

### **UNITED STATES NUCLEAR REGULATORY COMMISSION**

WASHINGTON, D.C. 20555-0001

March 5, 2003

MEMORANDUM TO: Melvyn N. Leach, Chief

Special Projects and Inspection Branch

Division of Fuel Cycle Safety

and Safeguards

Office of Nuclear Material Safety

and Safeguards

THRU:

FROM:

Special Projects Section
Special Projects and Inspection Branch
Division of Fuel Cycle Safety
and Safeguards, NMSS

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

SUBJECT:

FEBRUARY 6-7, 2003, MEETING SUMMARY: MEETING WITH DUKE

COGEMA STONE & WEBSTER TO DISCUSS MIXED OXIDE FUEL

FABRICATION FACILITY REVISED CONSTRUCTION

**AUTHORIZATION REPORT** 

On February 6-7, 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 the revised construction authorization request (CAR or revised CAR) submitted to NRC on October 31, 2002. The meeting agenda, summary, handouts, attendance list, and clarifying information provided by DCS are attached (Attachments 1, 2, 3, 4, and 5 respectively).

Docket: 70-3098

Attachments: 1. Meeting Agenda

2. Meeting Summary 3. Meeting Handouts 4. Attendance List

5. Clarifying Information

cc:

P. Hastings, DCS

D. Silverman, Esq., DCS

J. Johnson, DOE

H. Porter, SCDHEC

D. Curran, Esq., GANE

J. Conway, DNFSB

L. Zeller, BREDL

G. Carroll, GANE

2

MLeach

Docket: 70-3098

Attachments: 1. Meeting Agenda

Meeting Summary
 Meeting Handouts
 Attendance List

5. Clarifying Information

#### cc:

P. Hastings, DCS

J. Johnson, DOE

H. Porter, SCDHEC

J. Conway, DNFSB

L. Zeller, BREDL

G. Carroll, GANE

D. Silverman, Esq.,DCS

D. Curran, Esq., GANE

### DISTRIBUTION:

Docket: 70-3098

ADAMS PUBLIC Hearing File WGloers

PUBLIC SPIB r/f WGloersen DAyres, RII FCSS r/f JHull, OGC RPierson BSmith,EDO ELeeds NRC Attendees

ADAMS Accession NO: ML030630223

G:\SPB\AXP1\MOXmtgsumm2-6-03.wpd

\*See previous concurrence

OFC	SPIB*	SPIB*	SPIB*	SPIB
NAME	APersinko	DBrown	LGross	J.G.) HELD
DATE	2/ 28 /03	3/ 4 /03	3/ 4 /03	3/ 5 /03

OFFICIAL RECORD COPY

### MEETING AGENDA MOX FUEL FABRICATION FACILITY

February 6, 2003

9:00 AM

Introduction

9:15 AM

Discussions of fire safety

12:00 NOON

Lunch

1:00 PM

Discussions of chemical safety

5:00

Adjourn

February 7, 2003

9:00 AM

Discussions of chemical safety

12:00 NOON

Lunch

1:00 PM

Discussions of chemical safety

4:30

Summary / Actions

5:00

Adjourn

## MEETING SUMMARY MOX FUEL FABRICATION FACILITY February 6-7, 2003

#### Purpose:

The purpose of the meeting was to discuss chemical safety and fire protection issues related to the Mixed Oxide Fuel Fabrication Facility Construction Authorization Request (CAR) submitted by DCS on October 31, 2002, or identified in the NRC staff's Draft Safety Evaluation Report (DSER) dated April 30, 2002.

#### Summary:

The meeting was a technical, working level meeting that covered, in detail, chemical and fire protection issues.

A summary of the issues discussed is provide below:

#### **Chemical Safety**

1. Plutonium (Pu)(IV) Oxalate (MP-02)

DCS discussed the options that it was considering to prevent Pu can pressurization from radiolytic decomposition of residual moisture. DCS noted that any combination of moisture content limits, can pressure rating and storage time could be effectively manipulated to limit/prevent pressure buildup before placing a can into storage. DCS stated that it would provide the bases as part of the generic material handling controls.

To prevent re-oxidation of Pu(III), which could cause a pressure increase, DCS stated that it is considering 3 options: control of furnace parameters (time, temperature, moisture content); system performance; and, measurement of Pu(III). The exact method is to be decided. Items relied on for safety (IROFS) would be identified as part of the Integrated Safety Analysis (ISA) process. DCS stated that CAR sections 5.5.2.3.6.2 and 5.6.2.3 (Material Handling Controls) will be revised as necessary to reflect this information (See Attachment 5 for clarifying information and commitments made by DCS at the meeting).

This item is considered closed. Revised CAR pages pending.

#### 2. Pu(VI) Control System (AP-14)

The purification process is to prevent the introduction of Pu(VI) into the oxalic precipitation unit (furnace) through: valence state measurements of Pu; limiting the maximum Pu(VI) content (TBD); and developing a method to detect Pu(VI) as part of the final design process. DCS pointed out that methods under consideration included ultraviolet-visible spectrum (1E-5 resolution M) and alpha-spec (1E-9m resolution), as part of the sampling technique validation process. The sampling measurements would occur before the oxalate could be formed.

AP-14 is considered closed.

#### 3. Titanium (Ti): Prevention of Ti Fires (AP-03)

DCS agreed to provide an analysis of an electrolyzer failure (ground faults, etc.) as the initiator of a titanium fire for thick components (>1/30 inch). Any electrical protection schemes would be identified, if needed. DCS also noted that for thin walled components, inter-granular stress corrosion cracking (IGSC) played a major part. For this failure mechanism, NO<sub>2</sub> (from HNO<sub>3</sub> - Ti reaction) was the major contributor. By adding more water, the reaction is forced back. DCS agreed to provide operating history information on IGSC of Ti components in similar facilities and additional information that demonstrates the adequacy of the DCS glovebox fire strategy for fires involving bulk Ti (thermite reaction).

#### 4. Tri-butyl Phosphate (TBP) Degradation (CS-01)

DCS indicated that the "closed" system was limited to two evaporators. One would have a steam supply temperature of 90C and the other 133C. Aqueous phase evaporative cooling would provide the heat transfer mechanism preventing the evaporator contents from reaching the self-heating threshold. All would be vented, but DCS still needed to demonstrate adequate vent size to assure adequate mass transfer. DCS noted that the required venting for mass transfer was much less than that required for pressure relief during a "runaway" autocatalytic reaction. In order to provide an adequate margin to the initiation of "self-heating," DCS committed to: (1) provide process system controls to limit the steam temperature to less than or equal to 133C, and (2) provide a vent sized to relieve 1.2 x [energy generation + energy input into the system]. Testing would be conducted to better define the kinetics (effects of impurities included, etc.). Implicit in the vent size design is a demonstration that either the evaporator contents will not foam or that the vent is sized to accept foaming while maintaining adequate evaporative cooling, considering any back pressure (which has been shown to greatly reduce the initiation temperature for self-heating).

