ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN **657897**

Proj.
ECN

2. ECN Category (mark one) Supplemental ☐ Direct Revision ☒ Change ECN ☐ Temporary ☐ Standby ☐ Supersedure ☐ Cancel/Void ☐	3. Originator's Name, Organization, MSIN, and Telephone No. D. R. Duncan, SNF Project, R3-86, 372-1013	4. USQ Required? ☐ Yes ☒ No	5. Date 1/24/00	
	6. Project Title/No./Work Order No. SNF Project	7. Bldg./Sys./Fac. No. N/A	8. Approval Designator Q, S^N	
	9. Document Numbers Changed by this ECN (includes sheet no. and rev.) SNF-5488, Rev. 0	10. Related ECN No(s). N/A	11. Related PO No. N/A	

12a. Modification Work ☐ Yes (fill out Blk. 12b) ☒ No (NA Blks. 12b, 12c, 12d)	12b. Work Package No. N/A	12c. Modification Work Complete N/A Design Authority/Cog. Engineer Signature & Date	12d. Restored to Original Condition (Temp. or Standby ECN only) N/A Design Authority/Cog. Engineer Signature & Date
---	-------------------------------------	---	---

- 13a. Description of Change
- 13b. Design Baseline Document? ☐ Yes ☒ No
- Addition of paragraph in Section 2.1 discussing nonlinearity of reactive area change as a function of oxidation rate.
 - Revisions of Section 4.1 deleting discussion of stochastic fracture concept and Markov process.
 - Revisions of Section 4.2 to remove references to arrival time analyses and confine discussion to relating expected fragmentation behavior between TGA tests and cold vacuum drying.
 - Section 4.2, 2nd paragraph – explanation of Appendix A preparation added.
 - Section 4.3, 3rd paragraph – explanation of effective incremental rate multiplier added
 - The Review Comment Record from the peer reviewer is added as an attachment

USQ Categorical Exclusion B, Appendix C, AP NS-4-001

14a. Justification (mark one) Criteria Change ☐ Design Improvement ☒ Environmental ☐ Facility Deactivation ☐ As-Found ☐ Facilitate Const ☐ Const. Error/Omission ☐ Design Error/Omission ☐	14b. Justification Details Incorporation of review comments.
---	---

15. Distribution (include name, MSIN, and no. of copies)
 See attached distribution sheet

RELEASE STAMP

DATE: **JAN 24 2000**

STA: **MANFORD**

RELEASE

ID: **0**

[illegible]

DISTRIBUTION SHEET

To Distribution	From Process Engineering	Page 1 of 1
		Date 1/24/00
Project Title/Work Order Fuel Fracture (Crumbling) Safety Impact (OCRWM), SNF-5488, Rev. 1		EDT No. N/A
		ECN No. 657897

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
------	------	-----------------------------	-----------	------------------------------	-----------------

Spent Nuclear Fuel Project

R. L. Boyleston	R3-26	X			
J. D. Carlson	R3-26	X			
R. D. Crowe	R3-26	X			
D. R. Duncan (5)	R3-86	X			
J. R. Frederickson	R3-86	X			
R. L. Garrett	R3-26	X			
L. J. Garvin	R3-26	X			
R. L. McCormack	R3-11	X			
B. J. Makenas	H0-40	X			
W. C. Miller	R3-11	X			
A. L. Pajunen	R3-86	X			
A. V. Reed	R3-86	X			
J. A. Swenson	R3-11	X			
D. J. Trimble	H0-40	X			
SNF Project Files	R3-11	X			
SNF Project Training Organization	S2-45				X
SNF Project Procedures	X3-86				X

DOE/RL

P. G. Loscoe	S7-41	X	
--------------	-------	---	--

Offsite

M. G. Plys		X	
Fauske & Associates, Inc.			
16W070 W. 83 rd St.			
Burr Ridge, IL 60521			

R. G. Ballinger		X	
Altran Corporation			
Massachusetts Institute of Technology			
451 D Street			
Boston, MA 02210			

FUEL FRACTURE (CRUMBLING) SAFETY IMPACTS (OCRWM)

M. G. Plys* and D. R. Duncan

Fluor Hanford, Richland, WA 99352

U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: 657897

UC: 510

Org Code: 2F300

Charge Code: 105355/A010

B&R Code: EW7040000

Total Pages: 21

Key Words: Spent Nuclear Fuel, Crumbling, TGA, Oxidation, Reaction Rate

Abstract: The safety impact of experimentally observed N Reactor fuel sample fracture and fragmentation is evaluated using an average reaction rate enhancement derived from data from thermo-gravimetric analysis (TGA) experiments on fuel samples. The enhanced reaction rates attributed to fragmentation were within the existing safety basis. Peer review comments for the Revision 0 version were incorporated.

*Fauske & Associates, Inc.

