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HIGH-LEVEL RADIOACTIVE INSOLUBLE WASTE PREPARATION FOR VITRIFICATION

by

B. A. Hamm
R. E. Eibling
M. A. Ebra
T. Motyka
H. D. Martin

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

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DISCLAIMER

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B. A. HAMM, R. E. EIBLING, M. A. EBRA, T. MOTYKA, AND H. D. MARTIN
Savannah River Laboratory, Aiken, South Carolina 29808

ABSTRACT

At the Savannah River Plant (SRP), a process has been developed for immobilizing high-level radioactive waste in a borosilicate glass. The waste is currently stored as soluble salts and insoluble solids. Insoluble waste as stored requires further processing before vitrification is possible. The processes required have been developed and demonstrated with actual waste. They include removal of aluminum in some waste, washing soluble salts out of the insoluble waste, and mercury stripping. Each of the processes and the results with actual SRP waste will be discussed. The benefits of each step will also be included.

INTRODUCTION

After 10 years of research and development, construction was started in 1983 on the Defense Waste Processing Facility, known as the DWPF [1,2,3]. In the DWPF, high-level waste produced by defense activities at the Savannah River Plant will be processed into a solid form suitable for permanent off-site geologic disposal.

Borosilicate glass was chosen from seventeen possible forms as the preferred form for waste immobilization. The DWPF process, scheduled to be operational in 1989, will take the radioactivity contained in 30 million gallons of high-level waste, which has been accumulating in storage tanks since 1954, and will immobilize it in just one million gallons of glass. Once the present backlog of waste has been immobilized, about year 2005, the DWPF's production rate will be reduced to match the waste generation rate.

BACKGROUND

Acidic wastes generated from Savannah River Plant production processes are neutralized with sodium hydroxide prior to storage in underground carbon steel tanks having capacities from 0.75 to 1.3 million gallons. Neutralization of the wastes causes the formation of insoluble precipitates (sludges) of stable and radioactive fission products, actinide elements, and elements added in the separation processes.

The sludge is composed primarily of oxides and hydroxides of manganese, iron, and to a lesser degree, aluminum. It is a thick, brown substance which has the consistency of mud and contains almost all of the fission products originally in the irradiated fuel except cesium, and almost all of the actinides. The supernatant portion of the waste contains primarily dissolved salts and radioactive cesium. It is concentrated by evaporation to salt which is a white crystalline material similar in both appearance and chemical composition to ordinary fertilizer.

The main processing building of the DWPF is known as S-canyon. Within the canyon the process takes place within heavily shielded "cells" and is controlled remotely. Waste is currently stored in two separations areas known as F-area and H-area. As sludge and salt are removed from old waste tanks, the waste will be sent to processing tanks in H-area. Prior to processing in the canyon are several in-tank processing steps for waste preparation.

In-tank processing of salt involves dissolving the salt followed by a precipitation process to remove the radioactivity. The remaining liquid is mixed with a specially formulated cement and poured into an engineered disposal site. The precipitate containing the radioactivity is further processed in the canyon. In-tank processing of sludge involves several process steps. The sludge is slurried out of old tanks and transferred to processing tanks. Some sludges with high aluminum concentrations will undergo caustic dissolution to remove the aluminum which adversely affects glass viscosity and adds to the overall waste volume. Batch washing is performed on all sludges to remove soluble salts. A final gravity settling is used to concentrate the washed sludge to a solids loading between 13 and 19 wt% total solids.

After the sludge is transferred to S-canyon it will be treated with formic acid to reduce mercuric oxide to mercury metal and adjust slurry rheology. Radioactivity from the salt process is added and mercury is removed by steam distillation. Later, frit is added and excess water is evaporated prior to melter feeding. The process is illustrated in Figure 1 [1].