The staff notes that the above approach differs from the 1.5 maximum credible mass/vent area safety factor applied at Savannah River Site (SRS). However, it appears reasonable when considering that DCS still needs to perform a hazard and operability (HAZOP) evaluation. Such evaluations must consider the various failure modes such as a steam tube failure, any evaporator tray plugging, or vent system backpressure. As a result of the HAZOP, additional changes in safety features or margins may be identified.

The staff also noted that a review of foreign event investigations involving TBP degradation identified certain polymer derivatives of TBP (and alkyl radicals). DCS indicated that they had not seen any indications of these degradation products at their European facility.

See Attachment 5 for clarifying information and commitments made by DCS at the meeting.

CS-01 is considered closed.

#### 5. Azides (CS-04)

DCS discussed the safety concerns associated with azides. While electropositive metal azides, such as NaN<sub>3</sub> are not explosive, they can aid in the evolvement of hydrazoic acid. For other azides, dry out conditions can result in an explosive hazard. The DCS approach will be to prevent the formation of metal azides and their exposure to dry conditions and high temperatures. Administrative procedures, leak detection and avoidance of dryout conditions will be utilized on that portion of the process downstream of the stripping columns where hydrazine is used. The aqueous phase, which is most likely to contain any azides, is sent to the oxidation column. Prior to movement into the oxalic acid portion of the process, samples are taken to assure that no Pu(III) is present. The absence of Pu(III) is an indicator that the oxidation process is performing correctly and no azides will be present. However, if any Pu(III) is detected, then the oxidation process has not performed as expected and azides may be present. This strategy prevents the possible introduction of azides into the downstream evaporator.

Any azides in the organic phase will end up in solvent recovery where NaN<sub>3</sub> is produced in bulk to eliminate residual hydrazoic acid.

It is conceivable that azides could be formed in the liquid waste recovery unit. DCS noted that they would revise Chapter 8, page 8.34 to better describe the process.

DCS also presented proprietary information regarding preliminary mass balances that identified the maximum credible amount of azides (including uranium and plutonium) formed in various process areas. Based on the magnitude of the mass involved, DCS asserted that there was no significant safety concern and that they would provide a qualitative discussion on pages 8-32 and -33. The staff found this acceptable. See Attachment 5 for clarifying information and commitments made by DCS at the meeting.

CS-04 is considered closed. Revised CAR pages pending.

#### 6. Waste Unit Maximum Inventory (AP-05b)

DCS asserted that no formal inventory controls were needed on the waste unit because the total accumulated Am-241 over the estimated 13 year life of the project is bounded by a safety factor of at least 30. See Attachment 5 for clarifying information and commitments made by DCS at the meeting.

AP-05b is considered closed.

### 7. Use of Temporary Emergency Exposure Limits (TEELs) (CS-05b)

CAR section 8.4.2 will be revised to accurately reflect consideration of latent health effects. Additional information will be provided regarding indoor wind speed values used.

#### 8. Emergency Control Room Limits (CS-10)

DCS will justify the use of TEEL-3 values or present alternative values for protection of control room operators performing safety functions. (DCS will review Regulatory Guide 1.78 and use immediately dangerous to life and health (IDLH) values where available. For those chemical without an IDLH value, DCS will consult with a certified industrial hygenist to verify that the limits selected would not incapacitate an operator in the two minutes required to don protective equipment). See Attachment 5 for clarifying information and commitments made by DCS at the meeting.

9. NRC staff agreed to review items CS-9, AP-7, AP-8, AP-9 and clarify these issues with DCS.

#### Fire Protection

The adequacy of the fire barriers was discussed in detail, including the evaluation for flashover.

DCS presented their most recent evaluation of the MFFF fire severity calculations. Using the FPE tool fire model, DCS demonstrated that the fires in the MFFF did not exceed one hour. DCS considered this to be adequate since the MFFF fire barriers are rated for a minimum of 2 hours (in accordance with American Society for Testing and Materials (ASTM E)-119 standard fire test). However, the DCS analysis did not consider maximum credible fire growth rates which could result in a temperature rise outside of the standard fire test in the early stages of the fire, adding uncertainty to a comparison with the rating curve. For construction authorization, DCS agreed to re-evaluate those scenarios where room temperatures could exceed the ASTM E-119 time-temperature profile. DCS will revise the heat release rate and other input assumptions in FPEtool to determine the maximum credible room temperatures. If the ASTM E-119 temperatures are exceeded, DCS agreed to use methods which include more complete heat transfer calculations to determine the thermal impacts on the fire barriers.

For the license authorization, the applicant agreed to determine if flashover (room temperatures greater than 450C) can occur. Room flashover can impact fire area separation, because excess pyrolysates from combustion can spread through connected openings (such as ventilation openings, cracks around doors) and burst into flames in the adjoining spaces. In performing the ISA, the applicant committed to determine whether flashover is a credible event; if so, flashover will be accounted for in the consequence analyses.

See Attachment 5 for clarifying information and commitments made by DCS at the meeting.

### DUKE COGEMA STONE&WEBSTER SLIDES MOX FUEL FABRICATION FACILITY February 6-7, 2003



# MOX Fuel Fabrication Facility (MFFF) Fire Severity Calculation

NRC Technical Exchange Meeting 6 February 2003

Attachment 3

### **Outline of the Presentation**



- Fire Severity and the FHA
- Detailed Analysis with FPEtool
- Conservative Nature of Assumptions
- Results of Fire Severity Calculation
- Dealing with Flashover in FIRE SIMULATOR
- Conclusion

NRC Technical Exchange Meeting: Fire Severity

## Fire Severity and the FHA



- Fire severity determined for each fire area:
  - Determination based on assumption of equating averaged fire loading of 80,000 BTU per square foot to 1 hour fire severity.
  - Safety margin of 80% applied, i.e., 3 hour and 2 hour barriers required fire severities less than 2.4 hours and 1.6 hours, respectively.
- Of over 300 fire areas, 44 fire areas where 80% safety margin not met.
- Further analysis conducted for the 44 fire areas to include impact of HVAC flow to verify rating of fire barriers are acceptable.

