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GAS BEHAVIOR IN LARGE DIAMETER CONTAINERS (LDCs) DURING AND FOLLOWING LOADING WITH 105K EAST SLUDGE

Prepared For the U.S. Department of Energy
Assistant Secretary for the Environmental Management
Project Hanford Management Contract for the
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Fluor Hanford
P.O. Box 1000
Richland Washington

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J. L. Shelor, Technical Resources International, Inc
M. G. Plys, Fauske & Associates, Inc.
M Epstein, Fauske & Associates, Inc.
J. P. Sloughter, Numatec Hanford Company
John Abrefah, Pacific Northwest National Laboratory
C. H. Delegard, Pacific Northwest National Laboratory
A. J. Schmidt, Pacific Northwest National Laboratory

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J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

M. G. Plys
Vice President, Waste Technology
Fauske & Associates, Inc.

M Epstein
Vice President, Consulting
Fauske & Associates, Inc.

J. P. Sloughter, Numatec Hanford Company
Engineering Systems Manager
Spent Nuclear Fuel Project

C. H. Delegard
Staff Scientist
Pacific Northwest National Laboratory

A. J. Schmidt
Senior Engineer
Pacific Northwest National Laboratory

John Abrefah
Lead Scientist
Radiochemical Science & Engineering Group
Pacific Northwest National Laboratory

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EXECUTIVE SUMMARY

Hydrogen gas is generated within a Large Diameter Container (LDC) containing sludge by two mechanisms:

- Radiolysis
- The reaction of uranium directly with water.

The gas generated by these reactions can be released to the headspace of the LDC or it can be retained within the sludge as trapped bubbles and later exit the sludge by a mechanism known as an episodic release. Little is known about the exact mechanism of how the hydrogen gas is released from the sludge except to say:

For slow gas releases at the gas generation rate:

- Part of the gas will be released as it is generated and part will be retained.
- The proportions of how much is retained to how much is released are not well defined.
- The maximum gas retention for the sludge is postulated to be 35% (volume) (i.e., 2 m^3 of sludge can increase to a volume of 3.08 m^3 (sludge + gas). There is some evidence to indicate this is an accurate estimate of the maximum gas accumulation, but insufficient evidence to be conclusive.
- Once maximum gas retention is reached (postulated at 35% or less), the subsequently generated gas is released directly to the LDC headspace at the generation rate.

For episodic type gas releases:

- The rate and volume of the release are highly variable and are dependent on the manner in which the sludge retained the gas.
- There is strong evidence to suggest that gasses retained in the sludge will not be released except under extreme conditions of disturbance.
  - Attachment 12 describes experiments conducted at FAI that demonstrate the difficulty of causing gasses to release from sludge.
  - A report published by Purdue University, "Investigation of Sludge Material Response to Vibration", C. Wassgren, September 1999, Prepared for Westinghouse Savanah River Company under Purdue Research Foundation Award # AC07608-0, also describes the extreme difficulty and conditions necessary to cause retained gasses to release from the sludge.
- In general:
  - When the gasses are retained ~~high~~ in moderate to high strength sludge (≥1000 Pa) in small bubbles spread throughout the sludge, in much the same manner as bubbles in bread dough, releases are rare and slow, sometimes being spread over hours, with only a small fraction, less than 25%, of the gas being released.
  - When the gasses are trapped in large bubbles, such as vessel spanning bubbles, large magnitude disturbances are required to cause the gasses to

release and once the release starts, the release is generally quick, lasting only seconds, and the volume of gas released is large, 75 – 100%.

Two basic cases for the LDC are examined in this paper:

- A vented LDC and Cask containing air as the cover gas.
- A sealed/inerted LDC and Cask containing Argon as the cover gas.

For the vented case, two sub-cases are examined:

- Sub-case 1 – Episodic Release of Hydrogen. Assuming all generated hydrogen gas is retained in the sludge until there is ~~was~~ sufficient gas to cause a flammable condition in the headspace of the LDC. When sufficient gas exists, an episodic release occurs causing a flammable condition, 4% hydrogen in air. For this case, the generation time is measured from the start time for loading the first layer of sludge into the LDC to the time the sludge is first capable of containing 48 liters of hydrogen, 4% hydrogen in a 1200 liter LDC headspace.
- Sub-case 2 – Continuous Release of Hydrogen. Assuming all generated hydrogen gas is immediately released to the headspace of the LDC, the LDC is at the Safety Basis Temperature 25^0 C, and oxygen has been depleted from the sludge. Following the final decant of the LDC in preparation for shipping, how long would it take to develop a flammable condition? For this case, the time is measured from the completion of the final decant and calculated by dividing 48 Liters by the maximum hydrogen generation rate for the LDC at 25^0 C.

For the inerted LDC/Cask the only case requiring analysis is how long it takes to generate sufficient excess oxygen for a release of oxygen from the sludge to the LDC headspace to cause the headspace of the LDC to become a flammable mixture.

Attachment 13 discusses the flammability of hydrogen in an Argon/Oxygen atmosphere. From this discussion, the minimum oxygen required in an Argon/Hydrogen gas mixture to cause a flammable condition is 4%. Since a maximum of 1% oxygen is estimated to enter the LDC during the disconnect process and a maximum of 1% oxygen is estimated to enter the LDC during the final purge process, the permissible volume of oxygen that can be generated by the sludge is 2% (24 liters in a 1200 liter headspace). Accordingly, the oxygen calculations in this paper will be based on calculating the time to generate 24 liters of oxygen in the sludge.

Four cases are examined:

1. The Safety Basis Case. This is an analysis performed using only parameters contained in the current Safety Basis.

2. The Modified Safety Basis Case. This is an analysis performed using less conservative values of some conditions than are contained in the current Safety Basis but values that are either in the approval cycle now or will be in the approval cycle in the very near future. These less conservative conditions are:

   - Decay Power
   - Radiolysis Gas Generation Rate
   - Realistic operational temperature profiles
   - The effect of O_2 on the evolution of H_2 by the uranium-water reaction.

3. The Reasonably Bounding Case. This is an analysis performed using less conservative values of some parameters than are contained in the Modified Safety Basis Case but values that have a good technical basis and demonstrate the margin of safety available for these operations. These less conservative conditions are:

   - Uranium-Water Reaction Rate Enhancement Factor (Multiplier)
   - Uranium Metal Effective Particle Size
   - Uranium Metal Concentration
   - Total Uranium Concentration
   - Reactive Uranium Oxide Concentration
   - Radiolysis Gas Generation Rate
   - Decay Power.

4. The Nominal Case. This is an analysis performed using average (nominal) values of parameters for the sludge. This analysis is not being recommended for use in controlling the process. It is being shown as a method of displaying the average expected behavior of the gasses in the LDC as a comparison for the safety margin inherent in the system as designed. These less conservative conditions are:

   - Uranium-Water Reaction Rate Enhancement Factor (Multiplier)
   - Uranium Metal Concentration
   - Total Uranium Concentration
   - Reactive Uranium Oxide Concentration
   - Radiolysis Gas Generation Rate
   - Decay Power.

Vented LDC/Cask Conclusions/Recommendations.

Despite removal of substantial conservatisms, the time from the start of loading the first sludge layer to the time when sufficient hydrogen is potentially available to cause a flammable atmosphere in the event of an episodic release could not be sufficiently increased to justify routinely shipping the LDC/Cask in a vented condition. The results of the analyses are shown below:

Table ES-1 – Results of Vented LDC/Cask Flammability Intervals.

Condition/Case	Episodic Release (Note 1)	Continuous Release (Note 2)
Safety Basis Case	36.8 Hours	3.83 Hours
Modified Safety Basis Case	264 Hours	3.88 Hours
Reasonably Bounding Case	322 Hours	19.2 Hours
Nominal Case	527 Hours	134 Hours

Note 1: This time is measured from the start of fill of the first sludge layer until the sludge has generated 48 liters of hydrogen.

Note 2: This time is measured from the completion of the final decant to the time when the sludge would have released 48 liters of hydrogen assuming continuous release. Assumes all oxygen has been depleted, the LDC temperature is at 25^0 C, and all generated hydrogen is being released directly to the headspace of the LDC..

In view of the results above, it is considered imprudent to routinely to ship an LDC in a vented condition. An inerted LDC/Cask is needed, particularily for the transportation phase of the LDC production cycle.

Inerted LDC/Cask Conclusions/Recommendations.

The analysis of the inerted LDC/Cask was conducted to determine how long the inerted cask would remain non-flammable by determining how long it would take for the sludge to release a minimum of 24 liters of oxygen to the headspace of the LDC. The amount of oxygen required in an argon/hydrogen atmosphere to make a flammable mixture is 4% assuming at least 3.2% hydrogen is present. Since it is assumed that 1% oxygen will be introduced into the LDC during the disconnect process and 1% oxygen will be introduced during the final purge process, the oxygen that can be allowed to be released from the sludge is 2% (24 liters in a 1200 liter headspace).

Since the production of hydrogen from radiolysis is at least twice the production of oxygen gas from radiolysis and since hydrogen has a second source of production, the volume of hydrogen available will always be greater than the volume of oxygen available. Additionally, since the hydrogen volume necessary to produce a flammable condition is less than the required oxygen volume, this analysis deals only with determining when a total of 4% oxygen can be present.

The conclusion from this analysis is that only one reasonable case results in a very slow buildup of oxygen in the sludge with a possible release of oxygen to the headspace of the LDC. The only reasonable case in which oxygen is released to the LDC is the case of loading an LDC with pure floor sludge (i.e., no canister sludge is included in the mix) and maintaining LDC temperature at or below 15^0 C. In this case, 24 liters of oxygen would be available to be released to the headspace of the LDC in approximately 105 days.

A Bounding Oxygen Case has been added for the bounding oxygen analysis (see Attachment 26A, 26B, and 26C). In these analyses, the worst case conditions (reasonable) are combined to maximize the generation of oxygen and minimize the consumption of oxygen.

The results of all analysis cases except the Safety Basis case are shown in the table below:

Table ES-2 – Results of Inerted LDC/Cask Flammability Intervals.

Condition	Time to Deplete Oxygen in the Sludge Matrix from Start of Loading	Volume of Oxygen Released to the Headspace of the LDC in 90 days.
Modified Safety Basis Case	320 Hours	NONE
Reasonably Bounding Case	377 hours	NONE
Nominal Case	616 Hours	NONE
Bounding Oxygen Case	Not Depleted	20 Liters

In the final analysis, there is no case in which oxygen can be released to the headspace of the LDC at a rate that is capable of causing the headspace of the LDC to form a flammable mixture in any reasonable period of time. It can be concluded that the formation of a flammable atmosphere as a result of oxygen being released from the sludge to the headspace of the LDC is not a credible accident scenario.

In the Modified Safety Basis Case (Bounding Case), attachment 26A, 105 days are required to produce sufficient oxygen to cause the headspace of the LDC to become flammable (24 liters of oxygen produced by the sludge).

In the Reasonably Bounding Case, attachment 26B, 117 days are required to produce sufficient oxygen to cause the headspace of the LDC to become flammable.

In the Nominal Case, attachment 26C, 311 days are required to produce sufficient oxygen to cause the headspace of the LDC to become flammable.

This oxygen generation only occurs because the temperature of the LDC is held at 15^0 C. If the LDC is allowed to heatup to room temperature, 25^0 C, the oxygen generation is essentially stopped. See attachments 27A, 27B, and 27C.

In the Modified Safety Basis Case (Bounding Case), attachment 27A, oxygen never reaches a volume of 24 liters. All the dissolved oxygen is consumed in approximately 37 days and a flammable condition is never reached.

In the Reasonably Bounding Case, attachment 27B, greater than 100 years are required to produce sufficient oxygen to cause the headspace of the LDC to become flammable.

In the Nominal Case, attachment 26C, greater then 20 years are required to produce sufficient oxygen to cause the headspace of the LDC to become flammable.

CONCLUSIONS AND RECOMMENDATIONS

An inerting system using argon gas should be used to inert the LDC/Cask for transportation to T Plant. This inerting system should be available in K East for use during the loading sequence to be used as desired by facility management to inert the LDC whenever deemed appropriate.

Experience with primarily two samples, 96-05 and 96-06, described in Attachments 2 and 3, shows that layers of heavily concentrated metal sludge under layers of relatively metal poor sludge can lead to the formation of vessel spanning bubbles that are capable of lifting the sludge to the top of the LDC. It is recommended that large layers of pure canister sludge not be loaded into an LDC (more than about 0.1 m^3) under layers of relatively metal poor floor sludge. Rather, it is recommended that floor sludge be loaded first and then the LDC topped off with canister sludge. Otherwise, mixing canister and floor sludge is acceptable within layers in the LDC as long as the layer is at least 50% floor sludge. This is not intended to be a safety basis control or limiting condition for operation, only as a caution against setting up the conditions that could result in and have been observed in the laboratory to cause the formation of a vessel spanning bubble.

PURPOSE

The purpose of this paper is to describe the behavior of gasses in a Large Diameter Container (LDC) during and following the process of loading the LDC with sludge from 105K East and preparing to ship that sludge to T Plant for storage. This paper examines and makes conclusions and recommendations relative to two methods of loading and shipping an LDC containing K East Sludge:

1. A vented LDC/Cask and the associated flammability hazards.
2. An inerted LDC/Cask and the associated flammability hazards.

This paper examines physical and chemical phenomena and data that underlie the existing design and safety basis cases. This paper describes how a reasonably bounding case for hydrogen generation may be constructed by selecting a combination of parameters that differs from the compounding conservative method of pushing all parameter values simultaneously to their safety basis limits.

BACKGROUND

Current Spent Nuclear Fuel (SNF) Project design and safety basis calculations, such as those found in SNF-9955 for safety basis thermal and gas generation behavior of an LDC during shipping and storage at T Plant, uses parameter values found in the SNF Sludge Technical Databook, HNF-SD-SNF-TI-015, Vol 2, Rev 9. The technical basis for selection of these parameters appears in SNF-7765, Rev. 1, which cites and integrates many fundamental documents including laboratory data for sludge physical, chemical, and mechanical behavior. Important experimental and analytical contributions are summarized in two recent papers, HNF-16738 and HNF-16355.

Safety basis calculations for SNF sludge often simultaneously combine all parameters at their credible extreme, safety basis levels. While the conservatism of this approach is guaranteed, the results often appear unrealistic. Such results may even be physically impossible if the safety basis purposely neglects or discounts some phenomenon.

Current safety basis calculations for hydrogen production include sources from uranium metal water reactions and radiolysis that combine extreme values for metal content, decay power, reaction surface area, reaction rate multipliers (enhancement factors), and even operational conditions such as sludge temperature. A well-known phenomenon omitted by these calculations is oxygen poisoning of the uranium metal-water reaction: When dissolved oxygen is present in water, as is the case for K basins water, the reaction of the uranium metal does not evolve hydrogen.

The purpose of this paper, to provide reasonably bounding hydrogen and oxygen generation rates from sludge, is accomplished by systematically examining physical and chemical phenomena and operational characteristics that contribute to such a calculation. A major feature of the reasonably bounding case is inclusion of oxygen poisoning. These phenomena are summarized in the next section, and the reasonably bounding case is constructed thereafter.

TECHNICAL BASIS SUMMARY

Oxygen Poisoning. As described in Attachment 1, oxygen poisoning is a phenomenon that occurs when uranium is placed in water containing dissolved oxygen. The dissolved oxygen reacts with the uranium metal and with uranium oxides. While the oxygen is present, the uranium-water reaction, the reaction that causes the production of hydrogen from uranium metal, does not evolve hydrogen. When the oxygen is depleted, the uranium-water reaction will generate hydrogen that can be evolved from the sludge. This oxygen poisoning phenomenon provides for a delay from the time the sludge is loaded into the LDC until the sludge starts to produce hydrogen from the uranium-water reaction, examined in Attachment 1.

Gas Behavior of 96-05, 96-06. Attachment 2 examines the gas generation behavior of K East canister sludge samples 96-05 and 96-06 at ambient hot cell temperatures (35°C). These sludge samples (settled volume = 285 to 315 ml) were placed in 2-L glass cylinders, with an excess of water, and sparged with air for 5 minutes and then allowed to settle. Through air-sparging and settling, it is expected that the dense uranium metal in the samples concentrated at the bottom of the cylinders. About 90 minutes after air sparging, sample 96-06 began releasing gas (predominantly hydrogen). Sample 96-05 began generating and retaining gas about 7 hours after air sparging. Based on the gas generation rates, it is estimated that the samples, 96-06 and 96-05, contained 10.1% and 4.1 wt% uranium metal (settled sludge basis), respectively. Sample 96-06 exhibited a higher reactivity than any other K Basin sludge sample. The reactivity of 96-05 is about 20% less than safety basis KE canister sludge. While the rapid onset of gas generation in these samples after air-sparging (and oxygen saturation) appears to be in conflict with the predicted delay, Attachment 3 models these experiments, and presents a possible configuration (uranium metal distribution) that is consistent with the oxygen poisoning model.

Safety Basis Case Adjusted for Oxygen Poisoning, Decay Power, Radiolysis Rate, and Temperature (Modified Safety Basis) for Hydrogen. Before any comparison between the

Safety Basis case and any Reasonably Bounding case can be made, the Safety Basis case must have all the tools necessary for the comparison. That is to say, since the Reasonably Bounding case is dependent on the introduction of the concept of oxygen poisoning, the Safety Basis case must have the effects of oxygen poisoning applied. Further, the radiolysis rate must be adjusted to a more reasonable value, discussed in attachment 8. Additionally, since a recent revision to SNF-7765 is in review that contains a newly derived decay power that is less than the decay power used in the current Safety Basis, the effects of that decay power reduction must be provided to the Safety Basis case as well. The result of the calculation is the length of time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 48 liters of hydrogen (4% in a 1200 liter LDC headspace).

Reactions of Uranium Metal with Dissolved Oxygen. To accomplish this adjustment to the Safety Basis case, a modified Safety Basis case has been constructed that applies the principles of oxygen poisoning. Attachment 4 provides a detailed discussion on the consumption of oxygen by uranium metal, as well as the production of hydrogen by the uranium-water reaction when the oxygen has been depleted.

Reactions of Uranium Oxides with Dissolved Oxygen. A second source of oxygen consumption in the sludge is the reaction of oxygen with uranium oxides present in the sludge. Attachment 5 provides detailed discussions on these reactions and the rates of the reactions. The study of the reactions of oxygen with uranium oxides performed by Shoesmith resulted in two, nearly identical, correlations of reaction rates with radiolysis. Although these correlations are nearly identical, the correlations are different enough to cause one correlation to be more conservative when calculating the time to a flammable hydrogen atmosphere in a vented LDC (oxygen consumption maximized) while the other correlation is more conservative in calculating the time to a flammable atmosphere in an inerted LDC (oxygen consumption minimized) in the radiolysis and temperature ranges of interest. Accordingly, throughout this paper, one of the correlations is always used when hydrogen is the gas of interest and the other is always used when oxygen is the gas of interest (i.e., the gas controlling the potential flammable condition). As a result, all four cases (Safety Basis, Modified Safety Basis, Reasonably Bounding, and Nominal) are analyzed twice. One analysis is performed for the hydrogen control of the flammability and one for the oxygen control of the flammability.

Diffusion of Oxygen through KE Sludge in an LDC. To accomplish the delay associated with oxygen poisoning, the dissolved oxygen in the system must be capable of reaching the site of the uranium metal and the uranium oxide species. Attachment 6 provides a detailed discussion of the diffusion of oxygen to the needed locations and demonstrates that at all temperatures of interest; oxygen is sufficiently mobile to sustain the needed reactions. Attachment 6 also discusses the effects of uneven metal loading on the diffusion of oxygen within the LDC, an effect that was vividly demonstrated in the experiments with K East Sludge Samples 96-05 and 96-06.

K East Sludge Decay Heat (Decay Power). Attachment 7 summarizes the approach used to calculate the revised design and safety basis sludge decay power values (these values will be included in the SNF Technical databook, HNF-7765 Rev. 2 and HNF-SD-SNF-TI-015, Volume 2, Rev.10). Canister and floor sludge decay power were directly calculated from measured isotopic data from individual samples. This approach uses the data and includes appropriate statistical methods to consider variability, and it implicitly includes fission product losses during initial sludge formation by oxidation and any losses during sludge lifetime in the basins.

Radiolysis of Water in Sludge. The radiolysis of water provides a second source of oxygen to the water in the sludge and keeps the uranium-water reaction poisoned longer. Attachment 8 summarizes the derivation of radiolysis of water in sludge as a potential source of hydrogen and oxygen gases. However, the high chemical reactivity of uranium metal and oxide with oxidizing chemical species produced by radiolysis, and the low chemical reactivity of these with hydrogen while oxidizing species are present, implies that hydrogen will be the only significant gas to be evolved from the solution. The radiolytic production rate of hydrogen and oxidizing species (based on stoichiometric proportion) is calculated in Attachment 8. The hydrogen production rate from radiolysis is directly proportional to both decay power and the fraction of decay power absorbed by the water. The fraction of decay power deposited in water differs for alpha, beta, and gamma radiation due to the intrinsic absorption characteristics of each radiation type. Attachment 8 describes in detail how absorption by water is calculated, and shows that it depends upon absorption data for pure materials, the actual material composition, the volume fractions and densities of water and particles, and in the case of alphas and betas, upon the particle size distribution, and the distribution of path lengths through interstitial water. Standard values are used for $g(H_2)$, molecules H_2 per 100 eV absorbed by water, and it is possible that actual $g(H_2)$ values for sludge may be lower if liberated hydrogen species also react with the sludge.

Process for Producing the Modified Safety Basis Case for Hydrogen. The Safety Basis case is modified by:

1. Applying the effects of the revised decay power (see attachment 7).
2. Applying the effects of the revised radiolysis methodology (see attachment 8).
3. Allowing the temperature of the container to follow the normal profile rather that maintaining the temperature at 25^0 C artificially.
4. Applying the principle of Oxygen Poisoning to the evolution of hydrogen (see attachment 1).

The resultant Modified Safety Basis Case is shown in Attachment 16.

The result is the time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 48 liters of hydrogen.

Process for Producing the Reasonably Bounding Case for Hydrogen. The reasonably bounding case is constructed by applying the following corrections (reasonable bounds) on specific parameters used in the Safety Basis case:

1. Reducing the Reaction Rate Enhancement Factor from 3 to 1, as defined in Attachment 9.

2. Adjusting the radiolysis rate to conform to the derivation in Attachment 8.
3. Adjusting the effective metal particle size is from 500 microns to 750 microns as specified in SNF-7765, Revision 2.

4. Adjusting the uranium metal content from the safety basis, 64.8 Kg/m^3, to the Reasonably Bounding, 55.5 Kg/m^3 as specified in Attachment 10.

5. Adjusting the total uranium concentration from 740 Kg/m^3 to 632 Kg/m^3 as specified in attachment 10.

6. Adjusting the Reactive Uranium Oxide concentration from 515 Kg/m^3 to 439 Kg/m^3 as specified in attachment 10. Reactive uranium oxides are comprised of that portion of the uranium oxides that have not reached the final (chemically stable) form and are still reacting with oxygen and bonding with water.

7. Adjusting the decay power from the safety basis, 44.2 watts/m^3, to the reasonably bounding 36.2 watts/m^3', as specified in attachment 10 and discussed in attachment 7

   The Reasonably Bounding case is described in Attachment 17.

   The result is the time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 48 liters of hydrogen.

Reaction Rate Enhancement Factor (Multiplier). Attachment 9 summarizes results from Schmidt (et al. 2003) (i.e., Series III Gas Generation Testing) that support the reduction of the reaction rate enhancement factor from 3 (safety basis) to 1 (reasonably bounding case). Actual and theoretical particle radii were measured for eleven experiments performed with uranium metal fuel particles of varying initial size, at temperatures ranging from ~28 to 95°C, with and without overlying sludge burden. The theoretical and actual uranium metal particle sizes were derived for test intervals (each of the 11 tests provided a significant number of discrete test intervals appropriate for analysis) over the course of the testing program. The *actual* fuel particle sizes (i.e., nominal diameters determined from sieving, corrected by the amount of uranium lost to corrosion were compared to calculated *theoretical* particle sizes. The theoretical particle sizes were calculated by determining the "effective particle diameters" required to generate the measured gas rate if the uranium metal, as spheres, reacted in accordance with the SNF rate law. The ratio of the actual-to-theoretical particle size gives the enhancement factor. The rate enhancement (comparison) factor for the fuel particles was found to be about 0.28 ± 0.25 based on the SNF rate equation. That is, on average, the fuel particles in Series III reacted at about one-forth to one-third of the rate predicted by the SNF rate equation. The rate enhancement factor never exceeded unity at any measurement condition. Analysis of the data show that a rate enhancement factor of 1 is appropriate for the reasonably bounding case.

Reasonable Bounds for Parameters to be Varied. Attachment 10 provides tables of the parameters that will be varied during this analysis and the Safety Basis, Modified Safety Basis, Reasonably Bounding, and Nominal values for each parameter.

Comparison of Reasonably Bounding Case Predictions with Experimental Results. In Attachment 11 calculations were performed to compare the H_2 generation rate for the "Reasonably Bounding Case" to actual gas generation measurements from canister sludge samples. All rates were compared at 25°C. The reasonably bounding gas generation rate exceeds nearly all of the measured gas generation rates from KE and KW canister sludge samples. The gas generation rate from sample KC-2/3 (KE Canister sludge composite made up of sludge material from 10 sampling locations) is only 22% of that projected for the canister sludge component in the Reasonably Bounding Case.

With respect to the 1996 KE canister sludge samples, the gas generation rate for 1 of the 7 samples from fueled canisters, 96-06, significantly exceeds that of the Reasonably Bounding Gas Generation Rate (i.e., rate from 96-06 is 260% of the reasonably bounding rate). However, several of the fueled KE canister sludge samples collected in 1996 exhibited little or no gas generation. Assuming that the three samples with observed, but unmeasured, gas generation (96-08, 96-13, and 96-15) can be assigned a rate equal to one-half that of 96-05, and the other two from fueled canisters (with no observed gas generation) can be assigned a rate of zero, the mean rate for the 7 samples from fueled canisters would be 75% of the Reasonably Bounding Gas Generation Rate.

Process for Producing the Nominal Case for Hydrogen. The nominal case is constructed by applying three changes on specific parameters used in the Reasonably Bounding case:

1. Reducing the Reaction Rate Enhancement Factor from 1 to 0.4, as defined in Attachment 9.

2. Adjusting the radiolysis rate to conform to the derivation in Attachment 8.

3. Adjusting the uranium metal content from 55.5 Kg/m^3 to 18.4 Kg/m^3 as specified in Attachment 10.

4. Adjusting the total uranium concentration from 632 Kg/m^3 to 344 Kg/m^3 as specified in attachment 10.

5. Adjusting the Reactive Uranium Oxide concentration from 439 Kg/m^3 to 248 Kg/m^3 as specified in attachment 10. Reactive uranium oxides are comprised of that portion of the uranium oxides that have not reached the final (chemically stable) form and are still reacting with oxygen and bonding with water.

6. Adjusting the decay power from 36.2 watts/m^3 to 10.6 watts/m^3, as specified in attachment 10 and discussed in attachment 7

The Nominal case is described in Attachment 18.

The result is the time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 48 liters of hydrogen.

Technical Basis for Oxygen Lower Flammability Limit of 4% in an Ar-O_2-H_2-Air Atmosphere. The oxygen calculation performed in this analysis use a 4% Lower Flammability Limit for oxygen in an Ar-O_2-H_2-Air atmosphere. The basis for this 4% LFL is provided in attachment 13.

Safety Basis Case Adjusted for Oxygen Poisoning, Decay Power, Radiolysis Rate, and Temperature (Modified Safety Basis) for Oxygen. Before any comparison between the Safety Basis case and any Reasonably Bounding case can be made, the Safety Basis case must have all the tools necessary for the comparison. That is to say, since the Reasonably Bounding case is dependent on the introduction of the concept of oxygen poisoning, the Safety Basis case must have the effects of oxygen poisoning applied. Further, the radiolysis rate must be adjusted to a more reasonable value, discussed in attachment 8. Additionally, since a recent revision to SNF-7765 is in review that contains a newly derived decay power that is less than the decay power used in the current Safety Basis, the effects of that decay power reduction must be provided to the Safety Basis case as well. The result is the length of time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 48 liters of total oxygen, 2% (24 liters) generated by the sludge.

Process for Producing the Modified Safety Basis Case for Oxygen. The Safety Basis case is modified by:

1. Applying the effects of the revised decay power.

2. Applying the effects of the revised radiolysis methodology.

3. Allowing the temperature of the container to follow the normal profile rather that maintaining the temperature at 25^0 C artificially.

4. Applying the principle of Oxygen Poisoning to the evolution of hydrogen.

The resultant modified Safety Basis Case is shown in Attachment 20.

The result is the time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 24 liters of oxygen.

Process for Producing the Reasonably Bounding Case for Oxygen. The reasonably bounding case is constructed by applying four corrections (reasonable bounds) on specific parameters used in the Safety Basis case:

1. Reducing the Reaction Rate Enhancement Factor from 3 to 1, as defined in Attachment 9.
2. Adjusting the radiolysis rate to conform to the derivation in Attachment 8.
3. Adjusting the effective metal particle size is from 500 microns to 750 microns as specified in SNF-7765, Revision 2.
4. Adjusting the uranium metal content from the safety basis, 64.8 Kg/m^3, to the Reasonably Bounding, 55.5 Kg/m^3 as specified in Attachment 10.
5. Adjusting the total uranium concentration from 740 Kg/m^3 to 632 Kg/m^3 as specified in attachment 10.
6. Adjusting the Reactive Uranium Oxide concentration from 515 Kg/m^3 to 439 Kg/m^3 as specified in attachment 10. Reactive uranium oxides are comprised of that portion of the uranium oxides that have not reached the final (chemically stable) form and are still reacting with oxygen and bonding with water.
7. Adjusting the decay power from the safety basis, 44.2 watts/m^3, to the reasonably bounding 36.2 watts/m^3', as specified in attachment 10 and discussed in attachment 7

   The Reasonably Bounding case is described in Attachment 21.

   The result is the time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 24 liters of oxygen.

Process for Producing the Nominal Case for Oxygen. The nominal case is constructed by applying three changes on specific parameters used in the Reasonably Bounding case:

1. Reducing the Reaction Rate Enhancement Factor from 1 to 0.4, as defined in Attachment 9.
2. Adjusting the radiolysis rate to conform to the derivation in Attachment 8.
3. Adjusting the uranium metal content from 55.5 Kg/m^3 to 18.4 Kg/m^3 as specified in Attachment 10.
4. Adjusting the total uranium concentration from 632 Kg/m^3 to 344 Kg/m^3 as specified in attachment 10.
5. Adjusting the Reactive Uranium Oxide concentration from 439 Kg/m^3 to 248 Kg/m^3 as specified in attachment 10. Reactive uranium oxides are comprised of that portion of the uranium oxides that have not reached the final (chemically stable) form and are still reacting with oxygen and bonding with water.

6. Adjusting the decay power from 36.2 watts/m^3 to 10.6 watts/m^3, as specified in attachment 10 and discussed in attachment 7

   The Nominal case is described in Attachment 22.

   The result is the time from the start of loading of the first sludge layer to the time the sludge has generated, and potentially stored, 24 liters of oxygen.

Comparison of Loading Methods. For this analysis, three loading cases were examined.

1. Case 1 – All sludge layers loaded at 60% floor and 40% canister sludge. Results of this analysis are presented in Attachment 23.
2. Case 2 – Four layers of pure canister sludge are loaded followed by 6 layers of floor sludge. Results of this analysis are presented in Attachment 24.
3. Case 3 – Six layers of floor sludge are loaded followed by four layers of canister sludge. The results of this analysis are presented in Attachment 25.

Oxygen Bounding Case. This case was constructed to investigate an anomaly noted during the unbalanced loading analysis. It appeared that pure floor sludge layers produced oxygen. To investigate this possibility three cases were constructed that maximized oxygen generation from radiolysis, and minimized oxygen consumption from uranium metal and oxides. In this bounding oxygen generation case, it was determined that it is mathematically possible for floor sludge to generate oxygen and that 24 liters of oxygen could be generated in a period of 105 days. However, this oxygen generation takes place only when the temperature of the LDC is limited to 15^0 C. If the temperature of the LDC is allowed to increase to room temperature, 25^0 C, the oxygen generation is essentially stopped and several years are required to generate the 24 liters of oxygen necessary to cause the headspace of the LDC to form a flammable atmosphere.

Bubble Release from the Sludge as a Result of Vibration. Attachment 12 discusses the results of experiments conducted with sludge simulates where a vessel spanning bubble was formed and a vibrating table was used to simulate transporting the LDC containing the sludge and vessel spanning bubble. ~~Three~~ Four experiments were conducted and in all cases except one the sludge plug remained in tact and the vessel spanning bubble was not released. Although the results of these experiments show that the tendency of the sludge is to retain trapped bubbles, even under transportation conditions, these results are limited and do not completely discount the possibility of an episodic release of hydrogen from a large bubble during the transportation process. Bubbles as large as 1.2 m^3 could be formed before any outward signs (water at the LDC vent) would be evident to indicate the presence of the bubble. Although it is believed that the outlet filter mechanism would act to break up the sludge plug and release the bubble, the possibility that water and then sludge would be extruded from the open LDC vent ports cannot be completely discounted.

Sudden gas released was observed when the sludge thickness was reduced to 3.5 cm

HYDROGEN AND OXYGEN PRODUCTION IN AN LDC

Two analyses will be presented here:

- Shipping a vented LDC/Cask.
- Shipping an inerted LDC/Cask.

6.1 SHIPPING A VENTED LDC AND CASK.

The loading conditions assumed for all calculations in this paper are that a 0.2 m3 layer of sludge is loaded every 12 hours until the LDC is full ($2m^3$). The LDC is prepared for shipment to T Plant but is then kept in the transport bay at K East while the gas environment of the LDC is allowed to fully develop.

There are two issues of interest in the case of the vented LDC.

1. Assuming all hydrogen generated in the sludge is maintained within the sludge in a bubble until sufficient hydrogen exists to cause the LDC headspace to develop a flammable atmosphere. The bubble is then released in an episodic release to the headspace of the LDC. How long does it take for the bubble large enough to make the headspace flammable (48 Liters) to form in the sludge. This time is measured from the start of loading the first sludge layer to the time that 48 liters of hydrogen has been generated by the sludge.

2. Assuming loading has been completed, oxygen has been depleted, LDC temperature is 25^0 C, and all the hydrogen generated in the sludge is immediately released to the LDC headspace. How long will it take from the time of the final decant of the LDC for the headspace to contain a flammable atmosphere. This time is measured from the time of completion of the final decant to the time the sludge has released 48 liters of hydrogen to the headspace of the LDC.

6.1.1 CURRENT SAFETY BASIS FOR A VENTED LDC AND CASK.

The current Safety Basis predicts that one cubic meter of K East sludge will begin to evolve hydrogen from radiolysis at the rate of 0.2724 Liters/hr and at the rate of 6 Liters/hr from the uranium-water reaction immediately upon being loaded into the LDC. These hydrogen generation rates are based on the following Safety Basis parameters:

Sludge Mixture:	60% Floor Sludge / 40% Canister Sludge
Decay Power:	69.9 Watts/m^3
Metal Concentration:	63.85 Kg/m^3
Total Uranium:	740 Kg/m^3
Temperature:	25^0 C
Metal Particle Size:	500 microns
LDC Void Volume:	1.2 m^3

Under these Safety Basis conditions, approximately 36 hours 45 minutes would be required during loading operations to generate the required 48 liters of hydrogen to drive the LDC headspace to a flammable condition in the event of an episodic release. It should be noted that 36 hours 45 minutes is only 30% of the load time required for the LDC and only 3 layers of sludge have been loaded at this point in the process. Attachment 15 provides detailed calculations.

Assuming loading has been completed, oxygen has been depleted, LDC temperature is 25^0 C, and all the hydrogen generated in the sludge is immediately released to the LDC headspace, the headspace of the LDC would contain a flammable atmosphere 3 hours 50 minutes after the final decant.

6.1.2 MODIFIED SAFETY BASIS FOR A VENTED LDC AND CASK.

The Modified Safety Basis Case is composed of the Safety Basis Case modified for certain parameters that are in the approval cycle to be changed or in the process of being changed and are being used in this analysis for completeness. Four parameters/processes are in the change process for the current Safety basis and are used here:

1. Sludge Decay Power is being changed from 69.9 Watts/m3 to a value more consistent with the statistical analysis of the sludge samples and data available, 44.2 Watts/m3.
2. Gas generation rate from radiolysis is being changed from 13.08 Liters/day to a value more consistent with radioactive power absorbed in the water of 4.18 Liters/day.
3. The sludge temperature profile is being changed to be more realistic with the temperature profile during actual loading conditions, starting at 15^0 C and heating to 25^0 C at 1^0 C/day until reaching a stable temperature of 25^0 C. The current Safety Basis uses 25^0 C for all calculations in K East that are temperature related inflating the hydrogen generation rate by nearly a factor of 3.
4. The role of oxygen in the production of hydrogen in the sludge matrix. The current Safety Basis does not recognize or account for the fact that the presence of dissolved oxygen in the sludge matrix prevents the evolution of hydrogen from the uranium-water

reaction. This uranium-oxygen reaction can be easily shown to delay the onset of the evolution of hydrogen from the uranium-water reaction for days and even weeks. This is an extremely important reaction in the gas behavior of sludge in a LDC. The Modified Safety Basis Case introduces the oxygen reactions and demonstrates their effect on the gas behavior of the sludge.

6.1.2.1 SLUDGE DECAY POWER.

The current Safety Basis uses a decay power for the LDC (69.9 Watts/m^3) that is above the decay power observed in actual samples of the K East sludge in the laboratory. This paper uses a more appropriate value for Safety Basis Decay Power for K East sludge. The values and approach used in this paper will be incorporated into the next revision of the sludge technical databook (HNF-SD-TI-015, Vol. 2).

The change in the decay power for the Modified Safety Basis case comes about as a result of a reinterpretation of the available data for the sludge. Additionally, since the oxygen reactions in the sludge that are relatively highly dependent on decay power have not yet been introduced into the problem, the change in decay power shown here has no effect on the rate of hydrogen generation except for a small effect on the sludge radiolysis rate, discussed in the next section. The primary effect of the change in the decay power is to lower the heat up rate of the sludge following loading.

6.1.2.2 GAS GENERATION FROM RADIOLYSIS.

The current Safety Basis uses a gas generation rate from radiolysis that is in excess of any measured value for K East sludge during laboratory experiments. This paper establishes a revised Safety Basis Radiolysis Generation Rate that is being incorporated into the current Safety Basis.

The radiolysis rate of the sludge is controlled by many complex variables. For this reason, the calculation of the radiolysis rate for each sludge type (pure canister, pure floor, 60% floor/40% canister) under each case condition (Modified Safety Basis, Reasonably Bounding, and Nominal) has been performed separately in Attachment 8. The only variable of concern for the calculations performed in these attachments is the variation of the volume of the gas with temperature, since the generation rates provided in Attachment 8 are provided at STP, this is a simple application of the ideal gas law. The equation used is:

$$QR_{H_2}(T) = QR_{H_2} \times \left(\frac{273.15 + T}{273.15} \right)$$

Where:

$QR_{H2}(T)$ = H_2 Generation Rate as a function of temperature (liters/hr)
QR_{H2} = H_2 Generation Rate at STP for the sludge type and case (liters/hr)
T = Sludge/LDC temperature (^{0}K)

6.1.2.3 SLUDGE TEMPERATURE.

The current Safety Basis uses the safety basis temperature of 25^0 C for all hydrogen generation calculations in K East. Since the sludge is actually loaded at approximately 12^0 C, this paper uses a loading temperature of 15^0 C for hydrogen generation calculations during loading operations. Following loading operations the LDC increases to 25^0 C at 1^0 C per day until it stabilizes at 25^0 C in accordance with calculations in the current Safety Basis.

As discussed in section 6.1.2.2, the volume of hydrogen released from radiolysis varies with temperature as a function of the ideal gas law. The other source of hydrogen in the sludge is the reaction of uranium metal directly with water.

The uranium metal-water reaction is:

$$U + 2\,H_2O \rightarrow UO_2 + 2\,H_{2\,(g)}$$

One of the variables for the rate of the Uranium-Water reaction is temperature.

The base rate of the reaction is derived in Attachment 4 and is expressed as the volume of hydrogen generated in one hour from the uranium-water reaction with the water at 25^0 C and the hydrogen released at STP.

The base reaction rate for the Modified Safety Basis calculation is 5.585 liters/hr.

The temperature variation of the rate of reaction of uranium metal and water is defined by the following equation:

$$\mathrm{Log}_{10}K_W \quad = \quad 7.634 - 3016/T$$

?

Where: K_W = Reaction Rate of Uranium Metal-Water Reaction (mg U/m^2 day)
T = Temperature in ^{0}K

Solving for K_W the equation becomes:

$$K_W = 10^{\left(7.634 - \frac{3016}{T}\right)}$$

Solving for a final reaction rate in terms of the initial reaction rate as a function of temperature, the equation becomes:

$$K_{W2} = K_{w1} \times \left(\frac{10^{\left(7.634 - \frac{3016}{T2}\right)}}{10^{\left(7.634 - \frac{3016}{T1}\right)}} \right)$$

Simplifying the equation results in:

$$K_{W2} = K_{W1} \times 10^{\left(3016 \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)}$$

Where:
K_{W1} = The initial reaction rate (liters/hr)
K_{W2} = The final reaction rate (liters/hr)
T_1 = The initial Temperature (^{0}K)
T_2 = The final Temperature (^{0}K)

In Attachments 15 - 27, this calculation is performed in a table containing "Relative Um Rate" and "H_2 Rate Um liters/hr". In this calculation:

K_{W1} = Base rate at 25^0 C and STP gas conditions (5.585 liters/hr)
K_{W2} = The final reaction rate for each temperature of interest. (H_2 Rate Um liters/hr)
T_1 = 273.15 + 25 = 298.15^0 K
T_2 = 273.15 + Temp of interest (^{0}C)

The "Relative Um Rate" is calculated using the exponential part of the above equation.

As demonstrated above, the rate of the Uranium-Water reaction is an exponential function of the temperature of the sludge at the reaction site. For a 10^0 C increase in the reaction temperature, the rate of the reaction varies from slightly less than a factor of 2 to slightly greater than a factor of 2.5 with the more pronounced effect at the lower temperatures (< 35^0 C).

The total hydrogen volume in the sludge is a function of generation rate and sludge temperature.

The volume of hydrogen gas generated in each sludge layer after dissolved oxygen depletion is calculated by the following formula:

$$QL_{H_2} = \left(QU_{H_2} + QR_{H_2}\right) \times \left(\frac{VS_L}{VS_{LDC}}\right)$$

Where:
QL_{H2} = H_2 Generation Rate in the Layer (Liters/Hour)
QU_{H2} = H_2 Generation Rate from U-H_2O reaction for full LDC sludge load (2 m^3) (Liters/Hour)
QR_{H2} = H_2 Generation Rate from Radiolysis for full LDC sludge load (2 m^3) (Liters/Hour)
VS_L = Sludge Volume for the layer (m^3)
VS_{LDC} = Sludge Volume for a full LDC (2 m^3)

6.1.2.4 THE ROLE OF OXYGEN IN THE PRODUCTION OF HYDROGEN IN THE SLUDGE MATRIX

There are four processes/reactions that affect the time to oxygen depletion:

1. The concentration of oxygen in the water at the time the sludge enters the LDC. The concentration of oxygen is assumed to be the concentration for air saturated water at 15^0 C (loading temperature). The justification for this assumption is presented in section 6.1.2.4.
2. The generation of oxygen and oxidizing species by radiolysis. This generation rate is discussed in detail in Attachment 8.
3. The consumption of oxygen by uranium metal following loading in the LDC. This consumption rate is discussed in detail in Attachment 4.
4. The consumption of oxygen by reactive uranium oxides following loading of the LDC. This consumption rate is discussed in detail in Attachment 5.

It is reasonable to assume that the water mixed with the sludge as the sludge is loaded into the LDC is air saturated. This assumption is justified by three phenomena:

1. The basin is a very large pool of water with a very large surface area and only 17 feet deep making oxygenating of the water by the cover gas (air) easy.
2. The water in the basin is circulated by circulation systems, one of which is the skimmer system. The skimmer system takes the top 1 to 2 inches of the surface of the water that is in contact with the air and drains it to a centrifugal pump. The water is pumped through a sand filter and an ion exchanger and returned to the basin at the 12-foot level. The water entering this skimmer system does so through a gutter arrangement and moves into the system with entrained air. The flow rate of the skimmer system is 300 gallons per minute, which causes all the water in the basin to pass through this system approximately every 56 hours, keeping the water aerated.
3. The sludge retrieval system passes the sludge through 2 centrifugal pumps on the path to the LDC, which provides thorough, violent mixing of the sludge with the aerated water at the ratio of 3 parts water to one part sludge.

The CRC Tables were used to construct an oxygen concentration as a function of temperature table in each spreadsheet. This is used as the initial concentration of oxygen in the sludge matrix water. While the sludge is being loaded, the temperature of the sludge and LDC are maintained constant at 15^0 C. During this loading time, the effects on the oxygen content of the sludge matrix are generation by radiolysis, consumption by uranium metal and consumption by uranium oxides. However, after loading is complete, the temperature of the sludge and LDC starts to increase at the rate of 1^0 C per day until the temperature is 25^0 C. As the water in the sludge matrix heats up, the solubility of oxygen in the water decreases. Accordingly, after loading is complete, if the oxygen concentration exceeds the saturation value for the temperature of interest, oxygen may be released from the sludge in the form of very small bubbles as the oxygen is forced out of solution. Assuming the saturation value of oxygen to be a linear function over the small temperature range of interest ($15^0 - 25^0$ C), an equation was constructed for the saturation value of oxygen over the temperature range of operation of the LDC at K East.

$$O_{2ST} = O_{2ST1} + \left(\frac{(O_{2ST2} - O_{2ST1})}{T_1 - T_2} \right) \times (T_1 - T)$$

Note: This equation may only be used for temperature bands for which the value of oxygen saturation can be closely approximated by a linear function, such as between 15^0 and 25^0 C.

Where:

O_{2ST} = Oxygen Saturation Value for any Temperature T
O_{2ST1} = Oxygen Saturation Value at the High Temperature of Interest.
O_{2ST2} = Oxygen Saturation Value at the Low Temperature of Interest.
T_1 = High Temperature of Interest.
T_2 = Low Temperature of Interest.
T = Temperature of Interest. This value must be T2 <= T <= T1.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The volumes provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\,H_2O}\right]$$

Where:

QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)
22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the volume of gas released using the following expression:

$$V_{O_2}(T)\,[liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15 + T}{273.15}\right)$$

Where:

$V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

Two processes in the sludge perform the consumption of oxygen: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4. The reaction of uranium oxides with oxygen is described in detail in Attachment 5. Both of these reactions will be covered briefly here:

The uranium metal-oxygen reaction is:

$$U + O_{2\,(aq)} \rightarrow UO_2$$

The rate of reaction of uranium metal with oxygen is controlled by temperature as well as other factors. Only the temperature variation will be discussed in this section.

The base rate of the reaction is derived in Attachment 4 and is expressed in the number of hours required to deplete the oxygen contained in air saturated water at various reaction temperatures with the volume of the gasses expressed in liters/hr at STP. For purposes of these calculations, the liter/hr rate from Attachment 4 is converted to ppm/hr using the above equation and the base reaction rate is expressed as the concentration of oxygen in air saturated water at 25^0 C divided by the number of hours to deplete the oxygen calculated in Attachment 4 at a reaction temperature of 25^0 C (237 hours) producing a base reaction rate in terms of ppm/hr at 25^0 C.

The base reaction rate for the Modified Safety Basis calculation is 0.0359 ppm/hr.

The temperature variation of the rate of reaction of uranium metal and oxygen is defined by the equation:

$$\mathrm{Log}_{10}\mathrm{K}_\mathrm{O} \quad = \quad 8.333 - 3730/\mathrm{T}$$

Where: K_O = Reaction Rate of Uranium Metal-Oxygen Reaction (mg U/m^2 day)
T = Temperature in ^{0}K

Solving for K_O the equation becomes:

$$K_O = 10^{\left(8.333 - \frac{3730}{T}\right)}$$

Solving for a final reaction rate in terms of the initial reaction rate as a function of temperature, the equation becomes:

$$K_{O2} = K_{O1} \times \left(\frac{10^{\left(8.333 - \frac{3730}{T2}\right)}}{10^{\left(8.333 - \frac{3730}{T1}\right)}} \right)$$

Simplifying the equation results in:

$$K_{O2} = K_{O1} \times 10^{\left(3730 \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)}$$

Where: K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
T_1 = The initial Temperature (^{0}K)
T_2 = The final Temperature (^{0}K)

In attachments 16 – 27 where these calculations are performed, this calculation is performed in a table containing "Relative Um Rate" and "Um Rate ppm/hr". In this calculation:

K_{O1} = Base rate at 25^0 C (8.510 ppm/237 hours = 0.0359 ppm/hr)
K_{O2} = The final reaction rate for each temperature of interest. (Um Rate ppm/hr)
T_1 = 273.15 + 25 = 298.15^0 K
T_2 = 273.15 + Temp of interest (^{0}C)

The "Relative Um Rate" is calculated using the exponential part of the above equation.

As demonstrated above, the rate of the Uranium-Oxygen reaction is an exponential function of the temperature of the sludge at the reaction site. For a 10^0 C increase in the reaction temperature, the rate of the reaction varies from slightly less than a factor of 2.5 to slightly greater than a factor of 3.0 with the more pronounced effect at the lower temperatures (< 35^0 C).

The second process that consumes oxygen is the reaction of oxygen with uranium oxides. The reactions that cause this consumption are:

$$2\ UO_2 + O_2 + 4\ H_2O \rightarrow 2\ UO_3{\cdot}2H_2O$$
$$8\ UO_{2.25} + 3\ O_2 + 16\ H_2O \rightarrow 8\ UO_3{\cdot}2H_2O$$

At equal amounts of uranium present as UO_2 and $UO_{2.25}$, the combined reaction becomes:

$$8\ UO_2 + 8\ UO_{2.25} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

or

$$16\ UO_{2.125} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

Attachment 5 discusses these reactions in detail and provides the base rate of the reaction in the form of the number of hours required to deplete the oxygen in air saturated water at 25^0 C.

The rate of the reaction between oxygen and uranium oxides is governed by several factors. Only temperature is discussed in detail in this section.

The base rate of the reaction at 25^0 C is obtained from Attachment 5 and is identified in the spreadsheets that use this data as the "Uo Rate ppm/hr".

The variation in the Uranium Oxide – Oxygen Reaction Rate as a function of temperature is described in detail in Attachment 5. From Attachment 5, the equation describing the reaction rate as a function of temperature is:

> The rate of the reaction at 15°C can be as much as 1.61-times lower, according to the Arrhenius equation (rate = $Ae^{-Ea/RT}$) and an activation energy (E_a) for the reaction of 34 kJ/mole in non-complexing neutral solution (E_a = 29-34 kJ/mole reported in section 5.6 of Shoesmith, 2000):
>
> $$\frac{\text{Rate (25°C)}}{\text{Rate (15°C)}} = \frac{Ae^{-E_a/RT_{298}}}{Ae^{-E_a/RT_{288}}} = \frac{e^{[-34000\ \text{J/mole}]/[(8.314\ \text{J/mole·deg})\cdot 298]}}{e^{[-34000\ \text{J/mole}][(8.314\ \text{J/mole·deg})\cdot 288]}} = 1.61$$

Accordingly, the rate of the reaction at any temperature (T) can be expressed by the equation:

$$R_F = R_I \times \left(\frac{e^{\left[-34000\ J/mole \big/ ((8.314\ J/mole \bullet \text{deg}) \times T_F) \right]}}{e^{\left[-34000\ J/mole \big/ ((8.314\ J/mole \bullet \text{deg}) \times T_I) \right]}} \right)$$

Where:
R_I = Initial Reaction Rate (ppm/hr)
R_F = Final Reaction Rate (ppm/hr)
T_I = Initial Temperature (^{0}K)
T_F = Final Temperature (^{0}K)

In Attachments 16 – 18 and 20 - 27, the ratio of T_F over T_I is termed "Relative Uo Rate". By substituting 25^0 C (298.150 K) for the Initial Temperature and by simplifying the equation, "Relative Uo Rate" becomes:

$$RUo_R(T_F) = e^{\left(4089.5 \times \left(\frac{1}{298.15} - \frac{1}{273.15 - T_F} \right) \right)}$$

Where: $RUo_R(T_F)$ = Relative Reaction Rate at temperature T_F

Reaction Rate is the Relative Reaction Rate to the rate at 25^0 C.

