

### UNITED STATES NUCLEAR REGULATORY COMMISSION

WASHINGTON, D.C. 20555-0001

August 29, 2003

 MEMORANDUM TO: Kathy Halvey Gibson, Acting Chief Special Projects and Inspection Branch Division of Fuel Cycle Safety and Safeguards Office of Nuclear Material Safety and Safeguards
THRU: Brian W. Smith, Acting Table 2010

THRU: Brian W. Smith, Acting Chief **Special Projects Section** Special Projects and Inspection Branch Division of Fuel Cycle Safety and Safeguards, NMSS

FROM: Andrew Persinko, Sr. Nuclear Engineer Special Projects Section Special Projects and Inspection Branch Division of Fuel Cycle Safety and Safeguards, NMSS

SUBJECT: JULY 29 - AUGUST 1, 2003, MEETING SUMMARY: MEETING WITH DUKE COGEMA STONE & WEBSTER TO DISCUSS OPEN ITEMS RELATED TO MIXED OXIDE FUEL FABRICATION FACILITY

On July 29 - August 1, 2003, U.S. Nuclear Regulatory Commission (NRC) staff met with Duke Cogema Stone & Webster (DCS), the mixed oxide fuel fabrication facility (MFFF) applicant, to discuss chemical safety, nuclear criticality safety, and fire protection open items related to the construction authorization request for the MFFF. The meeting agenda, summary, handouts, and attendance list are attached. (Attachments 1, 2, 3, and 4, respectively).

Docket: 70-3098

- Attachments: 1. Meeting Agenda
  - 2. Meeting Summary
  - 3. Meeting Handouts
  - 4. Attendance List

cc: P. Hastings, DCS L. Zeller, BREDL

G. Carroll, GANE

J. Johnson, DOE

J. Conway, DNFSB

- D. Curran, GANE
- D. Silverman, DCS
- H. Porter, SCDHEC

### MEETING AGENDA MOX FUEL FABRICATION FACILITY July 29-August 1, 2003

### July 29, 2003

1:00PM Discussion of chemical safety open items

5:00PM Adjourn

### July 30, 2003

- 9:00AM Discussion of chemical safety open items
- 12:00 NOON Lunch
- 1:00PM Discussion of chemical safety open items
- 5:00PM Adjourn

#### July 31, 2003

- 9:00AM Discussion of chemical safety open items
- 12:00 NOON Lunch
- 1:00PM Discussion of nuclear criticality safety open item
- 5:00PM Adjourn

#### August 1, 2003

- 9:00AM Discussion of nuclear criticality safety open item
- 12:00 NOON Lunch
- 1:00PM Discussion of fire protection open item

#### 5:00PM Adjourn

### MEETING SUMMARY MOX FUEL FABRICATION FACILITY July 29-August 1, 2003

### Purpose:

The purpose of the meeting was to discuss the draft Safety Evaluation Report (SER) chemical safety, nuclear criticality safety, and fire protection open items related to the construction authorization request (CAR) for the MOX Fuel Fabrication Facility (MFFF).

### Meeting Summary:

The following issues were discussed:

### 1. <u>CS-01, Red-Oil</u>

DCS stated that it identified the chemical safety control system, the process control subsystem, and the offgas system as Principal Structures, Systems, and Components (PSSCs) to ensure that there will be an aqueous phase to prevent a red oil explosion. DCS stated that a runaway reaction can occur at a temperature of 137 degrees C. At the meeting, DCS provided information about evaporators in use at Savannah River. That information indicated that a runaway reaction occurs at a temperature greater that 130 degrees C; therefore, 130 degrees C is used as the point where a runaway reaction can occur. DCS identified the process steam temperature as a design basis value. The staff indicated that it was concerned about control of the solution temperature. The staff indicated that it would accept a solution temperature of 120.4 degrees C at the surface of the solution, a maximum temperature of 125 degrees C within the solution, and a maximum rate of temperature change of 1-2 degrees C/minute as design bases for the solution temperature. DCS subsequently explained that the design of the evaporator is such that the solution is at constant pressure and temperature everywhere in the solution.

Based on the design of the evaporator, the staff indicated that it would accept a maximum solution temperature of 122.4 degrees C and a maximum rate of temperature change of 1-2 degrees C/minute as design bases for the solution temperature. The reason for changing the acceptable maximum temperature from 125 to 122.4 degrees C is because, based on the evaporator design, the average temperature becomes the same as the maximum temperature for a well mixed solution.

DCS indicated that it would identify the following as design bases:

- (a) limit the energy generation resulting from the potential oxidation of tri-butyl phosphate degradation products by ensuring that the process fluid does not exceed 125 degrees C; and
- b) ensure that over-pressurization can be effectively prevented via the addition of an aqueous phase to the evaporators by limiting the heating rate to two degrees per minute.

Staff indicated that it would consider the DCS proposal. This item remains open pending resolution of the maximum allowable solution temperature for closed systems. NRC staff has this action.

DCS needs to identify a PSSC to ensure adequate evaporative cooling.

### 2. <u>CS-02, HAN/Hydrazine Analysis</u>

DCS stated that Table 1 of DCS letter dated July 28, 2003 (DCS-NRC-000151) constitutes the design bases for HAN/hydrazine.

The staff noted that it visited DCS offices on July 22, 2003, to review the calculations performed by DCS regarding its HAN model. Staff indicated that it was able to verify the DCS results during the visit. Initially, however, NRC staff was unable to verify the DCS model during the in-office review as a result of errors in DCS' May 30, 2003, and July 28, 2003, letters to NRC. Consequently, at the July 29 meeting, NRC staff emphasized the importance of following the quality assurance plan, and being clear in DCS' letters, whether the information being provided is draft or final.

During the meeting, NRC staff requested that DCS include iron as an impurity in the confirmatory tests that it plans to perform; DCS agreed (see Attachment 3).

DCS also agreed to: 1) notify NRC staff in the event that there are changes to the HAN model that result from additional external review; and 2) include design basis values from DCS' July 28, 2003, letter in the CAR.

The staff had no further questions and will continue its review of the proposed model.

### 2. <u>CS-09, AP-02, AP-08 and AP-09, Lower Flammability Limits (LFL)</u>

These items involve the use of 25% vs. 50% vs. 60% of the LFL for the design bases of solvent temperature, electrolyzer generated gases, offgas system flammable gases and vapors, and solvent flashpoint vapor pressure. DCS proposed to use:

- (a) 60% of the LFL in accordance with National Fire Protection Association (NFPA) 69-1997, as a design basis value inside process vessels in which solvent is present. NFPA 69 allows 60% of the LFL to be used provided the system is equipped with automatic instrumentation with safety interlocks. The flashpoint temperature of the solvent vapor will be based on measurement or application of LeChatelier's rule. These values are selected based on guidance from NFPA 30-1996 and NFPA 69-1997.
- (b) 50% of the LFL as the design basis value and 25% as the setpoint inside vessels containing hydrogen that are in the offgas treatment unit.
- (c) 25% of the LFL as the design basis value outside of process vessels(e.g., in rooms) with a setpoint to be determined by a setpoint analysis.

This proposal is different from the Mixed Oxide (MOX) Standard Review Plan, which indicates that 25% LFL would be acceptable. The staff requested that DCS provide specifics regarding the interlocks that DCS proposes to use for cases (a) and (b), considering that radiolysis/electrical phenomena may not be amenable to interlocks, and identify appropriate PSSCs and design bases. DCS has the action.

### 3. <u>CS-10, Control Room Habitability</u>

This item concerns the establishment of hazardous chemical concentration limits in the control room that would require operator use of protective equipment (breathing air, etc.) in order to assure that they could remain in the control room to perform required safety functions. In previous meetings, the staff noted that operating reactors used Regulatory Guide 1.78, which references Immediately Dangerous to Life and Health (IDLH) values. At these levels, operators have two minutes to don appropriate protective equipment without becoming incapacitated. DCS stated that they would use the IDLH values where available and Temporary Emergency Exposed Limits (TEEL) -2s for any hazardous chemicals without established IDLH levels. DCS had previously committed that Chapter 8 of the revised construction authorization request would be updated to include a table of the values to be used by the control room operators.

By letter dated July 28, 2003, DCS submitted revised CAR pages, including a separate table for hazardous chemical limits. NRC staff indicated that the revised Table submitted by DCS was acceptable. However, there was discussion at the meeting regarding whether the Self-Contained-Breathing Apparatus (SCBA) as described in the CAR was still accurate. It was agreed that the staff and DCS would look into this question, and clarify if necessary.

### 4. AP-3, Titanium Fires

The staff stated that it agreed with the DCS strategy of preventing a potential titanium fire. The staff stated that it does not believe that NFPA 70 is applicable in this case because it does not appear to address the time interval for the fuse/breaker; Institute of Electrical and Electronics Engineers (IEEE) 242 appears to be an appropriate standard. The staff stated its concern, namely, the adequacy of a protective device that would assure that the activation energy is not enough to initiate the event. Staff suggested that DCS use a current-time curve or characteristic curve for the device. At the conclusion of the meeting, the staff requested that DCS:

- (a) justify its design basis, proposed at the meeting, to limit leakage to 10 mA for 1 second;
- (b) justify the adequacy of the electrical protection device to protect against overcurrent that would cause a phase change in the titanium (believed to be around 450 degrees C); and
- (c) consider the contact area of the electrodes on the electrolyzer in its analysis.

### 5. MP-1, UO<sub>2</sub> Burnback

During the meeting, DCS stated that UO<sub>2</sub> burnback is not expected to affect the final High Efficiency Particulate Air (HEPA) filters because:

(a) during normal operations,  $UO_2$  would not be expected to be present on the final HEPA filters because intermediate HEPA filters would prevent any significant quantities of  $UO_2$  powder from reaching the final HEPA filter housing;

- (b) any particles passing through the prefilters would be micron-size particles that would be cooled by the time they reach the final HEPAs or do not contain enough energy to degrade the performance of the HEPAs; and
- (c) the energy associated with burnback is small when compared to the energies involved in an area fire.

DCS also provided a calculation which showed that approximately 36 kg of  $UO_2$  would have to collect on each element of the final HEPA filter units before the timetemperature rating of the filter is exceeded. DCS estimated that the maximum amount of uranium that could accumulate on a filter, using conservative assumptions, was 3.6 kg. Thus, DCS felt that this event is incredible for reasons provided in Attachment 3.

NRC staff stated that it is concerned about an ignition-type phenomena based on particle size (i.e., a small particle passing through the HEPA prefilters) and cited NRC Information Notice 92-14. Staff felt that the calculation provided by DCS did not address the potential ignition concern. The staff's concern is that small particles may become hot in the ventilation system and there are no pre-filters credited to remove these small particles.

In summary, at the meeting, the staff requested that DCS assume that 3.6 kg of  $UO_2$  converts to U3O8 on the filter surface and verify that the ignition temperature of the HEPA filters is not exceeded or that unacceptable damage, such as reducing the filter efficiency (e.g., by causing damage to the filter binder), does not occur. The staff is continuing to review the information provided by DCS at the meeting, including whether the 3.6 kg is an acceptable value.

6. NCS-4, Nuclear Criticality Safety

The following points were made during the meeting:

- a) for Areas of Applicability (AOA) 1, 2, and 5, NRC accepts k-effective for the range of parameters;
- (b) for AOAs 3 and 4, NRC has concerns and questions. NRC can approve the criticality part of the CAR now, but with different k-effectives than proposed by DCS and may limit the range of AOA 4. The staff may require additional margin for AOAs 3 and 4;
- (c) when DCS uses the term "dual parameter control", DCS means mass and moderation. The preferred approach is passive geometry control. There are no dual parameter controls so the facility uses passive geometry, and dual controls on one or more parameters, for example dual controls on mass and dual controls on moderation;
- (d) there was some confusion over the terms "normal conditions" and "abnormal conditions"; DCS agreed to clarify its use of these terms;
- (e) NRC staff questioned the footnote on CAR page change 6-20. DCS explained that the footnote was an explanation of two parameter control;
- (f) in DCS' July 25 letter regarding AOA 4, DCS needs to provide a revised CAR page change for Table 1-1 to correct the H/Pu ratio;
- (g) regarding Table 5-2 in AOA 4, DCS will change the design applicability to 1740ev;
- (h) similarly, the design applicability for AOA 3 will also be narrowed; and
- (i) NRC is continuing its review of AOA 4.