NRC Technical Exchange Meeting: Fire Severity

# DUKE COGEMA

STONE & WEBSTER

## **Detailed Analysis with FPEtool**

- Choice of FPEtool for Fire Severity Calculations
  - Simplicity of operation/manipulation.
  - Well-known among fire safety professionals.
  - Created by the National Institute of Standards and Technology (NIST).
  - Ability to handle HVAC flow in FIRE SIMULATOR module without necessity of detailed HVAC system layout.
  - Fire modeling provides more realistic results than use of 80,000 BTU per square foot thumbrule.

6 February 2003

NRC Technical Exchange Meeting: Fire Severity

## DUKE COGEMA STONE & WEBSTER

## **Conservative Nature of Assumptions**

- Assumptions to Maximize Duration of Fire:
  - Fire height at 0 feet to maximize time before descending smoke layer envelops fire.
  - Combustion efficiency of 100%.
  - Slow fire growth curve because faster fires will consume oxygen and combustibles quicker.
  - Allow fire to continue to 6% pre-flashover oxygen level instead of default 10% oxygen level.
  - Fire position is not critical factor for determining fire severity.

6 February 2003

NRC Technical Exchange Meeting: Fire Severity



## Results of Fire Severity Calculation

- Fire severities as determined by FPEtool substantially less than those presented in FHA.
- Predicted fire severity values per FPEtool range from 0.1 hour to 1.0 hour.

## DUKE COGEMA STONE & WEBSTER

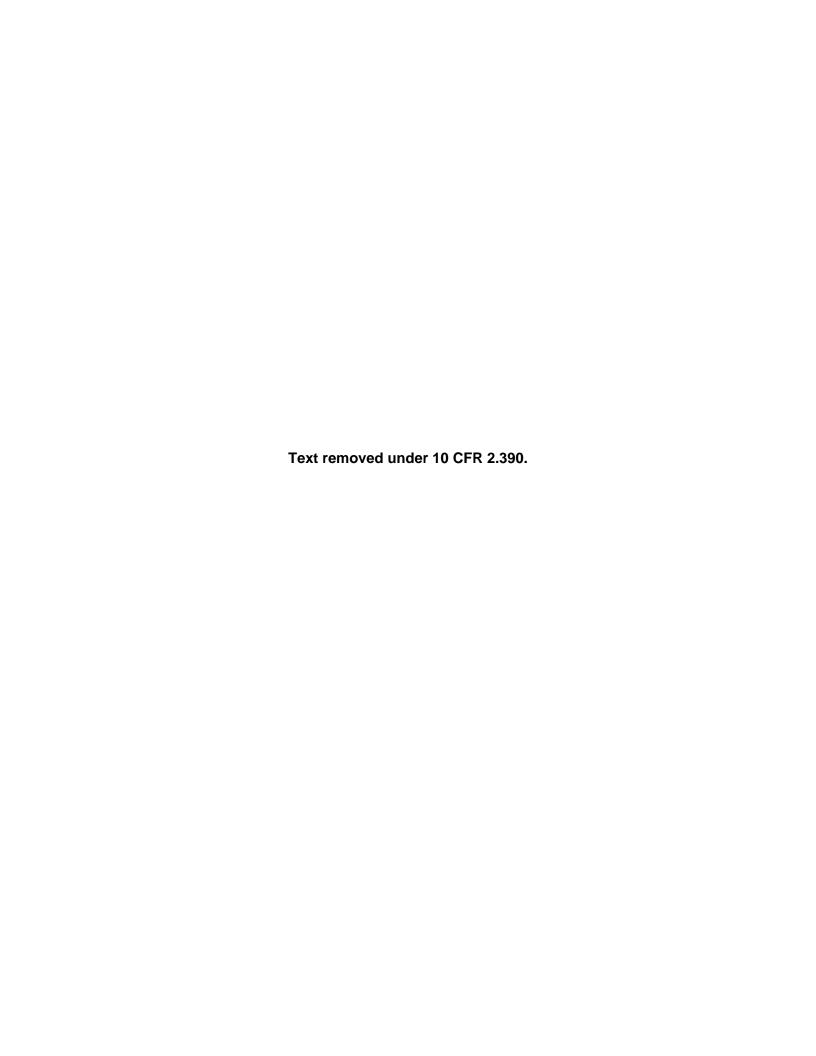
# Dealing With Flashover In FIRE SIMULATOR

- Flashover (FO) is generally accepted to occur at 1112 F (600 C).
- Model lessens fire severity if FO occurs at 842 F (450 C)
- If flashover occurs during a FIRE SIMULATOR run, various inputs are needed to continue run such as combustible load in room in pounds per square foot, orientation, and thickness.
- At this point, combustible load is conservatively assumed to be 100% of fire load in fire area, even though some material was consumed to reach flashover temperature.
- FIRE SIMULATOR post-FO run continues until all combustibles consumed or fire extinguished due to lack of oxygen (at 2%).
- Use of lower flashover temperature will shorten fire duration since more combustibles consuming oxygen.
- Selection of post-FO combustible load critical for determining remaining fire duration.

### **Conclusion**



• The fire severity for all MFFF fire areas is within the 80% safety margin of the fire barriers.





## Parametric Study of Changing Flashover Temperature to 842 F (450 C)

• For the six fire areas where flashover temperature was achieved and fire terminated:

FO

**End** 

- FA-MP-229: 277 seconds and 395 seconds

- FA-SR-001: 1031 seconds and 3531 seconds

- FA-AP-205: 358 seconds and 456 seconds

- FA-AP-217: 326 seconds and 518 seconds

- FA-AP-321: 326 seconds and 518 seconds

- FA-AP-403: 396 seconds and 556 seconds

6 February 2003

NRC Technical Exchange Meeting: Fire Severity

# DUKE COGEMA

# Impact of Fire Barrier Rating on Fire Areas Modeled by FPEtool

- Of the 44 fire areas modeled by FPEtool, 27 have 2-hour fire barriers and 17 have 3-hour fire barriers.
- Of the six fire areas that FIRE SIMULATOR indicates reach flashover temperature, five of six have 2-hour fire barriers.
- If these five fire areas had 3-hour fire barriers in lieu of 2-hour fire barriers, they would have not been modeled by FPEtool due to already demonstrating an adequate safety margin.

