DUKE COGEMA
STONE & WEBSTER

Document Control Desk
U.S. Nuclear Regulatory Commission
11545 Rockville Pike
Rockville, MD 20852-2738

09 February 2005
DCS-NRC-000179

Subject: Docket Number 070-03098
Duke Cogema Stone & Webster
Mixed Oxide (MOX) Fuel Fabrication Facility
Construction Authorization Request Page Changes

References:
1) R. L. Sweigart (DCS) letter to Document Control Desk (NRC), DCS-NRC-000177, dated 27 January 2005, *Construction Authorization Request Page Changes*
2) P. S. Hastings (DCS) letter to Document Control Desk (NRC), DCS-NRC-000157, dated 29 September 2003, *Response to Request for Additional Information – Chemical Safety Open Items CS-09, AP-02, AP-08, and AP-09*

This letter provides change pages to the Duke COGEMA Stone & Webster (DCS), LLC, Construction Authorization Request (CAR) concerning the Mixed Oxide (MOX) Fuel Fabrication Facility. The enclosed change pages replace pages in the CAR as updated through Reference 1. The changes incorporate the revisions discussed in Reference 2.

The enclosed change pages do not contain information which is considered to be proprietary to DCS. Enclosure 1 provides instructions for updating the CAR with the change pages. Enclosure 2 provides twenty-five copies of the CAR change pages.

If I can provide any additional information, please feel free to contact me at (980) 373-3787.

Sincerely,

Richard L Sweigart

Richard L. Sweigart
Vice President, Regulatory Affairs

RLS/KLA:gdh
Enclosures:
(1) Construction Authorization Request February 2005 Update Instructions
(2) Change Pages to the Mixed Oxide Fuel Fabrication Facility Construction Authorization Request

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Enclosure 1
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February 2005 Update Instructions

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Enclosure 2

Change Pages for Mixed Oxide Fuel Fabrication Facility Construction Authorization Request

25 copies enclosed

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- For temperature and hydrazine concentration at their respective design basis values, the system is stable for all HAN concentrations as long as the nitric acid concentration is less than 7.3 M.

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

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

- Process vessles containing HAN and hydrazine nitrate with addition of NO_x.

Each of these cases is described below.

5.5.2.4.6.4.1 Process Vessels Containing HAN and Hydrazine Nitrate Without Addition of NO_X

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

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

5.5.2.4.6.4.2 Process Vessels Containing HAN and Hydrazine Nitrate With Addition of NO_X

In the AP purification cycle, vessels designed to receive NO_x for reaction with hydrazine nitrate, HAN, and hydrazoic acid include the oxidation column KPA CLMN6000 and a recycling tank, KPA TK9500. Unlike other AP process vessels, these vessels are designed to eliminate hydrazine nitrate, HAN, and hydrazoic acid via reaction with excess nitrous acid produced from the introduction of NO_x. The temperature and pressure rise in these vessels as a result of these reactions is dependent on the concentrations of the reagents introduced into these vessels and the vent size of these vessels.

To reduce the risk of an over-pressurization/explosion event in these operations to the facility worker, site worker, IOC, and the environment, a preventative safety strategy is adopted. The principle SSCs utilized to implement this safety strategy are chemical safety control(s) and the off-gas treatment system. The safety function of chemical safety control is to limit the concentration of the HAN, hydrazine nitrate, nitric acid, and hydrazoic acid in the system ensuring the potential heat evolution and pressure increase do not exceed the design capabilities of the process vessel. The safety function of the off-gas treatment system is to provide an exhaust path for the removal of off-gases generated during the decomposition of these chemicals, which provides a means for heat transfer/pressure relief for affected process vessels.

5.5.2.4.6.5 Hydrogen Peroxide Explosion

A solution of 10 wt % hydrogen peroxide is used in the dissolution units. Explosive vapors can be produced from concentrated solutions higher than 75 wt %. To reduce the risk to the facility worker, site worker, IOC, and the environment associated with this postulated explosion group, a safety strategy utilizing prevention features is adopted. The principal SSC identified to implement this safety strategy is chemical safety control. The safety function of chemical safety control is to ensure that explosive concentrations of hydrogen peroxide do not occur. Details of this event are presented in Section 8.5.

5.5.2.4.6.6 Solvent Explosion

Some units within the AP process are fed with solvent. The potential for explosions exists due to high process temperatures and the possible attainment of a flammable/explosive mixture in the gaseous phase due to excessive heating. Solvent explosions resulting from chemical interactions with strong oxidizers are discussed in the following section. Section 8.5 presents more details related to this event.