### 7. FS-2, Fire Barriers

DCS described the results of its analysis regarding the effects on concrete where temperatures exceed the American Society for Testing and Materials (ASTM)-E119 fire curve. The analysis included calculating the room temperature as a function of time and then using finite difference methods to calculate the temperature as a function of depth in the concrete. The results are shown in Attachment 3. The conclusion is that under the time vs. temperature curve that was calculated for the compartment, the concrete temperature at a depth of one inch does not exceed 200 degrees F in the first ten minutes, and after the first five minutes, the fire temperature slevel off or decline. Spalling has been found to occur only when the temperature exceeds 200 degrees F about an inch into the concrete. Therefore, DCS concluded that spalling would not be a concern should a fire occur.

### DUKE COGEMA STONE&WEBSTER HANDOUTS MOX FUEL FABRICATION FACILITY July 29-August 1, 2003

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### 8.3.2.2.1 EXPLOSION — TBP-NITRIC ACID ("RED OIL") RUNAWAY REACTIONS

The H-Canyon PHA (Ref. 8) (PHA Events RR-02, WD-04, and AR-01) includes a possible uncontrolled runaway TBP/nitric acid reaction. The event frequency was classified Unlikely because of the use of 7.5% TBP by volume in most HM Processes that significantly limits the amount of TBP available for this reaction. The consequences were classified as high, resulting in a Scenario Class I event. In this classification, the only passive, engineered feature considered was the canyon building, thus the high consequences. When the active systems and ACs are considered (described below), the consequences are reduced to medium and the frequency to Extreme Unlikely, and the event becomes Scenario Class III.

### 8.3.2.2.1.1 <u>Release Pathways and Scenarios</u>

A brief description of the chemistry of TBP/nitric acid reactions and of previous accidents involving TBP/nitric acid reactions at SRS and elsewhere is given in ECS-SSS-950007 (Ref. 25). In this accident scenario, tri-butyl phosphate (TBP) and nitric acid or TBP and uranyl nitrate are mixed in the same process vessel and heated to the autocatalytic temperature of the TBP-nitrate reaction. The autocatalytic temperature, the temperature at which the reaction is self-sustaining, is above 130° C. To date none of the red oil reactions that have resulted in explosions originated from an unheated process vessel. All the known reactions have resulted from mixing thermally hot solutions or by applying heat to the TBP-nitrate mixture. The term nitrate as used here means either nitric acid or a uranyl nitrate solution and for simplicity the term "red oil" means either type mixture. Although called a TBP-nitric acid runaway reaction, most of the known explosions in the nuclear industry have resulted from a mixture of uranyl nitrate and TBP rather than the more simple mixture of TBP and nitric acid.

As the red oil mixture is heated, the TBP starts to decompose. The decomposition products further decompose releasing a tremendous amount of volatile and explosive gases. In an unvented vessel, the reactions generate a very large and very rapid pressure increase. This rapid pressure increase can rupture an unvented vessel releasing the volatile explosive gases into the environment. This type of pressure explosion occurred in the evaporator at the SRS TNX facility. If an ignition source (e.g., a spark or heat source to heat the gases above their autoignition temperature) is present, the gases released from the reaction will explode violently. Two types of explosions are known to have occurred from a TBP-nitrate reaction. One type is the Tomsk (mixing thermally hot solutions) type explosion in which the initial reaction occurred in an inadequately or improperly vented process vessel resulting in an initial pressure explosion of the vessel. The gases released were subsequently ignited and created a secondary explosion extensively damaging the building. The other type of explosion is the one that occurred at SRS (denitrator process vessel contents heated with an external heat source) in which the volatile gases are released from the vessel through vents or other means. These volatile gases then explode as a primary explosion if an ignition source is present.

A red oil explosion can occur in H-Canyon or OF-H-by mixing TBP and uranyl nitrate or nitric acid.

The resulting mixture will have to be heated above the autocatalytic temperature of >130° C, several controls will have to fail. These controls include ACs and operating procedures that require shutdown of the heat source if the temperature exceeds preset limits. Examples of some of the equipment which would have to also fail include the temperature sensors and alarms, the liquid level instruments, pressure indicators,

the passive vents on the vessels, the PVV System, and the interlocks on these instruments. Credit is not taken for the canyon ventilation system as a preventer for this accident. If the reaction occurs within the confines of the canyon, the canyon building and canyon ventilation system will mitigate the radiological effects of the event. If the reaction occurs outside the canyon, very limited if any protection is available to mitigate the event consequences. The radiological consequences to the onsite worker and the offsite population are from an airborne radiological dose. For the facility worker, the major concern is the immediate blast effects (shock wave and ejected chemicals and radionuclides) and potential long-term exposure to radioactive nuclides in the accident clean up process.

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The PHA (Ref. 8) indicated that a red oil event is in the Unlikely frequency category for the canyon liquid waste systems, the evaporators, and the Rerun processes. The Unlikely frequency and the high accident consequences made this a Scenario Class I event. For the Head End process and the recycle sump in OF-H, the PHA identified a red oil reaction as having an Extremely Unlikely frequency with medium consequences for a Scenario Class III event. A red oil reaction in the ARU is considered to be an Extremely Unlikely event with high consequences to the facility worker for a Scenario Class II event.

Additional analyses identified two different red oil events that are possible in the canyons. One event involves a red oil explosion in which greater than 3,000 pounds of TBP are involved and the other is an explosion in which less than 3,000 pounds of TBP is involved. Red oil events involving greater than 3,000 pounds of TBP can cause extensive damage to or destruction of the canyon structure. Below a 3,000 pound TBP mass, the canyon structure has been shown to remain intact without significant damage. The analysis identified additional administrative and physical controls which when implemented reduces the frequency of the greater than 3,000 pounds of TBP event to less than 1.0E–06/year or to a BEU event. These controls are summarized in Table 8.3–2 and in the TSRs. The controls necessary to reduce the frequency or mitigate the consequences of the less than 3,000 pounds of TBP event are also contained in Table 8.3–2 and the TSRs.

### 8.3.2.2.1.2 Preventive and Mitigative Features

The basic approaches to preventing a TBP-nitric acid reaction in H-Canyon include the following:

1. Maintain the vessel effective vent area to reduce constituent partial pressures in the vessel that could feed back to increase energy release rates and limit evaporative cooling. If the mixture is open to the atmosphere, evaporation of water, diluent, and nitric acid is an efficient heat loss mechanism, which will limit the temperature of the mixture to the atmospheric pressure boiling point. Also, adequate venting allows the escape of reactants and intermediates from the reaction mixture, and limits the extent of the reaction. In contrast, a closed or inadequately vented system allows the pressure to increase as gaseous reaction products accumulate, which raises the boiling point, suppresses the heat loss due to evaporation, and retains partially reacted intermediates which can continue to react and generate heat. Based on an experimental investigation and analysis (ECS-SSS-950007) (Ref. 25), the process vessel-vent and vessel overflow piping provide sufficient vent area for most canyon vessels. Adequate margin in vent areas will be ensured for those non-evaporator vessels with a potential for accumulating up to 3,000 pounds of TBP. Vessels that have small diameter overflow pipes will have one spare nozzle opened and specifically designated as a red oil vent (ROV) nozzle (DF). S-CLC-H-00228 (Ref. 26) indicates that a minimum vent area of 6.44 in<sup>2</sup> is sufficient to relieve the pressure from a red oil reaction. This reference identifies those H-Canyon vessels for which adequate venting exists. The vessels that require additional venting are identified in X-CLC-H-00304, Rev. 0, (Ref. 89) as Tanks 8.4, 8.6, 9.8, 11.4, 11.7, 12.2, 13.7, 14.2, 14.6, 14.8, 15.1, 15.2, 15.4, 16.1, 16.2, 16.6, 17.1, 17.3, 17.5, 18.1, and

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18.2. The ROV nozzle (SS items) covers with special markings were installed initially in August 1997 on the Hot and Warm Canyon vessels identified above as requiring ROVs at that time. Since 1997, additional tanks have had ROVs installed based on the more recent referenced calculation. The vent itself is simply a direct opening into the vessel through a short stubby pipe with a special flange to allow connection of the Hanford Connector. If there is no other pipe or jumper connected to the nozzle, it is assumed that the vent is open and adequate as a vent nozzle. The specially marked dust covers keep dust, dirt, and other debris out of the process vessel. The dust cover allows adequate pressure relief and venting of the tank. Periodically, the presence of the dust covers will be verified by visual inspection using the canyon cranes and procedures that identify which vessels have the ROV nozzles.

- 2. Not all H-Canyon tanks require additional vent area to relieve pressures generated by a potential red oil reaction. Most of the solvent extraction processes in H-Canyon use only 7.5 vol. % TBP which significantly limits the amount of TBP available for the reaction when compared to the 30 vol. % TBP used in F-Canyon processes. The tanks that require additional vent area in H-Canyon are typically those tanks in which 30 vol. % TBP can be used or in which there is the potential for significant TBP accumulation. For the other H-Canyon vessels in which TBP can be used but that are not specifically identified as requiring additional vent area to prevent a red oil explosion, the existing vent area (e.g., vent area provided by the vessel liquid overflow line and the PVV nozzle) is sufficient to limit the pressure build up from the reaction. Since the vessel overflow line is a passive DF of the equipment, the vessels which were designated as requiring additional vent area are those for which the liquid overflow line and PVV nozzle (DF) will not provide sufficient vent capacity.
- Prevent mixtures of TBP and nitric acid from reaching high temperature by ensuring cooling 3. mechanisms are capable of removing the heat being generated. The reaction will run away only if the temperature exceeds some critical value (dependent on TBP mass and vessel heat removal mechanisms), above which the rate of heat generation exceeds the rate of heat loss. The canyon air exhaust system, a SC system, maintains sufficient airflow to provide adequate heat removal through the tank walls provided the tank contents are mixed. Initial studies indicated that the agitator provides sufficient fluid motion for the necessary heat transfer although an unmixed organic layer may be present in certain circumstances. The initial studies indicated agitation is required only when there is a mechanism for heating the top layer of solution in the tank, (e.g., steam jetting solution into the tank). After the transfer has been completed, agitation can be stopped. In the original studies, indication of agitation for vessels, which could contain 3,000 lb. of TBP, was designated as an additional SC system based on a review of the incident in Russia at the Tomsk reprocessing facility. WSRC-RP-98-00171, Revision 1 (Ref. 27), reports the results of subsequent experiments and analyses that demonstrate adequate mixing and heat transfer is available to prevent overheating the top organic layer without agitation in the tank. The latest experiments determined that if the steam jet is left on for an extended period after all the liquid solution is transferred, the organic layer would not be overheated. Reference 27 proves that if the steam jet is left on without agitation being present, the maximum temperature the organic layer will reach is 128° C, still below the 130° C limit at which the runaway red oil reaction is assumed to occur in the safety analysis. Since agitation is not required to ensure that the organic layer will not exceed the 130° Climit the requirement for SG indication of agitation on tanks that can contain greater than 3,000 pounds of TBP is removed. Not all H-Canyon tanks can contain greater than 3,000 pounds of TBP based on the 7.5 vol. % TBP used in most H-Canyon processes. For those tanks, which cannot contain greater than 3,000 pounds of TPP, agitation is unnecessary because other natural features of the process provide adequate cooling to limit the temperature rise associated with the reaction. One natural feature is the cooling effect generated by the evaporation of the aqueous phase. WSRC-TR-94-0540 (Ref. 28) demonstrates that in unagitated vented vessels (e.g.,

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evaporators), the transport of water from the underlying aqueous phase to the TBP phase is sufficient to maintain continuous evaporation and a net cooling of the solution. This conclusion covers temperatures up to 120° C and organic depths to at least 6 feet.