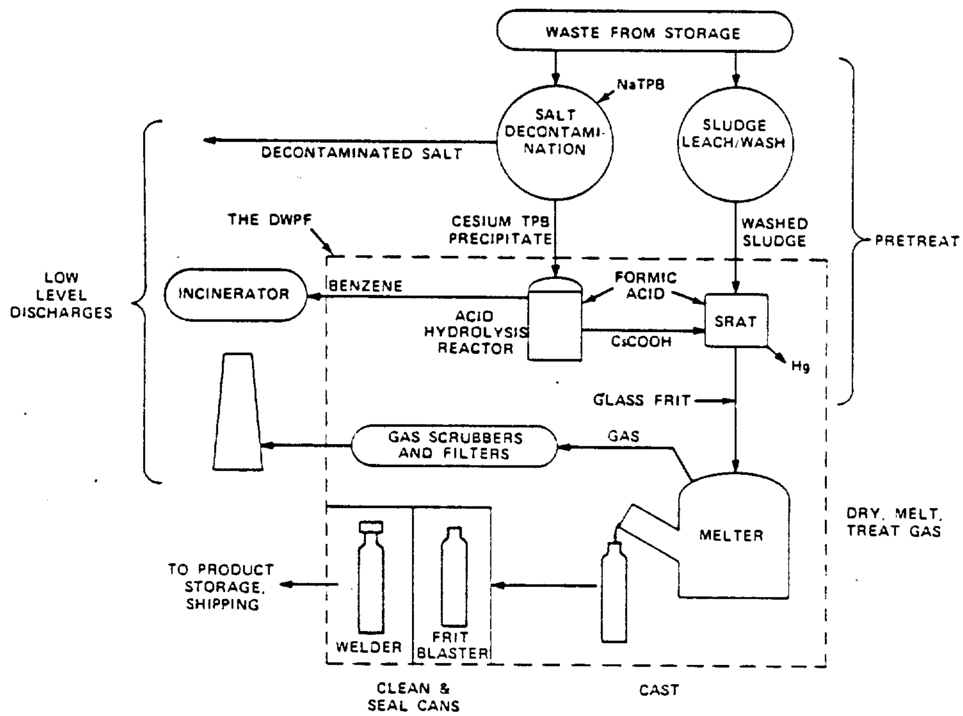

Figure 1. Defense High-Level Waste Treatment at the Savannah River Plant

The melter is an electric furnace designed to make about 230 pounds of glass per hour at an operating temperature of 2100°F. The molten glass is poured into stainless steel canisters, two feet in diameter and ten feet tall. The full canisters, which weigh about two tons, will be stored in the waste glass storage building. The building can hold 1,040 canisters or about two years of DWPF production.

Research conducted by DuPont has reduced the estimated cost of the facility. The detailed technology for the DWPF process was developed by scientists and engineers at the Savannah River Laboratory. Full-scale equipment testing has been conducted and all process steps have been demonstrated. In the following pages the results of some of the testing will be presented along with more detailed information about the steps involved in preparing high-level radioactive insoluble waste for vitrification.

In-Tank Processing

In-tank processing of sludge requires several process steps. Sludge is transported to processing tanks where some sludges may undergo aluminum dissolution. All sludges will be washed to remove soluble salts before gravity settling of sludge as feed to DWPF. A more detailed description of the processing steps follows.

Sludge Slurrying

Mixing of sludge is provided by slurrying during removal of aged sludge from waste tanks and during the sludge processing steps. Waste sludges are slurried with long-shaft centrifugal pumps inserted through risers in the top of the tank. The standard pumps at full speed can pump 600 gpm through each of two horizontally opposed, 1.5 inch nozzles, with a mixing radius of about 25 feet. Two higher capacity pumps, the quad volute and the single discharge have been developed.

The quad volute pump was developed for waste removal and waste processing in new tanks. Its higher capacity and larger mixing radius will allow the same degree of agitation with fewer pumps than the standard type pump. Its large diameter prevents its installation in tanks other than type III. The quad volute pump at full speed can pump 2000 gpm through each of two 3-inch nozzles, with a mixing radius of 40 feet. Improved mixing was observed when one pump nozzle was angled upwards at 30 to 45 degrees. When the pump is mounted near the tank bottom, the horizontal nozzle provides scouring action to prevent build-up of solids on the tank floor, the angled nozzle provides good top to bottom mixing. Four quad volute pumps are used to achieve a homogeneous sludge composition.

The single discharge pump was developed for use in older tanks with smaller riser openings for difficult sludge slurrying situations that cannot be efficiently handled by the standard pump. It is a modified version of the quad volute pump and has only one 3-inch nozzle, making it similar in width to the standard pump. The single discharge pumps 2000 gpm and has a 40 foot mixing radius.

