TANK FARM PROCESSING OF HIGH-LEVEL WASTE

FOR THE DEFENSE WASTE PROCESSING FACILITY

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ABSTRACT

The high-level radioactive waste that has accumulated at the Savannah River Plant is stored in large, underground steel tanks. Programs to remove the waste from the storage tanks and immobilize the radioactivity in borosilicate glass in the Defense Waste Processing Facility (DWPF) are currently in the construction phase. Much of the processing of the waste prior to vitrification is accomplished in the waste storage areas (tank farms). Tank farm processing includes resuspension and washing of the insoluble (sludge) waste, dissolution and decontamination of soluble (salt) waste, and waste transfer between the tanks and operations areas. The overall program for handling the waste in the tank farms, the research program that supports it, and the major concerns with implementing the program are described.

INTRODUCTION

The objective of the DWPF is to immobilize all the high-level waste at the Savannah River Plant (SRP) into one of two wasteforms: 1) borosilicate glass, a high-integrity wasteform that will contain virtually all of the radioactivity, and 2) saltstone, a less-expensive wasteform that will contain mainly the nonradioactive chemicals used in the SRP separations processes. An extensive program of waste removal and in-tank processing is currently underway in the SRP waste tank farms to prepare the feeds for these two DWPF processes. The purpose of processing waste in the tank farm is to reduce the cost of the DWPF process, thereby reducing the cost of the overall immobilization program.

Tank farm processing encompasses the following programs: 1) waste removal from the tanks, 2) aluminum dissolution and washing of the sludge, and 3) decontamination of the soluble waste. In addition to the actual construction and operations programs underway at the Savannah River Plant, there continues to be a significant research effort by the Savannah River Laboratory in support of these plans. This research effort includes further work on slurry transport between operations areas.

WASTE REMOVAL

The first step of DWPF feed preparation is to remove the waste from a particular storage tank and send it to the appropriate processing tank. The procedures for sludge removal and salt removal are similar and, for illustration, the procedure for sludge removal is described below.

First, a slurry medium, such as water or salt solution, is added to the tank. Then the sludge is suspended using long-shaft slurry pumps. These pumps draw in sludge slurry and discharge it through two nozzles 180° apart. Three of four pumps are used per tank. After several days to several weeks of agitation, the suspended sludge is transferred from the tank with a long-shaft transfer pump (a pump similar in design to the slurry pumps but with a discharge leg rather than nozzles).

Sludge is removed in batches of up to 570,000 liters each and a full sludge storage tank may require several batches to empty it. After sludge removal is complete, the tank is spray washed using two or three rotary sprays, which cover a complete spherical pattern, thus washing down the walls and roof of the tank. The spent water from spray washing is slurried and transferred similarly to suspended sludge.

This procedure has been used successfully at SRP to remove the sludge and salt from two leaking tanks and from seven single-wall tanks. This waste has been put in newer storage tanks with two containment walls. All future waste removal transfers will be to double-wall tanks designated for in-tank processing for the DWPF.

In 1986, the first interarea transfer of suspended sludge was completed through the 3.6-km interarea transfer line. This sludge transfer is significant because it is the first of many through long pipelines that will be needed to operate the DWPF. As of October 1986, 1.4 million liters of settled sludge had been successfully pumped through the 7.62-cm-diameter interarea line. Sludge settling and line pluggage while transferring the dilute sludge slurry were not encountered. The interarea transfer line was originally built for salt solution transfers only. The line was upgraded for sludge use by the addition of a higher capacity pump, an automatic control system, and additional leak detection and interlocks.

SLUDGE PREPARATION

Three 4.9-million-liter tank will be dedicated to processing the sludge prior to transfer to the DWPF canyon building. The purpose of the pretreatment is to remove nonradioactive ingredients such as soluble sodium salts and water-insoluble aluminum compounds, which may be sent to saltstone instead of the more costly glass.

