

IN-TANK PRECIPITATION PROCESS FOR
DECONTAMINATION OF WATER SOLUBLE RADIOACTIVE WASTE

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ABSTRACT

A precipitation and adsorption process has been developed to remove cesium, strontium, and plutonium from water-soluble, high-level radioactive waste. Sodium tetraphenylborate precipitates cesium and sodium titanate adsorbs strontium and plutonium. The solids are separated from the decontaminated salt solution by crossflow filtration. This new process offers significant capital savings over an earlier ion exchange process for salt decontamination. Chemical and engineering studies with actual and simulated waste are reported. The effect of many variables on the decontamination factors and filter performance are defined.

BACKGROUND

The Savannah River Plant is presently the nation's primary source of tritium, weapons plutonium, heat source plutonium, deuterium, and several other radionuclides for defense, space, medical, and energy applications. SRP was built by the DuPont Company for the U. S. Atomic Energy Commission in the early 1950's, and the plant is still operated by the DuPont Company for the U. S. Department of Energy. The plant, which is located near Aiken, SC, comprises a 300 square mile land area with extensive support facilities and a single operating contractor.

The radioisotopes produced at SRP are generated in nuclear reactors by irradiating appropriate target materials with neutrons from uranium fuels and then chemically separating the products in two onsite processing plants. In the 28 years of SRP operations, some 72 million gallons of high level waste have been generated and waste generation is expected to continue at the rate of 1.5 million to 4 million gallons a year depending on operating demands. This waste has been evaporated to about 28 million gallons which is now stored in large underground tanks. The principal radionuclides in the waste are strontium-90 and cesium-137. Some 10% of the waste is a sludge generated from precipitation of iron, manganese, and aluminum hydroxides; the sludge contains most of the strontium and small amounts of actinides not recovered in the reprocessing plants.

The remainder of the waste is liquid and salt cake, which consists primarily of sodium nitrate, sodium nitrite, sodium aluminate, and sodium hydroxide. This waste contains cesium and traces of other soluble radionuclides. A new reference process has recently been developed for decontamination of SRP supernate - the In-Tank Precipitation Process. This method removes virtually all of the ^{137}Cs and ^{90}Sr radionuclides which are the primary biological hazards in supernate. In addition, the process results in an approximate \$500 MM cost reduction over the previous Defense Waste Processing Facility (DWPF) Stage 2 ion exchange reference process, because the need for an additional canyon building is eliminated.

The In-Tank Precipitation Process involves addition of sodium tetraphenylborate and sodium titanate to a waste tank containing supernate. The cesium and potassium precipitates as cesium tetraphenylborate and potassium tetraphenylborate. The strontium is adsorbed by the sodium titanate, which remains a solid throughout the process. The supernate, with most of its radioactive constituents now in solid form, is then filtered through sintered stainless steel filters with a 0.5 micron pore size.

The decontaminated supernate filtrate will be incorporated into a soil and cement mixture and buried. The precipitate, which is unable to pass through the filters, is recycled back to the waste tank. This material is then concentrated and washed to remove residual salts. The washed precipitate, containing virtually all the radioactivity of the original supernate, will eventually be incorporated into borosilicate glass in the Defense Waste Processing Facility.

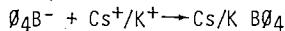
SRP recently successfully demonstrated this process in Waste Tank 48, in the In-Tank Salt Decontamination Demonstration. 427,000 gallons of high-level radioactive supernate were transferred from Tank 24 to Tank 48, then sodium tetraphenylborate and sodium titanate were added to Tank 48 and the precipitate was filtered. 518,000 gallons (goal 400,000) of decontaminated supernate were produced. The average ^{137}Cs activity of the decontaminated supernate was 7400 d/m/ml, corresponding to a ^{137}Cs decontamination factor of 43,000 (goal 10,000). After filtration, about 40,000 gallons of concentrated precipitate remained in Tank 48 which was water washed to remove sodium salts and reconcentrated.

The experience gained from the Demonstration is being applied to design of a permanent In-Tank Salt Decontamination Facility.

Chemistry of the Precipitation Process

The waste supernate contains about 4 Ci/gal cesium-137. This accounts for more than 99% of the total activity in 15-year-old water-soluble waste. The ion exchange flowsheet reduces the cesium activity by a factor of 10^4 , i.e., has a decontamination factor, DF, of 10^4 .