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Printed in the United States of America. To obtain copies of this document, contact: Document Control Services, P.O. Box 950, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

Release Approval 1/24/00
Date

Approved for Public Release

FAUSKE & ASSOCIATES, INC.
CALCULATION NOTE COVER SHEET

SECTION TO BE COMPLETED BY AUTHOR(S):

Page <u>1</u>	
Calc-Note Number <u>MGP111799</u>	Revision Number <u>2</u>
Title: <u>Fuel Fracture (Crumbling) Safety Impact</u>	
Project <u>Hanford Spent Nuclear Fuel</u>	Project No. or Shop Order <u>DESH02</u>
Purpose: Use moist air TGA data to evaluate reaction rate impact of fuel crumbling.	
Results Summary: Effects of crumbling are within the existing SNFP safety basis.	
References of Resulting Reports, Letters, or Memoranda (Optional): None	
Author(s):	Completion
Name (Print or Type)	Signature Date
<u>Martin Plys</u>	<u>M. Plys</u> <u>12/21, 1999</u>

SECTION TO BE COMPLETED BY VERIFIER(S):

Verifier(s):	Signature	Completion Date
Name (Print or Type)		
<u>Michael Epstein</u>	<u>Michael Epstein</u>	<u>12.21.1999</u>
Method of Verification: Design Review <u>Independent Review</u> or Alternate Calculations <u>or</u> Testing		
Other (specify)		

SECTION TO BE COMPLETED BY MANAGER:

Responsible Manager:	Signature	Approval Date
Name (Print or Type)		
<u>Martin Plys</u>	<u>M. Plys</u>	<u>12/21 1999</u>

CALCULATION NOTE METHODOLOGY CHECKLIST

CHECKLIST TO BE COMPLETED BY AUTHOR(S) (CIRCLE APPROPRIATE RESPONSE)

1.	Is the subject and/or the purpose of the design analysis clearly stated?	<u>YES</u>	NO	
2.	Are the required inputs and their sources provided?	<u>YES</u>	NO	N/A
3.	Are the assumptions clearly identified and justified?	<u>YES</u>	NO	N/A
4.	Are the methods and units clearly identified?	<u>YES</u>	NO	N/A
5.	Have the limits of applicability been identified?
(Is the analysis for a 3 or 4 loop plant or for a single application.)	<u>YES</u>	NO	N/A
6.	Are the results of literature searches, if conducted, or other background data provided?	<u>YES</u>	NO	N/A
7.	Are all the pages sequentially numbered and identified by the calculation note number?	<u>YES</u>	NO	
8.	Is the project or shop order clearly identified?	<u>YES</u>	NO	
9.	Has the required computer calculation information been provided?	YES	NO	<u>N/A</u>
10.	Were the computer codes used under configuration control?	YES	NO	<u>N/A</u>
11.	Were the computer code(s) used applicable for modeling the physical and/or computational problems identified?
(Is the correct computer code being used for the intended purpose.)	YES	NO	<u>N/A</u>
12.	Are the results and conclusions clearly stated?	<u>YES</u>	NO	
13.	Are Open Items properly identified	YES	NO	<u>N/A</u>
14.	Were approved Design Control practices followed without exception?
(Approved Design Control practices refers to guidance documents within NSD that state how the work is to be performed, such as how to perform a LOCA analysis.)	YES	NO	<u>N/A</u>
15.	Have all related contract requirements been met?	<u>YES</u>	NO	N/A

NOTE: If NO to any of the above, Page Number containing justification: _____

Fauske & Associates, Inc.

DATE: December 21, 1999

TO: Darrel Duncan, Jim Frederickson, Al Pajunen, and Joe Swenson, Hanford
Spent Nuclear Fuel Project

FROM: Martin Plys *M. Plys*

SUBJECT: Fuel Fracture (Crumbling) Safety Impact

1.0 SUMMARY

This memorandum evaluates the safety impact of experimentally observed N reactor fuel sample fracture and fragmentation using a technique that relies solely upon observations and is independent of theories for underlying cause. Data and theories are briefly summarized to introduce and motivate the approach.

Moist helium thermogravimetric analysis (TGA) data are used to derive an average reaction rate which is above average, i.e. an average enhancement factor. The frequency of the above-average reaction rates is also derived. Combining these leads to an overall enhancement factor to apply, regardless of fundamental cause.

The analysis is not claimed to be statistically robust because TGA experiments were not designed to look for fragmentation or its effects, and because variability is expected in the character of samples, so that the number of observations necessary to draw precise quantitative conclusions is not known. However, the effect of fragmentation based on current experimental data is small compared with the safety margin used in SNFP calculations.

An extra factor of 1.0 should be added to the reaction rate to account for peak reaction rates observed in TGA experiments. For example, when a safety-basis factor of 10 is applied to

reaction rates, $10 + 1 = 11$ would be appropriate for a long-term average. In contrast the current safety basis was made using an incremental factor of 12 to account for rapid weight gain events, so SNFP safety basis calculations for cold vacuum drying employ an overall enhancement factor of $10+12 = 22$. So the extra contribution due to above-average reaction rates is an order of magnitude less than the factor applied for rate law uncertainty, and an order of magnitude less than the incremental factor applied for rapid reaction rates.