NRC Technical Exchange Meeting: Fire Severity

## NFPA 251 Standard Time-Temperature Curve

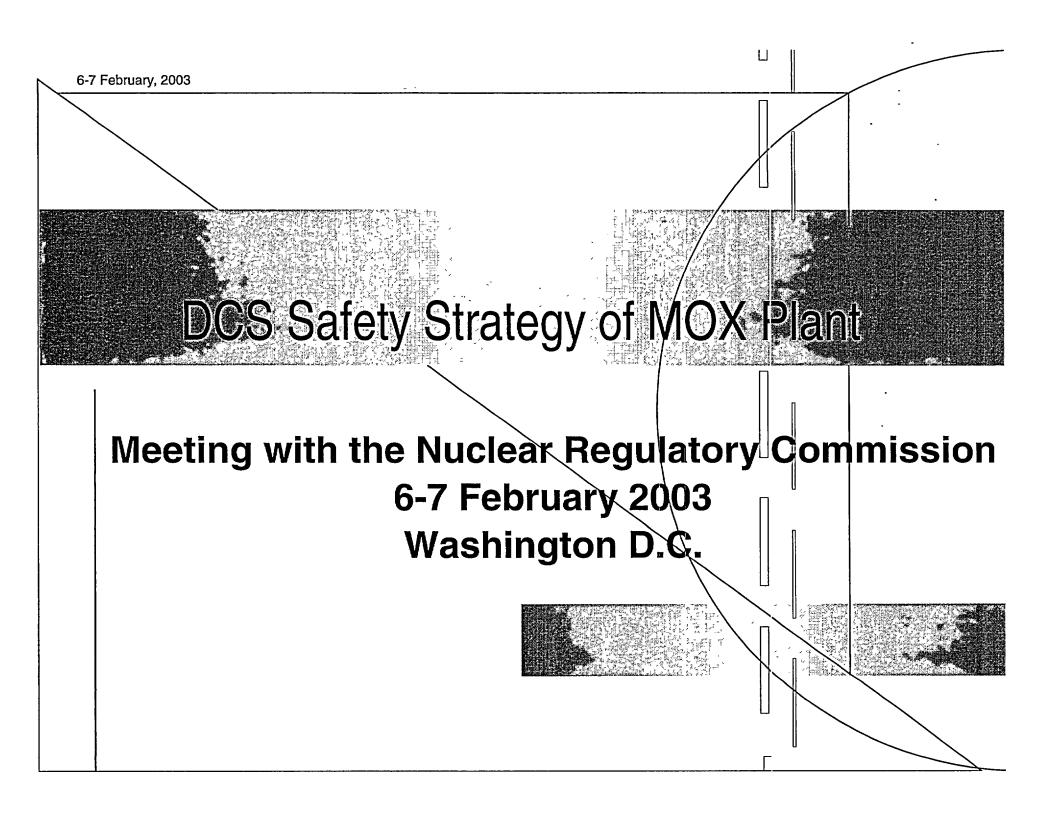


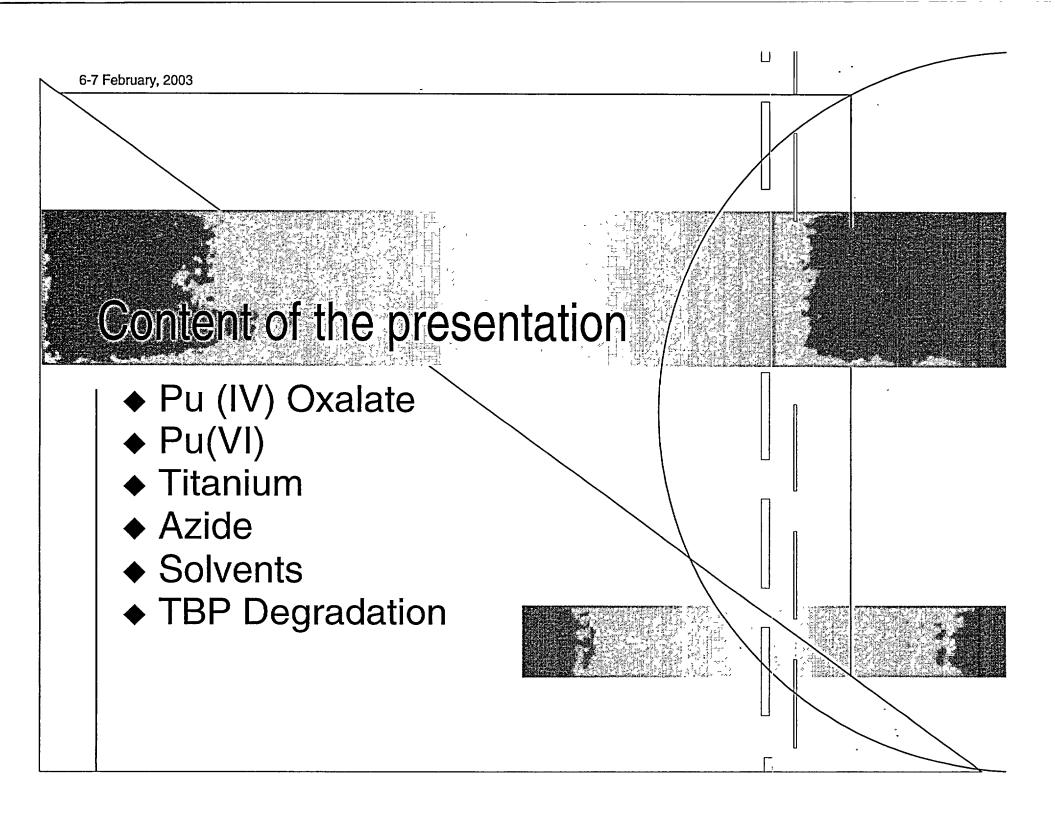
- Based on NFPA 251, fire-rated barriers can withstand the following fire exposures:
  - At 5 minutes, 1000 F
  - At 10 minutes, 1300 F
  - At 1 hour, 1700 F
  - At 2 hours, 1850 F
  - At 3 hours, 1925 F



# Comparison of Flashover Times to NFPA 251 Standard Time-Temperature Curve

- Based on NFPA 251, flashover temperature of 1112 F reached between 5 and 10 minutes since temperature at each time is 1000 F and 1300 F, respectively.
- Assuming linear relationship, flashover temperature on NFPA 251 curve achieved at 412 seconds.
- Although 3 out of 6 flashover rooms achieve flashover temperatures more rapidly than NFPA 251 curve, the maximum fire duration of these 3 rooms (approximately 9 minutes) is far less than the minimum fire barrier rating of 2 hours.
- Maximum post-flashover duration of approximately 60 minutes (1.0 hours) is less than the minimum 80% margin of 1.6 hours.