In the precipitation process, tetraphenylborate anion is added as the water soluble (0.9M at room temperature)³ sodium tetraphenylborate. The waste supernate contains about 2.5×10^{-4} M cesium and 0.031M potassium, and both are precipitated as the tetraphenylborates. Over 98% of the Cs⁺/K⁺ precipitate is the potassium salt. The precipitation reaction can be represented as:



The effects of several experimental variables on cesium removal via sodium tetraphenylborate precipitation have been studied. These variables include supernate feed composition [(Na⁺) = 2.8-6.2M, (OH⁻) = 1-3.8M, cesium activity = 0.08-4.0 Ci/gal], sodium tetraphenylborate excess, contact time, and purity of sodium tetraphenylborate. Sodium tetraphenylborate was used consistently as 0.5M solution in 0.01M sodium hydroxide.

The decontamination factor (DF) for cesium ranged from 10^4 to 10^6 depending on the cesium and sodium concentrations in the feed. The expected DF values for cesium in salt supernate can be calculated using data taken from plots of the solubility of cesium tetraphenylborate and sodium tetraphenylborate versus the concentration of sodium ion. The calculated DF values agree well with values measured on actual supernate.

The cesium DF is effected strongly by the sodium and potassium ion concentrations. The concentration of hydroxide ion and the radioactivity level have only a minor effect on cesium DF. With a sodium tetraphenylborate excess of 0.015M, a high cesium DF ($>10^5$) is always obtained when the supernate contains less than 4.5M sodium ion. However, the solubility product for sodium tetraphenylborate is exceeded when supernate containing more than 4.5M sodium is used. The cesium DF then varies with contact time because most of the tetraphenylborate anion added is precipitated at the high sodium concentration and is not available immediately to precipitate cesium. Sodium tetraphenylborate solubility decreases from about 0.9M in water to 0.0011M in supernate containing 7M sodium as shown in Table 1. A high cesium DF can be obtained if enough excess sodium tetraphenylborate is added and a longer contact time is used to allow the cesium to exchange with the sodium.

The effect of sodium tetraphenylborate excess on cesium DF for a supernate containing 5.3M Na⁺ is shown in Table 2. Given a contact time of 2 hours, cesium DF values of 10^5 were obtained when the sodium tetraphenylborate excess was 0.025M or greater.

When the sodium tetraphenylborate excess is insufficient, the contact time was also found to be important for high cesium DF values. This effect is seen clearly when the contact time is less than two hours. Table 3 indicates that at 4.3M sodium and 0.012M sodium tetraphenylborate excess, the cesium DF increases from 18 to $>1.1 \times 10^5$ in four days (no stirring) and reaches a constant value of $>3.3 \times 10^5$ after 11 days.

The improvement in cesium DF with time is a result of the slow exchange of ions between the sodium tetraphenylborate precipitate and cesium ions in the supernate. Longer times are required to reach high cesium DF values when the sodium level is high because ion exchange is much slower than precipitation.

TABLE I

Solubility of Sodium Tetraphenylborate as a Function of Sodium Concentration

[Na ⁺], M	Solubility* of Sodium Tetraphenylborate, M
0	0.80
2.5	0.32
4.0	0.0065
5.5	0.0018
7.0	0.0011

* Measured by Plasma Source Emission Spectroscopy (ICP) at room temperature.

TABLE II

Effect of Sodium Tetraphenylborate (NaTPB) Excess on the Cesium Decontamination Factor,* Two Hours Contact Time

[Na ⁺], M	NaTPB Excess, M	Cesium in Filtrate, dis/(min mL)	Cesium DF
5.3	0.02	2.51×10^7	89
5.3	0.025	$<2 \times 10^4$ **	$>1.12 \times 10^5$
5.3	0.035	$<1.8 \times 10^4$ **	$>1.24 \times 10^5$
5.3	0.040	$<1.4 \times 10^4$ II	$>1.60 \times 10^5$

* The feed was 2.24×10^9 dis/(min mL) in cesium and 0.0335M in potassium.

** Precise Cs-137 levels could not be obtained because of Ru-106 interference.

TABLE III

Effect of Contact Time on Cesium DF

[Na ⁺], M	NaTPB Excess, M	Contact Time	Cesium DF
4.3	0.012	2 hours	18
4.3	0.012	1 day	107
4.3	0.012	4 days	$>1.1 \times 10^5$
4.3	0.012	11 days	$>3.3 \times 10^5$
4.3	0.012	15 days	$>3.3 \times 10^5$

Adsorption of Strontium and Plutonium by Sodium Titanate

Most of the strontium in waste is precipitated as strontium hydroxide in the sludge. The remaining concentration of soluble strontium in supernate is about 5×10^{-7} M. A strontium DF of 200 to 300 can be obtained by adding 0.5 grams of sodium titanate (added as a 67 g/L slurry) per liter supernate.

