

CHEMICAL AND PROCESS SAFETY

1. NRC Staff Conduct of Review

- * **NRC regulates the following aspects of chemical and process safety:**
 - chemical hazards of radioactive materials (e.g., depleted uranium dioxide)
 - chemical hazards of chemicals produced from radioactive materials (e.g., NO_x release from plutonium nitrate/nitric acid solutions)
 - chemical hazards that affect the safe handling of licensed radioactive material (e.g., N₂O₄ reagent release upon plutonium handling operations)

- * **Performance requirements in 10 CFR 70.61**
 - High consequence: render acute chemical exposures highly unlikely if endanger life of worker or irreversible/other serious health effects outside controlled area boundary
 - Intermediate consequence: render acute chemical exposure unlikely if irreversible/other serious effects to worker or mild transient health effects outside controlled area boundary
 - applicant submits proposed quantitative standards for chemical health effects for NRC approval

- * **Staff review used the guidance provided in the MOX Standard Review Plan (NUREG-1718)**

- * **Staff obtained open literature documents and performed independent analyses as necessary to supplement the review**

2. Chemical Safety in the Application

- * Applicant has proposed the use of TEELs - Temporary Emergency Exposure Limits - for chemical health effects (Table 1)**

Table 1: Selected Chemicals, Inventories, and TEELs

Chemical	Approximate Chemical Quantity Onsite	TEEL-1 mg/m3	TEEL-2 mg/m3	TEEL-3 mg/m3
N ₂ O ₄	206 gal, 35%	15	15	75
HNO ₃	429 gal, 13.6 M	2.5	12.5	50
HAN	435 gal, 1.9 M	10	25	125
N ₂ H ₄ .H ₂ O	206 gal, 35%	0.006	0.04	0.04
UO ₂	37.5 tonnes	0.6	1	10

- * Staff review has identified potential concerns with chemical releases at the proposed facility**

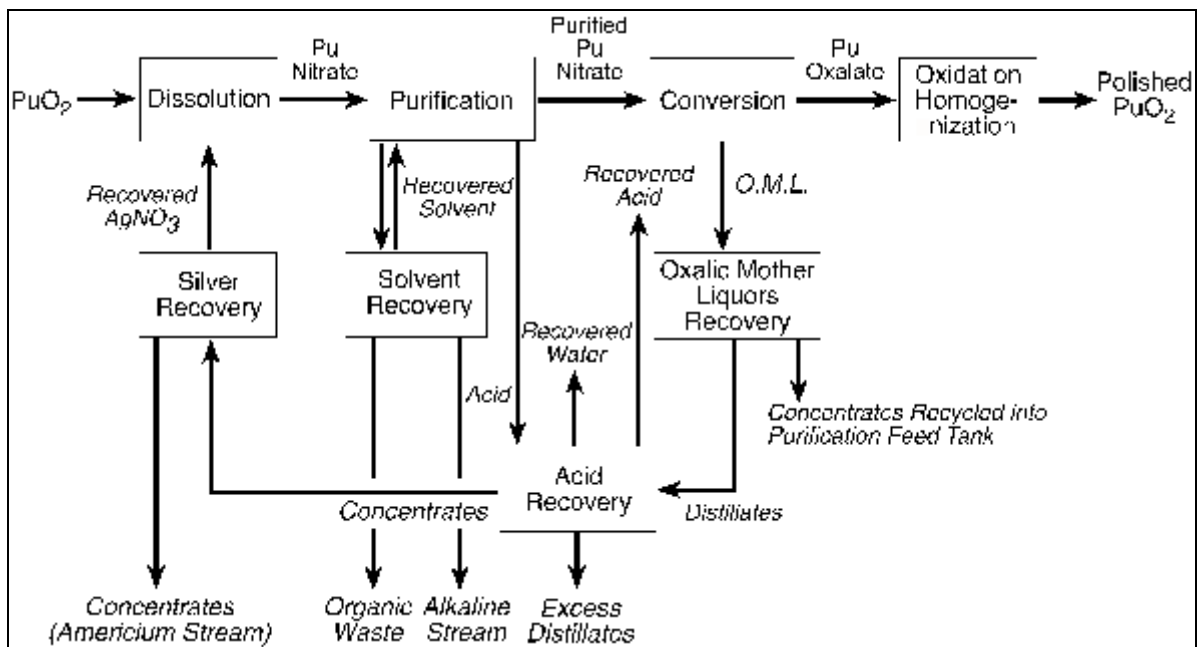
- * Special case of uranium compounds**
 - radiation hazards relatively small
 - chemical hazards and toxicity effects dominate potential risk for low enriched materials