Sludge from selected tanks that are high in aluminum will be treated with sodium hydroxide to dissolve the insoluble aluminum salts. In this process, the sludge solids are leached with excess sodium hydroxide at 80 to 90°C for three days. This dissolves about 75% of the hydrated alumina and reduces the volume of this type of sludge by 50%. Removing the aluminum reduces the viscosity and permits higher waste loading in the glass. The dissolved aluminum is sent to in-tank precipitation processing and eventually to saltstone.

All of the sludge, including that which has been treated with hydroxide, will be washed with water to remove soluble salts. This is done in batches by the following steps: 1) water addition, 2) mixing, 3) settling, and 4) decanting. These steps will be repeated 15 to 20 times on each batch until the soluble salt content of the sludge is reduced to less than 3.5% of the total solids weight. The washed sludge will be stored in a waste tank and eventually sent to the DWPF glass plant.

Sludge washing requires three processing tanks: one to hold a washed batch of sludge and two to process the next batch. The wash water from the first of the two washing tanks is passed on to the second washing tank, thereby decreasing the total amount of water required. After the sludge in the two tanks is completely washed, the two tanks are combined to provide a two-year supply (2,500,000 liters) of sludge feed to the DWPF. By producing the sludge in large batches, the number of changes in feed composition to the vitrification process is reduced, and the consistency of the glass product composition is improved.

IN-TANK PRECIPITATION PROCESS

The salt portion of the high-level waste will be dissolved using long-shaft slurry pumps, similar to the technique for sludge removal. Four 4.9 million-liter tanks will be dedicated to the in-tank precipitation process. The salt solution will be decontaminated by precipitating Cs-137 as its insoluble tetraphenylborate (TPB) salt and by absorbing Sr-90 on sodium titanate particles (1). The major reactions that occur in this process are shown in Fig. 1. Tetraphenylborate forms insoluble salts with cesium, potassium, and ammonium ions, effectively removing them from solution. The extent of the decontamination depends on the solubility of CsTPB, which in turn depends on the ionic strength of the salt solution, the concentration of TPB$^-$, and the temperature. Under the anticipated tank farm conditions, the process will reduce the cesium level to 2-4 nCi per milliliter of solution, corresponding to a decontamination factor in excess of 10^4. Any soluble mercury in the salt solution will react with the tetraphenylborate to produce diphenylmercury. This reaction will remove most of the mercury under the right conditions (2), and decontamination factors larger than 20 are expected in full-scale processing. Strontium is removed by adsorption on sodium titanate, and a decontamination factors of 200 have been demonstrated on actual waste.

The precipitation reaction will be carried out in a 4.9-million-liter stress-relieved carbon steel waste tank. Nine batches of salt solution will be processed each year, producing 23 million liters of decontaminated solution. The volumes of the solutions used in the batches are listed in Table I.

After the precipitation, the radioactive solids will be separated from the salt solution by cross-flow filtration (Fig. 2). The pressurized precipitate slurry is pumped through the filter at high velocities. The filtrate passes through the pores and is collected in the annular space between the filter tube and housing. The slurry is recycled to the waste tank until the desired solids concentration is reached. The decontamination filtrate is sent to a separate storage tank, it will be pumped to a separate facility where the saltstone grout is mixed and placed in aboveground vaults.

Precipitation

$$Cs^+ + B(C_6H_5)_4^- \longrightarrow CsB(C_6H_5)_4\,(s)$$

$$K^+ + B(C_6H_5)_4^- \longrightarrow KB(C_6H_5)_4\,(s)$$

$$NH_4^+ + B(C_6H_5)_4^- \longrightarrow NH_4B(C_6H_5)_4\,(s)$$

$$3\,Hg^{2+} + 2\,B(C_6H_5)_4^- + 4\,OH^- \longrightarrow 3\,(C_6H_5)_2Hg\,(s) + 2\,B(C_6H_5)(OH)_2$$

Adsorption

$$Sr^{2+} + 2\,NaTi_2O_5H\,(s) \longrightarrow Sr(Ti_2O_5H)_2\,(s) + 2\,Na^+$$

Fig. 1. Major reactions that occur during in-tank precipitation.