Since the adsorption is an ion exchange process, the DF should be contact-time dependent. Data was obtained showing strontium DF as a function of contact time at a sodium titanate level equivalent to 1% TiO₂ in glass. Based on these results, at least two days of contact time is required at this sodium titanate level.

It is preferable to carry out the adsorption of strontium in a waste tank instead of using an ion exchange column because the sodium titanate slurry can be mixed with sodium tetraphenylborate solution so that cesium and strontium can be removed in one operation. In addition, disposal of the used sodium titanate in the column is avoided.

Like strontium, most of the plutonium is in the sludge. However, small amounts of plutonium have been detected in the supernate in both soluble and insoluble form. In plutonium analysis of Tank 18 supernate, some very fine dark brown particles were seen. The particles were separated, and plutonium analyses were made for both liquid and solid portions. The solids contained approximately 580 times more plutonium than the liquid. This result agrees with the plutonium data for Tank 19 supernate before and after sand filtration.

Chemical and Radiolytic Stability of the Precipitate

The new precipitation process can be performed in existing waste tanks only if the precipitate remains chemically and radiolytically stable long enough to filter and wash it. Tests were therefore made to determine the effectiveness of cesium isolation in the precipitate as a function of time by using supernate from SRP Tank 19. No significant amount of Cs-TPB had returned to solution in this period. The cesium DF after 344 days of storage was 2.3×10^5 . This indicates that the precipitate is chemically stable in actual waste supernate and also stable in a beta radiation field for the expected processing times.

The gamma radiation intensity is much higher in a waste tank than the intensity in an isolated sample. To evaluate the effects of higher intensity gamma, the precipitate and sodium tetraphenylborate solution were irradiated in a high-intensity cobalt-60 source to an equivalent of seven years total gamma dose. Based on these results, the K/Cs TPB is about 15 times more stable than sodium tetraphenylborate in the radiation field. At an expected dose rate of 2000 Rad/hr, and if radiation stability is the controlling factor, sodium tetraphenylborate should decompose at $6E-7$ moles/hr and K/Cs tetraphenylborate at $4E-8$ moles/hr. The effects of K/Cs tetraphenylborate decomposition on the salt DF can easily be overcome by the presence of a small excess of sodium tetraphenylborate during the expected processing and storage period. Degradation of the organic fractions is still to be avoided for flammability and processing considerations.²

Engineering Studies with Actual and Simulated Waste

Cross-flow filtration was chosen as the process for separation of the solid tetraphenylborate and sodium titanate from the decontaminated supernate (Fig. 1). Cross-flow filtration is recommended with low solids loading, relatively small particle size, and in cases where power costs for pressure operation are not a problem. During filtration, the pressurized precipitate slurry is pumped through the filter at high velocities. The filtrate weeps through the pores and is collected in the annular space between the filter tube and its housing (Fig. 2). The high linear velocity of slurry helps sweep the filter surface clean and maintain high filtrate flux. The slurry is recycled to the precipitation/feed tank until the desired solid concentration is reached. An air backpulse pressure approximately 50 psi greater than the slurry pressure is applied to the filtrate side every 5 to 10 minutes. The filter is backpulsed for about 0.5 to 2 seconds.

A crossflow filtration system was installed in High Level Caves (HLC)* for testing and evaluation of the process and equipment concept (Fig. 3). These filters are made of sintered stainless steel powder and are fabricated in tubular form. The commercially

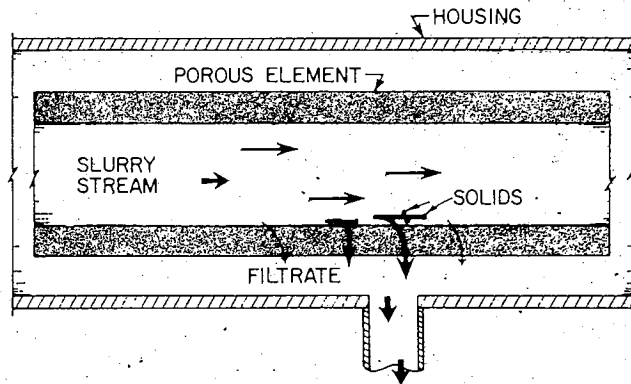


Fig. 1. Cross Section of a Single Tube Filter. (Taken from DP-1636 pg. 20)