- * Only specific design feature to mitigate consequences of chemical releases: special filters for chemicals on the emergency control room HVAC**

3. The Chemical Aspects of MOX Fabrication

- * **The Proposed MOX Facility (MFFF) consists of two basic processes**
 - AP - Aqueous Polishing
 - MP - MOX (powder) Process

Figure 1: AP Process Overview



- * **AP purifies the plutonium by removing chemical and radioactive impurities**
 - Similar to processes conducted at DOE facilities (Hanford and Savannah River)
 - NRC-licensed facilities have also used variations of the same process for scrap recovery and recycle
 - Currently applied on a significant scale in France, United Kingdom, Russia, and Japan
 - process operations are conducted in cells and gloveboxes

- * **The impure plutonium dioxide from DOE is dissolved in nitric acid, assisted by electrolysis**

- * **AP uses solvent extraction into an organic, kerosene-like solvent as the principal means of purification**
 - Based upon an updated PUREX process
 - Chemicals are tri-butyl phosphate (TBP) in dodecane (similar to kerosene)
 - Both columns and mixer-settlers used (Figures 2-4)

Figure 2: Typical Solvent Extraction Arrangement

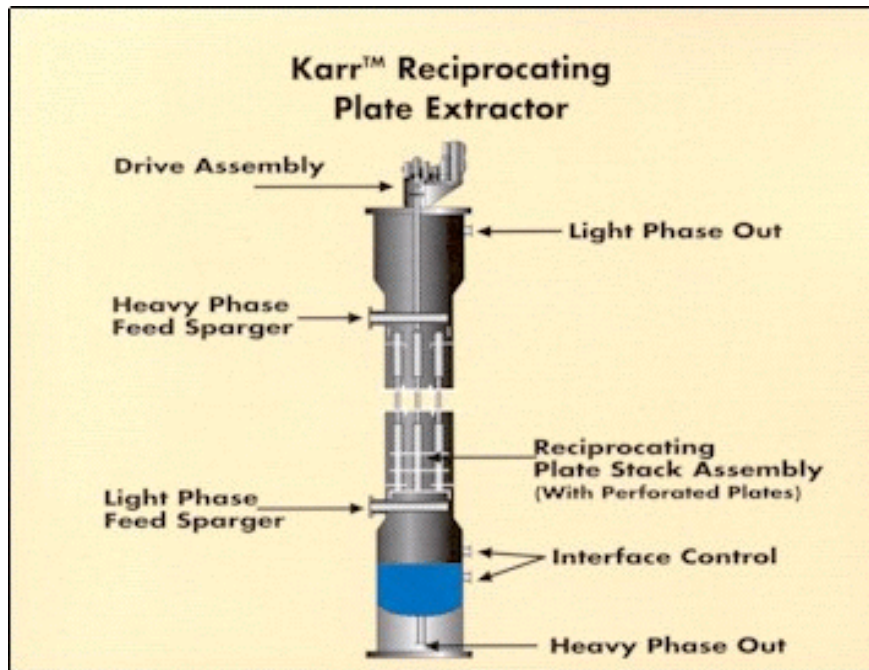


Figure 3: Schematic of Reciprocating Karr Column

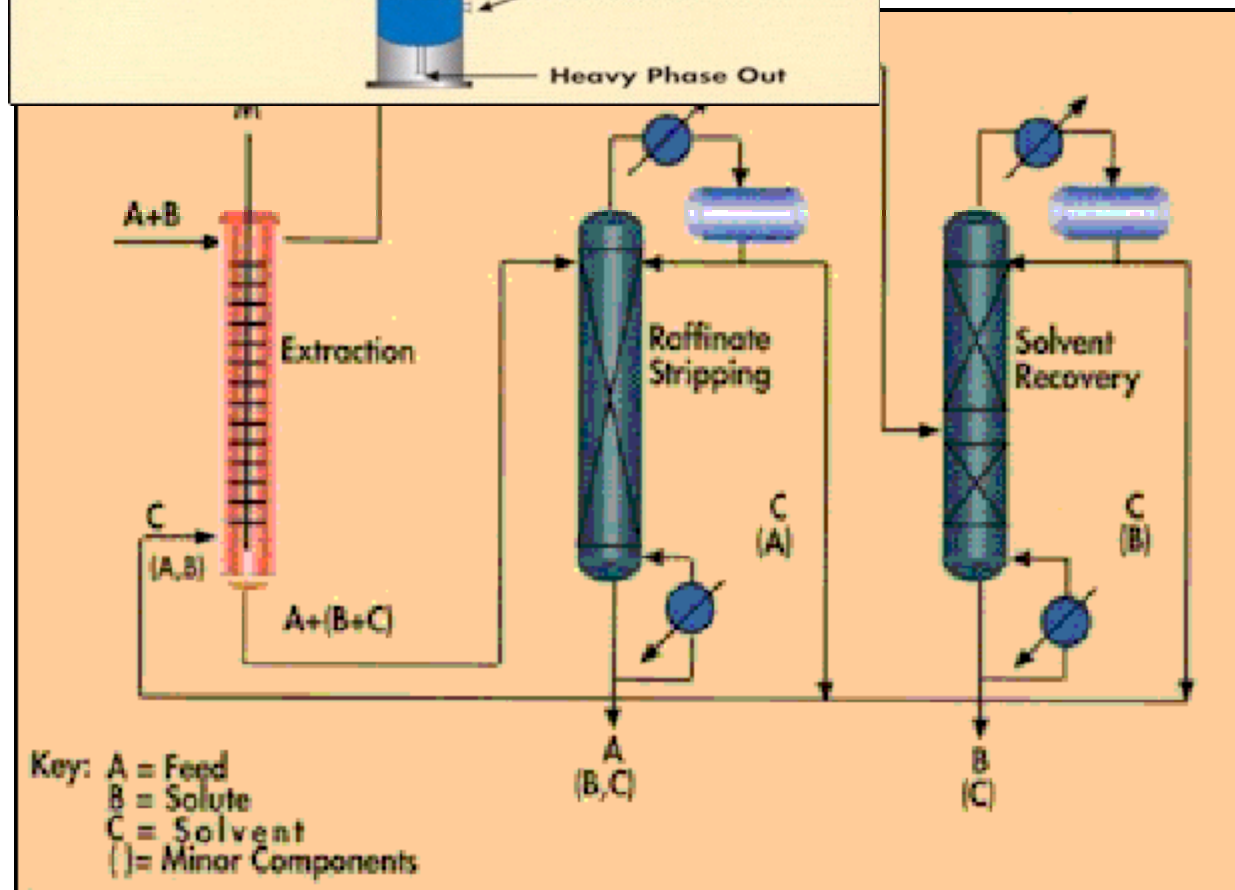


Figure 4: Example of Experimental Unit - Karr Column in Center

- * **Additional purification by precipitation**
- * **Purified plutonium nitrate converted to oxide by oxalate precipitation and calcination**
- * **About 50% of AP**



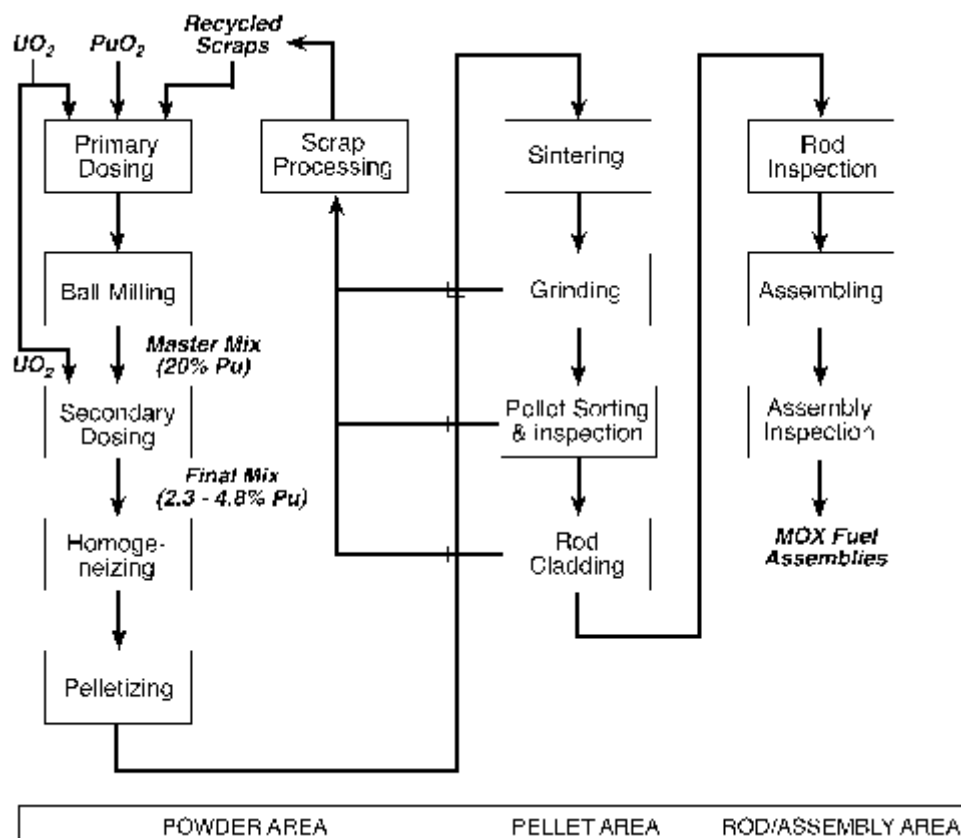
associated with reagent recovery and waste processing

