (122 cm) as described in Section 5.2.1.

5.5.2 Agitation

Since there is the potential for gel formation from the silicates in some of the sludge, a mechanical agitator will be used to agitate the solution in the dissolver vessel.

5.5.3 Cooling Equipment

The dissolver will be cooled by circulating water through an internal coil in the lower part of the vessel. The cooling system must be capable of removing the heat of generated by the dissolution of the uranium and other components in the sludge.

5.5.4 Heating Equipment

Heat will be supplied to the dissolver by either an external steam jacket or external electrical heaters. External heaters will be used to minimize internal structures that would interfere with agitation and sludge removal. Rapid heating of the dissolver will not be necessary so the additional heat transfer surface provided by internal heaters will not be necessary. External heaters will also reduce the number of penetrations through the dissolver wall. Depending on where the sludge processing facility is built, process steam may not be available.

5.5.5 Materials of Construction

The sludge dissolver will be used for nitric acid service so it must have good corrosion resistance to nitric acid. Design Guidelines for the Selection and Use of Stainless Steels lists 304L and 430 stainless steels for nitric acid service. Type 304L is an austenitic stainless steel which has better weld properties than the ferritic 430 stainless steel. Therefore, type 304L stainless steel is recommended as an acceptable material of construction for the dissolver.

Other materials may also be acceptable or even superior to 304L stainless steel. Additional evaluation will be performed in the early phases of conceptual design to determine how 304L is affected by the intergranular corrosion phenomena that can occur when oxidizing ions such as Fe^{+3} are present in solution along with HNO_3.

5.5.6 Instrumentation and Control

The following instrumentation is recommended to monitor and control the dissolver. This list should be considered the minimum required.

•   Solution conductivity to monitor the acid concentration

•   Solution temperature

•   Liquid level

•   Specific gravity

•   Dissolver vacuum control system

•   Sludge addition flow rate and control system

•   Acid addition flow rate and control system

•   Off gas flow rate

• NO_x concentration in the off gas

• H_2 concentration in the off gas

•   Kr-85 concentration in the off gas

•   Xe concentration in the off gas

•   Gamma monitor to detect fissile material heel left in the bottom of the dissolver

- Cooling water flow rate

- Heater controls

The vacuum control system should consist of an automatic control loop that would adjust a flow control valve in the off gas system as necessary to control the dissolver vacuum at the set point.

The sludge addition control system should be interlocked to the temperature instrument so that a high temperature indication will shut off the sludge addition. A series of steps that operators should take in response to an increasing dissolution reaction was presented in Section 4.2.4.

6.0 CONCLUSIONS

The major conclusions from this study on dissolution of the K Basin sludge are listed below.

1. The recommended batch size is 160 kgs of solids (dry basis) suspended in water as a 12 wt% slurry. Approximately 214 batches will be required to process all of the sludge with this batch size.

2. The dissolver should be operated in a semi-continuous mode. The sludge and nitric acid should be added continuously, but the dissolver product solution and undissolved solids should be removed as a batch.

3. The sludge should be fed to the dissolver continuously over an 8 hr period at a rate of approximately 20 kg solids/hr. This will control the reaction rate by limiting the amount of finely divided uranium that is available for reaction at any time. It will also level out the NO_x concentration in the dissolver off gas.

4. The recommended acid concentration and temperature for dissolving the sludge are 6 $\underline{M}$ HNO_3 at 95°C.

5. Mass limits and a soluble nuclear poison are recommended for criticality control. This will allow the use of a cylindrical dissolver vessel with a mechanical agitator.

7.0 REFERENCES

American Iron and Steel Institute, <u>Design Guidelines for the Selection and Use of Stainless Steel</u>, April 1977.

<u>Bibliography of the Kinetics of Dissolution of UO$_2$ in Nitric Acid</u>, CEA-TR-2216, December 1986.

Blaine, 1960, <u>Dissolution of Power Reactor Fuel Cores</u>, HW-66320, August 1960.

Blanco, R. E. and C. D. Watson, Reactor Handbook, Vol. II, <u>Fuel Reprocessing</u>", second ed., Stoller, S. M., and R. B. Richards, editors, 1961.

Bredt, P. R., C. H. Delegard, A. J. Schmidt, A. H. Zacher, B. M. Thorton, K. L. Silvers, 1998, "K Basin Sludge Scoping and Supplementary Analyses", letter report 28507-05, Pacific Northwest National Laboratory.