The product of the Relative Reaction Rate and the Reaction Rate at 25^0 C produces the reaction rate at any temperature of interest. This value is supplied in the spreadsheet as "Uo Rate ppm/hr".

As demonstrated above, the rate of the Uranium Oxide-Oxygen reaction is an exponential function of the temperature of the sludge at the reaction site. For a 10^0 C increase in the reaction temperature, the rate of the reaction varies from slightly less than a factor of 1.5 to slightly less than a factor of 1.7 with the more pronounced effect at the lower temperatures (< 35^0 C).

It should also be noted here that oxygen consumption is dominated by the Uranium Oxide-Oxygen reaction over the temperature range of interest (15^0 – 25^0 C) in that the consumption of oxygen by uranium oxides is between a 4.3 and 12.8 times higher than the consumption of oxygen by uranium metal with the more pronounced effect at the lower temperatures. Therefore, over the temperature range of interest, uranium oxides consume 82% to 93% of the oxygen consumed.

The sludge matrix contains dissolved oxygen present in the basin water as the sludge is pumped to the LDC and contains dissolved oxygen (or oxidizing species) produced from the radiolysis of water after the sludge is loaded into the LDC. Oxygen from both of these sources reacts with the uranium metal and uranium oxides present in the sludge. This oxygen dramatically affects the onset of the evolution of hydrogen from the uranium-water reaction, the reaction responsible for the majority of the hydrogen postulated to be generated in the LDC shortly after loading. The effect of this oxygen is to essentially "poison" the uranium-water reaction, preventing the evolution of hydrogen from this reaction until the oxygen in the sludge has been depleted. Although the possibility exists that extreme local metal distribution concentrations within the sludge may cause localized oxygen depletion earlier than in other areas with lesser metal concentrations, overall, the effect of metal distribution averaged over the volume of the container makes little or no difference in the time it takes for the sludge to generate the volume of hydrogen necessary to form a flammable atmosphere in air, 48 liters. The primary effect of these oxygen sources is to delay, by a substantial time, the onset of hydrogen evolution from the uranium-water reaction. The effect of the dissolved oxygen in the sludge and the oxygen generated from radiolysis is essentially ignored in the current Safety Basis. Attachment 1 provides a detailed discussion of the oxygen poisoning effect. Attachment 16 provides detailed calculations demonstrating the effect of oxygen.

Under these loading and operating conditions, 264 hours (11 days) is required to generate the necessary 48 liters of hydrogen to make the headspace of the LDC a flammable atmosphere in the event of an episodic release.

If, following loading, the hydrogen being generated were to be released directly to the headspace of the LDC, the headspace of the LDC could be a flammable atmosphere in as little as 144 hours (6.0 days).

The primary reason for the significantly longer time to reach 48 liters of hydrogen calculated for the Modified Safety Basis Case compared to the Safety Basis Case, a factor of 38, is the delay caused by reactions that effect the oxygen concentration in the sludge matrix. Oxygen must be depleted before the uranium-water reaction will generate hydrogen. The current Safety Basis does not recognize the effect of oxygen on the onset of hydrogen generation by the uranium-water reaction.

The oxygen depletion time is given by:

$$t = \frac{C_{O2}}{Q_{O2,met} + Q_{O2,ox} - Q_{O2,rad}}$$

where parameters are:

C_{O2} = Initial concentration of oxygen in the water.
Q = Rate

met = Consumption by metal oxidation
ox = Consumption by uranium oxide hydration
rad = Radiolytic production of oxidizing species in terms of equivalent O_2.

6.1.3 THE REASONABLY BOUNDING CASE

For the reasonably bounding case, the Safety Basis parameters that affect hydrogen generation rate are examined to determine if more conservatism than necessary exists in these parameters.

In addition to possible over conservatisms in the values of the Safety Basis parameters, all Safety Basis parameters are used in calculations effectively amplifying the magnitude of the conservatisms even more.

Attachment 10 displays tables of Safety Basis, Reasonably Bounding, and Nominal values for uranium metal concentration, total uranium, and decay power, three parameters of interest.

Two other parameters of interest will be examined in the Reasonably Bounding Case. Reaction Rate Enhancement Factor (Multiplier) and uranium metal particle size.

6.1.3.1 THE URANIUM-WATER REACTION RATE ENHANCEMENT FACTOR (MULTIPLIER).

The uranium-water reaction rate enhancement factor (multiplier) is set to 3 in the current Safety Basis. Experimental data shows that this multiplier should be between 0.25 and 0.4 for hydrogen generation by the uranium-water reaction in K East sludge. For the reasonably bounding analysis in this paper, a multiplier of 1 is used. Attachment 9 provides a discussion of the Reaction Rate Enhancement Factor (Multiplier) and the basis for reducing it.

For Hydrogen Generation.

The variation of Uranium Metal-Water reaction rate as a function of Reaction Rate Enhancement Factor (Multiplier) is a simple ratio of the final reaction rate enhancement factor ($RREF_F$) divided by the initial reaction rate enhancement factor ($RREF_I$).

$$KW_F = KW_I \times \frac{RREF_F}{RREF_I}$$

Where: KW_F = Final Reaction Rate (liters/hr)
KW_I = Initial Reaction Rate (liters/hr)
$RREF_F$ = Final Reaction Rate Enhancement Factor
$RREF_I$ = Initial Reaction Rate Enhance Factor

There is no corresponding factor for Oxygen depletion/generation.

6.1.3.2 URANIUM METAL PARTICLE SIZE EFFECTS.

Data from gas generation experiments conducted by PNNL suggests that it is reasonable to assume the average particle size for uranium metal in K East sludge is 750 microns rather than the safety basis number of 500 microns. The justification for this change is provided in SNF-7765, Revision 1, Section A.4.0.

For Hydrogen Generation.

The variation in the Uranium Metal-Water reaction rate as a function of particle size is a function of the surface area to volume ratio of the particles.

$$Q_{H2} \;=\; \xi K_w(T)\, A_V \frac{4}{32}\frac{1}{\rho_{H2}}$$

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
K_W = Rate law for $U+O_2 = UO_2$, 100% relative humidity, kg $O_2/m^2/s$,
A_V = Surface area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

Sludge surface area per unit volume is given by:

$$A_V \;=\; \frac{6\, C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal
ρ_m = U metal density
D = Particle size

Reaction rate as a function of particle size becomes:

$$Q_{H2F} = Q_{H2I} \times \left(\frac{D_I}{D_F}\right)$$

Where: Q_{H2F} = Final Reaction Rate (liters/hr)
Q_{H2I} = Initial Reaction Rate (liters/hr)
D_I = Initial Particle Size (microns)
D_F = Final Particle Size (microns)

For Oxygen Depletion/Generation.

The variation in the Uranium Metal-Oxygen reaction rate as a function of particle size is a function of the surface area to volume ratio of the particles.

$$Q_{O2} \;=\; K_O(T)\,A_V\,\frac{1}{\rho_{O2}}$$

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
K_O = Rate law for $U+O_2 = UO_2$, 100% relative humidity, kg $O_2/m^2/s$,
A_V = Surface area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

Sludge surface area per unit volume is given by:

$$A_V \;=\; \frac{6\,C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal
ρ_m = U metal density
D = Particle size

Reaction rate as a function of particle size becomes:

$$Q_{O2F} = Q_{O2I} \times \left(\frac{D_I}{D_F}\right)$$

Where:
Q_{O2F} = Final Reaction Rate (ppm/hr)
Q_{O2I} = Initial Reaction Rate (ppm/hr)
D_I = Initial Particle Size (microns)
D_F = Final Particle Size (microns)

In the case of hydrogen, the effect of this change is a reduction in the rate of the uranium-water reaction of a factor of 1.5 (a 33% reduction).

In the case of oxygen, given the dominance of the uranium oxide-oxygen reaction in the total consumption of oxygen, this change has little effect on the total time required to deplete the oxygen in the sludge matrix. For example, at 25^0 C a 6% reduction in consumption and a corresponding 6% increase in the time to depletion would be expected, however, at 15^0 C, this effect would be expected to be only 2%.

6.1.3.3 URANIUM METAL CONCENTRATION IN THE K EAST SLUDGE.

It is reasonable to assume that LDCs are not likely to contain the safety basis metal content. Careful review of the uranium metal content data for KE canister sludge shows that the safety basis value is not overly conservative and is therefore used for the reasonably bounding case. However, the safety basis uranium metal content value for KE floor sludge has been appropriately adjusted downward for the reasonably bounding case. Accordingly, the metal content is reduced from 63.8 Kg/m^3 to 55.5 Kg/m^3.

For Hydrogen Generation.

The variation in the Uranium Metal-Water reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final uranium metal concentration divided by the initial uranium metal concentration. The equation for this variation is:

$$K_{W2} = K_{W1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{W1} = The initial reaction rate (liters/hr)
K_{W2} = The final reaction rate (liters/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

For Oxygen Depletion/Generation.

The variation in the Uranium Metal-Oxygen reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final concentration divided by the initial concentration. The equation for this variation is:

$$K_{O2} = K_{O1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

As can be seen from the equations above, a reduction of 50% in the uranium metal concentration of the sludge reduces the uranium-water reaction rate by a factor of 2 (50%) while, because of the dominance of the uranium oxide-oxygen reaction to the total oxygen consumption rate, the same 50% change in the uranium metal concentration causes approximately a 9% change in total oxygen depletion rate at 25^0 C and approximately a 3.5% change in total oxygen depletion rate at 15^0 C.**6.1.3.4 REASONABLY BOUNDING DECAY POWER**

The Safety Basis Decay Power is 44.2 Watts/m^3. Attachment 7 discusses decay power in K East sludge and Attachment 10 provides a Reasonably Bounding value for decay power. That value is 36.2 Watts/m^3.

For Hydrogen Generation.

There is no effect on the volume of hydrogen gas evolved by the uranium-water reaction for a change in decay power, however there is a substantial change in the delay time to onset of hydrogen evolution as a result of the significant effect of a change in decay power on the oxygen consumption rate and the oxygen generation rate.

The radiolysis rate, therefore, the hydrogen generation rate from radiolysis is proportional to decay power, however, the radiolysis rate of the sludge is controlled by many complex variables. For this reason, the calculation of the radiolysis rate for each sludge type (pure canister, pure floor, 60% floor/40% canister) under each case condition (Modified Safety Basis, Reasonably Bounding, and Nominal) has been performed separately in Attachment 8. The only variable of concern for the calculations performed in attachments 15 – 27 is the variation of the volume of the gas with temperature, since the generation rates provided in Attachment 8 are provided at STP, this is a simple application of the ideal gas law. The equation used is:

$$QR_{H_2}(T) = QR_{H_2} \times \left(\frac{273.15 + T}{273.15} \right)$$

Where:

$QR_{H2}(T)$ = H_2 Generation Rate as a function of temperature (liters/hr)
QR_{H2} = H_2 Generation Rate at STP for the sludge type and case (liters/hr)
T = Sludge/LDC temperature (^{0}K)

For Oxygen Generation and Consumption.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The values provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\;H_2O}\right]$$

Where:

QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)
22.4 = Volume of 1 mole of any gas @ STP (liters)

32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the gas released using the following expression:

$$V_{O_2}(T)\ [liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15+T}{273.15}\right)$$

Where:
$V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

The consumption of oxygen is performed by two processes in the sludge: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4 and is unaffected by changes in decay power. The reaction of uranium oxides with oxygen is described in detail in Attachment 5 and is significantly affected by changes in decay power.

The variation of uranium oxide-oxygen reaction rate as a function of sludge decay power is a complex calculation involving several variables. This first variable is the concentration of uranium oxide present. For decay power to change, the total radioactivity present must have changed. Therefore, the total uranium present must have changed. Accordingly, a change in the concentration of total uranium results in a corresponding change in the concentration of reactive uranium oxides present.

The variation of uranium oxide – oxygen reaction rate as a function of uranium oxide concentration is a simple ratio of the final concentration divided by the initial concentration. The equation for the variation of uranium oxide-oxygen reaction rate as a function of uranium oxide concentration becomes:

$$R_{UOF} = R_{UOI} \times \frac{C_{UOF}}{C_{UOI}}$$

Where:
R_{UOF} = Final Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
C_{UOF} = Final Concentration of Reactive Uranium Oxides (Kg/m^3)
C_{UOI} = Initial Concentration of Reactive Uranium Oxides (Kg/m^3)

The other variables that change on a change of decay power all deal with the radiolysis rate affecting the reaction rate. These changes are:

1. The total power available for radiolysis is changed by the simple ratio of the final decay power divided by the initial decay power.
2. The sludge density changes because the total uranium concentration has changed. The sludge density change affects the fraction of the energy from radioactive decay that is deposited in the water as compared to the fraction of the energy that is deposited in the solids in the sludge. This change is applied through a ratio of the final water fraction divided by the initial water fraction.
3. Additionally, since the radiolysis rate that controls the rate of the uranium oxide-oxygen reaction is driven by power density, and the sludge density change directly results in a change to the power density, the radiolysis dose rate (grays/hr), a measure of energy per unit mass, is changed proportionately. This change is applied through a ratio of the initial density divided by the final density.

Taking these changes into account, the equation for the variation of the uranium oxide-oxygen reaction rate as a function of decay power becomes:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}}\right) \times \left(\frac{0.33 \times \left(DR_I \times \left(\frac{\rho_{SI}}{\rho_{SF}}\right) \times \left(\frac{WAF_F}{WAF_I}\right) \times \left(\frac{DP_F}{DP_I}\right)\right)^{0.33}}{0.33 \times (DR_I)^{0.33}}\right)$$

Where:
R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
DR_I = Initial Dose Rate (power deposited in the water) (grays/hr)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Simplifying the equation:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}}\right) \times \left(\left(\frac{\rho_{SI}}{\rho_{SF}}\right) \times \left(\frac{WAF_F}{WAF_I}\right) \times \left(\frac{DP_F}{DP_I}\right)\right)^{0.33}$$

Where:
R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Attachment 17 provides detailed calculations on the effect of the parameter changes necessary to produce the Reasonably Bounding Case. The time to reach 48 liters of hydrogen is extended from 264 hours for the Modified Safety Basis Case to 322 hours for the Reasonably Bounding Case.

6.1.4 THE NOMINAL CASE

For the Nominal case, the Reasonably Bounding parameters that affect hydrogen generation rate are examined to demonstrate the average expected hydrogen generation rates.

Attachment 10 displays tables of Safety Basis, Reasonably Bounding, and Nominal values for uranium metal concentration, and decay power, two parameters of interest.

One other parameter of interest will be examined in the Nominal Case. Reaction Rate Enhancement Factor (Multiplier).

6.1.4.1 THE URANIUM-WATER REACTION RATE ENHANCEMENT FACTOR (MULTIPLIER).

The uranium-water reaction rate enhancement factor (multiplier) is set to 3 in the current Safety Basis. Experimental data shows that this multiplier should be between 0.25 and 0.4 for hydrogen generation by the uranium-water reaction in K East sludge. For the nominal analysis in this paper, a multiplier of 0.4 is used. Attachment 9 provides a discussion of the Reaction Rate Enhancement Factor (Multiplier) and the basis for reducing it.

For Hydrogen Generation.

The variation of Uranium Metal-Water reaction rate as a function of Reaction Rate Enhancement Factor (Multiplier) is a simple ratio of the final reaction rate enhancement factor ($RREF_F$) divided by the initial reaction rate enhancement factor ($RREF_I$).

$$KW_F = KW_I \times \frac{RREF_F}{RREF_I}$$

Where:
KW_F = Final Reaction Rate (liters/hr)
KW_I = Initial Reaction Rate (liters/hr)
$RREF_F$ = Final Reaction Rate Enhancement Factor
$RREF_I$ = Initial Reaction Rate Enhance Factor

There is no corresponding factor for Oxygen depletion/generation.

6.1.4.2 URANIUM METAL CONCENTRATION IN THE K EAST SLUDGE.

Attachment 10 displays nominal values for uranium metal content as 18.6 Kg/m^3.

For Hydrogen Generation.

The variation in the Uranium Metal-Water reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final uranium metal concentration divided by the initial uranium metal concentration. The equation for this variation is:

$$K_{W2} = K_{W1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where: K_{W1} = The initial reaction rate (liters/hr)
K_{W2} = The final reaction rate (liters/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

For Oxygen Depletion/Generation.

The variation in the Uranium Metal-Oxygen reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final concentration divided by the initial concentration. The equation for this variation is:

$$K_{O2} = K_{O1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where: K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

As can be seen from the equations above, a reduction of 50% in the uranium metal concentration of the sludge reduces the uranium-water reaction rate by a factor of 2 (50%) while, because of the dominance of the uranium oxide-oxygen reaction to the total oxygen consumption rate, the same 50% change in the uranium metal concentration causes approximately a 9% change in total oxygen depletion rate at 25^0 C and approximately a 3.5% change in total oxygen depletion rate at 15^0 C.

6.1.4.3 NOMINAL DECAY POWER

Attachment 7 discusses decay power in K East sludge and Attachment 10 provides a Nominal value for decay power. That value is 10.6 Watts/m^3.

For Hydrogen Generation.

There is no effect on the volume of hydrogen gas evolved by the uranium-water reaction for a change in decay power, however there is a substantial change in the delay time to onset of hydrogen evolution as a result of the significant effect of a change in decay power on the oxygen consumption rate and the oxygen generation rate.

The radiolysis rate, therefore, the hydrogen generation rate from radiolysis is proportional to decay power, however, the radiolysis rate of the sludge is controlled by many complex variables. For this reason, the calculation of the radiolysis rate for each sludge type (pure canister, pure floor, 60% floor/40% canister) under each case condition (Modified Safety Basis, Reasonably Bounding, and Nominal) has been performed separately in Attachment 8. The only variable of concern for the calculations performed in attachments 15 – 27 is the variation of the volume of the gas with temperature, since the generation rates provided in Attachment 8 are provided at STP, this is a simple application of the ideal gas law. The equation used is:

$$QR_{H_2}(T) = QR_{H_2} \times \left(\frac{273.15+T}{273.15}\right)$$

Where: $QR_{H2}(T)$ = H_2 Generation Rate as a function of temperature (liters/hr)
QR_{H2} = H_2 Generation Rate at STP for the sludge type and case (liters/hr)
T = Sludge/LDC temperature (^{0}K)

For Oxygen Generation and Consumption.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The values provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\;H_2O}\right]$$

Where: QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)
22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the gas released using the following expression:

$$V_{O_2}(T)\ [liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15+T}{273.15}\right)$$

Where: $V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

The consumption of oxygen is performed by two processes in the sludge: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4 and is unaffected by changes in decay power. The reaction of uranium oxides with oxygen is described in detail in Attachment 5 and is significantly affected by changes in decay power.

The variation of uranium oxide-oxygen reaction rate as a function of sludge decay power is a complex calculation involving several variables. This first variable is the concentration of uranium oxide present. For decay power to change, the total radioactivity present must have changed. Therefore, the total uranium present must have changed. Accordingly, a change in the concentration of total uranium results in a corresponding change in the concentration of reactive uranium oxides present.

The variation of uranium oxide – oxygen reaction rate as a function of uranium oxide concentration is a simple ratio of the final concentration divided by the initial concentration. The equation for the variation of uranium oxide-oxygen reaction rate as a function of uranium oxide concentration becomes:

$$R_{UOF} = R_{UOI} \times \frac{C_{UOF}}{C_{UOI}}$$

Where: R_{UOF} = Final Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
C_{UOF} = Final Concentration of Reactive Uranium Oxides (Kg/m^3)
C_{UOI} = Initial Concentration of Reactive Uranium Oxides (Kg/m^3)

The other variables that change on a change of decay power all deal with the radiolysis rate affecting the reaction rate. These changes are:

1. The total power available for radiolysis is changed by the simple ratio of the final decay power divided by the initial decay power.
2. The sludge density changes because the total uranium concentration has changed. The sludge density change affects the fraction of the energy from radioactive decay that is deposited in the water as compared to the fraction of the energy that is deposited in the solids in the sludge. This change is applied through a ratio of the final water fraction divided by the initial water fraction.

3. Additionally, since the radiolysis rate that controls the rate of the uranium oxide-oxygen reaction is driven by power density, and the sludge density change directly results in a change to the power density, the radiolysis dose rate (grays/hr), a measure of energy per unit mass, is changed proportionately. This change is applied through a ratio of the initial density divided by the final density.

Taking these changes into account, the equation for the variation of the uranium oxide-oxygen reaction rate as a function of decay power becomes:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}} \right) \times \left(\frac{0.33 \times \left(DR_I \times \left(\frac{\rho_{SI}}{\rho_{SF}} \right) \times \left(\frac{WAF_F}{WAF_I} \right) \times \left(\frac{DP_F}{DP_I} \right) \right)^{0.33}}{0.33 \times \left(DR_I \right)^{0.33}} \right)$$

Where:

R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
DR_I = Initial Dose Rate (power deposited in the water) (grays/hr)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power ($watts/m^3$)
DP_F = Final Decay Power ($watts/m^3$)

Simplifying the equation:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}} \right) \times \left(\left(\frac{\rho_{SI}}{\rho_{SF}} \right) \times \left(\frac{WAF_F}{WAF_I} \right) \times \left(\frac{DP_F}{DP_I} \right) \right)^{0.33}$$

Where:

R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Attachment 18 provides detailed calculations on the effect of the parameter changes necessary to produce the Nominal Case. The time to reach 48 liters of hydrogen is extended from 322 hours for the Reasonably Bounding Case to 527 hours for the Nominal Case.

6.1.5 VENTED LDC AND CASK CONCLUSIONS AND RECOMMENDATIONS.

Although in the Reasonably Bounding Case, the time to reach 48 liters of generated hydrogen can be extended to 333 hours, 13.88 days, it is considered imprudent to routinely ship the LDC/Cask in a vented configuration containing air. One could easily envision malfunctions that could prevent the cask from being received at T Plant in the 13.88 days allotted from the time loading the first layer of sludge begins at K East. It is therefore considered necessary and prudent to provide for an inerting system that would prevent the hydrogen being generated from forming a flammable atmosphere in the LDC/Cask during the transportation phase of shipping the LDC to T Plant. It is also considered prudent to have the inerting system available in K East as a defense in depth system. Although nearly 14 days are available from the start of loading sludge into an LDC before a flammable atmosphere is possible, the possibility of a malfunction that would delay the LDC and result in a possible flammable atmosphere in K East cannot be completely discounted. Accordingly, the next step in this analysis will be to examine the time to form a flammable atmosphere in an inerted cask though the generation of oxygen released to the headspace of the LDC.

Table 6.1-1 – Summary of K East Sludge Characteristics, Parameters, and Hydrogen Behavior

Characteristic or Parameter	1.1 Safety Basis Case	Modified Safety Basis Case	Reasonably Bounding Case	Nominal Case
Sludge Mixture (% Volume) (Floor/Canister)	60/40	60/40	60/40	60/40
Decay Power (Watts/m^3)	69.9	44.2	36.2	10.6
Metal Concentration (Kg/m^3)	63.8	63.8	55.5	18.4
Reactive Uranium Oxide Concentration (Kg/m^3)	515	515	439	248
Total Uranium (Kg/m^3)	740	740	632	344
Metal Particle Size (microns)	500	500	750	750
Void Volume (m^3)	1.2	1.2	1.2	1.2
Temperature (^{0}C)	25	15-25	15-25	15-25
H_2 Generation (Radiolytic) (15^0 C) (L/Hr)	N/A	0.1741	0.1449	0.0449
H_2 Generation (Radiolytic) (25^0 C) (L/Hr)	0.5447	0.1801	0.1500	0.0465
H_2 Generation (Chemical) (15^0 C) (L/Hr)	N/A	5.16	1.01	0.134
H_2 Generation (Chemical) (25^0 C) (L/Hr)	12.0	12.0	2.36	0.313
H_2 Delay Time (Chemical) (Hours from completion of loading layer)	N/A	243	293	410
Time to Headspace Flammability (Episodic Release) (Hours) (Vented LDC – H_2 Limited) (Note 1)	36.75	264	322	527
Time to Headspace Flammability (Continuous Release) (Hours) (Vented LDC – H_2 Limited) (Note 2)	3.83	3.88	19.1	134
Time from start of loading to first layer loaded oxygen depletion (hours)	N/A	255	305	422
Time from start of loading to last layer loaded oxygen depletion (hours)	N/A	298	338	463

Note 1: This time is measured from the start of fill of the first sludge layer until the sludge has generated 48 liters of hydrogen.

Note 2: This time is measured from the completion of the final decant to the time when the sludge would have released 48 liters of hydrogen assuming continuous release. Assumes all oxygen has been depleted, the LDC temperature is at 25^0 C, and all generated hydrogen is being released directly to the headspace of the LDC.

6.2 SHIPPING AN LDC AND CASK INERTED WITH ARGON.

To analyze the issue of a flammable atmosphere in an LDC/Cask inerted with argon, one must examine the status of two gasses, hydrogen and oxygen. Two conditions must be met to form a flammable atmosphere in an LDC/Cask inerted with argon. Hydrogen concentration must be equal to or greater than 3.2% and oxygen concentration must be equal to or greater than 4%.

The LDC has two sources of hydrogen, radiolysis and the uranium-water reaction. Except for oxygen that enters the LDC during the closure process through the connections and during the final purge of the cask/LDC (a total of 2% oxygen), the only other significant source of oxygen to the LDC is the oxygen produced from radiolysis.

Since the oxygen produced from radiolysis and released as oxygen gas in a typical system is less than one-half the hydrogen released from radiolysis, and since an additional source of hydrogen exists, the uranium-water reaction, one can easily conclude that the hydrogen concentration in the LDC will always reach a value equal to or greater than 3.2% prior to the oxygen concentration reaching a value equal to or greater than 4%. Therefore, only oxygen concentrations will be calculated during this analysis. The hydrogen concentration will be assumed to always be higher than the oxygen concentration.

6.2.1 CURRENT SAFETY BASIS FOR AN INERTED LDC AND CASK.

The current Safety Basis predicts that K East sludge will begin to evolve oxygen from radiolysis at the rate of 0.1062 Liters/hr-m^3 immediately upon being loaded into the LDC. This oxygen generation rate is based on the following Safety Basis parameters:

Sludge Mixture:	60% Floor Sludge/40% Canister Sludge
Decay Power:	69.9 Watts/m^3
Metal Concentration:	63.85 Kg/m^3
Total Uranium:	740 Kg/m^3
Temperature:	25^0 C
Metal Particle Size:	500 microns
LDC Void Volume:	1.2 m^3

Under these Safety Basis conditions, and assuming that one layer of sludge 0.2 m^3 thick is loaded every 12 hours approximately 154 hours would be required during loading operations to generate the required 24 liters of oxygen to drive the LDC headspace to a flammable condition in the event of an episodic release. 24 liters is the additional 2% oxygen above the 2% assumed admitted to the LDC during disconnect and purge.

Following loading, if all oxygen had been cleared from the LDC, it would take approximately 88 hours for the required 24 liters of oxygen to be produced. Attachment 19 provides detailed calculations.

6.2.2 MODIFIED SAFETY BASIS FOR AN INERTED LDC AND CASK.

6.2.2.1 SLUDGE DECAY POWER.

The current Safety Basis uses a decay power for the LDC (69.9 Watts/m^3) that is above the decay power observed in actual samples of the K East sludge in the laboratory. This paper uses a more appropriate value for Safety Basis Decay Power for K East sludge. The values and approach used in this paper will be incorporated into the next revision of the sludge technical databook (HNF-SD-TI-015, Vol. 2).

The change in the decay power for the Modified Safety Basis case comes about as a result of a reinterpretation of the available data for the sludge. Additionally, since the oxygen reactions in the sludge that are relatively highly dependent on decay power have not yet been introduced into the problem, the change in decay power shown here has no effect on the rate of oxygen generation/consumption except for a small effect on the sludge radiolysis rate, discussed in the next section. The primary effect of the change in the decay power is to lower the heat up rate of the sludge following loading.

6.2.2.2 GAS GENERATION FROM RADIOLYSIS.

The current Safety Basis uses a gas generation rate from radiolysis that is in excess of any measured value for K East sludge during laboratory experiments. This paper establishes a revised Safety Basis Radiolysis Generation Rate that is being incorporated into the current Safety Basis.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The volumes provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right]\times\frac{1}{22.4}\left[\frac{moles}{liters}\right]\times 32\left[\frac{grams}{mole}\right]\times 1000\left[\frac{mg}{gram}\right]\times\frac{1}{1500}\left[\frac{2\,m^3}{Kg\,H_2O}\right]$$

Where:
QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)
22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the volume of gas released using the following expression:

$$V_{O_2}(T)\,[liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15 + T}{273.15}\right)$$

Where:
$V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

6.2.2.3 SLUDGE TEMPERATURE.

The current Safety Basis uses the safety basis temperature of 25^0 C for all gas generation and consumption calculations in K East. Since the sludge is actually loaded at approximately 12^0 C, this paper uses a loading temperature of 15^0 C for oxygen generation and consumption calculations during loading operations. Following loading operations the LDC increases to 25^0 C at 1^0 C per day until it stabilizes at 25^0 C in accordance with calculations in the current Safety Basis.

The uranium metal-oxygen reaction is:

$$U + O_{2\,(aq)} \rightarrow UO_2$$

The rate of reaction of uranium metal with oxygen is controlled by temperature as well as other factors. Only the temperature variation will be discussed in this section.

The base rate of the reaction is derived in Attachment 4 and is expressed in the number of hours required to deplete the oxygen contained in air saturated water at various reaction temperatures with the volume of the gasses expressed in liters/hr at STP. For purposes of these calculations, the liter/hr rate from Attachment 4 is converted to ppm/hr using the above equation and the base reaction rate is expressed as the concentration of oxygen in air saturated water at 25^0 C divided by the number of hours to deplete the oxygen calculated in Attachment 4 at a reaction temperature of 25^0 C (237 hours) producing a base reaction rate in terms of ppm/hr at 25^0 C.

The base reaction rate for the Modified Safety Basis calculation is 0.0359 ppm/hr.

The temperature variation of the rate of reaction of uranium metal and oxygen is defined by the equation:

$$\mathrm{Log}_{10}K_O \;=\; 8.333 - 3730/T$$

Where:
K_O = Reaction Rate of Uranium Metal-Oxygen Reaction (mg U/m^2 day)
T = Temperature in ^{0}K

Solving for K_O the equation becomes:

$$K_O = 10^{\left(8.333 - \frac{3730}{T}\right)}$$

Solving for a final reaction rate in terms of the initial reaction rate as a function of temperature, the equation becomes:

$$K_{O2} = K_{O1} \times \left(\frac{10^{\left(8.333 - \frac{3730}{T2}\right)}}{10^{\left(8.333 - \frac{3730}{T1}\right)}} \right)$$

Simplifying the equation results in:

$$K_{O2} = K_{O1} \times 10^{\left(3730 \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)}$$

Where:

K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
T_1 = The initial Temperature (^{0}K)
T_2 = The final Temperature (^{0}K)

In attachments 16 – 27 where these calculations are performed, this calculation is performed in a table containing “Relative Um Rate” and “Um Rate ppm/hr”. In this calculation:

K_{O1} = Base rate at 25^0 C (8.510 ppm/237 hours = 0.0359 ppm/hr)
K_{O2} = The final reaction rate for each temperature of interest. (Um Rate ppm/hr)
T_1 = 273.15 + 25 = 298.15^0 K
T_2 = 273.15 + Temp of interest (^{0}C)

The “Relative Um Rate” is calculated using the exponential part of the above equation.

As demonstrated above, the rate of the Uranium-Oxygen reaction is an exponential function of the temperature of the sludge at the reaction site. For a 10^0 C increase in the reaction temperature, the rate of the reaction varies from slightly less than a factor of 2.5 to slightly greater than a factor of 3.0 with the more pronounced effect at the lower temperatures (< 35^0 C).

The second process that consumes oxygen is the reaction of oxygen with uranium oxides. The reactions that cause this consumption are:

$$2\ UO_2 + O_2 + 4\ H_2O \rightarrow 2\ UO_3{\cdot}2H_2O$$
$$8\ UO_{2.25} + 3\ O_2 + 16\ H_2O \rightarrow 8\ UO_3{\cdot}2H_2O$$

At equal amounts of uranium present as UO_2 and $UO_{2.25}$, the combined reaction becomes:

$$8\ UO_2 + 8\ UO_{2.25} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

or

$$16\ UO_{2.125} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

Attachment 5 discusses these reactions in detail and provides the base rate of the reaction in the form of the number of hours required to deplete the oxygen in air saturated water at 25^0 C.

The rate of the reaction between oxygen and uranium oxides is governed by several factors. Only temperature is discussed in detail in this section.

The base rate of the reaction at 25^0 C is obtained from Attachment 5 and is identified in the spreadsheets that use this data as the "Uo Rate ppm/hr".

The variation in the Uranium Oxide – Oxygen Reaction Rate as a function of temperature is described in detail in Attachment 5. From Attachment 5, the equation describing the reaction rate as a function of temperature is:

> The rate of the reaction at 15°C can be as much as 1.61-times lower, according to the Arrhenius equation (rate = $Ae^{-Ea/RT}$) and an activation energy (E_a) for the reaction of 34 kJ/mole in non-complexing neutral solution (E_a = 29-34 kJ/mole reported in section 5.6 of Shoesmith, 2000):
>
> $$\frac{\text{Rate (25°C)}}{\text{Rate (15°C)}} = \frac{Ae^{-E_a/RT_{298}}}{Ae^{-E_a/RT_{288}}} = \frac{e^{[-34000\ \text{J/mole}]/[(8.314\ \text{J/mole}\cdot\text{deg})\cdot 298]}}{e^{[-34000\ \text{J/mole}][(8.314\ \text{J/mole}\cdot\text{deg})\cdot 288]}} = 1.61$$

Accordingly, the rate of the reaction at any temperature (T) can be expressed by the equation:

$$R_F = R_I \times \left(\frac{e^{\left[{}^{-34000\ J/mole}\!\big/\!_{((8.314\ J/mole\bullet\text{deg})\times T_F)} \right]}}{e^{\left[{}^{-34000\ J/mole}\!\big/\!_{((8.314\ J/mole\bullet\text{deg})\times T_I)} \right]}} \right)$$

Where:

R_I = Initial Reaction Rate (ppm/hr)
R_F = Final Reaction Rate (ppm/hr)
T_I = Initial Temperature (^{0}K)
T_F = Final Temperature (^{0}K)

In Attachments 16 – 18 and 20 - 27, the ratio of T_F over T_I is termed "Relative Uo Rate". By substituting 25^0 C (298.150 K) for the Initial Temperature and by simplifying the equation, "Relative Uo Rate" becomes:

$$RUo_R(T_F) = e^{\left(4089.5 \times \left(\frac{1}{298.15} - \frac{1}{273.15 - T_F}\right)\right)}$$

Where:

$RUo_R(T_F)$ = Relative Reaction Rate at temperature T_F

Reaction Rate is the Relative Reaction Rate to the rate at 25^0 C.

The product of the Relative Reaction Rate and the Reaction Rate at 25^0 C produces the reaction rate at any temperature of interest. This value is supplied in the spreadsheet as "Uo Rate ppm/hr".

As demonstrated above, the rate of the Uranium Oxide-Oxygen reaction is an exponential function of the temperature of the sludge at the reaction site. For a 10^0 C increase in the reaction temperature, the rate of the reaction varies from slightly less than a factor of 1.5 to slightly less than a factor of 1.7 with the more pronounced effect at the lower temperatures ($< 35^0$ C).

It should also be noted here that oxygen consumption is dominated by the Uranium Oxide-Oxygen reaction over the temperature range of interest ($15^0 – 25^0$ C) in that the consumption of oxygen by uranium oxides is between a 4.3 and 12.8 times higher than the consumption of oxygen by uranium metal with the more pronounced effect at the lower temperatures. Therefore, over the temperature range of interest, uranium oxides consume 82% to 93% of the oxygen consumed.

6.2.4.4 THE ROLE OF OXYGEN IN THE PRODUCTION OF HYDROGEN IN THE SLUDGE MATRIX

There are four processes/reactions that affect the time to oxygen depletion:

1. The concentration of oxygen in the water at the time the sludge enters the LDC. The concentration of oxygen is assumed to be the concentration for air saturated water at 15^0 C (loading temperature). The justification for this assumption is presented in section 6.1.2.4.
2. The generation of oxygen and oxidizing species by radiolysis. This generation rate is discussed in detail in Attachment 8.
3. The consumption of oxygen by uranium metal following loading in the LDC. This consumption rate is discussed in detail in Attachment 4.
4. The consumption of oxygen by reactive uranium oxides following loading of the LDC. This consumption rate is discussed in detail in Attachment 5.

It is reasonable to assume that the water mixed with the sludge as the sludge is loaded into the LDC is air saturated. This assumption is justified by three phenomena:

1. The basin is a very large pool of water with a very large surface area and only 17 feet deep making oxygenating of the water by the cover gas (air) easy.
2. The water in the basin is circulated by circulation systems, one of which is the skimmer system. The skimmer system takes the top 1 to 2 inches of the surface of the water that is in contact with the air and drains it to a centrifugal pump. The water is pumped through a sand filter and an ion exchanger and returned to the basin at the 12-foot level. The water entering this skimmer system does so through a gutter arrangement and moves into the system with entrained air. The flow rate of the skimmer system is 300 gallons per minute, which causes all the water in the basin to pass through this system approximately every 56 hours, keeping the water aerated.

3. The sludge retrieval system passes the sludge through 2 centrifugal pumps on the path to the LDC, which provides thorough, violent mixing of the sludge with the aerated water at the ratio of 3 parts water to one part sludge.

The CRC Tables were used to construct an oxygen concentration as a function of temperature table in each spreadsheet. This is used as the initial concentration of oxygen in the sludge matrix water. While the sludge is being loaded, the temperature of the sludge and LDC are maintained constant at 15^0 C. During this loading time, the effects on the oxygen content of the sludge matrix are generation by radiolysis, consumption by uranium metal and consumption by uranium oxides. However, after loading is complete, the temperature of the sludge and LDC starts to increase at the rate of 1^0 C per day until the temperature is 25^0 C. As the water in the sludge matrix heats up, the solubility of oxygen in the water decreases. Accordingly, after loading is complete, if the oxygen concentration exceeds the saturation value for the temperature of interest, oxygen may be released from the sludge in the form of very small bubbles as the oxygen is forced out of solution. Assuming the saturation value of oxygen to be a linear function over the small temperature range of interest ($15^0 - 25^0$ C), an equation was constructed for the saturation value of oxygen over the temperature range of operation of the LDC at K East.

$$O_{2ST} = O_{2ST1} + \left(\frac{(O_{2ST2} - O_{2ST1})}{T_1 - T_2} \right) \times (T_1 - T)$$

Note: This equation may only be used for temperature bands for which the value of oxygen saturation can be closely approximated by a linear function, such as between 15^0 and 25^0 C.

Where:
O_{2ST} = Oxygen Saturation Value for any Temperature T
O_{2ST1} = Oxygen Saturation Value at the High Temperature of Interest.
O_{2ST2} = Oxygen Saturation Value at the Low Temperature of Interest.
T_1 = High Temperature of Interest.
T_2 = Low Temperature of Interest.
T = Temperature of Interest. This value must be T2 <= T <= T1.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The volumes provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\,H_2O}\right]$$

Where:
QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)

22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the volume of gas released using the following expression:

$$V_{O_2}(T)\ [liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15 + T}{273.15}\right)$$

Where:
$V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

Two processes in the sludge perform the consumption of oxygen: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4. The reaction of uranium oxides with oxygen is described in detail in Attachment 5. Both of these reactions are covered briefly in section 6.4.2.3.

The sludge matrix contains dissolved oxygen present in the basin water as the sludge is pumped to the LDC and contains dissolved oxygen (or oxidizing species) produced from the radiolysis of water after the sludge is loaded into the LDC. Oxygen from both of these sources reacts with the uranium metal and uranium oxides present in the sludge. This oxygen dramatically affects the onset of the evolution of hydrogen from the uranium-water reaction, the reaction responsible for the majority of the hydrogen postulated to be generated in the LDC shortly after loading. The effect of this oxygen is to essentially "poison" the uranium-water reaction, preventing the evolution of hydrogen from this reaction until the oxygen in the sludge has been depleted. Although the possibility exists that extreme local metal distribution concentrations within the sludge may cause localized oxygen depletion earlier than in other areas with lesser metal concentrations, overall, the effect of metal distribution averaged over the volume of the container makes little or no difference in the time it takes for the sludge to generate the volume of hydrogen necessary to form a flammable atmosphere in air, 48 liters. The primary effect of these oxygen sources is to delay, by a substantial time, the onset of hydrogen evolution from the uranium-water reaction. The effect of the dissolved oxygen in the sludge and the oxygen generated from radiolysis is essentially ignored in the current Safety Basis. Attachment 1 provides a detailed discussion of the oxygen poisoning effect. Attachment 20 provides detailed calculations demonstrating the effects of the changes made to obtain the modified safety basis case. The oxygen in the sludge is depleted in approximately 325 hours. During this time the oxygen level in the sludge is continuously decreasing. No oxygen is released from the sludge to the headspace of the LDC and no flammable atmosphere is developed.

6.2.3 THE REASONABLY BOUNDING CASE

For the reasonably bounding case, the Safety Basis parameters that affect oxygen consumption and generation rates are examined to determine if more conservatism than necessary exists in these parameters.

In addition to possible over conservatisms in the values of the Safety Basis parameters, all Safety Basis parameters are used in calculations effectively amplifying the magnitude of the conservatisms even more.

Attachment 10 displays tables of Safety Basis, Reasonably Bounding, and Nominal values for uranium metal concentration, total uranium, and decay power, three parameters of interest.

Two other parameters of interest will be examined in the Reasonably Bounding Case. Reaction Rate Enhancement Factor (Multiplier) and uranium metal particle size.

6.2.3.1 THE URANIUM-WATER REACTION RATE ENHANCEMENT FACTOR (MULTIPLIER).

The uranium-water reaction rate enhancement factor (multiplier) is set to 3 in the current Safety Basis. Experimental data shows that this multiplier should be between 0.25 and 0.4 for hydrogen generation by the uranium-water reaction in K East sludge. For the reasonably bounding analysis in this paper, a multiplier of 1 is used. Attachment 9 provides a discussion of the Reaction Rate Enhancement Factor (Multiplier) and the basis for reducing it.

For Hydrogen Generation.

The variation of Uranium Metal-Water reaction rate as a function of Reaction Rate Enhancement Factor (Multiplier) is a simple ratio of the final reaction rate enhancement factor ($RREF_F$) divided by the initial reaction rate enhancement factor ($RREF_I$).

$$KW_F = KW_I \times \frac{RREF_F}{RREF_I}$$

Where:
KW_F = Final Reaction Rate (liters/hr)
KW_I = Initial Reaction Rate (liters/hr)
$RREF_F$ = Final Reaction Rate Enhancement Factor
$RREF_I$ = Initial Reaction Rate Enhance Factor

There is no corresponding factor for Oxygen depletion/generation.

6.2.3.2 URANIUM METAL PARTICLE SIZE EFFECTS.

The current Safety Basis uses a uranium metal particle size of 500 microns for all uranium metal particles. Experimental data obtained at PNNL demonstrates that the uranium particles in the K

East sludge behave like particles of approximately 780 microns, when modeled with the SNF databook rate equation. For this paper, a reasonably bounding particle size of 750 microns is used.

For Hydrogen Generation.

The variation in the Uranium Metal-Water reaction rate as a function of particle size is a function of the surface area to volume ratio of the particles.

$$Q_{H2} = \xi K_w(T) A_V \frac{4}{32} \frac{1}{\rho_{H2}}$$

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
K_W = Rate law for $U + O_2 = UO_2$, 100% relative humidity, kg $O_2/m^2/s$,
A_V = Surface area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

Sludge surface area per unit volume is given by:

$$A_V = \frac{6\, C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal
ρ_m = U metal density
D = Particle size

Reaction rate as a function of particle size becomes:

$$Q_{H2F} = Q_{H2I} \times \left(\frac{D_I}{D_F}\right)$$

Where:
Q_{H2F} = Final Reaction Rate (liters/hr)
Q_{H2I} = Initial Reaction Rate (liters/hr)
D_I = Initial Particle Size (microns)
D_F = Final Particle Size (microns)

For Oxygen Depletion/Generation.

The variation in the Uranium Metal-Oxygen reaction rate as a function of particle size is a function of the surface area to volume ratio of the particles.

$$Q_{O2} = K_O(T)\,A_V\,\frac{1}{\rho_{O2}}$$

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
K_O = Rate law for $U+O_2 = UO_2$, 100% relative humidity, kg $O_2/m^2/s$,
A_V = Surface area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

Sludge surface area per unit volume is given by:

$$A_V = \frac{6\,C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal
ρ_m = U metal density
D = Particle size

Reaction rate as a function of particle size becomes:

$$Q_{O2F} = Q_{O2I} \times \left(\frac{D_I}{D_F}\right)$$

Where:
Q_{O2F} = Final Reaction Rate (ppm/hr)
Q_{O2I} = Initial Reaction Rate (ppm/hr)
D_I = Initial Particle Size (microns)
D_F = Final Particle Size (microns)

In the case of hydrogen, the effect of this change is a reduction in the rate of the uranium-water reaction of a factor of 1.5 (a 33% reduction).

In the case of oxygen, given the dominance of the uranium oxide-oxygen reaction in the total consumption of oxygen, this change has little effect on the total time required to deplete the oxygen in the sludge matrix. For example, at 25^0 C a 6% reduction in consumption and a corresponding 6% increase in the time to depletion would be expected, however, at 15^0 C, this effect would be expected to be only 2%.

6.2.3.3 URANIUM METAL CONCENTRATION IN THE K EAST SLUDGE.

The current Safety basis uses a uranium metal content in the K East sludge that is well above the statistically reasonable value. Careful review of the uranium metal content data for KE canister sludge shows that the safety basis value is not overly conservative and is therefore used for the reasonably bounding case. However, the safety basis uranium metal content value for KE floor sludge has been appropriately adjusted downward for the reasonably bounding case.

For Hydrogen Generation.

The variation in the Uranium Metal-Water reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final uranium metal concentration divided by the initial uranium metal concentration. The equation for this variation is:

$$K_{W2} = K_{W1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{W1} = The initial reaction rate (liters/hr)
K_{W2} = The final reaction rate (liters/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

For Oxygen Depletion/Generation.

The variation in the Uranium Metal-Oxygen reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final concentration divided by the initial concentration. The equation for this variation is:

$$K_{O2} = K_{O1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

As can be seen from the equations above, a reduction of 50% in the uranium metal concentration of the sludge reduces the uranium-water reaction rate by a factor of 2 (50%) while, because of the dominance of the uranium oxide-oxygen reaction to the total oxygen consumption rate, the same 50% change in the uranium metal concentration causes approximately a 9% change in total oxygen depletion rate at 25^0 C and approximately a 3.5% change in total oxygen depletion rate at 15^0 C.

6.2.3.4 REASONABLY BOUNDING DECAY POWER

The Safety Basis Decay Power is 44.2 Watts/m^3. Attachment 7 discusses decay power in K East sludge and Attachment 10 provides a Reasonably Bounding value for decay power. That value is 36.2 Watts/m^3.

For Hydrogen Generation.

There is no effect on the volume of hydrogen gas evolved by the uranium-water reaction for a change in decay power, however there is a substantial change in the delay time to onset of hydrogen evolution as a result of the significant effect of a change in decay power on the oxygen consumption rate and the oxygen generation rate.

The radiolysis rate, therefore, the hydrogen generation rate from radiolysis is proportional to decay power, however, the radiolysis rate of the sludge is controlled by many complex variables. For this reason, the calculation of the radiolysis rate for each sludge type (pure canister, pure floor, 60% floor/40% canister) under each case condition (Modified Safety Basis, Reasonably Bounding, and Nominal) has been performed separately in Attachment 8. The only variable of concern for the calculations performed in attachments 15 – 27 is the variation of the volume of the gas with temperature, since the generation rates provided in Attachment 8 are provided at STP, this is a simple application of the ideal gas law. The equation used is:

$$QR_{H_2}(T) = QR_{H_2} \times \left(\frac{273.15 + T}{273.15} \right)$$

Where:
$QR_{H2}(T)$ = H_2 Generation Rate as a function of temperature (liters/hr)
QR_{H2} = H_2 Generation Rate at STP for the sludge type and case (liters/hr)
T = Sludge/LDC temperature (^{0}K)

For Oxygen Generation and Consumption.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The values provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\,H_2O}\right]$$

Where:
QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)

22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the gas released using the following expression:

$$V_{O_2}(T)\,[liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15+T}{273.15}\right)$$

Where:
$V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

The consumption of oxygen is performed by two processes in the sludge: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4 and is unaffected by changes in decay power. The reaction of uranium oxides with oxygen is described in detail in Attachment 5 and is significantly affected by changes in decay power.

The variation of uranium oxide-oxygen reaction rate as a function of sludge decay power is a complex calculation involving several variables. This first variable is the concentration of uranium oxide present. For decay power to change, the total radioactivity present must have changed. Therefore, the total uranium present must have changed. Accordingly, a change in the concentration of total uranium results in a corresponding change in the concentration of reactive uranium oxides present.

The variation of uranium oxide – oxygen reaction rate as a function of uranium oxide concentration is a simple ratio of the final concentration divided by the initial concentration. The equation for the variation of uranium oxide-oxygen reaction rate as a function of uranium oxide concentration becomes:

$$R_{UOF} = R_{UOI} \times \frac{C_{UOF}}{C_{UOI}}$$

Where:
R_{UOF} = Final Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
C_{UOF} = Final Concentration of Reactive Uranium Oxides (Kg/m^3)
C_{UOI} = Initial Concentration of Reactive Uranium Oxides (Kg/m^3)

The other variables that change on a change of decay power all deal with the radiolysis rate affecting the reaction rate. These changes are:

1. The total power available for radiolysis is changed by the simple ratio of the final decay power divided by the initial decay power.
2. The sludge density changes because the total uranium concentration has changed. The sludge density change affects the fraction of the energy from radioactive decay that is deposited in the water as compared to the fraction of the energy that is deposited in the solids in the sludge. This change is applied through a ratio of the final water fraction divided by the initial water fraction.
3. Additionally, since the radiolysis rate that controls the rate of the uranium oxide-oxygen reaction is driven by power density, and the sludge density change directly results in a change to the power density, the radiolysis dose rate (grays/hr), a measure of energy per unit mass, is changed proportionately. This change is applied through a ratio of the initial density divided by the final density.

Taking these changes into account, the equation for the variation of the uranium oxide-oxygen reaction rate as a function of decay power becomes:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}}\right) \times \left(\frac{0.22 \times \left(DR_I \times \left(\frac{\rho_{SI}}{\rho_{SF}}\right) \times \left(\frac{WAF_F}{WAF_I}\right) \times \left(\frac{DP_F}{DP_I}\right)\right)^{0.43}}{0.22 \times \left(DR_I\right)^{0.43}}\right)$$

Where:

R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
DR_I = Initial Dose Rate (power deposited in the water) (grays/hr)
er$_{SF}$ = Final Sludge Density (g/cm^3)
er$_{SI}$ = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Simplifying the equation:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}}\right) \times \left(\left(\frac{\rho_{SI}}{\rho_{SF}}\right) \times \left(\frac{WAF_F}{WAF_I}\right) \times \left(\frac{DP_F}{DP_I}\right)\right)^{0.43}$$

Where:

R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
er$_{SF}$ = Final Sludge Density (g/cm^3)
er$_{SI}$ = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Attachment 21 contains detailed calculations for the reasonably bounding case. Oxygen in the sludge is depleted in approximately 375 hours. No oxygen is released to the headspace of the LDC and no flammable atmosphere is developed.

