

DEFENSE NUCLEAR FACILITIES SAFETY BOARD

November 30, 1992

MEMORANDUM FOR: G.W. Cunningham, Technical Director
W.R. Kornack, Director, Engineering Group
A.G. Stadnik, Director, Materials Processing Group

COPIES: Board Members

FROM: David C. Lowe

THROUGH: Paul Gubanc, Savannah River Site Team Leader

SUBJECT: Savannah River Site Defense Waste Processing Facility
Vitrification Plant Trip Report (November 4-5, 1992)

- Purpose:** This trip report documents the Defense Nuclear Facilities Safety Board (DNFSB) technical staff and outside expert November 4-5, 1992 review of process technical issues, and ventilation and off-gas systems at the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) Vitrification Plant. DNFSB technical staff included David Lowe, Daniel Ogg, Roger Zavadoski, Joe Roarty, and Walter Moore, and outside expert David Strawson (MPR Associates).
- Summary:** Westinghouse Savannah River Company (WSRC) believe that they have developed sufficient understanding of the DWPF chemical process from pilot plant operation and the laboratory test program in order to commence cold chemical runs in December 1992. The Department of Energy (DOE) has not approved the new flowsheet, and the associated modifications, that will be used during cold chemical runs and subsequent radioactive operations. The new flowsheet mitigates a number of safety-related issues associated with DWPF operation, including the production of hydrogen, ammonium nitrate, and organic carryover. The DNFSB staff has requested documentation (Safety Envelope Report and Unreviewed Safety Question (USQ) for nitric acid and "Late Wash" flowsheets) that form the basis for operating DWPF during cold chemical runs.
- Background:** The DWPF Vitrification Plant is currently completing the DOE Operational Readiness Review (ORR) in preparation for cold chemical runs. Anticipated start of cold chemical run testing is December 1992.

4. **Discussion:** The DNFSB staff team review consisted of DOE-SR and WSRC technical briefings and discussions, and DWPF and TNX pilot plant walkthroughs.

a. Process Technical Issues: There have been several potentially significant safety issues identified over the last few years during operation of the DWPF TNX pilot plant facility. WSRC has proposed fixes (i.e., late wash and nitric acid flowsheet) for the process technical issues. Each of these issues, and proposed and alternative fixes were discussed with the DWPF staff. The results of these discussions are summarized below. It should be noted that these fixes have been proposed by WSRC, but have not been approved by DOE. But, WSRC will enter cold chemical runs using the modified flowsheet (i.e., late wash and nitric acid flowsheet) as the technical baseline. The applicable chemical reactions are provided in Attachment 1.

1. Hydrogen Generation: Hydrogen is generated by a noble metal catalyzed reaction of formic acid, which is used in the feed preparation process for mercury removal and pH adjustment of the feed prior to entering the melter. The noble metals (rhodium, ruthenium, palladium, and silver) are constituents of the waste stream and, in addition to causing hydrogen generation, have the potential for collecting in the bottom of the melter and reducing melter life.

It is planned to avoid the potential for a hydrogen explosion in the vent piping by supplying dilution air to the process vessels in order to keep the hydrogen concentration well below the lower flammable limit (LFL) in accordance with National Fire Protection Association (NFPA) Standard 69, *Explosion Prevention Systems 1992 Edition* (25% of LFL during cold chemical runs, and 60% of LFL during radioactive operations with in-line hydrogen monitoring and hard-wired shutdown interlocks). In addition, tests have shown that the hydrogen generation rate can be cut by about a factor of two by substituting nitric acid for formic acid during the final stage of feed preparation. Alternatives evaluated include use of a catalytic recombiner to remove the hydrogen, but DWPF personnel indicate this is not a viable approach due to catalyst poisoning. Ignition type hydrogen removal systems were also briefly considered, but it was concluded these would exacerbate concerns over vent systems explosions. This is considered a valid concern.

The air dilution approach appears viable, but has a down side, i.e., it increases the entrainment of mercury and other particles in the process vessel vent stream. WSRC indicated an alternative approach which would minimize entrainment would be to introduce the dilution air just downstream of the condensers located at the top of the process vessel. This would alleviate the entrainment concerns while ensuring that flammability controls are maintained. WSRC is analyzing this alternative approach.

