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U.S. Nuclear Regulatory Commission
Washington, DC 20555

28 July 2003
DCS-NRC-000151

Subject: Docket Number 070-03098
Duke Cogema Stone & Webster
Mixed Oxide (MOX) Fuel Fabrication Facility
Response to DSER Open Item CS-02

Reference: (1) Internal Memo from Dave Brown (NRC) to Kathy Halvey Gibson (NRC), *July 24, 2003 Summary of Phone Call with the Applicant: Resolution of Open Items in the April 30, 2003 Draft Safety Evaluation Report for the Mixed Oxide (MOX) Fuel Fabrication Facility*

Please find enclosed, responses to the questions identified in the in-office review conducted last week (22 & 23 July 2003) and documented in your letter dated 25 July 2003 Reference 1.

If you have any questions, please feel free to contact me at (704) 373-7820.

Sincerely,

Vincent Chevalier

for

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Enclosures: (1) Response to NRC Staff Questions regarding DSER Open Item CS-02

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Enclosure 1
Response to NRC Staff Questions Regarding DSER Open Item CS-02

Question 1:
For chemical concentrations and temperatures what are the design basis values? Provide a basis for the values, including the safety margin.

Response to Question 1:
DCS has identified design basis values for concentrations and temperatures to preclude an autocatalytic reaction between HAN and nitric acid. These values are provided in Table I.

Table I Design Basis Values

Temperature	50 C
HNO_3	6 M
HAN	1.9 M
N_2H_4	0.10
Pu	not limited

Note: For the purposes of determining the design basis values to preclude an autocatalytic reaction between HAN and nitric acid, the design basis value for hydrazoic acid previously identified in the Construction Authorization Request (CAR) was not specified i.e. the hydrazoic acid concentration is assumed to be zero due to the fact that it scavenges nitrous acid which stabilizes the system. However, the design basis value of 0.055 M still pertains to precluding a potential gas phase explosion involving hydrazoic acid.

The design basis values to preclude an autocatalytic HAN/nitric acid reaction were developed such that bounding values were selected for each parameter that affects the stability of the system e.g. nitric acid, hydrazine, HAN, and temperature. Thus, IROFS will be applied to each of the selected design basis parameters to ensure that the design basis value for each of the respective parameters is not exceeded. Furthermore, the design basis values were selected by simultaneously selecting worst case values for both the temperature and nitric acid and verifying that the system was stable for all concentrations of HAN and plutonium for a specified quantity of hydrazine. Additional detail on the safety margin provided by the DCS design bases is provided below.

The design basis values have been determined utilizing a kinetic model developed to predict the stability boundary for systems containing plutonium, HAN, hydrazine, and hydrazoic in conjunction with nitric acid. This model is based on an examination of each of the respective reactions that govern the system. The kinetic constants and rate equations are presented in Attachment A. These kinetic constants and rate equations are taken from previously published and peer reviewed experimental data. References for each of the respective reactions that govern the system are provided in Attachment B.

DCS has performed extensive statistical analyses of the kinetic data to verify the "goodness" of the fits for the reported rate constants. Furthermore, DCS has examined multiple fits to the data sets and examined the predictions of each of the respective fits on the predictions of the stability boundary. The determination of the "best" fits to the kinetic data is given by a comparison of the predictions of the kinetic model to the integral experiments that have been utilized to determine the instability

boundary. (These integral experiments have been utilized to develop the instability boundary presented in DOE/EH-0555.) In this manner the kinetic data and the rate equations are benchmarked to the global predictions of the experimental data utilized in deriving the instability index. The results of the benchmarking of the model are provided in Attachment C.