MP - MOX Powder Process (Figure 5)

Figure 5: MP Flow Diagram

- * **MP is a dry powder milling and blending process**
 - similar to uranium fuel fabrication at existing NRC licensees
 - applied on a significant scale in France, Belgium, and United Kingdom
 - comprised of some 38 process units in the proposed facility

- * **Purified plutonium dioxide powder is blended with depleted uranium dioxide powder (Figure 6) and milled**



(size reduced) to form a master mix (about 20% Pu)

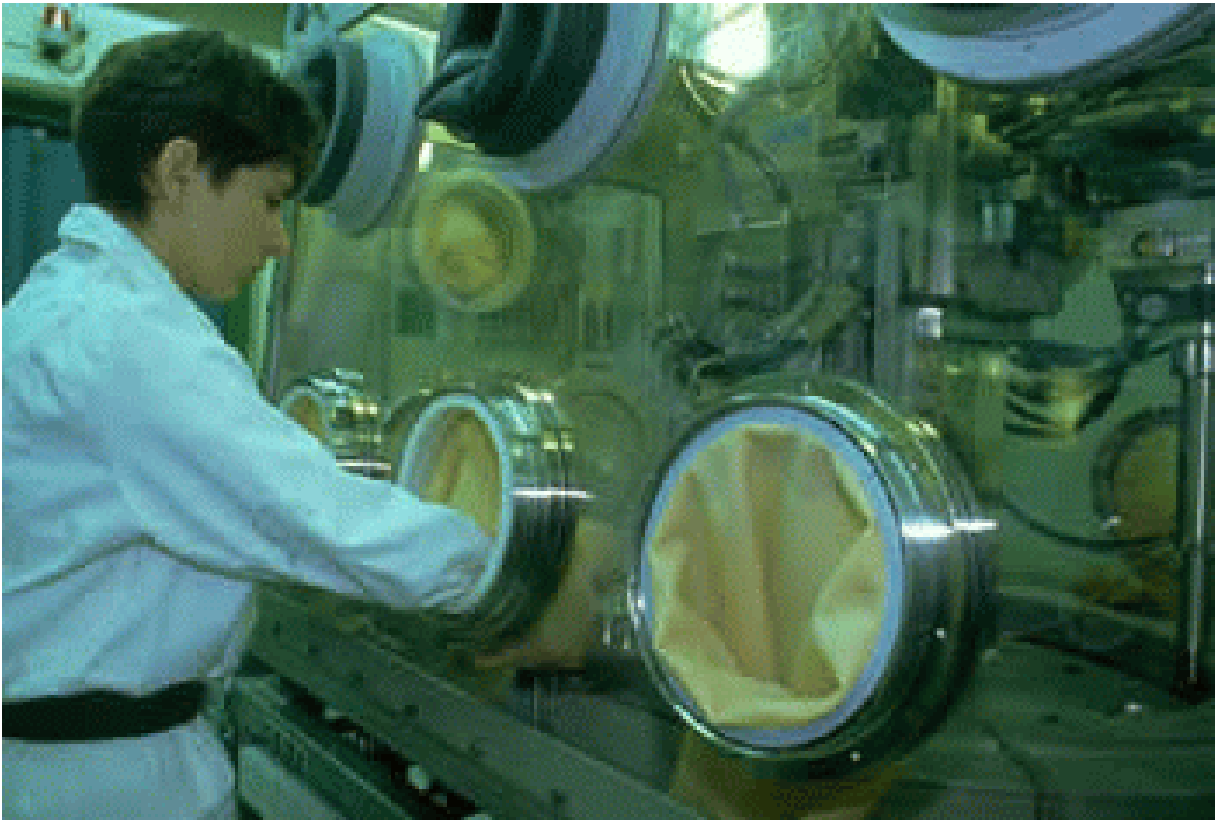
- all powder operations are conducted under a nitrogen gas atmosphere