TABLE I

Material Balance for In-Tank Precipitation Processing

Component	Volume/Year* (106 liters)
Salt solution (6.9 M Na$^+$)	17.2
NaTPB solution (0.5 M)	1.2
NaTitanate slurry (15 wt % solids)	0.1
Dilution water (recycled wash water)	6.3
Fresh wash water	6.3
Decontaminated salt solution (4.8 M Na$^+$)	22.8
Spent wash water	6.3
Precipitate slurry (10 wt % solids)	2.0

*Three batches per cycle, three cycles per year.

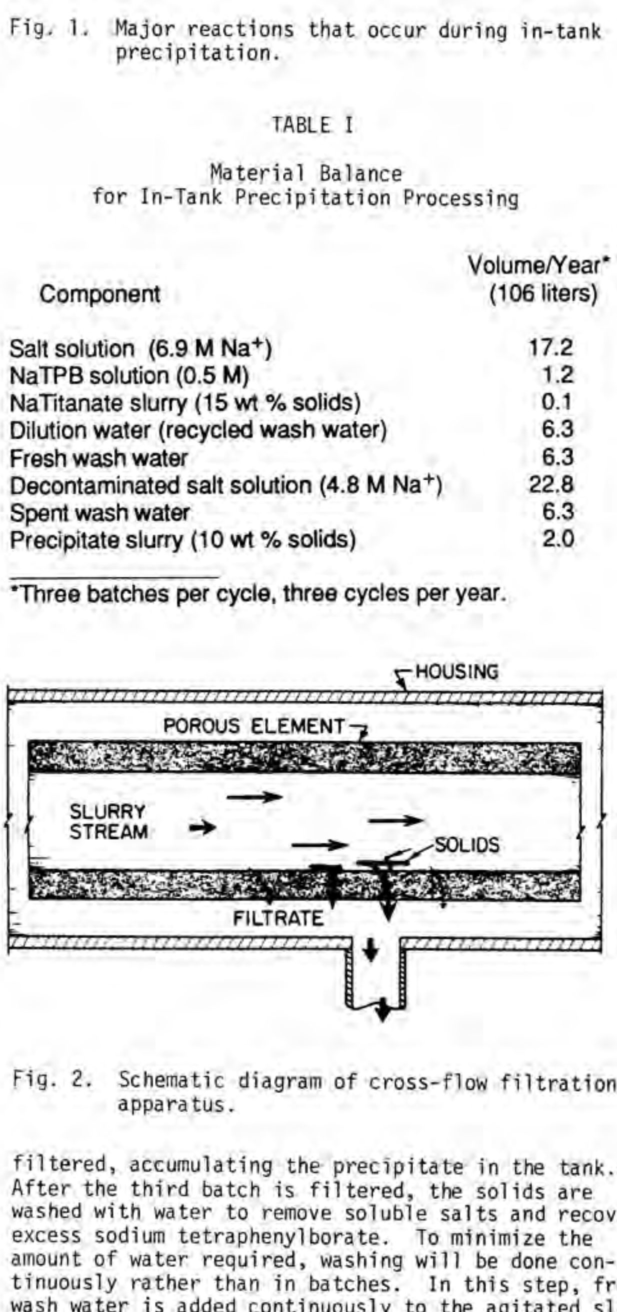

Fig. 2. Schematic diagram of cross-flow filtration apparatus.