The safety margin given by the DCS selected design basis values may be best examined via a parametric analysis. This parametric analysis is presented in Attachment D. The results of this sensitivity analysis indicate the following:

- The system is insensitive to nitrous acid from concentrations ranging from $1x10^{-4}$ to $1x10^{-2}$ M. That is, the system is stable for all credible nitrous acid concentrations in the aqueous phase.
- The system is insensitive to the plutonium concentration.
- For fixed concentrations of HAN, hydrazine, and nitric acid e.g. parameters taken at their respective design basis values the system is stable up to a temperature of 68 C.
- For fixed temperature, hydrazine concentration, and nitric acid concentrations at their respective design basis values the system is stable for all HAN concentrations as may be seen from examination of Table 1 of Attachment D.
- For fixed temperature, nitric acid concentration and all HAN concentrations at their respective design basis values the system is stable with a minimum of 0.001 M hydrazine utilizing a nitrous concentration of $1x10^{-4}$ M. Table 3 of Attachment D presents the results of this investigation.
- For temperature and hydrazine concentration at their respective design basis values the system is stable for all HAN concentrations as long as the nitric acid concentration is less than 7.3 M.

Question 2:
Address HNO_2 as an initial condition relied upon in the safety assessment.

Response to Question 2:
DCS has performed a sensitivity analysis to study the effect of a range of concentrations of nitrous acid. The results of this study are given in Table 2 of Attachment C for the selected design basis values of temperature (50 C), nitric acid (6 M), HAN (1.9 M), and hydrazine (0.1 M). Investigations were also performed on the influence of plutonium to the system. These investigations did not reveal any departure from the reported results i.e. negligible change to the stability of the system. The results of the study indicate that for nitrous concentrations ranging from the expected values on the order of $1x10^{-4}$ to $1x10^{-2}$ the DCS design basis values have negligible impact.

Question 3:
Provide an explanation of the "path forward" including confirmatory laboratory tests, Monte Carlo modeling- that will validate the model and design basis values derived.

Response to Question 3:
DCS has extended the validation of the kinetic model by examination of additional experiments. The validation of the kinetic model with additional experimental results are provided in Response to Question 5. In addition, DCS plans to conduct testing to further substantiate the results of the model. This testing will examine the reaction mechanism and kinetics of nitric and nitrous acid with dinitrogen tetraoxide. DCS also plans to conduct testing to examine the reaction kinetics and

mechanism for reactions between nitrous acid, hydrazine, and HAN. The investigations will be performed under a range of temperatures (0-70 °C), HAN concentrations (1 mM to 2.5 M), and hydrazine concentration (0.1 mM to 0.2 M). In addition, the Pu redox behavior in nitric acid will be examined. Lastly, integral experiments that confirm the kinetic model predictions are necessary. The experimental techniques that may be utilized to quantify the above reactions and produce the requisite kinetic data for inclusion into the model are described in Attachment E (It should be noted that these are typical techniques available for use; specific selection of analytical techniques will be based a detailed evaluation at a later date).

Question 4:
Staff would like to see that DCS has performed parametric studies using the model, such as would be performed to define the design basis values [e.g. sensitivity analyses for HNO_2)

Response to Question 4:
Parametric investigations and sensitivity analyses have been performed. Attachments C and D provide this demonstration.

Question 5:
Has DCS compared model data with any experimental results other than those presented in Section 7.2 in the calculation.

Response to Question 5:
DCS has performed benchmarking of the kinetic model with additional experimental results. This benchmarking of the model is provided in Table 4 of Attachment C. From Table 4 it should be noted that the kinetic model is generally conservative with respect to the prediction of the maximum stable concentration of nitric acid relative to the predictions of the instability index. However, at extremely low temperature, conditions not expected to be seen at the MFFF within process cells, the kinetic model tends to over estimate stability. Additional investigations will be performed during the ISA to reconcile this behavior.

Question 6:
Explain why flow controls were removed as a design basis function in the May 30, letter.