- all operations prior to rod inspection are conducted in glove boxes (Figure 7)

Figure 6: Uranium Dioxide Powder (PuO₂ appearance is similar)



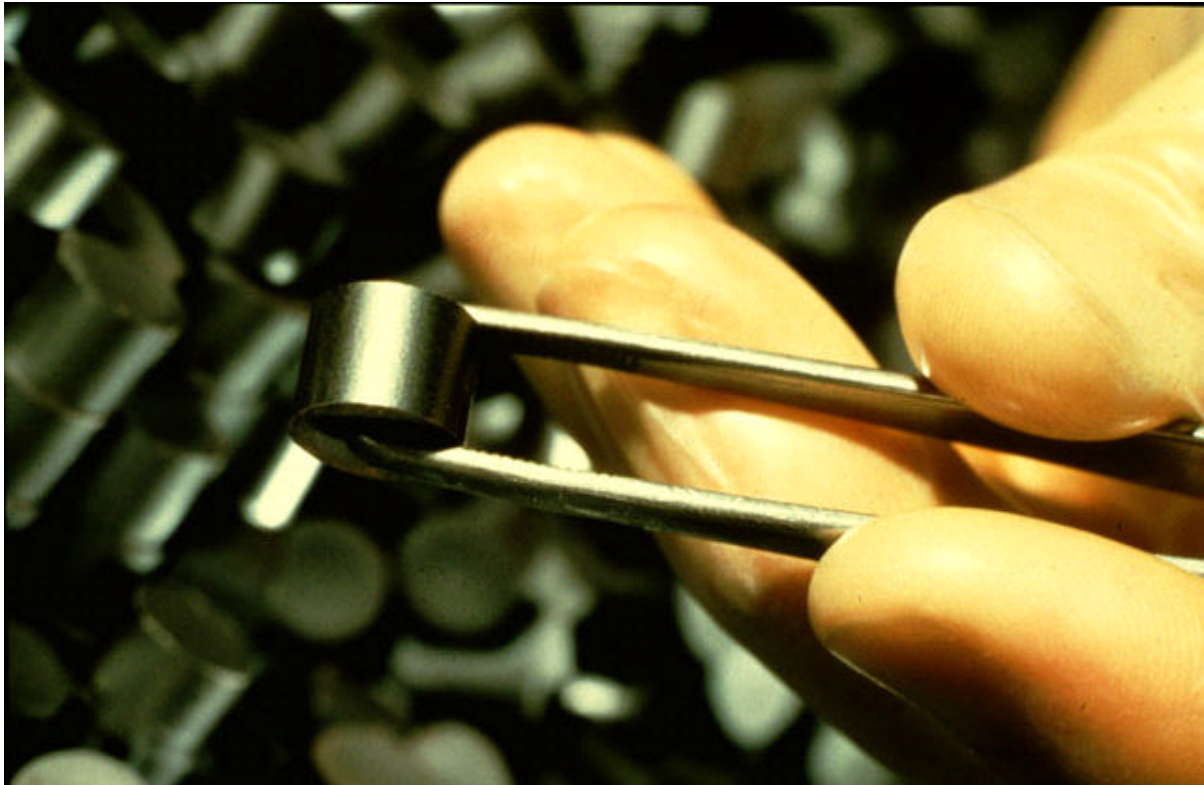
Figure 7 : A typical glovebox (Melox Plant, France)



- * **Additional depleted uranium dioxide and dry chemicals (such as soaps and binders) are added to the master mix, blended, and homogenized to form a final powder mix (2.3-4.8% Pu)**

- * **The final powder is pressed into pellets and sintered into a high density material using a furnace**
 - high temperatures in the furnace remove the organic materials
 - a hydrogen/argon gas mixture provides a reducing atmosphere in the furnace that produces higher pellet densities (Figure 8)

**Figure 8: Uranium Dioxide Fuel Pellets
(MOX pellets are similar)**



- * Pellets are ground to specific dimensions and inspected**

- * Pellets are loaded into rods and the rods are sealed and inspected (Figures 9 and 10)**

