

# DEFENSE NUCLEAR FACILITIES SAFETY BOARD

February 28, 1997

**TO:** G. W. Cunningham, Technical Director  
**FROM:** R.F. Warther, M.T. Sautman  
**SUBJECT:** RFETS Activity Report for Week Ending February 28, 1997

**Recommendation 94-1:** RFFO has decided that ash residues will be vitrified in a furnace. In addition, RFFO's *draft* recommendation for combustibles is to just use some of the proposed modifications. Recommended upgrades are those that require little testing (larger batch size, hot nitrogen drying, and filtered bags); sonication is not to be pursued. In addition, RFFO wants K-H to decide whether cryo-shredding is needed since the DOE trade study recommends it but the combustibles ACE does not. The site reps believe that cryo-shredding is probably not required in addition to a nitrogen atmosphere and a CO<sub>2</sub> fire suppression system. Pure nitrocellulose, which is much more reactive than the RFETS material, will exothermically react in an argon atmosphere, but this does not occur until 190-C. Hanford has found that similar nitrate-rich mixtures can react at room temperatures if ignited with red hot BBs, but sparks are not energetic enough. The use of liquid nitrogen in cryo-shredding would also increase industrial hazards and probably reduce equipment reliability.

In response to questions about the residue rebaselining treatments during last week's Board visit, a summary of the proposed technologies, their technical maturities, and development schedules is attached to the weekly report. This summary incorporates comments from the Board technical staff, Los Alamos staff at RFETS, and RFFO. Comparisons of the proposed technologies with other available methods was discussed in the staff's draft technical report.

**Hydrogen:** RFETS is finding that the hydrogen issue was not limited to plutonium solution tanks. In B707, gas samples were taken from operationally empty organic solution tanks that had been tapped. Hydrogen concentrations in the two raschig ring tanks were 6.3 percent and 3.9 percent. The hydrogen level in a group of eleven interconnected pencil tanks was 19.6 percent and 20.7 percent in another group of eight tanks. These tanks may contain as much as 150 g of plutonium holdup. although the very low oxygen levels (56 to 305 ppm) present make the gas mixtures non- explosive, the gas could become explosive if mixed with air. Therefore, argon or nitrogen gas will be used to purge these tanks.

In B776/777, gas samples from two organic solution tanks were between NFPA's 1 percent limit and the 4 percent hydrogen lower explosive limit (LEL). Gas samples from the head space of two other former feed tanks to the old fluidized bed incinerator showed 11 and 13 percent methanol. This exceeds methanol's 6 percent LEL. All four tanks will be purged. A degreaser line pipe containing sludge and plutonium was also found to contain 33 percent hydrogen. This pipe will be vented, drained, and removed. Other degreaser line pipes are being sampled.

**Deactivation, Decommissioning and Privatization:** The Site Reps held several discussions this week with SSOC, RMRS, and RFFO personnel on D&D. The discussions centered on two topics: endpoints for D&D and privatization of B779 and B886 D&D functions. The endpoints still have not been determined in detail. RMRS and SSOC continue to work in this area. With respect to privatizing D&D SNM facilities, the site reps understand that a request to fund privatization of B886 and B779 is in Congress at this time. However, the RFFO Manager and K-H have indicated that they may not be ready to privatize these functions. Part of the reason for not privatizing these D&D functions is that the site has not completed enough characterization and planning to write a detailed procurement specification. A substantial number of issues remain including the following:

a. RMRS and SSOC will not be assigned this work. However, both will be allowed to bid on the privatization contract if they choose. Two problems are evident. First, this ties up valuable resources that could otherwise be applied to risk reduction with bid activities. Second, RMRS and SSOC personnel both stated that are keeping an arm's distance from the procurement so that they are not precluded from bidding. As a result, communications between companies have been retarded, and lessons learned will suffer.

b. K-H is writing the RFP. RFFO's involvement to date is minimal.