Response to Question 6:
The May 30, 2003 DCS submittal provided a safety strategy for the safe use of HAN within the AP Process. This safety strategy included the PSSCs to address avoidance of autocatalytic HAN/nitric acid reactions where NO_x addition is performed. These PSSCs included both the chemical safety controls and the process off-gas treatment system. The safety function of chemical safety control is to limit the concentration of the HAN, hydrazine nitrate, nitric acid, and hydrazoic acid in the system ensuring the potential heat evolution and pressure increase do not exceed the design capabilities of the process vessel. The safety function of the off-gas treatment system is to provide an exhaust path for the removal of off-gases generated during the decomposition of these chemicals, which provides a means for heat transfer/pressure relief for affected process vessels.

Previously, the CAR contained an additional PSSC, the process safety control subsystem. The safety function of the process safety control subsystem was to control the liquid flowrate into the oxidation column, thereby regulating the quantity of HAN, hydrazine nitrate and hydrazoic acid added to the column ensuring the potential heat evolution and pressure increase do not exceed the design capabilities of the process vessel. However, this PSSC was removed due to the fact that an adequate selection of both the chemical safety controls and the off-gas treatment subsystem will ensure that control of the liquid flow rate into the oxidation column. Furthermore, as was previously noted the NOx addition also takes place in recycle tanks where the reagents are present. Hence flow control is not meaningful and thus safety is based on the identified PSSCs namely the off-gas treatment system and the chemical safety controls.

Differential System

$$\frac{\partial[Pu(IV)]}{\partial t} = -k_{redHAN}\frac{[NH_3OH^+]^2}{[H^+]^4(1+\beta[NO_3^-])^2}\frac{[Pu(IV)]^2}{[Pu(III)]^2} - k_{redHyd}\frac{[Pu(IV)][N_2H_4]}{K+[H^+]} + k_{reox}[H^+][NO_3^-][HNO_2][Pu(III)] \quad \text{(Eq. 1)}$$

$$\frac{\partial[HNO_2]}{\partial t} = \frac{3k_{aut1}[NO_3^-]}{\frac{k_{aut2}}{k_{aut3}} + 2[HAN]}[H^+][HNO_2][HAN] + k_{reox}[H^+][NO_3^-][HNO_2][Pu(III)] - \ldots \quad \text{(Eq. 2)}$$

$$\ldots - k_{hansc}[H^+][HNO_2][HAN] - k_{hydsc}[H^+][HNO_2][N_2H_4] - k_{hasc}[H^+][HNO_2][HN_3]$$

$$\frac{\partial[HAN]}{\partial t} = -k_{redHAN}\frac{[NH_3OH^+]^2}{[H^+]^4(1+\beta[NO_3^-])^2}\frac{[Pu(IV)]^2}{[Pu(III)]^2} - \left(\frac{k_{aut1}[NO_3^-]}{\frac{k_{aut2}}{k_{aut3}} + 2[HAN]} + k_{hansc}\right)[H^+][HNO_2][HAN] \quad \text{(Eq. 3)}$$

$$\frac{\partial[N_2H_4]}{\partial t} = -k_{hydsc}[H^+][HNO_2][N_2H_4] - k_{redHyd}\frac{[Pu(IV)][N_2H_4]}{K+[H^+]} - k_{nitric1}[H^+]^2[NO_3^-][N_2H_4] \quad \text{(Eq. 4)}$$

$$\frac{\partial[HN_3]}{\partial t} = k_{hydsc}[H^+][HNO_2][N_2H_4] - k_{hasc}[H^+][HNO_2][HN_3] - k_{nitric2}[HN_3] \quad \text{(Eq. 5)}$$