6.2.4 THE NOMINAL CASE

For the Nominal case, the Reasonably Bounding parameters that affect oxygen generation rate are examined to demonstrate the average expected oxygen generation rates.

Attachment 10 displays tables of Safety Basis, Reasonably Bounding, and Nominal values for uranium metal concentration, and decay power, two parameters of interest.

One other parameter of interest will be examined in the Nominal Case. Reaction Rate Enhancement Factor (Multiplier).

6.2.4.1 THE URANIUM-WATER REACTION RATE ENHANCEMENT FACTOR (MULTIPLIER).

The uranium-water reaction rate enhancement factor (multiplier) is set to 3 in the current Safety Basis. Experimental data shows that this multiplier should be between 0.25 and 0.4 for hydrogen generation by the uranium-water reaction in K East sludge. For the nominal analysis in this paper, a multiplier of 0.4 is used. Attachment 9 provides a discussion of the Reaction Rate Enhancement Factor (Multiplier) and the basis for reducing it.

For Hydrogen Generation.

The variation of Uranium Metal-Water reaction rate as a function of Reaction Rate Enhancement Factor (Multiplier) is a simple ratio of the final reaction rate enhancement factor ($RREF_F$) divided by the initial reaction rate enhancement factor ($RREF_I$).

$$KW_F = KW_I \times \frac{RREF_F}{RREF_I}$$

Where: KW_F = Final Reaction Rate (liters/hr)
KW_I = Initial Reaction Rate (liters/hr)
$RREF_F$ = Final Reaction Rate Enhancement Factor
$RREF_I$ = Initial Reaction Rate Enhance Factor

There is no corresponding factor for Oxygen depletion/generation.

6.2.4.2 URANIUM METAL CONCENTRATION IN THE K EAST SLUDGE.

Attachment 10 displays nominal values for uranium metal content as 18.6 Kg/m^3.

For Hydrogen Generation.

The variation in the Uranium Metal-Water reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final uranium metal concentration divided by the initial uranium metal concentration. The equation for this variation is:

$$K_{W2} = K_{W1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{W1} = The initial reaction rate (liters/hr)
K_{W2} = The final reaction rate (liters/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

For Oxygen Depletion/Generation.

The variation in the Uranium Metal-Oxygen reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final concentration divided by the initial concentration. The equation for this variation is:

$$K_{O2} = K_{O1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

As can be seen from the equations above, a reduction of 50% in the uranium metal concentration of the sludge reduces the uranium-water reaction rate by a factor of 2 (50%) while, because of the dominance of the uranium oxide-oxygen reaction to the total oxygen consumption rate, the same 50% change in the uranium metal concentration causes approximately a 9% change in total oxygen depletion rate at 25^0 C and approximately a 3.5% change in total oxygen depletion rate at 15^0 C.

6.2.4.3 NOMINAL DECAY POWER

Attachment 7 discusses decay power in K East sludge and Attachment 10 provides a Nominal value for decay power. That value is 10.6 Watts/m^3.
For Hydrogen Generation.

There is no effect on the volume of hydrogen gas evolved by the uranium-water reaction for a change in decay power, however there is a substantial change in the delay time to onset of hydrogen evolution as a result of the significant effect of a change in decay power on the oxygen consumption rate and the oxygen generation rate.

The radiolysis rate, therefore, the hydrogen generation rate from radiolysis is proportional to decay power, however, the radiolysis rate of the sludge is controlled by many complex variables. For this reason, the calculation of the radiolysis rate for each sludge type (pure canister, pure floor, 60% floor/40% canister) under each case condition (Modified Safety Basis, Reasonably Bounding, and Nominal) has been performed separately in Attachment 8. The only variable of concern for the calculations performed in attachments 15 – 27 is the variation of the volume of the gas with temperature, since the generation rates provided in Attachment 8 are provided at STP, this is a simple application of the ideal gas law. The equation used is:

$$QR_{H_2}(T) = QR_{H_2} \times \left(\frac{273.15 + T}{273.15} \right)$$

Where:
$QR_{H2}(T)$ = H_2 Generation Rate as a function of temperature (liters/hr)
QR_{H2} = H_2 Generation Rate at STP for the sludge type and case (liters/hr)
T = Sludge/LDC temperature (^{0}K)

For Oxygen Generation and Consumption.

Oxygen, as well as other oxidizing species, are produced from radiolysis. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The values provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\,H_2O}\right]$$

Where:
QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)
22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)

1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the gas released using the following expression:

$$V_{O_2}(T)\,[liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15+T}{273.15}\right)$$

Where:
$V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

The consumption of oxygen is performed by two processes in the sludge: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4 and is unaffected by changes in decay power. The reaction of uranium oxides with oxygen is described in detail in Attachment 5 and is significantly affected by changes in decay power.

The variation of uranium oxide-oxygen reaction rate as a function of sludge decay power is a complex calculation involving several variables. This first variable is the concentration of uranium oxide present. For decay power to change, the total radioactivity present must have changed. Therefore, the total uranium present must have changed. Accordingly, a change in the concentration of total uranium results in a corresponding change in the concentration of reactive uranium oxides present.

The variation of uranium oxide – oxygen reaction rate as a function of uranium oxide concentration is a simple ratio of the final concentration divided by the initial concentration. The equation for the variation of uranium oxide-oxygen reaction rate as a function of uranium oxide concentration becomes:

$$R_{UOF} = R_{UOI} \times \frac{C_{UOF}}{C_{UOI}}$$

Where:
R_{UOF} = Final Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
C_{UOF} = Final Concentration of Reactive Uranium Oxides (Kg/m^3)
C_{UOI} = Initial Concentration of Reactive Uranium Oxides (Kg/m^3)

The other variables that change on a change of decay power all deal with the radiolysis rate affecting the reaction rate. These changes are:

4. The total power available for radiolysis is changed by the simple ratio of the final decay power divided by the initial decay power.
5. The sludge density changes because the total uranium concentration has changed. The sludge density change affects the fraction of the energy from radioactive decay that is deposited in the water as compared to the fraction of the energy that is deposited in the solids in the sludge. This change is applied through a ratio of the final water fraction divided by the initial water fraction.
6. Additionally, since the radiolysis rate that controls the rate of the uranium oxide-oxygen reaction is driven by power density, and the sludge density change directly results in a change to the power density, the radiolysis dose rate (grays/hr), a measure of energy per unit mass, is changed proportionately. This change is applied through a ratio of the initial density divided by the final density.

Taking these changes into account, the equation for the variation of the uranium oxide-oxygen reaction rate as a function of decay power becomes:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}}\right) \times \left(\frac{0.22 \times \left(DR_I \times \left(\frac{\rho_{SI}}{\rho_{SF}}\right) \times \left(\frac{WAF_F}{WAF_I}\right) \times \left(\frac{DP_F}{DP_I}\right)\right)^{0.43}}{0.22 \times (DR_I)^{0.43}}\right)$$

Where:

R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
DR_I = Initial Dose Rate (power deposited in the water) (grays/hr)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Simplifying the equation:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}} \right) \times \left(\left(\frac{\rho_{SI}}{\rho_{SF}} \right) \times \left(\frac{WAF_F}{WAF_I} \right) \times \left(\frac{DP_F}{DP_I} \right) \right)^{0.43}$$

Where:

R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power (watts/m^3)
DP_F = Final Decay Power (watts/m^3)

Attachment 22 provides detailed calculations for the effects of applying nominal values for reaction rate enhancement factor (multiplier), metal concentration, and decay power. The oxygen in the sludge is depleted in approximately 562 hours and no oxygen is released to the headspace of the LDC. Therefore, no flammable atmosphere is developed.

Table 6.2-1 – Summary of K East Sludge Characteristics, Parameters, and Oxygen Behavior

Characteristic or Parameter	Safety Basis Case	Modified Safety Basis Case	Reasonably Bounding Case	Nominal Case
Sludge Mixture (% Volume) (Floor/Canister)	60/40	60/40	60/40	60/40
Decay Power (Watts/m^3)	69.9	44.2	36.2	10.6
Metal Concentration (Kg/m^3)	63.8	63.8	55.5	18.4
Reactive Uranium Oxide Concentration (Kg/m^3)	515	515	439	248
Total Uranium (Kg/m^3)	740	740	632	344
Metal Particle Size (microns)	500	500	750	750
Void Volume (m^3)	1.2	1.2	1.2	1.2
Temperature (^{0}C)	25	15-25	15-25	15-25
O_2 Generation (Radiolytic) (ppm/Hr)	0.2724 (L/Hr)	0.0786	0.0654	0.0203
O_2 Consumption (Chemical) (Umetal) (ppm/Hr)	N/A	0.0132	0.0077	0.0025
O_2 Consumption (Chemical) (Uoxides) (ppm/Hr)	N/A	0.0870	0.0706	0.0262
Net O_2 (ppm/Hr)	N/A	-0.0216	-0.0081	-0.0084
O_2 Release Rate to Headspace (L/Hr)	N/A	0	0	0
Time to Headspace Flammability (Episodic Release) (Hours) (Inerted LDC) (Note 1)	286	Infinite	Infinite	Infinite
Time to Headspace Flammability (Continuous Release) (Hours) (Inerted LDC) (Note 2)	220	Infinite	Infinite	Infinite
Time from start of loading to first layer oxygen depletion (Hours)	N/A	295	355	537
Time from start of loading to last layer oxygen depletion (Hours)	N/A	325	375	568
Time to 48 Liters of hydrogen available (Hours)	36.8	300	362	623

Note 1: This time is measured from the start of fill of the first sludge layer until the sludge has generated 24 liters of oxygen.

Note 2: This time is measured from the completion of the final decant to the time when the sludge would have released 24 liters of hydrogen assuming continuous release. Assumes the LDC temperature is at 15^0 C, and all generated oxygen is being released directly to the headspace of the LDC.

6.2.5 EFFECT OF LOADING METHOD ON HYDROGEN AND OXYGEN GENERATION.

The overall load of an LDC is limited to a mixture of 60% floor sludge and 40% canister sludge. Since the allowed sludge lift of 0.29 m^3 results in sludge layers that are approximately 16 cm thick, twice the oxygen diffusion length, it is appropriate to examine how loading sludge layers rich in metal content between layers poor in metal content will affect the gas generation within the LDC.

To conduct this analysis, three cases will be examined using the parameters for the Modified Safety Basis case:

1. Each sludge layer contains a 60/40 mix of floor and canister sludge. The LDC is loaded at the rate of one layer every 12 hours. Each layer will be 0.2 m^3. A delay of 5 days is encountered between the end of the loading process and shipping the LDC to T Plant. LDC temperature is maintained at 150 C to minimize oxygen consumption and maximize oxygen generation. The total delay time until 48 liters of hydrogen and/or 24 liters of oxygen have been produced will be calculated.
2. Same as case 1 except the sludge layers will be loaded with 4 layers of canister sludge on the bottom (first) and 6 layers of floor sludge on the top (last) of the LDC.
3. Same as case 1 except the sludge layers will be loaded with 6 layers of floor sludge on the bottom (first) and 4 layers of canister sludge on the top (last).

The results of Case 1 are presented in Attachment 23.

1. Oxygen depletion occurs in 717 hours. No oxygen gas is released to the headspace of the LDC or retained in the sludge.

2. Hydrogen volume reaches 48 liters in 342 hours.

The results of Case 2 are presented in Attachment 24.

1. Oxygen depletion occurs in the canister layers in 206 hours but the floor layers very slowly generate oxygen. The release of oxygen from the floor layers reaches a volume of 24 liters in 174 days.

2. Hydrogen volume reaches 48 liters in 193 hours

The results of Case 3 are presented in Attachment 25.

1. Oxygen depletion occurs in the canister layers in 279 hours but the floor layers very slowly generate oxygen. However, since the canister layers are on top of the floor layers, the oxygen cannot escape the sludge to the headspace of the LDC because the oxygen gets consumed by the canister sludge as the oxygen travels upward through the sludge.

2. Hydrogen volume reaches 48 liters in 261 hours

Care should be exercised in evaluating the results of this loading analysis. A simplification used in the spreadsheet consists of treating each sludge layer as an independent entity that does not interact/communicate with the layers around it. This simplification is causing an apparent significant variation in the time to reach 48 liters of hydrogen for unbalanced loads. The diffusion of oxygen within the sludge matrix is fast compared to the reaction rates of the reactants and oxygen will diffuse between layers. The outcome of this is that the result of an unbalanced load will most likely be that all three cases would start to produce hydrogen by chemical reaction at the same time and therefore reach 48 liters of hydrogen at the same time. The unbalanced loads may even start the chemical production of hydrogen earlier than the balanced load.

The point being demonstrated is that unbalanced loads will not change the behavior of the hydrogen generated appreciably. Further, combined with the experience with samples 96-05 and 96-06, which formed vessel spanning bubbles, it is recommended that large loads of canister sludge not be loaded underneath loads of floor sludge. This sets up the conditions for the formation of a vessel spanning bubble.

6.2.6 ANALYSIS OF AN LDC CONTAINING 100% FLOOR SLUDGE FOR POSSIBLE OXYGEN RELEASE.

As noted in two of the three unbalanced load cases in section 6.2.5, loads of pure floor sludge can produce oxygen under the right conditions. The following analysis uses an LDC loaded with 100% floor sludge to investigate the possibility that a flammable atmosphere may be produced in an inerted LDC from the oxygen released from a 100% floor sludge load.

To set the conditions for oxygen generation, 100% floor sludge is used and the temperature is maintained at 15^0 C (the loading temperature) to maintain oxygen consumption low.

The results of the analysis are presented in attachments 26A, 26B, and 26C.

For the low temperature case, the Modified Safety Basis case is bounding. In the Modified Safety Basis case, the sludge can release 24 liters (2% in the headspace) of oxygen in 105 days. 24 liters is half of the oxygen required to form a flammable atmosphere in an Ar-H_2-O_2 atmosphere with a minimum of 3.24% hydrogen available. These results are summarized in Table 6.2-2A.

For comparison purposes, since it is not reasonable to assume the LDC will not warm to room temperature, attachment 27 provides a duplicate analysis to the analysis conducted in attachment 26 except that the LDC temperature is allow to increase to 25^0 C (room temperature). In all cases the time to generated 24 liters of oxygen is substantially increased. In fact, the times to generated 24 liters of oxygen are so long that other reactions, such as corrosion of the stainless steel, would begin to dominate and consume the remaining oxygen. These results are summarized in Table 6.2-2B.

Table 6.2-2A – Summary of K East Sludge Characteristics, Parameters, and Bounding Oxygen Behavior with Temperature Maintained at 15^0 C.

Characteristic or Parameter	Modified Safety Basis Case	Reasonably Bounding Case	Nominal Case
Sludge Mixture (% Volume) (Floor/Canister)	100/0	100/0	100/0
Decay Power (Watts/m^3)	22.4	8.96	3.12
Metal Concentration (Kg/m^3)	23	9.17	4
Reactive Uranium Oxide Concentration (Kg/m^3)	211	84.4	42.7
Total Uranium (Kg/m^3)	300	120	60
Metal Particle Size (microns)	500	750	750
Void Volume (m^3)	1.2	1.2	1.2
Temperature (^{0}C)	15	15	15
O_2 Generation (Radiolytic) (ppm/Hr) @ 15^0 C	0.0434	0.0184	0.0066
O_2 Consumption (Chemical) (Umetal) (ppm/Hr) @ 15^0 C	0.0032	0.0013	0.00055
O_2 Consumption (Chemical) (Uoxides) (ppm/Hr) @ 15^0 C	0.0314	0.0093	0.0031
Net O_2 (ppm/Hr) @ 15^0 C	0.0088	0.0078	0.00295
O_2 Release Rate to Headspace (L/Hr) @ 15^0 C	0.0098	0.0087	0.0032
Time to Headspace Flammability (Episodic Release) (Hours) (Inerted LDC) (Note 1)	105 days	118 days	311 days
Time to Headspace Flammability (Continuous Release) (Hours) (Inerted LDC) (Note 2)	102 days	115 days	308 days
Time from start of loading to first layer oxygen depletion (Hours)	Infinite	Infinite	Infinite
Time from start of loading to last layer oxygen depletion (Hours)	Infinite	Infinite	Infinite
Time to 48 Liters of hydrogen available (Hours)	565	1440	3600

Note 1: This time is measured from the start of fill of the first sludge layer until the sludge has generated 24 liters of oxygen.

Note 2: This time is measured from the completion of the final decant to the time when the sludge would have released 24 liters of hydrogen assuming continuous release. Assumes the LDC temperature is at 15^0 C, and all generated oxygen is being released directly to the headspace of the LDC.

Table 6.2-2B – Summary of K East Sludge Characteristics, Parameters, and Bounding Oxygen Behavior with Temperature Allowed to Heat to 25^0 C.

Characteristic or Parameter	Modified Safety Basis Case	Reasonably Bounding Case	Nominal Case
Sludge Mixture (% Volume) (Floor/Canister)	100/0	100/0	100/0
Decay Power (Watts/m^3)	22.4	8.96	3.12
Metal Concentration (Kg/m^3)	23	9.17	4
Reactive Uranium Oxide Concentration (Kg/m^3)	211	84.4	42.7
Total Uranium (Kg/m^3)	300	120	60
Metal Particle Size (microns)	500	750	750
Void Volume (m^3)	1.2	1.2	1.2
Temperature (^{0}C)	15 - 25	15 - 25	15 - 25
O_2 Generation (Radiolytic) (L/Hr) @ 25^0 C	0.0434	0.0184	0.0066
O_2 Consumption (Chemical) (Umetal) (ppm/Hr) @ 25^0 C	0.0086	0.0034	0.0015
O_2 Consumption (Chemical) (Uoxides) (ppm/Hr) @ 25^0 C	0.0506	0.0149	0.0050
Net O_2 (ppm/Hr) @ 25^0 C	-0.0158	0.00000498	0.0000957
O_2 Release Rate to Headspace (L/Hr) @ 25^0 C	2.14 liters total	0.0000057	0.00011
Time to Headspace Flammability (Episodic Release) (Hours) (Inerted LDC) (Note 1)	Infinite	> 100 years	> 20 years
Time to Headspace Flammability (Continuous Release) (Hours) (Inerted LDC) (Note 2)	Infinite	> 100 years	> 20 years
Time from start of loading to first layer oxygen depletion (Hours)	881	Infinite	Infinite
Time from start of loading to last layer oxygen depletion (Hours)	881	Infinite	Infinite
Time to 48 Liters of hydrogen available (Hours)	565	1440	3600

Note 1: This time is measured from the start of fill of the first sludge layer until the sludge has generated 24 liters of oxygen.

Note 2: This time is measured from the completion of the final decant to the time when the sludge would have released 24 liters of hydrogen assuming continuous release. Assumes the LDC temperature is at 15^0 C, and all generated oxygen is being released directly to the headspace of the LDC.

6.2.7 INERTED LDC AND CASK CONCLUSIONS AND RECOMMENDATIONS.

The inerted LDC/Cask provides a better margin of safety for transportation of the cask from K East to T Plant. In the event of a malfunction that would prevent shipping a partially loaded LDC from K East, the inerting system provides a good defense in depth option.

Although it is possible to form oxygen in pure floor sludge, the rate of formation is so slow that no problems can be encountered in any reasonable timeframe. Formation of a flammable atmosphere by oxygen released from the sludge is not considered a credible event.

Care should be taken not to load sludge with high metal concentrations under sludge with low metal concentrations. This type of loading could result in the formation of a vessel spanning bubble.

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Attachment 1

Oxygen Poisoning

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

OXYGEN POISONING

The oxidation of uranium metal and uranium oxide compounds immersed in water relevant to K Basin sludge occurs by several reactions that involve the chemical consumption and production of gases:

$$U + 2\ H_2O \rightarrow UO_2 + 2\ H_{2\,(g)} \qquad (1)$$

$$U + O_{2\,(aq)} \rightarrow UO_2 \qquad (2)$$

$$U + 0.875\ N_{2\,(aq)} \rightarrow UN_{1.75} \qquad (3)$$

$$U + 1.5\ H_{2\,(g)} \rightarrow UH_3 \qquad (4)$$

$$UH_3 + 2\ H_2O \rightarrow UO_2 + 7\ H \text{ (or } 3.5\ H_{2\,(g)}) \qquad (5)$$

$$2\ UO_2 + O_2 + 4\ H_2O \rightarrow 2\ UO_3{\cdot}2H_2O \qquad (6)$$

$$8\ UO_{2.25} + 3\ O_2 + 16\ H_2O \rightarrow 8\ UO_3{\cdot}2H_2O \qquad (7)$$

In aerated waters uranium corrosion occurs by reactions with dissolved oxygen and nitrogen (reactions 2 and 3). In addition, dissolved oxygen is consumed by reactions with uranium oxide (reactions 6 and 7). However, if the system should become isolated and the dissolved oxygen is depleted by reactions 2, 6, and 7, the direct reaction of uranium with water becomes dominant and hydrogen gas is produced. While both reactions 1 and 2 occur to form UO_2, the rate of reaction 2 (that is the reaction of uranium with dissolved oxygen) is 30 to 40 times slower than reaction 1 (the direct reaction of uranium with water). Further, reaction 1 seemingly does not occur until the dissolved oxygen in the water has been depleted (anoxic conditions achieved).

There is seemingly conflicting data on the amount of dissolved oxygen necessary to "poison" the uranium water reaction, reaction 1:

1. In experiments conducted at PNNL designed to measure the effect of dissolved oxygen content, a coupon of uranium was placed into a flow through chamber and water was flowed through the chamber containing air saturated water at 25^0 C. The oxygen in the water prevented the uranium-water reaction. The water was then changed to argon-saturated water. The uranium-water reaction started, after some delay (discussed later), and continued until air-saturated water was again admitted to the chamber. When the air saturated water reentered the chamber, the uranium-water reaction stopped along with the production of hydrogen. However, it must be remembered that this experiment was conducted with a uranium coupon many times larger than the uranium particles present in the K Basin sludge and with only water as the cover surrounding the coupon, rather than the sludge/water mixture surrounding the particles in K Basin sludge. Accordingly, the possible slowdown of oxygen diffusion in the sludge must be considered when evaluating this phenomenon in sludge.

2. In a similar experiment to 1 above at PNNL, a coupon was maintained in a flow through chamber and air saturated water was pumped through the chamber at 25^0 C. Again the oxygen in the water prevented the uranium water reaction. Later, water was pumped through the chamber that contained only about 1-ppm oxygen and the oxygen in the water continued to prevent the uranium water reaction. However, it must be remembered that this experiment was conducted with a uranium coupon many times larger than the uranium particles present in the K Basin sludge and with only water as the cover surrounding the coupon, rather than the sludge/water mixture surrounding the particles in K Basin sludge. Accordingly, the possible slowdown of oxygen diffusion in the sludge must be considered when evaluating this phenomenon in sludge.

In seeming conflict with the results of the above experiments:

1. In 1945, experiments were conducted to measure gas generation rates from the corrosion of uranium in water. Again, sludge was not present and large uranium coupons were used rather than the smaller particles of interest in sludge. The experiments demonstrated the ability of oxygen to prevent the evolution of hydrogen from the uranium-water reaction but concluded that the evolution of hydrogen did not appear to be prevented at temperatures above approximately 60^0 C and only after a significant period of time.

2. In 1996, two samples of KE canister sludge were used for experiments (96-05 and 96-06). Shortly after air sparging, these samples generated hydrogen gas. The pertinent conditions associated with the behavior of these samples are described in detail in Attachment 2. A modeling calculation that describes the behavior of these samples, especially 96-06, is provided in Attachment 3.

The majority of the data surrounding the effect of dissolved oxygen on the uranium-water reaction and the production of hydrogen supports the conclusion that the presence of any dissolved oxygen will prevent the evolution of hydrogen from the uranium-water reaction from evolving hydrogen.

Oxygen diffusion calculations (Attachment 6) show that, even for dissolved oxygen inside sludge, diffusion rates for oxygen will support oxygen poisoning of the uranium water reaction until the oxygen is depleted within the sludge for relatively well distributed uranium metal concentrations.

Modeling calculations (Attachments 2 and 3) demonstrate that in extreme cases, conditions not likely to be encountered in an LDC, where the uranium metal is concentrated in a very small part of the sludge, the oxygen diffusion gradient can become so severe that local areas of oxygen depletion can be encountered and unusually short delay times can occur. This is believed to be the reason why sample 96-06 restarted within 90 minutes of being air sparged. In sample 96-06, the uranium metal concentration in one layer may have been ~75 times greater than that of uniformly distributed uranium metal in 60/40 KE floor/canister safety basis sludge. The modeling in Attachment 3 demonstrates that it is possible for the metal distribution in this sample of sludge to be so biased to the lower portion of the sample that the gradient set up for oxygen diffusion is unable to keep the uranium-water reaction from starting in the lower part of the sample. The restart of the reaction should have taken approximately 15 hours to occur, but the extremely high metal concentration in a small part of the sample caused a local oxygen depletion and caused the sample to restart in about one-tenth the expected time (approximately 90 minutes). This model demonstrates the possibility that, except in the extremely unlikely event that all the uranium metal would concentrate in the bottom 10% of the LDC, the distribution of the metal within the LDC has only a small overall effect on the gas behavior within the LDC. However, care should be exercised during the loading of the LDC to avoid producing thick (>0.2 m^3) layers of highly metal concentrated canister sludge with layers of floor sludge over top. This condition can also increase the potential formation of a vessel spanning hydrogen bubble, which can result in a relatively rapid release of gas when the bubble is ruptured.

Although oxygen in water surrounding, or covering a sludge layer is likely to play a role in poisoning of the uranium water reaction as the oxygen diffuses across sludge boundary layer, it is unclear how much of the oxygen present in the cover water is usable. Accordingly, the oxygen present in the cover water is not used in calculations presented later in this paper. This effect also applies to reoxygenating sludge after the oxygen has been depleted and the uranium water reaction has started.

It is therefore reasonable to conclude the following concerning the effect of dissolved oxygen on the uranium-water reaction in K Basin sludge:

1. For oxygen poisoning to take place in K Basin sludge it is necessary to thoroughly and violently mix the sludge with oxygenated water during the loading process into the LDC.

2. The dissolved oxygen originally contained within a sludge layer, the oxygen produced by radiolysis within a sludge layer, as well as oxygen present in adjacent sludge layers will contribute to oxygen poisoning.

3. The oxygen present in water adjacent to a sludge layer, although a probable contributor to the oxygen inventory in the sludge, is unpredictable and will be assumed to not be available to contribute to oxygen poisoning within a sludge layer.

4. Once the uranium-water reaction has begun to evolve hydrogen, it is difficult to stop the reaction short of thoroughly and violently remixing the sludge layer with oxygenated water in a manner similar to the original loading process or allowing the reactants to be consumed.

The above conclusions are made to a reasonably bounding certainty and are considered more than adequate to establish safety controls necessary to control the loading, transportation, and storage of K Basin sludge while incurring minimal, reasonable risk.

Release of Radiolytically Produced Oxygen from the Sludge. Questions have been raised about whether radiolytically generated oxygen could be released into the headspace of an LDC. Three chemical reactions occur in the sludge that consume oxygen:

$$U + O_{2\,(aq)} \rightarrow UO_2 \qquad (1)$$

$$2\ UO_2 + O_2 + 4\ H_2O \rightarrow 2\ UO_3{\cdot}2H_2O \qquad (2)$$

$$8\ UO_{2.25} + 3\ O_2 + 16\ H_2O \rightarrow 8\ UO_3{\cdot}2H_2O \qquad (3)$$

The oxygen balance in the sludge is defined by the following expression:

$$C_{O2} = C_{O2I} - (Q_{O2,met} + Q_{O2,ox} - Q_{O2,rad})*(t)$$

where subscripts are:

t = time
C_{O2I} = Initial concentration of oxygen in the water
C_{O2} = Concentration of oxygen in the water.
Q = Rate
met = Consumption by metal oxidation
ox = Consumption by uranium oxide hydration
rad = Radiolytic production of all oxidizing species in terms of equivalent O_2.

C_{O2I} – The initial concentration of dissolved oxygen in the water is a function of the temperature of the water entering the LDC. This concentration is affected by changes in temperature in the LDC and some gas could be formed in the sludge matrix as the LDC heats up following fill. Because it is conservative to do so, for purposes of this discussion and the calculations presented in this paper, the oxygen contained in the sludge will not be allowed to escape except during an episodic release in which the concentration of the LDC headspace would exceed flammable limits. For this reason, the concentration of the oxygen in a sludge layer will be expressed in ppm despite the fact that part of the oxygen will be dissolved in the water and part of the oxygen may be distributed throughout the sludge as small bubbles. For analysis purposes, a separate calculation of the estimate of the amount of gas (liters) contained in the sludge will be maintained for each calculation case so that the time when an episodic release would result in a flammable condition in the headspace of the LDC will be known.

$Q_{O2,met}$ – The rate of consumption of oxygen by uranium metal is affected by three primary variables. Temperature of the sludge, the concentration of reactive metal in the sludge, and the size of the metal particles (surface to volume ratio). In the temperature range of interest (10^0 C – 50^0 C), the rate of this reaction changes by a factor of 3.04 to 2.34 (average 2.66) for every 10^0 C change in temperature. The concentration of the reactive metal affects the rate of the reaction as a direct proportionality. If the metal concentration is doubled, the rate of the reaction doubles (assuming the added metal has the same or similar particle size distribution). The particle size distribution affects the rate of this reaction as a function of surface area to volume ratio. As the average particle size decreases, the rate of the reaction increases (assuming the metal concentration remains relatively constant). For K East sludge, it has been determined that the particles, on average, exhibit the characteristics of spherical particles that are approximately 750 microns in diameter.

$Q_{O2,ox}$ – The rate of consumption of oxygen by the uranium oxide species present. The rate of this reactions varies with temperature and the decay power of the sludge. For the temperature range of interest (10^0 C – 50^0 C), the reaction rate increases by a factor of 1.5 for each 10^0 C increase in temperature. For decay power, the rate of the reaction decreases by 16.5% for each 36% increase in the decay power.

$Q_{O2,rad}$ – Radiolysis of water defines the production rate of oxygen in the sludge. The radiolysis of water varies with the decay power of the sludge. As decay power is increased, radiolysis rates increase by the same factor.

C_{O2} – This is the concentration of oxygen in the sludge matrix. The number depicting this value will be expressed in ppm for all calculations in this paper. The total oxygen content in the sludge may be a combination of dissolved oxygen and trapped oxygen bubbles. Just as with all other gasses generated in a sludge, some fraction of the gas will escape the sludge matrix and enter the headspace of the LDC and some fraction will be captured and retained in the sludge matrix. For purposes of calculations done in support of this paper, all gasses produced by radiolysis or chemical reactions will be retained in the sludge and will only be released by episodic gas releases. This retention of all gasses generated will continue until the total gas retained in the sludge matrix is 35% of the volume of the matrix (approximately 1 m^3). After the sludge as reached the 3% retention, a headspace of 0.2 m^3 remains in the LDC, the hydrogen generated within the sludge matrix will be allowed to escape at a rate sufficient to compensate for both hydrogen and oxygen generation.

The above expression of oxygen concentration can be used to predict the number of hours from loading a sludge layer until that sludge layer will be depleted of oxygen. This time is generally known as delay time because it defines the time from loading of a sludge layer until the uranium-water reaction will evolve hydrogen.

The delay time is given by:

$$t = \frac{C_{O2}}{Q_{O2,met} + Q_{O2,ox} - Q_{O2,rad}}$$

where subscripts are:

C_{O2} = Initial concentration of oxygen in the water.
Q = Rate
met = Consumption by metal oxidation
ox = Consumption by uranium oxide hydration
rad = Radiolytic production of all oxidizing species in terms of equivalent O_2.

As can be seen from the above expression, as long as the consumption rates of the oxygen are greater than the generation rate of the oxygen, a positive number will be calculated for the delay time equal to the time from the completion of loading a sludge layer until that sludge layer is depleted of oxygen and the uranium-water reaction will evolve hydrogen. However, in some cases the generation rate of oxygen is higher than the consumption rate. In that case, "infinity" is indicated in the calculated time block. Infinity indicates that the uranium-water reaction will not evolve hydrogen at that temperature and eventually, enough oxygen will buildup in the sludge that an episodic release of gasses from the sludge will result in a flammable condition in the headspace of the LDC.

Since a revised calculation of the Safety Basis Decay Power has been made to SNF-7765, revising the Safety Basis Decay Power from 138 Watts per LDC loaded with 2 m^3 of sludge at 60% floor sludge and 40% canister sludge to 88.4 Watts per LDC loaded with 2 m^3 of sludge at 60% floor sludge and 40% canister sludge, a reexamination of the above Safety Basis case is warranted. In addition, a revised radiolysis calculation is being used in a change to SNF-9955. Accordingly, this change will also be examined. Attachment 14D, the Modified Safety Basis Case provides the results of the analysis of these changes. For the Modified Safety Basis conditions at 15^0 C:

Oxygen generation from Radiolysis = 0.0826 ppm/hr
Oxygen consumption from the reaction with uranium metal = 0.0388 ppm/hr
Oxygen consumption from the reaction with uranium oxide species = 0.0915 ppm/hr

Net oxygen = 0.0826 – 0.0388 – 0.0915 = -0.0477 ppm/hr

Since the consumption rate for oxygen exceeds the generation rate for oxygen by 0.0477 ppm/hr, the oxygen will be depleted from each layer of the sludge approximately 212 hours after the layer is loaded and that layer will begin evolving hydrogen from the uranium-water reaction. This compares to a generation rate for oxygen that exceeded the consumption rate of oxygen in the Safety Basis Case and resulted in the release of oxygen to the headspace of the LDC. In the Modified Safety Basis Case no oxygen will be released to the headspace of the LDC from the sludge matrix.

In the Modified Safety Basis Case, no oxygen will be released to the headspace of the LDC at any temperature greater than or equal to 10^0 C. At temperatures less than 10^0 C, it is possible using Modified Safety Basis parameters to have oxygen released to the headspace of the LDC. This compares to temperatures less than or equal to 23^0 C in the Safety Basis Case.

In an effort to define and examine a bounding case for oxygen consumption, the Modified Safety Basis Case was used but no uranium metal was present. In addition, the temperature was maintained at 15^0 C to minimize the consumption of oxygen by the uranium oxide species present.

Oxygen generation from Radiolysis = 0.0826 ppm/hr
Oxygen consumption from the reaction with uranium metal = 0.0 ppm/hr
Oxygen consumption from the reaction with uranium oxide species = 0.0915 ppm/hr

Net oxygen = 0.0826 – 0.0915 = -0.0089 ppm/hr

Since the consumption rate exceeds the generation rate by 0.0089 ppm/hr, no oxygen will be released to the headspace of the LDC and the oxygen will be depleted from each sludge layer approximately 1248 hours (52 days) after being loaded.

In addition to the above analysis, data gathered from experiments with actual K East sludge at PNNL indicates that it is extremely unlikely that oxygen would escape the sludge and be released to the headspace of the LDC.

Significant data were collected during gas generation testing (Delegard et al. 2000; Bryan et al., 2001; Schmidt et al., 2003) conducted with K Basin sludge and irradiated fuel fragments that provides insight into the fate of oxygen within proximity of sludge. These tests were conducted at temperatures ranging from 30°C to 95°C and ranged in duration from ~950 hrs to 10,000 hours. K Basin sludge samples, irradiated uranium particles, and an excess of water were placed into reaction vessels. The reaction vessels were connected to a gas line manifold system that allowed the gas generation in each reactor vessel to be independently monitored and sampled. Before the start of each test, and after each sampling event, the headspace of each reactor vessel was purged multiple times with neon gas to remove air. However, due to inefficient purging, and in leakage during gas sampling, traces of air were introduced to the reactor headspaces. In the course of the gas generation testing, approximately 130 gas samples were collected and analyzed via mass spectroscopy for H_2, CO_2, hydrocarbon gases, fission product gases, Ne, Ar, O_2 and N_2. Because N_2 and O_2 can potentially be generated or consumed in reactions with sludge, the results from the Ar (argon) analysis were used to determine the extent of air in leakage into the reaction vessel head spaces.

Atmospheric air contains 0.934 vol% Ar and 20.946 vol% O_2 (Weast, 1982). Therefore, if oxygen was neither consumed nor generated, the ratio of oxygen to argon in the reaction vessel gas samples would be: 22.4 (20.9346/0.934). A ratio higher than 22.4 would indicate that the sludge samples generated and released oxygen to the reaction vessel headspace. An O_2:Ar ratio less than 22.4 would be evidence that oxygen was dissolved into the slurry and was consumed by reactions. Of the 130 gas samples collected during the gas generation testing, only one sample was found to exhibit an O_2:Ar ratio greater than 22.4. For all other samples, the ratio indicated that oxygen was consumed during the testing.

The anomalous data point may be the result of an error, since oxygen is reported as about 6.5 times greater than the nitrogen for this sample. Also, in the four subsequent gas samples collected from this test, the O_2:Ar ratio was less than 22.4. Finally, the sludge material that gave the anomalous data point was a KE floor sludge sample that contained only 2.2 wt% uranium total (settled solids basis).

In addition to the data collected during the gas generation tests (Delegard et al. 2000; Bryan et al, 2001; and Schmidt et al, 2003), gas samples (total of 10 samples) were also collected and analyzed from KE and KW canister sludge shipping containers and during canister sludge characterization activities (Makenas et. al., 1997, Silvers 1997). This data set includes gas samples collected from KE canister sludge samples 96-05 and 96-06. All of these gas samples exhibited oxygen depletion relative to atmospheric air (i.e., O_2:Ar was less than 22.4).

In summary, based on the gas generation testing, there is no evidence to support that oxygen will be released to the headspace from sludge reactions or radiolysis. In fact, the data show that if air is introduced to the head space, that over time, the oxygen content will become depleted relative to atmospheric air.

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Attachment 2

Gas Behavior of Sludge Samples 96-05 and 96-06

A. J. Schmidt
Senior Engineer
Pacific Northwest National Laboratory

Evaluation of Gas Generation Behavior Exhibited by KE Canister Sludge Samples 96-05 and 96-06

Updated by AJ Schmidt 11/8/03

1.0 Scope

The purpose of this letter is to document and examine the gas generation behavior of KE canister sludge samples 96-05 and 96-06 at ambient hot cell temperatures and compare the time to onset of hydrogen gas generation with a model. Based on the gas generation rates, estimates were made of the uranium metal content in samples 96-05 and 96-06.

2.0 Background

Gas generation was observed and measured from certain KE canister sludge samples collected in 1996. The conditions and results of gas generation measurements from these studies (published previously in Appendix B of Makenas et al. 1997, discussed in Baker et al. 2000, and summarized in Delegard et al. 2000) are provided here for background.

Between June 11-20, 1996, nine K-Basin samples were delivered to the 325A High Level Radiochemistry Facility (325A HLRF). These samples were contained in sealed stainless steel shipping canisters with an approximate volume of 10.5 L each. At the start of the characterization effort four of the nine samples were vacuum transferred out of the stainless steel shipping canisters. Liquids were transferred into 10 L glass carboys while the settled sludge was transferred into 2 L glass graduated cylinders. In all four cases, supernatant was transferred back to the canister to aid in the recovery of the sludge remaining in the canisters. Supernatant was added to the graduated cylinders to bring the volume in each cylinder to approximately 1.7 L. Sample 96-05 was transferred on July 11, and samples 96-01, 96-06, and 96-08 were transferred on July 12. Upon opening the ball valves on canisters containing samples 96-05 and 96-06, supernatant was forced out of the valves to a height of approximately two feet indicating pressurization of the canisters had occurred. A fine particulate layer was noted on the bottom of the shipping canisters following the initial vacuum transfer. Repeated additions of supernatant followed by vacuum transfer were used to recover these fine particles. The fine particles were added to the slurry in the graduated cylinders.

Within a few days after samples were loaded into the graduated cylinders, bubbles were observed rising from the settled sludge layer. This gas release was not quantified nor was the gas collected.

The samples were sparged with air at 12:00 noon on July 29 for five minutes to mobilize the solid layer and obtain a homogeneous slurry. Air sparging was decided upon after attempts to mobilize the solid layer using magnetic stirrers as well as motorized blade mixers failed. The cell temperature was 35°C and the cells are maintained at a vacuum of approximately 0.26 inches of water relative to ambient air. Three video cameras were used to collect images both real time and time lapse as the slurry settled. Video images and visual observations showed gas generation in samples 96-05 and 96-06, with gas retention in 96-05. Gas generation was observed in sample 96-06 about 90 minutes after air sparging. Gas retention (an entrapped gas bubble was also observed in sample 96-05 a day after air sparging. The gas appeared to be generated at the bottom of 96-06 and released through preferred paths in the solids close to and along the walls of the graduated cylinder. In sample 96-05, a gas pocket formed near the bottom of the sludge layer and expanded across the cylinder lifting the overlying solid layer. The gas pocket continued to grow until July 31 when the gas quickly released from the sludge. The presence of the gas pocket near the bottom of the sludge along with the lack of gas release in the overlying sludge indicates the gas is generated predominantly in the faster settling portion of the sludge. The top of the sludge layer for sample 96-05 on July 30 at 4 pm was at the 290 ml mark on the graduated cylinder. Just before the gas pocket released, July 31 at 7:40 am, the top of the sludge was at the 320 ml mark. Given this volume and time data, an approximate generation rate of 1.9 ml/hr was calculated for 96-05. This gas generation rate should be considered a minimum since some gas could have been released from the sludge without being observed. The volume of the bubble in 96-05 at 4 pm on July 30 was estimated to be approximately 40 ml (based on the videotape image). At a gas generation rate of 1.9 ml/hr, it is estimated that the bubble began forming 21 hours earlier (i.e., 7 pm on July 29, or 7 hours after air sparging. Since the gas generated in sample 96-06 released through the sludge layer, the volume of gas generated by 96-06 during this time is not known, and therefore a generation rate cannot be calculated for this sample during this period. The graduated cylinders were then stoppered, and the evolved gases were collected from the 96-05 96-06 samples.

On August 20, 1996, the 96-05 and 96-06 (in 2 L cylinders) were resuspended using helium sparging. A gas sample was collected from sample 96-06 (gas generation continued, but was not sufficient to collect a good sample from the 96-05 sludge). On August 30, 1996, a gas pocket was observed at the bottom of Sample 96-06, and the volume growth of the bubbled was monitored over time, and an approximate generation rate of 5.2 ml/hr was calculated.

Several estimates were made of the overall gas generation rates for samples 96-05 and 96-06. Two techniques were used: in the first technique, generation rates were estimated by measuring the size of the gas pockets in the sludge column over time; for the second technique, the gas generation rate was determined by sealing the cylinders with stoppers fitted with Tedlar bags, and estimating the volume of gas collected over time in a Tedlar bag. The error associated with the Tedlar bag approach was estimated to be plus or minus 50%. Table 1 shows the estimated gas generation rates for samples 96-05 and 96-06. Analyses of gas samples indicated the gas generated was primarily hydrogen (i.e., 98 to 99%) with traces of fission gas, carbon dioxide and methane. This confirmed that the primary source of gases being observed was the reaction of uranium metal.

Table 2 provides additional information on the test conditions, properties, and gas generation relevant to modeling the behavior of 96-05 and 96-06.

The gas generation rates at ambient hot cell temperature (35°C) for the canister sludge samples collected in 1996 ranged from 0 to 150 ml/kg settled sludge-day (corrected to standard temperature and pressure). The average gas generation rates at ambient hot cell temperature (~35°C) from the canister samples collected in 1996 are 27 to 59 ml/kg settled sludge-day (corrected to standard temperature and pressure). These rates are much higher than observed for the large-scale test with KC-2/3 P250-L at ambient hot cell temperature (2.4 ml/kg settled sludge-day) (Delegard et al. 2000). Gas generation at ambient hot cell temperatures was also observed (though at lower rates than KE samples) in some sludge samples taken from storage canisters at the KW Basin (Baker et al. 2000). Relative to other canister sludge samples, the rate of gas generation from 96-06 was approximately 11 times greater than that projected for the KC-2/3 (whole) canister composite (made up of canister sludge collected from 10 different sampling locations) at ambient hot cell temperatures (Delegard et al. 2000).

Table 1. Estimated Total Gas Generation Rates from KE Canister Sludge Samples in 1996 at Hot Cell Temperature

Sludge Mass and Gas Generation Rates	**Date and (Method of Estimate)**	**KE Canister Sludge Sample 96-05**	**KE Canister Sludge Sample 96-06**
Mass of Settled Solids	N/A	667 g	733 g
2.1 Rates on a Per Sample Basis – STP			
Gas Generation Rate	7/31/96 (gas pocket)	1.7 ml/hr-STP (for 16 hr)	Not measured
Gas Generation Rate (After 5 min air sparge)	8/19/96 (Tedlar bag)	0.4 to 0.6 ml/hr-STP (for 107 hr)	0.6 to 1.2 ml/hr -STP (for 107 hr)
Gas Generation Rate (After 5 min helium sparge)	8/22/96 (Tedlar bag)	0.4 to 0.7 ml/hr - STP (for 40 hr)	0.9 to 1.7 ml/hr -STP (for 40 hr)
Gas Generation Rate	9/3/96 (gas pocket)	Not measured	4.6 ml/hr -STP (for 95 hr)
Average Gas Generation Rate	N/A	0.7 ml/hr - STP	1.8 ml/hr – STP
3.1 Rates on a Per kg Settled Sludge Basis – STP			
Maximum Gas Generation Rate	(gas pocket)	**61 ml/kg settled sludge-day**	**150 ml/kg settled sludge-day**
Average Gas Generation Rate	N/A	**27 ml/kg settled sludge-day**	**59 ml/kg settled sludge-day**

N/A – not applicable.
All gas volumes in Table 1 are given at STP conditions.

Table 2. Information for Modeling the Behavior of 96-05 and 96-06

Parameter	**96-05**	**96-06**
Ambient Hot cell temperature, °C	35	35
Volume of Settled sludge, ml	285	315
Diameter of Cylinder, cm	7.8	7.8
Height of settled sludge in cylinder	6.0	6.7
Volume of water above settled sludge	~1400 ml	~1400 ml
Estimated volume of sludge at bottom of cylinder after formation of spanning bubble, ml	~30(1)	~75(2)
Time between air sparging and observed onset of gas generation, hours	~7	1.5
Uranium content, dry basis, wt%	88	84
Settled density	2.34	2.33
Implied uranium metal content wt% settled sludge basis (see calculation below)	4.1	10.1

(1) Bubble formed after air sparging 7/30/96
(2) Bubble formed after helium sparging 8/30/06

3.0 Implied Uranium Metal Content in 96-05 and 96-06

Summary of Assumptions for Determining U metal content of Canister Sludge Samples 96-05 and 96-06.

Uranium metal content = to be determined for 96-05 and 96-06.

Uranium metal content for KE Canister Sludge Safety Basis = 0.125 g/cm^3 (5 wt%)

Reaction Rate Enhancement Factor = 1

Uranium metal particle size = 500 microns

Uranium metal particle shape = spherical

Reaction rate = log(rate) = 7.634 – 3016/T (Reilly 1998)(oxygen free water):
where rate = mg wt gain/hr-cm^2 and T = temperature, K

Surface Area of Uranium Metal in Sludge. The reaction rate is based on the surface area of the uranium metal; therefore, the uranium metal surface area per gram of settled sludge must be determined. For this determination it has been assumed that all uranium metal particles exist as 500-micron diameter spheres.

Surface area for a sphere = SA $= 4 \cdot \pi \cdot r^2$, where r = particle radius

Volume for a sphere = V $= 4/3 \cdot \pi \cdot r^3$

Mass of a sphere = m $= \rho \cdot V$, Where ρ = density

Substituting V from above, mass of a sphere is:

$$m = \rho \cdot 4/3 \cdot \pi \cdot r^3$$

Surface area per unit mass = SA/m

$$= (4 \cdot \pi \cdot r^2)/(\rho \cdot 4/3 \cdot \pi \cdot r^3)$$

$$= 3/(\rho \cdot r)$$

For the bounding case we have diameter = d = 500 µm = 0.050 cm.

And, r = d/2 = 0.025 cm.

And density of uranium metal, $\rho = 19.05\ g_{(u\text{-}metal)}/cm^3$

Surface area per unit mass uranium $= 3/(\rho \cdot r) = 3/(19.05\ g_{(u\text{-}metal)}/cm^3 \cdot 0.025\ cm)$

$$= 6.299\ cm^2/g_{(u\text{-}metal)}$$

Rate of Hydrogen Generation at 35°C.

The reaction for uranium metal with water is:

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

In oxygen free water, the rate is:

$\log(\text{rate}) = 7.634 - 3016/T$ where rate = mg wt gain/hr-cm^2
T = temperature, K

At 35°C, T = 273 + 35 = 308 K

Converting the rate from mg wt gain(oxygen)/hr-cm^2 to mg hydrogen generation/hr-cm^2, we can use the reaction stoiciometry and the rate equation to give:

Rate (mg$_H$ generation/hr-cm^2) $= 4\ \text{mg}_H/32\ \text{mg}_O \cdot 10^{(7.634-3016/308)}$

$= 8.684\text{E-}4$ mg$_H$ generation/hr-cm^2

$= 9.726\text{E-}3$ ml$_H$/hr-cm^2 (gas volume at STP)

For Sample 96-05, the maximum observed rate was 61 ml/kg settled sludge-day, or 2.54 ml/ kg settled sludge-hr. This rate implies a uranium surface area for 96-05 of:

(2.54 ml//kg settled sludge-hr)/ (9.726E-3 ml$_H$/hr-cm^2) = 261 cm^2/ kg settled sludge.

From the above assumptions we have: = 6.299 cm^2/g$_{(u\text{-metal})}$, Therefore, each kg of settled sludge contains: = 261 cm^2/ kg settled sludge/6.299 cm^2/g$_{(u\text{-metal})}$ = 41.4 g$_{(u\text{-metal})}$ / kg settled sludge.

= 4.1 wt%

For Sample 96-06, the maximum observed rate was 150 ml/kg settled sludge-day, or 6.25 ml/ kg settled sludge-hr. This rate implies a uranium surface area for 96-05 of:

(6.25 ml//kg settled sludge-hr)/(9.726E-3 ml$_H$/hr-cm^2) = 643 cm^2/ kg settled sludge.

From the above assumptions we have: = 6.299 cm^2/g$_{(u\text{-metal})}$, Therefore, each kg of settled sludge contains: = 643 cm^2/ kg settled sludge/6.299 cm^2/g$_{(u\text{-metal})}$ = 102 g$_{(u\text{-metal})}$ / kg settled sludge.

= 10.2 wt% U metal

4.0 References

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Attachment 3

Model of Sludge Samples 96-05 and 96-06

M Epstein
Vice President, Consulting
Fauske & Associates, Inc.

Fauske & Associates, Inc.

DATE: September 9, 2003

TO: James Shelor
Marty Plys

FROM: Mike Epstein

SUBJECT: Attachment 3: Model of Sludge Samples 96-05 and 96-06 (REVISED)

INTRODUCTION

K-East canister sludge samples 96-05 and 96-06 were loaded into 7.8-cm diameter graduated cylinders. To fluidize the solid sludge particulate air was blown through a tube that entered the settled, solid sludge from above and was forced to the bottom of the graduated cylinders. Hydrogen gas generation was observed about 1.5 hours after air bubbling sample 96-06 and gas generation was observed about 7.0 hours after air bubbling sample 96-05. Additional details with respect to the observations as well as estimates of the uranium metal content in samples 96-05 and 96-06 can be found in Schmidt (Attachment 2).

Most of the available data support the conclusion that hydrogen generation via the reaction of the sludge's interstitial water with the uranium metal does not begin until all the oxygen dissolved in the interstitial water is consumed by reaction with uranium. The question of interest is whether the rather short, 1.5 hour delay time to H_2 generation in sample 96-05 can be explained by oxygen depletion. It is demonstrated below that a plausible explanation for the short delay time is the inability of oxygen diffusion through the interstitial liquid to keep up with the kinetic rate of oxygen removal at the metal surfaces. However, the rationalization of the short delay time requires the assumption that as a result of air bubbling in sample 96-06 a highly concentrated, thin layer of essentially 100 percent uranium metal formed at the bottom of the cylinder.

