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Subject: Docket Number 070-03098
Duke Cogema Stone & Webster
Mixed Oxide (MOX) Fuel Fabrication Facility
Response to DSER Open Items AP-10 and CS-2

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. Enclosure 1 of this letter provides a response to close open items AP-10 and CS-2.

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

Sincerely,

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Enclosure 1
Response to DSER Open Items On Chemical Safety

Open Item AP-10:

Provide a design basis and PSSCs for removal of potentially toxic or reactive gases in the Offgas unit (DSER Section 11.2.1.3.10)

Clarifying statement in May 2003 Open Item Status Report issued by NRC 28 May 2003. DCS should address the following items:

1. Design basis requirements for protection of the HEPA filters from reactive gases in the offgas system.
2. Design basis requirements for protection of the site worker from toxic gases in the offgas system.

Response:

Item 1:

As stated on page 8 of Attachment 1 to Enclosure 1 of DCS to NRC letter (DCS-NRC-000128) dated 18 February 2003, to ensure HEPA filters are replaced as necessary, DCS will implement the following administrative controls:

- Periodic filter visual inspection and surveillance leak testing in accordance with ASME N510-1989, Testing of Nuclear Air Treatment Systems.
- Monitoring of HEPA filter differential pressure and filter replacement at specified filter differential pressures.
- Filter replacement at specified time intervals in accordance with ASME AG-1 or following identified exposures to water or chemicals [emphasis added].

This will ensure that the HEPA filters can withstand a differential pressure of at least 10 inches of water.

Item 2:

As discussed in the January public meeting, DCS committed to limiting chemical releases to "TEEL 2 type" values for the site worker. DCS understands that there is an open item (CS-5b) related to the identification of chemical release limits. DCS therefore, suggests that this open item be linked to the resolution of CS-5b.

Action:

Update the CAR to identify the PSSCs and the safety function above.

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Open Item: CS-02

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)

Response:

1. Safety Strategy and Principal SSCs for Preventing Autocatalytic HAN Reactions

The Aqueous Polishing (AP) process uses a mixture of hydroxylamine nitrate (HAN) and nitric acid (HNO_3) during the extraction step of the plutonium purification unit to strip plutonium from the solvent after removal of americium and gallium and other impurities. HAN has a number of advantages as a plutonium reductant. It is nonmetallic, it is readily decomposed to innocuous products by heating, the gaseous reaction products – nitrogen (N_2), nitrous oxide (N_2O), and water (H_2O) – contribute to minimization of the volume of solid wastes produced, and it possesses the proper Pu (IV) to Pu (III) reduction attributes. However, due to the potential for HAN to undergo an autocatalytic reaction with nitrous acid (HNO_2) under certain conditions, the use of HAN in the AP Process introduces an explosion/overpressure hazard. Control of systems containing both HAN and nitric acid (i.e., such that nitrous acid concentration does not increase) may be performed by utilizing a reducing agent (e.g., hydrazine nitrate (N_2H_4)) that consumes nitrous acid at a rate faster than the rate at which it is being produced by HAN reaction with nitric acid or via plutonium re-oxidation reaction.

Within the AP process, excess HAN/hydrazine nitrate and hydrazoic acid (a byproduct of the nitrous acid reaction with hydrazine nitrate) are destroyed by the introduction of NO_x into the purification cycle oxidation column, CLMN 6000 and recycling tanks. By destroying the HAN/Hydrazine nitrate and hydrazoic acid, they are not propagated to downstream process units and the front end of the purification cycle (PULS2000). PSSCs were identified in CAR Section 8.5.1.8 to preclude propagation of these reducing agents (i.e., HAN, Hydrazine, and Hydrazoic acid).

The principal SSCs that are implemented into the MFFF design to preclude the autocatalytic reaction of HAN with nitrous acid are represented by two cases:

- Process vessels containing HAN and hydrazine nitrate without addition of NO_x ;
- Process vessels containing HAN and hydrazine nitrate with addition of NO_x .

Each of these specific cases is described below. It should be noted that CAR Revision 1 described implementation of a third strategy for vessels containing HAN and no

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hydrazine nitrate. The design is being modified so that these vessels will contain hydrazine nitrate. Thus, a third strategy is no longer required.