Kinetic Constants used to describe the system

- $k_{redHAN}(T) = 1.44*10^{22}*e^{-\frac{137,068}{RT}}$, in M^5sec^{-1}; $k_{hydsc}(T) = 2.70*10^{14}e^{-\frac{56,500}{RT}}$, in M^2sec^{-1};
  $\beta = 3.62*10^4*e^{-\frac{22,163}{RT}}$, in M^{-1} ;
- $k_{redhyd}(T,\mu) = 3.91*10^{-2}*e^{0.3422\mu}*e^{-\frac{124,909}{RT}}$, in sec^{-1} ; $k_{hasc}(T) = 8.52*10^{11}e^{-\frac{54,600}{RT}}$, in M^2sec^{-1};
- $k_{reox}(T) = 1.02*10^{10}e^{-\frac{58,520}{RT}}$, in M^3sec^{-1}; $k_{hansc}(T) = 1.75*10^7 e^{2.19\sqrt{\mu}-\frac{51,106}{RT}}$, in M^2sec^{-1};
- $k(T,[HNO_3]) = 1.61x10^{-3}.e^{0.2318[HNO_3]+0.091e^{0.1281[HNO_3]}T}$, in M^2sec^{-1}; $k_{nitric1}(T) = 2*10^9 e^{-\frac{108,680}{RT}}$, in $M^{-3}sec^{-1}$;
- $\frac{k_{aut2}}{k_{aut3}} << 2[HAN]$; $k_{nitric2}(T,[HNO_3]) = 1.1*10^8 e^{0.8447[HNO_3]-\frac{89,000}{RT}}$, in sec^{-1};

Attachment B
References for the Development of the Kinetic Model

1. Barney, G.S.; *A Kinetic Study of the Reaction of Plutonium(IV) with Hydroxylamine*, J. Inorg. Nucl. Chem., **38**, pp 1677-88 (1976).
2. Yarbro, S.L. ; Schreiber, S.B. ; Ortiz, E.M.; Ames, R.L.; *Reducing Pu(IV) to Pu(III) with Hydroxylamine in Nitric Acid Solutions*, J. of Radioanalytical and Nuclear Chemistry, **235** (1-2), pp 21-24 (1998).
3. Koltunov, V.S.; Zhuravleva, G.I. ; *Kinetics of Reduction of plutonium by Hydrazine II. Reduction of Pu(IV)*, Radiokhimiya, **20**, p 80-83 (1978).
4. Dukes, E.K.; *Kinetics and Mechanisms for the Oxidation of Trivalent Plutonium by Nitrous Acid*, **82**, pp 9-13 (1960).
5. Biddle, P.; McKay, H.A.C.; Miles, J.H.; *The Role of Nitrous Acid in the Reduction of Plutonium(IV) by Uranium(IV)in TBP Systems*, Proc. Int. Conf. on Solvent Extraction of Metals, Harwell, Macmillan, London, pp 133-60 (1965).
6. Garley, M.S.; Phelan, K.G.; Stedman, G.; *Nitrogen Tracer Studies, on the Decomposition of Hydroxylamine in Nitric Acid*, Chem. Soc. Dalton Trans., pp 2835-37 (1984).
7. Bennett, M.R.; Brown, G.M.; Maya, L.; Posey, F.A.; *Oxidation of Hydroxylamine by Nitrous and Nitric Acids*, Inorg. Chem., **21**, pp 2461-68 (1982).
8. Gowland, R.J.; Stedman, G.; *Kinetic and product Studies on the Decomposition of Hydroxylamine in Nitric Acid*, Journal of Inorganic Nuclear Chemistry, **43**, pp 2859-62 (1981).
9. Bourke, G.C.; Stedman, G.; *The Chemistry of the Hydrazine-Hydroxylamine-Nitric Acid System at High Temperatures*, J. Chem. Research (S), pp 684-5 (1999).
10. Barney, G.S.; *The Reaction of Hydroxylamine with Nitrous Acid*, ARH-SA-97 (1971).
11. Fitzpatrick, J.; Meyer, T.A.; O'Neill, M.E.; Williams, D.L.H.; *Comparison of the Reactivity of Nine Nitrous Acid Scavengers*, Chem. Soc. Perkin Trans. II, pp 927-32 (1984).
12. Perrott, J.R.; Stedman, G.; *The Kinetics of Nitrite Scavenging by Hydrazine and Hydrazoic Acids at High Acidities*, J. of Inorg. Nucl. Chem., **39**(2), pp 325-7 (1977).
13. Biddle, P.; Miles, J.H.; *Rate of Reaction of Nitrous Acid with Hydrazine and with Sulphamic Acid: its application to nitrous acid control in two-phase industrial systems*, J. Inorg Nucl. Chem. **30**, pp 1291-97 (1968).
14. Karraker, D.G.; *Oxidation of Hydrazine by Nitric Acid*, Inorg. Chem., **24**, pp 4470-77 (1985).
15. Maya, B.M.; Stedman, G.; *Decomposition of Hydrazoic Acid in Nitric Acid*, J. Chem. Soc. Dalton Trans. (1983).