DPST-56-243 (Ref. 29) was used to establish 130° C as the always-safe temperature to prevent red oil explosions in the H-Canyon evaporators. This temperature was below the approximately 135° C minimum temperature at which initiation of a runaway reaction between TBP and concentrated (70-wt. %) nitric acid was observed to occur (Ref. 29). Gordon demonstrated that initiation did not occur until the temperature exceeded the 135° C minimum temperature observed in Reference 29 (Ref. 30). For example, initiation of the TBP-nitric acid runaway reaction was observed to start at temperatures above 140° C for an acid concentration of 50-wt. %, which is the maximum acid concentration typically used in the canyon processes. Literature data indicates that a runaway red oil reaction is not initiated in an open (vented to atmosphere) vessel below 135° C. The H-Canyon vessels have at least one passive vent to the canyon atmosphere.

SRTC completed experimental analysis to verify the 130°C obtained in Reference 29. The SRTC experiments also determined the effects of inextractable solids on the red oil runaway reaction initiation temperature. These SRTC experiments summarized in WSRC-TR-2000-00427 (Ref. 31), indicated or reported on "The initiation temperature for a runaway TBP/nitric acid reaction measured as a function of the nitric acid and dissolved solids concentration of the aqueous phase in equilibrium with pure TBP."

Reference 31 concludes "To obtain a runaway TBP/nitric acid reaction, it was necessary to seal the RSST<sup>™</sup> containment vessel at atmospheric pressure prior to initiation of an experiment." This conclusion supports previous literature data and experimental evidence that in an open vented system, such as the H-Canyon process vessels, a runaway TBP/nitric acid reaction will not occur.

The SRTC report (Ref. 31) also concluded that "The runaway reaction initiation temperatures for TBP in contact with nitric acid solutions containing no dissolved solids were in good agreement with the data from the 1950s." The minimum initiation temperature,  $137^{\circ}$  C, measured at 14-15M nitric acid was consistent with previously measured values in the 132 - 137° C range at nominally 15.7M nitric acid. The initiation temperature measured with TBP in contact with nitric acid solutions containing 5, 10, and 20% wt dissolved solids depicted a small dependence on the solids concentration; however, the temperatures were well above the minimum value for no dissolved solids." Data from Table 2 of this report shows that the minimum initiation temperature observed was 139° C with the lowest average initiation temperature for each group being 137° C.

The SRTC report supports the conclusion that with no agitation in the H-Canyon tanks, there is sufficient venting and a safe margin between the maximum theoretical temperature of 128°C in the tank and the actual TBP/nitric acid initiation temperature in excess of 130°C.

Reference 27 indicates that 128° C is the maximum theoretical temperature for organic layer self-heating in a two phase TBP-nitric acid mixture in which steam is blowing directly on the organic layer. The 128° C maximum temperature is 7° C below the 135° C minimum initiation temperature for a two phase system with 70-wt. % nitric acid, and is 12° C less than the observed 140° C initiation temperature of a two phase system with 50-wt. % nitric acid. The conservative results in Reference 27 demonstrate that agitation is not required to provide cooling

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of the TBP-nitric acid mixture, even if the steam is left on and blows on the organic layer after a liquid transfer is complete.

4. Limit the mass of TBP present by use of decanters. The total amount of heat generated and total amount of gases generated will be proportional to the amount of TBP that is reacted. With limited amounts of TBP, uncontrolled reactions can be accommodated with minimal consequences. The tank decanters and the administrative requirement to shut down the process in case of a high organic level in the decanter (TSR LCO), prevent the accumulation of excessive organic in vessels where red oil is a concern. These two features, combined with the relatively low volume percent TBP in the HM process, limit the amount of organic that can be fed to a particular vessel. The procedures used to control transfers into and from decanters 9.7 and 10.8 instruct the operator to stop all transfers involving the decanters if the decanter organic solution level weight factor exceeds 50. Use of the decanters to limit the TBP mass is required only for those processes in which more than 8.5 vol. % TBP is used. For those processes that use less than 8.5 vol. % TBP, decanters are not specifically required to prevent a red oil explosion involving 3,000 pounds or more of TBP since it is impossible to get more than 3,000 pounds of TBP in a single H-Canyon vessel using 8.5 vol. % or less TBP.

A low reaction rate and low boiling point of the weaker nitric acid solution makes the probability of a runaway TBP and nitric acid reaction for nitric acid concentrations below 2.5 Molar (M) negligible (SRT--CTS-95-0021, Ref. 32). Heat removal, venting, and solvent inventory controls have been applied to canyon vessels that have the potential to contain TBP in contact with a bulk solution concentration greater than 2.5M nitric acid. Indication of agitation for Tanks 8.7, 11.7, 11.8, 13.7, 13.8, 14.6, 15.2, 16.6, and 17.1 was the SC system used to prevent a red oil explosion in these tanks. Reference 27 demonstrates that agitation is not required to ensure sufficient heat transfer to prevent exceeding the 130° C limit to prevent a red oil explosion. Therefore, indication of agitation for the identified tanks has been removed as a SC requirement without increasing the frequency (i.e., the event is still BEU) of a red oil explosion in those tanks that can contain greater than 3,000 pounds of TBP (those tanks that can contain 30 vol. % TBP).

The two mechanisms for loss of aqueous from an evaporator are evaporation and displacement. By controlling the evaporator temperature and the loss of organic to the aqueous stream (decanter and solvent hold tank controls), the fraction of the evaporator contents that is aqueous will be indirectly controlled. With aqueous always in the evaporator when TBP could be present, the experimental results in WSRC-TR-94-0540 (Ref. 28) indicated temperatures will remain below 120° C. At these temperatures runaway reactions cannot occur. To prevent a potential problem, the following are required for evaporation of acidic solvent extraction waste and product in batch evaporators. Solvent extraction wastes may be neutralized and discarded without evaporation, if necessary. These features limit the evaporator temperatures, limit the organic that could enter the evaporator, and ensure that sufficient aqueous is present to provide the evaporative cooling necessary to prevent a red oil reaction in the evaporators.

Evaporator temperature sensors, interlocks, and alarms on 6.8E, 7.6E, 7.7E, 9.1E, 9.2E, 11.3E, and 17.8E are salety class. The temperature is maintained equal to or less than 120° C. The operator shall verify (via flow measurement) that steam is shut off (closing the steam block valve manually if needed) whenever the temperature alarms demand the steam valve to close. The operator will close the steam block valve within 30 minutes of the temperature alarm if steam interlocks do not operate properly. Additionally, safety significant interlocks limit steam pressure to a maximum of 25 psig. Some of the process

control signals for these interlocks pass through the input/output cards and/or programmable instruments in the temperature or pressure instrument loops. These interlocks are safety significant systems that prevent excessive heating of the evaporator solution.

- A control that limits TBP concentration used in some solvent extraction cycles to less than 8.5% TBP by volume (nominal 7.5 vol. % TBP used in First Cycle and Second U Cycle) ensures other H-Canyon evaporators cannot contain more than 3,000 pounds of TBP. During solvent extraction operations, evaporators have the potential to receive TBP although decanters are employed to eliminate this occurrence.
- A SC AC ensures that all Evaporator Feed which has been in contact with greater than 8.5 vol. % TBP shall be processed through a decanter prior to evaporation.
- Organic section level detectors and alarms on Decanters 9.7 and 10.8 are SC systems. Operating procedures require the operators to shutdown the decanters if a high organic tank level alarm is received for one of these decanters.
- An aqueous heel is required for the box decanter to work properly. The steam to the transfer jets that transfer aqueous from Box Decanters 13.6-1S and 16.1-1S are blanked off per a Safety Class AC to prevent the removal of aqueous to ensure proper operation of the decanters.
- The Warm Canyon sump solutions will be routed through a decanter that has a design efficiency equal to or greater than the 90% efficiency before processing in any evaporator. Additionally, the material in Tank 17.1 shall be processed through Decanter 16.1-1S, or another decanter with equal or greater efficiency, before being transferred to Tank 11.2 or Evaporator 11.3E. If the Warm Canyon sump solution is processed in an evaporator other than 17.2E, the sump solution may be passed through any other decanter that has an efficiency greater than or equal to the efficiency required for Decanter 16.1-1S. For example, if the Warm Canyon sump solution is processed in the LAW evaporators, the solution shall be passed through Decanter 9.7 before it is fed to the LAW evaporator. The requirement is to ensure that the sump solution is passed through a decanter that is at least 90% efficient in separating the organic and the aqueous components before the aqueous component is fed to the evaporator. WSRC-RP-98-00556 (Ref. 33) shows that the box decanter efficiency is greater than 98%, as compared to the 90% efficiency used in the accident analysis. The decanter efficiency of 90% was chosen in the accident analysis to provide a margin of safety between the actual expected decanter efficiency of >95% and the efficiency used in the accident analysis. As the expected efficiency of the decanter decreases the probability increases (e.g., becomes more frequent) that large amounts of solvent will enter the evaporator feed streams. This 90% efficiency limit is applicable to any decanter (e.g., 9.7, 10.8, 13.6–1S and 16.1–1S) that is used to control organic levels to prevent red oil explosions. Use of the decanters to limit the TBP mass present is required only for those processes in which more than 8.5 vol. % TBP is used in the process. For those processes that use less than 8.5 vol. % TBP, decanters are not specifically required to prevent a red oil explosion involving 3,000 pounds or more of TBP since it is impossible to get more than 3,000 pounds of TBP in a single H-Canyon vessel using 8.5% or less TBP by volume.
  - The evaporators are shut down, until the solvent inventory is accounted for, following large . solvent losses (more than 3,000 pounds of TBP) from the Second Product Cycle system. Some surveillance measures available to detect large solvent losses are: 1) activation of the low level alarm on the solvent hold tank for the process being operated (DiD); 2) daily

solvent inventory taken during process operations involving the 2A or 2B Banks (AC) (SC); or 3) routine monitoring of the solvent tank level during normal process operation (DiD).

• The transfer procedure for Decanters 9.7 and 10.8 includes a WARNING to the operator that decanter transfers must be stopped if the decanter organic section weight factor exceeds 50.

A red oil event involving greater than 3,000 pounds of TBP has been determined to be BEU in the HAW system evaporators, 9.1E and 9.2E, Evaporator 17.2E, and the Second Uranium Cycle evaporator, 17.6E, because these evaporators only receive material which has been in contact with 7.5 vol. % TBP. However, it is possible to get less than 3,000 pounds of TBP in these evaporators. Specific controls to prevent a red oil reaction involving less than 3,000 pounds of TBP in 9.1E, 9.2E, 11.3E, 17.2E, and 17.6E include:

- 1. Temperature alarms and interlocks on the 17.2E, and 17.6E evaporators that limit the temperature to 120° C or less are safety significant. This limit is chosen to ensure that if organic is present in the evaporator during the heat up or cool down phases of evaporator operation (when heat removal by active boiling is not taking place), the heat of reaction will be adequately removed.
- 2. Interlocks on the 9.1E, 9.2E, 17.2E, and 17.6E evaporators limit steam pressure to a maximum of 25 psig. This control applies to Evaporator 11.3E only when the evaporator is receiving or processing Rerun materials. These interlocks are SS systems to prevent excessive heating of the evaporator solution.