1.1. Process vessels containing HAN and hydrazine nitrate without addition of NO_x

In AP process vessels where HAN has been introduced to reduce the plutonium valence from IV to III (e.g., pulse column PULS3000 of the purification cycle), a preventative safety strategy is adopted to reduce the risk to the facility worker, site worker, public, and environment from an over-pressurization/explosion resulting from a potential autocatalytic HAN/nitric acid reaction. The principle SSCs to implement this safety strategy are the process safety control subsystem and chemical safety controls. The safety function of the process safety control subsystem is to ensure that the temperature of the solution containing HAN is limited to temperatures that are within safety limits. The safety function of the chemical safety controls is to ensure that the concentration of nitric acid, hydrazine, and HAN introduced into the process is within the established design basis limits.

An additional concern in systems composed of HAN and nitric acid, is the possible concentration of HAN and nitric acid due to long term evaporation and/or depletion of hydrazine via radiolysis thereby changing the concentrations of the reagents. To preclude unacceptable changes in the reagent(s) concentrations the chemical safety control subsystem is implemented as a principal SSC. The safety function of the chemical safety control subsystem is to administratively ensure that the concentrations of HAN, nitric acid, and hydrazine are maintained within their respective safety limits by limiting the residence time of solutions containing HAN in contact with nitric acid and/or plutonium bearing solutions. (Additional detail on the corresponding design basis is provided in Section 2.)

1.2. Process Vessels containing HAN and Hydrazine nitrate with addition of NO_x

In the AP purification cycle, vessels designed to receive NO_x for reaction with hydrazine nitrate, HAN, and hydrazoic acid include the oxidation column CLMN6000 and recycling tanks. Unlike other AP process vessels, these vessels are designed to eliminate hydrazine nitrate, HAN, and hydrazoic acid via reaction with excess nitrous acid produced from the introduction of NO_x. The temperature and pressure rise in these vessels as a result of these reactions is dependent on the concentrations of the reagents introduced into these vessels and the vent size of these vessels.

To reduce the risk of an over-pressurization/explosion event in these operations to the facility worker, site worker, public, and the environment, a preventative safety strategy is adopted. The principle SSCs utilized to implement this safety strategy are chemical safety control(s) and the 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

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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.

2. Determination of Design Basis for Principal SSCs

DCS has developed a kinetic model to determine the behavior of the system based on existing published kinetic data and rate equations governing the respective reactions to determine design basis values for the Construction Authorization. The equations governing the system are given by:

- Plutonium (IV) reduction by HAN (Eq. 1) [1,2];
- Plutonium (IV) reduction by Hydrazine (Eq. 1) [3];
- Plutonium (III) Re-oxidation (Eq. 1) [4,5];
- HAN reaction with nitric acid (Eq. 3) [6,7,8,9];
- HAN reaction with nitrous acid (Eq. 2 & Eq. 3) [7,10,11];
- Hydrazine reaction with nitrous acid (Eq. 4) [11,12,13,];
- Hydrazoic reaction with nitrous acid (Eq. 5) [11,12,13];
- Hydrazine oxidation by nitric acid (Eq. 4) [7,14];
- Hydrazoic oxidation by nitric acid (Eq. 5) [15];

Rate equations for each of these respective reactions were taken from peer-reviewed literature. Likewise, kinetic constants were obtained from published experimental results. The differential equations and rate constants governing the system are presented in Appendix A.

The results of this model serve as the basis for establishing the design basis limits on the principal SSCs that have been previously identified to ensure that over-pressurization events/explosions from autocatalytic HAN/nitric acid reactions are highly unlikely within the AP Process. Determination of the design basis values is dependent on the following parameters:

- temperature;
- HAN concentration;
- hydrazine concentration;
- plutonium loading;
- nitric concentration; and
- ionic strength.

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A temperature of 55°C was selected for the limiting temperature. This value represents the design basis for the process safety control subsystem. This value limits the production of N₂O₄ and consequently the production of nitrous acid.