Each processing cycle is composed of three precipitation batches and a washing stage. Three consecutive batches of salt solution are decontaminated and filtered, accumulating the precipitate in the tank. After the third batch is filtered, the solids are washed with water to remove soluble salts and recover excess sodium tetraphenylborate. To minimize the amount of water required, washing will be done continuously rather than in batches. In this step, fresh wash water is added continuously to the agitated slurry tank while the filters remove spent wash water at an equal rate. The spent wash water is recycled as dilution water in the next cycle. The washed slurry is transferred to a separate 4.9-million-liter storage tank from which it is pumped to the DWPF canyon building.

WASTE SCHEDULING

The tank-to-tank variability in waste composition presented a major difficulty in determining the order in which the waste tanks would be emptied. This variability could result in unacceptably wide swings in the DWPF feed composition if tank cleanout were not properly scheduled. Three waste components are of particular concern: Ru-106, Cs-137, and nonradioactive potassium. The concentration of each of these components has been estimated for each tank, and these estimates were used in preparing the waste removal schedules.

Ruthenium-106 is a major fission product with a half-life of one year. Its daughter isotope, Rh-106, emits a hard gamma ray when it decays. Although most of the ruthenium is insoluble and is found in the sludge, 25% remains with the soluble waste. The shielding requirements for the saltstone facility were based on processing only waste that had been aged long enough for the ruthenium to decay to low levels (8 to 15 years). However, to keep the tank farm evaporators running at full capacity, some waste aged only five years must be processed. The ruthenium concentrations in the proposed batches for the first several years of processing are shown in Fig. 3. The levels were predicted from actual analysis of the various tanks, projections of future waste production, models of ruthenium behavior in the evaporator systems, and blending in the precipitation process. The results of this analysis have shown that all but one of the planned batches are acceptable. It is anticipated that part of the salt solution for that batch will have to be pumped to a separate storage tank and allowed to age further before it can be processed.

Potassium in the waste is of concern because its tetraphenylborate salt is the major constituent of the precipitate . A salt tank high in potassium could produce enough precipitate to fill the slurry storage tank and prevent further salt processing. This is especially critical in the first two years of salt processing before the DWPF canyon building is completed.

The total inventory of potassium in the tank farm has been determined from the known quantities of potassium compounds used in SRP processes. This has been potassium permanganate and potassium fluroide used in the separations processes, and potassium hydroxide used to neutralize the oxalic acid from reactor heat exchanger cleaning. It is more difficult to determine the distribution of this potassium from tank to tank, but this has been estimated from records of the yearly consumption of potassium compounds, from monthly reports of waste transfers, and from limited sampling of tanks.

Figure 4 shows the projected inventory in the precipitate storage tank for the first nine years of operation of the in-tank precipitation process. It was generated from tank-by-tank estimates of the potassium distribution, from the salt removal schedule, and from the planned startup of the DWPF. The fill limit for the 4.9-million-liter tank is estimated to be 1.3 million moles of potassium, assuming the precipitate slurry will contain 0.27 moles of potassium per liter (10 wt% solids). The analysis shows that the current salt removal schedule presents no danger of overfilling the tank. This approach will be used in the future to assess the impact of changes in the schedule or the DWPF startup date.

Cesium-137 levels in the salt are important to DWPF emissions and to radiolytic decay of the tetraphenylborate precipitate. Using an onsite computer code that keeps track of the number of curies of certain radionuclides in each waste storage tank, it has been determined that the schedule for waste removal is compatible with the DWPF requirements. These estimates have been verified against actual tank analyses in many cases.