To reduce the risk to the facility worker, site worker, IOC, and the environment associated with this postulated event, a safety strategy utilizing prevention features is adopted.

> Within equipment in the solvent extraction, solvent recovery, and waste units and equipment not at elevated temperatures in the acid recovery unit the following are identified for control of the flammable hydrocarbon concentration:
>
> The principal SSCs identified to implement this safety strategy are the process safety control subsystem, and chemical safety controls. The safety function of the process safety control subsystem is to ensure that external sources of heat are limited so as to ensure that 60% of the LFL is not exceeded. This PSSC will be implemented by monitoring the process temperature and terminating the heat source prior to exceeding the temperature limit (e.g., 50 C for HPT). The safety function of the chemical safety controls is to ensure that the process temperature corresponding to the 60% LFL limit, which may result from exothermic chemical reactions is not exceeded. This will be implemented by controlling the concentrations and/or flow rates of reagents.

Within equipment in the oxalic precipitation and the oxalic mother liquor units and equipment at elevated temperatures (evaporator) in the acid recovery unit the following are identified for control of the flammable hydrocarbon concentration:

The Principle SSC identified to implement this safety strategy is the process safety control subsystem. The safety function of the process safety control subsystem is to prevent diluent from entering into equipment at elevated temperatures such that flammable concentrations of hydrocarbons above 25% of LFL do not occur. This will be implemented by online redundant measurements (density or conductivity for example).

5.5.2.4.6.7 TBP – Nitrate (Red Oils) Explosion

The acid-catalyzed hydrolysis of TBP and subsequent oxidation of the associated by-products introduces the risk of a runaway reaction and associated over-pressurization event. This risk exists in AP process units that may contain these by-products and reach high temperatures (e.g., acid recovery unit, oxalic mother liquors recovery unit, purification cycle and solvent recovery unit). These energetic reactions may involve TBP, nitric acid, plutonium nitrate TBP adduct, and TBP degradation products due to chemical reactions (nitration/oxidation/hydrolysis) and radiolysis. Runaway reactions involving TBP and nitric acid are referred to as "red-oil reactions."

To reduce the risk to the facility worker, site worker, IOC, and the environment, a preventative safety strategy is adopted. To implement this preventative safety strategy, principal SSCs are established to control the rate of energy production from the exothermic chemical reactions and the amount of energy liberated from the system (e.g., heat transfer). By ensuring that the rate of energy generation does not exceed the rate of heat removal, such runaway reactions are prevented. The principal SSCs established to implement this safety strategy are the offgas treatment system, the process safety control subsystem, and chemical safety control. These

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Table 5.5-19. Principal SSCs and Associated Safety Functions for all Receptors for the Explosion Event Type (continued)

Explosion Group	Principal SSC	Safety Function
HAN Explosion [Process vessels containing HAN and hydrazine nitrate with NO_x addition]	Chemical Safety Control	Ensure concentrations of HAN, hydrazine nitrate, and hydrazoic acid are controlled to within safety limits
	Offgas Treatment System	Provide an exhaust path for the removal of gases in process vessels
Hydrogen Peroxide	Chemical Safety Control	Ensure that explosive concentrations of hydrogen peroxide do not occur
Solvent Explosion	Process Safety Control Subsystem	Ensure the temperature of solutions containing solvents is limited to temperatures within safety limits
		Ensure that external sources of heat are limited so as to ensure that 60% of the LFL is not exceeded
		Prevent diluent from entering into equipment at elevated temperatures such that flammable concentrations of hydrocarbons above 25% LFL do not occur
	Chemical Safety Controls	Ensure that the process temperature corresponding to the 60% LFL, which may result from exothermic chemical reactions, is not exceeded
TBP – Nitrate (Red Oil) Explosion	Offgas Treatment System	Provide an exhaust path for aqueous phase evaporative cooling in process vessels, thereby providing a mechanism for heat removal
		Provide venting of vessels/equipment that potentially contain TBP and its associated by-products to prevent over-pressurization in the case of excessive oxidation of TBP and/or its degradation products
	Process Safety Control Subsystem	Ensure the temperature of solutions containing organic is restricted to temperatures within safety limits in order to limit the rate of energy generation. Ensure that the design basis heatup rate is not exceeded Limit the residence time of organics in process vessels containing oxidizing agents and potentially exposed to high temperatures and in radiation fields

Table 5.5-19. Principal SSCs and Associated Safety Functions for all Receptors for the Explosion Event Type (continued)