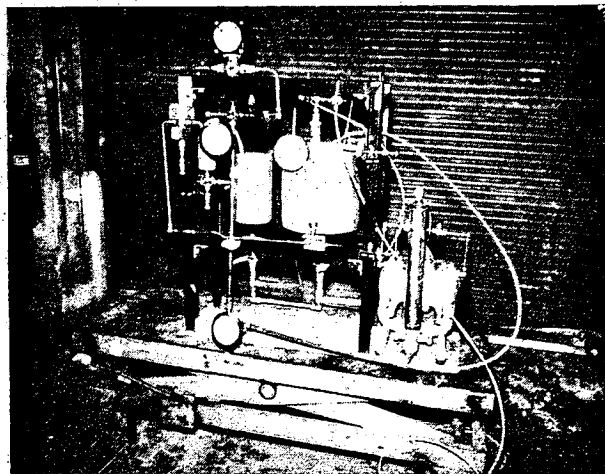


Fig. 2. Small Scale Cross-Flow Filtration Unit Tested in Shielded Cells (1-15401-1)

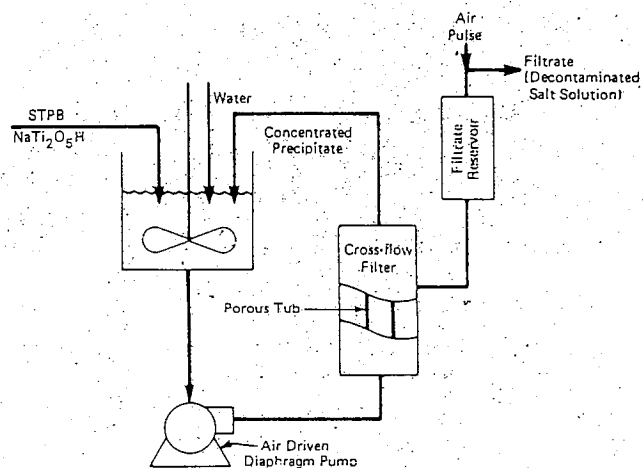


Fig. 3. Cross-Flow Filtration System Flow Diagram (Taken from DP-1636 pg. 21)

* The High Level Caves are shielded cells in which equipment can be tested by the use of remote manipulators.

available filters from Mott Metallurgical Corporation have pore sizes ranging from 0.2 to 20 microns, are enclosed in a housing, and are available in single tube or multitube configuration.

An intermediate scale filtration unit was built at the Equipment Test Facility (ETF)* and is shown in Fig. 4. The unit was used to define specific engineering variables on large equipment. Variables tested included main stream velocity, filter pressure differential, backpulse frequency and filter cleaning.

The cross-flow filter assemblies consist of 4 bundles, 7 tubes per bundle, each 10 foot long. Each bundle has a total of 11.5 sq. ft. of area for a total capability of 46 sq. ft. The tubes are made of 316 SS with a pore size of 0.5 micron. The 0.5 micron pore size gave high DF's in the HLC Precipitation Facility.

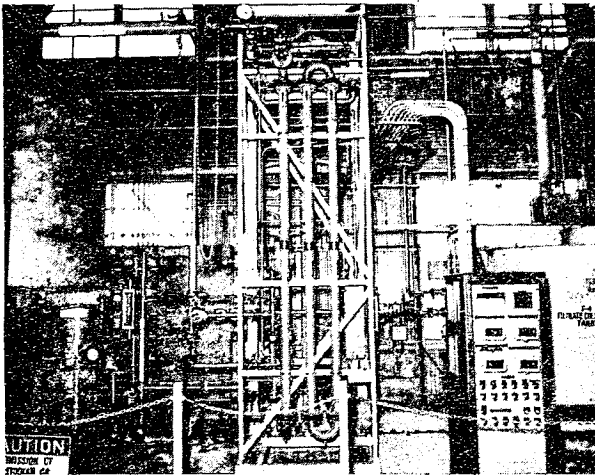


Fig. 4. Intermediate Scale Filtration Equipment for Engineering Studies (I-15427-3)

The filtrate passes to the shell side of the bundles and is collected in a backpulse reservoir. The reservoir is attached to an air source that delivers 90 psi backpulse air. This air source is periodically opened to reverse the flow of the filtrate forcing it through the filters and cleaning any plugging material off the filters. The filtrate passes to a collection tank and the main stream flow returns to the feed tank.

Initial filtration studies showed the potassium tetraphenylborate slurries to be shear sensitive. Tests conducted with a low-shear double diaphragm pump provided filtrate rates 4 to 5 times higher than a high-shear centrifugal pump. The diaphragm pump filtrate rates generally ranged from 0.15 to 0.33 gpm per square foot of filter area.