RADIOLYSIS EFFECTS ON TETRAPHENYLBORATE PRECIPITATE

In-tank processing of the soluble waste will begin two years before the DWPF canyon building is completed. The washed precipitate will be stored until the vitrification process is ready. During storage, radiolysis decomposes the tetraphenylborate precipitate, producing

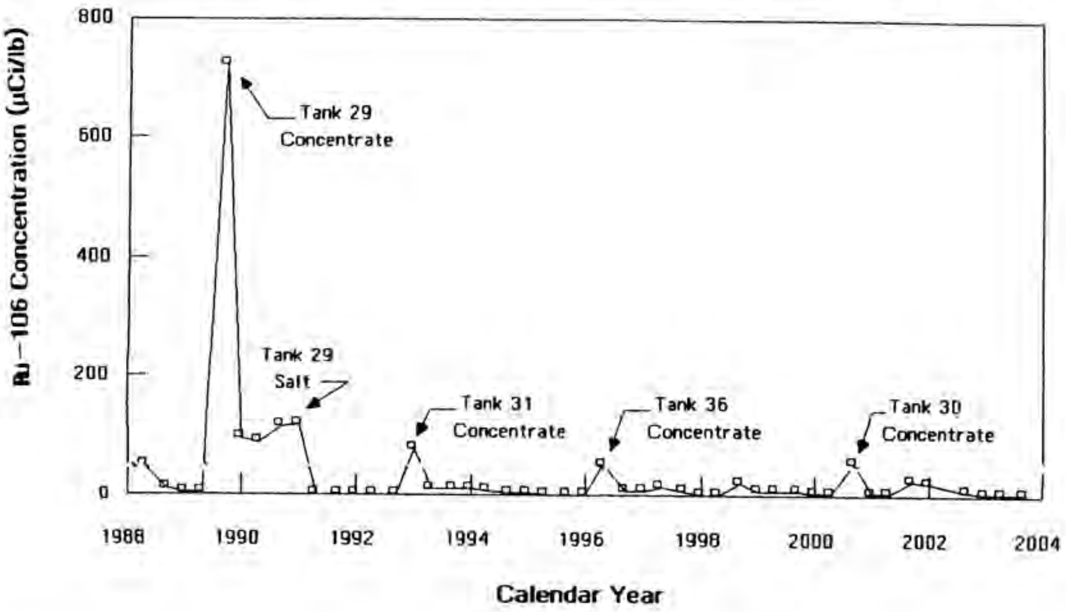

Fig. 3. Ruthenium-106 concentrations in feed solution to in-tank precipitation processing.

benzene, biphenyl, phenol, and phenylboric acid. Benzene, the major product, has been an important consideration in design of the process because of its flammability and toxicity. The net effect of radiolysis after two years of storage is shown in Table II. The presence of benzene in the precipitate has required that the tank ventilation be increased and other fire prevention measures be adopted in the tank farm.

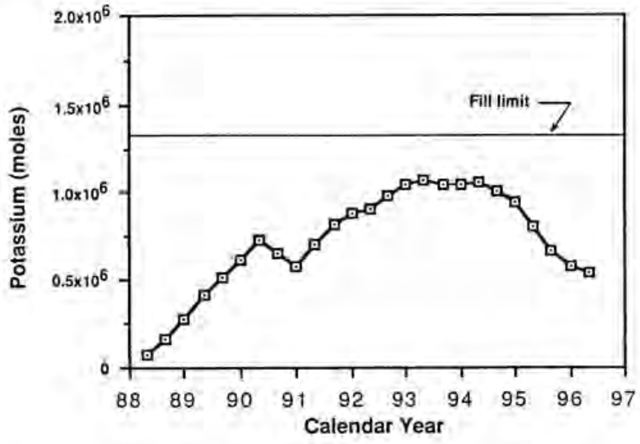

Fig. 4. Projected inventory of potassium in the precipitate storage tank.

TABLE II

Change in Composition of 10 Wt% Precipitate Slurry due to Radiolytic Decomposition

	Slurry Concentration (g/L)	
Component	Fresh	After 2 Years
KTPB	90.5	72.4
NH_4TPB	4.24	3.39
CsTPB	0.94	0.75
$NaTi_2O_5H$	4.21	4.21
$(C_6H_5)_2Hg$	1.06	1.06
Benzene	--	7.3
Biphenyl	--	3.3
Phenol	--	4.5
Nitrobenzene	--	0.033
Phenylboric acid	--	3.6
Boric acid	--	1.5

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*Two years of storage is equivalent to a dose of $2.9\text{x}10^8$ rads.