Because of a higher failure frequency than expected of RTD sensors installed in boiling acid evaporators, and the potential for the RTD to fail in a non-conservative mode, it was determined that an NI/PISA existed. The accident analyses assumed that the RTD is working properly and the fault tree analysis assumes that failure of the RTD will be detected within 24 hours (Ref. 88). To address this non-conservative failure of the RTD, an additional control was established. This control provides additional assurance that a failed RTD will not go undetected by ensuring that the structural integrity of the thermowell housing of the RTDs in the canyon acidic evaporators is maintained. If there is indication that the thermowell has failed, actions are taken to verify the operability of the RTD. The thermowell and/or the RTD are replaced as necessary, to ensure the operability of the RTD. A similar control was established for the ARU preheater and reboiler RTDs. Theses ACs protect against a failed RTD giving a low temperature reading which may cause the upper temperature limit to be exceeded.

The controls described above reduce the frequency of red oil events with a mass greater than 3,000 pounds to BEU (less than once in a million years).

To provide further assurance that a non-conservative failure of the RTD will be detected in the acidic evaporators and ARU, operating procedures require that the temperature readings be taken periodically. These temperature readings are compared against a known temperature that is expected during boiling conditions in the evaporators and the ARU. If the temperature reading is less than the comparison value or is not consistent with the other process operating parameters, an evaluation of the abnormal temperature is completed to determine the appropriate actions to take (e.g., continue operations or shut down the process). These procedural actions are not credited in the fault tree or the accident analysis and are simply process related and good conduct of operations activities that provide defense in depth to ensure that a RTD failure will be detected.

### WSRC-SA-2001-00008, Rev. 4 H-Canyon Safety Analysis Report

The consequences of events with a mass less than 3,000 pounds of TBP are acceptable in terms of the radiological hazard and potential doses to the onsite worker and the offsite public. Since the canyon structure, the sand filter and canyon exhaust system are expected to survive the effects of a red oil explosion involving less than 3,000 pounds of TBP, the accident consequences are mitigated by these SC systems. These mitigative systems reduce the event consequences from a high category to a medium category. Also since this event occurs within the canyon, the radiological doses from this event are expected to be less than the doses received from a transfer error to outside or a release to the cooling water systems. The consequences for a red oil explosion involving less than 3,000 pounds of TBP are in the consequence section of Addendum 1 to this SAR. The red oil explosion is not the bounding consequence event in the Extremely Unlikely frequency category. The controls identified do not move the frequency of the event involving less than 3,000 pounds of TBP from the Unlikely category into the Extremely Unlikely category.

An Unlikely frequency with medium consequences makes the red oil explosion with less than 3,000 pounds of TBP a Scenario Class II event.

An external heat source must be available to initiate the red oil reaction. Red oil events in OF-H, other than the ARU, are BEU since there are no external heat sources in the OF-H areas where solvent is present. Originally, an AC required that blanks be installed and maintained in the steam lines to the Segregated Solvent Tank coils. The steam lines to the steam coils in the Segregated Solvent Tanks in OF-H have been physically removed. An air gap now exists between the steam lines and the steam coils in the tanks. Since steam can no longer be applied to the Segregated Solvent Tanks, there is no method available to heat the organic material above the 130°C minimum temperature at which a runaway TBP-nitric acid reaction will occur. Therefore, the AC to maintain a blank or blank equivalent in the steam lines to the Segregated Solvent Tanks has been deleted as a red oil prevention control. If, for any reason, the steam lines are reconnected to the Segregated Solvent Tanks, this would be a physical change to the facility that is controlled by the Configuration Control Program, and will be evaluated by the Unreviewed Safety Question Process. Waste solutions originally containing solvent are evaporated in the canyon which removes solvent prior to being sent to OF-H. Therefore, red oil events, other than in the ARU, in OF-H are not considered further in this SAR. Specifically for the General Purpose (GP) Evaporators, additional red oil restrictions or controls are not required because these units are basic evaporators. Red oil reactions will not occur in a basic solution. Therefore, the single control that ensures other controls are not required to prevent a red oil explosion in the GP Evaporators is the AC that limits the GP Evaporator feed to minimum pH of 7.0 or greater. With this control, the GP Evaporator feed is basic and a red oil reaction is a BEU event. The pH 7.0 product feed limitation does not apply during the acid flush operations on the GP Evaporator when organic feed is discontinued.

The ARU in OF-H is a distillation column designed to concentrate dilute nitric acid from the canyon HAW and LAW evaporator overheads. Any organic material present in the canyon evaporators can be distilled into the evaporator overheads. The HAW and LAW evaporator overheads are the ARU feed. Unlike the canyon evaporators, the ARU is located outdoors in an area accessible to facility personnel. Therefore, the consequences of an explosion in the ARU are high for the facility workers. Gontrols are required to prevent a red oil explosion in the ARU to protect the facility worker.

The ARU aqueous phase is essentially nitric acid and water with very little if any potential for TBP to be present. The organic phase separates more completely and rapidly from the aqueous in the ARU and there is no mechanism for phase inversion. Control is simplified and achieved through maintaining the solution temperature in the ARU preheater and reboiler at or below 120°C by using the ARU

### WSRC-SA-2001-00008, Rev. 4 H-Canyon Safety Analysis Report

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Evaporator High Temperature Interlocks (SS items). This temperature protects against self-heating of the solution to the runaway point during periods when heat removal through active boiling is not occurring. The ARU Evaporator Feed Tank Low Liquid Level Pump Cutoff Interlock is an SS item. Since the feed tank is unagitated, the Low Liquid Level Pump Cutoff Interlock normally prevents accumulated organic from being fed to the ARU.

Although the ARU Feed Tank is inspected periodically and any accumulated organic is skimmed off as necessary, the ARU feed may still contain dissolved TBP in trace quantities as entrained organic. Evaporation can concentrate the entrained organic to about 90% and reduces the solubility of dissolved TBP from 100 mg TBP/liter in the feed to 32 mg TBP/liter in the concentrate (DPST-75-400). Inspections for accumulated organic have historically been completed weekly as a conservative approach. However, in actual operation, the dissolved TBP has tended to remain entrained as it comes out of solution rather than forming a layer, and very little accumulation has been observed between inspections. The typical method used to detect organic accumulation in OF-H has been rodding of the tank contents to detect the presence of organic in the feed tank. However, a visual inspection can also be used to detect the organic. An AC which requires annual inspection for and removal of a continuous layer of organic from the ARU Feed Tank prevents feeding an excessive amount of TBP to the evaporator. Any continuous layer of organic detected by the inspection shall be removed by skimming or flushing the tank.

These controls apply only when material that can contain TBP is available as a feed stream to the ARU. Typically, these controls will only apply when the solvent extraction processes are operating (or have just completed operation) and feed from the waste system evaporators can contain TBP. When the solvent extraction processes are not operating, the waste evaporators are used to concentrate liquids which have not been in areas where the aqueous and organic phases could be combined (e.g., rain water which collects in the OF-H sumps, dikes, and basins, and water from the canyon cell flushes). Since the material processed in the waste evaporators and the ARU is expected to contain very little if any organic material, application of the red oil controls is not necessary if the solvent extraction processes are not operational.



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## MOX Fuel Fabrication Facility (MFFF) Open Item Resolution CS-09, AP-02, AP-08 and AP-09

NRC Technical Exchange Meeting 29 July 2003



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A follow up teleconference to the Open Items AP-2 and CS-09, AP-08, and AP-09 from letter DSC-NRC-00142, dated 05 June 2003, was held on Wednesday, 11 June 2003. As a result of this teleconference, the NRC clarified its position regarding what constitutes an adequate margin between noncombustible and combustible conditions.

The NRC stated that 25% of the lower flammable limit (LFL) is used as a design basis safety margin by the DOE Hanford and Savannah River Sites. The NRC cited references [1] and [2] from these sites and NFPA 69-1997 to support this position. The NRC asked DCS to provide additional information to justify the use of different values for the design bases.



# **DCS Response Summary**

- DCS proposes to use 60% of the LFL in accordance with NFPA 69-1997 as a design basis value inside process vessels in which solvent is present. NFPA 69 allows 60% of the LFL to be used provided the system is equipped with automatic instrumentation with safety interlocks. The flash point temperature of the potentially combustible or flammable solvent vapor will be based upon measurement or application of Le Chatelier's rule. These values are selected based on guidance from NFPA 30-1996 and NFPA 69-1997.
- Inside of vessels containing  $H_2$  and in the KWG system the design basis value is 50% of the LFL with 25% of the LFL as a set point
- Outside of process vessels, e.g., in rooms, the design basis value is 25% of the LFL with a set point value determined by set point analysis
- DCS has reviewed the references provided by NRC and has concluded that the above safety philosophy is consistent with the practices performed at those DOE sites.
- It should be noted here that design bases identify the safety functions and the specific values and ranges of values chosen for controlling parameters as reference bounds for the design necessary to satisfy the performance requirements of 10 CFR §70.61.



### Pertinent Excerpts from NFPA 69-1997

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- "3-2.1 The following factors shall be considered in the design of a system to reduce the combustible concentration below the lower flammable limit (LFL):
- "(a) Required reduction in combustible concentration
- "(b) Variations in the process, process temperature and pressure, and materials being processed
- "(c) Operating controls
- "(d) Maintenance, inspection, and testing
- "3-2.2 The lower flammable limits of the combustible components shall be determined at all operating conditions, including startup and shutdown.
- "3-3 Design and Operating Requirements.
- "3-3.1 The combustible concentration shall be maintained at or below 25 percent of the lower flammable limit (LFL).
- Exception No. 1: When automatic instrumentation with safety interlocks is provided, the combustible concentration shall be permitted to be maintained at or below 60 percent of the lower flammable limit."

"3-4 Instrumentation.

"3-4.1 Instrumentation shall be provided to monitor the control of the concentration of combustible components."



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## The Applicable Codes

Two national fire protection codes govern the safety of process vessels handling flammable and combustible fluids:

- NFPA 30-1996 Flammable and Combustible Liquids Code
- NFPA 69-1997 Standard on Explosion Prevention Systems



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- The purpose of NFPA 30 is to provide reasonable requirements for the safe storage and handling of flammable and combustible liquids.
- NFPA 69 outlines the requirements for installing systems for the prevention of explosions in enclosures that contain flammable concentrations of flammable gases, vapors, mists, dusts, or hybrid mixtures.



- The first safety limit is set at a value of 25% of the LFL when the *control of the combustible components* is <u>not</u> <u>continuously monitored</u>. From NFPA 69 §3-3.1:
  - "The combustible concentration shall be maintained at or below 25 percent of the lower flammable limit (LFL)."
- When the control of the combustible components <u>is</u> <u>monitored with automatic instrumentation with safety</u> <u>interlocks</u>, the allowable value can be as high as 60% of the LFL. From NFPA 69 §3-3.1 Exception No. 1:
  - "When automatic instrumentation with safety interlocks is provided, the combustible concentration shall be permitted to be maintained at or below 60 percent of the lower flammable limit."



 These limits have been accepted by the NFPA 69 committee as providing a sufficient margin to prevent the initial ignition and onset of deflagration. These margins account for uncertainties in determining the limits between the explosive and non-explosive regimes when either the oxidant or combustible concentration is the control.



## **DCS Safety Commitments**

- To meet the requirements of 10 CFR §70.61, DCS has identified
  - The process safety control subsystem to ensure that process temperatures do not lead to flammable vapors e.g. exceedance of 60% of the LFL.
  - The PSSC will be implemented such that diverse/redundant IROFS are provided with automatic safety interlocks. Thus, using 60% of the LFL as a design basis safety limit is appropriate.