PHYSICAL MODEL

The settled sludge column in sample 96-06 is divided up into two regions. At the bottom of the sludge column is a layer of purely metal particulate that occupies the interval $0 < x \leq \delta_r$, where x is the vertical distance measured from the bottom of the column and δ_r is the thickness of the reactive metal layer. Above the metal layer is a semi-infinite region $\delta_r \leq x \leq \infty$ of inert (nonreactive) solid particulate material. In both regions the pore spaces are filled (saturated) with interstitial water containing an initial concentration Y_0 (mass fraction) of dissolved oxygen. The reaction between oxygen and uranium oxide particles and radiolytic O_2 generation are ignored.

The dissolved oxygen mass fraction Y in the lower reactive region obeys the partial differential equation

$$\frac{\partial Y}{\partial t} = D\frac{\partial^2 Y}{\partial x^2} - \frac{a_m \dot{m}''_{ox}}{\phi \rho_f} \qquad 0 \leq x \leq \delta_r \tag{1}$$

where t is time, D is the binary diffusion coefficient for the O_2/water solution, ρ_f is the density of the sludge's interstitial water, ϕ is the volume fraction of sludge occupied by water, $\dot{m}''_{ox}$ is the metallic particle oxidation rate per unit reactive area of the particles and a_m is the reactive surface area of the metallic particles per unit volume of the reactive layer. For the purely metal layer

$$a_m = \frac{6(1-\phi)}{d} \tag{2}$$

where d is the effective diameter of the metal particles. The safety basis metal particle diameter d = 500 μm. Using $\phi = 0.75$ the reactive area per unit volume is $a_m = 3000\ \text{m}^{-1}$. This value is a factor of 75 greater than the safety basis value 40 m^{-1}. The corresponding metal density in the reaction zone is 4750 kg m^{-3}.

The dissolved oxygen mass fraction Y in the upper, semi-infinite nonreactive layer obeys the partial differential equation

$$\frac{\partial Y}{\partial t} = D\frac{\partial^2 Y}{\partial x^2} \tag{3}$$

The boundary conditions for Eqs. (1) and (3) are the zero flux boundary conditions

$$\frac{\partial Y}{\partial x} = 0 \qquad \text{at} \qquad x = 0 \quad , \quad x = \infty \tag{4}$$

the continuity conditions

$$\left.\frac{\partial Y}{\partial x}\right|_{\delta_r -} = \left.\frac{\partial Y}{\partial x}\right|_{\delta_r +} \qquad ; \qquad Y|_{\delta_r -} = Y|_{\delta_r +} \quad \text{at} \qquad x = \delta_r \tag{5}$$

and the initial condition

$$Y = Y_0 \quad \text{at} \qquad t = 0 \tag{6}$$

In order to facilitate the solution of the above system of equations with a minimum number of parameters, the equations are converted to dimensionless forms by introducing the following dimensionless variables and parameters:

$$y = \frac{Y}{Y_0} \qquad \text{(dimensionless oxygen concentration)} \tag{7}$$

$$\tau = \frac{Dt}{\delta_r^2} \qquad \text{(dimensionless time)} \tag{8}$$

$$z = \frac{x}{\delta_r} \qquad \text{(dimensionless distance)} \tag{9}$$

$$R = \frac{a_m \dot{m}''_{ox} \delta_r^2}{\phi \rho_f Y_0 D} \quad \text{(dimensionless reaction rate parameter)} \tag{10}$$

The governing equations in dimensionless form are

$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial z^2} - R \qquad ; \qquad 0 \le z \le 1.0 \tag{11}$$

$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial z^2} \qquad ; \qquad 1.0 \le z \le \infty \tag{12}$$

$$\frac{\partial y}{\partial z} = 0 \qquad \text{at} \qquad z = 0, \infty \tag{13}$$

$$\left.\frac{\partial y}{\partial z}\right|_{1-} = \left.\frac{\partial y}{\partial z}\right|_{1+} \qquad ; \qquad Y\big|_{1-} = Y\big|_{1+} \qquad \text{at} \qquad z = 1.0 \tag{14}$$

$$y = 1.0 \qquad \text{at} \qquad \tau = 0 \tag{15}$$

NUMERICAL SOLUTION AND PARAMETER VALUES

Equations (11) to (15) were solved numerically by replacing $\partial^2 y/\partial z^2$ by the forward difference

$$\varepsilon^2 \frac{\partial^2 y}{\partial z^2} = y_{m+1} - 2y_m + y_{m-1} \tag{16}$$

where y_m is the value of m at regular intervals $z = m\varepsilon$, $m = 1,2,3,\ldots,N$. Actually Eq. (16) does not include the nodes n=1,N adjacent to the zero flux boundaries. For these nodes

$$\varepsilon^2 \frac{\partial^2 y}{\partial z^2} = 2(y_2 - y_1) \quad , \qquad m = 1 \tag{17}$$

$$\varepsilon^2 \frac{\partial^2 y}{\partial z^2} = 2(y_{N-1} - y_N) \ , \qquad m = N \tag{18}$$

In this manner Eqs. (11) and (12) are transformed to a system of N differential equations.

The dimensionless distance interval used in the calculations was $0 \le z \le 10$. This interval was divided into N = 250 nodes. A case was also run with 500 nodes and no difference was detected from the 250 node case. The calculations were carried out for the physical parameter values given in Table 1. Inserting these values into Eq. (10) gives R = 1.17 for the dimensionless reaction rate parameter.

Table 1 - Parameter Values

$a_m = 3.0 \times 10^3\ m^{-1}$	reactive area per unit volume of metal layer (Eq. 2)
$d = 500\ \mu m$	effective metal particle diameter
$D = 2.6 \times 10^{-9}\ m^2\ s^{-1}$	oxygen diffusion coefficient in water at 35°C
$\dot{m}''_{O_2} = 4.63 \times 10^{-10}\ kgO_2\ m^{-2}\ s^{-1}$	metal particle oxidation rate per unit area at 35°C
$Y_0 = 6.5 \times 10^{-6}$	dissolved oxygen mass fraction at 35°C
$\delta_r = 3.26$ mm	thickness of reactive layer based on 100% metal particulate of total mass 74 g
$\rho_f = 1000\ kg\ m^{-3}$	density of interstitial water
$\phi = 0.75$	volume fraction of water in sludge

Figure 1 shows the predicted dimensionless concentration profiles as a function of dimensionless time for the assumed sludge column morphology involving a highly concentrated layer of metal particles (4750 kg m^{-3}) at the bottom of the column. Note from Fig. 1 that complete oxygen depletion at the bottom of the column is achieved at the dimensionless time $\tau = 1.33$. Therefore, from Eq. (8) the actual predicted time delay to H_2 production is t = 1.51 hr; which is remarkably close to the observed time of 1.5 hr. As mentioned previously, the observed delay time to H_2 production in sample 96-05 was 7.0 hours. Clearly, to rationalize this observation it is only necessary to assume a less concentrated reaction zone in 96-05 relative to the purely metal layer assumed for 96-06. Table 2 shows the predicted times to oxygen depletion for selected uranium metal concentrations.

Table 2 - Time to Complete Oxygen Depletion Versus Uranium Metal Concentration (see Table 1 for physical parameter values)

Metal Concentration ($kg\ m^{-3}$)	**a_m m^{-1}**	**δ_r (mm)**	**Time to O_2 Depletion (hr)**
4750	3.0×10^3	3.26	1.51
3000	1895	5.16	2.0
1000	632	15.5	4.45
500	316	31.0	9.25

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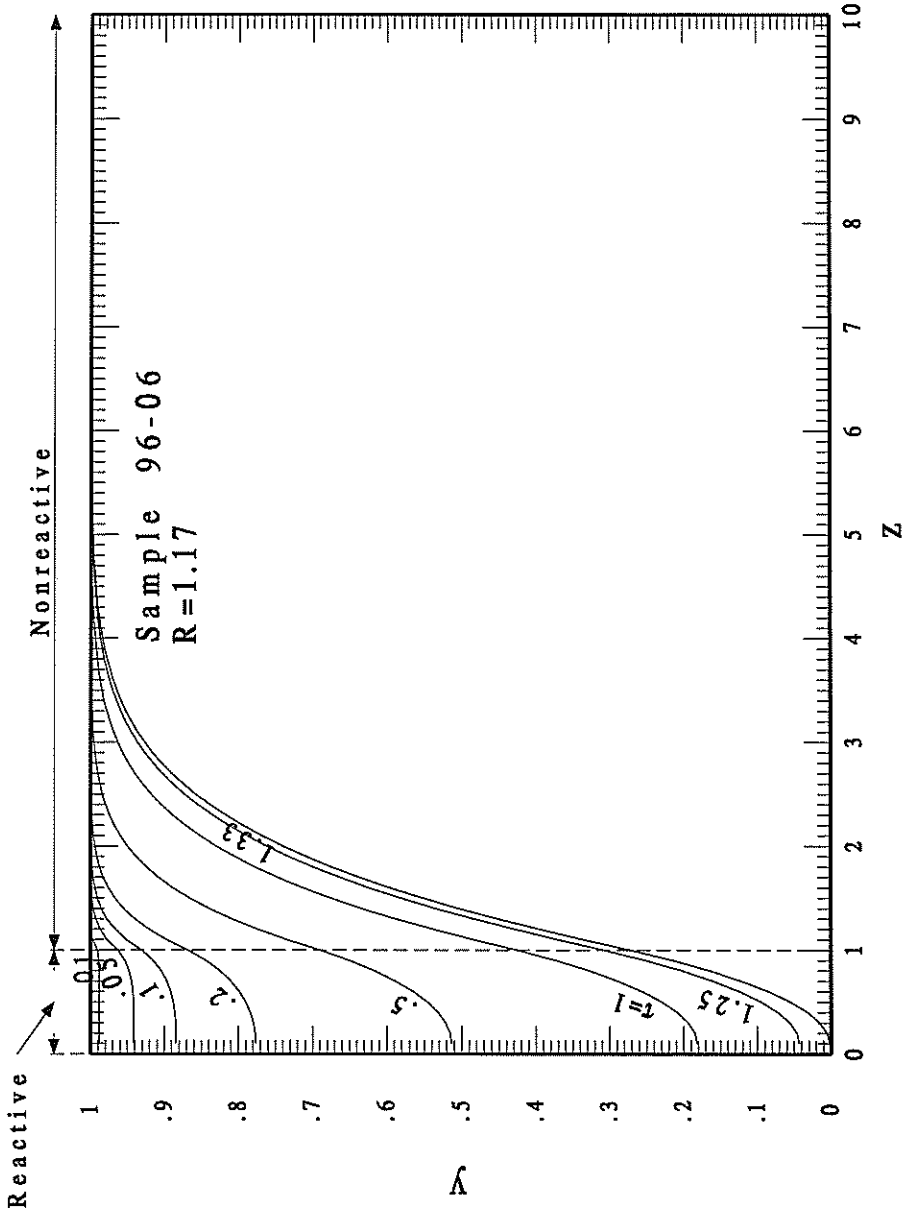

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Figure 1 Evolution of dimensionless oxygen concentration profiles for assumed concentrated layer of metal particles (4750 kg m^{-3}) at bottom of sludge sample 96-06.

Attachment 4

Consumption of Oxygen by Uranium Metal at 25^0 C

M. G. Plys
Vice President, Waste Technology
Fauske & Associates, Inc.

Fauske & Associates, Inc.

Date: October 16, 2003

To: Jim Shelor, Jim Sloughter, Darrel Duncan, Hanford SNFP

From: Martin G. Plys, FAI

Subject: **Sludge O2 Depletion (Rev. 3)**

In response to your request, I have evaluated the oxygen depletion rate from water saturated with dissolved oxygen inside an LDC. Oxygen is depleted via the U-O_2 reaction and this reaction must essentially proceed to completion before the uranium-water reaction commences. Oxygen may also be depleted by further oxidation and hydration of UO_2 and it may also be produced by radiolysis but these processes are not considered here.

Rates of hydrogen generation and oxygen depletion are given by:

$$Q_{H2} = \xi K_w(T) A_V \frac{4}{32} \frac{1}{\rho_{H2}}$$

$$Q_{O2} = K_O(T) A_V \frac{1}{\rho_{O2}}$$

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
ξ = Rate law multiplier (nominally 1; safety basis value is 3),
K_W = Rate law for $U+2H_2O = UO_2 + 2H_2$, oxygen-free, kg $O_2/m^2/s$,
K_O = Rate law for $U+O_2 = UO_2$, 100% relative humidity, kg $O_2/m^2/s$,
A_V = Reaction area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

A reaction rate law multiplier is used for the uranium-water reaction as a safety factor to consider uncertainty in literature data; its value appears in the SNF sludge databook (HNF-SD-SNF-TI-015, Vol. 2) and its origin is discussed in SNF-7765, Rev. 1. Use of a conservative uranium-water (or uranium-steam in the case of spent fuel processing) reaction rate is appropriate because of the hazard associated with the exothermic reaction and production of flammable gas. The rate law multiplier is not indicated in the equation above for oxygen consumption because a best-estimate approach to oxygen consumption is desired. If there were a significant question about heat generation from this reaction, for example, a conservative approach might be considered.

The ratio 4/32 appears in the hydrogen equation because the correlation is for weight gain, kg oxygen. Since products are UO_2 and $2H_2$, for every 32 kg weight gain there are 4 kg gas. Ideal gas STP densities of hydrogen and oxgyen at 1 atm (101325 Pa) and 0 °C are 0.08924 kg/m^3 and 1.428 kg/ m^3 respectively. Sludge reactive area per unit volume is given by:

$$A_V = \frac{6\,C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal, 64 kg/ m^3 at safety basis 40% canister sludge,
ρ_m = U metal density, 19000 kg/m^3, and
D = Particle size, 0.0005 m (500 microns)

so that $A_V = 40.42\ m^{-1}$.

Eq. (4) from the main SNF databook (HNF-SD-SNF-TI-015, Vol. 1) table 4-3 is used for the uranium-water reaction and Eq. (7) from table 4-4 is used for the uranium-oxygen reaction:

$$\begin{aligned} \text{Log}_{10}K_W &= 7.634 - 3016/T \\ \text{Log}_{10}K_O &= 8.333 - 3730/T \end{aligned}$$

where as written the units of K are mg weight gain (O_2) per square centimeter per hour. Unit conversions to SI are assumed when used in the formulas for Q (1 mg/cm^2/hr = $2.7778\text{x}10^{-6}$ kg/m^2/hr). For convenience the databook correlations are plotted in Figure 1 (using $\xi = 1$)and compared against the values for uranium reacting with saturated steam, often used as a surrogate for the reaction with liquid water, and uranium reacting in dry air. Also for convenience the ratio of these reaction rates is plotted in Figure 2.

Solubility data for oxygen are cast in the form of cc gas at STP per cc water at the given water temperature, given a cover gas pressure of 1 atm, using the symbol α for this concentration. These data are (CRC Handbook, 39th edition):

Table 1. Solubility of Oxygen in Water

Temperature, C	Solubility α cc O_2 (std) / cc H_2O @ 1 atm
10	0.03802
15	0.03415
20	0.03102
25	0.02831
30	0.02608
35	0.02440
40	0.02306

Dissolved oxygen concentration (volume gas per unit volume of sludge) is thus

$$C_{O2} = 0.21\,\alpha\,\phi$$

where 0.21 is the concentration of oxygen in air and ϕ is the water volume fraction in sludge, 0.75. The time for oxygen depletion is then simply $t = C_{O2} / Q_{O2}$.

Predicted oxygen depletion times are shown in Table 2. Note source values are per unit volume of sludge (and therefore apply to 1 m^3) but depletion time is independent of volume. Also for convenience the hydrogen generation rate per unit volume is given.

Table 2. Predicted Reaction Rates and Oxygen Depletion Times (volumetric rates at STP).

Temperature °C	Q_{H2}, L/hr	Q_{O2}, L/hr	Q_{O2}, m^3/s	C_{O2}, L/L (m^3/m^3)	O_2 depletion hrs
10	1.626	0.00409	1.14E-9	0.00599	1465.
15	2.489	0.00692	1.92E-9	0.00538	777.
20	3.754	0.0115	3.20E-9	0.00489	424.
25	5.585	0.0188	5.22E-8	0.00446	237.
30	8.201	0.0302	8.40E-8	0.00411	136.
35	11.89	0.0479	1.33E-8	0.00384	80.2
40	17.04	0.0747	2.08E-8	0.00363	48.6

The method used here can be extended to consider depletion due to hydration of uranium oxides and a radiolysis source. The depletion time is given by:

$$t = \frac{C_{O2}}{Q_{O2,met} + Q_{O2,ox} - Q_{O2,rad}}$$

where subscripts are: met = consumption by metal oxidation, same as given above, ox = consumption by uranium oxide hydration, and rad = radiolytic production rate of all oxidizing species in terms of equivalent O_2.

Figure 1. Comparison of uranium reaction rates with liquid water (top), saturated oxygen-free steam (second from top), moist air at 100% relative humidity, which is the surrogate for the uranium-oxygen reaction in water (second from bottom), and dry air (bottom), kg weight gain per square meter per second.

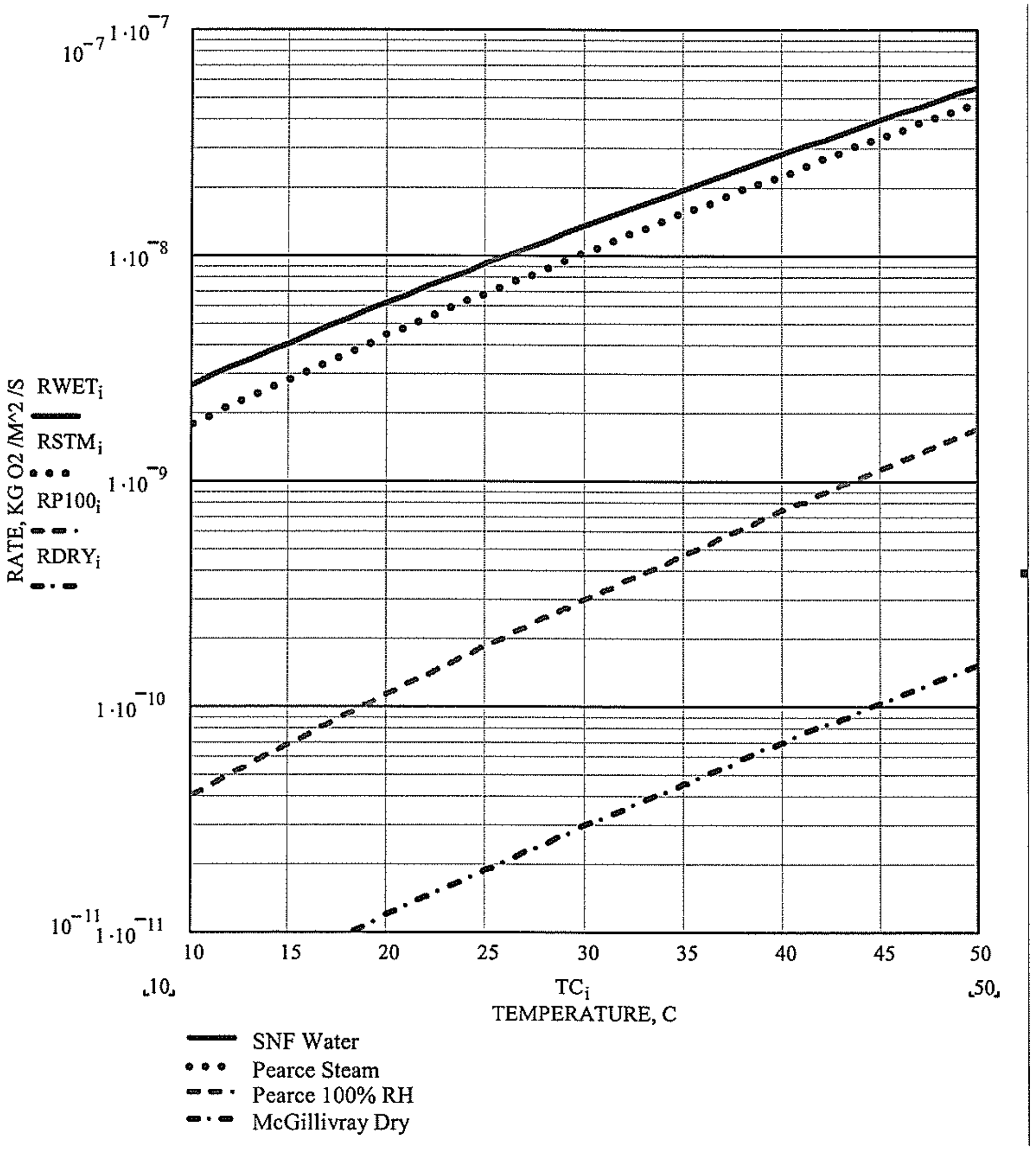
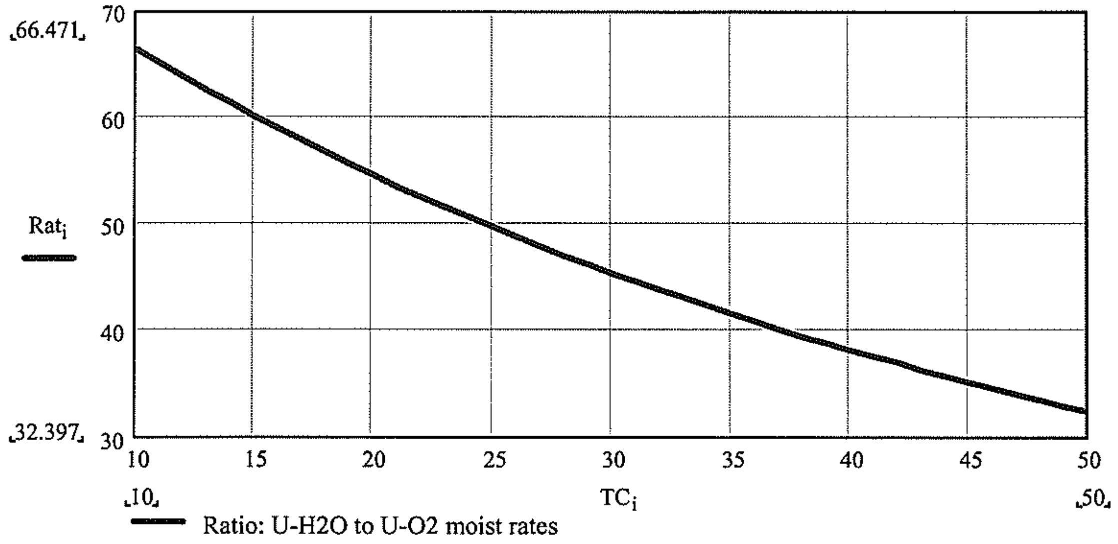


Figure 2. Ratio of uranium-water and uranium-oxygen reaction rates; the uranium-water reaction rate is oxygen-free and the uranium-oxygen reaction rate is at 100% relative humidity.



Attachment 5

Consumption of Oxygen by Uranium Dioxide Species present in K East Sludge at 25^0 C

C. H. Delegard
Staff Scientist
Pacific Northwest National Laboratory

John Abrefah
Lead Scientist
Radiochemical Science & Engineering Group
Pacific Northwest National Laboratory

DISSOLVED OXYGEN CONSUMPTION FROM ITS REACTION WITH $UO_{2.125}$

1. 1 cm^3 of sludge contains about 0.75 cm^3 of water and 0.25 cm^3 of solids. According to the "Safety Basis" estimate, the total uranium concentration in 40/60 canister/floor sludge is 0.74 g/cm^3. Metallic uranium constitutes about 0.0638 g/cm^3, which leaves 0.676 g/cm^3 of uranium in the form of oxides. It has been assumed that the non-metallic uranium in these sludge types starts with an equal uranium mole fraction of UO_2, $UO_{2.25}$, and $UO_3{\cdot}2H_2O$ (Plys and Pearce 2002 1). The formula weight of the nominal reduced uranium oxides (UO_2 and $UO_{2.25}$, or $UO_{2.125}$) is 272 g/mole. Therefore, the concentration of reactive reduced uranium oxide as $UO_{2.125}$ is:

$$\frac{\text{2 moles U in } UO_{2.125}}{\text{3 moles U in U oxide}} \times \frac{272\ \text{g/mole}\ UO_{2.125}}{238\ \text{g/mole U}} \times \frac{0.676\ \text{g U}}{\text{cm}^3\ \text{sludge}} = \frac{0.515\ \text{g}\ UO_{2.125}}{\text{cm}^3\ \text{sludge}}$$

   This is equivalent to 0.0464 cm^3 of $UO_{2.125}/cm^3$ of sludge based on a $UO_{2.125}$ particle density of 11.1 g/cm^3).2

2. Uranium dioxide (UO_2) and $UO_{2.25}$ in K Basin sludge can consume dissolved oxygen by the following reactions:

$$2\ UO_2 + O_2 + 4\ H_2O \rightarrow 2\ UO_3{\cdot}2H_2O$$

$$8\ UO_{2.25} + 3\ O_2 + 16\ H_2O \rightarrow 8\ UO_3{\cdot}2H_2O$$

   At equal amounts of uranium present as UO_2 and $UO_{2.25}$, the combined reaction becomes:

$$8\ UO_2 + 8\ UO_{2.25} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

   or

$$16\ UO_{2.125} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

   The weight ratio of uranium (as $UO_{2.125}$) being oxidized to oxygen consumed is 16.98 g U/g O_2.

3. According to Figure 32 of the review by Shoesmith (2000) 3, the rate of this surface area-limited reaction in aerated water at 25°C under irradiated conditions can be defined by two equations taken from two similar sets of data. These equations are:

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1 Plys, M. G., and K. L. Pearce. 2002. *Supporting Basis for Spent Nuclear Fuel Project Sludge Technical Databook*. SNF-7765, Rev. 1, Fluor Hanford, Richland, WA.

2 Assume 1.0 g of U metal with half, 0.5 g $U_{(metal)}$, to produce 0.576 g of $UO_{2.25}$ (density 11.29 g/cm^3) and the other half, 0.5 g $U_{(metal)}$, to produce 0.567 g of UO_2 (density 10.95 g/cm^3); densities from Table 5.22 of The Chemistry of the Actinide Elements, 2nd edition, J. J. Katz, G. T. Seaborg, and L. R. Morss, Chapman and Hall, New York (1986). The density of the product $UO_{2.125}$ is:

$$\text{Density } UO_{2.125} = \frac{\text{Mass}\,[UO_{2.25} + UO_2]}{\text{Volume}\,[UO_{2.25} + UO_2]} = \frac{[0.576 + 0.567]\ \text{g}}{[0.0510 + 0.0518]\ \text{cm}^3} = 11.12\ \text{g/cm}^3$$

3 Shoesmith, D. W. 2000. "Review – Fuel Corrosion Processes Under Waste Disposal Conditions," *Journal of Nuclear Materials* 282:1-31.

$$\text{Rate}, \frac{\text{mg U}}{\text{m}^2 \cdot \text{day}} = \frac{0.22\ \text{mg U}}{\text{m}^2 \cdot \text{day}} \times \text{DR}^{0.43} \qquad \text{(A)}$$

and

$$\text{Rate}, \frac{\text{mg U}}{\text{m}^2 \cdot \text{day}} = \frac{0.33\ \text{mg U}}{\text{m}^2 \cdot \text{day}} \times \text{DR}^{0.33} \qquad \text{(B)}$$

where DR is the radiolytic power, in Grays/hr, deposited into the water from radiolysis. Shoesmith observes that at absorbed power levels of 1 Gray/hr or less, the effect of this radiolytic power deposition is negligible. Accordingly, by entering 1 Gray/hr into the equations, the base rates of the reactions from equations (A) and (B) are found to be 0.22 mg/m^2·day and 0.33 mg/m^2·day, respectively. Note that these values are near, but not exactly equal to, the base rate given in Figure 32 of Shoesmith (2000) for unirradiated aerated solution of 0.2 mg/m^2·day.

From this base uranium consumption rate in the absence of irradiation, the equivalent oxygen consumption rate for reduced uranium oxide ($UO_{2.125}$) is:

$$\frac{0.2\ \text{mg U}}{\text{m}^2 \cdot \text{day}} \times \frac{\text{m}^2}{10^4 \text{cm}^2} \times \frac{\text{day}}{24\ \text{hr}} \times \frac{\text{mg O}_2}{16.98\ \text{mg U}} = \frac{4.91 \times 10^{-8}\ \text{mg O}_2}{\text{cm}^2 \cdot \text{hr}} \qquad \text{(C)}$$

The expected field in the 40/60 canister/floor sludge mix is 83.7 Gray/hr but only 23.9% is absorbed in the water to generate radiolytic products.

The oxygen consumption rate for a dose rate of 83.7 Grays/hr at 23.9% absorption (i.e., 20.0 Gy/hr absorbed dose rate) can be determined for both data sets:

From equation (A), uranium consumption is 0.798 mg U/m^2·day, equivalent to 1.96 x 10^{-7} mg O_2/cm^2·hr. This is 0.798/0.2 = 3.99-times greater than the base rate in the absence of irradiation.

From equation (B), uranium consumption is 0.887 mg U/m^2·day, equivalent to 2.18 x 10^{-7} mg O^2/cm^2·hr. This is 0.887/0.2 = 4.44-times greater than the base rate in the absence of irradiation.

The analysis conducted through this paper evaluates two conditions defined by equations (A) and (B) at the nominal 19.0 Gray/hr irradiation rate and compares them with the condition in the absence of irradiation shown by equation (C):

a. <u>The minimum time to reach a flammable atmosphere in the LDC through release of hydrogen to the headspace of a vented LDC containing air as the cover gas.</u> For conservatism, equation (B) will be used for the oxygen consumption by reduced uranium oxides to maximize oxygen consumption rate and therefore minimize time to onset of hydrogen generation.

b. <u>The minimum time to reach a flammable atmosphere in the LDC through release of oxygen to the headspace of a sealed and inerted LDC containing argon as the cover gas.</u> For conservatism, equation (A) will be used for the oxygen consumption by reduced uranium oxides to minimize oxygen consumption and therefore maximize oxygen generation rate.

4. The rate of the reaction at 15°C can be as much as 1.61-times lower, according to the Arrhenius equation (rate = $Ae^{-Ea/RT}$) and an activation energy (E_a) for the reaction of 34

kJ/mole in non-complexing neutral solution (E_a = 29-34 kJ/mole reported in section 5.6 of Shoesmith, 2000):

$$\frac{\text{Rate (25°C)}}{\text{Rate (15°C)}} = \frac{Ae^{-E_a/RT_{298}}}{Ae^{-E_a/RT_{288}}} = \frac{e^{[-34000\ \text{J/mole}]/[(8.314\ \text{J/mole·deg})\cdot 298]}}{e^{[-34000\ \text{J/mole}][(8.314\ \text{J/mole·deg})\cdot 288]}} = 1.61$$

5. The particle size distribution of $UO_{2.125}$ from U metal corrosion is taken from Figure I.6.2-15 of Makenas et al. (1997[4]) for particles from 96-06M, a sludge containing 82.6 wt% uranium, taken to high shear rates. The volumetric particle size distribution was presented in 41 "bins" with diameter ranging from ~0.3 to 300 µm. Spherical particles of $UO_{2.125}$ were assumed (valid based on reported particle aspect ratios near unity). Starting arbitrarily with 100 g of particles, the number of $UO_{2.125}$ particles in each bin was calculated by dividing the bin mass, in grams, by the mass of each particle (density 11.1 g/cm^3) of that particular bin size.

   The surface areas of the particles in each bin were calculated by the formula $4\pi r^2$ (where r is radius) multiplied by the number of particles in each bin. The sum of the surface areas for 100 grams of $UO_{2.125}$ found over the entire particle size distribution was 1.0425×10^5 cm^2. The volumes of the particles in each bin also were calculated by determining the volume, $4\pi r^3/3$, of each particle and multiplying by the number of particles in each bin.

   The total volume, calculated by summing over all bins, should be 9.01 cm^3. The surface area-to-volume ratio for these sludge particles therefore is 1.0425×10^5 cm^2/9.01 cm^3 particles = 1.157×10^4/cm (see the attached Table 1).[5] Assuming the particle size distribution of $UO_{2.125}$ is the same as the sludge, the volume-specific $UO_{2.125}$ surface area in the sludge is:

$$\frac{0.0464\ \text{cm}^3\ UO_{2.125}}{\text{cm}^3\ \text{sludge}} \times \frac{1.157\times10^4\ \text{cm}^2\ UO_{2.125}\ \text{surface}}{\text{cm}^3\ UO_{2.125}} = \frac{5.37\times10^2\ \text{cm}^2\ UO_{2.125}\ \text{surface}}{\text{cm}^3\ \text{sludge}}$$

6. The oxygen consumption rate at 25°C for the non-irradiated condition defined by equation (C) is:

$$\frac{5.37\times10^2\ \text{cm}^2\ UO_{2.125}\ \text{surface}}{\text{cm}^3\ \text{sludge}} \times \frac{4.91\times10^{-8}\,\text{mg}\ O_2}{\text{cm}^2\cdot\text{hr}} = \frac{2.64\times10^{-5}\ \text{mg}\ O_2}{\text{hr}\cdot\text{cm}^3\ \text{sludge}}$$

$$\frac{2.64\times10^{-8}\,\text{g}\,O_2}{\text{hr}\cdot\text{cm}^3\ \text{sludge}} \times \frac{1\ \text{g mole}\ O_2}{32\ \text{g}\ O_2} \times \frac{22.4\,\text{liters}\,O_2}{1\ \text{g mole}\,O_2} = \frac{1.85\times10^{-8}\ \text{liters}\,O_2}{\text{hr}\cdot\text{cm}^3\ \text{sludge}}$$

   The rate at 15°C would be less by a factor of 1.61, or 1.64×10^{-5} mg O_2/hr·cm^3 sludge.

7. At 8.5 ppm O_2 in air-saturated 25°C water, the sludge contains:

$$\frac{0.75\ \text{cm}^3\ H_2O}{\text{cm}^3\ \text{sludge}} \times \frac{8.5\times10^{-3}\,\text{mg}\ O_2}{\text{cm}^3\ H_2O} = \frac{6.38\times10^{-3}\ \text{mg}\ O_2}{\text{cm}^3\ \text{sludge}}$$

   Therefore, the time to deplete the oxygen in the non-irradiated sludge at 25°C is:

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[4] Makenas, B. J., T. L. Welsh, R. B. Baker, E. W. Hoppe, A. J. Schmidt, J. Abrefah, J. M. Tingey, P. R. Bredt, and G. R. Golcar. 1997. *Analysis of Sludge from Hanford K East Basin Canisters.* HNF-SP-1201, Duke Engineering and Services Hanford, Inc., Richland, WA.

[5] The surface area-to-volume ratio for 96-04L (54.6 wt% uranium; Figure I.6.2-6 of Makenas et al. 1997) was calculated to be 1.125×10^4/cm (Table 2), within 3% of the 1.157×10^4/cm ratio found for 96-06M (Table 1).

$$\frac{\dfrac{6.38\times10^{-3}\ \text{mg O}_2}{\text{cm}^3\ \text{sludge}}}{\dfrac{2.64\times10^{-5}\ \text{mg O}_2}{\text{hr}\cdot\text{cm}^3\ \text{sludge}}}=242\ \text{hr}$$

8. At 10.25 ppm O_2 in air-saturated 15°C water, the sludge contains:

$$\frac{0.75\,\text{cm}^3\ \text{H}_2\text{O}}{\text{cm}^3\ \text{sludge}}\times\frac{10.25\times10^{-3}\text{mg O}_2}{\text{cm}^3\ \text{H}_2\text{O}}=\frac{7.69\times10^{-3}\ \text{mg O}_2}{\text{cm}^3\ \text{sludge}}$$

Therefore, the time to deplete the oxygen from the non-irradiated sludge at the lower 15°C rate is:

$$\frac{\dfrac{7.69\times10^{-3}\ \text{mg O}_2}{\text{cm}^3\ \text{sludge}}}{\dfrac{1.64\times10^{-5}\ \text{mg O}_2}{\text{hr}\cdot\text{cm}^3\ \text{sludge}}}=469\ \text{hr}$$

9. If the effect of the radiation field is accounted, the respective times to exhaust the O_2 decrease. The energy available for radiolytic decomposition is the decay power of 44.2 μW/cm^3 of sludge.

The dose rate in “Modified Safety Basis” sludge containing 0.74 g U_{total}/cm^3, assuming a sludge density of 1.9 g/cm^3, and given a total decay power of 44.2μW/cm^3 , is 83.7 Gy/hr:

$$\frac{44.2x10^{-6}\ J}{\text{sec}.cm^3 sludge}\times\frac{3600\,\text{sec}}{hr}\times\frac{Gray}{J/kg\ sludge}\times\frac{cm^3\ sludge}{1.9\times10^{-3}\ kg\ sludge}=\frac{83.7\ Gy}{hr}$$

About 23.9% (see the attached Sludge Radiolysis Analysis report by Plys of FAI) of this total energy of 83.7 Gy/hr is deposited in the water for radiolytic decomposition. The balance is deposited, without effect, in the sludge solids. Thus the total for energy for water radiolysis is 20.0 Gy/hr.

From equations (A) and (B), the minimum and maximum rates of uranium corrosion, accounting for the effect of radiolysis at 20.0 Gy/hr, are:

Minimum, equation (A):

$$Rate,\frac{mg\ U}{m^2\cdot day}=\frac{0.22\ mg\ U}{m^2\cdot day}\times DR^{0.43}=\frac{0.22\ mg\ U}{m^2\cdot day}\times\left(\frac{20.0\ Gy}{hr}\right)^{0.43}=\frac{0.798\ mg\ U}{m^2\cdot day}$$

Maximum, equation (B):

$$Rate,\frac{mg\ U}{m^2\cdot day}=\frac{0.33\ mg\ U}{m^2\cdot day}\times DR^{0.33}=\frac{0.33\ mg\ U}{m^2\cdot day}\times\left(\frac{20.0\ Gy}{hr}\right)^{0.33}=\frac{0.887\ mg\ U}{m^2\cdot day}$$

These corrosion rates produce minimum and maximum oxygen consumption rates of:

Minimum, equation (A):

$$\frac{0.798\,mg U}{m^2\cdot day}\times\frac{m^2}{10^4 cm^2}\times\frac{day}{24\,hr}\times\frac{mg\,O_2}{16.98\,mg\,U}\times\frac{5.37\times10^2 cm^2\ sludge}{cm^3\ sludge}=\frac{1.05\times10^{-4}mg\,O_2}{cm^3\ sludge\cdot hr}$$

Maximum, equation (B):

$$\frac{0.887\,mg\,U}{m^2 \cdot day} \times \frac{m^2}{10^4\,cm^2} \times \frac{day}{24\,hr} \times \frac{mg\,O_2}{16.98\,mg\,U} \times \frac{5.37\times10^2\,cm^2\ sludge}{cm^3\ sludge} = \frac{1.17\times10^{-4}\,mg\,O_2}{cm^3\ sludge \cdot hr}$$

The minimum time to oxygen depletion in 25°C sludge is:

$$\frac{\dfrac{6.38\times10^{-3}\ mg\ O_2}{cm^3\ sludge}}{\dfrac{1.17\times10^{-4}\ mg\ O_2}{cm^3\ sludge \cdot hr}} = 54.5\ hours\ at\ 25°\,C$$

The maximum time to oxygen depletion in 25°C sludge is:

$$\frac{\dfrac{6.38\times10^{-3}\ mg\ O_2}{cm^3\ sludge}}{\dfrac{1.05\times10^{-4}\ mg\ O_2}{cm^3\ sludge \cdot hr}} = 60.8\ hours\ at\ 25°\,C$$

The corrosion rate is 1.61 times slower at 15°C than at 25°C (see step 4 above). Therefore, the maximum and minimum oxygen consumption rates become 7.27×10^{-5} and 6.52×10^{-5} mg O_2/(cm^3 sludge·hr), respectively. The oxygen concentration in the 15°C sludge water also is higher than at 25°C.

The minimum time to oxygen depletion in the oxygen-richer 15°C sludge is:

$$\frac{\dfrac{7.69\times10^{-3}\ mg\ O_2}{cm^3\ sludge}}{\dfrac{7.27\times10^{-5}\ mg\ O_2}{cm^3\ sludge \cdot hr}} = 105.8\ hours\ at\ 15°C$$

The maximum time to oxygen depletion in 15°C sludge is:

$$\frac{\dfrac{7.69\times10^{-3}\ mg\ O_2}{cm^3\ sludge}}{\dfrac{6.52\times10^{-5}\ mg\ O_2}{cm^3\ sludge \cdot hr}} = 117.9\ hours\ at\ 15°C$$

10. The results of the calculations of the time to depletion in the sludge of its contained dissolved oxygen are summarized in the following table.

Temperature	**Time to O_2 Depletion, hours**		
	Non-Irradiated	**21.5 Gy/hr Absorbed Irradiation Rate**	
		Equation (A)	**Equation (B)**
25°C	242	54.5	60.8
15°C	469	105.8	117.9

Table 1. Particle Size Distribution for 96-06M After Ultrasonication (Makenas et al. 1997, Figure I.6.2-15)

Diameter, µm	Wt%	100-gram basis			Cumulative, %	
		Number of Particles	Area, cm^2	Volume, cm^3	Volume or Mass	Surface Area
0.3	0.4	2.55E+12	7.2072E+03	3.60E-02	0.4	6.91
0.4	0.4	1.08E+12	5.4054E+03	3.60E-02	0.8	12.10
0.5	0.4	5.51E+11	4.3243E+03	3.60E-02	1.2	16.25
0.6	0.5	3.98E+11	4.5045E+03	4.50E-02	1.7	20.57
0.7	0.7	3.51E+11	5.4054E+03	6.31E-02	2.4	25.75
0.8	0.9	3.02E+11	6.0811E+03	8.11E-02	3.3	31.59
0.95	1.2	2.41E+11	6.8279E+03	1.08E-01	4.5	38.13
1.15	1.3	1.47E+11	6.1105E+03	1.17E-01	5.8	44.00
1.38	1.5	9.82E+10	5.8754E+03	1.35E-01	7.3	49.63
1.7	1.6	5.60E+10	5.0874E+03	1.44E-01	8.9	54.51
2	1.7	3.66E+10	4.5946E+03	1.53E-01	10.6	58.92
2.3	2	2.83E+10	4.7004E+03	1.80E-01	12.6	63.43
2.8	2.2	1.72E+10	4.2471E+03	1.98E-01	14.8	67.50
3.3	2.5	1.20E+10	4.0950E+03	2.25E-01	17.3	71.43
3.8	2.9	9.09E+09	4.1252E+03	2.61E-01	20.2	75.39
4.8	3.2	4.98E+09	3.6036E+03	2.88E-01	23.4	78.84
5.8	3.5	3.09E+09	3.2619E+03	3.15E-01	26.9	81.97
6.5	3.6	2.26E+09	2.9938E+03	3.24E-01	30.5	84.84
8	3.5	1.18E+09	2.3649E+03	3.15E-01	34.0	87.11
9.5	3.5	7.02E+08	1.9915E+03	3.15E-01	37.5	89.02
11	3.4	4.40E+08	1.6708E+03	3.06E-01	40.9	90.63
13.5	3.6	2.52E+08	1.4414E+03	3.24E-01	44.5	92.01
16	4.1	1.72E+08	1.3851E+03	3.69E-01	48.6	93.34
18.5	4.4	1.20E+08	1.2856E+03	3.96E-01	53.0	94.57
23	4.5	6.36E+07	1.0576E+03	4.05E-01	57.5	95.58
27	4.5	3.93E+07	9.0090E+02	4.05E-01	62.0	96.45
31	4.6	2.66E+07	8.0209E+02	4.14E-01	66.6	97.22
38	5	1.57E+07	7.1124E+02	4.50E-01	71.6	97.90
45	5.2	9.82E+06	6.2462E+02	4.68E-01	76.8	98.50
52	5	6.12E+06	5.1975E+02	4.50E-01	81.8	99.00
64	4.1	2.69E+06	3.4628E+02	3.69E-01	85.9	99.33
76	3.3	1.29E+06	2.3471E+02	2.97E-01	89.2	99.56
88	2.7	6.82E+05	1.6585E+02	2.43E-01	91.9	99.71
108	2.2	3.00E+05	1.1011E+02	1.98E-01	94.1	99.82
128	1.5	1.23E+05	6.3345E+01	1.35E-01	95.6	99.88
148	1.3	6.90E+04	4.7480E+01	1.17E-01	96.9	99.93
180	1	2.95E+04	3.0030E+01	9.01E-02	97.9	99.96
210	0.8	1.49E+04	2.0592E+01	7.21E-02	98.7	99.97
248	0.7	7.90E+03	1.5257E+01	6.31E-02	99.4	99.99
300	0.6	3.82E+03	1.0811E+01	5.41E-02	100.0	100.00
Sum	100		1.0425E+05	9.01		
Surface area / volume ratio = 1.0425×10^5 cm^2 / 9.01 cm^3 = 1.157×10^4/cm						

Table 2. Particle Size Distribution for 96-04L Without Ultrasonication (Makenas et al. 1997, Figure I.6.2-6)

Diameter, µm	Wt%	100-gram basis			Cumulative, %	
		Number of Particles	Area, cm^2	Volume, cm^3	Volume or Mass	Surface Area
0.3	0	0.00E+00	0.00	0.00E+00	0.0	0.00
0.4	0.3	8.07E+11	4054.05	2.70E-02	0.3	4.00
0.5	0.4	5.51E+11	4324.32	3.60E-02	0.7	8.27
0.6	0.6	4.78E+11	5405.41	5.41E-02	1.3	13.60
0.7	0.8	4.01E+11	6177.61	7.21E-02	2.1	19.70
0.8	1.1	3.70E+11	7432.43	9.91E-02	3.2	27.03
0.95	1.6	3.21E+11	9103.84	1.44E-01	4.8	36.01
1.15	2	2.26E+11	9400.71	1.80E-01	6.8	45.29
1.38	2	1.31E+11	7833.92	1.80E-01	8.8	53.02
1.7	2	7.00E+10	6359.30	1.80E-01	10.8	59.29
2	2	4.30E+10	5405.41	1.80E-01	12.8	64.62
2.3	2	2.83E+10	4700.35	1.80E-01	14.8	69.26
2.8	2.2	1.72E+10	4247.10	1.98E-01	17.0	73.45
3.3	2.3	1.10E+10	3767.40	2.07E-01	19.3	77.17
3.8	2.4	7.53E+09	3413.94	2.16E-01	21.7	80.54
4.8	2.3	3.58E+09	2590.09	2.07E-01	24.0	83.09
5.8	2.5	2.20E+09	2329.92	2.25E-01	26.5	85.39
6.5	2.6	1.63E+09	2162.16	2.34E-01	29.1	87.52
8	2.7	9.07E+08	1824.32	2.43E-01	31.8	89.32
9.5	2.6	5.22E+08	1479.37	2.34E-01	34.4	90.78
11	2.4	3.10E+08	1179.36	2.16E-01	36.8	91.95
13.5	2.4	1.68E+08	960.96	2.16E-01	39.2	92.90
16	2.9	1.22E+08	979.73	2.61E-01	42.1	93.86
18.5	3.5	9.51E+07	1022.64	3.15E-01	45.6	94.87
23	3.9	5.52E+07	916.57	3.51E-01	49.5	95.78
27	3.9	3.41E+07	780.78	3.51E-01	53.4	96.55
31	3.7	2.14E+07	645.16	3.33E-01	57.1	97.18
38	3.6	1.13E+07	512.09	3.24E-01	60.7	97.69
45	4	7.55E+06	480.48	3.60E-01	64.7	98.16
52	4.2	5.14E+06	436.59	3.78E-01	68.9	98.59
64	4.1	2.69E+06	346.28	3.69E-01	73.0	98.93
76	3.8	1.49E+06	270.27	3.42E-01	76.8	99.20
88	3.4	8.58E+05	208.85	3.06E-01	80.2	99.41
108	3	4.10E+05	150.15	2.70E-01	83.2	99.56
128	2.9	2.38E+05	122.47	2.61E-01	86.1	99.68
148	2.7	1.43E+05	98.61	2.43E-01	88.8	99.77
180	2.5	7.38E+04	75.08	2.25E-01	91.3	99.85
210	1.9	3.53E+04	48.91	1.71E-01	93.2	99.90
248	1.1	1.24E+04	23.98	9.91E-02	94.3	99.92
300	1	6.37E+03	18.02	9.01E-02	95.3	99.94
350	1.3	5.22E+03	20.08	1.17E-01	96.6	99.96
420	3.4	7.90E+03	43.76	3.06E-01	100.0	100.00
Sum	100.0		101352.47	9.01		
Surface area / volume ratio = 101352.47 cm^2 / 9.01 cm^3 = 1.125×10^4/cm.						

Attachment 6

Oxygen Diffusion and Effects of Metal Distribution in K East Sludge Loaded in LDCs

M Epstein
Vice President, Consulting
Fauske & Associates, Inc.

Fauske & Associates, Inc.

DATE: September 9, 2003

TO: James L. Shelor
Marty Plys

FROM: Mike Epstein

SUBJECT: **Attachment 6: Oxygen Diffusion in K East Sludge and Effect of Uranium Metal Distribution on Hydrogen Generation Rate and Delay Time (REVISED)**

In this memo the diffusion equation that describes the dissolved oxygen concentration history in a finite composite sludge layer of reactive and nonreactive material within an LDC is solved. In the LDC each reactive sludge layer containing metallic particles is "sandwiched" between two layers that, for all practical purposes, do not contain metallic particles. The composite sludge layer is hereafter referred to as the "layer"; the reactive and nonreactive layers that comprise the layer are called sublayers. The solutions to the diffusion equation are used to predict the "delay" time to the onset of H_2 gas generation, based on the understanding that H_2 gas generation begins at those locations where dissolved oxygen has vanished owing to reaction with uranium metal. The solutions to the diffusion equation are also used to predict the time to generate a flammable volume of H_2 gas (48L when instantaneously mixed with LDC headspace air). The main finding of the present oxygen diffusion in sludge study is:

The time to produce a flammable volume of H_2 gas is not very sensitive to the way in which the uranium metal sublayers are distributed. For example the time to generate 48L of H_2 when the metallic particles are uniformly distributed throughout the layer (or sludge column) is 442 hr. If, instead, the metal particles in each layer are concentrated by one order of magnitude relative to the uniform distribution case, so that the thickness of each reactive sublayer is one-tenth that of each layer, the time to generate 48L of H_2 is reduced by about one-half to 233 hr.

STATEMENT OF PROBLEM

On the basis of symmetry, the solution space of interest extends from the center of a typical reactive sublayer to the center of an adjacent nonreactive sublayer. Note that O_2 is free to diffuse from one sublayer to an adjacent sublayer through the sludge's interstitial water. Owing to sludge consolidation forces the water is a spatially continuous component of the sludge. The partial differential equation for the dissolved oxygen concentration Y (mass fraction) in the reactive region half-subspace is

$$\frac{\partial Y}{\partial t} = D\frac{\partial^2 Y}{\partial x^2} - \frac{a_m \dot{m}''_{ox}}{\phi \rho_f} \qquad ; \qquad 0 \le x \le \delta_r \tag{1}$$

where t is time, δ_r is the half-thickness of the reactive region, x is the distance measured from the center of the reactive sublayer, D is the binary diffusion coefficient for the O_2/water solution, ρ_f is the density of the sludge's interstitial liquid, ϕ is the volume fraction of the sludge occupied by water, $\dot{m}''_{ox}$ is the metallic particle mass oxidation rate per unit reactive area of the particles and a_m is the reactive surface area of the metallic particles per unit volume of the reactive sublayer. The partial differential equation for the nonreactive sublayer of half-thickness $\delta_{nr} - \delta_r$ is

$$\frac{\partial Y}{\partial t} = D\frac{\partial^2 Y}{\partial x^2} \qquad ; \qquad \delta_r \le x \le \delta_{nr} \tag{2}$$

Equations (1) and (2) are subject to the following boundary conditions: zero diffusion flux at the boundaries of the composite layer

$$\frac{\partial Y}{\partial x} = 0 \qquad \text{at} \qquad x = 0 \;,\; x = \delta_{nr} \tag{3}$$

and concentration and diffusion flux continuity at the interface of the reactive and nonreactive media

$$\left.\frac{\partial Y}{\partial x}\right|_{\delta_r-} = \left.\frac{\partial Y}{\partial x}\right|_{\delta_r+} \quad ; \quad Y|_{\delta_r-} = Y|_{\delta_r+} \quad \text{at} \quad x = \delta_r \tag{4}$$

Equations (1) and (2) are also subject to the initial condition

$$Y = Y_0 \quad \text{at} \quad t = 0 \tag{5}$$

where Y_0 is the initial dissolved oxygen concentration.