# DCS Approach to Safety

The DCS Safety Strategy is based on a fundamental understanding of the system through an exhaustive review of the literature, cooperation with world experts, experiments that will be performed to address the technical question identified during the ISA as necessary, and, industrial experience from COGEMA — La Hague

# Plutonium (IV) Oxalate

# Plutonium Oxide Production

## DCS Salety Strategy

- DCS limits the moisture content to less than 3 wt% in the cans due to both gas production and criticality safety constraints in the reusable cans (storage)
- ◆ Radiolysis has been examined and controls on the pressure rating of the can and limitations on the storage time to ensure safety will be determined during the ISA. However, the cans are in a glovebox as described in the CAR.

## Plutonium Oxide Formation

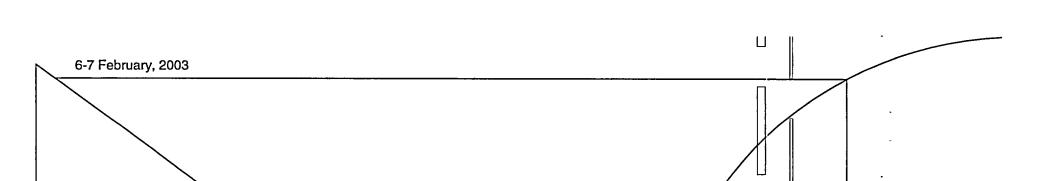
Multi-Step Mechanism – two major type of reactions:

◆ Plutonium Oxalate Endothermic Dehydration

At the inlet of the furnace the plutonium, under its tetravalent form, is complexed with exalate and the whole molecule is hexahydrated. The first part of the furnace is set to dehydrate it.

◆ Plutonium Oxalate Exothermic Decomposition

The plutonium oxalate *mono-hydrate* is reduced to its trivalent state. Water is still present in the system. Ru(III) oxalate, then is then oxidized to plutonium oxide.



## Mechanism of formation of Plutonium:Oxide

♦ Kozlova et al's model [1] in an Oxidative Medium

$$Pu(C_2O_4)_2.6H_2O \to Pu(C_2Q_4)_2.H_2O + 5H_2O$$

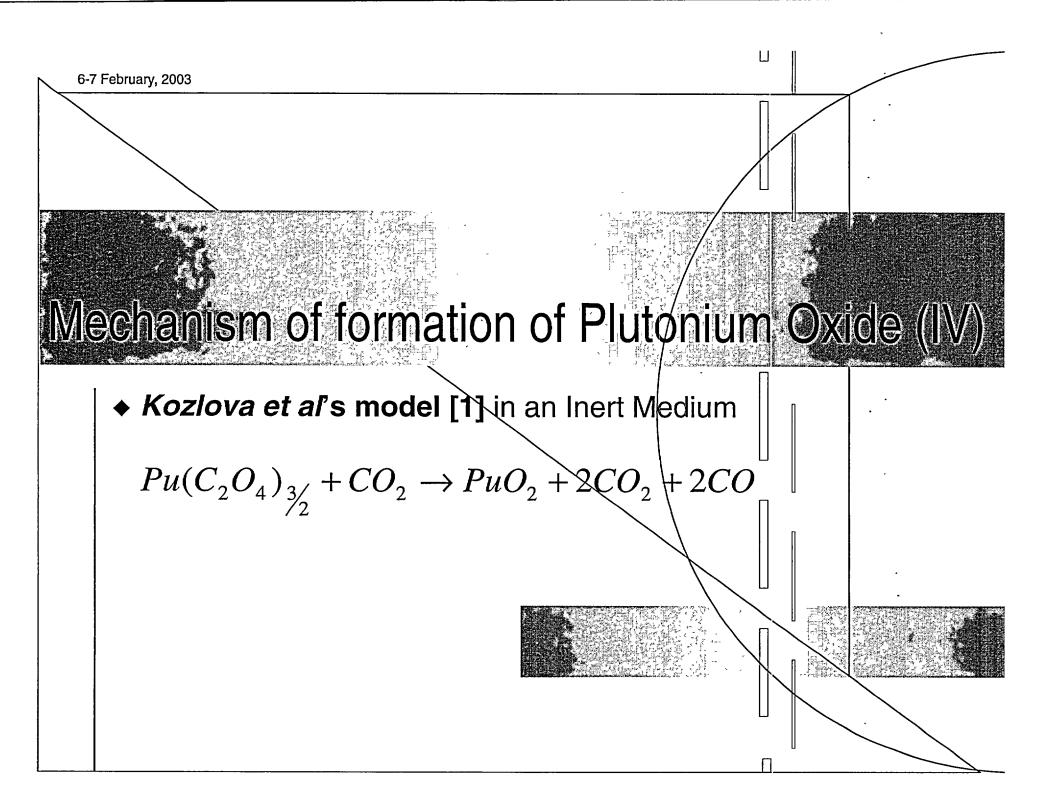
$$Pu(C_2O_4)_2.H_2O \to Pu(C_2O_4)_{3/2} + H_2O + CO_2$$

$$Pu(C_2O_4)_2.H_2O \xrightarrow{O_2} PuOCO_3 + 3CQ_3$$

$$Pu(C_2O_4)_{\frac{3}{2}} + O_2 \rightarrow PuOCO_3 + 2CO_2$$

$$PuOCO_3 \rightarrow PuO_2 + CO_2$$

6-7 February, 2003



## Prevention of re-oxidation in cans

Three acceptable options have been identified to prevent over pressurization once the plutonium oxide is stored:

- > Control furnace parameters:
  - (1) Residence time and,
  - (2) Temperature to ensure complete oxidation
  - (3) Moisture content of plutonium oxalate entering the furnace
- Experimental determination of the minimum moisture content accompanying Pu(III) at the exit of the furnace to prevent any over-pressurization due to the energy liberated during resolution (59kcal/mol)
- Measurement of Pu(III) content in the plutonium oxide powder

# Plutonium (VI)

# Plutonium (VI) Control System

## Plutonium (VI) Analysis

- ◆ The maximum quantity of Pu(VI) acceptable will be determined during the ISA using the methodology as described in the December 10-12 meeting.
- Appropriate Pu(VI) Detection Systems will be implemented; some possible analytical instruments are:
  - ✓ UV-Vis. spectroscopy: resolution to 10-5 M
  - $\checkmark$   $\alpha$ -spectroscopy: resolution to 10 $^{\circ}$  M



## Titanium Properties

- ◆ The excellent resistance of titanium to corrosion in most environments is due to its strong affinity of oxygen and the formation of a protective surface film of oxide. Film consists of TiO₂ at the metal environment interface with underlying layers of Ti₂O₃ and TiO.
- Titanium oxide forms naturally on the metal surface and is maintained when the metal is exposed to moisture or air.
- Titanium has been used in environments containing high temperatures (approximately 380°C), high nitric acid concentrations up to 60%, and high pressure without substantial corrosion.
- Titanium is used extensively in the production of nitric acid (20-70% HNO<sub>3</sub> reactors, tube bundles, heaters and thermowells at temperatures from boiling to 315°C.

