

DEFENSE WASTE PROCESSING FACILITY

PRECIPITATE HYDROLYSIS PROCESS

Joseph P. Doherty, Russell E. Eibling, and James C. Marek
E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

ABSTRACT

Sodium tetraphenylborate and sodium titanate are used to assist in the concentration of soluble radionuclides in the Savannah River Plant's high-level waste. In the Defense Waste Processing Facility, concentrated tetraphenylborate/sodium titanate slurry containing cesium-137, strontium-90 and traces of plutonium from the waste tank farm is hydrolyzed in the Salt Processing Cell forming organic and aqueous phases. The two phases are then separated and the organic phase is decontaminated for incineration outside the DWPF building. The aqueous phase, containing the radionuclides and less than 10% of the original organic, is blended with the insoluble radionuclides in the high-level waste sludge and is fed to the glass melter for vitrification into borosilicate glass. During the Savannah River Laboratory's development of this process, copper(II) was found to act as a catalyst during the hydrolysis reactions, which improved the organic removal and simplified the design of the reactor.

INTRODUCTION

The Savannah River Plant (SRP) has generated approximately 2.85×10^5 cubic meters of high-level radioactive waste since plant startup in the early 1950's. The waste generation is expected to continue at the rate of 5.7 to 15×10^3 cubic meters per year. The existing waste inventory has been concentrated through evaporation to about 1.1×10^5 cubic meters, currently stored in underground tanks. Approximately 10 volume percent of the waste is sludge which contains most of the radionuclides. The other 90 volume percent of the waste is salt cake and salt solution which are estimated to contain 39% of the total radioactivity present in the SRP waste.

The supernatant salt solution consists primarily of sodium nitrate, nitrite, aluminate, and hydroxide. In addition, the supernate contains traces of potassium, radioactive cesium, strontium, and plutonium. As a part of the permanent waste disposal plan, virtually all of the cesium-137 and strontium-90 and most of the plutonium will be removed from the salt solution by the In-Tank Salt Decontamination Process. In the Salt Decontamination Process, sodium tetraphenylborate is used to precipitate cesium, and sodium titanate is used to adsorb strontium and plutonium. Potassium tetraphenylborate, which also precipitates, is the major insoluble component of the resulting slurry. This material is then concentrated via crossflow filtration, and washed with water to decrease the amount of soluble solids in the solution. The washed slurry contains essentially all of the radioactivity of the original liquid waste.¹

The objective of the Defense Waste Processing Facility (DWPF) is to incorporate the waste radionuclides into borosilicate glass. The Salt Decontamination Process concentrates the soluble radionuclides in the waste tanks so that the DWPF can achieve its objective while processing less volume. Prior to blending the insoluble radionuclides in the waste sludge with the soluble radionuclides in the

precipitate, the organic content of the precipitate must be reduced by at least 90% for proper glass melter operation. The primary subject of this paper is to describe the development of the DWPF Precipitate Hydrolysis Process used to separate the organics from the soluble radionuclides.

In the DWPF, concentrated tetraphenylborate/sodium titanate slurry from the waste tank farm is hydrolyzed in the Salt Processing Cell forming organic and aqueous phases. The two phases are then separated, and the organic phase is decontaminated for incineration outside the DWPF building. The aqueous phase, containing the radionuclides and less than 10% of the original organic, is blended with waste sludge and is fed into the glass melter for vitrification into borosilicate glass.

PROCESS DESCRIPTION

Figure 1 shows a flow diagram of the DWPF Precipitate Hydrolysis Process. The Precipitate Reactor is operated as a semi-batch reactor. First, formic acid and copper formate catalyst solutions are charged into the reactor containing about 25% of the aqueous product from the previous batch. This reactor solution is heated to 90°C. Tetraphenylborate precipitate slurry, with a twelve weight percent total solids content, is pumped from the waste tank farm into the agitated, hot, reactor solution. The hydrolysis reactions begin almost immediately. Benzene and other aromatic compounds are produced as the tetraphenylborate is hydrolyzed. As it forms, benzene flashes out of the 90°C reaction mixture because it is above the normal boiling point (80.1°C). The precipitate for one batch is fed within one hour. The reactor is then heated and the solution attains its normal boiling point of 102°C.