- Jain, V., R. Pabaian, D. Daruwalla, J. Weldy and D. Pickett; "Review of BNFL Inc. Design Safety Features Deliverable: Hydrogen Control in High-Level Waste Storage Tanks," CNWRA 99-001, Rev. 1 April, 1999
- Hobbs, D. T., "Possible Explosive Compounds in the Savannah River Site Waste Tank Farm Facilities (U)", Savannah River Technology Center, WSRC-TR-91-444, Revision 3, February 15, 2000



# BNFL CNWRA 99-001

- Concentration of hydrogen is primary concern
- Safety goal is to stay below 25% of the LFL using active vessel ventilation system (AVVS)
- Failure of AVVS can occur
- Upon failure of AVVS, combustible gas concentration can exceed 25% of the LFL in finite time: between 1.37 hrs and 15.4 hrs
- Passive vessel ventilation system may not keep combustible gas concentration below 100% of the LFL
- Includes the following warning about exceeding the LFL
  - "during a failure of the AVVS, the residual hydrogen...can form rich pockets in the offgas piping, scrubber, filters, fans and the like...These pockets will need to be cleared safely during restart of the AVVS." [pp 8-1.]
- NRC agreed in their cover letter stating:
  - "Estimates in the report imply that the time periods required for reaching 25% and 100% of the lower flammability limit may be significantly shorter than those currently being used by the contractor."



### WSRC-TR-91-444

- Similar limits for H<sub>2</sub>
  - Type III waste tanks are set to alarm when the  $H_2$  concentration reaches 10% of the LFL
  - In the event that the ventilation system is shut down, administrative procedures require that the ventilation system be returned to operating condition within a period of time determined by the decay heat load of the tank.
- For tanks that contain benzene
  - Nitrogen purge is used to keep the oxygen concentration below 6.9% by volume
  - The concentration of benzene vapor is deemed to exceed 60% LFL
- For SRS F and H Area Separations Facilities and the DWPF
  - Waste temperature at the waste generator is limited to < 70°C to provide a 4°C margin to the flashpoint of dodecane (74°C), approximately 80% of the LFL based on vapor pressure
- For organic wastes tanks
  - Organic concentrations, temperature, and ventilation controls were established to prevent the formation of flammable vapor concentrations in waste tanks
  - AVVS required to keep concentrations below 25% of the LFL
  - Administrative controls control heat input and AVVS



# **Safety Position from References**

- DUKE COGEMA STONE & WEBSTER
  - Exceeding 25% of the LFL is credible, thus this is not a "not to exceed" safety limit
  - Automatic and administrative controls used to prevent exceeding 100% of the LFL when the 25% LFL safety goal is exceeded
  - When the 60% LFL limit is exceeded by the process, 2 approaches used
    - Temperature control to stay below flash point of liquid
    - Inert gas purge to stay below the limiting oxidant concentration

### Enclosure 1 Response to DSER Open Items On Chemical Safety

### Open Item CS-09, AP-02, AP-08 and AP-09:

A follow up teleconference to the Open Items AP-2 and CS-09, AP-08, and AP-09 from letter DSC-NRC-00142, dated 05 June 2003, was held on Wednesday, 11 June 2003. As a result of this teleconference, the NRC clarified its position regarding what constitutes an adequate margin between noncombustible and combustible conditions.

The NRC stated that 25% of the lower flammable limit (LFL) is used as a design basis safety margin by the DOE Hanford and Savannah River Sites. The NRC cited references [1] and [2] from these sites and NFPA 69-1997 to support this position. The NRC asked DCS to provide additional information to justify the use of different values for the design bases.

### **Response:**

- DCS proposes to use 60% of the LFL in accordance with NFPA 69-1997<sup>1</sup> as a design basis value inside process vessels in which solvent is present. NFPA 69 allows 60% of the LFL to be used provided the system is equipped with automatic instrumentation with safety interlocks. The flash point temperature of the potentially combustible or flammable solvent vapor will be based upon measurement or application of Le Chatelier's rule. These values are selected based on guidance from NFPA 30-1996 and NFPA 69-1997.
- Inside of vessels containing H2 and in the KWG system the design basis value is 50% of the LFL with 25% of the LFL as a set point
- Outside of process vessels, e.g., in rooms, the design basis value is 25% of the LFL with a set point value determined by set point analysis
- DCS has reviewed the references provided by NRC and has concluded that the above safety philosophy is consistent with the practices performed at those DOE sites.

<sup>&</sup>lt;sup>1</sup> Pertinent excerpts from NFPA 69-1997:

<sup>&</sup>quot;3-2.1 The following factors shall be considered in the design of a system to reduce the combustible concentration below the lower flammable limit (LFL):

<sup>&</sup>quot;(a) Required reduction in combustible concentration

<sup>&</sup>quot;(b) Variations in the process, process temperature and pressure, and materials being processed

<sup>&</sup>quot;(c) Operating controls

<sup>&</sup>quot;(d) Maintenance, inspection, and testing

<sup>&</sup>quot;3-2.2 The lower flammable limits of the combustible components shall be determined at all operating conditions, including startup and shutdown.

<sup>&</sup>quot;3-3 Design and Operating Requirements.

<sup>&</sup>quot;3-3.1 The combustible concentration shall be maintained at or below 25 percent of the lower flammable limit (LFL).

Exception No. 1: When automatic instrumentation with safety interlocks is provided, the combustible concentration shall be permitted to be maintained at or below 60 percent of the lower flammable limit." "3-4 Instrumentation.

<sup>&</sup>quot;3-4.1 Instrumentation shall be provided to monitor the control of the concentration of combustible components."

### Enclosure 1 Response to DSER Open Items On Chemical Safety

• It should be noted here that design bases identify the safety functions and the specific values and ranges of values chosen for controlling parameters as reference bounds for the design necessary to satisfy the performance requirements of 10 CFR §70.61.

The rational for this response is provided in Attachment A.

Two national fire protection codes govern the safety of process vessels handling flammable and combustible fluids: NFPA 30-1996 *Flammable and Combustible Liquids Code* and NFPA 69-1997 *Standard on Explosion Prevention Systems*. The purpose of NFPA 30 is to provide reasonable requirements for the safe storage and handling of flammable and combustible liquids. It provides safety requirements based on the fire risk inherent in the liquid being handled, thus it makes a distinction between flammable and combustible fluids. NFPA 69 is more specific than NFPA 30. NFPA 69 outlines the requirements for installing systems for the prevention of explosions in enclosures that contain flammable concentrations of flammable gases, vapors, mists, dusts, or hybrid mixtures.

Unlike NFPA 30, which defines requirements based on the relative risk posed by various fluids, NFPA 69 assumes that the process vapors are inherently hazardous under normal process or atmospheric conditions and thus it makes no distinction between flammable and combustible fluids. In order to provide a sufficient working margin between a flammable atmosphere and a nonflammable atmosphere when the goal is to prevent explosions, NFPA 69 sets two safety limits. The first safety limit is set at a value of 25% of the LFL when the *control of the combustible components* is <u>not continuously</u> monitored. From NFPA 69 §3-3.1:

"The combustible concentration shall be maintained at or below 25 percent of the lower flammable limit (LFL)."

When the control of the combustible components <u>is monitored with automatic</u> <u>instrumentation with safety interlocks</u>, the allowable value can be as high as 60% of the LFL. From NFPA 69 §3-3.1 Exception No. 1:

"When automatic instrumentation with safety interlocks is provided, the combustible concentration shall be permitted to be maintained at or below 60 percent of the lower flammable limit."

These limits have been accepted by the NFPA 69 committee as providing a sufficient margin to prevent the initial ignition and onset of deflagration. These margins account for uncertainties in determining the limits between the explosive and non-explosive regimes when either the oxidant or combustible concentration is the control.

To meet the requirements of 10 CFR §70.61, DCS has identified the process safety control subsystem to ensure that process temperatures do not lead to flammable vapors e.g. exceedance of 60% of the LFL. The PSSC will be implemented such that diverse/redundant IROFS are provided with automatic safety interlocks. Thus, using 60% of the LFL as a design basis safety limit is appropriate.

DCS has reviewed the two references supplied by the NRC and concludes that the national standard NFPA 69<sup>1</sup> Standard on Explosion Prevention Systems has been applied only as a guideline by the Savannah River Site (SRS) and Hanford Site to prevent explosions caused by deflagrations. When 25% of the LFL is referred to by the referenced documents, it seems to be in terms of a safety goal and not as a design basis i.e. a limit not to exceed, where the definition of design bases is taken from 10 CFR §50.2 and analytical limit is taken from the section Setpoints for Safety Instrumentation (Attachment B).

The distinction between the safety goal and design basis, i.e., a limit not to exceed, is seen in References [1] and [2]. In both references, for tanks in which the predominant combustible load consists of radiolysis-generated hydrogen, the sites use 10% of the LFL as the trip set point and 25% of the LFL as a de facto safety goal based on measurement (either continuous or periodic) and subject to time restrictions upon failure of the active vessel ventilation system (AVVS). These goals can be exceeded under some specifically identified instances. For example, tanks in which varying concentrations of organic compounds are present may have multiple safety action limits based on the amount of other flammable compounds present and the degradation or decomposition time. For other tanks in which the amount of the other flammable compounds is credited with being low, both the amount of combustible material present and the time to reach the 25% of the LFL is specifically mentioned. In tanks in which the quantity of other flammable compounds is present in significant quantities or cannot be otherwise bounded, the design basis safety limit is to remain below 100% of the LFL or the combustibles are deemed to exceed the LFL and the tank is inerted with nitrogen.

The tank systems at both the SRS and Hanford Site generally use an active vessel ventilation system (AVVS) similar to the MFFF process off gas system (KWG) to control the combustible gas concentration in the tanks to below 25% of the LFL; however, this limit may be exceeded upon failure of the AVVS. Upon failure of the AVVS, the accumulation of combustible gases can occur and a passive vessel vent system (PVVS) is used, if present, to keep the combustible gas concentration in the tank below the LFL or to extend the allowable shutdown time for tanks that can exceed the safety limit. The time to reach the 25% LFL safety goal is mentioned several times in both documents; however, the safety significance of this value is not. For example, these documents do not state that the AVVS is designed to handle x times the maximum possible combustible gas evolution rate, where x is the amount of air required to dilute the combustible gas to 25% of the LFL. Discussions with the authors of these papers failed to shed any light on the issue, because the percentage of LFL values were treated by the authors as generally accepted guideline values that could be assumed to ensure that the concentration of combustible vapors remained below the LFL. The authors' goal was to verify that the systems generally stayed below 25% of the LFL, and to determine where or how this goal

<sup>&</sup>lt;sup>1</sup> Version referenced is NFPA 69-1997. The documents submitted for review only refer to NFPA 69 generically without an issue date. Comparisons to earlier versions of the Standard have not been performed as part of this review.

could be exceeded. For these cases, the authors estimated how much time would elapse between the times the 25% LFL safety goal was exceeded and when a process limit was reached or the safety limit was breached.

### Review of Reference [1]

"CNWRA 99-001, Review of BNFL Inc. Design Safety Features Deliverable: Hydrogen Control in high-level waste storage tanks, Rev. 1 April, 1999," states in the Executive Summary that NFPA 69 limits the accumulation of hydrogen in air to less than ¼ of the LFL (1 percent hydrogen in the tank). [Ref. [1]: pp ix and 1-1] The thrust of the report is to suggest that the radiolytic hydrogen generation rate estimated by BNFL may be non-conservative because the radionuclide inventory selected by BNFL for their hydrogen generation rates did not consider the uncertainty estimates in their calculations. [Ref. [1]: pp 2-9 and 9-1.] In addition, BNFL has not considered the hydrogen generation from the thermal degradation of organics that could be as much as 17% of the radiolytic hydrogen generation. [Ref. [1]: pp 4-2 and 9-1.]