## Potential Conditions Detrimental to Til

- ◆ Bulk titanium will ignite spontaneously on contact with liquid oxygen; Ignition also possible in pure oxygen at pressures 350 psi. Under no condition does spontaneous heating occur if the oxygen content is less than 35%.
- A pyrophoric titanium reaction has been observed in environments of anhydrous chlorine gas and in red-fuming nitric acid.
- ♦ Excessive heating of very thin wall tranium (1/30" or less)

## Titanium Fire: Definition

- ◆ Titanium fires may potentially occur due to a strong exothermic oxidation reaction of titanium(0) metal to titanium(IV) oxide / anhydrous tetravalent complex.
- ◆ Titanium is an extremely good corrosion resistant material. It can however, under extreme conditions, create pyrophoric residue (intragranular corrosion / surface of finely divided particles of metallic titanium, e.g. increase of the reactive surface).

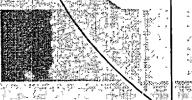
## Corrosion Mechanism

◆ Corrosion Reaction

$$Ti + 2nHNO_3 \Rightarrow nNQ_2 + 2nH_2O + Ti(NO_3)_n$$

With n the oxidized valence

◆ Required Reactant HNO₃ in large quantity (2n)





## Properties of Nitric Acid



$$4HNO_{\beta} \rightarrow 4NO_{2} + 2H_{2}O + O_{2}$$

 $2HNO_3 \rightarrow NO_2^+ + NO_3^- + H_2O_3$ 

Decomposition: Ionization of Furning Nitric Acid (FNA; i.e. hot and

concentrated nitric acid):

$$2HNO_3 
ightarrow N_2O_3 + II_2O_3 \ N_2O_5 
ightarrow NO_2^+ + NO_3^-$$

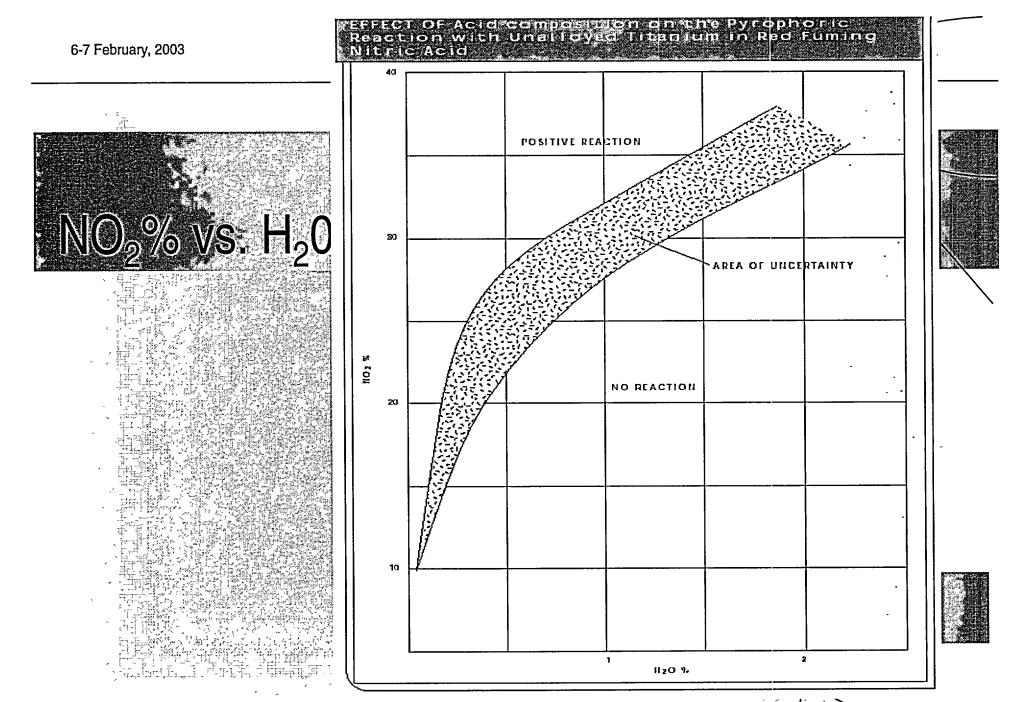
## Parameters driving the System (I)

## Factors effecting corrosion:

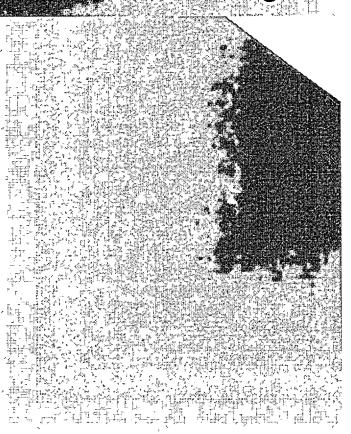
- Corrosion rate increase with decreasing water concentration
- ✓ Corrosion rate increases with increasing NO₂ concentration
- ✓ Stress corrosion cracks only occurs in anhydrous FNA

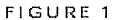
# Parameters effecting Corrosion (II)

	り」、Cartist 緑巻		
Parameters	Influen	ce on Corr	osion Rate
		+++	
$\mathrm{H}_2\mathrm{O}$ . Here $\mathrm{H}_2\mathrm{O}$			
HNO <sub>3</sub>		++	
Temperature		++	
Conductance of Liq. Phase		+	
Pressure			
· 特别的"一种"的"一种"。			
		•	

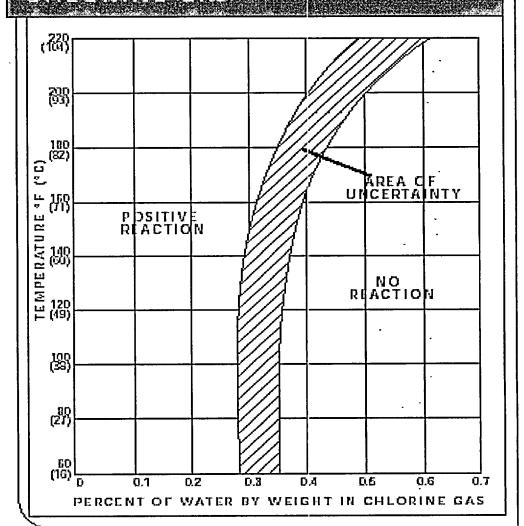


Temperature vs. H<sub>2</sub>0% in Chlorine gas

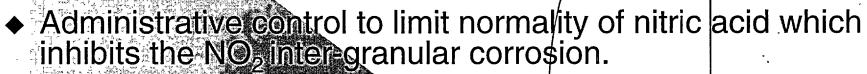




PRELIMINARY DATA REFLECTING PERCENT WATER CONTENT NECESSARY TO PASSIVATE UNALLOYED TITANIUM IN CHLORINE GAS



# DCS Safety Strategy



◆ Calculation will be performed during the ISA to ensure that the energy available due to the electrolyzer is not sufficient to cause tranium fire given the thickness of the electrolyzer.