Figure 9: Visual Inspection of Fuel Rods

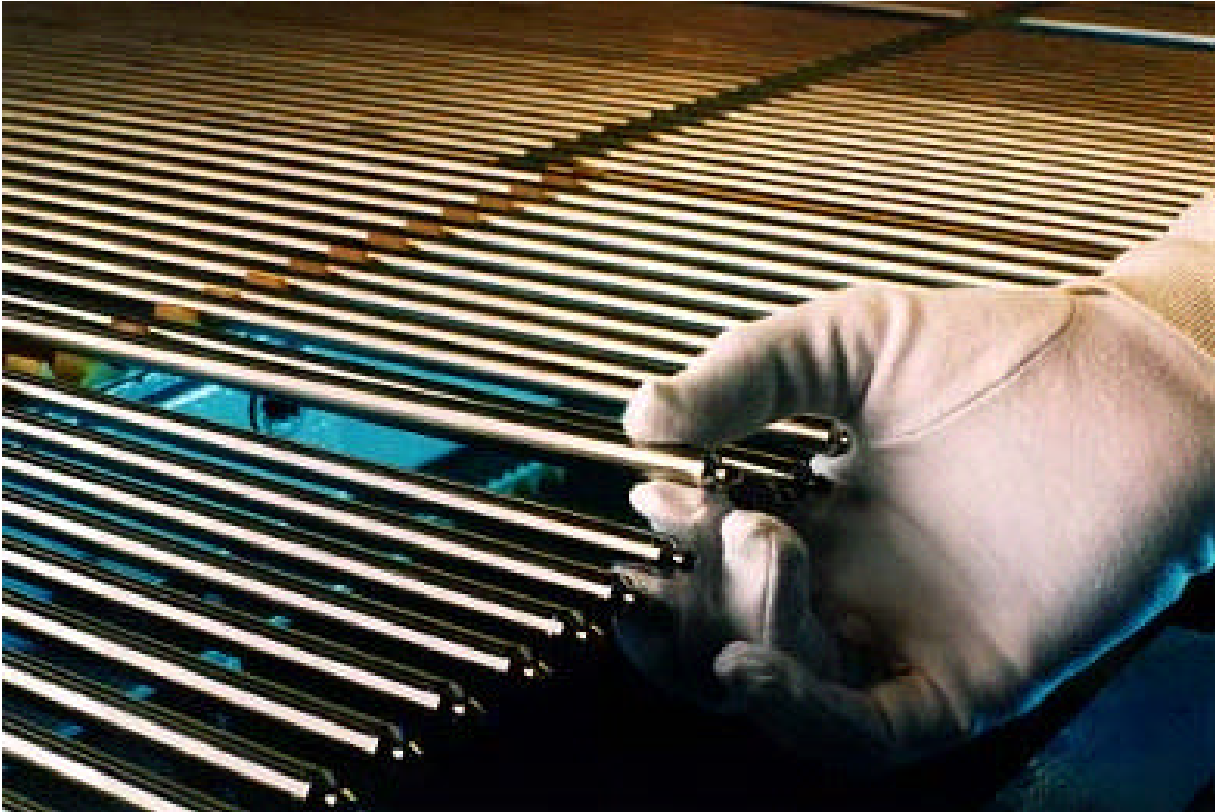


Figure 10 : Typical Fuel Rods (uranium fuel - MOX rods are identical)

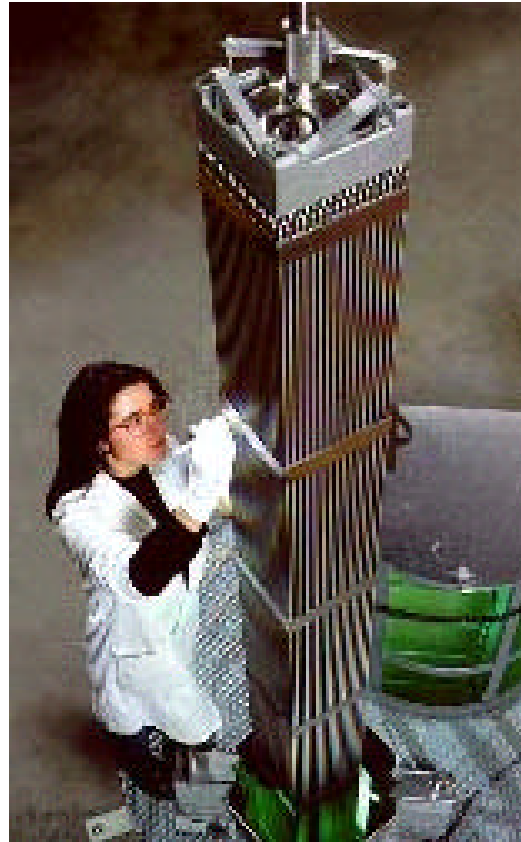


- * **Rods are inserted into grid straps and spacers to form assemblies (Figures 11 and 12)**