Explosion Group	Principal SSC	Safety Function
TBP – Nitrate (Red Oil) Explosion (continued)	Chemical Safety Control	Ensure a diluent is used that does not contain cyclic chain hydrocarbons
AP Vessel Over-Pressurization	Fluid Transport Systems	Ensure that vessels, tanks, and piping are designed to prevent process deviations from creating over-pressurization events
	Offgas Treatment System	Provide an exhaust path for the removal of gases in process vessels
	Chemical Safety Control	Ensure control of the chemical makeup of the reagents and ensure segregation/ separation of vessels/components from incompatible chemicals
Pressure Vessel Over-Pressurization	Pressure Vessel Controls	Ensure primary confinements are protected from the impact of pressure vessel failures (bulk gas, breathing air, service air and instrument air systems)
Hydrazoic Acid Explosion	Chemical Safety Control	Ensure the proper concentration of hydrazine nitrate is introduced into the system Ensure that hydrazoic acid is not accumulated in the process or propagated to units that might lead to explosive conditions
	Process Safety Control Subsystem	Ensure the temperature of solutions potentially containing hydrazoic acid is limited to prevent an explosive concentration of hydrazoic acid from developing

Table 5.6-1. MFFF Principal SSCs

Principal SSC	Safety Function	SA Design Basis Reference
3013 Canister	Withstand the effects of design basis drops without breaching	11.4.11
3013 Transport Cask	Withstand the design basis fire without breaching	11.4.11
	Withstand the effects of design basis drops without release of radioactive material	
Backflow Prevention Features	Prevent process fluids from back-flowing into interfacing systems.	11.8.7
C2 Confinement System Passive Barrier	Limit the dispersion of radioactive material	11.4.11
C3 Confinement System	Provide filtration to mitigate dispersions from the C3 areas	11.4.11
	Remain operable during design basis fire and effectively filter any release	
	Limit the dispersion of radioactive material	
	Provide exhaust to ensure that temperature in the 3013 canister storage structure is maintained within design limits	
	Provide cooling air exhaust from designated electrical rooms	
C4 Confinement System	Maintain a negative glovebox pressure differential between the glovebox and the interfacing systems	11.4.11
	Maintain minimum inward flow through small glovebox breaches	
	Remain operable during design basis fire and effectively filter any release	
	Ensure that C4 exhaust is effectively filtered	
	Operate to ensure that a negative pressure differential exists between the C4 glovebox and the C3 area	
	Contain a chemical release within a glovebox and provide an exhaust path for removal of the chemical vapors	

Table 5.6-1. MFFF Principal SSCs (continued)

Principal SSC	Safety Function	SA Design Basis Reference
Chemical Safety Controls*	Ensure that explosive concentrations of hydrogen peroxide do not occur Ensure a diluent is used that does not contain cyclic chain hydrocarbons Ensure that hydrazoic acid is not accumulated in the process or propagated to units that might lead to explosive conditions Ensure metal azides are not introduced into high temperature process equipment Ensure the sodium azide has been destroyed prior to the transfer of the alkaline waste into the high alpha waste of the waste recovery unit Ensure the valance of the plutonium prior to oxalic acid addition is not VI Ensure that nitric acid, metal impurities, and HAN concentrations are controlled and maintained to within safety limits Ensure concentrations of HAN, hydrazine nitrate, and hydrazoic acid are controlled to within safety limits Ensure the proper concentration of hydrazine nitrate is introduced into the system Ensure control of the chemical makeup of the reagents and ensure segregation/ separation of vessels/components from incompatible chemicals Ensure that the process temperature corresponding to the 60% LFL, which may result from exothermic chemical reactions, is not exceeded	5.6.2.1

Table 5.6-1. MFFF Principal SSCs (continued)

Principal SSC	Safety Function	SA Design Basis Reference
Process Safety Control Subsystem (continued)	Control the flowrate into the oxidation column	8.5
	Ensure the temperature of solutions containing organic is restricted to temperatures within safety limits in order to limit the rate of energy generation	8.5
	Limit the residence time of organics in process vessels containing oxidizing agents and potentially exposed to high temperatures and in radiation fields	8.5
	Ensure the temperature of solutions potentially containing hydrazoic acid is limited to prevent an explosive concentration of hydrazoic acid from developing	8.5
	Limit and control conditions under which dry-out can occur	8.5
	Ensure the temperature of solutions potentially containing metal azides is insufficient to overcome the activation energy needed to initiate the energetic decomposition of the azide	8.5
	Ensure the normality of the nitric acid is sufficiently high to ensure that the offgas is not flammable and to limit excessive hydrogen production	8.5
	Warn operators of glovebox pressure discrepancies prior to exceeding differential pressure limits	11.4.11
	Shut down process equipment prior to exceeding temperature safety limits	11.4.11
	Ensure the temperature of solutions containing solvents is limited to temperatures within safety limits	8.5
	Ensure the flow rate of nitrogen dioxide/ dinitrogen tetroxide is limited to the oxidation column of the purification cycle	8.5
	Ensure that the design basis heatup rate is not exceeded	8.5