It is convenient to convert the above set of equations to nondimensional form by introducing the following dimensionless variables and parameters:

$$y = \frac{Y}{Y_0} \qquad \text{(dimensionless oxygen concentration)} \tag{6}$$

$$\tau = \frac{Dt}{\delta_r^2} \qquad \text{(dimensionless time)} \tag{7}$$

$$z = \frac{x}{\delta_r} \qquad \text{(dimensionless distance)} \tag{8}$$

$$R = \frac{a_m \dot{m}''_{ox} \delta_r^2}{\phi \rho_f Y_0 D} \qquad \text{(dimensionless reaction rate parameter)} \tag{9}$$

The governing equations in dimensionless form are

$$\frac{\partial y}{\partial \tau}=\frac{\partial^2 y}{\partial z^2}-R \qquad ; \qquad 0\le z\le 1.0 \tag{10}$$

$$\frac{\partial y}{\partial \tau}=\frac{\partial^2 y}{\partial z^2} \qquad ; \qquad 1.0\le z\le \frac{\delta_{nr}}{\delta_r} \tag{11}$$

$$\frac{\partial y}{\partial z}=0 \qquad \text{at} \qquad z=0,\frac{\delta_{nr}}{\delta_r} \tag{12}$$

$$\left.\frac{\partial y}{\partial z}\right|_{1-}=\left.\frac{\partial y}{\partial z}\right|_{1+} \quad ; \quad Y\big|_{1-}=Y\big|_{1+} \quad \text{at} \quad z=1.0 \tag{13}$$

$$y=1.0 \qquad \text{at} \qquad \tau=0 \tag{14}$$

NUMERICAL SOLUTION, H_2 GENERATION AND PARAMETER VALUES

Equations (10) to (14) were solved numerically by replacing $\partial^2 y/\partial z^2$ by the forward difference

$$\varepsilon^2\frac{\partial^2 y}{\partial z^2}=y_{m+1}-2y_m+y_{m-1} \tag{15}$$

where y_m is the value of m at regular intervals $z = m\varepsilon$, $m = 1,2,3,\ldots,N$. Actually Eq. (15) does not include the nodes n=1,N adjacent to the zero flux boundaries. For these nodes

$$\varepsilon^2\frac{\partial^2 y}{\partial z^2}=2(y_2-y_1) \quad , \qquad m=1 \tag{16}$$

$$\varepsilon^2\frac{\partial^2 y}{\partial z^2}=2(y_{N-1}-y_N) \quad , \qquad m=N \tag{17}$$

In this manner Eqs. (10) and (11) are transformed to a system of N differential equations.

During the course of the solution the reaction rate R is set equal zero at each location m where the oxygen concentration y is reduced to zero. In the model the oxygen depleted nodes will begin to generate H_2 gas at a rate

$$\frac{dQ'''}{dt} = \frac{\dot{m}'''_{H_2} a_m}{\rho_{H_2}} \tag{18}$$

where $\dot{m}'''_{H_2}$ is the hydrogen mass generation rate per unit reactive area of the metallic particles, ρ_{H_2} is the density of H_2 gas at the prevailing LDC pressure and temperature and Q'''_m is the volume amount of H_2 gas generated in node m at time t per unit volume of the node. Replacing the physical time t in Eq. (18) with the dimensionless time τ from Eq. (7) gives

$$\frac{dQ'''_m}{d\tau} = R_H \tag{19}$$

where R_H is the dimensionless H_2 production parameter

$$R_H = \frac{\dot{m}''_{H_2} a_m \delta_r^2}{D\rho_{H_2}} \tag{20}$$

The total volume of H_2 gas generated in the sludge column Q_{tot} is found by evaluating the sum

$$Q = \sum_{m=1}^{N} Q'''_m \tag{21}$$

and noting that

$$Q = \frac{NQ_{tot}}{V} \tag{22}$$

where V is the total volume of the sludge column.

The interval of interest $0 \le z \le \delta_{nr}/\delta_r$ was divided into N = 250 nodes. Cases were also run with 500 nodes and no differences were detected from the 250 node cases. The calculations were carried out for the physical parameter values given in Table 1.

Table 1 - Parameter Values

$a_m = 40.0\ m^{-1}$	reactive area per unit volume of reactive region for uniformly distributed metal particles
$D = 1.8 \times 10^{-9}\ m^2\ s^{-1}$	oxygen diffusion coefficient in water at 20°C
$\dot{m}'''_{H_2} = 7.6 \times 10^{-10}\ kg\ m^{-2}\ s^{-1}$	particle H_2 generation rate per unit area at 20°C
$\dot{m}''_{ox} = 1.11 \times 10^{-10}\ kg\ m^{-2}\ s^{-1}$	particle oxidation rate per unit area at 20°C
$Q_{tot} = 4.8 \times 10^{-2}\ m^3$	H_2 gas volume above which instantaneously mixed LDC headspace is flammable
$V = 2.0\ m^3$	volume of sludge column
$Y_0 = 8.0 \times 10^{-6}$	dissolved oxygen mass fraction at 20°C
$\delta_{nr} = 8.0 \times 10^{-2}\ m$	half thickness of composite layer
$\rho_f = 1000\ kg\ m^{-3}$	density of interstitial water
$\rho_{H_2} = 8.21 \times 10^{-2}\ kg\ m^{-3}$	density of H_2 gas at 20°C and 1.0 atm
$\phi = 0.75$	volume fraction of water in sludge

Inserting the numerical values of N, Q_{tot} and V into Eq. (22) reveals that the H_2 generation parameter

$$Q = 6.0 \tag{23}$$

when the volume of hydrogen generated is 48L

RESULTS AND DISCUSSION

The predicted evolution of the dissolved oxygen concentration profile for a layer in which the metal particles are uniformly distributed, hereafter referred to as the UD layer (UD standing for uniformly distributed), is shown in Fig. 1. In this case $\delta_{nr} = \delta_r = 0.08$ m. The UD layer is uniformly and completely depleted of dissolved oxygen at dimensionless time $\tau = 0.38$. From Eq. (7) and Table 1 the corresponding physical time to complete oxygen depletion is t = 375 hr. Hydrogen production begins at this time everywhere in the layer. The hydrogen generation function defined by Eq. (21) versus dimensionless time τ is plotted in Fig. 2. From this figure and Eq. (23), 48L of H_2 gas is generated at $\tau = 0.4$ or, equivalently, after an elapsed physical time t = 393 hr.

Figure 3 shows the oxygen concentration profile history in a layer containing a reactive sublayer of thickness $\delta_r = 0.032$ m. This sublayer is 2.5 times more concentrated in uranium metal than the UD layer. Note that the UD layer and the concentrated sublayer contain the same total mass of uranium metal. The dissolved oxygen concentration in the reactive sublayer decreases rapidly with time relative to the UD layer due to concentrated uranium metal oxygen uptake. Some of the reacted oxygen is replaced by oxygen diffusion from the nonreactive sublayer. Nevertheless complete oxygen depletion occurs at the center of the reactive sublayer at 234 hr ($\tau = 1.48$), which is about 141 hr earlier than the onset of H_2 generation in the UD layer. However, unlike the UD layer, not all of the uranium metal participate in H_2 production. At 316 hr ($\tau = 2$) only 50% of the reactive sublayer is producing H_2 (see Fig. 3). The remaining portion of the sublayer receives oxygen from the nonreactive layer and about 24% of the initial dissolved oxygen is still available in the water (Fig. 4). As a result the time from the onset of H_2 generation to H_2 buildup to 48L is longer in the concentrated sublayer than in the UD layer, 58 hr versus 18 hr respectively. The H_2 generation parameter history $Q(\tau)$ for the reactive sublayer is shown in Fig. 5. The time to generate 48L (Q = 6.0) in the concentrated layer is 292 hr ($\tau = 1.85$).

Two more numerical cases were run involving highly concentrated reactive sublayers: five and ten times more concentrated than the layer of uniformly distributed metal particles (i.e., the UD layer). All the numerical results are summarized in Table 2.

Table 2

Predicted Times to Onset of H_2 Generation and to Generation of 48L of H_2

Half-Thickness of Composite Layer (δ_{nr},m)	Half-Thickness of Reactive Sublayer (δ_r,m)	Concentration of Uranium Metal (multiple of concentration in uniformly distributed layer)	Time to Onset of H_2 Generation (hr)	Time to Generate 48L of H_2 (hr)	Dissolved O_2 Fraction Remaining in Layer When 48L of H_2 is Generated (percent)
0.08	0.08	1.0	375	393	0.0
0.08	0.032	2.5	234	292	27.0
0.08	0.16	5.0	174	234	42.5
0.08	0.008	10.0	144	200	50.0

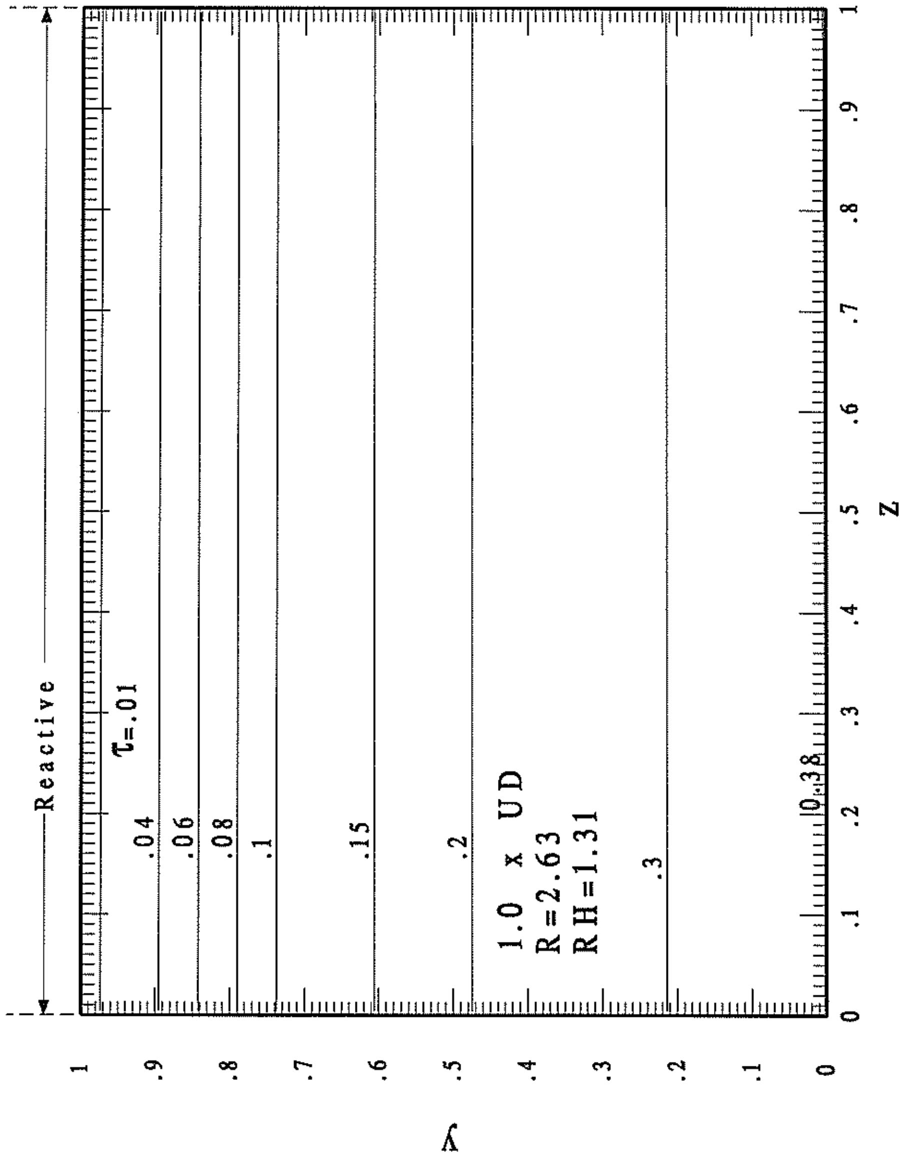

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Figure 1 Dimensionless oxygen depletion profiles in a sludge layer with uniformly distributed metal particles; dimensionless time as a parameter.

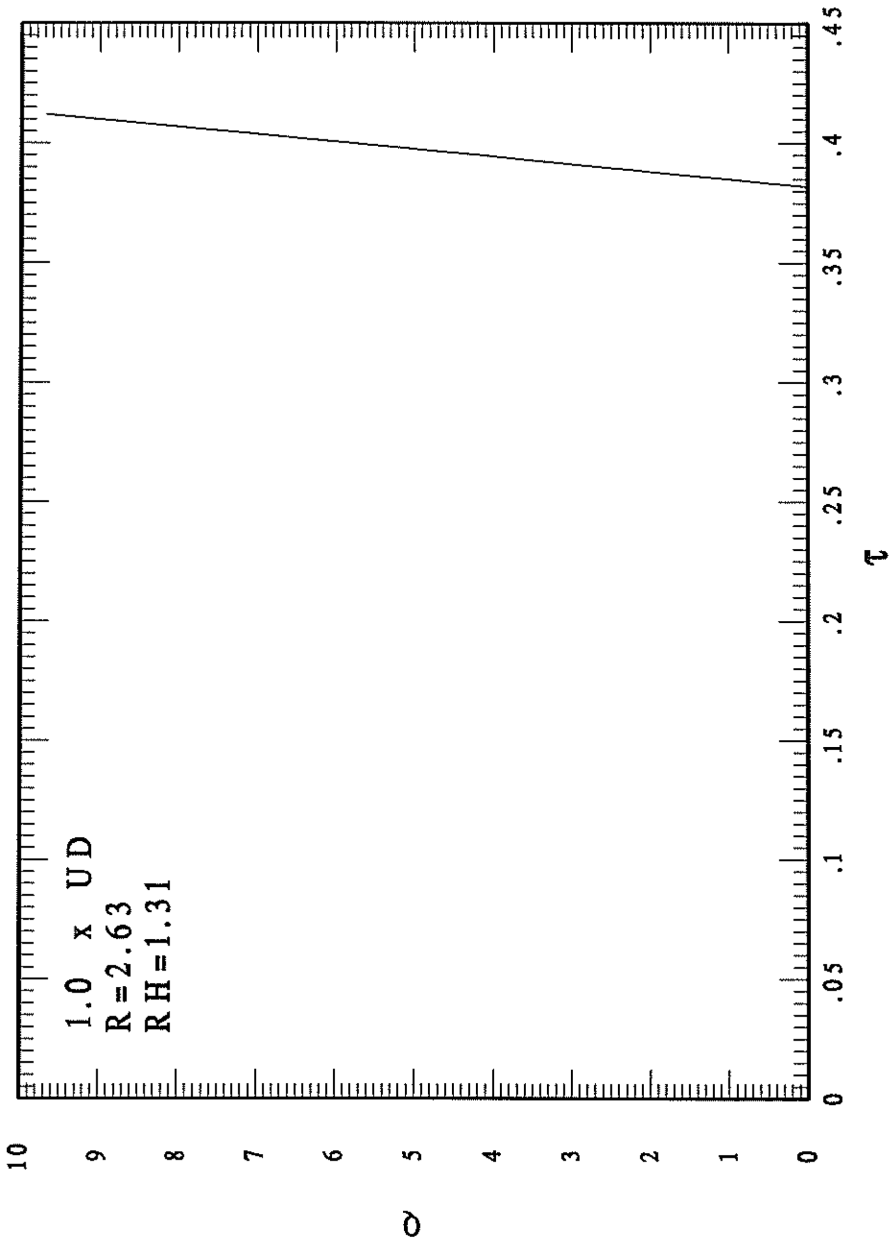

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Figure 2 Hydrogen generation function (Eq. 21) versus dimensionless time for a layer with uniformly distributed metal particles. Q = 6 corresponds to 48L of H_2 gas.

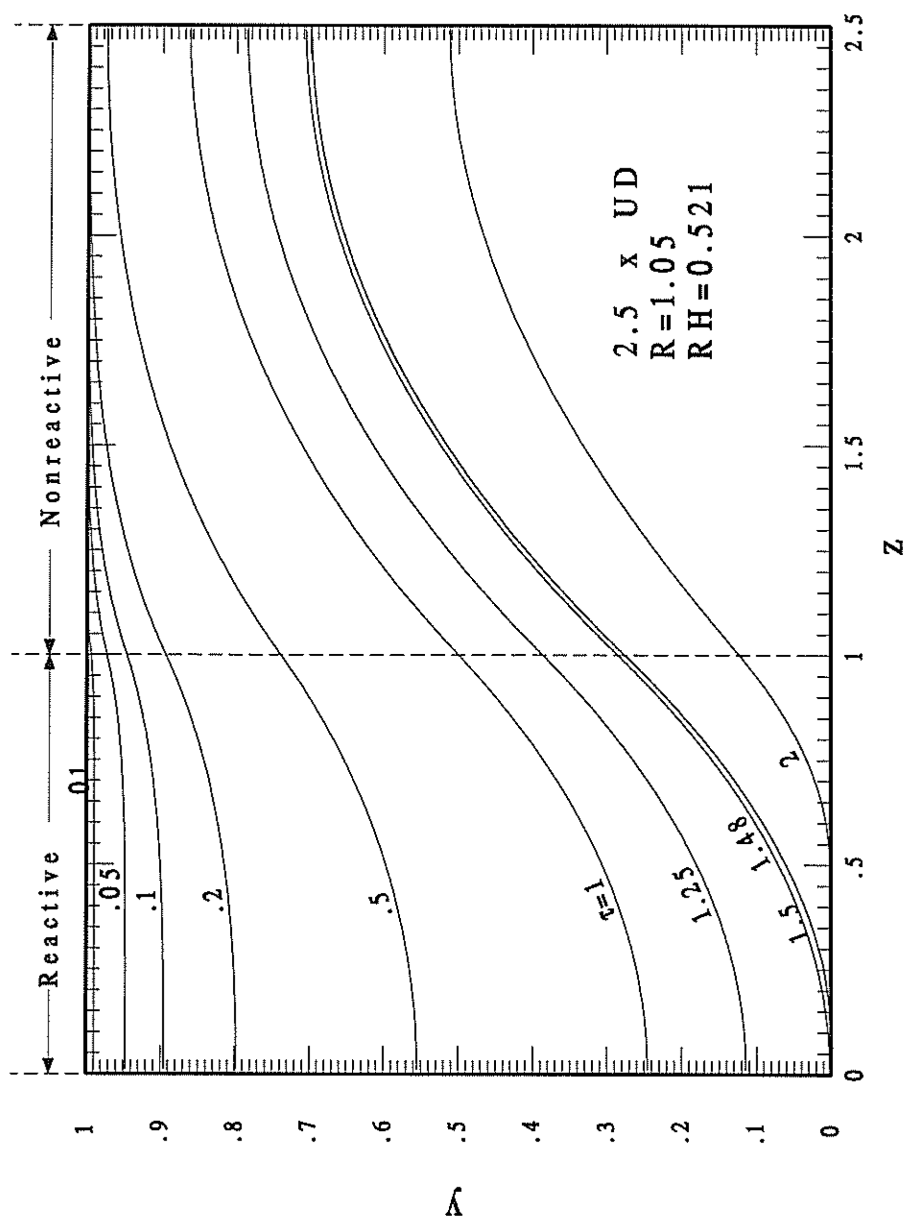

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Figure 3 Dimensionless oxygen depletion profiles in a sludge layer with a concentrated sublayer of metal particles (2.5 times the concentration in the UD layer); dimensionless time as a parameter.

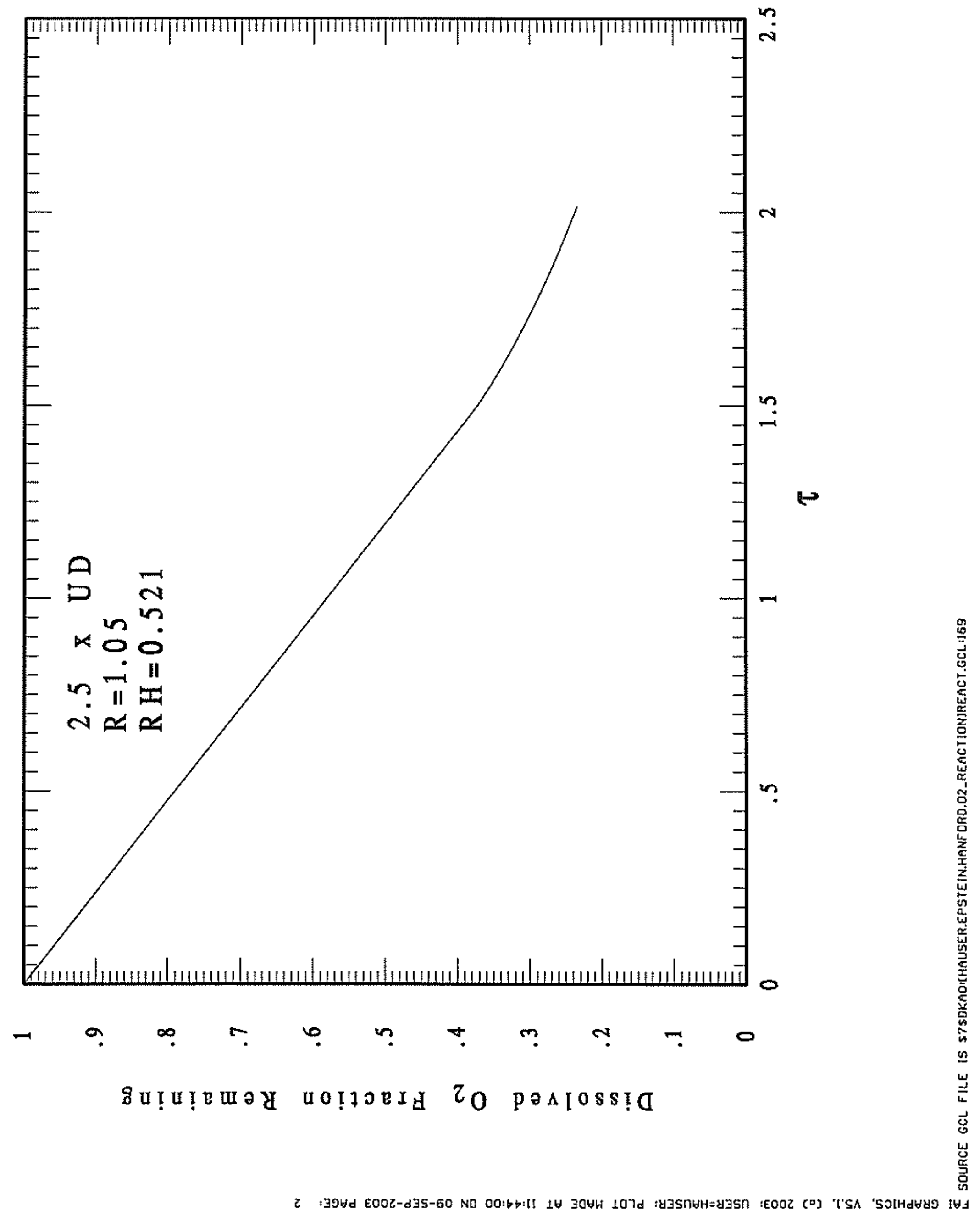

Figure 4 Dissolved oxygen as a fraction of the initial concentration versus dimensionless time in a sludge layer with a concentrated sublayer of metal particles (2.5 times the concentration in the UD layer).

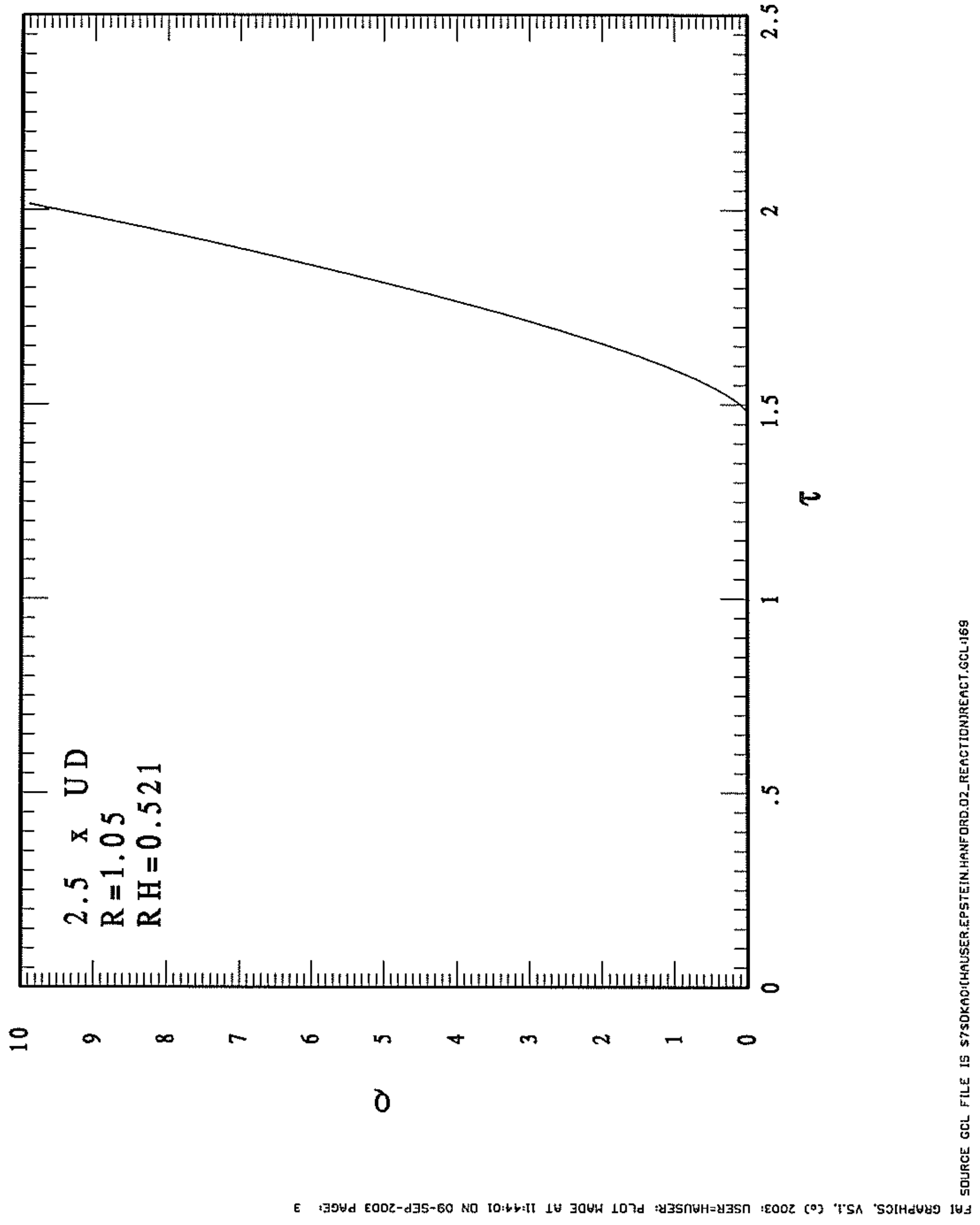

Figure 5 Hydrogen generation function (Eq. 21) versus dimensionless time in a sludge layer with a concentrated sublayer of metal particles (2.5 times the concentration in the UD layer).

Attachment 7

K East Sludge Decay Heat

A. J. Schmidt
Senior Engineer
Pacific Northwest National Laboratory

DECAY POWER
(Revised 9/4/03)

The following discussion and selection of safety basis decay power for KE Canister sludge and KE floor sludge is being incorporated into HNF-7765, Revision 2 and HNF-SD-SNF-TI-015, Rev 10.

Decay power of sludge is less than that of decay power in fuel and in fuel pieces (fuel piece sludge) because the fuel oxidation process by which sludge is created leads to the loss of fission products, notably cesium. There are two fundamentally different ways to evaluate decay power: Using isotopic concentrations based on fuel, whether by measurement or reactor physics evaluation, and using isotopic concentrations based on sludge sample data. The former method was used for fuel piece sludge, and the latter method was used for floor and canister sludge.

Canister and floor sludge decay power were directly calculated from measured isotopic data, typically given in curies per unit volume of sludge. This approach uses the data and includes appropriate statistical methods to consider variability, and it implicitly includes fission product losses during initial sludge formation by oxidation and any losses during sludge lifetime in the basins.

There are two approaches to analyzing sludge sample isotopic information. In the development of isotopic source terms for dose consequence evaluations, the variability in each individual isotope was considered independently, and a safety basis source term was constructed by selecting extreme values of each isotope. This approach is pertinent to creating bounding predictions of isotopic content of very small amounts of sludge characteristic of released quantities. An alternate and preferred approach is to take each sludge sample and use its isotopic information to calculate decay power, and then to evaluate the distribution of decay power and select a confidence limit value to represent the safety basis. This alternate approach is superior for the application of decay power estimates because the variance in decay power arises from the combination of variances of each isotope, and it is this combination that is the desired figure of merit.

In general, decay power based on source term isotopics exceeded decay power based on statistical analysis of integrated sample decay power. However, examination of the parameters used to calculate the decay power based on source term isotopics implied a physically impossible uranium total concentration in the KE canisters sludge [(i.e., the implied uranium total concentration in wet sludge (3.36 g/cm^3) exceeds the safety settled sludge density of safety of 2.5 g/cm^3].

Therefore, the decay power values based on the measured isotopics of individual sludge samples are judged to be the appropriate values to use for design and safety basis calculations. Design basis values based on sludge sample isotopic concentrations are the mean values, and safety basis values are selected as the 95/95 TL values for KE canister sludge (sample isotopic data was shown to exhibit a goodness-of-fit to a normal distribution). For KE floor sludge, the safety basis value was selected as the 95/99 TL value, as the sample data for some isotopes did not exhibit a goodness-of-fit to a normal distribution. The decay power values for KE floor, KE canister, and a 40/60 KE floor/canister mixture (volume basis) are presented in the table below:

KE Floor and Canister Sludge Decay Power,
Base on Sludge Sample Isotopic Values

Sludge Stream	Decay Heat, W/m^3 (μW/cm^3)	
	Design Basis (mean)	Safety Basis
KE Canister Sludge	21.7	77.0(1)
KE Floor Sludge	3.12	22.4(2)
40/60 Canister/Floor	10.6	44.2

(1) Based on 95/95 TL.
(2) Based on 95/99 TL.

References:

Plys M. G. and K. L. Pearce. 2003 (draft). *Supporting Basis for Spent Nuclear Fuel Project Sludge Technical Databook*, SNF-7765, Rev. 2. Fluor Hanford, Richland Washington.

Pearce, K. L. Pearce 2003 (draft). *Spent Nuclear Fuel Project Technical Databook*, Volume 2, Rev. 10, HNF-SD-SNF-TI-015. Fluor Hanford, Richland Washington.

Attachment 8

Production of Hydrogen and Oxygen by Radiolysis of K East Sludge

M. G. Plys
Vice President, Waste Technology
Fauske & Associates, Inc.

Fauske & Associates, Inc.

Date: October 30, 2003

To: Jim Shelor, Jim Sloughter, Darrel Duncan, Hanford SNFP

From: Martin G. Plys, FAI

Subject: **Sludge Radiolysis, Rev. 3**

1.0 Purpose

The purpose of this work is to estimate the radiolysis rate of liquid water in K East Basin sludge and contribute to calculations of gas behavior in a large diameter container in SNF-18133. This memorandum is intended to be Attachment 8 of SNF-18133, and it refers to other attachments of that document. Results of this work supersede estimates in SNF-9955, Rev. 1. Values are provided for floor, canister, and 60%/40% floor/canister sludge at the modified safety basis (same safety basis for this work), reasonably bounding, and nominal levels described in Attachment 10.

2.0 Radiolysis Rate Equation, Background, and Approach

The rate of hydrogen production from radiolysis W_{H2}, kg/s, is

$$W_{H2} = C\,Q\left[f_{q\alpha}e_{\alpha}g_{\alpha} + f_{q\beta}e_{\beta}g_{\beta} + f_{q\gamma}e_{\gamma}g_{\gamma}\right]$$

where

C = Units conversion factor,

$$C = \frac{1}{100\text{ eV}} \times \frac{1\text{ eV}}{1.602\times10^{-19}\text{ J}} \times \frac{0.002\text{ kg}}{6.02\times10^{23}\text{ molecules}} = 2.07\times10^{-10}$$

Q = Decay power, W,

f_q = Fraction of decay power for the given radiation type,

e = Fraction of power absorbed by water for the given radiation type, and

g = $g(H_2)$, molecules H_2 per 100 eV absorbed by water, and alpha, beta, and gamma radiation are respectively considered. An average g value G may be defined for convenience,

$$G = f_{q\alpha}e_{\alpha}g_{\alpha} + f_{q\beta}e_{\beta}g_{\beta} + f_{q\gamma}e_{\gamma}g_{\gamma}$$

which results in a simplified version of the equation,

$$W_{H2} = C\,Q\,G$$

Also, the power fraction absorbed by water F_Q may be desired, and is simply given by

$$F_Q = f_{q\alpha}e_{\alpha} + f_{q\beta}e_{\beta} + f_{q\gamma}e_{\gamma}$$

The form of the equation presupposes that we can determine the amount of energy deposited in water (or hydrogen-bearing material), and that $g(H_2)$ values are defined on the same basis. Such an approach is mentioned in several SNFP and Hanford background references. Specifically, this approach was used to examine radiolysis of Hanford sludge samples to determine its impact relative to hydrogen production from metal-water reactions in Appendix C of PNNL-13320; this reference discusses a rationale for selecting the fraction of energy absorbed by water for each radiation type. An evaluation of radiolysis from sludge prior to SNF-9955, Appendix C of FAI/01-44, Scoping Calculations of SNF Sludge Behavior in a Large Diameter Container, used this PNNL-13320 information with an updated safety basis decay power. The approach was used to calculate radiolysis in MCOs in HNF-SD-SNF-TI-040, although the hydrogen-bearing materials in this instance also included hydrates of uranium oxide, aluminum oxide, and iron oxide.

When it is not possible or appropriate to consider power absorbed in the hydrogen-bearing medium, the effective $g(H_2)$ value is based upon power absorbed in the entire material matrix and therefore represents the product e*g. This is pointed out in a Hanford review of radiolysis data from waste forms, "Hydrogen Control in the Handling, Shipping and Storage of Wet Radioactive Waste," RHO-WM-EV-9P. This is for example the case with grout as discussed in PNL-7644.

Present $g(H_2)$ values that appear in TI-040 are based upon power absorbed in the matrix of combined solids and water or hydrogen-bearing compounds. Notable background references containing these data include PNL-7644 and two reports by Bibler, [Bibler, 1980] and DP-1464. Bibler studied generation of H_2 and O_2 from concrete containing alpha emitters, Pu-238, and beta-gamma emitters, Sr-90 and Cs-137.

A key question to ask for application of these data to SNF sludge is: How appropriate are the materials, i.e. are they appropriate surrogates? Radiolysis is the term for the process by which energy loss from radiation causes ionization of a medium and formation of oxidizing and reducing species. These species react with one another and with the materials present. In an aqueous system, the net result of formation of these species by ionization of water, back reactions to re-form water, and reactions with any solids or other materials present is manifest in the measured $g(H_2)$ and $g(O_2)$ values. Therefore, the chemistry of the system is crucial to the relative amounts of hydrogen and oxygen created. For example, $g(O_2)$ values are in less than stoichiometric proportion to the $g(H_2)$ values in TI-040. This quantifies the net result of chemical reactions that consume oxidizing species produced by radiolysis.

Uranium has a strong affinity for oxidizing species: Oxidation of U metal is discussed in Attachment 4 and oxidation of U oxides is discussed in Attachment 5. Therefore, reactions of radiolytically produced oxidizing species are a priori expected to be different in SNFP sludge than in concrete or grout. Furthermore, the high atomic number of uranium immediately implies that relative power deposition between the solids and liquids in a composite matrix will also be different for SNFP sludge than in concrete or grout. Therefore, it is concluded that concrete and grout materials that form the basis for the TI-040 recommended $g(H_2)$ and $g(O_2)$ values are not necessarily representative surrogate materials, although clearly the data base can be used for guidance in sludge application. This work proceeds with the full knowledge of the references, but seeks to understand how best to predict radiolysis in sludge rich in uranium compounds.

In this work, the power fraction deposited in water will be estimated, and standard $g(H_2)$ values for water will be applied as discussed below. The production rate of oxidizing species is in stoichiometric proportion to that of hydrogen and is given here in terms of equivalent O_2. The outcome of this work may then be combined with an analysis of oxygen reactions with uranium metal and oxides, Attachments 4 and 5 respectively, to determine the net release of O_2, if any.

The positive benefit of the approach is that consideration is explicitly given to water fraction, material composition, fundamental energy loss data, sludge particle sizes, and the distribution of path lengths through water. A drawback of the approach is that the evaluation is commensurately more complicated than an approach relying upon total energy deposited in the medium, especially for alpha energy deposition. It is difficult to conceive of an improved approach without directly applicable experimental data for the substances considered.

The essence of the approximation is therefore: Radiolytic decomposition of water is assumed as the basis for evolution of hydrogen and oxidizing species: The power fraction deposited in water is estimated and used to define the production rate of species from radiolysis. Decomposition of water-bearing hydrates in the solids is neglected as a trivial effect. Transfer of deposited energy from solids to water, or vice versa, is not considered. Back-reactions in water itself implicitly form the basis for the production rate of hydrogen. However, chemical reactions of the oxidizing species are known to reduce or eliminate the production of oxygen. In essence, hydrogen produced is assumed to be available for release, but oxidizing species produced are available for recombination with solids as quantified in Attachment 5.

3.0 Data to Evaluate Radiolysis Rate

3.1 Decay Power, Power Fractions, and G values

A revised safety basis decay power of 88.4 W is used for this calculation, taken from Attachment 10, and assuming 2 m^3 of sludge. Power for other cases is: Reasonably bounding, 72.4 W; Nominal, 21.2 W. For unmixed streams, power per unit volume is: Reasonably bounding canister, 77 W/m^3; and reasonably bounding floor, 8.96 W/m^3.

Consistent with SNF-9955, decay power fractions are respectively $f_{q\alpha} = 0.3217$, $f_{q\beta} = 0.5146$, and $f_{q\gamma} = 0.1637$. Appropriate g values are 1.5 for alpha and 0.5 for beta and gamma as discussed in PNNL-13320, TI-040, and FAI/01-44.

3.2 Power Fractions Absorbed by Water

Power fractions absorbed by water were found using fundamental data for radiation absorption in sludge components. Sludge physical properties and particle size distributions, described later, were also required for this step.

The National Institute of Standards (NIST) maintains an on-line library and computational method to examine absorption of alphas, betas, and gammas as described in the website link http://physics.nist.gov/PhysRefData/Star/Text/contents.html; these are the ASTAR, ESTAR, and PSTAR programs, respectively. As noted in PNNL-13320, we are concerned with alpha particles born near 5 MeV; beta particle energies are 0.545 MeV for Sr-90 and 2.27 for Y-90, and the gamma energy of interest is the 0.66 MeV for Cs-137. Briefly, ASTAR data were used to construct values of stopping power S (Mev cm^2/g) and range R (g/cm^2) for alphas and betas in water and in idealized particles made of U metal, UO_2, and SiO_2 as a function of energy. Dividing the range R by the density yields the linear range L in cm. Also, ASTAR data for particle deflection from Rutherford scattering, the so-called detour factor, are used to reduce the linear range to an effective measured distance. PSTAR data for the gamma ray mass energy absorption coefficient μ/ρ (cm^2/g) were similarly used. The continuous slowing down approximation (CSDA) is the heart of the method employed in all cases.

NIST data were used to calculate alpha absorption by a Monte Carlo method described in Section 6, and to support an averaging approach to calculate beta absorption described in Section 7 and gamma absorption described in Section 8. Results are summarized in Section 4.

3.3 Sludge Physical Properties

Sludge has 75% water by volume and a safety basis mixture is defined by 40% canister sludge and 60% floor sludge. Using safety basis values for these two streams, a safety basis sludge mixture has a wet density of 1.9 g/cc, a uranium element mass fraction of 0.56, and a particle density of 4.6 g/cc. Further sludge property background and data required for this work are given in Section 8. A key feature sludge for this work is that following SNF-7765 its composition is idealized as a mixture of uranium metal, uranium oxides at a density of 7.5 g/cc, and non-uranium material at a density of about 1.9 g/cc (see Section 8) which is represented using SiO2 as a surrogate for radiation energy loss.

3.4 Particle Size Distributions and Water Pore Size Distribution

Particle size distributions (PSDs) are required for the uranium metal, uranium oxide, and non-uranium compounds for the alpha energy deposition calculation, as is the distribution of water pore sizes. Details are discussed in Section 9 below. Because the homogeneous medium approximation is used for beta and gamma energy deposition, only the ratio of the path length in particles to the path length in water is needed for these two calculations, and this depends only upon the water volume fraction.

4.0 Calculation

The bottom line of these approaches is summarized here for various sludge cases considered. Table 4-1 contains the power fraction to water calculated per the methods described in Sections 6, 7, and 8 for alpha, beta, and gamma radiation respectively, and the overall power fraction to water based the decay power fraction for each radiation type listed in Section 3.1. Here SB/MS = safety/modified safety basis, RB = reasonably bounding, N = nominal.

Table 4-1. Power Fraction to Water.

Sludge Type	Alpha	Beta	Gamma	Power-weighted total F_Q
SB/MS Canister	0.320	0.191	0.0253	0.205
RB Canister	0.320	0.191	0.0253	0.205
N Canister	0.324	0.241	0.0418	0.235
SB/MS Floor	0.325	0.311	0.0838	0.278
RB Floor	0.327	0.346	0.139	0.306
N Floor	0.325	0.359	0.184	0.319
60/40 SB/MS	0.324	0.248	0.0434	0.239
60/40 RB	0.324	0.261	0.0492	0.247
60/40 N	0.325	0.300	0.0762	0.271

Note that the alpha values are the result of 3 or more trials apiece, and are subject to some variation in the third decimal place. For practical purposes the alpha power fraction to water is slightly over 32% for all sludge types, but the minor variation among sludge types is consistent with that of beta and gamma radiation, i.e, the less the U content, the higher the water absorption fraction.

Using values developed above, the average g value, power fraction absorbed by water, and radiolytic production rate of hydrogen and oxidizing species are:

Sludge Type	Power Fraction to Water F_Q	Overall $g(H_2)$, molecule/100 eV	Hydrogen rate Q_{H2} L/hr per cubic meter sludge	Equivalent oxidizing species rate Q_{O2} L/hr per cubic meter sludge
SB/MS Canister	0.205	0.206	0.1321	0.0661
RB Canister	0.205	0.206	0.1321	0.0661
N Canister	0.235	0.222	0.0402	0.0201
SB/MS Floor	0.278	0.244	0.0456	0.0228
RB Floor	0.306	0.258	0.0193	9.6543e-3
N Floor	0.319	0.264	0.0069	3.4407e-3
60/40 SB/MS	0.239	0.224	0.0825	0.0413
60/40 RB	0.247	0.228	0.0687	0.0344
60/40 N	0.271	0.240	0.0213	0.0106

For the an LDC containing 2 m^3 of a 60/40 floor/canister mixture, the hydrogen production rate and equivalent oxidizing species rates in L/hr are:

Sludge Type	Q_{H2} L/hr, 2 m^3 sludge	Q_{O2} L/hr, 2 m^3 sludge
60/40 SB/MS	0.1650	0.0825
60/40 RB	0.1375	0.0687
60/40 N	0.0425	0.0213

5.0 Scaling and Sensitivity

Results scale directly with decay power which is obvious from the equation for hydrogen production. Scaling for uranium content, such as canister versus floor sludge, is deemed a second-order effect because of competing phenomena. Reducing the uranium content should reduce total power. However, reduced uranium content will lead to lower stopping power in the solids, and hence more absorption in water relative to the present for each radiation type.

Radiolysis results are influenced by factors that affect alpha deposition as identified in Section 6. Overall results are deemed most sensitive to actual $g(H_2)$ values, as discussed in Section 2: The current approach estimates dose to water, but presumes pure water $g(H_2)$ values when in fact some of the ions produced by radiolysis may effectively combine with the solid matrix to form uranium oxide hydrates. In an experiment, this would change the inferred $g(H_2)$ value.

6.0 Alpha Power Deposition by Monte Carlo Technique

Alpha particles have a relatively short range, on the order of tens of microns as will be seen, but this length scale is comparable to the size of sludge particles and interstitial water gaps. Thus a calculation of alpha energy deposition can only really be done via a detailed numerical method. A Monte Carlo technique is described here which relies upon the continuous slowing down approximation, valid for alphas, and the so-called detour factor to consider changes in direction during scattering.

As mentioned above, the NIST ASTAR database and program provided the source of fundamental data for this work. Data were obtained for O, Si, U, and liquid water, and these were used to construct data for UO_2 and SiO_2 as surrogates for particle solids. The fundamental piece of data is a table of stopping power S (Mev cm^2/g) defined as $S = -(1/\rho)\ dE/dx$ as a function of energy. The range R (g/ cm^2) of a particle in a substance is given by the integral

$$R(T) \;=\; \int_0^T -\left(\frac{1}{\rho}\frac{dE}{dx}\right)^{-1} dE$$

where T is the initial particle energy in MeV, and the linear range L is simply $L = R/\rho$. Since scattering causes deviation from a straight path, the actual distance an alpha penetates a medium is less than L. The ratio of the actual range to the value of R given above is known as the detour factor, denoted here as D, and it has been calculated and tabulated in the ASTAR database. Selected ASTAR data for liquid water and uranium are given in Tables 1 and 2.

Table 1. Selected ASTAR data for liquid water.

Kinetic Energy MeV	Electron. Stp. Pow. MeV cm2/g	Nuclear Stp. Pow. MeV cm2/g	Total Stp. Pow. MeV cm2/g	CSDA Range g/cm2	Projected Range g/cm2	Detour Factor
2.500E-01	1.743E+03	9.253E+00	1.752E+03	2.450E-04	2.238E-04	0.9135
5.000E-01	2.178E+03	5.214E+00	2.184E+03	3.699E-04	3.478E-04	0.9402
1.000E+00	2.190E+03	2.898E+00	2.193E+03	5.931E-04	5.702E-04	0.9615
2.000E+00	1.624E+03	1.594E+00	1.625E+03	1.123E-03	1.099E-03	0.9789
3.000E+00	1.255E+03	1.119E+00	1.257E+03	1.829E-03	1.804E-03	0.9867
4.000E+00	1.034E+03	8.686E-01	1.035E+03	2.711E-03	2.686E-03	0.9907
5.000E+00	8.848E+02	7.132E-01	8.855E+02	3.759E-03	3.733E-03	0.9931

Table 2. Selected ASTAR data for uranium.

Kinetic Energy MeV	Electron. Stp. Pow. MeV cm2/g	Nuclear Stp. Pow. MeV cm2/g	Total Stp. Pow. MeV cm2/g	CSDA Range g/cm2	Projected Range g/cm2	Detour Factor
2.500E-01	3.148E+02	1.903E+00	3.167E+02	1.662E-03	8.134E-04	0.4894
5.000E-01	4.190E+02	1.220E+00	4.202E+02	2.331E-03	1.390E-03	0.5966
1.000E+00	4.454E+02	7.456E-01	4.461E+02	3.453E-03	2.431E-03	0.7041
2.000E+00	3.396E+02	4.402E-01	3.400E+02	6.021E-03	4.897E-03	0.8133

```
3.000E+00 2.767E+02 3.196E-01 2.770E+02 9.310E-03 8.092E-03 0.8692
4.000E+00 2.417E+02 2.535E-01 2.420E+02 1.319E-02 1.188E-02 0.9007
5.000E+00 2.186E+02 2.113E-01 2.188E+02 1.755E-02 1.614E-02 0.9200
```

Alpha particle initial energies important to this work are: U-238, 4.2 MeV, U-235, 4.4 MeV, Pu-239, 5.15 MeV, and Am-241, 5.46 MeV. Since most of the alpha activity is due to the latter two, an average energy of 5.25 MeV is used for this work. Variation of this value in the range near 5 MeV does not change results for the fraction of energy absorbed by water, therefore, the alpha energy does not need to be selected randomly in the Monte Carlo process and an average suffices.

Stopping power, range, and detour factor data for alpha particles in the four material types (uranium metal, uranium oxide as a surrogate for all uranium oxides, silicon dioxide as a surrogate for all non-uranium material, and water) are shown in Figures 1a to 1c. Note that the detour factor is only important for alpha energies less than 1 MeV in sludge solids; when it is neglected, overall results for alpha absorption in water only change by a few percent. Figure 2 provides the linear range in sludge particles using the densities stated in SNF-7765 and Section 8 below. The range in water is slightly more than twice that in uranium oxide surrogate: About 37 microns at 5 MeV in water and 17 microns in uranium oxide surrogate.

An alpha particle of energy T_0 will be absorbed if the thickness Δs of the medium is greater than or equal to $D(T_0)L(T_0)$. If the thickness Δs is less than this value, the alpha particle will emerge from the medium with a reduced energy T_1 given by

$$\Delta s/\rho \;=\; D(T_0)R(T_0) \;-\; D(T_1)R(T_1)$$

and since T_1 is the upper value of the integral for $R(T_1)$ its value must be found numerically. Figure 3 provides the remaining alpha energy as a function of distance traveled through sludge particles and water, respectively, using an initial energy of 5.25 MeV. These figures may be used to illustrate the fate of an alpha particle, as follows:

Suppose a 5.25 alpha particle travels 9.5 microns through its sludge particle of origin, a uranium oxide particle, before entering water. It therefore departs this particle with 3 MeV remaining energy, and it has deposited 2.25 MeV in the solid (the solid curve of the upper figure shows 3 MeV remaining at about 9.5 microns) The alpha enters the water with an energy corresponding to 22 microns of passage through pure water (the solid curve of the lower figure shows at 22 microns the remaining alpha energy is 3 MeV). Suppose it crosses 10 microns of water; it therefore departs the water with an energy of about 1.6 Mev, having deposited 1.4 MeV in the water (at 32 microns range the remaining energy is 1.6 MeV). An alpha particle of 1.6 MeV energy has a remaining range of only about 2 microns in U metal (the range for 1.6 MeV in metal is 7 microns and remaining energy is 0 at 9 microns), a remaining range of about 4 microns in U oxide (1.6 MeV, 13.5 microns, and 0 MeV, 17.5 microns), and a remaining range of about 5 microns in non-uranium (1.6 MeV, 22 microns, 0 MeV, 27 microns). So, if the alpha particle encounters a sludge particle greater than the given sizes, it has a good chance of being completely absorbed, depending upon its angle of incidence. Supposing this is the case, the total energy absorbed by solids is 2.25 + 1.6 = 3.85 MeV and the fraction deposited is 3.85/5.25 = 73%; the fraction absorbed by water is 1.4/5.25 = 27%.