Attachment C
Benchmarking the Kinetic Model with Instability Index

Benchmarking of Kinetic Model with the predictions utilizing the instability index are given in Tables 1 through 4. **Table 1** to **Table 3** present the maximum quantity of nitric acid before the system starts running away as a function of temperature and initial nitrous acid concentration:

T [°C]	[HAN]	[HNO2]	Kinetic Model	Instability Index	T [°C]	[HAN]	[HNO2]	Kinetic Model	Instability Index
30	0.01	1.00E-04	0.3	2.2	40	0.01	1.00E-04	0.2	1.99
30	0.01	1.00E-03	0.16	2.2	40	0.01	1.00E-03	0.11	1.99
30	0.01	1.00E-02	0.0065	2.2	40	0.01	1.00E-02	0.004	1.99
30	0.3	1.00E-04	6.4	4.6	40	0.3	1.00E-04	4.9	4.2
30	0.3	1.00E-03	6.3	4.6	40	0.3	1.00E-03	4.8	4.2
30	0.3	1.00E-02	6	4.6	40	0.3	1.00E-02	4.5	4.2
30	0.5	1.00E-04	7.1	5.4	40	0.5	1.00E-04	5.5	4.9
30	0.5	1.00E-03	7	5.4	40	0.5	1.00E-03	5.4	4.9
30	0.5	1.00E-02	6.8	5.4	40	0.5	1.00E-02	5.2	4.9
30	0.8	1.00E-04	7.6	6.3	40	0.8	1.00E-04	6	5.7
30	0.8	1.00E-03	7.6	6.3	40	0.8	1.00E-03	5.9	5.7
30	0.8	1.00E-02	7.4	6.3	40	0.8	1.00E-02	5.8	5.7
30	1	1.00E-04	7.9	6.7	40	1	1.00E-04	6.2	6.1
30	1	1.00E-03	7.8	6.7	40	1	1.00E-03	6.2	6.1
30	1	1.00E-02	7.7	6.7	40	1	1.00E-02	6.1	6.1
30	1.9	1.00E-04	8.5	8.4	40	1.9	1.00E-04	6.8	7.6
30	1.9	1.00E-03	8.5	8.4	40	1.9	1.00E-03	6.8	7.6
30	1.9	1.00E-02	8.4	8.4	40	1.9	1.00E-02	6.7	7.6

Table 1: Influence of the Initial Nitrous Acid Concentration on the Stability of the System – Temperatures: 30 and 40°C