The standard pump had a lubricating water leakage rate of 1 gpm, adding a large quantity of excess water during processing. To reduce the amount of leakage, a mechanical bellows seal was developed. Extensive testing showed seal leakage rates were less than 1 ml/min. Inspection after 10,000 hours showed undetectable seal face wear and insignificant shaft bushing wear.

Sludge Transport

SRP waste sludge is transferred out of waste tanks using 10-hp, long-shafted, vertical submerged pumps (Barret-Haentjens). The pumps are rated at 100 gpm at 70 feet of total dynamic head. H-area sludge is pumped from the waste tank to an intermediate pump tank and then to a sludge processing tank. F-area sludge (about one million gallons) will be transferred to H-area through an existing two-mile transfer line.

The inter-area line or IAL is actually a pair of 3-inch stainless steel schedule 40 lines encased in a 4-inch carbon steel jacket. The lines were designed for transferring salt solutions between areas to make more efficient use of the high-level-waste evaporators in each area. Modifications have been initiated to upgrade the line for slurry service.

Due to the long length of the line, the lack of intermediate pumping stations, and the pressure limitations imposed by jumper connections, only a limited range of slurries can be transported through the IAL. Transport conditions are limited to slurry concentrations with a yield stress between 30 and 50 dynes/cm^2.

Aluminum Dissolution

Aluminum adversely affects glass viscosity and adds to overall waste volume. It is dissolved from some sludges into the supernate where it is subsequently removed by decantation and water washing.

Studies to identify sludges recommended that aluminum dissolution be limited to sludge in four waste tanks. The four tanks contain 45% of the sludge volume and 80% of the aluminum solids. The average aluminum in the combined washed sludge from all 23 tanks will be reduced from 12.7 to 6.6 wt% and the amount of sludge solids reduced by 22%. Contacting the remaining sludges would only increase the solids reduction to 27% and therefore does not warrant the extra processing.

Aluminum solids in the sludge are believed to be present in three forms - aluminum trihydrate or gibbsite, alumina monohydrate or boehmite, and aluminosilicate. Only the gibbsite form is readily soluble at the relatively low dissolving temperatures possible in the waste tanks.

Aluminum dissolution is performed by adding 50 wt% $NaOH$ to the process tank and heating, using steam spargers, to hold the slurry temperature at 85°C for three to five days while slurrying continuously. The caustic is added in sufficient quantity to provide a minimum initial ratio of 3 moles of free hydroxide per mole of acid-soluble aluminum (gibbsite) and to provide a final liquid phase free hydroxide molarity of 3. To avoid problems with post-precipitation of aluminum, final aluminate concentrations should be kept at less than 1M $NaAlO_2$ at a 3M caustic concentration.

A full-scale demonstration of in-tank aluminum dissolution was performed in July of 1982. A total of 104,000 gallons of 50 wt% sodium hydroxide and 118,000 gallons of dissolved salt solution were added to 125,000 gallons of high aluminum sludge. Initial dissolving conditions were 1.3M NO_3^-, 0.28M NO_2^-, and 3.64M OH^-. The tank was heated from 63 to 83°C in 38 hours with steam spargers (6000 lb/hr) and was continuosly agitated. Thereafter a steam flow of 1000 lb/hr was used to maintain tank temperatures between 83 and 85°C. After five days of digestion, sample analyses indicated that 79% of the total aluminum in the sludge had dissolved. The shift of aluminum from the insoluble solids to the liquid is illustrated in Figure 2.