# Azide System Analysis





## Administrative Control of Azides

- Azides present a potential risk in dry conditions
- ◆ DCS Safety Strategy is to avoid dry-out conditions:

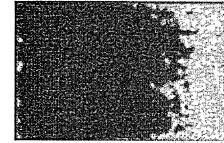
Tanks in the purification process that may potentially contain azides are rinsed after draining / leakage

## Design Bases for U/Pu Azides

- Avoid Dry-out conditions
- ◆ Limit the locations where U/Pu azides may be present so as to avoid high temperatures e.g. restrict azides from entering evaporators or furnace (sampling controls for azides have previously been identified as principal SSCs in the CAR)

# Destruction of Sodium Azide

◆ Sodium Azide from solvent recovery unit is destroyed by NaNO₂ addition prior to acidification so as to avoid retransformation to hydrazoic acid.



# TBP Degradation

# Temperature Limit for TBP/nitric acid systems

# Presentation of the Research Tests and \ \ Limitation of the Applicability of their Results

- ◆ For an adiabatic system there is no minimum initiation temperature for runaway reaction
- Minimum temperature for a "closed system" has been previously evaluated based on conductive heat transfer from the side of the tank without considering the evaporative heat transfer capability of the system

# DCS Approach for determination of Avoiding Runaway TBP/nitric acid reactions:

- To determine the actual dynamics of the system and determine the safety margin DCS will evaluate the following interactions:
  - Energy generation through chemical reactions
  - Heat transier through the vessel
  - Evaporative cooling through venting
- Experimental analysis will be performed to model the system and the safety regime of operation (and its limits) will be consequently determined

#### **Chemical Limit Comparison Table**

Chemical Concentrations	Nitric Acid	Cl2	NO2	TBP	N2O4	Hydrazine	Monohydr		Diluent: C10-C13	UO2
	<u> </u>						ate	Nitrate	Isoalkanes	
	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3	mg/m3
					4-	0.0	0.0075	3	5	0.6
TEEL-1	2.5	3	7.5	6	15	0.6	0.0075	Il		
1 hr AEGL-1 (interim)	1.3	1.5	N/A	N/A	N/A	0.1	N/A	N/A	N/A	· N/A
							approxim			
CAB Concentration for	0.00	0.002	0.02	0.01	0.14	×	ately 0	0.0002	0.06	0.0059
Doubled Inventory	0.09	0.002	0.02	0.01	0.14	1		0.0002	0.00	0.0000
TEEL-2	15	7.5	7.5	10	15	6	0.06	5	35	1
	10	5.8	N/A	N/A	N/A	17	N/A	N/A	N/A	N/A
1 hr AEGL-2 (interim)	10	0.0	IN/A	IN/A	N/A		14//	N/A	NA	IN/A
Worker Concentration (at 100 meters) for Doubled										
Inventory	4.6	0.4	3.5	0.6	7.5	x	0.033	0.03	3.2	0.974
TEEL-3	200	60	35	300	75	40	50	5	200	10
IDLH	62	30	36	375	N/A	65	N/A	N/A	N/A	10
1 hr AEGL-3 (interim)	55	58	N/A	N/A	N/A	45	N/A	N/A	N/A	N/A
Control Room Concentration*	0.3	×	×	0.21	62	×	0.1	x	0.8	. x

Note: x is not calculated. Calculation is being revised to account for current design information



# MOX Fuel Fabrication Facility (MFFF) Miscellaneous Questions 6 February 2003



- Is the UO<sub>2</sub> drum emptying unit glovebox nitrogen blanketed?
  - Yes, for process reasons. N<sub>2</sub> blanket is not required for safety.
  - CAR page in chapter 11 will be updated to reflect this information.

6 February 2003

NRC Technical Exchange Meeting



- Open Item AP-5b Identify any PSSCs and design bases for the waste unit, such as maximum inventories (Clarify if inventory information provided in CAR Table 5.5-3a are maximum inventories and identify any actions that would be taken if maximum inventories are exceeded).
  - Yes, values are bounding values

\*Text removed under 10 CFR 2.390.

Waste transfers expected every 2 weeks

6 February 2003

NRC Technical Exchange Meeting



- What are the release rates for chlorine and NOx?
  - Chlorine with scrubber <0.01 kg/batch (~12 hours)
  - Chlorine without scrubber < 0.8kg/batch
  - NOx with scrubbers <0.2kg/hr
  - NOx without scrubber <10.2 kg/hr (largest
    - vessel)
  - NOx without scrubbers <11.2 kg/hr (total)



- Is the site worker PSSC to control N<sub>2</sub>O<sub>4</sub> flow also required for the facility worker?
  - No, the facility worker is protected by different PSSCs
    - ◆ KWG offgas system ensures chemicals are vented through the stack.
    - ◆ Facility worker action ensures workers leave the area
  - These PSSCs protect facility worker from all chemical releases originating from KWG

6 February 2003

NRC Technical Exchange Meeting

5



- Other than chlorine, are there other chemicals where the PSSC facility worker action (worker leaves the area or takes other protective action) is required?
  - Yes, as described in CAR chapter 5.5.2.10.6.2, this PSSC is applied to any release of hazardous chemicals produced from licensed material. Facility workers will be trained to take appropriate action to protect themselves in the event of any chemical release.