The report notes without comment that BNFL uses an AVVS designed to maintain the  $H_2$ concentration in the vessel vapor space at 25% of the LFL (1 percent hydrogen in the tank). In addition, a PVVS is used to maintain the  $H_2$  concentration in the vessel vapor space at less than 100% of the LFL (4 percent hydrogen in the tank), if the AVVS fails. Even with the PVVS, the report warns that "during a failure of the AVVS, the residual hydrogen...can form rich pockets in the offgas piping, scrubber, filters, fans and the like...These pockets will need to be cleared safely during restart of the AVVS." [Ref. [1], pp 8-1.] The report then estimates that it will take between 1.37 hrs and 15.4 hrs to exceed 25% of the LFL in the vessel air space without considering the effects of either a PVVS or AVVS. [Ref. [1]: Table 2-3, pp 2-9.] Exceeding 25% of the LFL is shown to be possible under conditions of passive ventilation. Thus we conclude that the report assigns a safety goal at 25% of the LFL and a design basis safety limit at 100% of the LFL. This position is clearly supported in the cover letter from Robert Pierson (NRC) to Dr. Clark Gibbs (DOE) which transmitted Reference 1. This letter refers to both the 25% safety goal value and the 100% LFL design basis value stating: "Estimates in the report imply that the time periods required for reaching 25% and 100% of the lower flammability limit may be significantly shorter than those currently being used by the contractor." Mentioning that 100% of the LFL could be reached implies that 25% of the LFL is not a design basis, i.e., not to exceed, value because if 25% of the LFL really was a design basis value then one would have to assume that an event would occur upon its exceedance thus rendering moot the importance of exceeding 100% of the LFL.

### Review of Reference [2]

"Possible Explosive Compounds in the Savannah River Site Waste Tank Farm Facilities (U)," states that H<sub>2</sub> monitors on Type III waste tanks are set to alarm when the H<sub>2</sub> concentration reaches 10% of the LFL (0.4 percent hydrogen in the tank). In the event that the ventilation system is shut down, administrative procedures require that the

ventilation system be returned to operating condition within a period of time determined by the decay heat load of the tank. Not all tanks have permanently installed H<sub>2</sub> monitors. The vapor space in these tanks is periodically sampled to determine the flammable gas concentration. The report does not specify a safety limit for these conditions. A different safety set point is used for tanks that contain benzene. In these tanks the benzene concentration in air may exceed the LFL and form a combustible vapor, thus exceeding the 25% LFL control limit. For this case, a nitrogen purge is used to keep the oxygen concentration below 6.9% by volume. This is below the limiting oxidant concentration (LOC) to account for measurement uncertainties. [Ref. [2]: pp 13.]

The report also states that in the SRS F and H Area Separations Facilities and the DWPF, waste temperature at the waste generator is limited to  $<50^{\circ}$ C to ensure that the waste temperature in the pump tanks is  $<70^{\circ}$ C to provide a 4°C margin to the flashpoint of dodecane (74°C). The vapor pressure of dodecane at 70°C is much higher than 25% of the LFL (approximately 80% of the LFL based on vapor pressure).

The safety argument is presented differently for other tank systems. "For the organic pump tanks and waste tanks, the active ventilation system keeps the flammable organic concentration below the LFL, just as in the case for hydrogen." [Ref. [2]: pp 18.] Administrative controls minimize heat introduction into the organic tanks and maintain ventilation during waste transfer. For non-organic pump and waste tanks, the liquid waste temperature is restricted. At the time of the report, the stated controls (organic concentrations, temperature, and ventilation) were established to prevent the formation of flammable vapor concentrations in waste tanks, but not in transfer pump tanks and evaporators. Analysis of the organic content of the vapor space showed that the concentration was several orders of magnitude below that which would be a flammability concern. The same was found for the liquid samples.

The conclusion to be drawn from References 1 and 2 is that the design basis concentration of hydrogen generation is 100% of the LFL for the waste tanks at both Hanford and SRS. Neither reference stipulates use of a design basis concentration<sup>2</sup> of 25% of the LFL.

The use of 100% of the LFL as an acceptable safety limit value may also be inferred from NFPA 30-1996, the Flammable and Combustible Liquids code applicable to the storage,

<sup>&</sup>lt;sup>2</sup> Design basis concentration used in this sense cannot be the safety limit (or never to exceed) value because the system would be under-designed for the normal expected operating conditions. It is clear that for the referenced tank systems, the AVVS is designed to vent at least 4 times the highest volume of gas calculated and the backup PVVS is designed to provide only enough vent flow to ensure that a sufficient amount of time is present to perform additional protective actions prior to exceeding the control limit value of 25% of the LFL. These values are clearly "restraints derived from generally accepted "state of the art" practices for achieving functional goals" [10CFR50.2 Definitions]. Because the functional goal is a safety goal, the values represent the reference safety bounds for design.

handling, and use of flammable and combustible liquids<sup>3</sup>. In the section of NFPA 30-1996 pertaining to liquid handling, transfer and use of flammable or combustible liquids, inert gas is required at all times when transferring Class I liquids and only when Class II and Class III liquids are heated above their flash points. A liquid heated to its flash point forms a barely flammable mixture, i.e., a vapor at the LFL. Unlike sections of NFPA 30-1996 which discuss minimum ventilation requirements to dilute fugitive emissions from tanks, NFPA 30-1996 allows the transfer of combustible fluids using air when the fluids are (a) in piping systems designed to withstand the transfer pressures and to relieve any over pressure events, (b) Class II or Class III liquids, and (c) below their flash point. The difference between Class I and Class II/III liquids is that Class I liquids are ignitable when at normal room temperatures while Class II and III liquids must be heated well above normal room temperatures in order to be ignitable.

### **References**

- Jain, V., R. Pabaian, D. Daruwalla, J. Weldy and D. Pickett; "Review of BNFL Inc. Design Safety Features Deliverable: Hydrogen Control in High-Level Waste Storage Tanks," CNWRA 99-001, Rev. 1 April, 1999
- [2] Hobbs, D. T., "Possible Explosive Compounds in the Savannah River Site Waste Tank Farm Facilities (U)", Savannah River Technology Center, WSRC-TR-91-444, Revision 3, February 15, 2000

<sup>&</sup>lt;sup>3</sup> Flammable and combustible liquids are defined by NFPA 30 in Sections 1-7.3.1 (Class IA, IB and IC) and 1-7.3.2 (Class II, IIIA and IIIB). Flammable (Class I et al) liquids are defined as any liquid that has a closed-cup flash point below 37.8°C (100°F). Combustible (Class II) liquids are defined as any liquid that has a closed-cup flash point at or above 37.8°C (100°F) and below 60°C (140°F). Combustible (Class III et al) liquids are defined as any liquid that has a closed-cup flash point at or above 37.8°C (100°F) and below 60°C (140°F). Combustible (Class III et al) liquids are defined as any liquid that has a closed-cup flash point at or above 60°C. Flash point is a direct measure of a liquid's volatility, i.e., its tendency to vaporize. The lower the flash point, the greater the volatility and the greater the risk of fire.

### Setpoints for Safety Instrumentation

Instrument trip setpoint uncertainty allowances and trip setpoint discrepancies for safety instrumentation are determined in accordance with ISA S67.04.01-2000 using the 95/95 criterion identified in section C.1 of Regulatory Guide 1.105. This methodology has been selected to ensure that a margin exists between the limiting conditions of operation (LCO) and the safety limit by minimizing the risk of operating outside of the specified LCO as a result of normal instrumentation calibration drift and errors in calibration procedures.

These safety limits protect soft barriers such as the point at which a gas or vapor becomes flammable in air, i.e., the LFL, much like the inherent strength and toughness of a physical barrier can prevent radioactive material release out of a protected space, such as the glovebox walls designed to prevent the uncontrolled release of radioactivity out of the process systems. The physical barrier in this case represents the event horizon. Passing through the barrier, i.e., loss of confinement is an event. The presence of the barrier for non-quantum scale particles, i.e., particles much larger than the Planck distance, precludes the passage of solid radioactive particles into unprotected space. Ensuring that these barriers are intact, free from wear, corrosion, cracks and through-holes is necessary to maintain the leak free state of the barrier. While the physical properties of solid materials can be described in terms of their resistance to various forces which can be readily understood, the analogous properties of the LFL of a vapor seem to require more explanation.

Simply put, the LFL is the point at which a quiescent mixture of gas/vapor in air when exposed to an ignition source has an identifiable flame front that traverses a fixed distance at least half the time it is tested.

Safety limits are chosen to maintain the integrity of these physical barriers. The safety limits are approached only by passing through multiple process safety limits as seen in the attached figure and they are controlled by the normal, protective and safety control subsystems (or in the case of the utility systems the normal, auxiliary and emergency control subsystems.) The hierarchy of safety limits is the upper safety limit, the analytical safety limit, the process safety limit, the protective limit (not credited for safety) and the normal limit (also not credited for safety.) Figure 1 graphically shows the safety limit hierarchy.

The normal control subsystems serve as the primary process controllers and are expected to maintain the process parameters within an allowable normal range. Should the process parameters exceed the normal range limits, the normal control subsystem performs the actions necessary to prevent the event or to mitigate the risk of the event. The point at which these actions occur is called the normal trip setpoint. The normal trip setpoints of the normal control subsystem may be below or at the same trip setpoints as the safety control subsystem trip setpoints depending on the risk of the event. Higher risk events are provided with more margin between the normal limit and the analytical safety limit.



- A. Allowance described in paragraph 4.3.1
- B. Allowance described in paragraph 4.3.1
- C Region where channel may be determined inoperable
- D. Plant operating margin
- E Region of calibration tolerance (acceptable as left condition) described in paragraph 4.3.1

Figure 1—Nuclear safety-related setpoint relationships (Ref. ANSI/ISA—S67.04.01—2000)

### Action:

None



## MOX Fuel Fabrication Facility (MFFF) Open Item Resolution MP-01

NRC Technical Exchange Meeting 29 July 2003



STONE & WEBSTER

## **Open Item MP-01**

One Issue Remaining

Accumulation of unreacted UO<sub>2</sub> powder on the final HEPA filters is postulated to occur based on CAR crediting only the final HEPA filters with LPF

- This unreacted  $UO_2$  powder subsequently undergoes pyrophoric oxidation to  $U_3O_8$
- The heat released by this reaction damages the HEPA filter elements



## **DCS Evaluated the Event**

- Thermal load required to damage HEPA filters determined based on AG-1 Thermal Load Test
- This thermal load was compared against the pyrophoric heat of reaction and equated to a mass loading of unreacted UO<sub>2</sub> powder
- Amount of powder was determined to be 36 kg per filter element
- Event deemed incredible—Total amount of powder required was at least 10 times maximum credible inventory in the process
- DCS commits to surveillance as PSSC to ensure event is incredible



# **Calculation of Critical Thermal Mass**

- Assuming air is 79% N2 and 21% O2 and at a constant temperature of 672°K during the test run, Cp for air becomes
  - Cpair(T) = 0.79.Cp N2 + 0.21.Cp O2 = 10.4 + 0.00348T 39417/T2 cal/°K mol
  - $Cpair(672) = 12.651 \text{ cal/}^{\circ} \text{K mol}$
- Mass passing through the filter is the density of the gas r times the volumetric flow rate q times the elapsed time t of 5 minutes divided by the molecular weight Mw of air
  - m = rqt/Mw = 1.185 kg/m3 . 298/672 °K/°K . 42.5m3 . 5 minutes / 0.028951 kg/mol = 3,869 mol
- Heat load Q = mCpDT
  - $Q = 3,869 \cdot 12.651 \cdot (672 298) / 4.1868 \text{ cal/J} = 4.372 \text{ x } 106 \text{ J}$
- U3O8 can form from the oxidation of UO2 between the temperatures of 1,396 to 1,723°K. Heat of formation of U3O8 under these conditions is
  - 1.5 UO2 + 0.5 O2 → 0.5 U3O8 166,900 + 84T J (from 1,396 to 1,723°K) [Ref. 4]
- Multiplying by 2 to obtain a molar heat of formation
  - Dhf = -333,800 + 168T J per mol U3O8
- Assuming the reaction takes place at 1,396°K and 1,723 °K to cover the temperature range of the model
  - Dhf U3O8 = -99,272 J / mol at 1,396 °K to -44,336 J / mol at 1,723 °K
- Dividing by the highest heat of formation corresponding to the Dhf at 1,396 °K
  - x mol U3O8 = Q / Dhf =  $4.372 \times 106 / 99,272 = 44$  mols of U3O8 or 132 mols of UO2 =>  $\sim 0.270 \cdot 132 \approx 36$  kg UO2



## The Bounding Event

- The event that could release the most depleted uranium powder would be an explosion located in the fire containing the final dosing unit. This area contains a largest amount of depleted UO2 in powder form. The powder is located in the UO2 receiving hopper that has a maximum capacity of 400-kg, and a predosing hopper with a capacity of 120-kg. The airborne release fraction for an explosion in this unit is unity. Thus the total amount of airborne powder due to an explosion in the final dosing unit is 520-kg UO2.
- A release to the C4 ventilation system that would throw up enough dust to cause a thermal event in the VHD final HEPA filters (6 elements) without breaching the glovebox confinement boundary was deemed to be incredible. A simple spill does not provide enough dust or energy to create a dust cloud. Dust in gloveboxes is limited to a few jars (80 kg J80 or 2 60 kg J60). Even if 2 J60 jars spilled powder, the 120 kg of powder is well below the 216 kg critical value.