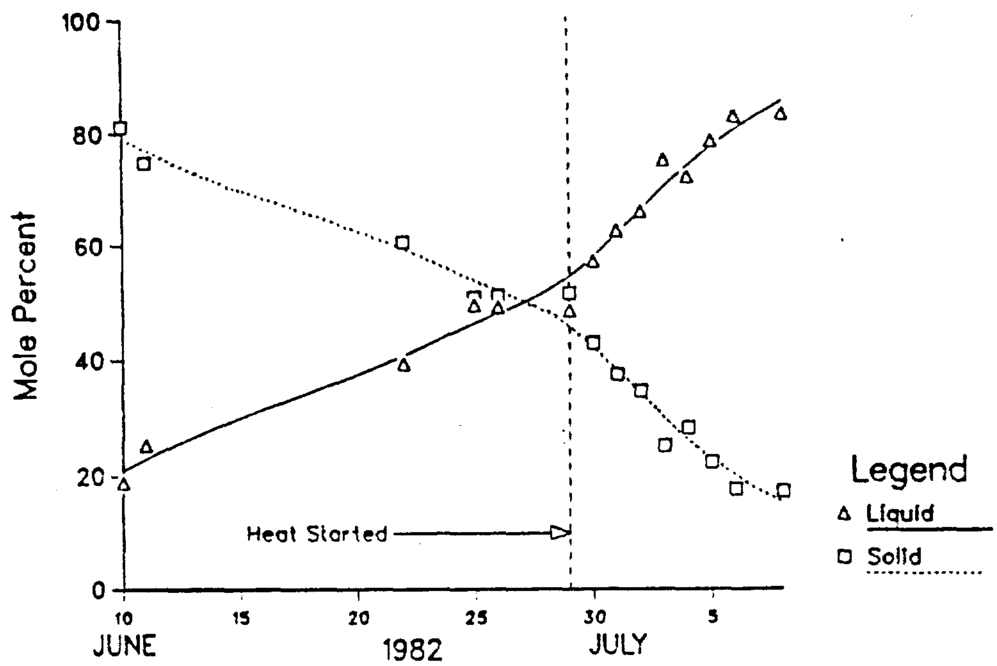

Figure 2. Aluminum Concentration During Dissolution Step

Sludge Washing

All waste sludges, whether aluminum dissolved or not, will be washed to reduce the level of soluble salts since the sludge contains too much sodium and sulfate for optimum glass durability. During the fullscale demonstration the sludge underwent two full washes and one partial wash. The concentration of soluble salts follows a simple dilution model. The results for sodium are illustrated in Figure 3. An optimal wash level of 3% total solids in the sludge on a dry weight basis was determined after the demonstration based on concentrations in the glass.

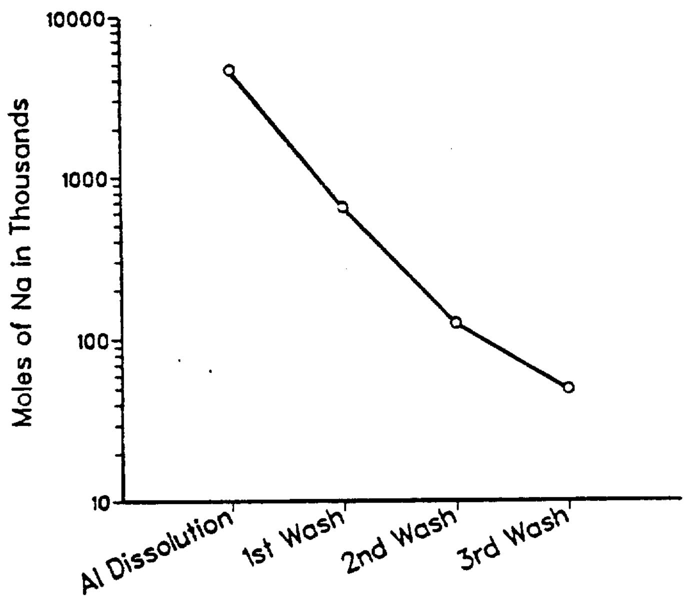

Figure 3. Sodium During Wash Steps

Sludge Settling

Gravity settling plays a key role in the in-tank process. After each step of the process, settling is required to concentrate the sludge before the start of the next step. It is estimated that about 75% of the overall time required to process a complete batch of sludge will be devoted to settling periods.

The settling rates of sludge slurries are dependent on the concentration of the solids and the type and history of the sludge. Therefore, settling data from one waste sludge or simulated sludge can only be used for an initial estimate of a different sludges settling behavior. Data in the hindered settling range (1 to 10 wt% solids concentration) can, however, be taken on sludge from each waste tank in lab-scale settling tests. A limited amount of lab-scale data exists at the present time. A general observation is that F-area sludges settle faster and are somewhat less gelatinous that H-area sludges at equivilent solids concentrations. This difference might be attributed to the higher aluminum content of H-area sludge.