Design basis values of 6 M nitric acid and 1.9 M HAN were selected to also restrict the production of nitrous acid production. [It is important to emphasize that nominal acidity within the stripping column is less than 1 M.] The ionic strength was also selected to be 6M. A concentration design basis of 0.055 M in the aqueous phase for hydrazoic acid has also been previously established to ensure that potentially explosive concentrations of hydrazoic acid are not present in the gaseous phase. Based on the selection of these variables the limiting quantity of hydrazine required to stabilize the system was determined to be 7×10^{-3} M. This concentration of hydrazine represents the minimum quantity of hydrazine that is required to be introduced into the process to ensure that an autocatalytic HAN/nitric reaction do not occur for multiple years in the event of long term process shutdown. A sensitivity analysis was performed on the plutonium concentration and determined not to affect the results. It should be noted that DCS currently introduces hydrazine into the process with a concentration of 0.14 M.

A comparison of the predictions of the kinetic model developed by DCS to experimental work to determine the limiting hydrazine concentration confirms the DCS model for the conditions examined. Utilizing the experimental parameters of:

- [HNO₃] = 10 M;
- T = 70°C; and
- [HAN] = 1.67×10^{-2} M,

a minimum hydrazine concentration of 2×10^{-3} M was determined whereas the experimental results yielded a value of 5×10^{-4} M [9,13].

As previously noted, the concentrations of the reagents may change due to evaporation and/or radiolytic reactions. During the ISA a residence time limit will be established to limit the concentration of the nitric acid and HAN concentrations due to long term evaporation as well as the loss of hydrazine due to radiolysis to ensure that the conditions within the system do not change in a way that would enable the autocatalytic HAN/nitric acid reaction to occur. [This is expected to be on the order of months, so as to not require immediate action by either engineered or administrative features.]

As noted in previous meetings, DCS will perform confirmatory experiments during the ISA to verify the design bases discussed above.

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APPENDIX A: Presentation of the differential system used to model the purification unit - KPA

1. Differential System

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

$$\begin{aligned} \frac{\partial [HNO_2]}{\partial t} = & \frac{3k_{aut1}[NO_3^-]}{k_{aut2} + 2[HAN]} [H^+] [HNO_2] [HAN] + k_{reox} [H^+] [NO_3^-] [HNO_2] [Pu(III)] - \dots \\ & \dots - k_{hansc} [H^+] [HNO_2] [HAN] - k_{hydsc} [H^+] [HNO_2] [N_2H_4] - k_{hasc} [H^+] [HNO_2] [HN_3] \end{aligned} \quad \text{Eq. 2}$$

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

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

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

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2. Kinetic Constants used to describe the system

- $k_{redHAN}(T) = 1.17 * 10^{21} * e^{-\frac{131,062}{RT}}$, in $M^5 \cdot sec^{-1}$; $k_{hydsc}(T) = 5.33 * 10^{13} e^{-\frac{56,500}{RT}}$, in $M^2 \cdot sec^{-1}$;
- $k_{redhyd}(T, \mu) = 1.83 * 10^{17} * e^{0.3466\mu} * e^{-\frac{122,623}{RT}}$, in sec^{-1} ; $k_{hasc}(T) = 9 * 10^{11} e^{-\frac{54,500}{RT}}$, in $M^2 \cdot sec^{-1}$;
- $k_{reox}(T) = 1.02 * 10^{10} e^{-\frac{58,520}{RT}}$, in $M^3 \cdot sec^{-1}$; $k_{hansc}(T) = 8.79 * 10^9 e^{-\frac{51,836}{RT}}$, in $M^2 \cdot sec^{-1}$;
- $k_{aut1}(T, [HNO_3]) = 2.07 * 10^8 \cdot e^{-\frac{57,949}{RT}} \cdot e^{4.51 * 10^4 \cdot \frac{27,933}{RT} * [HNO_3]}$, in $M^2 \cdot sec^{-1}$; $k_{nitric1}(T) = 2 * 10^9 e^{-\frac{108,680}{RT}}$, in $M^3 \cdot sec^{-1}$;
- $\frac{k_{aut2}}{k_{aut3}} \ll 2[HAN]$; $k_{nitric2}(T, [HNO_3]) = 1.1 * 10^8 e^{0.8447[HNO_3] - \frac{89,000}{RT}}$, in sec^{-1} ;
- $[Pu(III)] = [Pu(IV)]_0 - [Pu(IV)]$

Notes: All the activation energies that are presented are in Joules per mole, the temperatures in degree Kelvin and the concentrations in mol per liter (M).

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