Vapors from the Precipitate Reactor condense in the Precipitate Reactor Condenser. The condensed aqueous and organic phases are separated in the Precipitate Reactor Decanter. The aqueous phase returns by gravity to the reactor. The lighter benzene-rich organic phase flows by gravity to the Organic Evaporator. Boiling continues in the reactor for five hours to allow the reactions to approach

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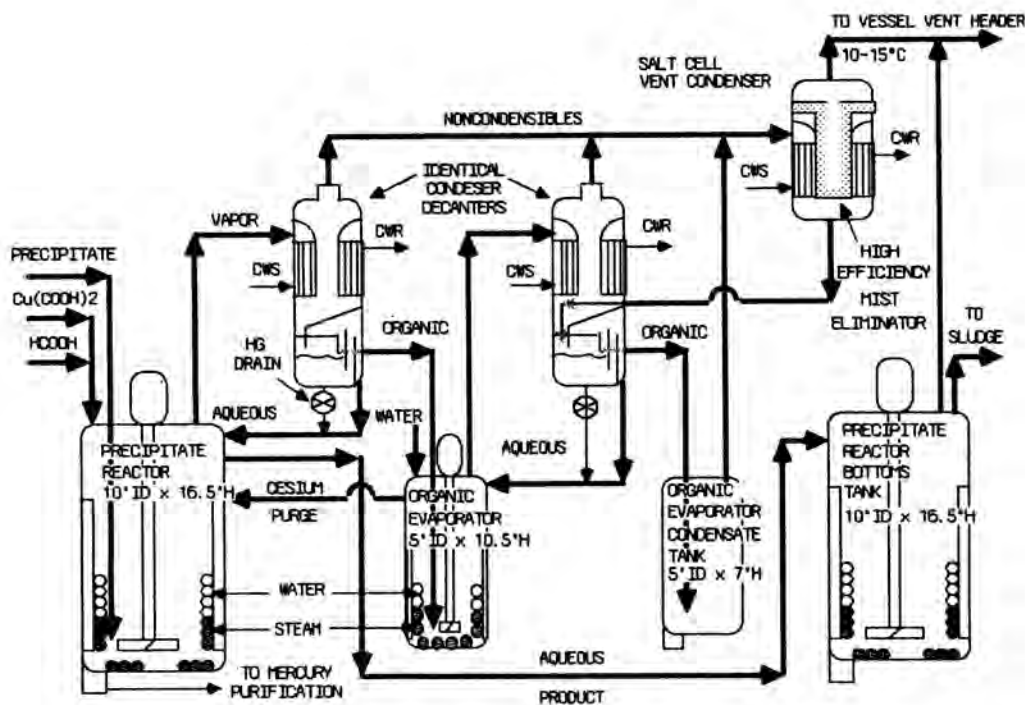


Fig. 1. DWPf Precipitate Hydrolysis Process Flow Diagram.

completion and to steam strip the higher boiling aromatic compounds from the aqueous phase.

The organic phase is decontaminated in the Organic Evaporator by water washing and evaporation. By agitating the organic with water, cesium is extracted from the organic phase into the water. The Organic Evaporator is then heated to boiling. Benzene is evaporated around 80°C. Then, as the temperature is increased to 100°C, the water steam strips heavier organics from the aqueous phase. No volatile cesium compounds are produced by the reactions. Liquid entrainment in the vapor is the only mechanism by which radionuclides can contaminate the condensate. The Organic Evaporator Condenser and Decanter cool the vapor and separate condensate in the same manner as the Precipitate Reactor Condenser and Decanter. Boiling in the evaporator continues until the same amount of water is boiled as in the reactor. The organic phase collects in the Organic Evaporator Condensate Tank. Water from the evaporator is pumped to the reactor to purge the cesium.

The Organic Evaporator Condensate Tank is sampled and analyzed for contamination. Clean organic will be pumped outside the shielded DWPf and held for incineration. Otherwise, the organic will be returned to the evaporator for a repeated wash and evaporation. The aqueous phase in the reactor is sampled and analyzed for adequate organic removal (greater than 90%). This solution is pumped to the Precipitate Reactor Bottoms Tank and held until the time cycle is right for blending and processing with the high-level waste sludge in preparation for vitrification.