A Monte Carlo simulation using the data described above is carried out as follows:

1.0 An alpha particle interacts in its "birth" solid particle:

1.1 The metal or oxide birth particle is chosen randomly using the relative volume fractions of metal and oxide to weight the choice from a uniform pdf.
1.2 A random particle size is selected from the appropriate PSD, see Section 10.
1.3 A random location of alpha particle birth is found. This distribution is uniform throughout the volume, therefore, radius of birth goes as volume fraction to the 1/3 power -- the majority of particles are born nearer the surface. So, a random volume fraction is selected from the range 0 to 1, and its value to the 1/3 power yields the radius fraction of birth.
1.4 A random direction of alpha flight is selected from a uniform pdf for the angle from 0 to 180 degrees.
1.5 The distance the alpha travels in particle is obtained from law of cosines given the birth radius and particle radius:

$$\Delta s(r,d,\theta) = d\cos(\pi-\theta)+\sqrt{r^2-d^2\left(1-\cos^2(\pi-\theta)\right)}$$

1.6 Energy loss in the solid is obtained using the relationship between range, detour factor, and Δs, Figure 3, when the distance is less than the total range of a 5.25 MeV alpha. Metal or oxide properties are used as determined from step 1.1. If the distance exceeds the range, the alpha is absorbed in its particle of origin, else the remaining energy is passed on to the water.

2.0 An alpha particle interacts with water.

2.1 A next particle type to possibly interact with, if the alpha passes through water, is chosen by using the volume fractions of metal, oxide, and non-uranium to weight the choice from a uniform pdf.
2.2 The particle size of a next particle to interact with, if the alpha passes through water, is chosen from the PSD appropriate to the particle type just chosen.
2.3 The average path length through water from the source solid particle (the sludge particle from which the alpha particle emerges into water) to the next particle is given by $\lambda = \pi/4\left(d_1+d_2\right)\beta$ where d_1 and d_{12} are the particle diameters and β is the function of water volume fraction in Section 10.
2.4 Energy loss in the water is obtained using same method as for a particle, but with water data. Energy remaining, if any, is passed on to the next particle.

3.0 An alpha particle interacts with a new solid particle.

3.1 The next particle size used to evaluate the interaction with water is retained.
3.2 A random angle of entry is selected from 0 to 90 degrees.
3.3 The distance traveled is found via law of cosines:

$$\Delta s(r,\theta) \;=\; r\sqrt{2\left(1-\cos(\pi-2\theta)\right)}$$

3.4 Energy loss in the solid is obtained as before.

4.0 Steps 2 and 3 are repeated as required until complete absorption.

Steps described above are followed for a large number of alphas. For each alpha, the amount of energy deposited in solids and in water are tracked and the number of absorption steps is tracked. Also, to help interpret results, total energy absorbed during each absorption step is summed and then averaged. Note that the first absorber is always the birth solid particle, and that the second, fourth, sixth, etc. even-numbered absorbers are water, and that remaining odd-numbered absorbers are solid particles.

The bottom line result of the evaluation is that just over 32% of alpha energy is absorbed by water, and the result is rather insensitive to sludge type. There is slight variation in energy absorption fraction by water: it increases slightly as uranium content decreases. Section 4 summarizes numerical results.

Detailed results are shown in Figures 4 and 5 for reasonably bounding sludge to explain the overall results. Figure 4 shows the average energy absorbed in each absorption step, and Figure 5 shows the frequency for a given total number of absorbers. Again, an odd numbered absorber is a solid particle, and an even numbered absorber is water. Just under 60% of alpha energy is deposited in the birth particle (Fig. 4, absorber 1) and about 50% of the time all the alpha energy is absorbed in the birth particle (Fig. 5, 1 absorber). Just under 25% of alpha energy is absorbed in the first passage through water (Fig. 4, absorber 2) and about 25% of the time this is the final absorption step (Fig. 5, 2 absorbers). About 6% of the energy is deposited in the 3rd and 4th absorbers each, so that 4 absorption steps account for almost 97% of the alpha energy. About 8% of the alphas stop in absorber 3 and about 9% make it to absorber 4, so that 92% of the alphas are stopped in up to four absorption steps.

Alpha absorption results are influenced by:

- Particle size distribution. Reasonable variation in the PSD will not influence the fact that the largest particles absorb most alpha energy but there are many small particles that cannot completely stop a single alpha particle.
- Distance traveled through water. The distance through water is directly related to particle sizes as shown in Section 10. Therefore, this is not an independent selection, it is directly related to the PSD.
- Particle composition. This is a second-order effect as shown by results for the various sludge types. This furthermore means that selection of silicon dioxide as a non-uranium surrogate does not influence results.
- Alpha energy. Experience with the model indicates that results are unchanged for reasonable variation in alpha source energy among the various isotopes.

7.0 Beta Power Deposition by Homogeneous Approximation

Beta particles have a relatively long range compared to the majority of particle sizes as will be shown. Therefore, it is appropriate to use a homogeneous medium approach to estimate their absorption. Beta energy loss with distance in a medium is used to define the stopping power mentioned above in Section 6. The differential energy loss using the continuous slowing down approximation is

$$dE = -\rho\, S(E)\, dx$$

and when an beta particle travels through a composite matrix, if a fraction of the distance ϕ is spent in each material, there follows:

$$dE = -\sum \rho_i\, S_i(E)\, \phi_i\, dx$$

Therefore, at any energy E, the fraction of energy absorbed by water is simply

$$f_{q\beta} = \frac{\rho_w\, S_w(E)\, \phi_w}{\sum \rho_i\, S_i(E)\, \phi_i}$$

The average value is the integral of this fraction over all energies. The distance fractions may be algebraically replaced by the average distances through each medium derived in Section 10.

Figure 6 shows the electron range, microns, for the surrogate materials, and Figure 7 shows the electron range, microns, for solid particles with an average composition defined by the various sludge compositions investigated here. It is evident that while stopping power is a strong function of energy, the ratio of water to particle stopping power does not vary appreciably over the energy range of interest. Also from Figures 6 and 7, it is clear that the homogeneous approximation for beta energy absorption breaks down for particles near 1000 microns in size, but it is excellent for particles less than 100 microns in size. In particular, the approximation is not very good for metal particles alone, but they constitute such a small volume fraction that as a composite the homogeneous approximation is valid.

Results of the evaluation are shown in the table in Section 4 for various sludge types. Figures 8a and 8b show the sensitivity of results to beta energy and water volume fraction for reasonably bounding sludge. In the range from 65% to 75% water, the beta energy fraction to water varies from about 21% to 26%.

8.0 Gamma Power Deposition by Homogeneous Approximation

Gamma rays have a long range compared to sludge particles, and the homogeneous approximation is valid for all sludge particle sizes and compositions as shown by the derived data for the attenuation coefficeint μ, cm^{-1}, for the surrogate compositions, Figure 9. However, unlike the case for beta radiation, relative gamma absorption in uranium increases significantly compared to that of water as gamma energy decreases (due to the photoelectric effect). The continuous slowing down energy loss formula for gamma radiation is:

$$dE = -\rho \left[\frac{\mu}{\rho}\bigg|_{en} (E) \right] E\, dx$$

where the fundamental data for (μ/ρ) are a function of energy. When the fraction of energy deposited in water is found, the energy cancels and

$$f_{q\gamma} = \frac{\rho_w \left[(\mu/\rho)_{en,w} (E) \right] \phi_w}{\sum \rho_i \left[(\mu/\rho)_{en,i} (E) \right] \phi_i}$$

Results of the evaluation are given in the table in Section 4. Figures 10a and 10b show the sensitivity of results to gamma energy and water volume fraction for reasonably bounding sludge

9.0 Sludge Composition Background and Values for Radiolysis

9.1 Reference Definitions

Definitions and relationships between parameters used to describe sludge composition and density are given in SNF-7765 Appendix C.1, and some are mentioned here for convenience to explicitly show how they are used to calculate radiolysis.

There are four Sludge Databook (TI-015/2) density and composition parameters:

ρ_{wet}	Wet sludge density, g/cc,
α	Water volume fraction (also called void fraction), cc water /cc wet sludge,
C_U	Total uranium concentration, g U / cc wet sludge, and
C_{Umet}	Uranium metal concentration, g U metal / cc wet sludge

In addition to these parameters, a complete and self-consistent description of K East sludge composition is based upon two simplifying assumptions:

1. Sludge can be idealized as a mixture of three components: Uranium metal, uranium oxide, and non-uranium. True material densities must be assigned to these components.
2. The uranium oxide component represents an average oxidation state higher than that of UO_2 and it includes hydrate compounds such as schoepite $UO_3.2H_2O$. An average molecular weight must be assigned to the uranium oxide component reflecting the range of oxidation and hydration.

Implementing these assumptions, the following densities are assigned in SNF-7765:

ρ_m = 19 g/cc,
ρ_o = 7.5 g/cc (partial hydration),
ρ_{nu} = to be derived based on other sludge properties, and
ρ_w = 1 g/cc

where subscripts indicate uranium metal (m), uranium oxide (o), non-uranium compounds (nu), and water (w). The uranium oxide component is an equimolar mixture of UO_2, $UO_{2.25}$, and $UO_3.2H_2O$, with a formula weight $FW_O = 288.6$. The ratio of the oxide to metal formula weight is designed $r = FW_O / 238 = 1.213$ given this choice.

It is important to note that the non-uranium material density is uniquely defined by the basic sludge input parameters, with no guarantee that it is physically realistic unless the parameters were chosen to ensure this fact. This is the case for values selected in SNF-7765.

Stream definitions for this work are defined in terms of constant values for the water volume fraction (α=0.75) and the assumed oxide stoichiometry ($FW_O = 288.6$), but with potential variation in the uranium metal and total uranium content. Therefore, there is only one independent variable left to choose for a stream: Either the wet density or the non-uranium material density. It is consistent to choose to preserve the non-uranium material density given by SNF-7765 for the canister and floor sludge streams. Then, any variation on U metal and total U content unambiguously implies a variation in total density for the canister and floor sludge streams, and for any mixture of canister and floor sludge. Wet sludge density given defined values for all other stream parameters is:

$$\begin{aligned}\rho_{wet} &= \rho_w\alpha + C_{Umet} + C_O + C_{nu} \\ C_O &= r\left(C_U - C_{Umet}\right) \\ C_{nu} &= \rho_{nu}\left[1-\alpha-C_{Umet}/\rho_m - C_O/\rho_o\right]\end{aligned}$$

where C_O is the uranium oxide concentration and C_{nu} is the non-uranium concentration, and the non-uranium material density is ρ_{nu}.

A priori, the wet density of a mixture of floor and canister sludge is found by volume weighting the densities of the floor and canister sludge streams. The equation for wet sludge density indicates also that the component concentrations (U metal, total U, and non-U) may also be volume weighted. However, it is important to note that the average non-uranium material density is not a constant for a combined stream. The non-uranium material density is different for canister and floor sludge streams because it is a dependent variable defined by selection of the four parameters listed at the beginning of this discussion, plus the assumed uranium oxide formula weight and the metal and oxide material densities. The non-uranium material density for a mixed stream is simply an average value that may be derived.

9.2 Values for Radiolysis and LDC Gas Calculations

Specific dose rate is required by the uranium oxide oxidation rate law, and it is defined by the power deposited in water divided by the sludge density. The sludge density is defined for safety and design basis sludge in SNF-7765 but modified safety basis and nominal values of sludge density are required. These are "built up" from the definitions of canister and floor sludge streams at the reasonably bounding and nominal levels, then weighted to combine the two streams. The safety basis value of non-uranium material density is preserved for canister and floor sludge in order to derive the wet densities at the reasonably bounding and nominal levels in order to be consistent, since the only intended changes are in U metal and total U. The non-uranium densities for safety basis canister and floor sludge are, respectively, 2.1173 g/cc and 1.9172 g/cc, and these are used with values from Attachment 10 to define the reasonably bounding and nominal canister and floor sludge definitions (SB/MS = safety/modified safety basis; RB = reasonably bounding, N = nominal):

	Total Uranium g/cc	Uranium metal g/cc	Sludge density g/cc
SB/MS Canister	1.400	0.125	2.500
RB Canister	1.400	0.125	2.500
N Canister	0.770	0.0399	1.9502
SB/MS Floor	0.300	0.023	1.500
RB Floor	0.120	0.00917	1.3376
N Floor	0.060	0.004	1.2834

From these, the 60/40 stream parameters are derived:

	Total Uranium g/cc	Uranium metal g/cc	Sludge density g/cc	Non-U density g/cc
60/40 SB/MS	0.740	0.0638	1.900	1.9389
60/40 RB	0.632	0.0555	1.802	1.9366
60/40 N	0.344	0.01836	1.538	1.9700

Dry basis volume fractions for particle components are given by:

Volume Fraction in Particle	U Metal	U Oxide	Non-U
SB Canister	0.0263	0.8246	0.1491
RB Canister	0.0263	0.8246	0.1491
N Canister	0.0084	0.4722	0.5194
SB Floor	0.0048	0.1791	0.8160
RB Floor	0.0019	0.0717	0.9264
N Floor	0.000842	0.0362	0.9629
60/40 SB/MS	0.0134	0.4373	0.5493
60/40 RB	0.0117	0.3728	0.6155
60/40 N	0.0039	0.2106	0.7855

10.0 Sludge Particle Size Distributions and Water Pore Size

The PSD for uranium metal is taken to be uniform from 200 to 1000 microns diameter based upon SNF-7765 App. B. The key points of this work are that there is very little metal below 250 microns in size, and a "birth" or maximum size of about 1000 microns is consistent with observations. A uniform distribution is assumed because no details are available.

The PSD for uranium oxides is found by merging a fine-grain PSD from Attachment 5, Table 1 with an overall PSD from TI-040 Vol. 2 table 4-8 for KE canister sludge, and is shown in Fig. 11. The PSD from attachment 5 is for material below 300 microns diameter. The PSD from TI-040 goes up to 6250 microns and has 66% of the volume below 500 microns. So, cumulative values from Attachment 5 are multiplied by 0.66 to merge the distributions. The canister sludge PSD is representative of uranium oxides because of its high U content.

The PSD for non-uranium is taken from TI-040 Vol. 2 Table 4-8 for KE floor sludge and is shown in Fig. 12. This PSD is representative of non-uranium due to the its U content.

The distance that a radiation particle travels through a solid sludge particle is equal to the average chord length c for a sphere of diameter D, c = π/4 D. The distance that a radiation particle travels through water is found by associating a unit cell of water with each particle, so that the water volume fraction in the unit cell is 75%. For a spherical unit cell around a particle of diameter D, the average distance traveled through water is λ given by:

$$\lambda = \frac{\pi}{4}D\left[(1-\alpha)^{-1/3} - (1-\alpha)^{1/3}\right] = \frac{\pi}{4}D\beta$$

When D is the mean particle size, the resulting value of λ is the mean interparticle distance through water. For a given particle size D_p, the average distance traveled to all other particles is half the value associated with D_p plus half the value associated with the mean particle size. The probability distribution of water distances can be viewed as a joint probability of traveling from one particle to another, which is simply the product of the probabilities of the two particle sizes assuming that they are independent, times the associated chord length. Alternately, given a starting particle size, the probability of water distances can be viewed as the conditional probability of travel to another particle (simply the probability of selecting any particle diameter) times the associated chord length. For the given water volume fraction of 75%, the term in brackets above is 0.9574, coincidentally nearly unity, and the product of this value and π/4 is 0.752 or very nearly 75%.

11.0 References

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Fig. 1a. Stopping power for alpha particles in solid particles and water.

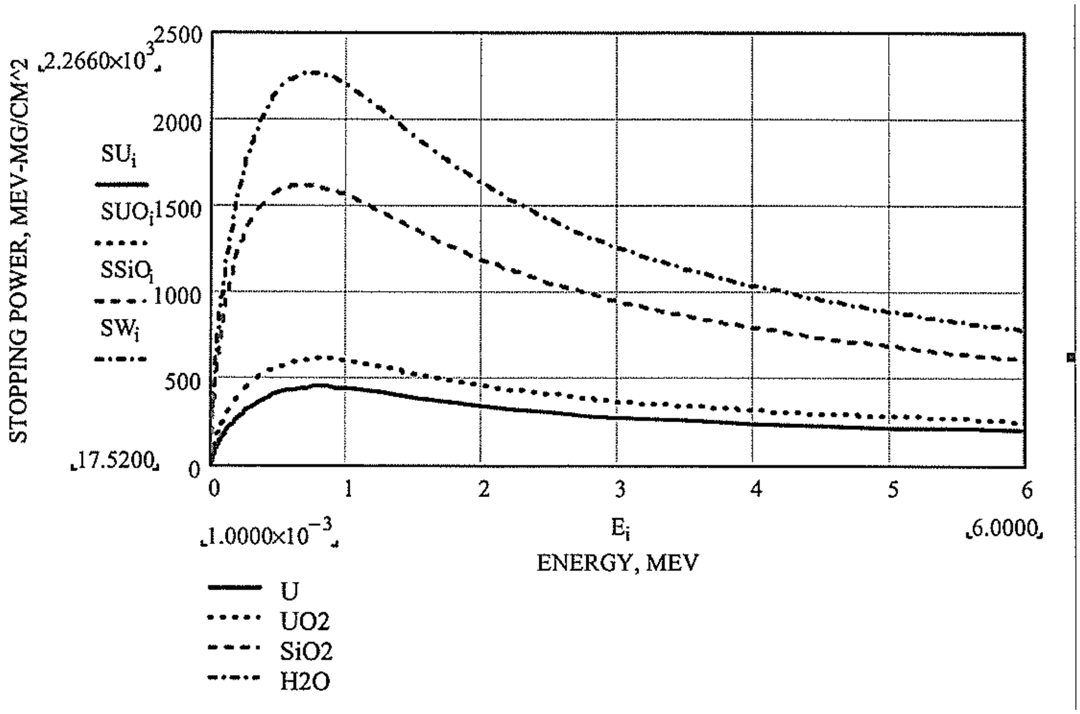


Fig. 1b. Range for alpha particles in solid particles and water.

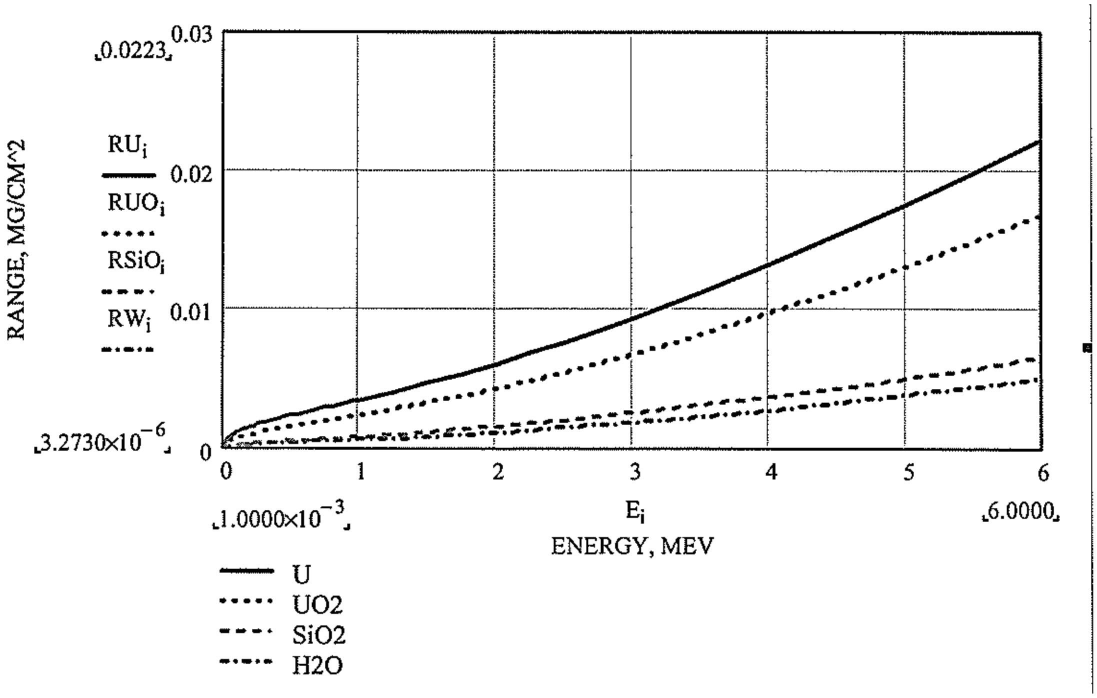


Fig. 1c. Detour factor for alpha particles in solid particles and water.

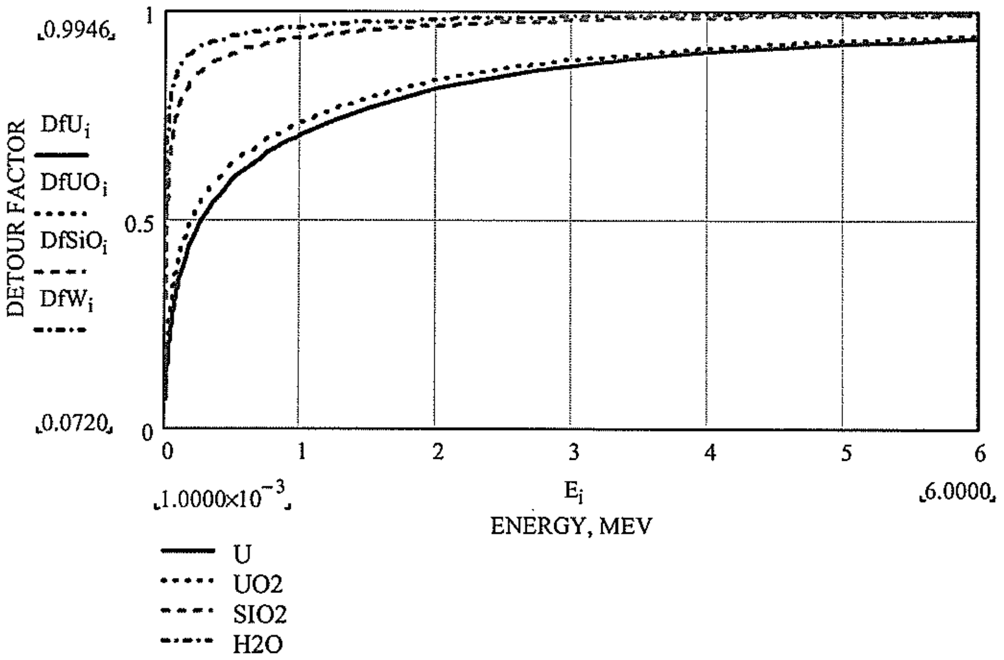


Fig. 2. Linear ranges, micron, as function of alpha energy, MeV, using SNF-7765 material densities and SiO2 surrogate for non-uranium. Densities are: U, 19 g/cc, UOx, 7.5 g/cc, non-uranium, 1.90 g/cc, and water, 1.0 g/cc.

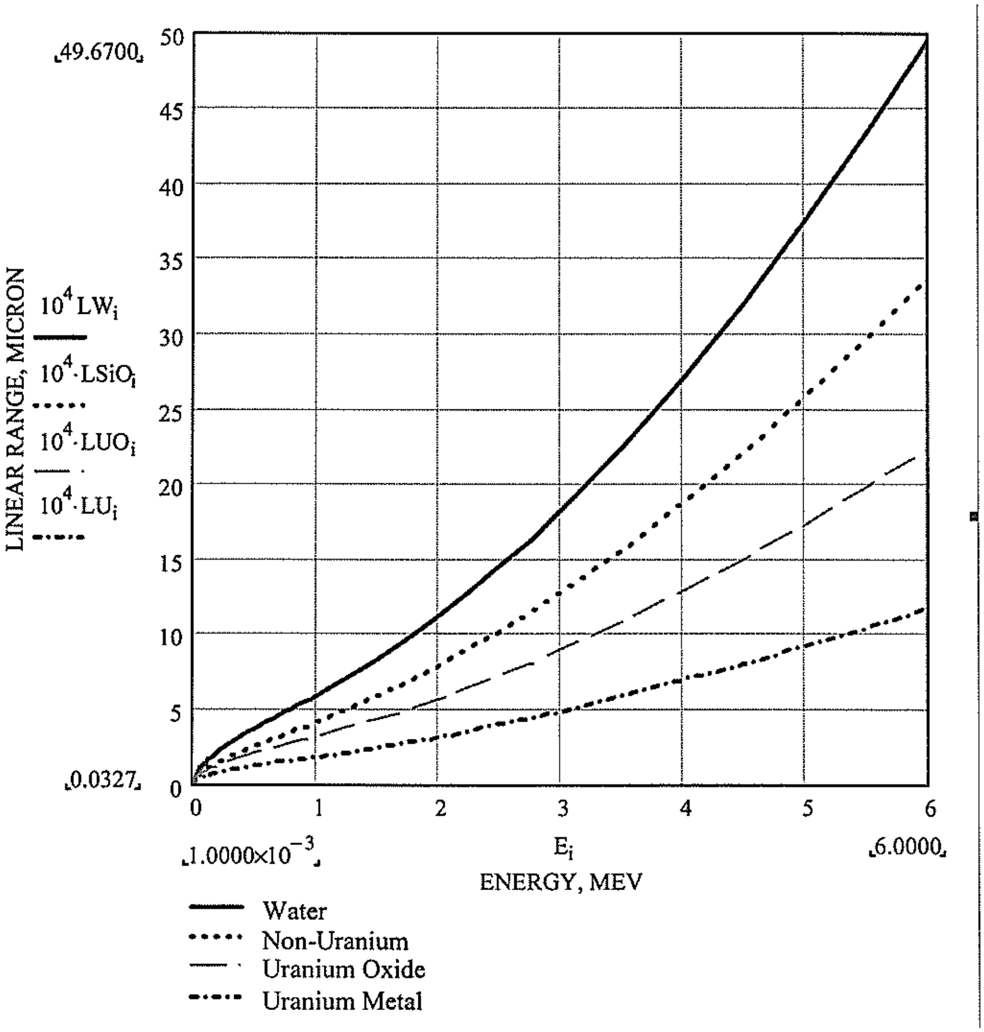
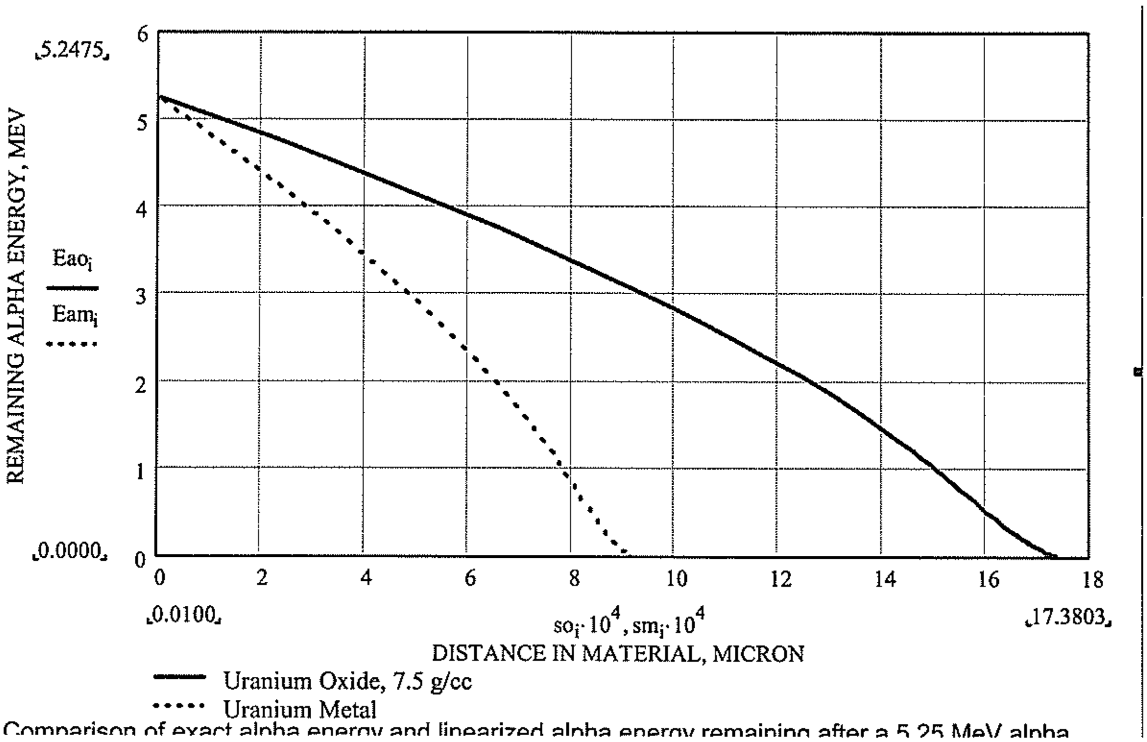


Fig. 3a,b. Remaining alpha energy, MeV, after a 5.25 MeV alpha travels a given distance, micron, through the indicated material, including the detour factor.



Comparison of exact alpha energy and linearized alpha energy remaining after a 5.25 MeV alpha

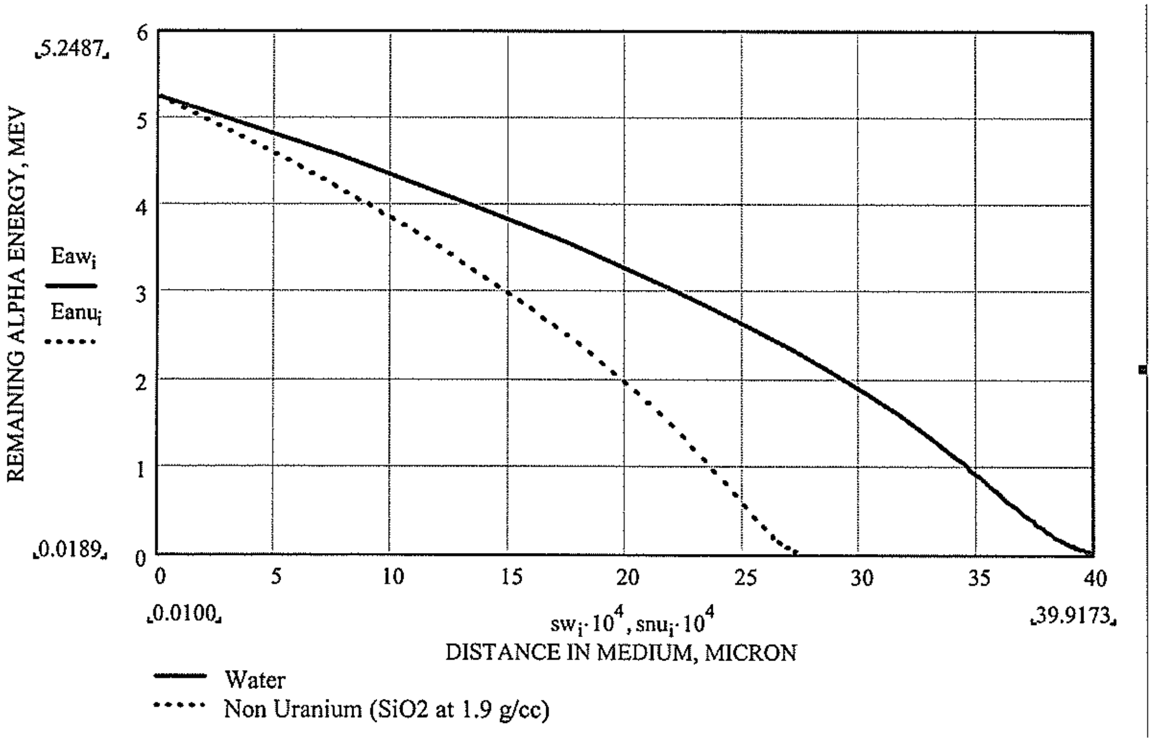


Fig. 4. Alpha energy fraction absorbed by successive absorbers for reasonably bounding sludge, 1 = particle of birth, 2 = water, 3 = next particle, 4 = water, etc.

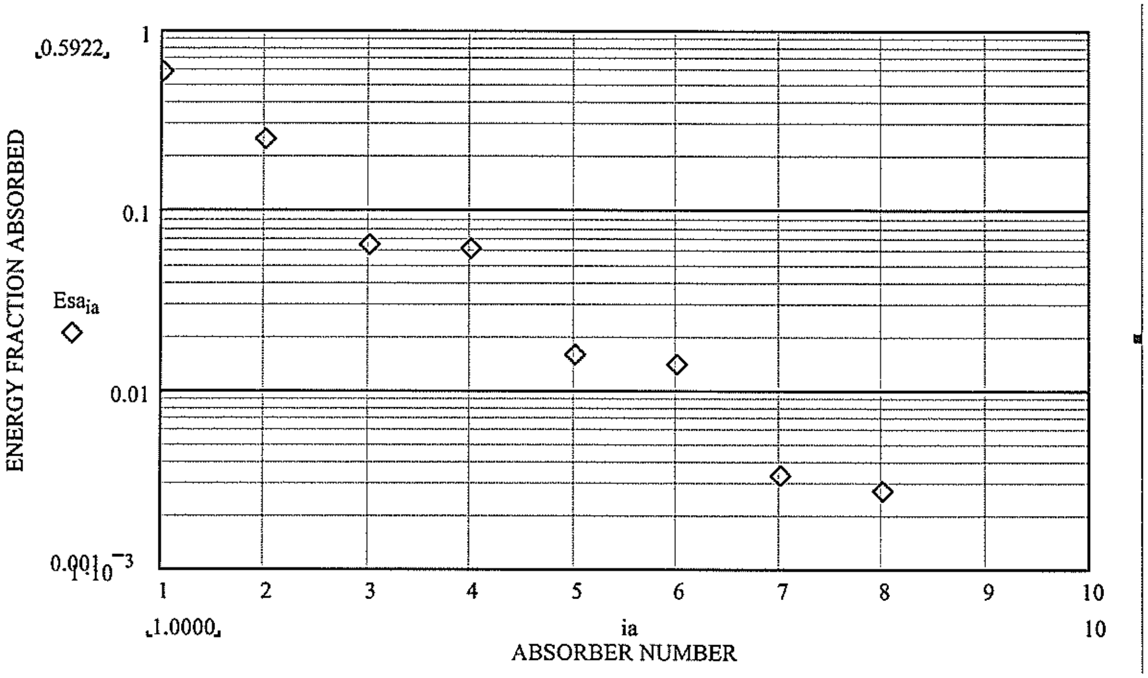


Fig. 5. Frequency of total number of absorbers for reasonably bounding sludge, 1 = particle of birth, 2 = water, 3 = next particle, 4 = water, etc.

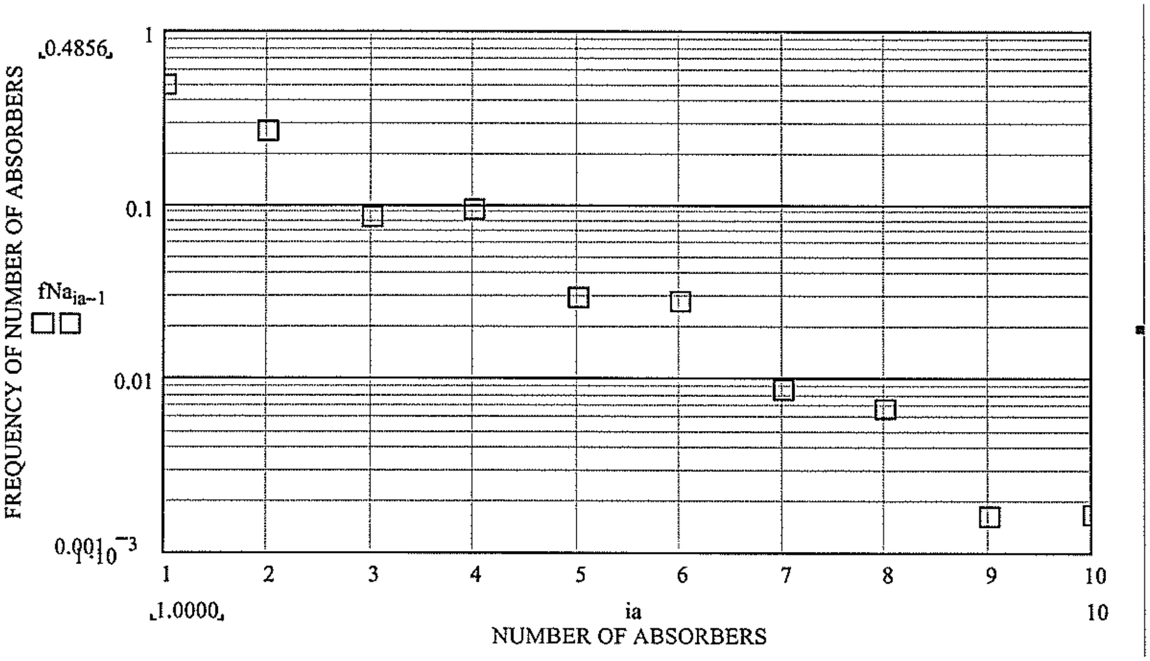


Fig. 6. Electron range, micron, in indicated materials.

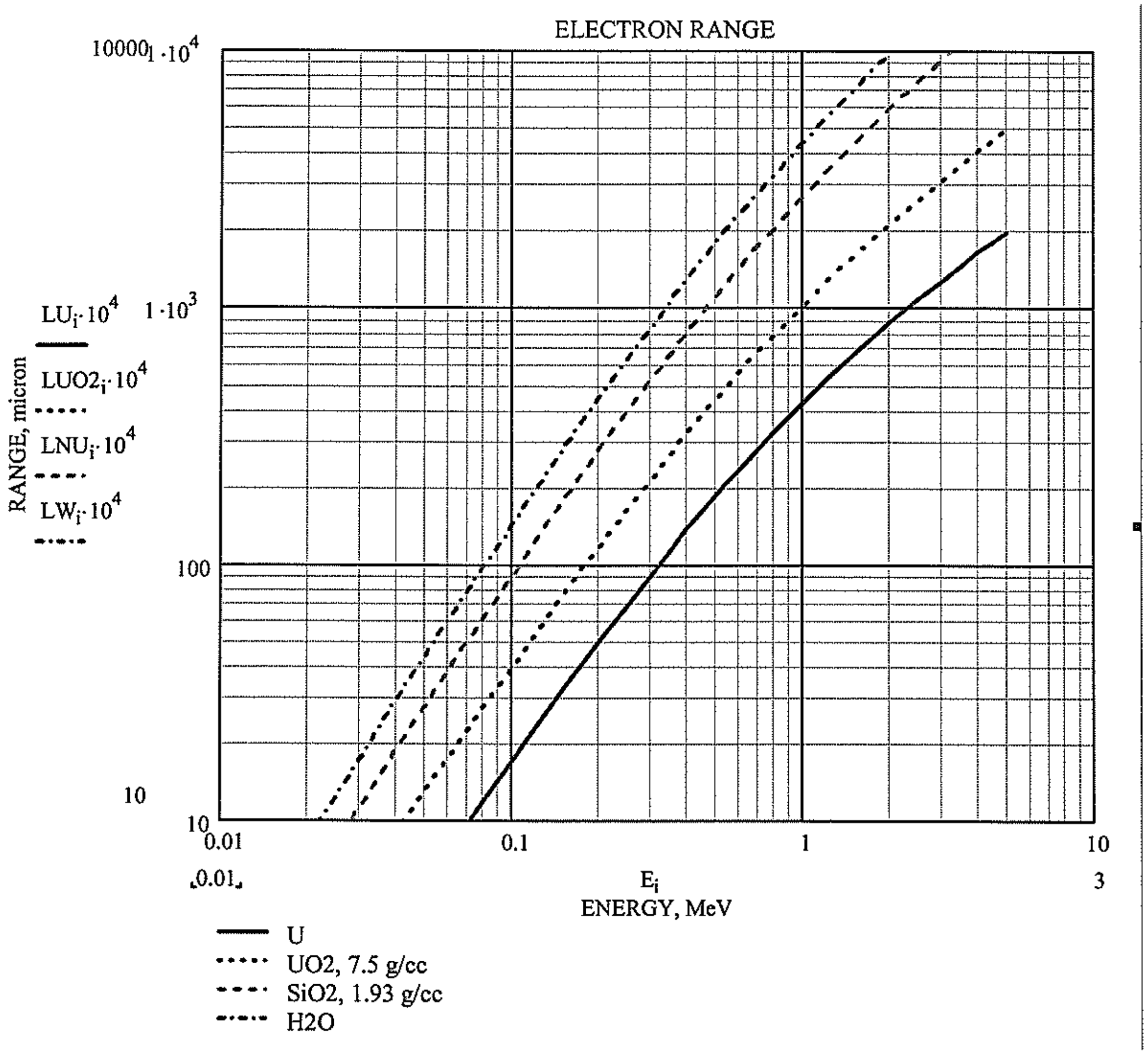
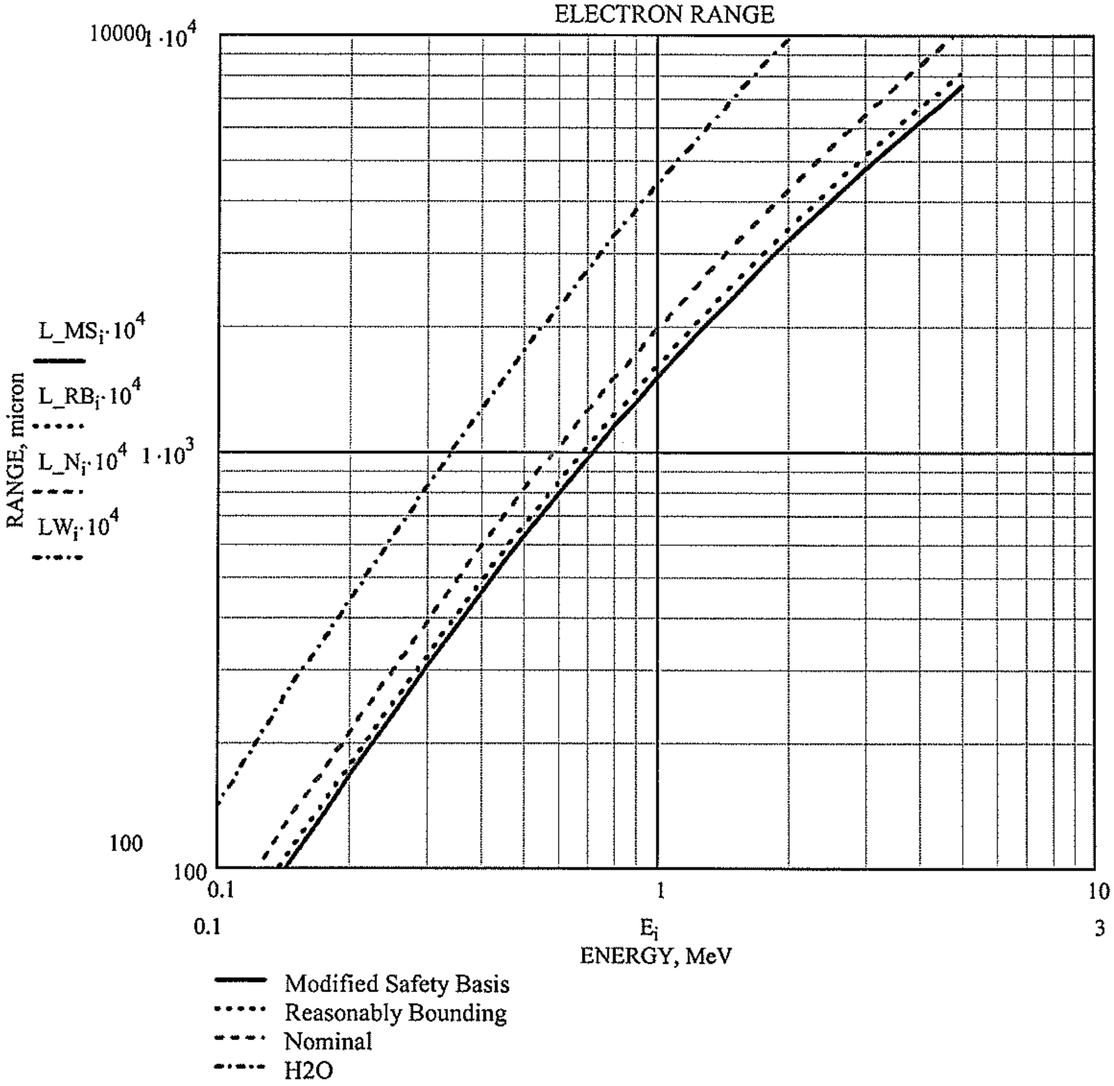


Fig. 7. Electron range, micron, in homogeneous sludge particles and water.



Figs. 8a,b. Sensitivity of beta energy deposition to beta energy (top) and water fraction (bottom).

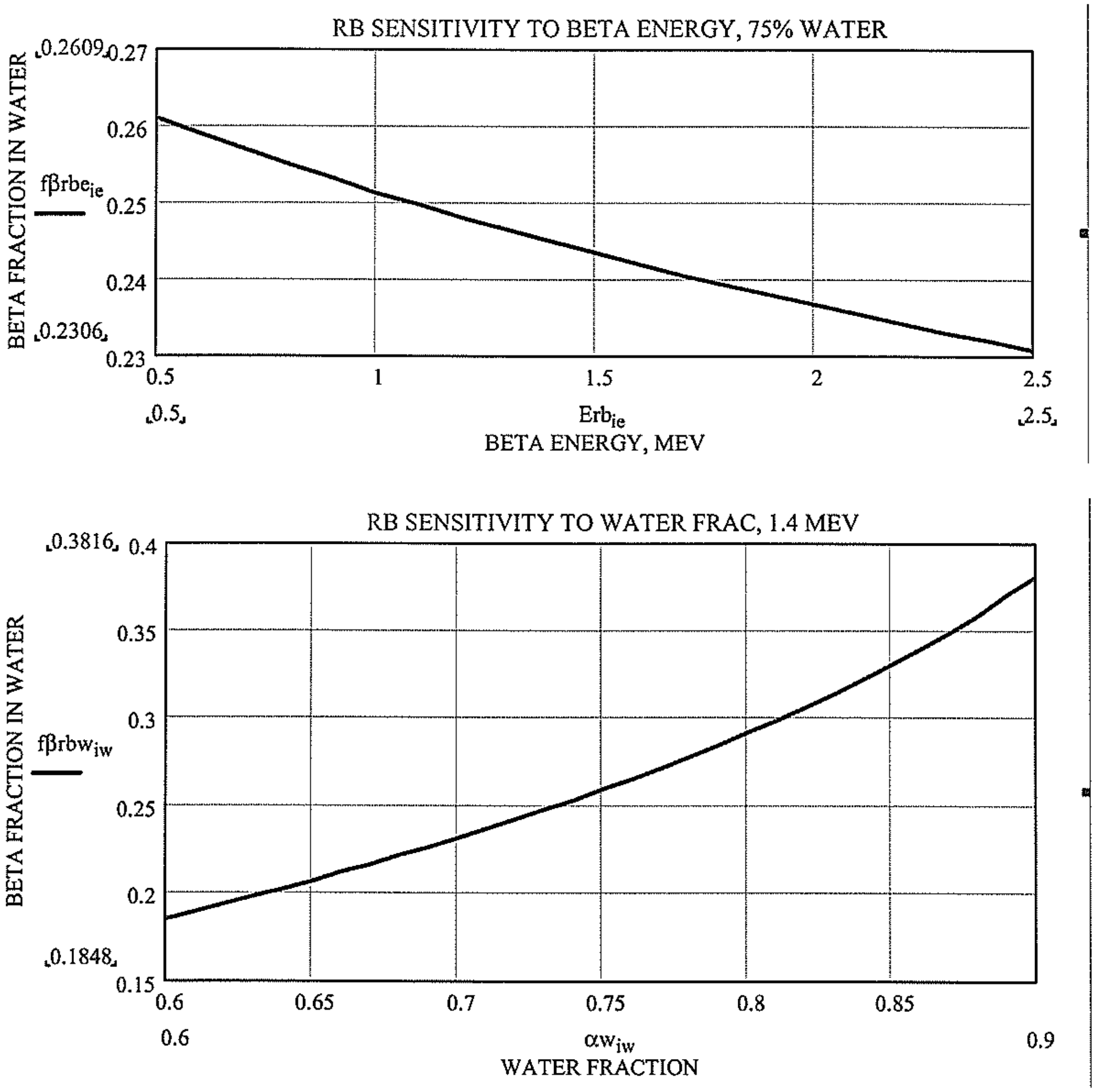
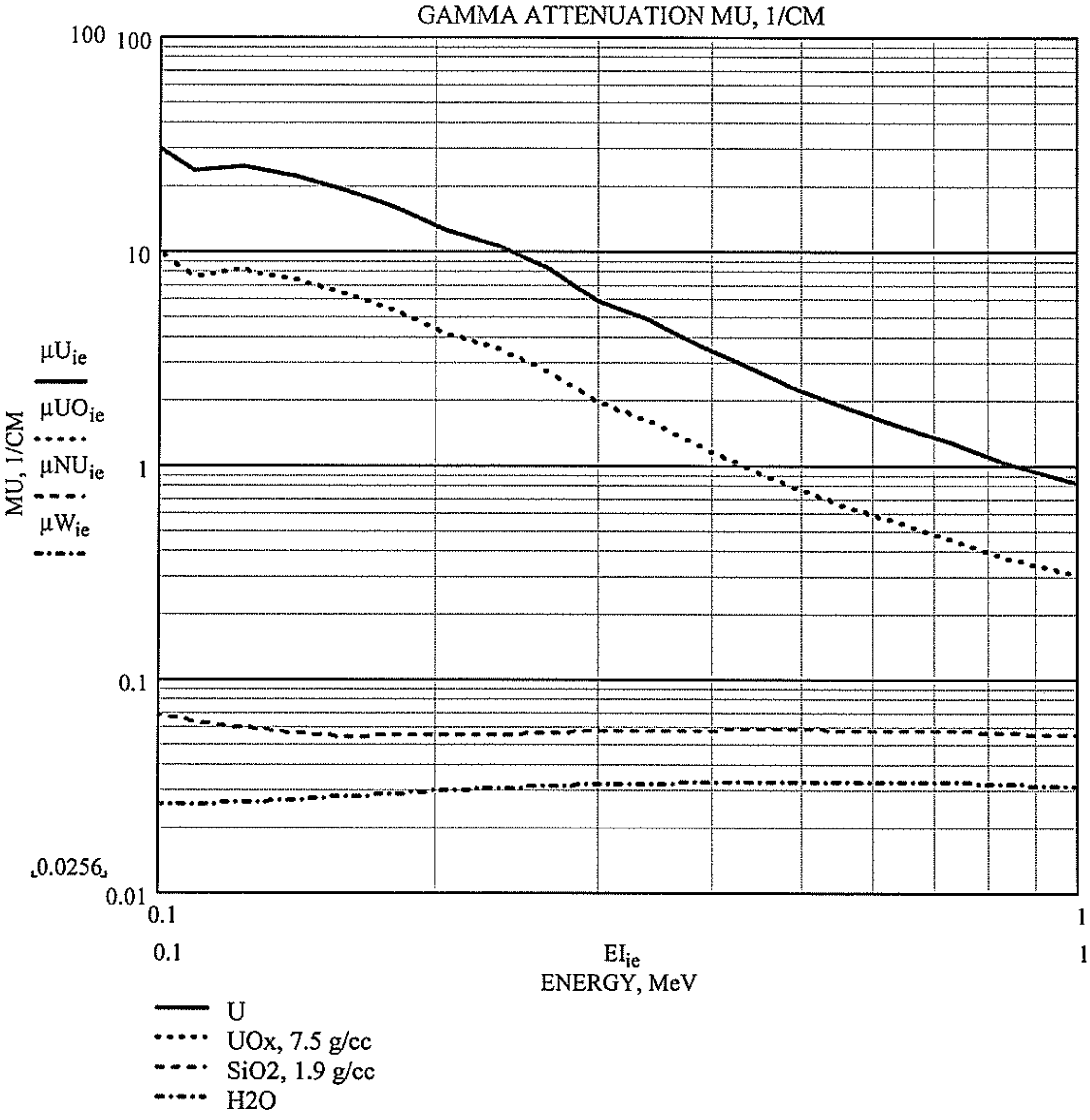


Fig. 9. Gamma attenuation μ cm^{-1}, for indicated materials as a function of energy, MeV.



Figs. 10a,b. Sensitivity of gamma energy deposition to gamma energy (top) and water fraction (bottom).