Attachment C
Benchmarking the Kinetic Model with Instability Index

T [°C]	[HAN]	[HNO2]	Kinetic Model	Instability Index	T [°C]	[HAN]	[HNO2]	Kinetic Model	Instability Index
45	0.01	1.00E-04	0.16	1.8	50	0.01	1.00E-04	0.13	1.8
45	0.01	1.00E-03	0.09	1.8	50	0.01	1.00E-03	0.07	1.8
45	0.01	1.00E-02	0.001	1.8	50	0.01	1.00E-02	0.0009	1.8
45	0.3	1.00E-04	4.3	3.9	50	0.3	1.00E-04	3.7	3.7
45	0.3	1.00E-03	4.2	3.9	50	0.3	1.00E-03	3.6	3.7
45	0.3	1.00E-02	3.9	3.9	50	0.3	1.00E-02	3.4	3.7
45	0.5	1.00E-04	4.8	4.6	50	0.5	1.00E-04	4.3	4.3
45	0.5	1.00E-03	4.8	4.6	50	0.5	1.00E-03	4.2	4.3
45	0.5	1.00E-02	4.6	4.6	50	0.5	1.00E-02	4	4.3
45	0.8	1.00E-04	5.3	5.3	50	0.8	1.00E-04	4.8	4.9
45	0.8	1.00E-03	5.3	5.3	50	0.8	1.00E-03	4.7	4.9
45	0.8	1.00E-02	5.2	5.3	50	0.8	1.00E-02	4.6	4.9
45	1	1.00E-04	5.7	5.7	50	1	1.00E-04	5	5.3
45	1	1.00E-03	5.5	5.7	50	1	1.00E-03	4.9	5.3
45	1	1.00E-02	5.4	5.7	50	1	1.00E-02	4.8	5.3
45	1.9	1.00E-04	6.2	7.1	50	1.9	1.00E-04	5.6	6.6
45	1.9	1.00E-03	6.1	7.1	50	1.9	1.00E-03	5.5	6.6
45	1.9	1.00E-02	6.1	7.1	50	1.9	1.00E-02	5.5	6.6

Table 2: Influence of the Initial Nitrous Acid Concentration on the Stability of the System – Temperatures: 45 and 50°C

Attachment C
Benchmarking the Kinetic Model with Instability Index

T [°C]	[HAN]	[HNO2]	Kinetic Model	Instability Index	T [°C]	[HAN]	[HNO2]	Kinetic Model	Instability Index
55	0.01	1.00E-04	0.1	1.6	60	0.01	1.00E-04	0.081	1.5
55	0.01	1.00E-03	0.059	1.6	60	0.01	1.00E-03	0.047	1.5
55	0.01	1.00E-02	0.0023	1.6	60	0.01	1.00E-02	0.0016	1.5
55	0.3	1.00E-04	3.3	3.4	60	0.3	1.00E-04	2.8	3
55	0.3	1.00E-03	3.2	3.4	60	0.3	1.00E-03	2.8	3
55	0.3	1.00E-02	2.9	3.4	60	0.3	1.00E-02	2.5	3
55	0.5	1.00E-04	3.8	3.9	60	0.5	1.00E-04	3.4	3.4
55	0.5	1.00E-03	3.7	3.9	60	0.5	1.00E-03	3.3	3.4
55	0.5	1.00E-02	3.6	3.9	60	0.5	1.00E-02	3.1	3.4
55	0.8	1.00E-04	4.3	4.5	60	0.8	1.00E-04	3.8	3.9
55	0.8	1.00E-03	4.2	4.5	60	0.8	1.00E-03	3.8	3.9
55	0.8	1.00E-02	4.1	4.5	60	0.8	1.00E-02	3.6	3.9
55	1	1.00E-04	4.5	4.8	60	1	1.00E-04	4	4.2
55	1	1.00E-03	4.4	4.8	60	1	1.00E-03	4	4.2
55	1	1.00E-02	4.3	4.8	60	1	1.00E-02	3.9	4.2
55	1.9	1.00E-04	5	5.9	60	1.9	1.00E-04	4.6	5.2
55	1.9	1.00E-03	5	5.9	60	1.9	1.00E-03	4.5	5.2
55	1.9	1.00E-02	4.9	5.9	60	1.9	1.00E-02	4.5	5.2

Table 3: Influence of the Initial Nitrous Acid Concentration on the Stability of the System – Temperatures: 55 and 60°C

Case #	[HAN]	Experimental $[HNO_3]$	T	Kinetic Model $[HNO_3]$
1	0.05	4	5	Stable
2	0.05	3.5	13	7.9
3	0.05	3	25	4.3
4	0.02	4	2	Stable
5	0.02	3.5	11	5.6
6	0.02	3	17	3.4
7	0.02	2.5	30	1.3
8	0.01	3.5	2	10.9
9	0.01	3	10	1.2
10	0.01	2.5	19	0.6
11	0.01	2	30	0.3
12	0.005	3	4	0.22
13	0.005	2.5	12	0.18
14	0.005	2	21	0.13

Table 4: Additional Benchmark Experiments

Attachment D
Sensitivity Analysis

Sensitivity analyses were performed to examine the behavior of the system to changes in the design basis parameters to quantify the margin of safety.