An observation from both synthetic and actual slurry settling tests is that at about twice the initial settled volume the slurry's settling rate drops dramatically. This indicates the start of the relatively slow compressive settling regime. The solids concentration at which this occurs will depend upon the type of solids but is typically between 5 and 15 wt% suspended solids.

Canyon Processing

Slurry Receipt Adjustment Tank

After sludge is transferred to the DWPF, the first process vessel it is sent to is the Slurry Receipt Adjustment Tank, known as the SRAT. In the SRAT, formic acid is added in a quantity sufficient to react with primarily the Mn,Ca,Ni and Hg in the sludge. The formic acid is added to modify the rheology of the sludge and to reduce Hg. The formic acid (90 wt%) is added at the rate of 0.1 lb(100%)/hr/lb of sludge solids to sludge at 85°C. Following formic acid addition, the temperature of the sludge is slowly increased to boiling (101°C).

During boiling, the radioactive material from salt decontamination is added to the slurry. Boiling is then continued until mercury is steam stripped to an endpoint of 0.45 wt% in the sludge. Hg is stripped at a rate of 1 lb/750 lbs of steam for concentrations of Hg down to 0.8 wt%. This is equivalent to three times the theoretical amount of steam based on vapor pressures. As the mercury in the sludge drops below 0.8 wt%, the multiple of the theoretical steam requirement increases rapidly. The mercury recovered from the SRAT undergoes additional purification prior to bottling and storage.

The full-scale SRAT is 12 feet in diameter and 18 feet tall. It is equipped with two concentric steam coils and one cooling coil. The tank pressure is maintained at a draft of two inches of water. Water and mercury vapor are condensed in a top mounted condenser and collected in a condensate tank.

There are three small scale research vessels. Two are used strictly for simulated sludge work, one is 1/3 scale and the other is 1/200 scale. A full-scale design demonstration vessel is being assembled for use with simulated sludge. There is a 1/240 scale SRAT for research using actual radioactive waste.

Slurry Mix Evaporator

After sludge has been steam stripped in the SRAT it is transferred to the Slurry Mix Evaporator, known as the SME. In this vessel frit slurry is added as excess water is evaporated off. The final product is 50 wt% in is total solids. Water that is evaporated is condensed and sent back to in H-area.

The SME process tank is of the same dimensions as the SRAT and is equipped with identical coils.

Melter Feed Tank

After SME processing, the sludge-frit mixture is transferred to a melter feed tank. Total feed rate is equivalent to a glass melting rate of 228 lb/hr.

CONCLUSION

DWPF will produce glass at the rate of two canisters per day until the back log of old waste has been processed. At that time the processing rate will be reduced to match the waste generation rate.

The operations which will take place in the tank farm have been demonstrated full scale with actual waste. The canyon operations have been demonstrated small scale. Work is under way on a design demonstration SRAT/SME which will be used with simulated sludge. Small scale work with actual and simulated waste will be continued. Samples will be taken from several waste tanks and the sludge will be processed through all of the steps described including the actual vitrification step.

REFERENCES

1. M. D. Boersma, "Process Technology for Vitrification of Defense High-Level Waste at the Savannah River Plant," Presented at Meeting of the American Nuclear Society Meeting, Fuel Reprocessing and Waste Management, Jackson Hole, Wyoming, August 26-29, 1984.

2. R. Maher, L. F. Shafranek, W. R. Stevens, III, "Solidification of Savannah River Plant High Level Waste," Report No. CONF-8311117-1, American Institute of Chemical Engineers, Washington DC, November 4, 1983.

3. Defense Waste Processing Facility, DOE/SR-0011.

ACKNOWLEDGMENT

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CC: E. L. Bowser, DOE-SR
D. L. McIntosh, SRP
J. T. Lowe - W. R. Stevens, SRL
G. W. Wilds
M. A. Ebra - B. A. Hamm
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DP-MS-84-63, "HIGH-LEVEL RADIOACTIVE INSOLUBLE WASTE PREPARATION FOR VITRIFICATION", by B. A. Hamm, R. E. Eibling, M. A. Ebra, T. Motyka and H. D. Harmon.

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G. W. Wilds, Research Manager
Waste Processing Technology Division
Savannah River Laboratory