- An explosion would throw dust into the C3 confinement area (the room) outside of the gloveboxes where the HDE ventilation system would collect the dust instead of the glovebox ventilation system, VHD.
- Dividing 520 kg by the number of filter elements 144 yields a little over 3.6 kg per filter element or one-tenth the critical value of 36 kg.
- The factor of safety is 10.



## **HEPA Filter Element Thermal Test**

 HEPA filter elements are tested in accordance with standard ASME AG-1 to withstand exposure to high temperatures without failing at rated flow. The test consists of exposing the filter element to a flowing temperature of 700 to 750°F for a minimum of 5 minutes followed by a high stress flow with humid (95%RH) air set to create at least 10 inches of water differential pressure across a clean filter for one hour.



## Conclusion

- Previous studies show a few kg of powder are detectable by the automatic instrumentation
- Long term accumulation is thus detectable and correctable
- The glovebox HEPA filters (2-stages), room HEPA filter (1-stage), the duct run, the expansion zones (i.e., the exhaust plenums upstream of the final filter units), the high strength stainless roughing filter and the high strength stainless/glass fiber prefilter do not have to be credited with any removal efficiency to ensure this event is incredible

# <u>MP-01</u>: PSSC and design basis information associated with the pyrophoric nature of some UO<sub>2</sub> powders (DSER Section 11.3.1.2.1)

### Clarification of MP-01: Address uranium dioxide burnback in analysis of soot loading (FS-1).

### Response:

At elevated temperatures, finely divided  $UO_2$  can undergo further oxidation to higher uranium oxides, specifically  $U_3O_8$ . This reaction results in spontaneous heating of the oxide and is typically referred to as "burnback."  $UO_2$  burnback is not expected to affect MFFF final HEPA filters for the following reasons:

- During normal operations, UO<sub>2</sub> is not expected to be present on the final HEPA filters because the Glovebox and VHD intermediate HEPA filters prevent any significant quantities of UO<sub>2</sub> powder from reaching the final HEPA filter housing, and the high strength roughing and prefilters remove nearly all of the remaining particles before they reach the final HEPA filters.
- During a fire, UO2 powder is just one of many potential embers. Large embers are removed by the high strength roughing and prefilters. The remaining micron size particles are either cooled by the time they reach the final HEPA filters or do not contain enough energy to degrade the performance of the final HEPA filters.
- The energy associated with the burnback phenomenon is small when compared to the energies involved in a MFFF area fire. The process unit containing the largest quantity of UO<sub>2</sub> is the Final Dosing Unit (520 kg UO<sub>2</sub>). The energy generated by the oxidation of this quantity of UO<sub>2</sub> in a fire is approximately 50,000 Btu. The MFFF FHA assumes a Btu loading for this area of 134,701 Btu /ft<sup>2</sup> with an area of 1123 ft<sup>2</sup>. This yields a total Btu loading of over 151 million Btu. The quantity of energy released as a result of burnback is negligible when compared to that involved in the process unit fire.

### **Additional Clarification to Response:**

The amount of unreacted  $UO_2$  that will cause a problem with excessive thermal loading on the HEPA filter elements is deemed to be incredible based on the calculation shown below. This calculation shows that approximately 36 kg of  $UO_2$  must collect on each element of the final HEPA filter units before the temperature-time rating of the filter is exceeded. To prevent the accumulation of this much dust, the PSSC is periodic surveillance. From previous analyses, we know that the differential pressure across the final filter elements will be significant when loaded with a few kg of dust. We can thus

be assured that a small amount of dust is detectable by the automatic differential pressure instrumentation. We also know that no mechanism exists that will throw 36 kg of dust into the air during any given event; therefore the accumulation of 36 kg of material will occur only over a long period of time. Thus, periodic surveillance of the filters/ducts will be an effective control to prevent the accumulation of too much unreacted dust. This is deemed to be true; even though, the glovebox HEPA filters (2-stages), room HEPA filter (1-stage), the duct run, the expansion zones (i.e., the exhaust plenums upstream of the final filter units), the high strength stainless roughing filter and the high strength stainless/glass fiber prefilter are not credited with any removal efficiency.

The conclusion that this event is incredible is also reached when we consider the bounding quantity of material at risk (MAR) in any given fire area as being 520 kg. The event that could release the most depleted uranium powder would be an explosion located in the fire containing the final dosing unit. This area contains the largest amount of depleted UO<sub>2</sub> in powder form. The powder is located in the UO<sub>2</sub> receiving hopper that has a maximum capacity of 400-kg, and a predosing hopper with a capacity of 120-kg. The airborne release fraction for an explosion in this unit is unity. Thus the total amount of airborne powder due to an explosion in the final dosing unit is 520-kg UO<sub>2</sub>. An explosion would throw dust into the C3 confinement area (the room) outside of the gloveboxes where the HDE ventilation system would collect the dust instead of the glovebox ventilation system, VHD. Considering that the HDE ventilation system has 144 first-stage HEPA filter elements and that flow across the face of the HEPA filters is balanced in accordance with ASME AG-1 requirements; then, we can calculate that the dust load across each filter element is the total dust load in the air divided by the number of filter elements. Hence, dividing 520 kg by the number of filter elements 144 yields a little over 3.6 kg per filter element or one-tenth the critical value of 36 kg. Thus, the factor of safety is 10.

A release to the C4 ventilation system that would throw up enough dust to cause a thermal event in the VHD final HEPA filters (6 elements) without breaching the glovebox confinement boundary was deemed to be incredible. A simple spill does not provide enough dust or energy to create a dust cloud. Dust in gloveboxes is limited to a few jars (80 kg J80 or 2 60 kg J60). Even if 2 J60 jars spilled powder, the 120 kg of powder is well below the 216 kg critical value. Direct fire load upon dust is not energetic enough to cause dust to become airborne.

Normal ventilation rates through gloveboxes averages a little over 1 air change per hour (ach) or about 7 scfm. This can be compared to the normal room air ventilation rates which is closer to 3 ach and is hundreds of scfm. Upon breach of a glove in a glovebox, the emergency dump valves increase the air flow through the glovebox proportional to differential pressure requirement. Under this scenario, there is not enough dust to cause a problem.

#### Calculation Summary

HEPA filter elements are tested in accordance with standard ASME AG-1 to withstand exposure to high temperatures without failing at rated flow. The test consists of exposing

the filter element to a flowing temperature of 700 to 750°F for a minimum of 5 minutes followed by a high stress flow with humid (95%RH) air set to create at least 10 inches of water differential pressure across a clean filter for one hour. The severity of this test is such that test conditions exceed the design rating of the filter element and thus can be considered to bound the design ratings of the filter for temperature and flow.

The heat flux through the filter may be estimated by taking the differential between the average temperature of the flow stream and standard temperature (298°K), multiplied by the specific heat capacity of the gas and the mass of the gas passing through the filter for 5 minutes.

Temperature of air stream in degrees K is

 $750^{\circ}F - 32^{\circ}F / 1.8 + 273 = 672^{\circ}K$  $\Delta T = 672 - 298 = 374^{\circ}K$ 

Heat capacity of air at constant pressure Cp is

Cp =  $\int$  CpdT , where Cp is estimated by taking 0.79<sup>•</sup>Cp<sub>N2</sub> + 0.21<sup>•</sup>Cp<sub>O2</sub> Cp<sub>N2</sub> = 11.00 + 0.00433T cal/°K mol (273 - 700 °K) Cp<sub>O2</sub> = 8.27 + 0.000258T - 187700/T<sup>2</sup> cal/°K mol (300 - 5,000 °K)

Assuming air is 79%  $N_2$  and 21%  $O_2$  and at a constant temperature of 672°K during the test run, Cp for air becomes

 $Cp_{air}(T) = 0.79^{\circ}Cp_{N2} + 0.21^{\circ}Cp_{O2} = 10.4 + 0.00348T - 39417/T^{2} cal/^{\circ}K mol$ 

 $Cp_{air}(672) = 12.651 \text{ cal/}^{\circ} \text{K mol}$ 

Mass passing through the filter is the density of the gas  $\rho$  times the volumetric flow rate q times the elapsed time t of 5 minutes divided by the molecular weight Mw of air

 $m = \rho qt/Mw = 1.185 kg/m^3 \cdot 298/672 °K/°K \cdot 42.5m^3 \cdot 5 minutes / 0.028951 kg/mol = 3,869 mol$ 

Heat load  $Q = mCp\Delta T$ 

 $Q = 3,869 \cdot 12.651 \cdot (672 - 298) / 4.1868 \text{ cal/J} = 4.372 \text{ x } 10^6 \text{ J}$ 

 $U_3O_8$  can form from the oxidation of  $UO_2$  between the temperatures of 1,396 to 1,723°K. Heat of formation of  $U_3O_8$  under these conditions is

 $1.5 \text{ UO}_2 + 0.5 \text{ O}_2 \rightarrow 0.5 \text{ U}_3\text{O}_8 - 166,900 + 84\text{T J}$  (from 1,396 to 1,723°K) [Ref. 2]

Multiplying by 2 to obtain a molar heat of formation

$$\Delta h_f = -333,800 + 168T J \text{ per mol } U_3O_8$$

Assuming the reaction takes place at 1,396°K and 1,723 °K to cover the temperature range of the model

$$\Delta h_f U_3 O_8 = -99,272 \text{ J} / \text{mol at } 1,396 \text{ }^\circ\text{K} \text{ to } -44,336 \text{ J} / \text{mol at } 1,723 \text{ }^\circ\text{K}$$

Dividing by the highest heat of formation corresponding to the  $\Delta h_f$  at 1,396 °K

x mol U<sub>3</sub>O<sub>8</sub> = Q /  $\Delta h_f$  = 4.372 x 10<sup>6</sup> / 99,272 = 44 mols of U<sub>3</sub>O<sub>8</sub> or 132 mols of UO<sub>2</sub> => ~0.270 · 132 ≈ 36 kg UO<sub>2</sub>

Where, Mw of  $UO_2$  is assumed to be 270. Note that these results are slightly higher than the values previously quoted for the heat of oxidation from a fire in the response to MP-1. The response to MP-1 assumed that the reaction occurred at the bulk temperature of the fire which lowered the heat of formation. The higher heat of formation value is used in this calculation because it places a lower limit on the quantity of  $UO_2$  required to achieve the undesired thermal effect.