An underlying cause of fragmentation is believed by the present author, and by authors of reference documents, to be oxidation. The rate and amount of fragmentation is therefore lower at CVD temperatures than at temperatures used for moist helium TGA experiments. Therefore the present assessment, using these TGA data, is conservative.

Fragmentation implies an increase of reaction area with time. The area increase is directly proportional to the amount of oxidation, presuming that oxidation is an underlying cause. Therefore, any increases in reaction rate to account for this effect should be initially zero in a calculation. The safety basis rate law multipliers discussed above are applied at all times during calculations, and therefore the calculations are conservative.

2.0 N REACTOR FUEL SAMPLE FRACTURE AND FRAGMENTATION DATA

2.1 Summary of Observations and Inferences

Oxidation rate data for N reactor fuel in dry air and moist helium atmospheres were obtained at PNNL using TGA and are reported in [Trimble, 1999] and [Abrefah, 1999]. Oxidation and fuel fracture with partial fragmentation, colloquially called crumbling, are also discussed by [Ballinger, Loscoe, and DeVine, 1999].

Oxidation rates for N reactor fuel in moist helium follow first-order Arrhenius kinetics as expected a priori. However, values for the rates fall somewhat below literature values. This is explained in the references as a result of some oxygen contamination in the system. For practical purposes, N reactor fuel oxidation rates in moist helium are therefore well-represented by literature values.

In moist helium atmospheres, specimen fracture and partial fragmentation was observed in some TGA experiments conducted at 160 °C and above, but not in experiments at lower temperatures. In particular fracture occurred in TGA runs 80, 81, and 82 at a nominal 160 °C.

Various hypotheses have been postulated for fracture and are described in the following section. TGA experiments were not designed to investigate fracture or provide data to support model development. For example, it is difficult to infer when fracture occurred. In TGA 80, a period of relatively high rate of weight gain, followed by a slight but noticeable change in slope, is evident at about 1300 minutes. This is an expected signature of fracture with partial fragmentation. Unfortunately, the rate of weight gain in TGA 82 was relatively constant, and the weight gain history for TGA 81 was marred by a series of weight loss events.

Observations pertinent to this work are:

1. While there appears to be a temperature threshold effect for fracture and fragmentation, this could be an artifact of experiment duration. It is difficult to tell from the data whether the threshold should really be a relationship between time and temperature. Fragmentation was observed at about the same temperature range for moist helium experiments and dry air experiments.
2. Fragmentation is localized to portions of the specimens, although we cannot a priori discern whether experimental duration or sample characteristics are a cause. There are generally distinct portions of the original specimen that did not crumble, even on originally exposed surfaces, and crumbled fragments that therefore represent a fraction of the original specimen.
3. Fragment sizes are generally visible to the naked eye and are orders of magnitude greater than the fuel grain size.
4. New surface area of fuel fragments is comparable to the original specimen reactive area. This is based on a visual estimate of the fraction of specimen mass that is fragmented, and observations of particle size discussed below. The implication here is that it is difficult to conclusively infer a fragmentation event from inspection of sample weight gain history. Also, experiment duration may influence this observation.
5. It is difficult to determine if fracture is a discrete event during TGA tests, or a series of events that approximates a continuous process. For example, the weight gain history of TGA 80 suggests one major such event and a few minor events, while TGA 81 has continuous noise that suggests frequent fragmentation. TGA 82 data appear to have similar noise, but are not plotted on an appropriate scale to compare with TGA 81.

As a final note on the observations, because the rate of weight gain per unit area is constant for steady state uranium reacting with water vapor, a change in the reactive area during an experiment logically implies a nonlinear weight gain history. For example, if reactive area changed in direct proportion to the amount of oxidation, a quadratic weight history curve would be observed. On the other hand, the extra area of crumbled surfaces in TGA 80, 81, and 82 is stated above to be comparable to the original area, so this effect is not easy to discern in existing experimental data.

2.2 Particle Size Data

A combination of weight gain and particle size data are available at this time for TGA tests conducted in moist helium at a nominal 160 °C; these are TGA runs 80, 81, and 82. These data are:

Table 2-1. TGA Data for Runs at 160 °C in Moist Helium

TGA Run	Surface Area, cm ²	Initial Weight mg	Weight Gain mg	Average Particle Size micron
80	1.24	1626	33	852
81	1.59	2649	3*	1160
82	1.94	3244	36	896

*Partial sample loss during experiment.

Note that in TGA 81 the oxidation rate obtained during time periods without sample loss was between values obtained for runs 80 and 82.

Figure 2-1 contains a particle histogram from combined TGA runs 80, 81, and 82 data reported by [Abrefah, 1999]. The largest particles, near and above 4000 microns, account for most of the mass and surface area. The average size reported by Abrefah and appearing in Table 2-1 is the numerical average of data in Figure 2-1. The surface area mean particle size turns out to be larger than the numerical average by a factor of about two, and it is this value which is of interest in extrapolating reactive area from experiment to application.

Figure 2-1. Particle counts from PNNL TGA runs 80, 81, 82.