All the vessels in this process are maintained at a slightly negative pressure relative to the surrounding cell environment. Nitrogen is purged into the tanks to maintain the oxygen concentration below the level required for benzene combustion. Vapors and gas from the two process condensers and the Organic Evaporator Condensate Tank pass through the chilled Salt Cell Vent Condenser. This condenser operates at 10 to 15°C. Condensate returns to the process via the

Evaporator Decanter. The saturated gas stream exiting the vent condenser enters the building vessel vent system header and exits the DWPf stack.

PRECIPITATE FEED DESCRIPTION

The tetraphenylborate precipitate slurry nominally contains 10 ± 1 weight percent insoluble solids and 1.8 ± 0.2 weight percent dissolved salt. Table I shows the average composition of the insoluble solids. The majority of the dissolved salts are nitrate (NaNO_3), nitrite (NaNO_2), and aluminate (NaAl(OH)_4). Slight variations in the relative concentrations will be expected as 30 years of high-level waste is processed. Cesium-137 activity in the average 15-year aged salt solution will contain 9.5×10^3 Ci/cubic meter, but may range from 2.6 to 26×10^3 Ci/cubic meter. Cesium-137 decay accounts for greater than 99% of the activity in the precipitate solution.

TABLE I

Average Insoluble Solids Composition of DWPf Precipitate Feed

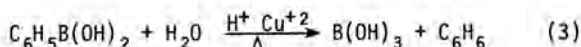
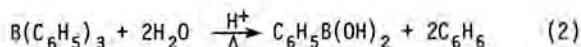
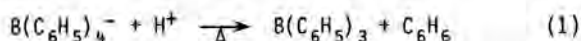
Compound	Dry Weight Percent
$\text{KB(C}_6\text{H}_5)_4$	89.5
$\text{NH}_4\text{B(C}_6\text{H}_5)_4$	4.2
$\text{NaTi}_2\text{O}_5\text{H}$	4.2
$\text{Hg(C}_6\text{H}_5)_2$	1.1
$\text{CsB(C}_6\text{H}_5)_4$	1.0

The density of the solid tetraphenylborate precipitate is slightly greater than the density of the salt solution. However, the precipitate traps air very easily. Some of the precipitate will rise to the surface and produce a foam. The concentrated precipi-

tate is best described as having the rheology similar to that of a Bingham Plastic.² An initial yield stress of about 200 dynes per square centimeter must be overcome before the precipitate will flow. Bingham Plastics are known to produce stable foams.³ Cesium-137 decay radiation alters the rheology with increased exposure. The yield stress is virtually lost after the equivalent of half a year of average exposure. The resulting Newtonian rheology makes the precipitate easier to pump, but it still foams when air is entrained or gases pass through it.

REACTION CHEMISTRY

Salts of the tetraphenylborate anion decompose in aqueous acid solutions and are converted to triphenylboron and benzene. Triphenylboron then undergoes hydrolysis to phenylboric acid and benzene.⁴ Phenylboric acid is stable in aqueous solutions below 150°C, except in the presence of certain metal catalysts. Phenylboric acid is then cleaved to form boric acid and benzene. Copper(II) has been found to be an effective catalyst to cleave phenylboric acid at 100°C. Investigations by SRL and others⁵ have not found a more efficient catalyst than copper(II). The reaction rates of the tetraphenylborate and triphenylboron decomposition are also increased. The stoichiometry for the above reactions is:

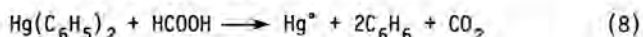
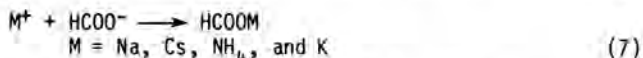
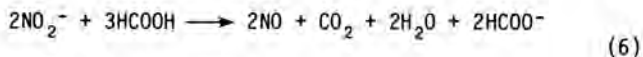
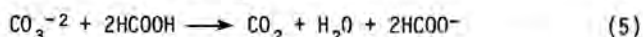
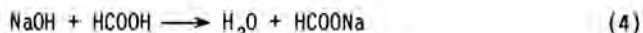


Tetraphenylborate and triphenylboron decompose completely. Phenylboric acid decomposes about 85 to 90%.