Figure 11 : Typical Grid Straps and Spacers



Figure 12 : Typical UO₂ PWR Assembly (MOX Assemblies Similar)



- * **Assemblies are inspected, stored, and shipped to the reactor site (Figure 13)**

Figure 13: Typical Fuel Assembly Storage (UO2 - MOX storage is similar)



4. STAFF EVALUATION AND FINDINGS

- * **Applicant has not met regulations due to open items**

- * **Section 8 of Draft SER: Chemical and Process Safety**
10 Open Items:
 - "red oil" analysis is not complete
 - HAN/hydrazine analysis is incomplete
 - HAN/hydrazine/azide
 - pH control for avoiding precipitation in waste unit
 - modeling of hazardous chemical releases
 - potential controls to protect the worker from a laboratory explosion
 - safety functions for the delivery of chemicals
 - chemical toxicity impacts from DUO2
 - adequate margin for the solvent temperature design basis
 - design basis for habitability in the Emergency Control Room

- * **Section 11.2 of Draft SER: Aqueous Polishing Process and Chemistry**
13 Open Items:
 - protection of the electrolyzer against overtemperature
 - potential fires/explosions from flammable gases around and in the electrolyzer
 - electrolyzer events involving titanium
 - corrosion monitoring of alloys susceptible to silver(II) corrosion
 - confirm that wastes will meet the SRS WACs and that SRS will accept these wastes
 - identify design bases and safety functions for the high alpha waste system
 - identify design bases for the feed material to the proposed facility
 - provide a design basis and PSSCs for flammable gases and vapors in the Offgas unit
 - provide a design basis and PSSCs for the maximum solvent temperature
 - provide a design basis and PSSCs for the removal of toxic and potentially reactive gases in the Offgas unit
 - corrosion monitoring of components exposed to aggressive species in the Offgas unit
 - provide design basis and PSSC information on the sampling system
 - identify a safety strategy for hazardous chemical releases from the loss of confinement of radioactive materials

- * **Section 11.3 of Draft SER: Mixed Oxide Process System Description and Review**
4 Open Items:
 - provide design basis and PSSC information associated with the pyrophoric/burnback nature of some UO₂ powders
 - provide design basis and PSSC information associated with the pyrophoric nature of some PuO₂/PuO_x powders
 - provide design basis and PSSC information associated with potential steam explosion events in the sintering furnace
 - provide design basis and PSSC information associated with potential explosions in the sintering furnace room

- * **Staff reviewing additional information as it is submitted by applicant**

- * **Staff found the following areas acceptable at the preliminary design/construction stage**
Closed Items:
 - mass, energy, and radioactivity balances
 - overall process description
 - completeness of chemical listing and quantities
 - general approach of using EPA ALOHA code and NUREG/CR-6410 for guidance in modeling chemical releases
 - feed concentration controls for peroxide and hydrazine hydrate
 - design basis temperatures for gloveboxes and cells