The fraction of material that is crumbled is not available. Ballinger, Loscoe, and DeVine have opined that about 1/3 of the sample mass is fragmented based on post-test photographs for TGA 80 and 81, and about 3/4 for TGA 82.

The new reaction area due to fragmentation can be estimated from the above figures. For TGA 80, using an average particle diameter of 850 microns = 0.085 cm, the area/volume ratio is $A/V = 6/d = 71 \text{ cm}^{-1}$. The crumbled volume is estimated using the fraction of 1/3, yielding $1/3 * 1.626/19 = 0.028 \text{ cm}^3$. The particle area is the product of these values, about 2.0 cm^2 , which is a factor of 1.6 larger than the original area of 1.24 cm^2 . Since the particle area is comparable to the original reaction area, it is difficult to discern the effect of fragmentation during the course of these TGA experiments.

3.0 HYPOTHESES FOR FUEL FRACTURE AND FRAGMENTATION

Two hypotheses for fuel fracture and fragmentation are presented to date, those of [Ballinger, Loscoe, and DeVine, 1999] and [Abrefah, 1999]. The former hypothesis, known hereafter as the Technical Assistance Group (TAG) crumbling model, is developed into a mathematical model for application to TGA experiments and MCO behavior. The latter hypothesis, known hereafter as the PNNL crumbling concept, consists of a mechanistic cause for fragmentation but is not quantified into a mathematical model at the present time.

3.1 PNNL Concept

In the PNNL concept, microcracks are present in the uranium matrix of corroded or damaged regions of N reactor fuel. These cracks have been observed and are clearly seen in photomicrographs [Marschman, Pyecha, and Abrefah, 1997] to extend on a scale of at least millimeters through fuel. The PNNL concept is that these microcracks are the underlying contributor to fracture and fragmentation of samples during oxidation. These cracks propagate during oxidation; cracks are initially much larger than grain sizes, and cracks may also propagate along grain boundaries. Particulate varies in size depending on the density of the crack network.

Not stated, but evidently implied by the PNNL references, oxidation in the cracks causes stresses which cause crack propagation and ultimately fragmentation. Stresses are due to the low density of the oxide product compared to that of the metal, about a factor of two. Buildup of oxide in the cracks causes stresses that cannot be borne by the small samples which are not constrained mechanically, for example by cladding.

3.2 TAG Model

The TAG crumbling model also identifies stresses due to oxidation as the mechanism for fragmentation. Fuel is represented as an ensemble of "cells" that correspond roughly to the grain size of the material. Residual stresses from irradiation damage exist but are balanced in the fuel before oxidation. Oxidation along cell boundaries increases the stress and causes crack tip propagation. A crack propagates when the "oxide wedge" between adjacent cells has grown to a critical thickness called the crack tip opening displacement, or CTOD. When this threshold amount of oxide is built up, a fuel fragment is released. The fuel fragment size is much greater than the cell size, and corresponds to observations.

The model assumes that fragmentation occurs on a fraction of the original specimen exterior reactive surfaces that is not a priori known because the residual stresses are not a priori known. For the same reason, it is not possible to a priori predict whether a given specimen will fragment. Parameters that determine the CTOD are shown to depend strongly on physical properties and irradiation-induced effects that are not a priori known, and this explains the high variability in TGA results. For example, this explains qualitatively why it is possible to observe

fragmentation during TGA 80, 81, and 82, but not at experiments conducted at higher temperature.

On the bottom line, the TAG model predicts a direct proportion between the amount of crumbling and the amount of oxidation. Specifically, the model can be manipulated to derive the ratio: (grams crumbled material) / (grams weight gain due to oxidation). This means that the precise temperature history of a specimen or of fuel in an MCO is not important, just the cumulative effect of all oxidation. The ratio is not dependent upon fragment size. It does depend on two parameters that are difficult to determine, the cell size, which is set equal to the grain size, and a parameter known as the crack tip opening displacement, which is derived from further parameters. Also the TAG model predicts a ratio of new surface area produced per unit of weight gain due to oxidation, and this ratio is directly proportional to fragment size.

4.0 APPLICATION OF FRACTURE DATA TO SNF PROCESS SAFETY

4.1 Discussion of Data and Models

Both the PNNL concept and the TAG model have in common an appeal to variability in fuel character, whether this is in the density of cracks or in variation of the required crack tip opening displacement. We cannot a priori know these facts for a given specimen. A fuel assembly is for practical purposes an ensemble of hundreds of specimens, and a fuel or scrap basket is for practical purposes an ensemble of thousands of specimens. Fragmentation can occur at different times in different locations. We seek an overall average effect of fragmentation events that occur randomly.

A key feature shared by the PNNL concept and TAG model is that the rate of crumbling should depend on temperature because oxidation is the underlying cause. We unfortunately do not have sufficient data at this time to quantify temperature dependence. However, if oxidation

is an underlying cause of fracture, then it is reasonable to expect that the Arrhenius temperature dependence of oxidation would be followed.

The effect of fuel fracture is to increase reactive surface area and to increase the reaction rate for a brief period of time, as exemplified by TGA 80 data. Thus a given location in fuel normally has the nominal reaction rate, but periodically endures an increased reaction rate. As pointed out above, increased reaction area implies a cumulative increase in reaction rate, but such an effect has not been quantified using existing TGA data.

