



DUKE COGEMA
STONE & WEBSTER

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Washington, D.C. 20555

06 October 2003
DCS-NRC-000158

Subject: Docket Number 070-03098
Duke Cogema Stone & Webster
Mixed Oxide (MOX) Fuel Fabrication Facility
Response to Request for Additional Information – Chemical Safety Open Items
CS-01 and CS-02

References: 1) R. C. Pierson (NRC), *Draft Safety Evaluation Report on Construction of Proposed Mixed Oxide Fuel Fabrication Facility, Revision 1*, Dated 30 April 2003

As part of the review of Duke Cogema Stone & Webster's (DCS') Mixed Oxide Fuel Fabrication Facility (MFFF) Construction Authorization Request (CAR) documented in the Draft Safety Evaluation Report (Reference 1), NRC Staff identified open items related to Chemical Safety. In addition to items identified in Reference 1 above, NRC clarified their requests in a July 2003 public meeting. To facilitate resolution to the request for additional information, DCS has enclosed additional information regarding Open Items CS-01 and CS-02.

If I can provide any additional information, please feel free to contact me at (704) 373-7820.

Sincerely,

Peter S. Hastings, P.E.
Manager, Licensing and Safety Analysis

Enclosure 1: Chemical Safety DSER Open Item Responses

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xc (with enclosure):

David Alberstein, NNSA/HQ
Kenneth L. Ashe, DCS
Andrew Persinko, USNRC/HQ
Donald J. Silverman, Esq., DCS
PRA/EDMS: Corresp\Outgoing\NRC\2003 NRC\DCS-NRC-000158

xc (without enclosure):

Marc Arslan, DCS
David A. Ayres, USNRC/RII
Timothy S. Barr, NNSA/CH
Jean-Marc Belmont, DCS
Edward J. Brabazon, DCS
James R. Cassidy, DCS
Vincent Chevalier, DCS
Mosi Dayani, NNSA/CLT
Sterling M. Franks, III, NNSA/SR
Joseph G. Giitter, USNRC/HQ
Joseph J. Holonich, USNRC/HQ
Robert H. Ihde, DCS
James V. Johnson, NNSA/HQ
J. David Nulton, NNSA/HQ
J. Olencz, NNSA/HQ
Robert C. Pierson, USNRC/HQ
Luis A. Reyes, USNRC/RII
Patrick T. Rhoads, NNSA/HQ
Brian W. Smith, USNRC/HQ
Phillipe Sordelet, DCS
Thomas E. Touchstone, DCS
Martin J. Virgilio, USNRC/HQ

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CS-01 Red Oil

The staff concludes that the red oil phenomena analysis in Chapter 5.5 of the CAR is not complete and that PSSCs and their design bases for preventing red oil explosions are not adequate for all potentially affected components. At a minimum, this applies to the following areas: purification, solvent recovery, calciner, oxalic mother liquor, acid recovery, and offgas. (DSER Section 8.1.2.5.2.5)

Clarification:

In the 29 August 2003 NRC letter providing minutes from the 29 July 2003 - 01 August 2003 meeting, the NRC requested DCS “to identify a PSSC to ensure adequate evaporative cooling” in the evaporator

Response:

The principle being addressed is to ensure evaporative cooling is available to prevent self-heating of the solution which may lead to a runaway reaction. The two PSSCs identified are the Offgas Treatment System (previously identified to prevent the AP Vessel Over-Pressurization [Construction Authorization Request Table 5.5-19]), and the Process Safety Control subsystem (not previously identified as a PSSC for this event).

The Process Safety Control subsystem has two safety functions:

1. To ensure adequate aqueous phase to provide evaporative cooling.
2. To ensure that the bulk temperature of the solutions that may contain degraded organic is restricted within safety limits to control the energy generation rate.

The design basis for the Process Safety Control subsystem is:

1. The bulk fluid design basis (safety limit) temperature is a maximum (i.e., not to exceed) temperature of 125 °C (as previously identified in the July 29 – August 1, 2003 meeting to discuss open items related to the Mixed Oxide Fuel Fabrication Facility).
2. The bulk fluid design basis heatup rate is limited to a maximum value of 2°C/min after startup.
3. The heating of the evaporator is stopped and aqueous phase is added when triggered by either of the above design basis values.

Various design options exist to ensure adequate aqueous phase is available in the evaporator (e.g., continuous feed or injection); these design options can be selected

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during final design and confirmed in the ISA without significant changes to the design or constructed facility.

Detailed evaluation of startup operations will be conducted as part of the ISA to ensure an appropriate margin of safety exists (such as additional aqueous phase, sampling to verify lack of degraded organics, or operation below credible initiation temperature) to account for regimes where the temperature rate of change during startup may exceed 2°C/min.

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CS-02 HAN

The staff concludes that the HAN/hydrazine analysis in Chapter 5.5 of the revised CAR is not complete and that PSSCs and their design bases for preventing Han/hydrazine explosions are not adequate for all potentially affected units and components. At a minimum this applies to the following areas: purification event, solvent recovery, offgas. (DSER Section 8.1.5.2.3)

Clarification:

In their 29 August 2003 NRC letter to DCS, NRC requested that DCS notify NRC staff in the event that there are changes to the HAN model that result from additional external review and include design basis values in the CAR.