Carlson, C. D., C. H. Delegard, I. E. Burgeson, A. J. Schmidt, K. L. Silvers, 1998a, "K Basin Sludge Conditioning Testing - Nitric Acid Dissolution Testing of K East Area Sludge Composite, Small and Large Scale Testing", letter report 29317-10, Pacific Northwest National Laboratory.

Carlson, C. D., C. H. Delegard, I. E. Burgeson, A. J. Schmidt, K. L. Silvers, 1998b, "K Basin Sludge Conditioning Testing - Nitric Acid Dissolution Testing of K East Canister Sludge", letter report 29317-09, Pacific Northwest National Laboratory.

Ikeda, Y., Y. Yasuike, K. Nishimura, S. Hasegawa, Y. Takashima, 1995, <u>Kinetic Study on Dissolution of UO2 Powders in Nitric Acid</u>, Journal of Nuclear Materials, 224: 266-272, March 1995.

Inoue, A., 1986, <u>Mechanism of the Oxidative Dissolution of UO_2 in HNO_3 Solution</u>, Journal of Nuclear Materials, 138: 152-154.

Katz, J. J., E. Rabinowitch, 1951, <u>The Chemistry of Uranium</u>, Chapman and Hall, New York.

Kessler, S. F., 1998, <u>Criticality Safety Evalution Report for the Cold Vacuum Drying Facility's Process Water Handling System</u>, HNF-SD-SNF-CSER-006, Rev 1.

Nevers, A. C., T. A. Flament, 1998, <u>Dissolution of Sludges Containing Uranium Dioxide and Metallic Uranium in Nitric Acid</u>, HNF-3119, Rev 0.

Nishimura, K., T. Chikazawa, S. Hasegawa, H. Tanaka, Y. Ikeda, Y. Yasuike, Y. Takashima, 1995, <u>Effect of Nitrous Acid on the Dissolution of UO_2 Powders in Nitric Acid</u>, Journal of Nuclear Science and Technology, 32: 157-159, February 1995.

Pearce, K. L., S. C. Klimper, and T. L. Flament, 1998, <u>105-K Basin Material Design Basis Feed Description for Spent Nuclear Fuel Project Facilities, Volume 2, SLUDGE</u>, HNF-SD-SNF-TI-009, Vol 2, Rev 2, Numatec Hanford Corporation, Richland, Washington.

Pool, K. H., C. H. Delegard, A. J. Schmidt, K. L. Silvers, 1998, Results from Test 1, "Acid Digestion of Zeolite and Hydrated Iron Oxide in Proportions Representative of Analyzed KE Sludge Materials", letter report 28510-04, Pacific Northwest National Laboratory.

Pool, K. H., C. H. Delegard, A. J. Schmidt, B. M. Thorton, K. L. Silvers, 1998, Results from Test 4, "Acid Digestion of Mixed-bed Ion Exchange Resins", letter report 28510-10, Pacific Northwest National Laboratory.

Shabbir, M. and R. G. Robbins, 1968, <u>Kinetics of the Dissolution of Uranium dioxide in Nitric Acid</u>, Journal of Applied Chemistry, May 1968.

Swanson, J. L., L. A. Bray, H. E. Kjarmo, J. L. Ryan, C.L. Matsuzak, S. G. Pitman, J. H. Haberman, 1985, <u>Laboratory Studies of Shear/Leach Processing of Zircaloy Clad Metallic Uranium Reactor Fuel</u>, PNL-5708, Pacific Northwest Laboratory, December 1985.

Swanson, J. L., 1988, <u>Recent Studies Related to Head-End Fuel Processing at the Hanford PUREX</u>, PNL-6609, Pacific Northwest Laboratory, August 1988.

Taylor, R. F., E. W. Sharratt, L. E. M. de Chazal, D. H. Logsdail, 1963, <u>Dissolution Rates of Uranium Dioxide Sintered Pellets in Nitric Acid Systems</u>, Journal of Applied Chemistry, January 1963.

Terry, B., 1983a, <u>The Acid Decomposition of Silicate Minerals Part I. Reactivities and Modes of Dissolution of Silicates</u>, Hydrometallury, 10: 135-150, 1983.

Terry, B., 1983a, <u>The Acid Decomposition of Silicate Minerals Part II. Hydrometallurgical Applications</u>, Hydrometallury, 10: 151-171, 1983.

Uriarte, A. L., R. H. Rainey, 1965, <u>Dissolution of High-density UO_2, PuO_2, and UO_2-PuO_2 Pellets in Inorganic Acids</u>, ORNL-3695, April 1965.

Wooten, D. W., February 28, 1995, "K Basin Sludge Retrieval Assay Evaluation", letter report.

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