One way to account for these features in safety analysis is simply to multiply the correlation-based reaction rate law by a factor that represents either the effect of peak reaction rates or a cumulative reaction rate increase. If a rate law multiplier is used, then a temperature effect is automatically considered.

4.2 Temperature Effect on Fracture

Experimentally observations of fuel fracture can be related to expected behavior in an MCO through the oxygen-free uranium-water vapor reaction rate law:

$$K(T,P) = P^{1/2} 2.14 \cdot 10^4 \exp\left(-\frac{4937}{T}\right)$$

K = Weight gain, mg/cm² / hr

P = Water Vapor Pressure, kPa

T = Temperature, K

Given that the time to fracture depends upon cumulative oxidation, the times to first fracture at any two temperatures (when steam partial pressure is equal) are related by

$$\frac{t}{t_0} = \exp\left[4937\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

For example, relating the temperatures at CVD ($T = 75\text{ }^{\circ}\text{C} = 348\text{ K}$) to those in TGA 80, 81, and 82 ($T_0 = 160\text{ }^{\circ}\text{C} = 433\text{ K}$) yields $t / t_0 = 16$. The ratio of rates would be higher if the steam pressure varied with pressure according to the saturation line. Note that experimentally used steam pressures, about 7 kPa, are typical of the steam pressure expected during vacuum drying.

Therefore, an expected time to fracture during cold vacuum drying is about an order of magnitude longer than the fragmentation time of TGA experiments where fragmentation was clearly observed. Also, the cumulative amount of fragmentation during cold vacuum drying should be an order of magnitude less than observed in TGA experiments. Bear in mind that we cannot conclusively tell the characteristic time to fragmentation in TGA experiments. However, any model based solely upon the observations must be conservative. The extent of conservatism is estimated to be about an order of magnitude, based upon the above discussion.

4.3 Peak Observed TGA Reaction Rates

For present purposes, it is sufficient to compare a bounding rate of above-average reaction to the safety basis rate previously given for rapid reactions. Base reaction rates (literature correlations) are increased by a factor of 10 to account for uncertainty in SNFP calculations. An incremental factor of 12 is added to account for above-average reaction rates that may periodically occur. The total rate used in the safety basis is the sum of the constant and rapid reaction effects, $10 + 12 = 22$.

Data for this assessment were assembled by the SNFP [Pajunen, 1999] and are shown in Appendix A. Pajunen compared peak rates of weight gain with the reported average constant rate of weight gain for all the moist air TGA experiments, including those where extensive crumbling was not observed. All these peak rates will be considered here.

Consider first TGA experiments 80, 81, and 82 which were described in detail above. The highest peak rate in TGA 80 was 21 times the average, over a duration of about 50 minutes, or 2% of the total experiment duration. Other peak to average rate ratios are much lower. The frequency-averaged peak rate ratio may be defined by summing each individual rate ratio times

its duration and normalizing by all above average durations: $\sum R_i \Delta t_i / \sum \Delta t_i$. The result for TGA 80 is an average of 3.60 over a total duration of 700 minutes out of 2700 minutes. One way to translate this to an average over the whole experiment is to derive an effective incremental rate multiplier for the whole experiment as $\sum (R_i - 1) \Delta t_i / t_{\text{exp}}$. Applied to TGA80 this yields $(700/2700) * (3.60 - 1.0) = 0.68$ or about 0.70. This ignores times when the overall reaction rate is below average. Clearly an extra incremental factor of 1.0 on the rate, to multiply an effective rate of reaction by 2.0, bounds the effect of these above-average rates when applied over the duration of a whole experiment. Examining TGA 81, only modest increments of a factor of 1.3 above average were observed, and this is not worth further pursuit to establish bounding behavior. Examining TGA 82, a frequency-averaged above-average rate is by inspection about 1.7 (it is somewhat lower) and again results from TGA 80 bound these.

Turning to other experiments, the highest ratio of peak to average rates is 41, and it occurred for 50 minutes out of 8600 during TGA 95, i.e. less than 1% of the duration of this single experiment alone. TGA 95 in fact has the highest set of peak to average rates among those in the table, and provides a bounding case. The frequency-averaged peak rate ratio is about 4. These occur over a total of 2850 minutes out of 8600, i.e. about 1/3 of the experiment. So the time-averaged value of all above average rates is only about $(2850/8600) * (4 - 1) = \text{about } 1.0$.

The next highest above average rate is found in TGA 77, where a rate ratio of 33 is observed for 25 minutes out of 4700, or about 0.5% of the experiment duration. For TGA 77, the frequency-averaged peak rate is 3.1. The total duration of these above average rates is 2175 minutes out of 4700 total minutes, about 46% of the total time, so the time-averaged value of all above-average events is about $(2175/4700) * (3.1 - 1) = \text{about } 1.0$ again.