c. It is not clear who will establish the AB for these activities. Nor is it clear who will train the workers independent of their employer.

d. It is not clear if another private contractor will have to use the site infrastructure and S/RIDs. For example, will they be required to use a RFETS Radiological Work Permit to conduct work. If they implement their own procedures, it is not clear who will assess the adequacy of these procedures.

e. It is not clear if the private company can rely on existing site programs (e.g., EOC, security, fire department). It also is not clear if they will subsidize those services or if these services will continue to be funded by K-H.

f. Security clearances have been a problem at the site. It taking a long time to complete security checks, and personnel cannot readily enter the buildings in the interim. If a new contractor brings in uncleared personnel, a delay will likely ensue.

**Vault Fire Protection:** DOE Orders and NFPA standards require that vault doors be rated for a 1½ hour fire and the floor, walls, and ceilings rated for 2 hours. Doors for three vaults in B371 are not rated for 1½ hours. The site reps and RFFO are concerned that the vault door for the brand new B371 vault, which was to enter into usage on Friday, does not meet NFPA standards. The water wall windows for the X-Y retriever and the stacker-retriever are not rated for a 2 hour fire. In addition, the eight I/O stations for the stacker-retriever are considered unprotected openings, but are not fire dampered. Combustibles are restricted around the unrated fire doors and the stacker-retriever (which is along an egress area) as a compensatory measure. Fire protection features inside the vaults vary across site depending on when the vault was built, the money available, and what equipment was already installed before the room was converted into a vault. Fire detection and suppression inside the vaults may consist of either a) nothing, b) an inert atmosphere, c) sprinklers, d) smoke detectors, or e) heat detectors. The new B371 vault was equipped with state-of-the-art smoke detectors not to address safety concerns, but because of the vault's cost and perceived value of the plutonium to be stored inside it.

**Discussions with Public:** The Site Reps met with LT Gov. Gail Schoettler on Monday 2/24 to provide her with an update to progress at the site, continuing issues the Board has with RFFO and K-H, as well as provide information regarding RFCA implementation. Doug Young, Gov. Romer's Environmental Policy assistant attended as well. The brief seemed to go very well. Both Young and the LT Governor asked specific questions regarding risks at the site, risk reduction completed to date, and were very interested in assessments of remaining risks. The LT Governor indicated that she would appreciate regular briefs. The site reps interpreted this to be at a frequency between three and six months.

cc: Board Members

## **Attachment 1 - Summary of Residue Rebaselining Treatments**

Process Name: Salt Pyro-oxidation

Process Description: Sodium carbonate is added to a molten salt matrix to oxidize any metallic species (Pu, Na, K, Ca, Mg) present.

Demonstration Status:Over 100 runs completed. Have demonstrated with 3 kg batches and are testing 5 kg batches. Most of the process parameters have been determined for MSE, ER, and DOR salt residues.

Feasibility Issues:None.

Optimization Issues:Parameters have already been varied to optimize the process. May be modified to include molten salt filtration as a pre-treatment step for subsequent distillation and dissolution processes. Can start pyro-oxidation without salt filtration.

Production Issues:May be modified to include liquation (see below) to avoid additional processing needed to meet safeguards termination limits. If oxidized salts will be distilled or dissolved, may use larger batch sizes.

Current Schedule:Start pyro-oxidation operations 8/97

Salt filtration demonstration and testing 10/96 - 9/97

Comments: This is the current baseline treatment and is covered by the EA. Only issue is that most of the oxidized salt will not meet safeguards termination limits (STL).

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Process Name: Liquation

Process Description: After pyro-oxidation, the much denser Pu and Am oxides settle out of the molten salt. The puck of concentrated actinide oxide (dark salt) is then separated from the essentially actinide-free bulk salt (white salt). The dark salt contains 10 to 20 percent entrained salt.