5. DISCUSSION OF SEVERAL OPEN ITEMS

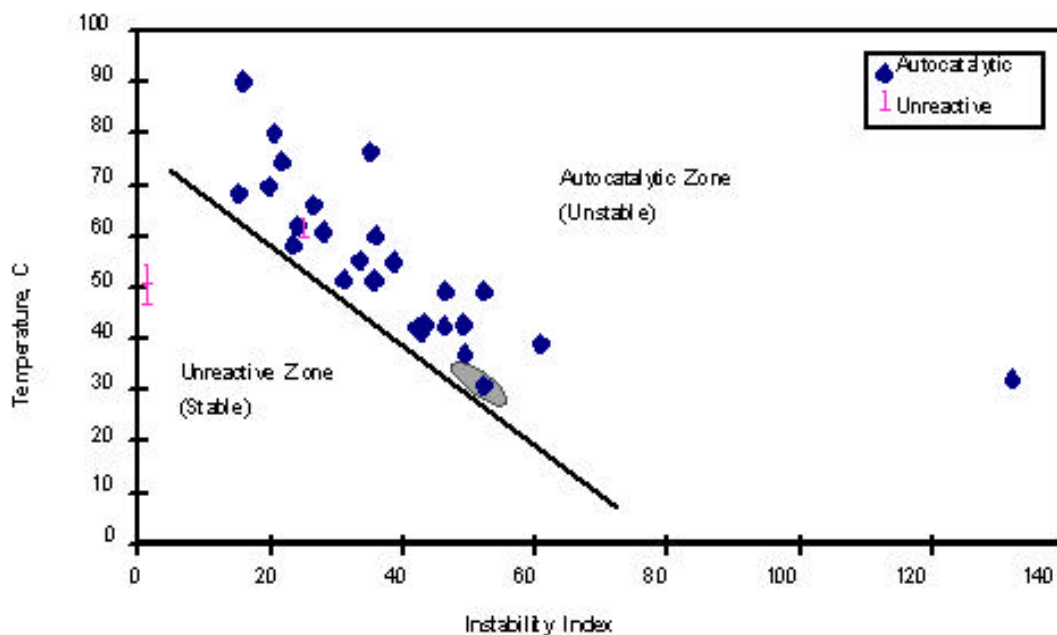
*** Red Oil Phenomena**

- formation of nitrated intermediates in TBP/solvent/nitric acid systems
- under certain conditions, the intermediates are potentially explosive
- several explosive events have occurred in nuclear facilities
- most recently at Tomsk in FSU, in 1994
- applicant has identified the potential for the phenomena and a temperature limit design basis
- staff review indicates proposed approach may not be consistent with the experience and literature
- staff concludes a lower temperature, and additional design bases and PSSCs may be needed

*** HAN/Hydrazine**

- Used as reducing agents and scavengers in the (oxidizing environment of) nitric acid/nitrate solutions
- under certain conditions, the mixture and intermediates are potentially explosive (Figure 14)
- several explosive events have occurred in nuclear and chemical facilities
- most recently at DOE Hanford, Washington State, in 1997
- applicant has identified the potential for the phenomena and design basis
- staff review indicates the proposed approach has not adopted all DOE recommendations for design bases and identified design bases and PSSCs to prevent explosive intermediate formation (e.g., azides)
- staff concludes additional design bases and PSSCs may be needed

Figure 14: HAN Stability Index



* **Hazardous Chemical Releases**

- applicant has concluded that chemical releases do not exceed the performance requirements of 10 CFR 70.61
- staff review indicates several chemicals have the potential for significant effects at 100 m and/or adequate margin needed
- staff review found some operator actions for safety may be needed outside of the emergency control room
- applicant has indicated PSSCs that protect the worker from radioactive releases also provide protection from chemical releases
- staff review found that these PSSCs may not be adequate for chemical releases to the worker and the SRS worker nearby
- potential toxicity of DUO2 powders not addressed
- staff concludes additional design bases and PSSCs may be needed

*** Electrolyzer**

- applicant has identified a prevention strategy for over-temperature, based upon a temperature limit
- staff review found credible events (electrolytic reactions and titanium interactions) that might not be prevented by the strategy
- staff review noted that mitigative strategies may not be effective for chemical release events
- staff concludes additional design bases and PSSCs may be necessary

*** Waste Area**

- applicant indicated there will be design bases and PSSCs for this area
- staff review found limited information on wastes (Table 2)
- staff will review additional information when it is submitted by the applicant

Table 2: Waste Stream Descriptions and Quantities in the Waste Reception Unit

Waste Stream Designation	Maximum Flow Rate, Gal/year (note 1)	Normal Flow Rate, Gal/yr	Concentration or Annual Quantity (note 2)
Excess Acid	1,321	1,321	Americium < 14 mg/yr
Stripped Uranium	42,530	35,400	Uranium = 16 g/L or 2,150 kg/yr U-235 concentration < 1% Plutonium < 0.1 mg/L
Liquid Americium	10,000	8,350	Americium = 24.5 kg/yr Gallium = 42 kg/yr Plutonium < 150 g/yr
Alkaline Wash	2,980	2,483	Uranium < 13 g/yr Plutonium < 13 g/yr
Total Flow Rates	56,831	47,554	
Note 1: Maximum flow includes unplanned recycling. Note 2: Concentrations are based on normal flow rate. Total radioactive material quantities are the same for maximum or normal flow rate. Concentrations based on maximum flow rates would be less.			

These values are based upon the original applicant's submittal and are expected to be revised because of the program changes.

* **Sintering Furnace**

- applicant's proposed approach uses a furnace with an argon/hydrogen mixture as the cover gas; a good fraction of the proposed operating range is flammable in air (Figure 15)
- sintering furnace is not located in a glovebox
- applicant has proposed a prevention strategy for hydrogen/leaks based upon hydrogen detectors, oxygen sensors, and pressure controls
- staff review found that hydrogen flow is not terminated by sensors in the room or over-pressure conditions
- staff review found analyses by the applicant did not include a potential steam explosion

Figure 15: MOX Pellets entering sintering furnace at Melox