Table 5.6-1. MFFF Principal SSCs (continued)

Principal SSC	Safety Function	SA Design Basis Reference
Process Safety Control Subsystem (Continued)	Monitor the electrolyzer for faults that could result in arcing or other imparting of electrical energy with the risk of initiation of titanium fire	11.6.7 System Description – 11.3.2.4
	Ensure that external sources of heat are limited so as to ensure that 60% of the LFL is not exceeded	5.5.2
	Prevent diluent from entering into equipment at elevated temperatures such that flammable concentrations of hydrocarbons above 25% of LFL do not occur	5.5.2
Seismic Monitoring System and Associated Seismic Isolation Valves	Prevent fire and criticality as a result of an uncontrolled release of hazardous material and water within the MFFF Building in the event of an earthquake	11.6.7 – for system 11.8.7 – for valves
Sintered silicon nitride barrier	Physically separate cathode from anode	5.5.2
Sintering Furnace	Provide a primary confinement boundary against leaks into C3 areas	11.4.11
Sintering Furnace Pressure Controls	Maintain sintering furnace pressure within design limits	11.4.11
Supply Air System	Provide unconditioned emergency cooling air to the storage vault and designated electrical rooms	11.4.11
Transfer Container	Withstand the effects of design basis drops without breaching	11.4.11
Waste Containers	Ensure that hydrogen buildup in excess of limits does not occur while providing appropriate confinement of radioactive materials	11.4.11
Waste Transfer Line	Ensure that the waste transfer line is protected from activities taking place outside the MOX Fuel Fabrication Building	10.5
	Prevent damage to the line from external fires, explosions, earthquakes, extreme winds, tornadoes, missiles, rain, and snow and ice loadings	10.5

* Administrative control

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Explosion Phenomena

Hydrogen gas mixtures can become explosive if a sufficient amount of fuel and oxidant is distributed throughout the mixture while the mixture is not exposed to an ignition source or it is below the spontaneous ignition temperature. Even if the mixture is exposed to an ignition source or raised to high enough temperature, the mixture will only ignite and explode under certain conditions. The explosiveness of the mixture depends on the gas concentration, temperature, pressure (i.e., the flammability limits), the container surface conditions and the container size. Gas concentrations below or above the LFL and UFL are nonexplosive. Because the flammability limits vary with temperature and gas composition, these variables are considered when choosing the applicable lower and upper explosive limits (the LEL and UEL).

Outside of the sintering furnace in the BMP and BAP, the MFFF intends to control combustible gas concentrations to levels below 25% of the LFL to ensure that the LEL is not exceeded and to

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prevent explosions in the BMP and BAP. Inside of the sintering furnace, the MFFF intends to control the combustible gas concentrations to levels above the UFL at high temperatures, prevent or limit the introduction of air or other oxygen sources into the furnace, and to provide enhanced administrative controls during startup and shutdown of the furnace to ensure that the supply of combustible gas is stopped or the furnace is purged of combustible gases whenever the furnace is offline and prior to energizing the resistor heaters.

Explosions due to lean hydrogen concentrations below 8% in air will result in a peak pressure rise slightly above 1 bar (14.5 psi) because the low H_2 concentration does not allow downward propagation of the flame. At slightly higher concentrations of 9 to 10% H_2 (i.e., above the downward lower flammability limit) the peak pressures may be close to 3 to 4 bar (44 to 58 psi). The hydrogen concentration and temperature also play strong roles in determining whether the mixtures burn or explode. Thus, physical structures that mitigate or contain potential explosions are designed with these limits in mind.