Demonstration Status:LANL has demonstrated an average of 97% Pu removal from the white salt (average 0.5 wt% Pu in salt) using oxygen sparging. Have demonstrated liquation (with oxygen sparging) on the different types of salts. Expect equivalent or better removal using pyro-oxidation, but this has not been demonstrated yet.

Feasibility Issues: It is not expected that liquation can consistently reduce the Pu in the bulk salt to meet STLs (0.2 wt%). The goal is to consistently reduce the Pu in the bulk salt to a level that a STL variance may be granted (0.5wt%)?

Optimization Issues:Is an hour adequate settling time? What is the largest batch size that can be used and still have enough Pu settle out?

Production Issues:Based on batch size and processing time, are there enough units to provide an adequate throughput to meet the IP milestones?

Current Schedule:Proof of concept 3/97 - 5/97

Determine processing, certification, and heel disposition 5/97 - ?/97

Comments:Liquation was not included in the original RFFO rebaselining decision. However, it is being investigated as a means to avoid further treatment required to meet STLs.

Should be covered by the EA.

The presence of chlorides in the heel is believed to make the Pu unacceptable for MOX fuel or vitrification. It is expected that the heel would be dissolved or distilled to separate the Pu before putting it in 3013 containers.

Otherwise it may be hard for the heel to satisfy loss-on-ignition requirements.

Liquation eliminates foaming during subsequent distillation, if performed, because sodium carbonate is removed.

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Process Name: Salt distillation

Process Description: Oxidized salts are heated to 850 - 950· C under a vacuum. Because of the large differences in vapor pressure between NaCl/KCl and actinide oxides, the salts evaporate and are transferred to another chamber where the salts condense. 99.996% of Pu is removed from the distilled salt. The remaining heel averaged 63% Pu, but was sometimes below 50%.

Demonstration Status: Demonstrated on a pilot scale (0.5 - 1 kg batch sizes, 50 kg total)

Undergoing full scale demonstration (3 kg batch)

Feasibility Issues: Not practical for CaCl<sub>2</sub> salts because they require much higher temperatures

Optimization Issues: Relatively slow throughput (3 kg in 12 hours)

Need to reduce excess sodium carbonate added during pyro-oxidation so that the heel exceeds 50 percent Pu, but still oxidize all the reactive metals. In addition, the sodium carbonate can lead to foaming.

Provide adequate heat removal at the condenser to prevent condensation from slowing down or occurring in other areas.

Try to lower Pu and Am concentrations in the distilled salt so that it can be consistently disposed as low-level waste rather than TRU waste.

There have been problems with breaking out the salt button. The salt sometimes condenses around the sides which makes later removal of the receiving container difficult.

Production Issues: Long cycle time may require several units or extend processing period.

Equipment reliability in a high temperature and salt environment

The current design has an overabundance of instruments and other equipment attached to it. Needs to be simplified if a vendor is going to build up.

Current Schedule: Prototype I testing 10/96 - 7/97

Prototype II design and development 1/97 - 9/97

Prototype II construction/delivery 1/98 - 4/98

Prototype II testing 4/98 - 7/98

Production unit design, construction, and installation 4/98 - ?/98 or ?/99

Comments: RFFO recommended rebaselining process.

Believed to require an EIS.

Process has been "almost ready" for several years.

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Process Name: Aqueous dissolution of oxidized DOR salts

Process Description: Neutral pH water is used to dissolve the CaCl<sub>2</sub> salt matrix. The solution is filtered to collect the undissolved metal oxides which are then dried, calcined, and stored. The solution is evaporated and the salt disposed.

Demonstration Status: Demonstrated on a lab scale at RFETS, LANL (2 samples), and UK

Feasibility Issues: Testing to date demonstrates the need for a pyro-oxidation first step

Optimization Issues: Ca oxide and hydroxide form cement once hydrated. These hard agglomerates dissolve very slowly (8 - 12 days to dissolve 2.7 - 5.5 kg samples) even if crushed beforehand. Will probably use hydrochloric acid to speed up dissolution.