T [°C]	[HAN]	[HNO2]	Kinetic Model	T [°C]	[HAN]	[HNO2]	Kinetic Model	T [°C]	[HAN]	[HNO2]	Kinetic Model
45	0.01	1.00E-04	8	50	0.01	1.00E-04	7.5	55	0.01	1.00E-04	7.1
45	0.01	1.00E-03	7.9	50	0.01	1.00E-03	7.5	55	0.01	1.00E-03	7
45	0.01	1.00E-02	7.7	50	0.01	1.00E-02	7.2	55	0.01	1.00E-02	6.8
45	0.3	1.00E-04	8	50	0.3	1.00E-04	7.5	55	0.3	1.00E-04	7.1
45	0.3	1.00E-03	7.9	50	0.3	1.00E-03	7.5	55	0.3	1.00E-03	7
45	0.3	1.00E-02	7.7	50	0.3	1.00E-02	7.3	55	0.3	1.00E-02	6.8
45	0.5	1.00E-04	8	50	0.5	1.00E-04	7.5	55	0.5	1.00E-04	7.1
45	0.5	1.00E-03	8	50	0.5	1.00E-03	7.5	55	0.5	1.00E-03	7
45	0.5	1.00E-02	7.7	50	0.5	1.00E-02	7.3	55	0.5	1.00E-02	6.8
45	0.8	1.00E-04	8	50	0.8	1.00E-04	7.5	55	0.8	1.00E-04	7.1
45	0.8	1.00E-03	8	50	0.8	1.00E-03	7.5	55	0.8	1.00E-03	7
45	0.8	1.00E-02	7.8	50	0.8	1.00E-02	7.3	55	0.8	1.00E-02	6.8
45	1	1.00E-04	8	50	1	1.00E-04	7.5	55	1	1.00E-04	7.1
45	1	1.00E-03	8	50	1	1.00E-03	7.5	55	1	1.00E-03	7
45	1	1.00E-02	7.8	50	1	1.00E-02	7.3	55	1	1.00E-02	6.8
45	1.9	1.00E-04	8	50	1.9	1.00E-04	7.5	55	1.9	1.00E-04	7.1
45	1.9	1.00E-03	8	50	1.9	1.00E-03	7.5	55	1.9	1.00E-03	7
45	1.9	1.00E-02	7.8	50	1.9	1.00E-02	7.3	55	1.9	1.00E-02	6.8

Table 1: Influence of the Initial Nitrous Acid Concentration on the Stability of a System with 0.1M N_2H_4 – Temperatures: 45, 50 and 55°C