Besides increasing the temperature of a combustible hydrogen mixture to above its spontaneous ignition temperature, the mixture can be ignited by a weak spark, such as one caused by the discharge of static electricity from a human body; open flames; hot surfaces or matches. Ignition of a gas mixture can result in the generation of a variety of different combustion regimes ranging from slow flames to detonations. Under certain conditions after ignition, slow flame fronts may be accelerated and transformed into detonations by the phenomenon of flame acceleration (FA) and deflagration to detonation transition (DDT). The conditions necessary to accelerate a flame to detonation are specific to the properties of the burned and unburned gas mixture and the physical layout and dimensions of the containment structure. Explosions may be prevented by controlling critical dimensions in the containment structure or by preventing the conditions necessary to sustain combustion or initiate ignition. Because of the complexity of the internal structures of the sintering furnace, the MFFF intends to prevent these types of explosions by controlling the conditions necessary to support combustion or initiate ignition.

Hydrogen Formation by High Temperature Reactions

Hydrogen can be formed at high temperatures by reactions with burning metals in which the oxygen atoms in the water are stripped off by unoxidized metal, thus releasing free hydrogen atoms. Hydrogen explosions in furnaces processing certain reactive metals (especially titanium) have been reported as a result of this reaction. The sintering furnace only processes a mixture of oxidized forms of uranium and plutonium. Therefore, any water that could come into contact with these oxides from excessive humidity in the process gas will only form steam and is not expected to become dissociated into free hydrogen. Explosions caused by increasing the hydrogen content of the process gas by this mechanism are thus precluded. Chapter 5.5.2.4.6.2 discusses the hazards involved with steam overpressure events.

8.5.1.1.1 Argon-Hydrogen Mixture in Sintering Furnace and Hydrogen Storage

A mixture of argon and hydrogen gas is used in the sintering furnace to provide the required atmosphere for pellet sintering. The gases are mixed outside of the MFFF building in the proper proportion and transferred to the pellet sintering areas via facility piping. Inherent with the use of hydrogen are the associated hazards of fire and explosion. These hazards are present at the gas storage/mixing area, sintering furnace area, furnace gloveboxes and airlocks, sintering furnace exhaust and associated HVAC system, and the sintering furnace itself. Control of the hazards associated with hydrogen in these areas is discussed in the following paragraphs.

Fire and explosion events are prevented in the sintering furnace area, furnace gloveboxes and airlocks, sintering furnace exhaust, and associated HVAC system by the process safety control subsystem. The process safety control subsystem prevents the formation of flammable mixtures of hydrogen. The design basis for this control is 25% of the lower flammability limit (LFL) of hydrogen in air. Actual setpoints will be determined as part of final design.

Fire and explosion events are prevented in the sintering furnace by the use of design features and procedures (administrative controls) that prevent the formation of flammable mixture of hydrogen in air. The basis for these engineered and administrative controls is NFPA 86C, *Industrial Furnaces Using a Special Processing Atmosphere.* As stated in Chapter 7.0, Fire Protection, fire safety for the sintering furnace is in accordance with the applicable requirements of NFPA 86C-1995.

The design bases of PSSCs associated with fire and explosion at the facility gas storage area (external events) are discussed in Section 11.1.7.

8.5.1.1.2 Hydrogen Production due to Radiolysis

Radiolysis is the process of hydrogen gas production by radiolytic dissociation of hydrogenous materials. Within the MFFF process, the hazards associated with radiolysis are present in some AP processes and in some waste drums. The potential for hydrogen production in the MOX process is low due to the negligible quantity of hydrogenous materials.

The design bases associated with the control of the hazards associated with hydrogen gas is in accordance with standard NFPA practices. The lower flammable limit (LFL) is considered the safety limit. This is the value at which an event may occur because the hydrogen concentration may be flammable. 25% of the LFL is the design basis value. This is the value used to design the process and as necessary, is used to initiate control actions during normal operations.

In the AP processes, the risk associated with radiolysis is mitigated by maintaining adequate dilution airflow and ensuring an exhaust path exists. Calculations will be performed as part of detailed design to determine appropriate air flow rates and summarized in the ISA. Should normal airflow be lost to an AP process vessel, emergency scavenging air will be provided as described in Section 11.9. These airflow rates will ensure that 25% of the LFL is not exceeded during normal or off-normal conditions.

Hydrogen production and accumulation may occur in the waste and byproducts, such as contaminated organic waste or organic-additive-bearing waste containing significant amounts of plutonium, scraps in transuranic (TRU) waste containers, and other liquid waste. Where this may become a hazard, the containers are equipped with a filtered vent system that limits hydrogen accumulation by providing an exhaust flow path while maintaining confinement of radioactive materials.