- CS-5b For chemical limits, commit to specific values and provide methodology
  - Specific values are provided in CAR revision 1
  - Methodology is based on use of TEELs
    - ◆ Statement of considerations identify AEGLs, ERPGs, other
    - ◆ No final AEGLs for MFFF chemicals
    - ◆ TEELs use ERPGs when available
    - ◆ When ERPGS not available, TEELS provide consistent method for approximations of ERPGs



- Have the revised TEEL values affected the conclusions regarding latent health effects due to accidental release of chemicals?
  - No
  - TEEL-2 values take into account latent (i.e. cancer) effects based on acute exposures.
  - Only 2 potential carcinogens at MFFF, hydrazine and uranium.
  - CAR Section 8.4.2 will be revised to reflect this information



- Are there any safety related functions provided by the fire detection system?
  - Room fire detection and suppression systems in rooms with dispersable material are designated as defense in depth and thus are classified as PSSCs.
  - Fire detection systems also provide signals to other systems such as pellet conveyer systems and some support systems (e.g. H<sub>2</sub>/Ar). During final design, it will be determined if these signals are required for safety (IROFS).

#### **MEETING ATTENDEES**

#### NAME AFFILIATION

February 6-7, 2003:

Andrew Persinko Nuclear Regulatory Commission (NRC)

Melvyn Leach **NRC** Joe Giitter NRC David Brown **NRC** Rex Wescott **NRC** Sharon Steele **NRC** Norma Garcia Santos NRC William Troskoski **NRC** Donna Skay **NRC** Tim Johnson **NRC** Ivelisse Cabrera **NRC** 

Peter Hastings Duke Cogema Stone & Webster (DCS)

Gary Kaplan DCS Ken Ashe DCS Tom St. Louis DCS Marc Klasky DCS Jean-Francois Weiss DCS Marc Vial DCS Steven Kimura **DCS** Larry Rosenbloom DCS

David Alberstein Department of Energy

Geoff Kaiser SAIC

Alan Russel MPR

Bill Shields Defense Nuclear Facilities Safety Board

Steven Dolley Nuclear Control Institute (NCI)

### CLARIFYING INFORMATION AND COMMITMENTS PROVIDED BY DUKE COGEMA STONE & WEBSTER (DCS) AT THE MEETING

The information below was provided by DCS at the meeting.

#### FS-02 (fire modeling)

<u>For Construction Authorization</u>, DCS will provide an evaluation (heat flux method or alternative) of 44 fire areas exceeding the 80% criterion where maximum temperature exceeds the E119 curve, using ultra-fast growth curve for solvent and fast for everything else. DCS will draw conclusion about need to assess other areas, based on criterion of no changes to fire barrier rating in the 44 areas evaluated.

For the License Application, fire barrier performance under credible fire conditions (including flashover as applicable) will be demonstrated in the Integrated Safety Analysis (ISA), or barrier failure (unexpected) will be accounted for in consequence analyses.

#### MP-02 (Pu in reusable can)

Leakage from reusable can is covered by the spill event discussed in 5.5.2.3.6.4 (Load Handling Controls – C4 Confinement).

In the event radiolysis in the reusable can results in a buildup of pressure, the can lid is deterministically assumed to impact the glovebox. This event is included in 5.5.2.3.6.2 AP/MP C3 Glovebox Areas. To mitigate this event, the Material Handling Control, Principal Structures, Systems and Components is used. In this case, material handling controls may include control of moisture content of the material, residence time of the canned material, and/or design pressure of the reusable can. The specific items relied on for safety (IROFS) will be determined as part of the ISA.

CAR section 5.5.2.3.6.4 does not require revision; CAR section 5.5.2.3.6.2 and 5.6.2.3 (Material Handling Controls) will be revised as necessary to reflect this information.

Over-pressurization from the oxidation of Pu(III) oxalate contained within stored cans may be prevented through one of the following:

- 1. Controls on furnace parameters, such as furnace residence time and minimum temperature to ensure complete oxidation and moisture content of plutonium oxalate entering the furnace;
- 2. Experimental confirmation of the minimum moisture content accompanying Pu(III) at the exit of the furnace to prevent any over-pressurization due to the energy liberated during re-oxidation;
- 3. Measurement of Pu(III) content in the plutonium oxide powder.

The specific IROFS will be identified as part of the ISA.

#### CS-01 (TBP/red oil)

To ensure that the performance requirements of 10.CFR 70.61 are met for systems that may potentially contain TBP/nitric acid and whose venting system may not sufficiently accommodate the consequences of a runaway reaction, DCS has implemented controls on the input energy to the system via the process safety Instrumentation and Controls (I&C) system. The safety function of the I&C system is to limit the energy input to the system e.g., limit the steam temperature to 133 C. In addition, the Process Vent System has been identified as a principal Structure, System and Component (SSC). The safety function of the Process Vent System is to provide a means to ensure that adequate evaporative cooling, is provided to preclude a runaway reaction. The margin of safety is provided by ensuring that excess heat transfer is afforded to the system. This margin is 1.2 times the energy generation and energy input to the system.

The safety margin of 1.2 is consistent with the 10% margin for overpressure indicated in CAR §11.8, doubled to account for uncertainty. It is conceivable that analyses and experiments conducted in support of the ISA could require an increase or support a decrease of the safety margin. As discussed previously, the phenomenon is a function of organics content, nitric acid concentration, system pressure, and extent of venting available. DCS anticipates these parameters can likely be varied as part of detailed design without significant impact to the constructed facility.

#### CS-04 (Azides)

The CAR will be revised to indicate sampling in a Liquid Waste Reception Unit to confirm destruction of azides.

#### CS-04 (Plutonium and Uranium Azides)

The azide anion can form soluble weakly bonded azido complexes with uranium (U) and plutonium (Pu) at molar ratios of  $HN_3/Pu$  and  $HN_3/U$  less than one. Considering that the bounding hydrazoic acid ( $HN_3$ ) concentration developed in the previous section is 0.055mol/L, the Pu/U concentration in process vessels in which this condition could exist is very low. Furthermore, the production of hydrazoic acid which may be formed in the process via CAR Equation 8.5-7 is limited by the quantity of nitrous acid that is available to react with the hydrazine to form hydrazoic acid, which could potentially form uranium or plutonium azides. In addition, the hydrazoic acid that may be present in the system is distributed between the organic and aqueous phases further limiting the quantity of uranium and plutonium azide that may be produced. The quantity of nitrous acid present in the system is limited by the moderate temperatures, controlled with principal SSCs, as described in Section 8.5.1.8, and the low acidity, approximately 1 N HNO3.

This information will be reflected in a CAR change page.

#### **CS-10**

DCS will justify the use of TEEL-3 values or present alternative values for protection of control room operators performing safety functions.

#### CS-05b Additional Discussion

CAR section 8.4.2 will be revised to accurately reflect consideration of latent health effects.

Additional information will be provided regarding indoor wind speed values used.