Results from recent bench-scale tests of actual radioactive wastes obtained from the tank farm indicate that hydrogen generation may be significantly lower than expectations based on pilot plant runs. It is theorized that some unknown chemical has poisoned the noble metals (catalyst) in the waste tanks. This poisoning is not reflected in the noble metals used during the pilot plant runs. WSRC has recently contracted with Georgia Tech to study the noble metal poisoning mechanism. The unknown poison also has an effect on the copper catalyst used in the precipitate hydrolysis process which will result in additional copper formate added to the process.

WSRC indicated that it is not planning to add noble metal during DWPF cold chemical runs, since this would cost on the order of \$200K to \$400K, and would likely not provide significant information beyond that obtained in running the one-fifth scale pilot plant facility with noble metals. The staff will continue to review this issue.

2. Ammonium Nitrate Generation: Ammonium nitrate is generated in the feed preparation process and can plate out in the vessel vent system piping. This is potentially explosive when dried, particularly in the presence of organics, which are also carried over into the vent system. To resolve this potential hazard, ammonia scrubbers are being installed upstream of the vent system, and it is planned to periodically clean the vent piping to remove the ammonium nitrate. In addition, a "late-wash" process has been proposed by WSRC. The ammonium nitrate is produced by reaction of sodium nitrite, added to the wastes to prevent corrosion of the carbon steel storage tanks, with downstream chemicals. In the "late wash" process, the sodium nitrite, as well as any organics produced as a result of radiolysis of the stored organic precipitated wastes, are largely removed by rinsing the wastes in stainless steel vessels. This appears to be a viable approach, which has undergone initial evaluation in the TNX pilot plant facility. Concern was raised over the additional time needed to construct and integrate the "late-wash" system into DWPF. WSRC indicated that the "late-wash" facility would not be operational until October 1995. Until the "late-wash" system is operational, DWPF cannot process precipitate feed using the modified flowsheet. This will delay DWPF startup because the chemical processing cell requires precipitate feed for mercury removal and in order to maintain melter feed composition requirements. But, delaying the startup of DWPF until October 1995 would cause capacity problems at the H-Area tank farm. As an alternative, WSRC stated that it could operate DWPF using a simulated precipitate feed until the "late-wash" facility is ready to operate. WSRC stated that the use of a simulated precipitate feed would result in approximately an eight percent increase in the total number of glass canisters produced at DWPF.

An alternative approach, which has been briefly evaluated, is to process the wastes in smaller batches so that stainless steel tanks can be used, and sodium nitrite addition can be avoided. This would reduce ammonium nitrate and organic high-boiler production. WSRC indicated that this alternative requires the addition of about 500,000 gallons of expensive stainless steel tanks, and is not considered practical. The DNFSB staff will review the rationale for this decision.

3. Organic Carryover: High boiling point organic compounds such as bi-phenylamines, tri-phenylamines, and tars are formed by radiolytic decomposition of the organic precipitating chemical. They are also formed during downstream feed processing, primarily as a result of reactions associated with the sodium nitrite used for carbon steel tank corrosion control. These organics are not removed from the process stream during the precipitate hydrolysis process because of their high boiling points. So they are retained in the process stream that feeds into the chemical processing cell. The high boiling organics have the potential for fouling vent process heat exchange surfaces in the chemical processing cell and therefore need to be minimized. The "late-wash" process for minimizing the production of ammonium nitrate would also be effective in minimizing organic carryover.
4. Ion Exchange Instead of In-Tank Precipitation (ITP): The process flowsheet employed to separate soluble cesium from liquid radioactive wastes prior to vitrification is based on the addition of an organic material (sodium tetraphenylborate) to precipitate the cesium. This results in the generation of undesirable chemicals; including benzene, ammonium nitrate, and high boiling organics. The Government Accounting Office (GAO) issued a report in June 1992, *Defense Waste Processing Facility - Cost, Schedule, and Technical Issues (GAO/RCED-92-183)*, in which GAO recommended that evaluations be performed on an alternative pretreatment process using ion exchange. Ion exchange was the process used at West Valley and is the leading candidate at Hanford. It should be noted that early in the DWPF design process ion exchange was considered, but ion exchange resin technology was not fully developed and the in-tank-precipitation pretreatment process was selected for SRS.

WSRC performed a study of switching to an ion exchange process, and reached the following major conclusions:

- The cost of using ion exchange is expected to exceed \$200 million.
- Eight to ten years would be required to implement ion exchange.
- Ion exchange development should be continued, but only as a contingency technology.