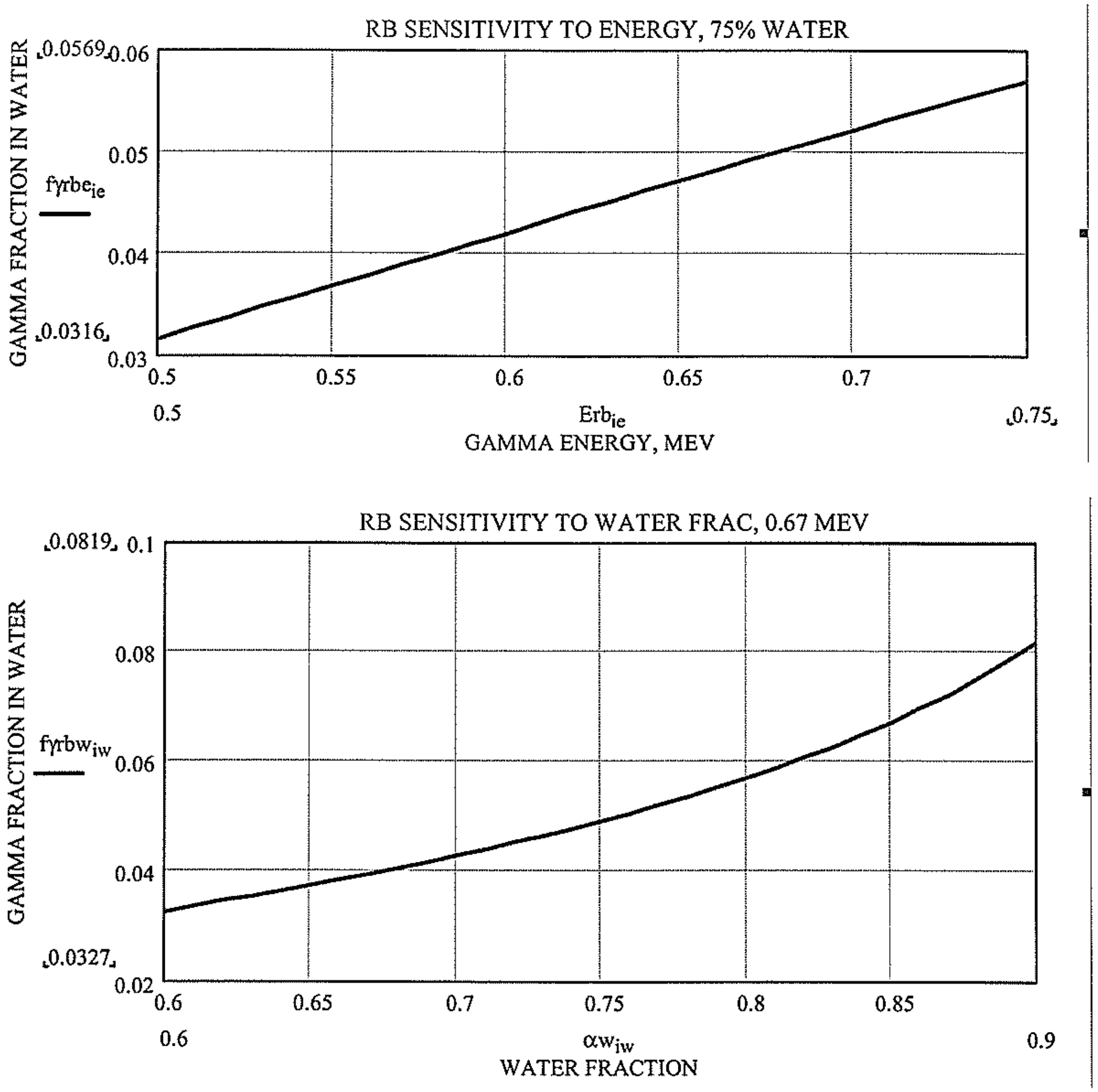


Fig. 11. Particle size distribution for uranium oxides, merging Att. 5 data below 300 microns with TI-015, Vol. 2, KE Canister data for 500 microns and above.

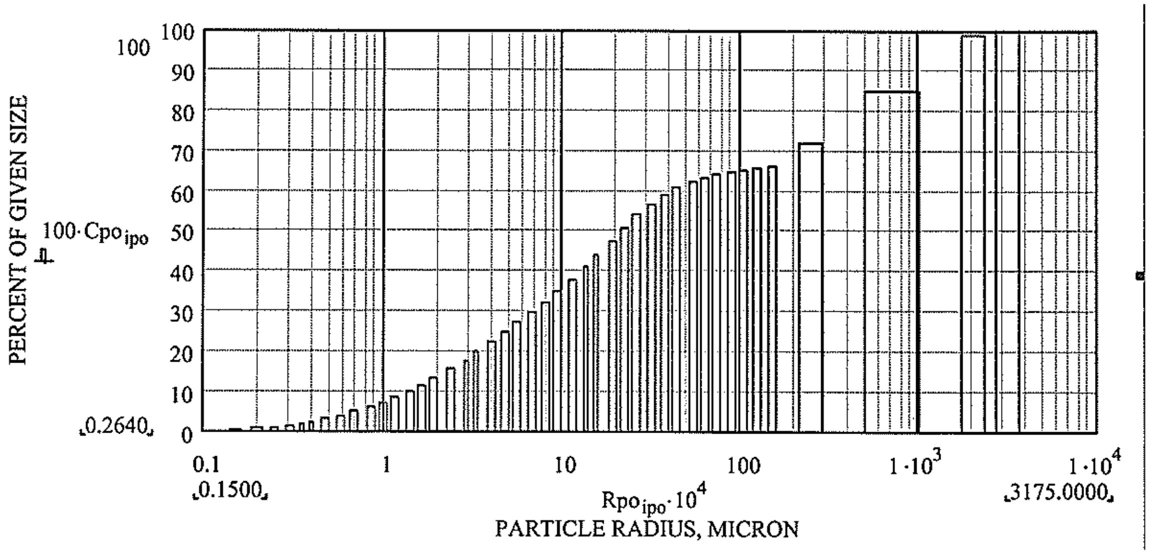
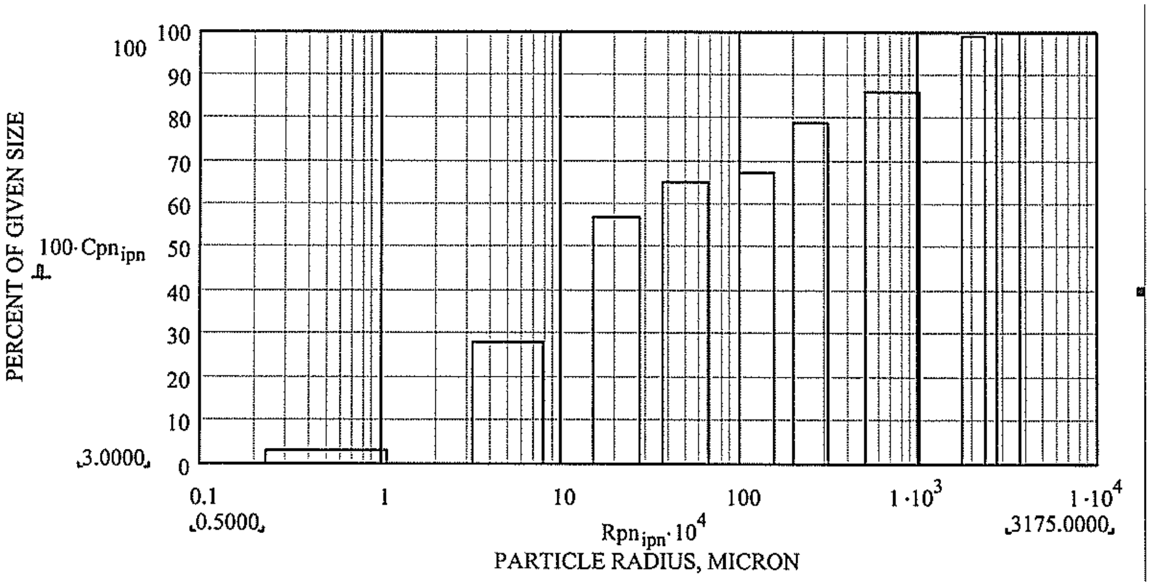


Fig. 12. Particle size distribution for non-uranium, using KE Floor sludge from TI-015, Vol. 2, Table 4-8.



Attachment 9

Justification for Lowering the Uranium-Water Reaction Rate Enhancement Factor (Multiplier) from 3 to 1

A. J. Schmidt
Senior Engineer
Pacific Northwest National Laboratory

Uranium Metal Reaction Enhancement Factor

The safety basis rate enhancement factor for the uranium metal reaction in water

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

is 3 for uranium metal in sludge according to the SNF project (SNF Project Sludge Technical Databook, Volume 2; Plys and Pearce 2001). While Appendix A of HNF-7765, Rev. 1 concludes that an enhancement factor of 1.0 is appropriate for design based on the sludge data (based on Delegard et. al. 2000), a safety basis value of 3.0 was selected because it represents approximately the 97.5% upper limit of observed reaction rate data in the literature. Recent corrosion testing work performed with crushed irradiated N Reactor fuel having known particle size distributions (Schmidt et al. 2003) provides assurance that the rate enhancement factor of 3 is overly conservative.

The baseline SNF reaction equation (Reilly 1998) for uranium metal corrosion in oxygen-free water:

$$\log \text{rate}\left(\text{U weight loss, mg/cm}^2 \cdot \text{hr}\right) = 8.505 - \frac{3016}{T}$$

is stated in units of $mg/cm^2 \cdot hr$ (i.e., the rate is proportional to the uranium metal surface area). Because the rate is proportional to the metal surface area, the enhancement factor can be determined as the ratio between the apparent uranium metal surface area (i.e., the uranium metal surface area needed to provide the experimentally observed gas generation rate assuming the uranium metal reacted according to the SNF rate equation) to the actual (measured) metal reaction surface area.

The equation for the enhancement factor based on the surface area ratios is shown immediately below. It is seen in the subsequent equation that the enhancement factor is proportional to the ratio of the actual to the theoretical particle radii (or diameters).

$$\text{Enhancement factor} = \frac{\text{Surface area (theoretical) / Unit mass}}{\text{Surface area (actual) / Unit mass}}$$

$$\text{Enhancement factor} = \frac{4\pi r_{theo.}^2 \,/\, \frac{4}{3}\pi r_{theo.}^3 \rho}{4\pi r_{act.}^2 \,/\, \frac{4}{3}\pi r_{act.}^3 \rho} = \frac{r_{act.}}{r_{theo.}}$$

The actual and theoretical particle radii were measured for eleven experiments performed with uranium metal fuel particles of varying initial size, at temperatures ranging from ~28 to 95°C, with and without overlying sludge burden. The theoretical and actual uranium metal particle sizes were derived for test intervals (each of the 11 tests provided a significant number of discrete test intervals appropriate for analysis) over the course of the testing program and results reported (Appendix C of Schmidt et al. 2003).

The *actual* fuel particle sizes (i.e., nominal diameters determined from sieving, corrected by the amount of uranium lost to corrosion as determined by the total gas as H_2, Kr, or Xe evolution) were compared to calculated *theoretical* particle sizes. As noted above, the theoretical particle sizes were calculated by determining the "effective particle diameters" required to generate the measured gas rate if the uranium metal, as spheres, reacted in accordance with the rate law summarized from the technical literature (SNF Databook, Vol. 1; Reilly 1998). The experimental results giving the actual and theoretical particle sizes are given in the Table 1.0 for the eleven experiments – seven with metal only and four with metal and overlying sludge. The ratio of the actual-to-theoretical particle size gives the enhancement factor.
Table 2.0 summarizes the rate comparison factors data provided in Table 1.0. The comparison factors generated from the tests conducted with fuel particles (no added sludge) are listed separately from those generated from tests that included both fuel particles and added sludge. The factors for Kr and Xe were developed from the test intervals for which gas samples were collected and analyzed. The factors for H_2 were developed from total gas generation data, and taking into account that >94% of the gas was H_2. Because the gas production (predominantly H_2) in the testing was monitored continuously, there are numerous data points on the particle diameters based on the H_2 gas release. The number of data points for the particle diameters based on the Kr and Xe release are limited to those having a discrete gas sampling event followed by mass spectrometric analysis.

The rate enhancement (comparison) factor for the fuel particles is about 0.33 ± 0.16, based on the SNF rate equation (Reilly 1998) and fission product gas data; that is, the fuel particles in Series III reacted at about one-third of the rate predicted by the SNF rate equation (Table 2.0). The fission product (Kr and Xe) gas data, both with and without sludge addition, give the same values for the enhancement factors. Overall, the H_2 data set, without sludge addition, exhibits greater scatter, but agrees with the fission product data sets.

From Table 1.0, it is seen that the rate enhancement factor never exceeds unity at any measurement condition. The enhancement factors as functions of the test temperature are plotted in Figures 1 and 2 for those tests with metal only and with metal plus sludge based on the hydrogen generation rate data. Similar plots based on the fission product xenon gas generation data are shown in Figures 3 and 4 for metal only and with metal plus sludge, respectively.

The figures show that the enhancement factors based on hydrogen gas rates generally decrease with temperature. It is seen that the enhancement factors in tests with metal plus sludge are at or below ~0.2 in the temperature range below 40°C.

The enhancement factors from the H_2 data for tests containing both fuel particles and sludge are 35% to 40% lower than those derived from the other data sets. This finding strongly suggests that the sludge blanket consumes or entraps a significant fraction of the H_2 that is released during uranium metal corrosion. This observation also indicates that the enhancement factors developed for the H_2 data sets with both fuel particles and sludge are biased low.

The enhancement factors based on the H_2 data for the individual tests containing fuel particles but no added sludge (Table 1.0) generally decrease as metal continues to corrode. This observation would support the hypothesis that the reaction rate decreases as the uranium metal surface becomes buried in a sludge corrosion product layer.

The rate decrease caused by sludge blanketing becomes more pronounced as the depth of the overlying sludge increases. This is shown in Figure 5 for SNF Databook (Reilly 1998) based on Xe generation rate data (the most reliable measurements) for the 80°C tests (which are the most extensive in the Series III testing). The sludge depth was determined from post-test examination and measurements of sludge density. In general, these figures show that, as the sludge depth increases, observed reaction rates decrease and deviate away from those predicted by the literature rate laws.

Table. 1.0 Fit to Reilly (log rate, µm/hr = 8.226 - 3016/T)

Metal Alone	Time, hr	Fraction U Reacted	Temp., °C	Theoretical Diameter, µm			Actual Diameter, µm	Ratio, Actual:Theoretical[a]		
				Kr	Xe	H_2		Kr	Xe	H_2
SNF Mid 60S	70-130	0.99	33.33	--	--	6730	1246	--	--	0.19
	300-964.6	0.95	60.80	5173	5492	4743	1229	0.24	0.22	0.26
	959.6-1223	0.82	60.75	--	--	6008	1170	--	--	0.19
	1223-1294	0.79	80.54	4637	4493	3810	1156	0.25	0.26	0.30
	1294-1323.3	0.73	95.47	3482	3731	2807	1126	0.32	0.30	0.40
	1323.3-1413.3	0.70	39.42	--	--	14511	1110	--	--	0.08
	1503.3-1583.3	0.70	36.47	--	--	14400	1110	--	--	0.08
	1643.3-2523.3	0.70	31.22	--	--	22647	1110	--	--	0.05
SNF Mid 40S	70-130	0.99	33.03	--	--	6928	1246	--	--	0.18
	140-1266	0.97	42.49	7198	6828	7728	1237	0.17	0.18	0.16
	1266-1577	0.93	61.28	--	--	5096	1220	--	--	0.24
	1577-1624.3	0.89	80.10	--	--	3398	1202	--	--	0.35
	1629.3-1724.3	0.86	39.37	--	--	13725	1189	--	--	0.09
	1804.3-2724.3	0.86	34.70	--	--	33935	1189	--	--	0.04
SNF P2000 80S	70-130	0.99	33.04	--	--	16702	3299	--	--	0.20
	145-500	0.90	80.86	5724	5733	5325	3196	0.56	0.56	0.60
	1900-2570.3	0.45	80.00	--	--	23832	2536	--	--	0.11
	2640.3-2870.3	0.50	29.10	--	--	63380	2627	--	--	0.04
SNF M500 80L	70-130	0.99	34.28	--	--	2827	289	--	--	0.10
	150-220	0.92	80.26	737	638	498	282	0.38	0.44	0.57
SNF Mid 80L	70-130	0.99	33.14	--	--	2274	1246	--	--	0.55
	150-400	0.80	80.85	2554	2779	3433	1160	0.45	0.42	0.34
	420-900	0.40	81.10	--	--	1650	921	--	--	0.56
SNF Mid 80L Dup	70-130	0.99	34.25	--	--	1837	1246	--	--	0.68
	150-400	0.80	81.20	2164	2290	1277	1160	0.54	0.51	0.91
	420-900	0.35	81.20	--	--	4315	881	--	--	0.20
Fuel Fragment (SNF Fragment)	70-130	0.99	80.00	--	--	81208	7126	--	--	0.09
	150-220	0.99	80.00	100874	77409	80668	7126	0.07	0.09	0.09
	1600-2100	0.85	80.00	21147	23700	17477	6773	0.32	0.29	0.39
							Metal Alone Average	0.33	0.33	0.28
							Metal Alone Standard Deviation	0.16	0.15	0.22
Metal Plus Sludge										
SNF + Can Fines 60S	70-130	0.98	38.17	--	--	3014	288	--	--	0.10
	650-900	0.80	63.67	2220	2294	3159	269	0.12	0.12	0.09
	1206-1278	0.65	81.16	2812	2716	3011	251	0.09	0.09	0.08
	1278-1307.3	0.60	94.62	3254	3227	2979	245	0.08	0.08	0.08
	1307.3-1567.3	0.58	40.69	--	--	29695	242	--	--	0.01
	1607.3-2473.3	0.58	35.14	--	--	85850	242	--	--	0.00
SNF + Can 60S	70-130	0.99	33.94	--	--	109428	1246	--	--	0.01
	660-1239.6	0.90	60.06	5814	5848	9064	1207	0.21	0.21	0.13
	1239.6-1312.3	0.87	80.24	4351	4765	4584	1193	0.27	0.25	0.26
	1312.3-1341.6	0.82	94.74	3627	3631	3010	1170	0.32	0.32	0.39
	1341.6-1591.6	0.80	36.99	--	--	23615	1160	--	--	0.05
	1661.6-2998.6	0.80	30.82	--	--	39106	1160	--	--	0.03
SNF + Can 60L	70-130	0.99	32.26	--	--	23057	1545	--	--	0.07
	150-1234	0.92	60.26	3300	3599	4591	1508	0.46	0.42	0.33
	1234-1305	0.80	80.21	2265	2777	3743	1439	0.64	0.52	0.38
	1305-1352.6	0.72	94.64	2545	2877	3008	1389	0.55	0.48	0.46
	1352.6-2452.6	0.67	33.25	--	--	12766	1356	--	--	0.11
	2752.6-3010.6	0.67	28.68	--	--	70031	1356	--	--	0.02
SNF + Floor 60L	70-130	0.99	30.87	--	--	9161	1545	--	--	0.17
	150-1241	0.92	60.29	2798	2912	4934	1508	0.54	0.52	0.31
	1241-1312	0.80	79.59	4269	3783	3415	1439	0.34	0.38	0.42
	1312-1359.6	0.72	92.78	3295	3228	2248	1389	0.42	0.43	0.62
	1359.6-3017.6	0.67	28.09	--	--	10574	1356	--	--	0.13
							Metal Plus Sludge Average	0.34	0.32	0.18
							Metal Plus Sludge Standard Deviation	0.19	0.16	0.17
							Total Average	0.33	0.32	0.24
(a) Actual: theoretical particle diameter = rate enhancement factor.							Total Standard Deviation	0.17	0.15	0.21

Table 2.. Rate Comparison/Enhancement Factors

Reilly (1998)	log k' (µm/hr) = 8.226 - 3016/T	No. of Data Points	Average	Standard Deviation
Kr Release	Fuel Particles Only	10	0.33	0.16
	Fuel Particles+Sludge	12	0.34	0.19
Xe Release	Fuel Particles Only	10	0.33	0.15
	Fuel Particles+Sludge	12	0.32	0.15
H_2 Generation	Fuel Particles Only	29	0.28	0.22
	Fuel Particles+Sludge	23	0.18	0.17
All Data (Reilly 1998)		96	0.28	0.25

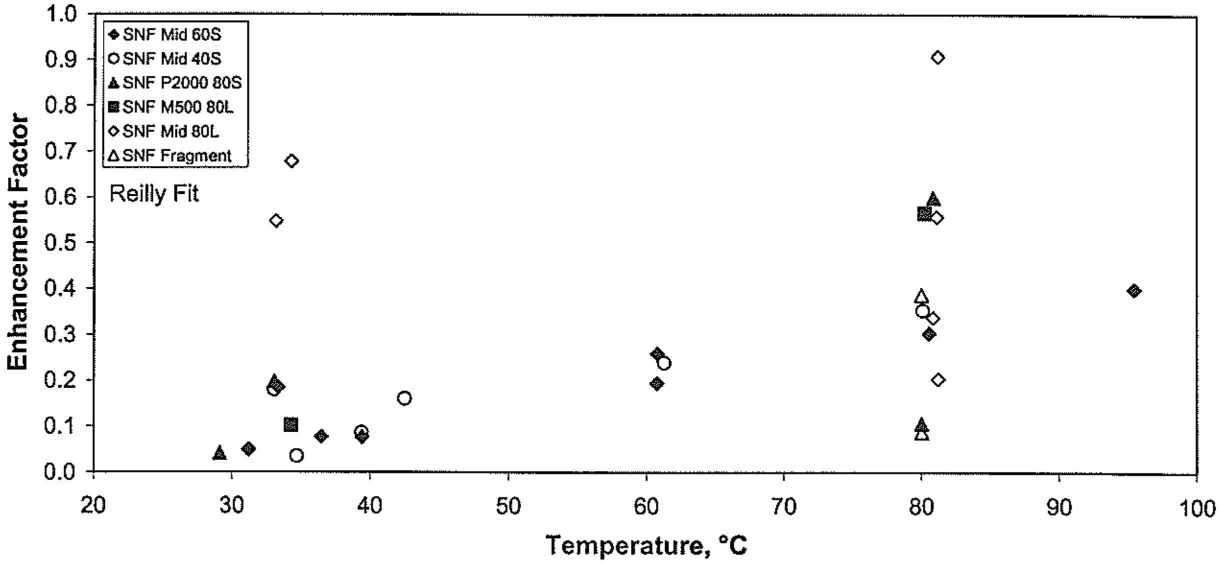


Figure 1. Enhancement Factor for Tests with Metal Only Based on Hydrogen Generation Rates.

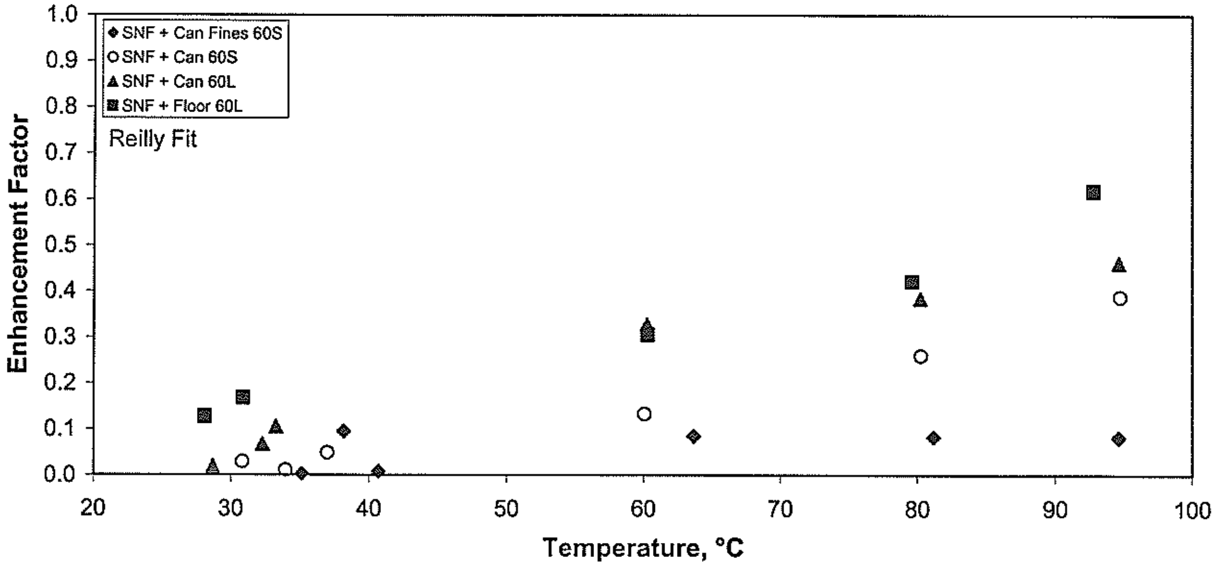


Figure 2. Enhancement Factor for Tests with Metal Plus Sludge Based on Hydrogen Generation Rates.

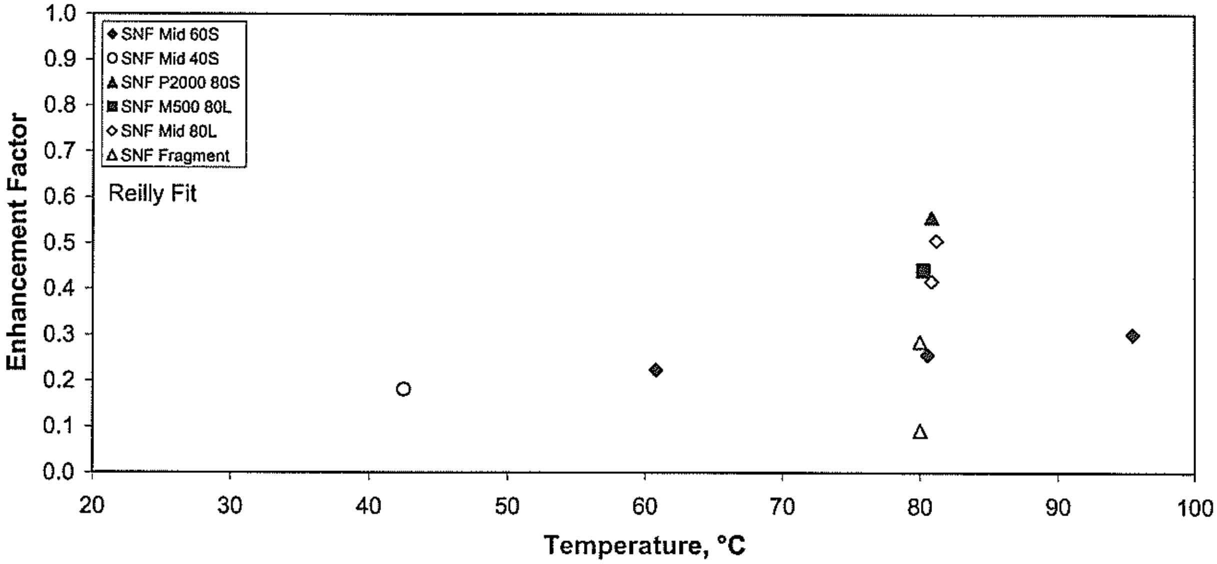


Figure 3. Enhancement Factor for Tests with Metal Only Based on Xenon Generation Rates.

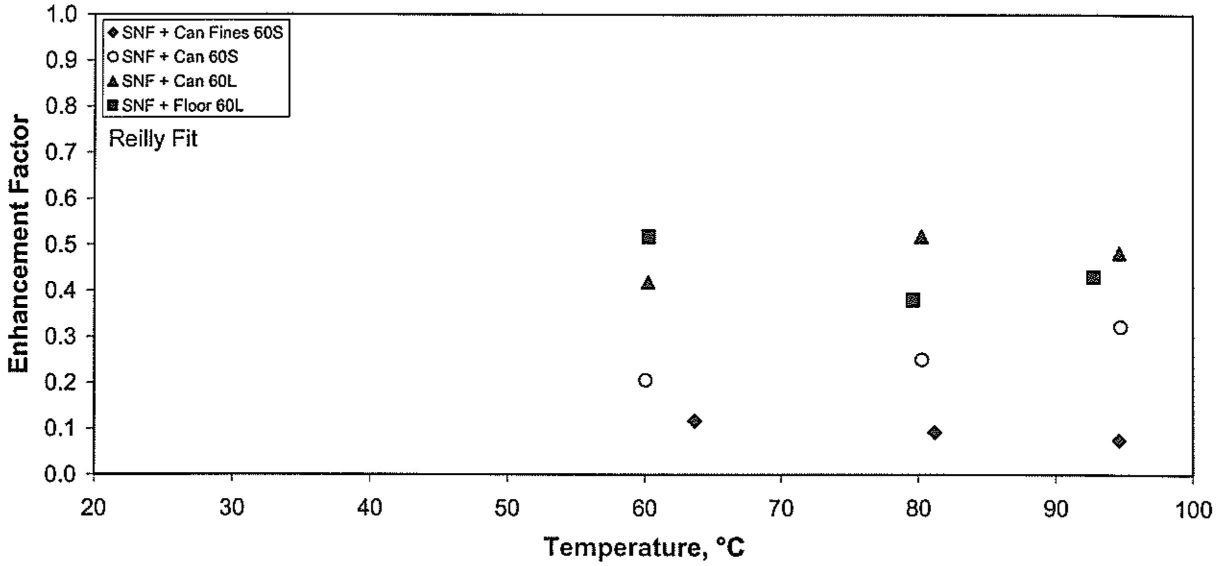


Figure 4. Enhancement Factor for Tests with Metal Plus Sludge Based on Xenon Generation Rates.

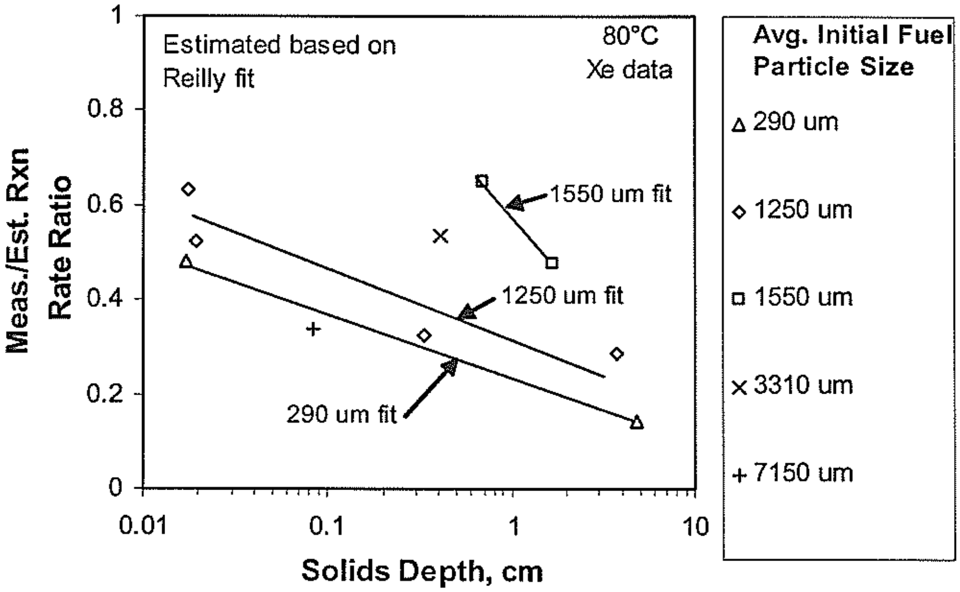


Figure 5. Ratio of Actual to Theoretical Fuel Particle Diameters (Enhancement Factor) as a Function of Solids Depth (Sludge Blanket) in the Gas Generation Reaction Vessels (Reilly Fit). The theoretical particle diameters were determined from the measured Xe gas release and the SNF Databook (Vol. 1) reaction rate equation for uranium metal in oxygen-free water provided in Reilly (1998). Solids depth was determined by dividing the known solids volume by the vessel cross-sectional area.

References:

Delegard, C. H., S. A. Bryan, A. J. Schmidt, P. R. Bredt, C. M. King, R. L. Sell, L. L. Burger, and K. L. Silvers. 2000. *Gas Generation from K East Basin Sludges – Series I Testing.* PNNL-13320, Pacific Northwest National Laboratory, Richland, WA.

Reilly, M. A. 1998. *Spent Nuclear Fuel Project Technical Databook, Fuel.* HNF-SD-SNF-TI-015, Rev. 6, Vol. 1, Fluor Hanford, Richland, WA.

Plys, M. G., and K. L. Pearce. 2001. *Supporting Basis for Spent Nuclear Fuel Project Sludge Technical Databook.* SNF-7765, Rev. 0, EDT 629145, Fluor Hanford, Richland, WA.

Schmidt, A. J., Delegard, C. H., S. A. Bryan, M. R. Elmore, R. L. Sell, K. L. Silvers, S.R. Gano, B. M. Thornton, 2003. *Gas Generation from K East Basin Sludges and Irradiated Metallic Uranium Fuel Particles – Series III Testing.* PNNL-14346, Pacific Northwest National Laboratory, Richland, WA.

Attachment 10

Tables of Metal Content, Decay Power, and Total Uranium Content for the Safety Basis, Reasonably Bounding, and Nominal Cases

A. J. Schmidt
Senior Engineer
Pacific Northwest National Laboratory

Table 1. Uranium Metal Concentration in KE Canister and Floor Sludge

Case	U Metal Concentration, Kg/m^3			Reference (SNF-7765 Rev. 1)
	KE Floor Sludge	KE Canister Sludge	40/60 (vol%) Can/Floor	
Safety Basis Case	23	125	63.8	Sec 4.3.4 and 4.3.2
Modified Safety Basis Case	23	125	63.8	Sec 4.3.4 and 4.3.2
Reasonably Bounding (Safety Basis Canister Sludge) [UL (95%) U_{met} Floor Sludge)]	9.17	125	55.5	Table B-3 and Sec 4.3.2
Nominal Case (Design Basis Canister Sludge) Design Basis Floor Sludge)	4	39.9	18.4	Sec 4.3.5 and 4.3.3

Table 2. Uranium Total Concentration in KE Canister and Floor Sludge

Case	U Total Concentration, Kg/m^3			Reference (SNF-7765 Rev. 1)
	KE Floor Sludge	KE Canister Sludge	40/60 (vol%) Can/Floor	
Safety Basis Case	300	1400	740	Table 4-4 and Table 4.3
Modified Safety Basis Case	300	1400	740	Table 4-4 and Table 4.3
Reasonably Bounding (Safety Basis Canister Sludge) [UL (95%) U_{met} Floor Sludge)]	120(1)	1400	632	Table 4.3 for canister sludge
Nominal Case (Design Basis Canister Sludge) Design Basis Floor Sludge)	60	770	344	Table 4-4 and Table 4.3

(1) For KE Floor, assumed U_{total} (Reasonably Bounding) is proportional to U_{metal} (Reasonably bounding), relative to U_{metal} (safety basis): 120 = 300 x (9.17/23)

Table 3. Reactive Uranium Oxide[(1)] Concentration in KE Canister and Floor Sludge

Case	Reactive U Oxide Concentration, Kg/m^3			Reference
	KE Floor Sludge	KE Canister Sludge	40/60 (vol%) Can/Floor	
Safety Basis Case	211	971	515	See Note 1.
Modified Safety Basis Case	211	971	515	
Reasonably Bounding (Safety Basis Canister Sludge) [UL (95%) U_{met} Floor Sludge)]	84.4	971	439	
Nominal Case (Design Basis Canister Sludge) Design Basis Floor Sludge)	42.7	556	248	

(1) It has been assumed that the non-metallic uranium in these sludge types is an equal uranium mole fraction of UO_2, $UO_{2.25}$, $UO_3 \cdot 2H_2O$ [SNF-7765 Rev. 1; Schmidt and Delegard (2003)]. Of these three uranium oxide species only UO_2 and $UO_{2.25}$ are assumed to react with oxygen (i.e., reactive uranium oxides).

Table 4. Decay Heat in KE Canister and Floor Sludge

Case	Decay Heat, W/m^3			Reference
	KE Floor Sludge	KE Canister Sludge	40/60 (vol%) Can/Floor	
Safety Basis Case				SNF-7765, Rev. 1
Modified Safety Basis Case	22.4	77.0	44.2	Table 4-9, (SNF-7765 Rev. 2 –Draft)
Reasonably Bounding (Safety Basis Canister Sludge) [UL (95%) U_{met} Floor Sludge)]	8.96[(1)]	77.0	36.2	Table 4-9 for canister sludge (SNF-7765 Rev. 2 –Draft)
Nominal Case (Design Basis Canister Sludge) Design Basis Floor Sludge)	3.12	21.7	10.6	Table 4-9, (SNF-7765 Rev. 2 –Draft)

(1) For KE Floor, assumed decay heat (Reasonably Bounding) is proportional to U_{total} (Reasonably bounding) relative to U_{total} (Safety Basis): 8.96 = 22.4 x (120/300).

References:

Plys, M. G., and K. L. Pearce. 2002. *Supporting Basis for Spent Nuclear Fuel Project Sludge Technical Databook.* SNF-7765, Rev. 1, Fluor Hanford, Richland, WA.

Schmidt A.J. and C.H. Delegard, 2003. *Updated Volumetric Expansion Factors for K Basin Sludge During Storage*, PNNL-14228, Pacific Northwest National Laboratory.

Attachment 11

Comparison of results of /reasonably Bounding Case with Measured Data from Experiments and Observations.

A. J. Schmidt
Senior Engineer
Pacific Northwest National Laboratory

To: Jim Sloughter and James Shelor

From: AJ Schmidt

Date: 11/08/03

Subject: Comparison of "Reasonably Bounding Gas Generation Rate" to Measured Gas Generation Rates from Canister Sludge Samples

Calculations were performed to compare the H_2 generation rate for the "Reasonably Bounding Case" to actual measurements from canister sludge samples. All rates (and gas volumes) were compared at 25°C. [rates at different temperatures were adjusted using the SNF rate equation for the reaction of uranium metal with oxygen free water (Duncan, 2002)]:

Temperature	Relative Reaction Rate
15	0.445
25	1.0
35	2.13
40	3.05

Reasonably Bounding Gas Generation Rate

The Reasonably Bounding Gas Generation Rate from a LDC loaded with 2 m^3 of 40/60 KE Canister sludge/KE floor sludge is given as: **2.32 liter/hr (@ 25°C).**

The Reasonably Bounding Case sludge contains 111 kg of uranium metal. Of this total, 100 kg (90.1 wt%) is associated with the canister sludge component of the 40/60 sludge.

For comparisons to measured rates, it is useful to calculate the volumetric gas generation rate of the canister sludge component of the Reasonably Bounding Sludge. For each 2 m^3 of 40/60, sludge, there is 0.8 m^3 (or 800 L) canister sludge.

Volumetric Gas Generation Rate Associated with Canister Sludge in Reasonably Bounding Case:

$$2.32\ \text{L/hr-2 m}^3 \times (2\ \text{m}^3/800\ \text{L}) \times 0.901\ (\text{wt fraction U met canister sludge}) \times (24\ \text{hr/day})$$

$$= 0.063\ \text{L H}_2\text{/L-canister sludge-day}$$

= 0.063 ml-gas/ml-sludge-day (@ 25°C).

Gas Generation Rate from KC-2/3 (KE Canister Sludge Composite)

KE Canister Composite, KC-2/3 was prepared from canister sludge collected from 10 KE canister barrels (5 barrels containing highly damaged fuel, and 5 barrels containing moderately damaged fuel). A subsample of the KC-2/3 composite was wet sieved to divide the material into a fraction containing particles larger than 250 μm (KC-2/3 P250) and a fraction containing particles less than 250 μm (KC-2/3 M250). On a wet sludge basis, 22 wt% of the KC-2/3 sample composite was made up of particles greater than 250 μm. Gas generation tests were performed with the samples of KC-2/3 P250 and KC-2/3 M250 at various temperatures (Delegard et al. 2000).

For KC-2/3 P250, at 40°C, a maximum gas generation rate of 80 ml/kg-day was measured (gas volume at STP).

The gas generation tests were run until all gas generation stopped (i.e., all uranium metal was reacted), and the uranium metal fractions in the various samples were determined. KC-2/3 P250 was found to contain 7.4 wt% U metal. KC-2/3 whole was calculated to contain 1.9 wt% U metal (i.e. KC-2/3 M250 contained very little uranium metal).

Also the density of KC-2/3 was 2.1 g/cc.

Therefore the rate, based on the whole KC-2/3 sample is:

> 80 ml/kg-day (@ 40°C) x (kg/1000g) x 1.9/7.4 x 2.1 g/ml = 0.043 ml/ml-day (gas volume at STP).
>
> Using the rate equation to adjust the rate to 25°C and adjusting the gas volume from STP to 25°C:
>
> = 0.043 ml/ml-day x 1/3.05 x (298K/273K) =
>
> **= 0.015 ml/ml-day (@ 25°C)**

Thus, the rate measured for KE Canister composite sludge KC-2/3 (whole), extrapolated to 25°C, is rate is only 24% of that projected for the canister sludge component in the Reasonably Bounding Case.

KE Canister Sludge (1996)

In 1996, 9 KE canister sludge samples were collected and transported to the 325 Building for characterization (Makenas et al., 1997). Each sample was collected from a single canister barrel. Two of the samples were collected from barrels containing no fuel (unfueled), 1 sample was collected from a canister containing fuel in good conditions; 5 samples were collected from canisters containing damaged fuel, and 1 sample was collected from a canister containing highly damaged fuel. In the 325 Building, gas generation was observed during settling tests with 5 of the 9 samples. These tests were conducted at 35°C. For two of the samples, 96-05 (from canister containing highly damaged fuel) and 96-06 (from canister containing damaged fuel) gas generation measurements were made. The gas generation rates from these samples on a volumetric basis are provided below:

Maximum Rate measured at 35°C for 96-05: 0.14 ml/ml-day (gas volume at STP)

Using the rate equation to adjust the rate to 25°C and adjusting the gas volume from STP to 25°C:

= 0.14/2.13 x 298/273 = **0.072 ml/ml-day (@25°C)**

Thus, the rate measured for KE Canister sludge 96-05 is 114% of that projected for the canister sludge component in the Reasonably Bounding Case.

Maximum Rates measured at 35°C for 96-06: 0.35 ml/ml-day (gas volume at STP)

Using the rate equation to adjust the rate to 25°C and adjusting the gas volume from STP to 25°C:

= 0.35/2.13 x 298/273 = **0.18 ml/ml-day (@25°C)**

Thus, the rate measured for KE Canister sludge 96-06 is 286% of that projected for the canister sludge component in the Reasonably Bounding Case.

The maximum gas generation rates for sample 95-05 and 96-06 were measured by monitoring the growth of a vessel spanning bubble (gas pocket). During these measurements, the ambient hot cell temperature was measured at ~35°C. It is possible that the temperature at the bottom of the graduated cylinders, where a small layer of sludge was generating the gas, could have been higher than 35°C, due to the heat of the reaction of the uranium metal reacting with water.

Gas generation (bubble release) was also observed in Samples 96-08, 96-13, and 96-15. The rates of gas generation from these samples were not measured, but were described as being less than that of Samples 96-05 and 96-06.

KW Canister Sludge (1997)

In 1996, 9 KW canister sludge samples were collected. These samples were transported to the 325 Building for characterization in March 1997 (Makenas et al., 1998). Each sample was collected from a single canister barrel. In the 325 building, gas generation testing was performed, and 5 of the 9 samples were observed to generate gas 96-02, 96-17, 96-23, 95-25, and 96-26. (Silvers 1997). When connected to traps, gas generation was measured for samples 96-23 (2.4 ml/day) and 96-26 (0.77 ml/day). After a settling test, a gas pocket formed in sample 96-17, and a gas generation rate of 0.76 ml/day was measured. The gas generation rates for samples 96-17, and 96-23 expressed as volumetric gas generation rates are provided below. The volumetric gas generation rate of sample 96-26 cannot be determined because no material was recovered (i.e., recovered sample volume is listed as zero).

Maximum Rate measured at 35°C for 96-17: 0.040 ml/ml-day (gas volume at STP)

Using the rate equation to adjust the rate to 25°C, and adjusting the gas volume from STP to 25°C :

= 0.040/2.13 x 298/273 = **0.020 ml/ml-day (@25°C)**

Thus, the rate measured for KW Canister sludge 96-17 is only 32% of that projected for the canister sludge component in the Reasonably Bounding Case.

Maximum Rate measured at 35°C for 96-23: 0.106 ml/ml-day (gas volume at STP)

Using the rate equation to adjust the rate to 25°C and adjusting the gas volume from STP to 25°C:

= 0.106/2.13 x (298/273) = **0.054 ml/ml-day (@25°C)**

Thus, the rate measured for KW Canister sludge 96-23 is 86% of that projected for the canister sludge component in the Reasonably Bounding Case.

Safety basis KW canister sludge contains 0.2 g uranium metal/cm^3 sludge. Safety basis KE canister sludge contains 0.125 g uranium metal/cm^3 sludge. Therefore, to compare the KW canister sludge gas generation rate values directly to that projected for the canister sludge component in the Reasonably Bounding Case, the volumetric gas generation rates for the Reasonable Bounding Case should be multiplied by 1.60 (0.200/0.125). Using this factor, the adjusted rate for the Reasonably Bounding Case (for the canister sludge component) would be 0.099 ml/ml-hr, a value that is significantly greater than that measured for the KW Canister sludge samples.

Conclusions

With respect to KC-2/3 (KE Canister sludge composite made up of sludge material from 10 sampling locations) the Reasonably Bounding Gas Generation Rate is indeed reasonably bounding.

With Respect to the 1996 KE canister sludge samples, the gas generation rate for 2 of the 7 samples from fueled canisters exceeds that of the Reasonably Bounding Gas Generation Rate. However, several of the KE canister sludge samples collected in 1996 exhibited little or no gas generation. Assuming that the three samples with observed, but unmeasured, gas generation (96-08, 96-13, and 96-15) can be assigned a rate equal to one-half that of 96-05, and the other two fuel canisters (with no observed gas generation) can be assigned a rate of zero, the mean rate for the 7 samples from fueled canisters at 25°C would be: 0.051 ml/ml-day (i.e., 81% of the Reasonably Bounding Gas Generation Rate).

The Reasonably Bounding Gas Generation Rate exceeds that of the KW Canister sludge samples. After accounting for the fact that KW canister sludge has more metal than KE canister sludge the Reasonably Bounding Gas Generation Rate significantly exceeds the KW canister gas generation rates.

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Silvers K. L. 1997. *K West Basin Canister Sludge Sample Analysis*, Rev 0, Pacific Northwest National Laboratory, Richland, WA.

Attachment 12

Effect of Vibrations Normally Encountered During Transport on the Gas Trapped within the Sludge in an LDC

M Epstein
Vice President, Consulting
Fauske & Associates, Inc.

Fauske & Associates, Inc.

DATE: December 2, 2003

TO: James Shelor
Marty Plys

FROM: Mike Epstein

SUBJECT: Response of Simulant Sludge Over Gas to Vibration

INTRODUCTION AND SUMMARY

Experiments have been performed on the response of a simulant sludge-over-gas configuration to vibration. The purpose of the experiments is to determine whether or not sludge liquefaction sufficient to release retained gas occurs when the sludge column is being transported and thereby agitated. A vessel spanning bubble capped by a sludge column is probably the retained gas morphology that is most susceptible to gas release and this was the morphology investigated.

The sludge-over-gas columns were subjected to an oscillatory horizontal motion of amplitude 2.0 cm and frequency 2.0 cycles s^{-1}. This means that twice a second the column experienced an acceleration of 0.32 g's. The simulant sludge used was kaolin and three sludge strengths were tested: 100, 180 and 300 Pa. Each test was carried out for about a 15 min period within which the shaker device was cycled on and off. The "on periods" lasted 1.0 min while the "off periods" lasted 15 s. In this way the sludge column was subjected to numerous vibration start-up transients. During each experiment one of the on periods was video taped.

Ten tests were performed (see Table 1). In Tests 1 to 3 the thickness H of the sludge column was approximately equal to the diameter D of the column and the sludge strength was varied from 100 to 300 Pa. In Tests 4 to 6 the sludge strength was 300 Pa and the sludge thickness-to-diameter ratio (H/D) was varied. In Tests 7 to 10 the sludge strength was 180 Pa and H/D was varied.

.1.1 Table 1

Summary Results of Sludge Column Vibration Tests

Test	Sludge Strength (Pa)	Thickness of Sludge Column (cm)	Thickness-to-Diameter Ratio*	Liquefaction and Gas Release
1	100	14.0	1.0	No
2	180	12.0	0.86	No
3	300	14.0	1.0	No
4	300	7.0	0.5	No
5	300	3.5	0.25	No
6	300	1.75	0.125	+
7	180	6.0	0.43	No
8	180	5.0	0.36	No
9	180	4.0	0.29	No
10	180	3.5	0.25	Yes

*Column diameter, 13.9 cm.

+Failed while attempting to load column.

The following observations were made:

(1) 100 Pa Simulant Sludge (Test 1): During the procedure of removing the platform that separated the 100 Pa sludge column from the underlying bubble (see next section) a portion of the column was mobilized and flowed downward into the bubble. Upon starting the vibration test more of the sludge was liquefied and again a sludge flow was observed to enter the gas region. Despite these partial sludge drainage events most of the sludge plug remained intact and no gas escaped from the trapped gas bubble. No additional sludge mobilization events were observed during the remainder of the test.

(2) 180 Pa Simulant Sludge (Test 2): Much like the 100 Pa sludge, a small fraction of the 180 Pa sludge column drained into the gas bubble while the separation platform was removed. No further sludge mobilization and no gas release occurred during the vibration test.

(3) 300 Pa Simulant Sludge (Test 3): No mobilization and no gas released was observed.

(4) 300 Pa Simulant Sludge (Tests 4 to 6): No mobilization and no gas release was observed when the sludge thickness was 7.0 or 3.5 cm. The 1.75-cm thick sludge failed while removing the platform that separated the sludge column from the underlying bubble. Attempts to load the apparatus with sludge columns of thickness less than about 3.0 cm were not successful.

(5) 180 Pa Simulant Sludge (Tests 7 to 10): Liquefaction was observed at the center of the upper surface of all the columns investigated, but failure and gas release did not occur until the column thickness was reduced to 3.5 cm.

4.1 EXPERIMENT APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. The main component of the apparatus is a plexiglass column of 13.9 cm ID and 42.6 cm length. Actually two sections comprise the column: a lower 12.6-cm long section and an upper 30-cm long section. During an experiment the two sections are connected by a flange (Fig. 1b). The upper section contains the simulant sludge plug and the lower section contains air.