Minimization of liquid waste generated

Salt filtration during pyro-oxidation may speed up dissolution.

Production Issues: Building an aqueous dissolution line in B371 and treating all the liquid waste will be expensive considering the relatively small amount of material to be processed.

Current Schedule: Preparations, development and testing 10/96 - 8/97

Transfer process to RFETS 8/97 - 9/97

Comments: Only required to enable DOR salts to meet STLs. RFFO is planning to request a waiver from STLs to avoid doing dissolution.

RFFO believes dissolution would require an EIS.

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Process Name: In-furnace vitrification of graphite fines and sand, slag, and crucible (SS&C)

Process Description: Residues are mixed with glass frit in a can and melted in a furnace.

Demonstration Status: Tested only on surrogate materials

Feasibility Issues: Need to determine appropriate glass formulation, but no problems are expected.

Optimization Issues: Maximize residue loadings in glass. May blend graphite fines and incinerator ash together and vitrify the mixture

Production Issues: May require modification of off-gas system to handle higher temperatures.

Need to determine how to NDA glass with minimal uncertainty.

Current Schedule:Proof-of-principle (SS&C)1/97 - 4/97

Proof-of-principle (graphite fines)1/97 - 7/97

Demonstration, testing, and optimization 10/96 - 2/98

Start operations 2/98

Comments: Vitrification has been chosen for graphite fines. No official decision for SS&C.

Addresses dispersibility concerns (94-3).

Vitrification will address STL issues if Safeguards agrees that it is microencapsulated, which does not have specific criteria.

Most of the calcining equipment and other preparations can be used for in-furnace vitrification with little modification.

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Process Name: Modified Wash and Dry (Cryo-shred, low temperature thermal desorption, wash, sonication)

Process Description:Cryogenic shredding is a size reduction technique in which material is frozen in liquid nitrogen and then shredded. The primary benefit is that it should eliminate the possibility of something sparking and igniting nitrated material. Organic-contaminated combustibles are heated to 110· C to evaporate the organic and exposed to steam to oxidize any Pu metal. All combustibles are then washed twice with dilute base to neutralize any acid and dissolve any nitrates present. Sonication uses an ultrasonic cleaner to shake Pu and other heavy material off the matrix. The Pu oxide is removed from solution with ceramic filters and vitrified. The combustible matrix is dried with hot nitrogen gas.

Demonstration Status:LANL has used their cryo-shredder demonstration unit (a modified commercial shredder) on Ful-Flo filters, rubber gloves, and other generic combustibles (plastic, cloth, etc.). Low temperature thermal desorption has been used to treat organically contaminated waste at RFETS. Steam oxidation has been demonstrated on a Pu surrogate at LANL. The washing process involves simple chemistry and has been demonstrated on several kg of nonradioactive waste at RFETS. LANL has only performed one set of beaker-scale experiments for sonication that involved Pu-doped combustibles.

Feasibility Issues:Does sonication work and what amount of separation is achievable?

Will steam oxidation work for various particle sizes of Pu and how long does this process take?

Optimization Issues:Increase batch size to 5 kg using a criticality safe vessel.

Maximizing the Pu separation achieved by sonication

How long does hot nitrogen drying take? Estimate is 4 hours.

Production Issues:Equipment wear from shredding liquid nitrogen-frozen material.

Based on the processing time per batch, is the number of planned units adequate for meeting milestones?

Current Schedule:D&T of washing and steam passivation2/96 - 1/98

Develop a 5 kg unit with hot nitrogen drying 1/97 - 3/98

Demonstration and testing of sonication 1/97 - 3/98

Demonstration and testing of cryo-shred 95 - 12/97

Design and installation 1/97 - 3/98

Start operations 3/98

Comments: No formal decision by RFFO yet for treating wet combustibles.

The purposes of the modifications are to minimize the number of drums going to WIPP, reduce resource requirements, and increase safety. The combustibles already meet STLs.

The residue EA should cover the modifications.