#### References

- 1. Perry, Robert H., Don W. Green; "Perry's Chemical Engineers' Handbock", McGraw-Hill, 1999
- 2. Roberge, Pierre R., "Handbook of Corrosion Engineering", McGraw-Hill, 1999

#### Action:

Update the CAR to include the PSSC and safety function identified above.

### DUKE COGEMA STONE & WEBSTER

### **FS-2 FIRE BARRIERS**

# **Fire Resistance of MFFF Fire Barriers**

## **OVERVIEW**

DUKE COGEMA STONE & WEBSTER

## • Results of Peak Temperature Calculation

- There are 28 fire areas that have temperatures which exceed the ASTM-E119 curve.
- There are only 2 fire areas that have time-temperature profiles that are above the ASTM-E119 test parameters for furnace temperature. (FA-MP-229, FA-AP-111).
- All fire areas are under the E119 curve after 5 minutes.
- After 8 minutes, the fire impact on the concrete for all areas is under the E119 curve.

## **OVERVIEW**



### • Concrete

- Spalling of concrete and temperature
- Concrete cover
- Concrete mix

DUKE COGEMA Stone & Webster

ROOM WITH TEMPFRATURE OVER AS TM-ELL9 CURVE							
	Heat Load	Агеа	Peak Fire Temperatu re	ASTM E- 119 Curve Exceeded	Approxima te Time ASTM E- 119 Curve Exceeded (max		
Fire Area	(BTU)	(ft <sup>2</sup> )	°F	(Yes or No)	seconds)	Comments	
FA-MP-120	78,924,154	600	1113	Yes	100		
FA-MP-126	56,826,457	530	1113	Yes	20		
FA-MP-142	165,590,425	730	1112	Yes	30		
FA-MP-229	2,899,950	55	1060	Yes	280	Outside E119 parameters	
FA-MP-342	15,786,075	150	1113	Yes	120		
FA-MP-365	154,170,666	1,215	1049	Yes	60	·	
FA-SR-117	39,718,050	186	1113	Yes	130		
FA-SR-209	45,178,950	295	1114	Yes	100		
FA-SR-212	45,118,200	290	1113	Yes	110		
FA-SR-304	6,024,375	180	1046	Yes	130		
FA-SR-306	127,922,008	670	1113	Yes	30		
FA-SR-317	21,181,250	610	1112	Yes	70		
FA-SR-319	4,590,000	140	837	Yes	20		
FA-AP-102	9,228,879	350	1115	Yes	70		
FA-AP-103	21,463,113	160	1113	Yes	130		
FA-AP-111	8,686,905	100	1065	Yes	· 260	Outside E119 parameters	
FA-AP-126	20,185,000	85	1122	Yes	90	·	
FA-AP-138	7,454,060	120	1062	Yes	130		
FA-AP-205	3,274,800	80	1075	Yes	120		
FA-AP-209	12,352,770	90	1003	Yes	120		
FA-AP-217	5,876,859	70	1066	Yes	140		
FA-AP-225	8,308,050	135	1065	Yes	130		
FA-AP-321	5,803,359	70	1063	Yes	130		
FA-AP-403	6,290,100	90	1088	Yes	130		
FA-AP-404	13,154,195	260	1113	Yes	100		
FA-AP-415	5,177,643	90	1062	Yes	130		
FA-AP-417	13,683,954	100	1015	Yes	130		
FA-AP-427	3,709,500	110	1080	Yes	140		
FA-AP-514	35,479,778	550	1129	Yes	130		
FA-EF-101	247,105,000	900	1122	Yes	80		
FA-E7-102	247,105,000	900	1122	Yes	80		

August 1, 2003

NRC Fire Barriers

DUKE COGEMA STONE & WEBSTER



Worst-Case Simulations - FA-MP-229, FA-AP-403, and FA-AP-514

All fire areas have temperatures under the E119 curve within 5 minutes and level off at this point.

DUKE COGEMA STONE & WEBSTER



The fire curves during the first 5 minutes with the ASTM-E1529 curve for a comparison.

DUKE COGEMA STONE & WEBSTER



Since two fire areas, even for a short duration, fall outside the E119 curve, a onedimensional implicit finite difference analysis was performed to determine the temperature effects within the concrete.

The graph above and the following graphs show the results of this analysis.

### **Results of Peak Temperature Calculation** DUKE COGEMA STONE & WEBSTER **TEMPERATURE PROFILE AT 8 MINUTES** 1600.00 1400.00 í. 1200.00 *<b>TEMPERATURE* \_\_\_\_ASTM-E1529 1000.00 ASTM-E119 800.00 **FA-MP-514** 600.00 <del>×---</del> FA-MP-229 400.00 200.00 0.00 0.5 0 1.5 2 **DEPTH OF CONCRETE (IN.)**

It can be seen from this graph that within 8 minutes, the concrete is within the E119 curve and the concrete temperatures are below 200 °F at 1 inch into the concrete.

DUKE COGEMA STONE & WEBSTER



The concrete temperatures at 1 inch are still less than 200°F for the fire areas and E119 curve.



• Spalling is the removal (sluffing off) of concrete due to pressure build-up in the concrete due to heating.

- Spalling affects the concrete by reducing the area of concrete, thereby increasing the stress on the concrete and potentially exposing the rebar to the fire.
- Large spalling appears to happen during rapid heating when the temperature reaches 200 °F about an inch into the concrete.
- Based on a review of fire tests, spalling does not occur until the furnace temperature is above 1,300 °F.
- Spalling is a function of moisture content, porosity and rating of heating.
- Spalling is also affect by geometry. Outside corners are more susceptible to spalling than flat surfaces (e.g., columns compared to walls).

- Based on the finite difference analysis, the concrete one inch in does not reach 200 °F in the first 10 minutes.
- Based on the results of the peak temperature calculation, after the first 5 minutes the fire temperatures level off or decline so over time the rate of heating is reduced.





- Concrete cover is the clear distance from the surface of the concrete to the rebar.
- Thickness of cover affects the performance of a concrete member.



- Performance is improved as cover is increased.
- Most of the tests were performed with a cover slightly over 1 inch.
- MOX design calls for a minimum cover of 1.5 inches for exterior walls and 2 inches for everything else.
- This increase in cover, especially at corners, increases the protection of the rebar and reduces the effect from loss of cover.



### • Concrete mix

- High strength concrete is more susceptible to spalling than normal strength concrete.
- MOX mix is classified as high strength due to the amount of fly ash in the mix.
- Even though the mix is classified as high strength, it is being used as normally strength (i.e., 4 Ksi). Therefore, the actual stresses in the concrete are lower.
- The actual strength is probably around 5-6 Ksi, so the margin of safety is increased by at least 20%.
- The reduction in concrete due to spalling will not cause over-stressing of the concrete.
- Therefore, even if spalling does occur, it is not a concern.



# CONCLUSION

- Fires are bounded by the E-119 curve.
- Spalling, if any, is not a concern.

The following clarifications and/or additions to previous responses are submitted by DCS as a result of discussions that occurred during the public meeting held 29 July through 1 August 2003.

### CS-01 – Red Oil

In addition to the commitments that have already been presented in the CAR, DCS commits to the following safety functions/design bases of the process safety control subsystem (PSCS) to prevent over-pressurization of the evaporators:

- 1. Limit the energy generation resulting from the potential oxidation of TBP degradation products by ensuring that the process fluid does not exceed 125°C;
- 2. Ensure that, overpressurization can be effectively prevented via the addition of an aqueous phase to the evaporators by limiting the heating rate to 2°C per minute.

Setpoints for these design bases will be established as described in Section 11.6.7 of the CAR. Exceedance of either of these values will result in the shut down of the steam supply and the addition of an aqueous solution to the evaporator.

### Action:

The above safety functions/design bases will be incorporated into the CAR.

### CS-02 - HAN

In addition to the response provided in the letter dated 28 July 2003 (letter # DCS-NRC-000151) DCS adds the following:

• Response to Question 3 in Enclosure 1 of the above referenced letter is amended to include Fe as an impurity in the confirmatory testing to be performed.

DCS will also notify NRC staff in the event of any changes to the kinetic model (described in the referenced letter above) that result from the additional external review being conducted.

### Action:

Design Basis values from DCS letter dated 28 July 2003 (letter # DCS-NRC-000150) will be included in the CAR.

### **AP-3** - Titanium fire

In addition to the response provided in the 28 July 2003 letter (number DCS-NRC-000150) DCS provides the following design basis information for the Process Safety Control Subsystem:

The design basis is to limit the current leakage to 10 mA for 1 second.

### Action:

The above design basis information will be incorporated into the CAR.

### **MEETING ATTENDEES**

### NAME

### **AFFILIATION**

Andrew Persinko David Brown Brian Smith Bill Troskoski Alex Murray Joel Klein Scott Gordon Norma Garcia-Santos Fred Burrows Wilkins Smith Nader Mamish Sharon Steele Bob Pierson Rex Wescott Margaret Chatterton Harry Felsher Chris Tripp	Nuclear Regulatory Commission (NRC) NRC NRC NRC NRC NRC NRC NRC NRC NRC NRC
John Lubinski	NRC
Ken Ashe Peter Hastings Steve Kimura Marc Klasky Marc Vial Sophie Gvenais Philippe Bretault Bob Foster Charles Henkel Frank Collins Larry Rosenblum	Duke Cogema Stone & Webster (DCS) DCS DCS DCS DCS DCS DCS DCS DCS DCS DCS
Dave Alberstein Joe Olencz	Department of Energy (DOE) DOE
David Notley Herb Feinroth	Gamma Engineering Gamma Engineering
Tom Clements	Greenpeace International
Dan Horner	McGraw-Hill

MEMORANDUM TO:	Kathy Halvey Gibson, Acting Chief		
	Special Projects and Inspection Branch		
	Division of Fuel Cycle Safety		
	and Safeguards		
	Office of Nuclear Material Safety		
	and Safeguards		

THRU: Brian W. Smith, Acting Chief /RA/ Special Projects Section Special Projects and Inspection Branch Division of Fuel Cycle Safety and Safeguards, NMSS

FROM: Andrew Persinko, Sr. Nuclear Engineer /RA/ Special Projects Section Special Projects and Inspection Branch Division of Fuel Cycle Safety and Safeguards, NMSS

SUBJECT: JULY 29 - AUGUST 1, 2003, MEETING SUMMARY: MEETING WITH DUKE COGEMA STONE & WEBSTER TO DISCUSS OPEN ITEMS RELATED TO MIXED OXIDE FUEL FABRICATION FACILITY

On July 29 - August 1, 2003, U.S. Nuclear Regulatory Commission (NRC) staff met with

Duke Cogema Stone & Webster (DCS), the mixed oxide fuel fabrication facility (MFFF) applicant, to discuss chemical safety, nuclear criticality safety, and fire protection open items related to the construction authorization request for the MFFF. The meeting agenda, summary, handouts, and attendance list are attached. (Attachments 1, 2, 3, and 4, respectively).

Docket: 70-3098

- Attachments: 1. Meeting Agenda
  - 2. Meeting Summary
  - 3. Meeting Handouts
  - 4. Attendance List
- cc: P. Hastings, DCS
  - L. Zeller, BREDL
  - G. Carroll, GANE
  - J. Johnson, DOE
- D. Curran, GANE D. Silverman, DCS

J. Conway, DNFSB

- H. Porter, SCDHEC
- DISTRIBUTION: SPIB r/f FCSS r/f RPierson, FCSS JHolonich, FCSS Hearing File JHull, OGC RVirgilio,OSP DMcIntyre,OPA WGloersen, RII Attendees DAyres

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OFC	SPIB	SPIB	SPIB	SPIB
NAME	APersinko	DBrown	LGross	BSmith
DATE	8/27/03	8/27/03	8/27/03	8/29/03