The DNFSB staff has requested and will review reports relating to the ion exchange process.

b. Systems Issues: The DNFSB staff identified several issues considered to warrant further evaluation. In summary:

1. Approximately three percent of the radioactive cesium entering the melter escapes by volatilization into the melter off-gas system. It is removed from the off-gas stream by several scrubbers which recycle the cesium back to the waste storage tanks, two HEPA filters, and a sand filter. It is anticipated that the first HEPA filter will collect several thousand curies of cesium during an operating cycle. The irradiation effects on the filter components (seals, gaskets, etc.) have not been analyzed.
2. The potential for hydrogen gas leakage from the process, and collection at the top of the canyon has not been analyzed by WSRC.
3. The DNFSB staff plans on further reviewing the transportation of the waste sludge/slurry solutions over long distances.
4. Operational Safety Requirements (OSR) have been developed for the forthcoming cold chemical runs. The OSR identifies specific limits for cold chemical runs, and provides the basis for the limits. However, the evaluations performed to ensure that all potential hazards associated with cold chemical runs have been adequately addressed are contained in the "Safety Envelope" document which was recently approved by DOE. This document has been requested, but not yet received.

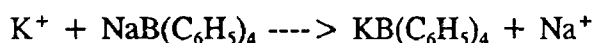
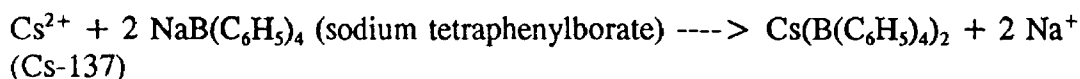
c. Other Safety Issues: Criticality control is based on assurance that there is no credible mechanism for concentration of fissile materials at any point throughout the DWPF process. The DNFSB staff has requested the analyses which support this position.

Attachment 1

Primary Chemical Reactions

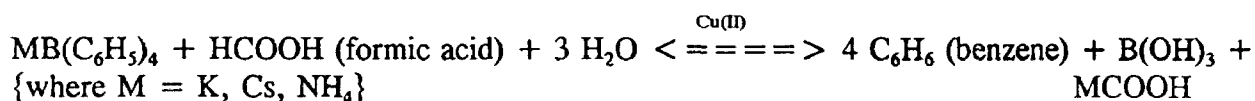
Normal Reactions

In-Tank Precipitation (ITP) Reactions:

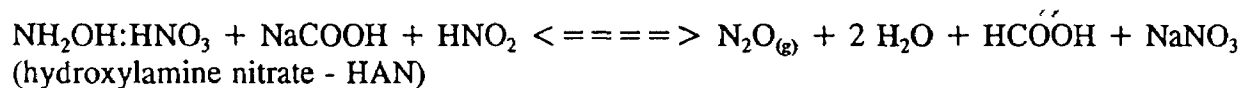


Also: Sodium Titanate (in an isopropanol/methanol solution) added to absorb Sr-90 and Pu in solution

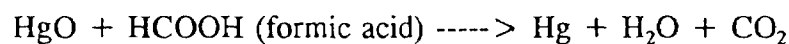
Hydrolysis Reaction:



Nitrite Destruction Reactions:



Mercury Reduction: {when pH adjusted to approximately 4}



Adverse Reactions

Organic Carryover:

$\text{HNO}_2 + \text{Organics} \rightleftharpoons \text{Organic high boilers (Di- \& Tri-Phenylamines) and tars}$

Ammonium Nitrate Formation: {occurs when pH adjusted to 6-8}

$4 \text{NH}_2\text{OH}:\text{HNO}_3 \text{ (HAN)} \rightleftharpoons 2 \text{NH}_4\text{NO}_3 + 2 \text{HNO}_3 + 3 \text{H}_2\text{O} + \text{N}_2\text{O}_{(\text{g})}$

$\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_{3(\text{g})} \text{ (ammonia)} + \text{H}_2\text{O}$

$\text{NH}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{v})} + \text{NO}_{\text{x}(\text{g})} \rightleftharpoons \text{NH}_4\text{NO}_3 \text{ (ammonium nitrate)}$
{occurs in process off-gas system}

Hydrogen Generation:

$\text{HCOOH} \text{ (formic acid)} \xrightarrow{\text{Rh/Ru/Pd/Ag}} \text{H}_{2(\text{g})} + \text{CO}_{2(\text{g})}$