Radiolysis also changes the rheological properties of the precipitate, markedly affecting the pumping characteristics in the 2.4-km transfer line to the DWPF. Relatively small radiation doses, compared to that received in two years of storage, significantly reduce the precipitate's yield stress and consistency. Figure 5 shows the changes in these properties with storage time (radiation dose). In one year of storage the precipitate will receive a radiation dose of $1.45\text{x}10^8$ rads. Because of this effect, the pump requirements for transferring the precipitate were reduced, and sludge and precipitate transfer pumps are now equivalent.

FURTHER WORK

Although sludge has been successfully transferred between areas, some aspects of sludge pumping are still being investigated. A nonradioactive mockup facility has been constructed for testing various aspects of sludge pumping. The facility consists of 168 meters of 7.62-cm-diameter stainless steel pipe. The pipe is looped in seven 24-meter sections, with each section angled upward at a 0.5% to 4% slope. Instrumentation is provided to measure flow and pressure drop across segments of the line. The variable speed pump on the mockup line has characteristics identical to the pumps used for the interarea transfers. This facility has been used to measure the plugging potential of low solids transfers, and the amount of water required to flush the interarea lines after transfers. Further work on methods for unplugging lines and on the plugging potential dependence on particle size is planned.

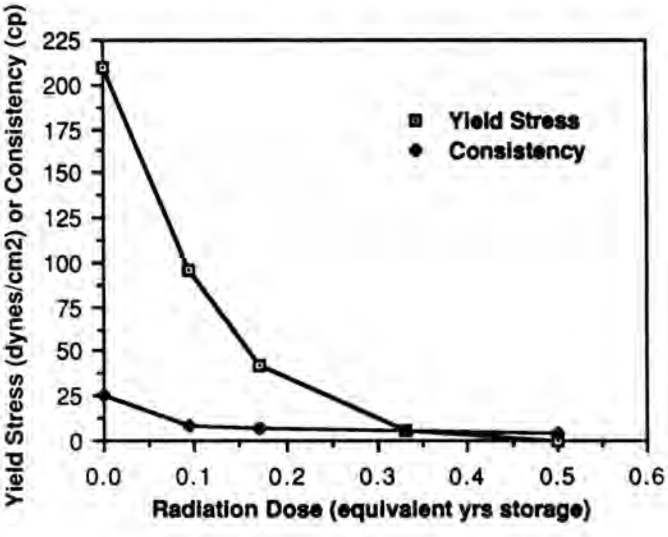

Fig. 5. Changes in rheological properties of 10 wt% KTPB slurry due to irradiation. One year of storage is equivalent to a radiation dose of 1.45x108 rads.

CONCLUSIONS

Tank farm processing of high-level waste for the DWPF encompasses several programs that are underway or under construction. Waste transfers have already started, and the first interarea sludge transfer has been made. Sludge processing has begun, and the first batch of sludge feed for the DWPF is currently being washed. Construction of the facilities for in-tank precipitation processing are underway and are scheduled for completion in 1988. Actual processing will begin in late 1988. Experimental and development work continues on inter-area sludge transfer problems.

ACKNOWLEDGEMENT

This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

REFERENCES

1. H. Dale Martin, Mark A. Schmitz, Martha A. Ebra, Darrel D. Walker, Lester L. Kilpatrick, and Lien-Mow Lee, "In-Tank Precipitation Process for Decontamination of Water Soluble Radioactive Waste", Proc. Symposium on Waste Management, Vol. 1, Tucson, Arizona, March 11-15, 1984, (291-296).

2. A. Heyrovsky, "Mercurimetric Titrations of Aromatic Boron Compounds", Z. anal. Chem., 173, 301-309 (1960).