Formic acid is used to acidify the precipitate because it is a strong reducing acid that does not provide an anion to substitute onto the benzene ring. Benzene has a very high vapor pressure and is easier to separate from the aqueous phase by batch distillation than chloro-, nitro-, or sulfo-substituted aromatic compounds with lower vapor pressures. Also, because it is used to chemically reduce the high-level waste sludge, formic acid use for precipitate hydrolysis is compatible with downstream DWPF chemical processing.

The large variety of dissolved salts in the precipitate feed cause side reactions to occur also. Nitrogen-containing aromatic compounds are formed due to the reaction of formic acid with the nitrite anion (NO_2^-) to form a weak nitrous acid (HNO_2) solution. Nitrite also undergoes an oxidation-reduction reaction with formic acid to generate NO_x and CO_2 . Oxidation reactions cause the production of biphenyl ($(C_6H_5)_2$), terphenyl ($(C_6H_5)_3$), and phenol (C_6H_5OH).^{5,6} These compounds are found only in trace amounts when the nitrite is left out of the feed. Since nitrite is formed by the radiolysis of nitrate and is added to the waste as a corrosion inhibitor, it will always be present in the feed.

In addition to hydrolyzing the tetraphenylborate, formic acid neutralizes sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3), combines with the tetraphenylborate salt cation released during reaction (1), and reduces diphenylmercury to mercury metal. The stoichiometry of the other reactions is:



Generation of CO_2 and NO in reactions (5) and (6) occurs faster than the tetraphenylborate is decomposed. As a result, these gases pass through the precipitate and produce a large quantity of foam. This drawback was eliminated by developing the reactor feeding method discussed under the Reaction Engineering and DWPF Design section.

PRODUCT DESCRIPTION

The aqueous product contains principally dissolved potassium formate, sodium formate, boric acid, sodium nitrate, and residual formic acid. Phenylboric acid and phenol are the principal dissolved organic compounds that remain in the aqueous phase. Sodium titanate particles do not react but do get coated with insoluble and higher boiling compounds of biphenyl, terphenyl, and diphenylamine ($C_6H_5NHC_6H_5$). These coated particles account for the total insoluble solids concentration of approximately 0.8 ± 0.1 weight percent. Excess formic acid, added to keep the pH below 5.0 during the hydrolysis reactions, will make up about 10% of the total formic acid required later in the process to chemically reduce the sludge.

Over 90% of the organic carbon in the tetraphenylborate precipitate ends up in the decontaminated organic phase. Over 30 compounds have been identified in this stream. Benzene accounts for 90% by weight of the organic compounds, with biphenyl, phenylboric acid, diphenylamine, and phenol accounting for an additional 8 to 9%. This stream has a density of 0.89 ± 0.005 g/mL at 25°C and is highly flammable.

Elemental mercury is the one other product from this process. Even though it will steam strip into the decanter, it will be returned to the reactor. When enough mercury accumulates in the reactor sump, it will be pumped out to be blended and purified with mercury produced during the sludge processing.

REACTION ENGINEERING AND DWPF DESIGN

Statistically designed experiments were used to develop the Precipitate Hydrolysis Process operating conditions and to provide DWPF design data. The key to the success of this process in meeting the DWPF criteria is the use of copper(II) as a catalyst. Copper(II) cleaves the phenylboric acid, increasing the organic removal from 75% to 90%. Increasing the rates of the other reactions also enabled the development of a reactor feeding method that did away with the need to use a pressurized reactor to contain the foam mentioned earlier.

Previously, the most efficient reaction conditions were found to be:

- 1) 100% stoichiometric formic acid to satisfy reactions (4), (5), and (6) plus 125% stoichiometric formic acid to satisfy reactions (1) and (8);
- 2) 400 parts per million copper(II);
- 3) 100°C reaction temperature;

- 4) 5 hours reaction time; and
- 5) 3.5 kg of water boiled/kg of precipitate feed solids.