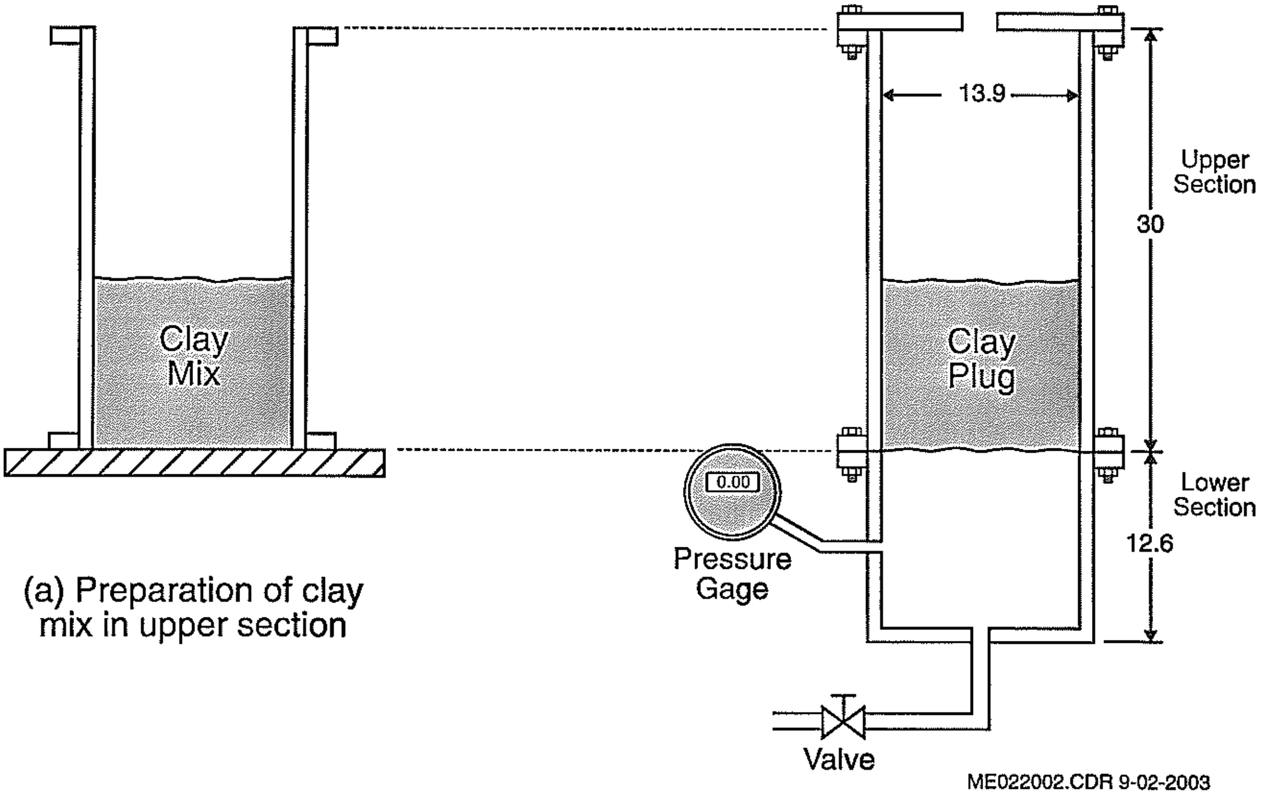
Mixtures of water and kaolin were used to represent the sludge plug in all the tests. The yield stress of this simulant as functions of concentration are known (Gauglitz et al., 2002). The simulant sludge plug was prepared in the bottom of the upper section of the plexiglass column. To accomplish this the upper section was separated from the lower section and the upper section was fitted with a temporary bottom (Fig. 1a). The kaolin and water were mixed until a uniform bubble free consistency similar to peanut butter was obtained. The mixture was kept in the upper section for up to about an hour to allow the mixture to consolidate. The upper section was then placed on top of the lower section. The temporary bottom (platform) was removed and the clay plug-containing upper section was sealed to the lower section by tightening the connecting flange bolts. The result was the desired initial configuration of a gas column trapped under a plug of simulant sludge. Finally the sludge-over-gas column was fastened to the platform of a commercially available sieve shaker.

At the end of each vibration test the valve in the line leading from the bottom of the test section to the outside was opened. The sludge column was observed to rapidly settle to the bottom of the test section, displacing the air as it translated downward. Indeed during the vibration experiments the sludge column was floating on the container spanning bubble.

REFERENCE

Gauglitz, P. A., Muller, S. J., and Rossen, W. R., 2002, "Mechanics of Bubbles in Sludges and Slurries," Pacific Northwest National Laboratory Report PNNL-13748.

ME:lak



(b) Upper section connected to lower section.

Figure 1 Schematic diagram of experimental apparatus (all dimensions in cm).

Attachment 13

Lower Flammability Limit for Oxygen in an Argon-Hydrogen-Oxygen Gas Mixture

M. G. Plys
Vice President, Waste Technology
Fauske & Associates, Inc.

Fauske & Associates, Inc.

Date: September 24, 2003

To: Jim Shelor, Jim Sloughter, Darrel Duncan, Hanford SNFP

From: Martin G. Plys, FAI

Subject: **Flammability and Combustion of H2, Air or O2, and Ar Gas Mixtures**

Flammability and combustion characteristics for hydrogen, air or oxygen, and argon are discussed here to assist evaluation for the KE sludge removal process with an argon gas purge.

For the case where a large diameter container (LDC) is purged by Ar, but H_2 and O_2 may evolve, flammability data given by Coward and Jones are available for the case of the ratio of O_2/Ar equal to the ratio of $O_2/(N_2+Ar)$ in air, which is 0.21/0.79. The lean flammability limit is 3.2% H_2, 76.5% Ar, and 20.3% O_2. This is slightly lower than the value of 4% hydrogen in air. The rich flammability limit is 76.4% H_2, 18.6% Ar, and 5% O_2 which is exactly the same oxygen content for the case of hydrogen in air. For practical purposes the rich limit of 5% O_2 is the value of interest to the project and is recommened except as follows.

A reference cited by Coward and Jones, Van Heiningen 1936, provides flammability data for the case of H_2-Air-Ar mixtures, which may be pertinent to the case of an LDC containing only hydrogen and argon but with in-leakage of air or incomplete purging of air. These data are reproduced in Figures 1, 2, and 3, which provide the overall flammability limit, a closeup of the lean limit, and the equivalent oxygen at the rich limit, respectively. Both lean and rich limit data for low Ar concentrations lie between today's known upward and downward propagation limits, and are an artifact of the experiment size and ignition location. Thus the fuel concentration decreases toward 4% on the lean limit as Ar is added, and the oxygen concentration also decreases. However, the oxygen concentration goes below 5% near 50% Ar, an unexpected result, and is about 4.1% at 70% Ar. This cannot be explained by the apparatus alone and cannot be discounted for industrial application. Thus, for the case of air ingression into an existing H_2-Ar mixture, a lower oxygen limit between 4% and 5% is recommended by using a linear fit: $x_{O2} = 5 - (x_{Ar}-50)/20$ where x is mole percent and $50\% < x_{Ar} < 70\%$. Use 5% O_2 when $x_{Ar} < 50\%$ and use 4% O_2 when $x_{Ar} > 70\%$. However, the mixture is completely inert when $x_{Ar} > 76\%$.

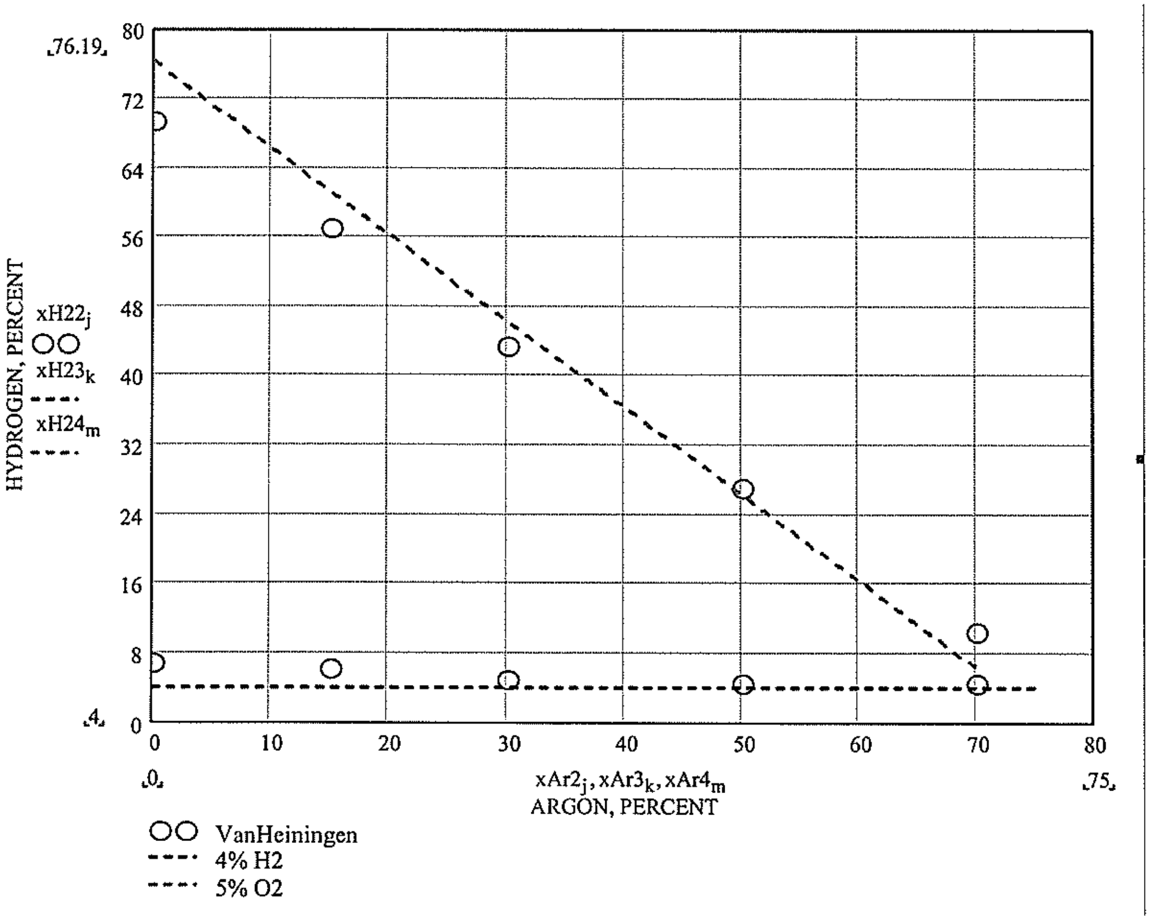
Lastly, it should be noted that because Ar has a lower heat capacity than air, the post-combustion pressure of a flammable mixture is higher with Ar than with air. Figure 4 provides the post-combustion pressure for a set of mixtures with various O_2 concentrations as indicated, beginning with a minimum stoichiometric quantity of hydrogen, so that rich mixture results are shown. Complete combustion is assumed in the absence of data near the rich limit.

References:

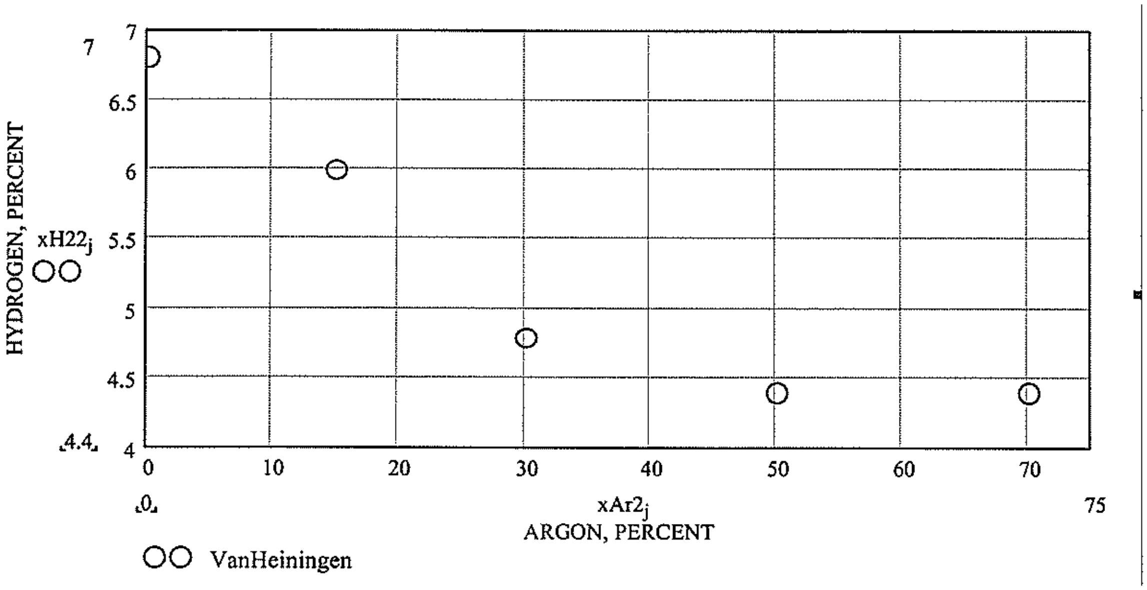
H.F. Coward and G.W. Jones, Limits of Flammability of Gases and Vapors, U.S. Bureau of Mines Bulletin 503, 1952.

J. Van Heiningen, Explosion Limits I: On the Influence of Argon, Nitrogen, Helium, and Carbon Dioxide on the Explosion Limits of Hydrogen, Carbon Monoxide, Methane, and Butane in Air, Receuil des Travaux Chimiques des Pays Bas, Vol. 55, pp. 65-75, 1936.

Figure 1. Flammability Limit Data for H_2-Air-Ar mixtures, Van Heiningen, 1936. For reference lines of 4% H_2 and 5% O_2 are drawn.



Figures 2 and 3. Closeup of Figure 1 lean flammability limit (top) and oxygen percentage at the rich flammability limit (bottom).



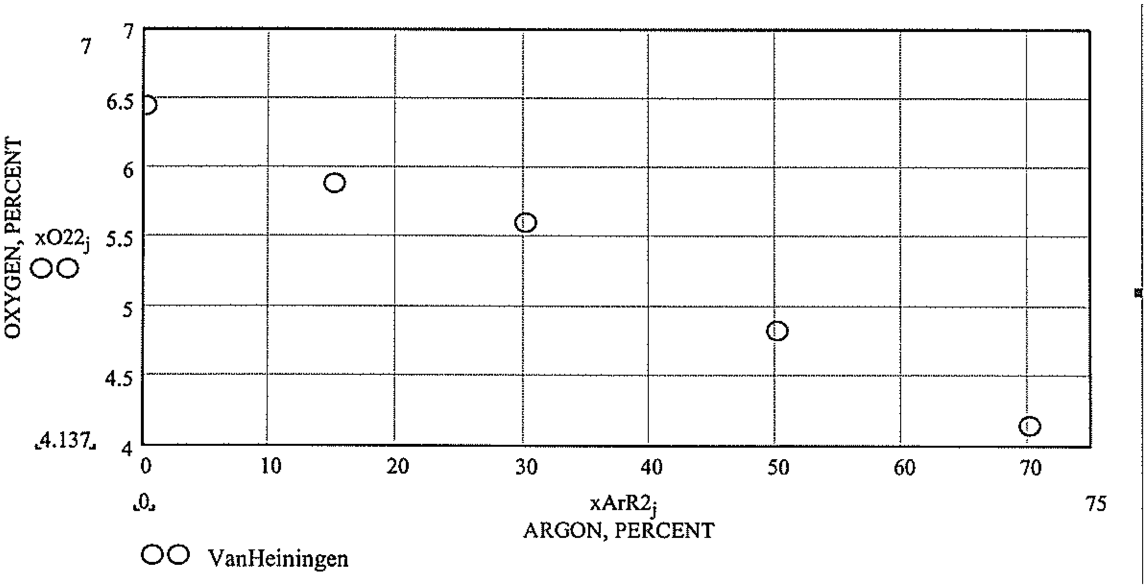
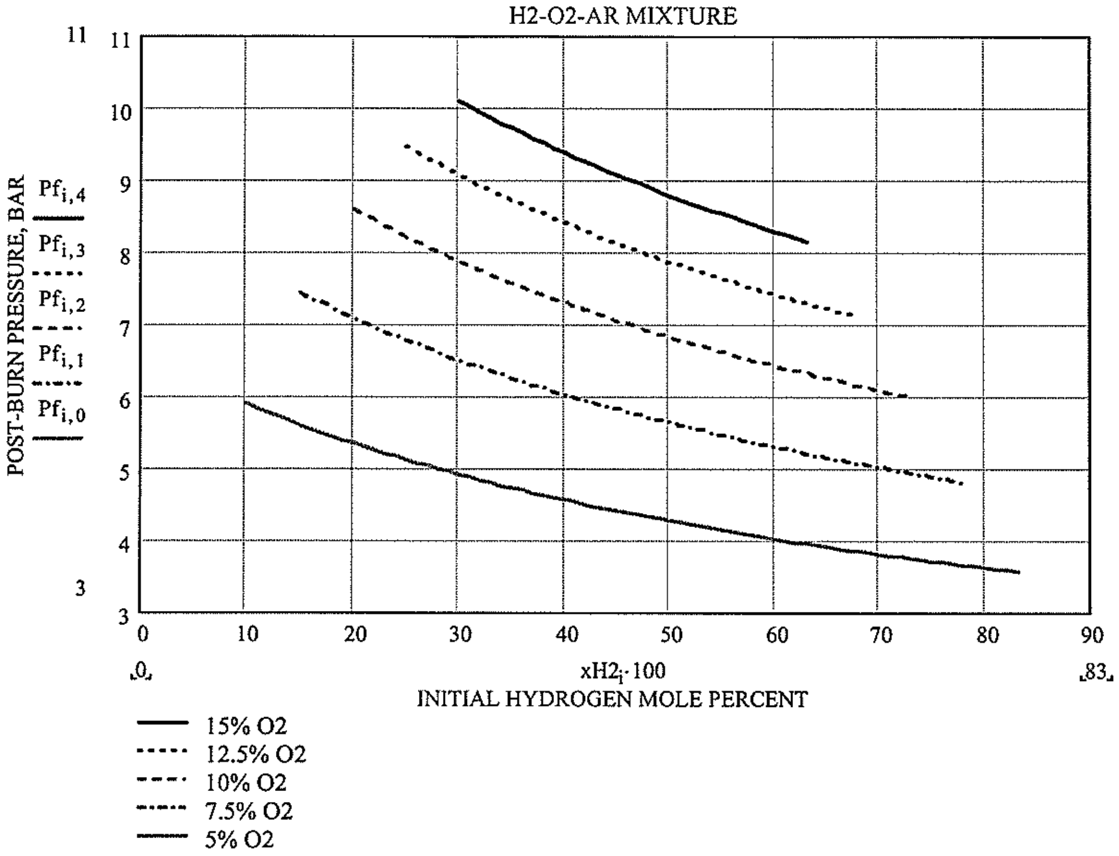


Figure 4. Post-combustion pressure for H_2-O_2-Ar mixtures with various O2 proportions and a minimum H2 stoichiometric content.



Attachment 14

Description of Calculations Performed in Support of this Analysis

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

CALCULATION OF HYDROGEN AND OXYGEN GENERATION FOR LARGE DIAMETER CONTAINERS (LDCs).

Introduction. This attachment provides the derivation of equations used to calculate the generation of hydrogen and the depletion (or generation as appropriate) of oxygen in Large Diameter Containers (LDCs) loaded with 2 m^3 of various mixtures of floor and canister sludge from the K East Basin. This attachment supports the calculations presented in Attachments 15 – 27.

Attachments 15 and 19, vented and inerted cases respectively, provide calculations of the hydrogen and oxygen generation using only parameters and processes approved in the currently approved Safety Basis.

Attachments 16 and 20, vented and inerted cases respectively, provide calculations of the hydrogen and oxygen generation using parameters and processes that are less conservative than those approved in the currently approved Safety Basis, but are being introduced as changes to the currently approved Safety Basis. This case is termed the Modified Safety Basis Case. The changes introduced by the Modified Safety Basis Case are:

1. A more realistic calculation of the Decay Power of the sludge that is more consistent with literature data on Decay Power of nuclear materials and experimentally observed data.
2. More realistic gas generation rates (H_2 and Oxidizing Species (O_2)) produced from the radiolysis of water.
3. Realistic operational temperature profiles for the sludge in the LDC rather than always considering the sludge to be at the maximum temperature at all times.
4. Introducing the role of O_2 in the gas behavior of the sludge including acknowledging the effect of O_2 in preventing the evolution of H_2 from the Uranium-Water Reaction as well as acknowledging the chemical behavior of O_2 and other oxidizing species formed during radiolysis.

Attachments 17 and 21, vented and inerted cases respectively, provide calculations of the hydrogen and oxygen generation using parameters and processes that are less conservative than those used for the Modified Safety Basis Case, but that reasonably bound the literature and experimental data on the processes taking place in the LDC during and following loading of the sludge into the LDC. This case is termed the Reasonably Bounding Case. The changes introduced by the Reasonably Bounding Case are:

1. Reducing the Reaction Rate Enhancement Factor from 3 to 1, as defined in Attachment 9.
2. Adjusting the radiolysis rate to conform to the derivation in Attachment 8.
3. Adjusting the effective metal particle size is from 500 microns to 750 microns as specified in SNF-7765, Revision 2.
4. Adjusting the uranium metal content from 64.8 Kg/m^3 to 55.5 Kg/m^3 as specified in Attachment 10.
5. Adjusting the total uranium concentration from 740 Kg/m^3 to 632 Kg/m^3 as specified in attachment 10.

6. Adjusting the Reactive Uranium Oxide concentration from 515 Kg/m^3 to 439 Kg/m^3 as specified in attachment 10. Reactive uranium oxides are comprised of that portion of the uranium oxides that have not reached the final (chemically stable) form and are still reacting with oxygen and bonding with water.
7. Adjusting the decay power from 44.2 watts/m^3 to 36.2 watts/m^3 as specified in attachment 10 and discussed in attachment 7

Attachments 18 and 22, vented and inerted cases respectively, provide calculations of the hydrogen and oxygen generation using parameters and processes that are averages of the data observed in literature and in experiments conducted with K East sludge. It is not suggested that these calculations be used in any way for safety basis calculations, however, it is suggested that these calculations will be more accurately predictive of the actual behavior that will be observed in the average LDC. This case is termed the Nominal Case. The changes introduced by the Nominal Case are:

1. Reducing the Reaction Rate Enhancement Factor from 1 to 0.4, as defined in Attachment 9.
2. Adjusting the radiolysis rate to conform to the derivation in Attachment 8.
3. Adjusting the uranium metal content from 55.5 Kg/m^3 to 18.4 Kg/m^3 as specified in Attachment 10.
4. Adjusting the total uranium concentration from 632 Kg/m^3 to 344 Kg/m^3 as specified in attachment 10.
5. Adjusting the Reactive Uranium Oxide concentration from 439 Kg/m^3 to 248 Kg/m^3 as specified in attachment 10. Reactive uranium oxides are comprised of that portion of the uranium oxides that have not reached the final (chemically stable) form and are still reacting with oxygen and bonding with water.
6. Adjusting the decay power from 36.2 watts/m^3 to 10.6 watts/m^3 as specified in attachment 10 and discussed in attachment 7

Attachments 23 – 25, inerted case, provide calculations to demonstrate the effect of uneven loading of sludge in the LDC. Modified Safety Basis parameters are used for these calculations. In Attachment 23, all sludge layers are 60% floor/40% canister sludge. In Attachment 24, the first four layers are pure canister sludge while the last six layers are pure floor sludge. In Attachment 25, the first six layers are pure floor sludge and the last four layers are pure canister sludge.

Attachments 26A – 26C, inerted case, provide calculations of an LDC loaded with pure floor sludge and maintained at low temperature (15^0 C) for the Modified Safety Basis (26A), Reasonably Bounding (26B), and Nominal Cases (26C). Attachment 26A provides the calculation of the bounding oxygen generation case.

Attachments 27A – 27C, inerted case, provide calculations of an LDC loaded with pure floor sludge and allowed to warm up to room temperature (25^0 C) for the Modified Safety Basis (27A), Reasonably Bounding (27B), and Nominal Cases (27C).

Enabling Assumptions. After making the changes in each case shown above, a simple calculation of the time required from the start of fill of an LDC to the time when a 48 liter hydrogen bubble could exist in the sludge is performed. As part of the calculation of the time to generate 48 liters of hydrogen, the time to deplete the dissolved oxygen and the volume of oxygen released by the sludge (if any) are calculated. The following general assumptions are used in these calculations; parameter values and assumptions specific to a particular case are provided in the specific attachment containing that calculation:

1. Sludge is loaded as a safety basis sludge mixture – sludge mixed as 60% floor sludge and 40% canister sludge.
2. The temperature of the sludge during loading is 15^0 C based in a normal basin water temperature of 53^0 F (11.5^0 C).
3. As long as at least one layer of sludge is loaded per day, the LDC temperature remains at 15^0 C based on more than 30,000 gallons of water at 11.5^0 C passing through the LDC during a loading cycle.
4. Each day that sludge is not loaded into the LDC, sludge (and LDC) temperature increase at 1^0 C per day until sludge (and LDC) temperature reaches 25^0 C. At 25^0 C the temperature stabilizes and remains at 25^0 C for as long as the LDC is maintained in the loadout bay in K East.
5. Sludge is loaded in 0.2 m^3 lifts every 12 hours until 2 m^3 of sludge has been loaded.
6. Hydrogen generated from both radiolysis and the uranium-water reaction is retained in the sludge immediately after a sludge layer is completely loaded and settled (i.e., at the end of the 12 hour loading period). Prior to the completion of the 12 hour loading period, any hydrogen generated by either the radiolysis or the uranium-water reaction process escapes the unsettled sludge and is swept out of the LDC by the water being pumped through the LDC.
7. The void volume in the LDC is the Safety Basis Void Volume – 1.2 m^3.
8. The LDC and Cask are vented to atmosphere through Nucfil filters; therefore, hydrogen and/or oxygen gas generation does not result in a pressure change in the LDC.
9. The hydrogen generated in settled sludge is retained within the sludge until a sufficient volume of hydrogen is available to cause the headspace (void volume) of the LDC to become flammable. The hydrogen is then released from the sludge by a mechanism known as an episodic release.

Derivation and Calculation.

Oxygen Generation and Depletion.

There are four processes/reactions that affect the time to oxygen depletion:

1. The concentration of oxygen in the water at the time the sludge enters the LDC. The concentration of oxygen is assumed to be the concentration for air saturated water at 15^0 C (loading temperature). The justification for this assumption is presented in section 6.1.2.4.
2. The generation of oxygen and oxidizing species by radiolysis. This generation rate is discussed in detail in Attachment 8.

3. The consumption of oxygen by uranium metal following loading in the LDC. This consumption rate is discussed in detail in Attachment 4.
4. The consumption of oxygen by reactive uranium oxides following loading of the LDC. This consumption rate is discussed in detail in Attachment 5.

The CRC Tables were used to construct an oxygen concentration as a function of temperature table in each spreadsheet. This is used as the initial concentration of oxygen in the sludge matrix water. While the sludge is being loaded, the temperature of the sludge and LDC are maintained constant at 15^0 C. During this loading time, the effects on the oxygen content of the sludge matrix are generation by radiolysis, consumption by uranium metal and consumption by uranium oxides. However, after loading is complete, the temperature of the sludge and LDC starts to increase at the rate of 1^0 C per day until the temperature is 25^0 C. As the water in the sludge matrix heats up, the solubility of oxygen in the water decreases. Accordingly, after loading is complete, if the oxygen concentration exceeds the saturation value for the temperature of interest, oxygen may be released from the sludge in the form of very small bubbles as the oxygen is forced out of solution. Assuming the saturation value of oxygen to be a linear function over the small temperature range of interest ($15^0 - 25^0$ C), an equation was constructed for the saturation value of oxygen over the temperature range of operation of the LDC at K East.

$$O_{2ST} = O_{2ST1} + \left(\frac{(O_{2ST2} - O_{2ST1})}{T_1 - T_2} \right) \times (T_1 - T)$$

Note: This equation may only be used for temperature bands for which the value of oxygen saturation can be closely approximated by a linear function, such as between 15^0 and 25^0 C.

Where:
O_{2ST} = Oxygen Saturation Value for any Temperature T
O_{2ST1} = Oxygen Saturation Value at the High Temperature of Interest.
O_{2ST2} = Oxygen Saturation Value at the Low Temperature of Interest.
T_1 = High Temperature of Interest.
T_2 = Low Temperature of Interest.
T = Temperature of Interest. This value must be T2 <= T <= T1.

Oxygen is produced from radiolysis as well as other oxidizing species. For purposes of this analysis, all oxidizing species produced from radiolysis will be treated as equivalent oxygen. Attachment 8 provides a detailed discussion and analysis of radiolysis in K East sludge. Attachment 8 provides specific values of oxygen generation for pure canister, pure floor, and 40% canister/ 60% floor sludge for all analysis conditions including safety basis, modified safety basis, reasonably bounding and nominal. The values provided in Attachment 8 are at STP, and are converted to ppm in the water in the sludge matrix by the following conversion:

(by mass)

$$QW_{O_2}\left[\frac{ppm}{hr}\right] = QR_{O_2}\left[\frac{liters}{hr\ m^3}\right] \times \frac{1}{22.4}\left[\frac{moles}{liters}\right] \times 32\left[\frac{grams}{mole}\right] \times 1000\left[\frac{mg}{gram}\right] \times \frac{1}{1500}\left[\frac{2\,m^3}{Kg\ H_2O}\right]$$

X

1.9 ✓

Where:
QWO2 = Generation rate of oxidizing species (eq O2) (ppm/hr)
QRO2 = Generation rate of equivalent O2 gas at STP (liters/hr)

per m³

22.4 = Volume of 1 mole of any gas @ STP (liters)
32 = Molecular weight of one mole of O2 (grams)
1000 = Number of milligrams per gram
1500 = Kg of water in 2 m3 of sludge (Kg)

Factors affecting the production of oxygen (oxidizing species) through radiolysis are covered in Attachment 8 and will not be covered here. If the production of oxygen by radiolysis were to result in the release of oxygen from the sludge, the only calculations required would be to convert from ppm to liters using the above expression and to apply an adjustment factor to temperature compensate the gas released using the following expression:

$$V_{O_2}(T)\,[liters\ @\ Temp] = V_{O_2}(STP) \times \left(\frac{273.15 + T}{273.15}\right)$$

Where: $V_{O2}(T)$ = Volume of O_2 at the temperature of interest (liters)
$V_{O2}(STP)$ = Volume of O_2 at 0^0 C (STP).
273.15 = 0^0 C in ^{0}K
T = Temperature of interest in ^{0}C

The consumption of oxygen is performed by two processes in the sludge: the reaction of uranium metal with oxygen and the reaction of uranium oxides with oxygen. The reaction of uranium metal with oxygen is described in detail in Attachment 4. The reaction of uranium oxides with oxygen is described in detail in Attachment 5. Both of these reactions will be covered briefly here:

The uranium metal-oxygen reaction is:

$$U + O_{2\,(aq)} \rightarrow UO_2$$

The rate of reaction of uranium metal with oxygen is controlled by several factors:

1. Temperature.
2. Metal concentration in the sludge.
3. Surface to Volume ratio of the metal in the sludge.

The base rate of the reaction is derived in Attachment 4 and is expressed in the number of hours required to deplete the oxygen contained in air saturated water at various reaction temperatures with the volume of the gasses expressed in liters/hr at STP. For purposes of calculations in this spreadsheet, the liter/hr rate from Attachment 4 is converted to ppm/hr using the above equation and the base reaction rate is expressed as the concentration of oxygen in air saturated water at 25^0 C divided by the number of hours to deplete the oxygen calculated in Attachment 4 at a reaction temperature of 25^0 C (237 hours) producing a base reaction rate in terms of ppm/hr at 25^0 C.

The base reaction rate for the Modified Safety Basis calculation is 0.0359 ppm/hr.

The temperature variation of the rate of reaction of uranium metal and oxygen is defined by the following equation:

$$\mathrm{Log}_{10}\mathrm{K}_{\mathrm{O}} = 8.333 - 3730/\mathrm{T}$$

Where: $\mathrm{K_O}$ = Reaction Rate of Uranium Metal-Oxygen Reaction (mg U/m^2 day)
T = Temperature in ^{0}K

Solving for $\mathrm{K_O}$ the equation becomes:

$$K_O = 10^{\left(8.333 - \frac{3730}{T}\right)}$$

Solving for a final reaction rate in terms of the initial reaction rate as a function of temperature, the equation becomes:

$$K_{O2} = K_{O1} \times \left(\frac{10^{\left(8.333 - \frac{3730}{T2}\right)}}{10^{\left(8.333 - \frac{3730}{T1}\right)}} \right)$$

Simplifying the equation results in:

$$K_{O2} = K_{O1} \times 10^{\left(3730 \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)}$$

Where: $\mathrm{K_{O1}}$ = The initial reaction rate (ppm/hr)
$\mathrm{K_{O2}}$ = The final reaction rate (ppm/hr)
$\mathrm{T_1}$ = The initial Temperature (^{0}K)
$\mathrm{T_2}$ = The final Temperature (^{0}K)

In the spreadsheets where these calculations are performed, this calculation is performed in a table containing "Relative Um Rate" and "Um Rate ppm/hr". In this calculation:

$\mathrm{K_{O1}}$ = Base rate at 25^0 C (8.510 ppm/237 hours = 0.0359 ppm/hr)
$\mathrm{K_{O2}}$ = The final reaction rate for each temperature of interest. (Um Rate ppm/hr)
$\mathrm{T_1}$ = 273.15 + 25 = 298.15^0 K
$\mathrm{T_2}$ = 273.15 + Temp of interest (^{0}C)

The "Relative Um Rate" is calculated using the exponential part of the above equation.

The variation in the Uranium Metal-Oxygen reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final concentration divided by the initial concentration. The equation for this variation is:

$$K_{O2} = K_{O1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where: K_{O1} = The initial reaction rate (ppm/hr)
K_{O2} = The final reaction rate (ppm/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

The variation in the Uranium Metal-Oxygen reaction rate as a function of particle size is a function of the surface area to volume ratio of the particles.

$$Q_{O2} = K_O(T)\, A_V \frac{1}{\rho_{O2}}$$

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
K_O = Rate law for $U+O_2 = UO_2$, 100% relative humidity, kg O_2/m^2/s,
A_V = Surface area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

Sludge surface area per unit volume is given by:

$$A_V = \frac{6\, C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal
ρ_m = U metal density
D = Particle size

Reaction rate as a function of particle size becomes:

$$Q_{O2F} = Q_{O2I} \times \left(\frac{D_I}{D_F} \right)$$

Where: Q_{O2F} = Final Reaction Rate (ppm/hr)
Q_{O2I} = Initial Reaction Rate (ppm/hr)
D_I = Initial Particle Size (microns)
D_F = Final Particle Size (microns)

The second process that consumes oxygen is the reaction of oxygen with uranium oxides. The reactions that cause this consumption are:

$$2\ UO_2 + O_2 + 4\ H_2O \rightarrow 2\ UO_3{\cdot}2H_2O$$
$$8\ UO_{2.25} + 3\ O_2 + 16\ H_2O \rightarrow 8\ UO_3{\cdot}2H_2O$$

At equal amounts of uranium present as UO_2 and $UO_{2.25}$, the combined reaction becomes:

$$8\ UO_2 + 8\ UO_{2.25} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

or

$$16\ UO_{2.125} + 7\ O_2 + 32\ H_2O \rightarrow 16\ UO_3{\cdot}2H_2O$$

Attachment 5 discusses these reactions in detail and provides the base rate of the reaction in the form of the number of hours required to deplete the oxygen in air saturated water at 25^0 C.

The rate of the reaction between oxygen and uranium oxides is governed by several factors:

1. Reaction Temperature.
2. Concentration of reactive oxides present.
3. Decay Power
    a. Radiolysis Rate (total power (dose rate) in grays/hour).
    b. Fraction of Decay Power Absorbed in Water
    c. Sludge Density

The base rate of the reaction is derived in Attachment 5. For purposes of attachments 16 through 18, the goal is to calculate the minimum time required to generate 48 liters of hydrogen in an LDC containing 2 m^3 of sludge. Accordingly, the appropriate equation to use for this calculation is the equation that results in the shortest time to deplete the oxygen, thereby, maximizing the hydrogen generation rate. That equation, from Attachment 5, is:

$$Rate, \frac{mg\ U}{m^2 \cdot day} = \frac{0.33\ mg\ U}{m^2 \cdot day} \times DR^{0.33}$$

Where: DR = Radiolytic power (Dose Rate) deposited in the water (grays/hr)

From Attachment 5, using this equation results in a base reaction rate for the Modified Safety Basis Case of 8.51 ppm/54.5 hrs = 0.1561 ppm/hr. In the Part B spreadsheet, this reaction rate is identified as the "Uo Rate ppm/hr".

The variation in the Uranium Oxide – Oxygen Reaction Rate as a function of temperature is described in detail in Attachment 5. From Attachment 5, the equation describing the reaction rate as a function of temperature is:

> The rate of the reaction at 15°C can be as much as 1.61-times lower, according to the Arrhenius equation (rate = $Ae^{-Ea/RT}$) and an activation energy (E_a) for the reaction of 34 kJ/mole in non-complexing neutral solution (E_a = 29-34 kJ/mole reported in section 5.6 of Shoesmith, 2000):

$$\frac{\text{Rate (25°C)}}{\text{Rate (15°C)}} = \frac{Ae^{-E_a/RT_{298}}}{Ae^{-E_a/RT_{288}}} = \frac{e^{[-34000\ \text{J/mole}]/[(8.314\ \text{J/mole}\cdot\text{deg})\cdot 298]}}{e^{[-34000\ \text{J/mole}][(8.314\ \text{J/mole}\cdot\text{deg})\cdot 288]}} = 1.61$$

Accordingly, the rate of the reaction at any temperature (T) can be expressed by the equation:

$$R_F = R_I \times \left(\frac{e^{\left[{}^{-34000\ J/mole}\!\big/\!{}_{((8.314\ J/mole \bullet \text{deg}) \times T_F)}\right]}}{e^{\left[{}^{-34000\ J/mole}\!\big/\!{}_{((8.314\ J/mole \bullet \text{deg}) \times T_I)}\right]}} \right)$$

Where:
R_I = Initial Reaction Rate (ppm/hr)
R_F = Final Reaction Rate (ppm/hr)
T_I = Initial Temperature (^{0}K)
T_F = Final Temperature (^{0}K)

In Attachments 16 – 18 and 20 - 27, the ratio of T_F over T_I is termed "Relative Uo Rate". By substituting 25^0 C (298.150 K) for the Initial Temperature and by simplifying the equation, "Relative Uo Rate" becomes:

$$RUo_R(T_F) = e^{\left(4089.5 \times \left(\frac{1}{298.15} - \frac{1}{273.15 - T_F}\right)\right)}$$

Where: $RUo_R(T_F)$ = Relative Reaction Rate at temperature T_F

Reaction Rate is the Relative Reaction Rate to the rate at 25^0 C.

The product of the Relative Reaction Rate and the Reaction Rate at 25^0 C produces the reaction rate at any temperature of interest. This value is supplied in the spreadsheet as "Uo Rate ppm/hr".

The variation of uranium oxide – oxygen reaction rate as a function of uranium oxide concentration is a simple ratio of the final concentration divided by the initial concentration. The equation for the variation of uranium oxide-oxygen reaction rate as a function of uranium oxide concentration becomes:

$$R_{UOF} = R_{UOI} \times \frac{C_{UOF}}{C_{UOI}}$$

Where:
R_{UOF} = Final Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide-Oxygen Reaction Rate (ppm/hr)
C_{UOF} = Final Concentration of Reactive Uranium Oxides (Kg/m^3)
C_{UOI} = Initial Concentration of Reactive Uranium Oxides (Kg/m^3)

The variation of uranium oxide-oxygen reaction rate as a function of sludge decay power is a complex calculation involving several variables. This first variable is the concentration of uranium oxide present, described above. For decay power to change, the total radioactivity present must have changed. Therefore, the total uranium present must have changed. Accordingly, a change in the concentration of reactive uranium oxides present occurs and is defined by the equation shown above.

The other variables that change on a change of decay power all deal with the radiolysis rate affecting the reaction rate. These changes are:

1. The total power available for radiolysis is changed by the simple ratio of the final decay power divided by the initial decay power.
2. The density of the sludge changes because the total uranium concentration has changed. The density change affects the fraction of the energy from radioactive decay that is deposited in the water as compared to the fraction of the energy that is deposited in the solids in the sludge. This change is applied through a ratio of the final water fraction divided by the initial water fraction.
3. The density of the sludge changes because the total uranium concentration has changed. This change in density affects the radiolysis dose rate (grays/hr) because a gray is a measure of energy per unit mass. This change is applied through a ratio of the initial density divided by the final density.

Taking these changes into account, the equation for the variation of the uranium oxide-oxygen reaction rate as a function of decay power becomes:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}} \right) \times \left(\frac{0.33 \times \left(DR_I \times \left(\frac{\rho_{SI}}{\rho_{SF}} \right) \times \left(\frac{WAF_F}{WAF_I} \right) \times \left(\frac{DP_F}{DP_I} \right) \right)^{0.33}}{0.33 \times \left(DR_I \right)^{0.33}} \right)$$

Where:
R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
DR_I = Initial Dose Rate (power deposited in the water) (grays/hr)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power ($watts/m^3$)
DP_F = Final Decay Power ($watts/m^3$)

Simplifying the equation:

$$R_{UOF} = R_{UOI} \times \left(\frac{C_{UOF}}{C_{UOI}} \right) \times \left(\left(\frac{\rho_{SI}}{\rho_{SF}} \right) \times \left(\frac{WAF_F}{WAF_I} \right) \times \left(\frac{DP_F}{DP_I} \right) \right)^{0.33}$$

Where:
R_{UOF} = Final Uranium Oxide Reaction Rate (ppm/hr)
R_{UOI} = Initial Uranium Oxide Reaction Rate (ppm/hr)
C_{UOF} = Final Reactive Uranium Oxide Concentration (Kg/m^3)
C_{UOI} = Initial Reactive Uranium Oxide Concentration (Kg/m^3)
ρ_{SF} = Final Sludge Density (g/cm^3)
ρ_{SI} = Initial Sludge Density (g/cm^3)
WAF_I = Initial Water Absorption Fraction (unitless)
WAF_F = Final Water Absorption Fraction (unitless)
DP_I = Initial Decay Power ($watts/m^3$)
DP_F = Final Decay Power ($watts/m^3$)

Hydrogen Generation Prior to Dissolved Oxygen Depletion.

The volume of hydrogen gas generated in each sludge layer prior to dissolved oxygen depletion is calculated by the following formula:

$$QL_{H_2} = \left(QR_{H_2}\right) \times \left(\frac{VS_L}{VS_{LDC}}\right)$$

Where:
QL_{H2} = H_2 Generation Rate in the Layer (Liters/Hour)
QR_{H2} = H_2 Generation Rate from Radiolysis for full LDC sludge load (2 m^3) (Liters/Hour)
VS_L = Sludge Volume for the layer (m^3)
VS_{LDC} = Sludge Volume for a full LDC (2 m^3)

The radiolysis rate of the sludge is controlled by many complex variables. For this reason, the calculation of the radiolysis rate for each sludge type (pure canister, pure floor, 60% floor/40% canister) under each case condition (Modified Safety Basis, Reasonably Bounding, and Nominal) has been performed separately in Attachment 8. The only variable of concern for the calculations performed in these attachments is the variation of the volume of the gas with temperature, since the generation rates provided in Attachment 8 are provided at STP, this is a simple application of the ideal gas law. The equation used is:

$$QR_{H_2}(T) = QR_{H_2} \times \left(\frac{273.15 + T}{273.15}\right)$$

Where:
$QR_{H2}(T)$ = H_2 Generation Rate as a function of temperature (liters/hr)
QR_{H2} = H_2 Generation Rate at STP for the sludge type and case (liters/hr)
T = Sludge/LDC temperature (^{0}K)

Hydrogen Generation Following Dissolved Oxygen Depletion.

The volume of hydrogen gas generated in each sludge layer after dissolved oxygen depletion is calculated by the following formula:

$$QL_{H_2} = \left(QU_{H_2} + QR_{H_2}\right) \times \left(\frac{VS_L}{VS_{LDC}}\right)$$

Where:

QL_{H2} = H_2 Generation Rate in the Layer (Liters/Hour)
QU_{H2} = H_2 Generation Rate from U-H_2O reaction for full LDC sludge load (2 m^3) (Liters/Hour)
QR_{H2} = H_2 Generation Rate from Radiolysis for full LDC sludge load (2 m^3) (Liters/Hour)
VS_L = Sludge Volume for the layer (m^3)
VS_{LDC} = Sludge Volume for a full LDC (2 m^3)

The uranium metal-water reaction is:

$$U + 2\,H_2O \rightarrow UO_2 + 2\,H_{2\,(g)}$$

The rate of reaction of uranium metal with water is controlled by several factors:

1. The presence of dissolved oxygen in the water.
2. Temperature.
3. Reaction Rate Enhancement Factor (Multiplier)
4. Metal concentration in the sludge.
5. Surface to Volume ratio of the metal in the sludge.

The base rate of the reaction is derived in Attachment 4 and is expressed as the volume of hydrogen generated in one hour from the uranium-water reaction with the water at 25^0 C and the hydrogen released at STP.

The base reaction rate for the Modified Safety Basis calculation is 5.585 liters/hr.

As shown in the Uranium-Oxygen Reaction discussion, the Uranium-Water reaction does not evolve hydrogen as long as there is dissolved oxygen present in the water. Accordingly, it must be remembered that the reaction discussed here (Uranium-Water) will not evolve the hydrogen shown until after all dissolved oxygen has been depleted.

The temperature variation of the rate of reaction of uranium metal and water is defined by the following equation:

$$\mathrm{Log}_{10}\mathrm{K}_{\mathrm{W}} = 7.634 - 3016/\mathrm{T}$$

Where: $\mathrm{K_W}$ = Reaction Rate of Uranium Metal-Water Reaction (mg U/m^2 day)
T = Temperature in ^{0}K

Solving for $\mathrm{K_W}$ the equation becomes:

$$K_W = 10^{\left(7.634 - \frac{3016}{T}\right)}$$

Solving for a final reaction rate in terms of the initial reaction rate as a function of temperature, the equation becomes:

$$K_{W2} = K_{w1} \times \left(\frac{10^{\left(7.634 - \frac{3016}{T2}\right)}}{10^{\left(7.634 - \frac{3016}{T1}\right)}} \right)$$

Simplifying the equation results in:

$$K_{W2} = K_{W1} \times 10^{\left(3016 \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)}$$

Where: $\mathrm{K_{W1}}$ = The initial reaction rate (liters/hr)
$\mathrm{K_{W2}}$ = The final reaction rate (liters/hr)
$\mathrm{T_1}$ = The initial Temperature (^{0}K)
$\mathrm{T_2}$ = The final Temperature (^{0}K)

In Attachments 15 - 27, this calculation is performed in a table containing "Relative Um Rate" and "H_2 Rate Um liters/hr". In this calculation:

$\mathrm{K_{W1}}$ = Base rate at 25^0 C and STP gas conditions (5.585 liters/hr)
$\mathrm{K_{W2}}$ = The final reaction rate for each temperature of interest. (H_2 Rate Um liters/hr)
$\mathrm{T_1}$ = 273.15 + 25 = 298.15^0 K
$\mathrm{T_2}$ = 273.15 + Temp of interest (^{0}C)

The "Relative Um Rate" is calculated using the exponential part of the above equation.

The variation of Uranium Metal-Water reaction rate as a function of Reaction Rate Enhancement Factor (Multiplier) is a simple ratio of the final reaction rate enhancement factor ($RREF_F$) divided by the initial reaction rate enhancement factor ($RREF_I$).

$$KW_F = KW_I \times \frac{RREF_F}{RREF_I}$$

Where:

KW_F = Final Reaction Rate (liters/hr)
KW_I = Initial Reaction Rate (liters/hr)
$RREF_F$ = Final Reaction Rate Enhancement Factor
$RREF_I$ = Initial Reaction Rate Enhance Factor

The variation in the Uranium Metal-Water reaction rate as a result of changes in uranium metal concentration can be calculated using a simple ratio of the final uranium metal concentration divided by the initial uranium metal concentration. The equation for this variation is:

$$K_{W2} = K_{W1} \times \left(\frac{C_{U_{MET2}}}{C_{U_{MET1}}} \right)$$

Where:

K_{W1} = The initial reaction rate (liters/hr)
K_{W2} = The final reaction rate (liters/hr)
C_{UMET1} = The initial Uranium Metal Concentration (Kg/m^3)
C_{UMET2} = The final Uranium Metal Concentration (Kg/m^3)

The variation in the Uranium Metal-Water reaction rate as a function of particle size is a function of the surface area to volume ratio of the particles.

$$Q_{H2} \quad = \quad \xi K_w(T) A_V \frac{4}{32} \frac{1}{\rho_{H2}}$$

define ξ

where

Q = Volumetric rate, m^3 gas / m^3 sludge, at STP,
K_W = Rate law for $U+O_2 = UO_2$, 100% relative humidity, kg $O_2/m^2/s$,
A_V = Surface area per unit volume, and
ρ = Gas density, kg/m^3, evaluated at STP.

Sludge surface area per unit volume is given by:

$$A_V \quad = \quad \frac{6\, C_{Umet}}{\rho_m D}$$

where

C_{Umet} = Concentration of U metal
ρ_m = U metal density
D = Particle size

Reaction rate as a function of particle size becomes:

$$Q_{H2F} = Q_{H2I} \times \left(\frac{D_I}{D_F} \right)$$

Where:
Q_{H2F} = Final Reaction Rate (liters/hr)
Q_{H2I} = Initial Reaction Rate (liters/hr)
D_I = Initial Particle Size (microns)
D_F = Final Particle Size (microns)

The total volume of hydrogen retained in the sludge as a function of time becomes:

$$V_{H_2}(T) = \sum_{a=10}^{a=1} \left(L_a QL_{H_2} \times L_a t_s \right)$$

Where:
$V_{H2}(T)$ = The total volume of H2 present in the sludge at any time (T) after loading began. (Liters)
L_a = Each specific layer of sludge loaded. In this example, 10 layers of sludge are loaded; accordingly the values of a are 1 through 10.
L_aQL_{H2} = The total hydrogen generation rate for the specific sludge layer. (Liters/Hour)
t_s = The time since the specific sludge layer completed the settling process and commenced retention of the hydrogen generated. (Hours)

Hydrogen Flammability in Air.

The total hydrogen volume of interest is that hydrogen volume that when released to the headspace of the LDC will result in a flammable atmosphere in the headspace (void volume) of the LDC. This volume is calculated by the following equation:

$$VF_{H_2} = V_{SB} \times LFL_{H_2}(air)$$

Where: VF_{H2} = Volume of hydrogen required to produce a flammable atmosphere in the headspace of the LDC. (Liters)
V_{SB} = Safety Basis Void Volume of the LDC. (1200 Liters)
LFL_{H2}(air) = Lower Flammability Limit for hydrogen in air. (4%)

The total hydrogen volume of interest, from the above equation, is 48 liters.

Lower Flammability Limit for Oxygen in an Ar-H_2-O_2 Atmosphere

The total oxygen volume of interest is that oxygen volume that when released to the headspace of the LDC will result in a flammable atmosphere in the headspace (void volume) of the LDC. This volume is calculated by the following equation:

$$VF_{O_2} = V_{SB} \times LFL_{O_2}(Ar - H_2 \text{ gas mixture})$$

Where: VF_{02} = Volume of oxygen required to produce a flammable atmosphere in the headspace of the LDC. (Liters)
V_{SB} = Safety Basis Void Volume of the LDC. (1200 Liters)
LFL_{O2} (Ar – H_2 gas mixture) = Lower Flammability Limit for oxygen in an Argon – Hydrogen Gas Mixture. (4%)

The technical basis for the use of 4% as the Lower Flammability Limit for oxygen in an Ar-H_2-O_2 atmosphere is provided in attachment 13. The total oxygen volume of interest, from the above equation, is 48 liters. However, since it is assumed that 1% oxygen is admitted to the LDC during the disconnect process and 1% oxygen is admitted to the LDC during the final purge process, calculations in this paper will used 24 liters (2%) oxygen as the limit for oxygen from the sludge.

Attachment 15

Safety Basis Case – Vented LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 16

Modified Safety Basis Case – Vented LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 17

Reasonably Bounding Case – Vented LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 18

Nominal Case – Vented LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 19

Safety Basis Case – Sealed/Inerted LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 20

Modified Safety Basis Case – Sealed/Inerted LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 21

Reasonably Bounding Case – Sealed/Inerted LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 22

Nominal Case – Sealed/Inerted LDC

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 23

Unbalanced Load Analysis – 10 60/40 Layers

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 24

Unblanced Load Analysis – 4 Canister Layers Followed By 6 Floor Layers

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 25

Unblanced Load Analysis – 6 Floor Layers Followed By 4 Canister Layers

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 26A

Modified Safety Basis Case – 100% Floor Sludge – No Heatup

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 26B

Reasonably Bounding Case – 100% Floor Sludge – No Heatup

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 26C

Nominal Case – 100% Floor Sludge – No Heatup

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 27A

Modified Safety Basis Case – 100% Floor Sludge – Heatup to Room Temperature

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 27B

Reasonably Bounding Case – 100% Floor Sludge – Heatup to Room Temperature

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project

Attachment 27C

Nominal Case – 100% Floor Sludge – Heatup to Room Temperature

J. L. Shelor, TRI, Inc
Senior Technical Advisor
Spent Nuclear Fuel Project