Several tests were run at various main stream velocities from 1.5 to 20 ft/s through the 5/8 in. ID filter tube. In general the filtrate rate was fairly independent of main stream velocity although at all filter differentials a small peak in filtrate rate could be observed between 2-4 ft/s. Filtrate rate was shown to be directly proportional to filter pressure

differential. Care must be taken in selecting the pressure drop; the rate and permanence of filter plugging increases with higher filter pressure drop. Generally the main stream pressure was maintained below 40 psi, at least 50 psi below the backpulse pressure.

Backpulse duration and interval was optimized at 0.5 sec and 5 min respectively at nearly all filter conditions. Although the backpulse significantly retards the rate of filter plugging, as with all filter operations, plugging is inevitable. After considerable run time the intermediate equipment plugged and cleaning methods were explored. In all tests a 0.2 M solution of oxalic acid returned the filters to their "as received" filtrate rates. Metallurgical results have shown that repeated washings of the filters with dilute oxalic acid exhibits no detrimental effects on the filter-pore size.

A full scale filter test unit was constructed at the ETF and is shown in Fig. 5. Four filter bundles, each containing 31 tubes, 10 foot long with 50 sq. ft. of filter per bundle were assembled in series operation. The facility provided confirmation of data obtained in intermediate and small scale equipment. One of the key functions of the full scale filter facility was to act as a host for equipment to be used in a plant test with actual radioactive waste. The filter bundles to be used in the radioactive test were approved at the ETF to be used in the plant test.

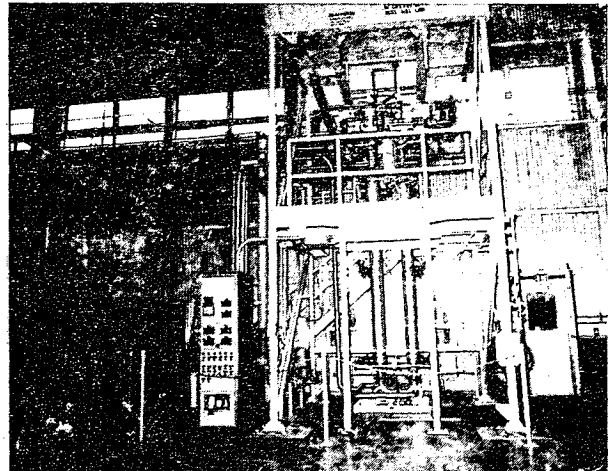


Fig. 5. Full-Scale Precipitation Test Facility (35784-6)

In-Tank Salt Decontamination Demonstration

In January 1983 the Precipitation Process for Salt Decontamination was demonstrated with actual High Level Waste. Approximately 450,000 gallons of waste supernate was transferred from Tank 24H at SRP to Tank 48, a new, double walled, 1.3 million gallon tank designed for supernate processing. The total Na^+ molarity in the solution was then adjusted to 5.5M. To the waste tank was added sufficient sodium tetraphenylborate and sodium titanate to remove the cesium and strontium.

* The Equipment Test Facility is a semiworks plant for testing large scale equipment with simulated waste.

After two days of reaction and mixing filtration was started. The filters, which were suspended in Tank 48 during construction, performed well throughout the three month demonstration. Both a diaphragm and a centrifugal feed pump were used during the testing and each produced satisfactory filtrate rates. Cesium DF for the entire demonstration was in excess of 43,000. Strontium was removed to the lower analytical detection limit, proving a DF of at least 200. During the demonstration all process chemistry and equipment functioned very well. Over 450,000 gallons of decontaminated supernate was produced during the three months of operation.

In conclusion, the Precipitation process for the decontamination of SRP supernate has been tested from the laboratory to full scale equipment. Using actual SRP waste the In-Tank Salt Decontamination Process has been shown to be a highly feasible and economical step toward the final disposition of liquid radioactive waste at the Savannah River Plant.

ACKNOWLEDGEMENT

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

REFERENCES

1. R. Maher, et al, "The Defense Waste Processing Facility - A Remote Process for Solidification of SRP High Level Waste," DPSPU-81-30-16, March 1982.
2. L. M. Lee and L. L. Kilpatrick, "A Precipitation Process for Supernate Decontamination," DP 1639, November 1982
3. E. B. Snell and C. J. heng, "Salt Decontamination Demonstration Test Results, DPSP-83-17-8, June 20, 1983