Without performing a detailed analysis of every experiment, it is clear that an enhancement factor of 2 bounds the observations. That is, the above-average increment is bounded by an increment of 1.0, and above-average rates are bounded by a factor equal to the underlying rate.

The incremental factor of 1.0 derived here is much less than the incremental factor of 12 derived in the reference document for the safety basis. Even the largest average of above-average rates, about 4.0 from TGA 95-- without regard to the fact that this should only be applied to a fraction of the time -- is still below the incremental factor of 12 used in the safety basis.

Based on the assessment above, there is no need to examine these reaction rates in the same level of detail as in the reference.

For the following reasons, I conclude that fuel reaction rates due to fragmentation during cold vacuum drying are within the existing SNFP safety basis:

1. Extrapolating experimental data, the time to fuel fracture and accompanying fragmentation during cold vacuum drying is about an order of magnitude greater than observed in experiments. Therefore, an experimentally-based approach is conservative.

2. Examining experimental data for the frequency and magnitude of above-average reaction rates, the peak above-average reaction rate (while above-average reactions occur) is about 4 times the average reaction rate. This is within the incremental factor of 12 used in the current safety basis. Considering the frequency of above-average reactions, an increment of 1.0, equal to the average, should be applied.

3. Experimental data imply an increase of reactive area about equal to the original reactive area over a duration equal to that of cold vacuum drying, and at much higher temperature. This is equivalent to an incremental factor of 1.0.

4. The analysis is recognized to not be statistically rigorous because TGA experiments were not designed to look for or quantify effects of fragmentation. For this reason a numerical analysis of all the data was not conducted here, only worst case examples were chosen. However, experimental observations are well within the current safety basis which assumes a rate law uncertainty factor of 10 plus a rapid reaction contribution of 12, for a total of $10+12 = 22$.

The incremental factor of 1.0 suggested by experimental data is an order of magnitude less than either contribution to the safety basis.

5.0 REFERENCES

- Abrefah, J., PNNL, letter to D.J. Trimble, Numatec Hanford Company, Letter Report: Particle Sizes of Disintegrated SNF Samples from TGA Oxidation Testing in Moist Helium, Sep. 17, 1999.
- Abrefah, J. and Sell, R.L., Oxidation of K-West Basin Spent Nuclear Fuel in Moist Helium Atmosphere, PNNL-12167, Pacific Northwest National Laboratory, Richland, WA, 1999.
- Ballinger, R.G., Loscoe, P.G., and DeVine, J.C., N Reactor Spent Nuclear Fuel Crumbling: Analysis and Modeling, SNFPR 99-01, Rev. 3, Nov. 18, 1999, EDT # 628219.
- Duncan, D.R., and Plys, M.G., Simulation of Normal and Off-Normal Multi-Canister Overpack Behavior, HNF-2256, Rev. 2, DE&S Hanford, Inc., Richland, WA, 1998 (b).
- Marschman, S.C., Pyecha, T.D., and Abrefah, J., Metallographic Examination of Damaged N Reactor Spent Nuclear Fuel Element SFEC5,4378, PNNL-11438, Pacific Northwest National Laboratory, Richland, WA, 1997.
- Pajunen, A.L., Rapid Reaction Episodes from N Reactor Fuel Oxidation Tests in Moist Helium, SNFP Memorandum to J.R. Frederickson, 99-SNF/ALP-001, Numatec Hanford, Richland, WA, Nov. 11, 1999.
- Trimble, D.J., Oxidation Kinetics of K Basin Fuel, HNF-4206, Duke Engineering & Services Hanford, Inc., Richland, WA, March, 1999.

APPENDIX A. Excerpt from "Rapid Reaction Episodes from N Reactor Fuel Oxidation Tests in Moist Helium" by A.L. Pajunen [Pajunen, 1999].

J. R. Frederickson
Page 2
November 11, 1999

99-SNF/ALP-001

Table 1. Summary of Potential Rapid Reaction Episodes in Moist Helium TGA Experiments

Run	Temperature, °C	Total Run Duration, min	Episode	Duration, min	Episode Rate, mg/min	Episode Rate Run Linear Rate
80	161	2700	1	100	0.068	5.3
			2	50	0.267	21
			3	125	0.031	2.5
			4	150	0.020	1.6
			5	275	0.018	1.4
81	161	2580	1	50	0.0182	1.3
			2	50	0.0176	1.3
82*	160	2700	1	100	0.022	1.6
			2	100	0.024	1.7
			3	100	0.024	1.7
			4	100	0.024	1.7
			5	100	0.024	1.7
			6	100	0.024	1.7
			7	150	0.0146	1.1
			8	50	0.0189	1.4
			9	100	0.0189	1.4
			10	100	0.0227	1.6
83	100	3050	1	50	0.0017	1.3
84	99	2950	1	150	0.0024	2.0
			2	75	0.0014	1.2
			3	50	0.0026	2.2
85	99	2950	1	250	0.0013	3.3
			2	300	0.0013	3.3
			3	100	0.0056	14
			4	520	0.0007	1.8
			5	75	0.0014	3.5
86	133	2900	1	100	0.0028	1.2
			2	50	0.0056	2.3
88	162	2700	No episodes with slope greater than rate reported for test			
89*	163	2700	1	150	0.0065	1.4
			2	150	0.0058	1.2
91*	134	2900	1	350	0.0031	2.6
			2	500	0.0015	1.2
			3	100	0.0039	3.3
			4	100	0.002	1.7
92*	105	2900	1	750	0.0008	1.3
			2	450	0.0011	1.8
			3	225	0.002	3.3