Response:

As agreed to in the 29 July 2003 meeting, DCS has completed an external review of the HAN model shown to the NRC during the NRC's 22-23 July 2003 in-office visit. No significant changes have been made to the differential system or the rate constants. A few refinements to the model have been made pursuant to review comments, but these changes did not affect the design basis values previously provided. The refinements are summarized below:

1. The reduction rate of plutonium by HAN, k_{redhan} , is presented utilizing the rate constant obtained from G. Richardson (Ref 1) with a rate constant in M^3/s .
2. A dissociation constant β in M^{-1} is presented separately, while previously β was incorporated in the rate constant ($k=k_{Richardson}/\beta^2$). (Either representation of the rate constant for plutonium reduction by HAN is acceptable.)
3. The rate constant for reduction of plutonium by hydrazine, k_{redhyd} , is now presented as a constant times an exponential. The previous version presented only one exponential.

The constant that was previously in the exponential ($124909/(8.314*343.15)$) has been factorized and incorporated into the pre-exponential term 4×10^{17} . There is no impact from this change (i.e., the pre-exponential term was changed from 3.91×10^{-2} to $3.91 \times 10^{-2} * \exp(124909/(8.314*343)) = 4 \times 10^{17}$).

4. The rate constant for the production of di-nitrogen tetraoxide, k_{aut1} , was previously in ° Celsius. However, all the other rate constants are in ° Kelvin. Therefore to avoid confusion, the term in k_{aut1} has been modified from T to (T-273.15).
5. Finally, the pre-exponential terms of k_{hydsc} and k_{hansc} have been modified.
 - a. Refined calculations have determined that that new value of k_{hydsc} is 2.06×10^{14} compared to 2.7×10^{14} previously. Detailed analysis has confirmed that this results in no change in design-basis results.

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- b. Similarly, a refinement has been made in the pre-exponential term for k_{hansc} from 3.28×10^8 to 3.26×10^8 , which has no impact on the output of the analysis.

The resulting design basis values are presented in Table 1 below. As compared to the data previously submitted, for each value it is specified whether it is a maximum or a minimum quantity.

Table 1: Design Basis Values.

Temperature	<50°C
HNO ₃	<6 M
HAN	< 2.5 M
N ₂ H ₄	≥ 0.10 M
Pu	not limited

It should be noted that the design basis value for HAN has been increased from 1.9M to 2.5M to more accurately reflect anticipated operating conditions, and as further analysis has confirmed the stabilizing role of HAN. This change resulted in no impact to other parameters.

In addition to the above information, DCS includes in Table 2 below the equations and constants from the model shown to the NRC during the 22-23 July in office visit, updated to include the above refinements. These equations and constants are reproduced in their entirety in this response and supersede the responses provided in the letters previously transmitted by DCS to NRC on 30 May 2003 and 28 July 2003.

Reference 1:

Richardson, G.L.; Swanson, J.L.; *Plutonium Partitioning in the PUREX Process with Hydrazine Stabilized Hydroxylamine Nitrate*, HEDL-TME-75-31 (1975)

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Table 2

Differential System

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

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

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

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

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

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

Rate and equilibrium constants used to describe the system

$$\bullet k_{redHAN}(T) = 1.89 * 10^{31} * e^{-\frac{181,394}{RT}} \quad , \text{ in } M^3 \text{ sec}^{-1}; \quad k_{hydsc}(T) = 2.06 * 10^{14} e^{-\frac{56,500}{RT}} \quad , \text{ in } M^{-2} \text{ sec}^{-1};$$

$$\beta = 3.62 * 10^4 * e^{-\frac{22,161}{RT}} \quad , \text{ in } M^{-1} \quad ; \quad K = 0.14 \quad ;$$

$$\bullet k_{redhyd}(T, \mu) = 4 * 10^{17} * e^{0.3422\mu} * e^{-\frac{124,909}{RT}} \quad , \text{ in } \text{sec}^{-1} \quad ; \quad k_{hasc}(T) = 8.6 * 10^{11} e^{-\frac{54,600}{RT}} \quad , \text{ in } M^{-2} \text{ sec}^{-1};$$

$$\bullet k_{reox}(T) = 1.02 * 10^{10} e^{-\frac{58,520}{RT}} \quad , \text{ in } M^{-3} \text{ sec}^{-1}; \quad k_{hansc}(T) = 3.26 * 10^8 e^{2.16\sqrt{\mu}} e^{-\frac{51,106}{RT}} \quad , \text{ in } M^{-2} \text{ sec}^{-1};$$

$$\bullet k_{aut1}(T, [HNO_3]) = 1.61 * 10^{-3} * e^{0.2318[HNO_3] + 0.091e^{0.1281[HNO_3]}(T-273.15)} \quad , \text{ in } M^{-2} \text{ sec}^{-1}; \quad k_{nitric1}(T) = 2 * 10^9 e^{-\frac{108,680}{RT}} \quad , \text{ in } M^{-3} \text{ sec}^{-1};$$

$$\bullet \frac{k_{aut2}}{k_{aut3}} \ll 2[HAN] \quad ; \quad k_{nitric2}(T, [HNO_3]) = 1.1 * 10^8 e^{0.8447[HNO_3]} e^{-\frac{89,000}{RT}} \quad , \text{ in } \text{sec}^{-1};$$