When the formic acid/copper/precipitate slurry mixture was heated, gas evolution generated a foam that could not be contained within the reactor. As a result, step 4 had to be done in a vessel that was sealed before heating, followed by step 5 after the pressure (40 to 45 psig) was relieved. The foam generated in this reaction sequence hindered agitation and heat transfer.

The alternative method that was developed is performed at ambient pressure. This method is now the reference method for the DWPF and follows this sequence:

- 1) leave an aqueous heel in the reactor equivalent in volume to at least 25% of the precipitate feed batch,
- 2) add the formic acid and copper(II) required for this batch (steps 1 and 2 above),
- 3) agitate and heat the reactor solution to $90 \pm 5^\circ\text{C}$,
- 4) maintain $90 \pm 5^\circ\text{C}$ while adding the precipitate at a constant rate and over a time period no shorter than 30 minutes,
- 5) when all the precipitate has been fed, heat the reactor solution to boiling, and maintain this condition until the 5-hour reaction time and the water boiling criteria (step 5 above) are met.

The combined effect of these steps is that the precipitate is diluted and decomposes very quickly. The gas evolution rate is controlled by the feed rate and the tetraphenylborate concentration is so low that foaming does not occur. Reaction (6) is autocatalytic and dependent on the formic acid concentration and the temperature. Figure 2 shows the rate of gas evolution at two different feeding temperatures. The downside of the peak shown during the 60°C run coincides with the collapse of the foam. At temperatures below 70°C the reaction rate is dominated by the buildup of an intermediate compound that serves as a catalyst. At temperatures above 80°C , the reaction rate is dependent on the formic acid concentration and the temperature. As more formic acid is consumed, the gas evolution rate decreases. The catalytic intermediate does not accumulate.

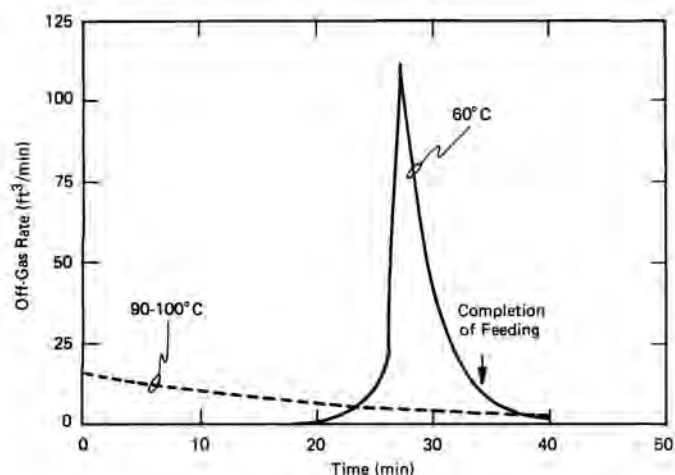


Fig. 2. Effect of Temperature on Gas Generation.

Laboratory studies using natural cesium and cesium-137 tracers have not detected any cesium dissolved in the organic phase. For the purposes of design, it is assumed that the organic phase will be saturated with the aqueous phase in the decanter. This assumption means that cesium will be present in the organic phase due to its known presence in the aqueous phase. To keep entrainment to a minimum during distillation, the reactor and evaporator are operated half full and at a low boiling flux (vapor rate/boiling area). In addition, an impingement plate is located at the entrance to the vapor line leaving these vessels. By washing the organic phase with clean water prior to final organic decontamination, an additional decontamination factor of at least 1000 is expected. For the entire process, a minimum cesium decontamination factor (weight in feed/weight in product) of 10^9 is expected for the organic phase.

CONCLUSION

The Defense Waste Processing Facility is currently under construction at the Savannah River Plant. It is scheduled to begin radioactive service in September 1989. The concentrated tetraphenylborate precipitate fed to the DWPF represents about 60% of the total waste volume fed to the DWPF. Development of the Precipitate Hydrolysis Process has contributed to the objective of disposing of the nation's high-level defense waste.

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