J. R. Frederickson

99-SNF/ALP-001

Page 3

November 11, 1999

Run	Temperature, °C	Total Run Duration, min	Episode	Duration, min	Episode Rate, mg/min	Episode Rate Run Linear Rate
93*	75	5800	1	200	0.0069	17
			2	350	0.0006	1.5
			3	200	0.0005	1.2
			4	150	0.0006	1.5
			5	100	0.0007	1.8
94*	77	8600	1	500	0.0006	2.0
			2	300	0.0008	2.7
			3	200	0.0009	3.0
			4	400	0.0007	2.3
			5	75	0.0025	8.3
			6	300	0.0005	1.7
			7	100	0.003	10
95*	78	8600	1	400	0.0007	2.3
			2	50	0.0123	41
			3	200	0.0013	4.3
			4	300	0.0022	7.3
			5	150	0.0027	9.0
			6	1600	0.0005	1.7
			7	150	0.0024	8.0
96*	211	500	1	30	0.0357	1.3
97*	211	500	1	120	0.0188	1.2
98*	129	2900	1	125	0.0048	2.1
			2	575	0.0028	1.2
			3	375	0.0029	1.3
75*	169	2150	1	150	0.0155	1.2
77*	108	4700	1	25	0.0114	33
			2	550	0.0011	3.1
			3	350	0.0011	3.1
			4	450	0.0008	2.3
			5	350	0.0012	3.4
			6	150	0.001	2.9
			7	300	0.0006	1.7
79*	132	2750	1	100	0.0081	12
			2	150	0.0033	4.9
			3	375	0.0025	3.7
			4	200	0.0021	3.1
			5	225	0.0043	6.4
87*	162	2700	1	150	0.0109	2.8
			2	400	0.0051	1.3
			3	250	0.0046	1.2
90*	162	1450	1	130	0.0137	1.8

* - Rapid reaction episodes may be attributed to noise or drift in the experimental apparatus.

REVIEW COMMENT RECORD (RCR)

1. Date 12/9/99	2. Review No.
3. Project No. SNF Project	4. Page 1 of 4

5. Document Number(s)/Title(s) SNF-5488/Fuel Fracture (Crumbling) Safety Impact (OCRWM)	6. Program/Project/ Building Number SNF Project/MO285	7. Reviewer Dr. D. R. Olander	8. Organization/Group Process Engineering	9. Location/Phone MO285/A-167/372-1013
---	---	----------------------------------	--	---

17. Comment Submittal Approval:

10. Agreement with indicated comment disposition(s) 11. CLOSED

Organization Manager (Optional)

Date 1/19/00 Reviewer/Point of Contact Author/Originator

1/19/00 Date Reviewer/Point of Contact Author/Originator

12. Item	13. Comment(s)/Discrepancy(s) (provide technical justification for the comment and detailed recommendation of the action required to correct/ resolve the discrepancy/problem indicated.)	14. Hold Point	15. Disposition (provide justification if NOT accepted.)	16. Status
1	<p>The document's assessment that oxidation is the underlying cause of fragmentation is reasonable, although it leads to the following logical inconsistency: The rate of oxidation is proportional to the exposed surface area of the specimen multiplied by the rate given by the equation on p. 11. The quantity of exposed area is a function of oxidation (p. 4, 2nd paragraph). If both of these are true, the weight-gain rate is given by:</p> $M = A(m)K(T,p)$ <p>Where $A(m)$ is the area for reaction as a function of the extent of prior oxidation, m. Integration of this equation (if the function $A(m)$ were known) would give a nonlinear relation between m and t, in contradiction to the observed linear kinetics.</p>		<p>Yes, indeed, if you use the Ballinger model, you get quadratic kinetics.</p>	DO

REVIEW COMMENT RECORD (RCR)