8.5.1.1.3 Hydrogen Production by Electrolysis

The dissolution unit and the dechlorination and dissolution unit utilize a catholyte loop in which nitric acid is used to dissolve plutonium oxide. This electrolytic dissolution process introduces the risk of generating hydrogen gas.

The design bases associated with the control of the hazards associated with hydrogen gas is in accordance with standard NFPA practices. The LFL is considered the safety limit, the value at which an event may occur because the hydrogen concentration may be flammable. 25% of the LFL is the design basis value. This is the value used to design the process and as necessary is used to initiate control actions during normal or off normal operations.

The production of hydrogen during electrolysis is a function of the nitric acid normality. As described in Section 5.5.2.4, the normality of the nitric acid will be maintained sufficiently high to ensure that the off-gas is not flammable. Calculations will be performed as part of detailed design and summarized in the ISA to determine the appropriate nitric acid limits. These limits will ensure that 25% of the LFL is not exceeded during normal or off-normal conditions.

8.5.1.2 Solvent Related Hazards

Some units within the AP process are fed with solvent. The potential for solvent related fires and explosions exists due the possible attainment of a flammable/explosive mixture in the gaseous phase due to excessive heating.

As described in section 5.5.2, a combination of IROFS will be in place to ensure that explosive conditions associated with solvent vapors are prevented from occurring. DCS uses the guidance of NFPA 69-1997 as the design basis for control of flammable mixture concentrations within the AP process vessels. NFPA 69 provides various options to accomplish this, including the following:

- The combustible concentration shall be maintained at or below 60% of the LFL when automatic instrumentation with safety interlocks is provided, or

- The combustible concentration shall be maintained at or below 25% of the LFL.

8.5.1.3 Hydroxylamine Nitrate (HAN) and Hydrazine (N_2H_4) in Nitric Media

The Aqueous Polishing (AP) process uses a mixture of hydroxylamine nitrate (HAN) and nitric acid (HNO_3) during the extraction step of the plutonium purification unit (KPA) to strip plutonium from the solvent after removal of americium and gallium. HAN has a number of advantages as a plutonium reductant. It is nonmetallic, it is readily decomposed to innocuous products by heating, the gaseous reaction products – nitrogen (N_2), nitrous oxide (N_2O), and water (H_2O) – contribute to minimization of the volume of solid wastes produced, and it possesses the proper Pu (IV) to Pu (III) reduction attributes. However, due to the potential for HAN to undergo an autocatalytic reaction with nitrous acid under certain conditions, the use of HAN in the AP Process introduces an explosion/overpressure hazard.

Experience and insights gained from previous accidents involving HAN and experimental data from the Hanford and Savannah River sites are utilized in conjunction with La Hague Plant experience to assist in the determination of safe operating conditions for the storage and the handling of HAN, hydrazine and nitric acid.

The HAN-nitric acid system is a complex multi-parametric system involving the interdependence of the following four parameters:

- Chemical concentration of each reactant
- Molar ratio of nitric acid to HAN
- Temperature of the mixture
- Concentration of metal ion catalysts.

A general feature that has characterized many of the previous accidents with HAN mixtures without hydrazine is the inadvertent increase of solution temperature and/or concentration of or an inadvertent acid addition to these solutions. Experimental results indicate that high nitric acid concentrations or the presence of impurities (such as metal ions) increase the likelihood of the initiation of an autocatalytic reaction. Furthermore, for systems without metal catalyst, a trend of decreasing the autocatalytic reaction temperature threshold when increasing the nitric acid to HAN ratio has been found. Maintaining low nitrous acid concentrations has been indicated as important to storage and use of HAN, with respect to autocatalytic reactions. Previous attempts to characterize the stability of a system have examined both experimental and accident conditions in which the concentrations of nitric acid and HAN have increased. In these systems the energy liberated as a result of an autocatalytic reaction also increases as a function of the original energy content of the solution and the initial concentrations of HAN.

To understand the behavior of systems comprised of HAN, hydrazine, plutonium and metal ions with nitric acid, the various associated reactions are modeled. In this manner the kinetic rates for reactions governing production and consumption of nitrous acid are used to describe the stability of the system under normal, abnormal, and accident conditions. The chemical reactions that govern the solutions that may contain HAN include:

- Plutonium (IV) reduction by HAN
- Plutonium (IV) reduction by Hydrazine
- Plutonium (III) Re-oxidation
- HAN reaction with nitrous acid
- Hydrazine reaction with nitrous acid
- Catalyzed Nitrous Reactions with Metal Ions

Additional discussion of the safety strategies and specific controls associated with control of these reactions is found in Section 5.5.

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