Attachment D
Sensitivity Analysis

T [°C]	[HAN]	[HNO2]	Kinetic Model	T [°C]	[HAN]	[HNO2]	Kinetic Model	T [°C]	[HAN]	[HNO2]	Kinetic Model
45	0.01	1.00E-04	8	50	0.01	1.00E-04	7.5	55	0.01	1.00E-04	7.1
45	0.01	1.00E-03	7.9	50	0.01	1.00E-03	7.5	55	0.01	1.00E-03	7
45	0.01	1.00E-02	7.7	50	0.01	1.00E-02	7.2	55	0.01	1.00E-02	6.8
45	0.3	1.00E-04	8	50	0.3	1.00E-04	7.5	55	0.3	1.00E-04	7.1
45	0.3	1.00E-03	7.9	50	0.3	1.00E-03	7.5	55	0.3	1.00E-03	7
45	0.3	1.00E-02	7.7	50	0.3	1.00E-02	7.3	55	0.3	1.00E-02	6.8
45	0.5	1.00E-04	8	50	0.5	1.00E-04	7.5	55	0.5	1.00E-04	7.1
45	0.5	1.00E-03	8	50	0.5	1.00E-03	7.5	55	0.5	1.00E-03	7
45	0.5	1.00E-02	7.7	50	0.5	1.00E-02	7.3	55	0.5	1.00E-02	6.8
45	0.8	1.00E-04	8	50	0.8	1.00E-04	7.5	55	0.8	1.00E-04	7.1
45	0.8	1.00E-03	8	50	0.8	1.00E-03	7.5	55	0.8	1.00E-03	7
45	0.8	1.00E-02	7.8	50	0.8	1.00E-02	7.3	55	0.8	1.00E-02	6.8
45	1	1.00E-04	8	50	1	1.00E-04	7.5	55	1	1.00E-04	7.1
45	1	1.00E-03	8	50	1	1.00E-03	7.5	55	1	1.00E-03	7
45	1	1.00E-02	7.8	50	1	1.00E-02	7.3	55	1	1.00E-02	6.8
45	1.9	1.00E-04	8	50	1.9	1.00E-04	7.5	55	1.9	1.00E-04	7.1
45	1.9	1.00E-03	8	50	1.9	1.00E-03	7.5	55	1.9	1.00E-03	7.1
45	1.9	1.00E-02	7.8	50	1.9	1.00E-02	7.3	55	1.9	1.00E-02	6.9

Table 2: Influence of the Initial Nitrous Acid Concentration on the Stability of a System with 0.2M Pu and with 0.1M N_2H_4 – Temperatures: 45, 50 and 55°C

T [°C]	[HAN]	[HNO2]	Min Hyd
50	0.01	1.00E-04	7.30E-03
50	0.3	1.00E-04	6.60E-03
50	0.5	1.00E-04	6.20E-03
50	0.8	1.00E-04	5.50E-03
50	1	1.00E-04	5.00E-03
50	1.9	1.00E-04	1.00E-03

Table 3: Influence of the HAN Concentration on the Minimum Required N_2H_4 Concentration Stability with 0.2M Pu at a Temperatures: 50

Attachment E
Experimental Techniques to Investigate the Kinetic Behavior of the HAN System

Infrared spectroscopy has been a widely used technique to evaluate thermodynamic and kinetic data for HAN [i,ii]. When coupled with a flow through cell the decomposition of HAN can be evaluated in real time under a variety of temperature and solution conditions, yielding the required kinetic parameter. In a similar way Raman spectroscopy coupled with flow cells can provide similar real time data [iii,iv]. The IR and Raman techniques used in tandem can be utilized to evaluate a wide range of nitrogen containing molecules resulting from the investigations.

Nuclear Magnetic Resonance (NMR) can also provide spectroscopic data for the evaluation of HAN [v,vi]. The method relies upon a linear relationship between the chemical shift and HAN concentration. The technique is time limited by the pulse sequence used in the experiments. Spectra can be collected between 10 seconds and 1 minute. NMR can utilize protons, ^{13}C, and ^{15}N. The applicability of ^{13}C to the system of interest is limited. The ^{15}N NMR can be applied to HAN due to the high concentration of N in the molecule.

A wide variety of thermal techniques can be used to evaluate the degradation of HAN and the conditions for an autocatalytic reaction [vii]. The techniques include bomb calorimetry, differential scanning calorimetry, thermal gravimetric analysis, and thermogravimetric/differential thermal analysis. These techniques evaluate the change in the examined system upon the application of heat. The thermal methods have determined the initiation temperatures of the autocatalytic HAN reaction under a variety of conditions.

For the evaluation of Pu redox, UV-Visible spectroscopy and laser induced photoacoustic spectroscopy are excellent techniques for evaluating Pu speciation and oxidation state [viii,ix]. Both techniques can be utilized to obtain real time Pu speciation results in a variety of systems.

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