1. Date 12/9/99	2. Review No.
3. Project No. SNF Project	4. Page 2 of 4

12. Item	13. Comment(s)/Discrepancy(s) (Provide technical justification for the comment and detailed recommendation of the action required to correct/resolve the discrepancy/problem indicated.)	14. Hold Point	15. Disposition (Provide justification if NOT accepted.)	16. Status
2	The statement on the bottom of p. 2 is puzzling. It asserts that fragmentation occurs during tests at 160°C but not at lower temperatures. Reading the manuscript gives the strong impression that the high-rate 'episodes' listed in Table 1 (pp. 17 and 18) are the result of fuel fragmentation. If this interpretation is correct, the episodes in runs 93, 94, 95, and others suggest that fragmentation occurred during these tests. Yet all were oxidized at temperatures less than 160°C. If the high-rate episodes in the low-temperature tests were <u>not</u> due to fragmentation, what was the cause?		Yes, this is a contradiction. I'm really just using above average rates whether or not I believe fragmentation occurred, and this can be clarified.	<i>SA</i>
3	I assume that the meaning of the last column in Table 1 is episode rate divided by run linear rate. Is this correct? By the way, a linear rate means that the weight increases as t. I think the term 'run linear rate' means a constant rate and a linear rate gain with time.		Ok, we mean a constant rate of weight gain. Will clarify.	<i>SA</i>
4	Section 3 contributes nothing of significance to the report. One model is qualitative and the other is quantitative but unusable because of lack of input properties and the nondeterministic nature of fragmentation. This section, along with Section 4.1, should be deleted. Its removal would not affect the assessment of the fragmentation effect on the oxidation rate, which eventually is based on examination of the data, not on theories. The discussion of Poisson, binomial, and normal distributions, transition state probabilities and Markov processes is reminiscent of medieval scholars' attempts to determine the number of angels that fit on the head of a pin.		Section 3 was present to briefly describe the PNWL and TAG interpretations in one place, and it will be kept. Section 4.1 is supposed to be used to help us define the maximum rate we ever need to consider. Instantaneously, a given location can be reacting at a higher than average rate. Why not for safety calculations assume all surfaces can react at much higher than normal rates at the same time?..because these are independent events. The discussion appears like rambling to you because it relates to similar discussions we had about two years ago on this topic. I will revise the discussion.	<i>SA</i> m1

REVIEW COMMENT RECORD (RCR)

1. Date	2. Review No.
12/9/99	
3. Project No.	4. Page
SNP Project	3 of 4

5	<p>The variable P in the equation on p. 11 is defined as the vapor pressure (of what?). Shouldn't p be the partial pressure of water vapor in the gas? This equation is used to determine the ratio of the time-to-fracture at two temperatures. It should be stated that the premise is that fracture occurs when the specimen gains a critical mass of oxygen, m*, which is assumed to be independent of temperature. This the fracture times at different temperatures are related by:</p> $M^* = K(T)t = K(T_0)t_0$ <p>From which the equation on the bottom of p. 11 follows.</p>	<p>Yes. Also I agree on the critical mass needed for first rupture.</p>		
6	<p>This equation predicts that the time-to-fracture at 75°C should be 16 times that at 160°C. It is then claimed that the expected fragmentation time during CVD is an order of magnitude longer than that observed in experiments. This statement implies that there exists somewhere measurements on the fracture times in the TGA tests. If so, why were they not included in the report?</p>	<p>True, there is no measured fracture time. Will reword.</p>		
7	<p>Table 1 only gives the duration of the high-rate episodes without indicating when during the run they started. For example, did the first episode in run 93 start near time zero or towards the end of the run? Without this information, it is impossible to verify that fragmentation times have ever been observed.</p>	<p>True, although now the mission has mutated into simply tallying the above-average rates. I'll mention this point but proceed as before.</p>		
8	<p>The second paragraph on p. 12 is a collection of caveats and mystifying claims. What are the 'fundamental reasons' that fragmentation will be slower in CVD than in the TGA experiments (at the same temperature)?</p>	<p>Bottom line is that temperature is lower at CVD. I'll focus on this point.</p>		

SNF-5488
m1

REVIEW COMMENT RECORD (RCR)

1. Date 12/9/99	2. Review No.
3. Project No. SNF Project	4. Page 4 of 4

9

The discussion on the peak TGA reaction rates suggests that the high-rate periods do not result in a very large (i.e., >2) factor of oxidation enhancement. I agree with this claim, but believe it can be made more clearly quantifiable by the following analysis.

Let:

M_{avg} = average constant oxidation weight gain rate in an experiment

T_r = total run duration

M_r = weight gain rate during a high-rate episode

T_i = duration of the episode

$M_{avg}T_r$ = total weight gain in the absence of high-rate episodes

$(m_i - m_{avg})t_i$ = weight gain during high-rate episode in excess of normal weight gain during the period of the high-rate

Summing the latter over all episodes observed during a run and dividing by the former gives a gain factor for the run. This quantity is defined as the total excess oxidation due to fragmentation divided by the normal oxidation that would have been observed had the specimen remained intact:

$$\text{Gain factor} = \frac{\sum_i (m_i - m_{avg})t_i}{m_{avg}T_r} = \sum_i \left(\frac{m_i}{m_{avg}} - 1 \right) \frac{t_i}{T_r}$$

The last column in Table 1 in the report gives m_i/m_{avg} and t_i/T_r is obtained by dividing the times in column 5 by those in column 3. With this algorithm, it is straightforward to provide a quantitative measure of the fragmentation-induced oxidation. The following table shows the gain factors for three of the runs in Table 1:

TGA Run No.	Gain factor
80	0.67
95	0.98
77	1.34

As can be seen from the above table, the gain factors are about unity. This means that excess oxidation due to fragmentation roughly doubles the weight gain that would have occurred in a nonfragmenting specimen.

Looks interesting. I may adopt this.
Thanks!

SNF

SNF.5488
m1