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SEPARATION OF SRP WASTE SLUDGE AND SUPERNATE

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ABSTRACT

Sludges and supernates were separated from Savannah River Plant waste slurries by centrifugation and sand filtration. This separation, a portion of a conceptual process for solidification and long-term storage of high-level radioactive wastes, was tested in shielded cells with small-scale process equipment. Procedures for the separation were developed in tests with nonradioactive materials. Then, in 13 tests with actual sludges and supernates, solids removal ranged from 90 to 99.2 vol % and averaged 96.4 vol % after two passes through a basket-type centrifuge. Centrates from the tests, containing 0.05 to 0.2 vol % solids, were clarified by sand filter columns to produce solutions of the soluble salts with <0.01 vol % solids. About 700 liters of salt solution and 8 kilograms of washed, dried sludges were separated in the tests. Effects of sludge type, flocculant, flow rates, and batch size were evaluated. Washing and drying of centrifuged sludges were studied, and two types of dryers were tested. Ruthenium volatility during drying was negligible. Washing efficiency was determined by analyses of wash solutions and sludge products.

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SEPARATION OF SRP WASTE SLUDGE AND SUPERNATE

INTRODUCTION

High-level radioactive wastes from operation of the Savannah River Plant (SRP) separations areas are made basic and stored in underground tanks. More than 20 million gallons (76 million liters) of high-level wastes are stored on the plantsite. A conceptual process for long-term management of these wastes has been proposed.[1] The process would include removal of wastes from the tanks, solidification in either concrete or glass, and storage in a retrievable surface storage facility (RSF) until shipment to a federal repository.

The operations shown in Figure 1 have been designated as the conceptual process for development studies and cost estimates. The process is divided into seven independent major operations or modules, including:

1. Removal of waste from tanks. Sludge, supernate, and salt cake are slurried with recycled water; most of the salt cake dissolves. Development of Module 1 includes studies on waste-tank cleaning that were made several years ago.[2]

2. Separation of sludge and supernate. A clarified salt solution containing most of the ^{137}Cs is produced. Solids are washed and dried to form sludge powder containing most of the ^{90}Sr, other fission products, and plutonium. A small-scale process study on Module 2 is the subject of this report.

3. Separation of ^{137}Cs from supernate. The ^{137}Cs is removed by ion-exchange sorption and elution. The cesium eluate is then concentrated and fixed on zeolite. Decontaminated salt solution (effluent from cesium sorption step) is produced. Small-scale studies on Module 3, reported separately,[3] proceeded in conjunction with work on Module 2.

4. Solidification of sludge and ^{137}Cs-zeolite. The conceptual process uses concrete as a matrix for immobilizing the powdered sludge and zeolite. Each concrete-waste casting is packaged in two containers. Glass has been proposed as an alternative to concrete as the solid waste form. Development studies on Module 4 have been made with both concrete[4] and glass[5,6] waste forms.

5. Evaporation of decontaminated salt solution produced in Module 3. The solution is evaporated in wiped film evaporators,[7] to yield monolithic salt that is packaged in single-walled containers. Evaporated water is used to slurry waste in the next tank.

6. Storage of concrete waste forms. Canisters of solidified waste are stored in an RSF.

7. Storage of decontaminated salt cake. Packaged salt is stored in an RSF.

This report focuses on Module 2 of the conceptual process. Steps in the sludge-supernate separation are described in the following section. Tests were made with small-scale process equipment at full levels of radioactivity. The equipment and the test procedures are described. Results of the tests with both simulated and actual SRP waste provide a technical basis for design of a large-scale process.
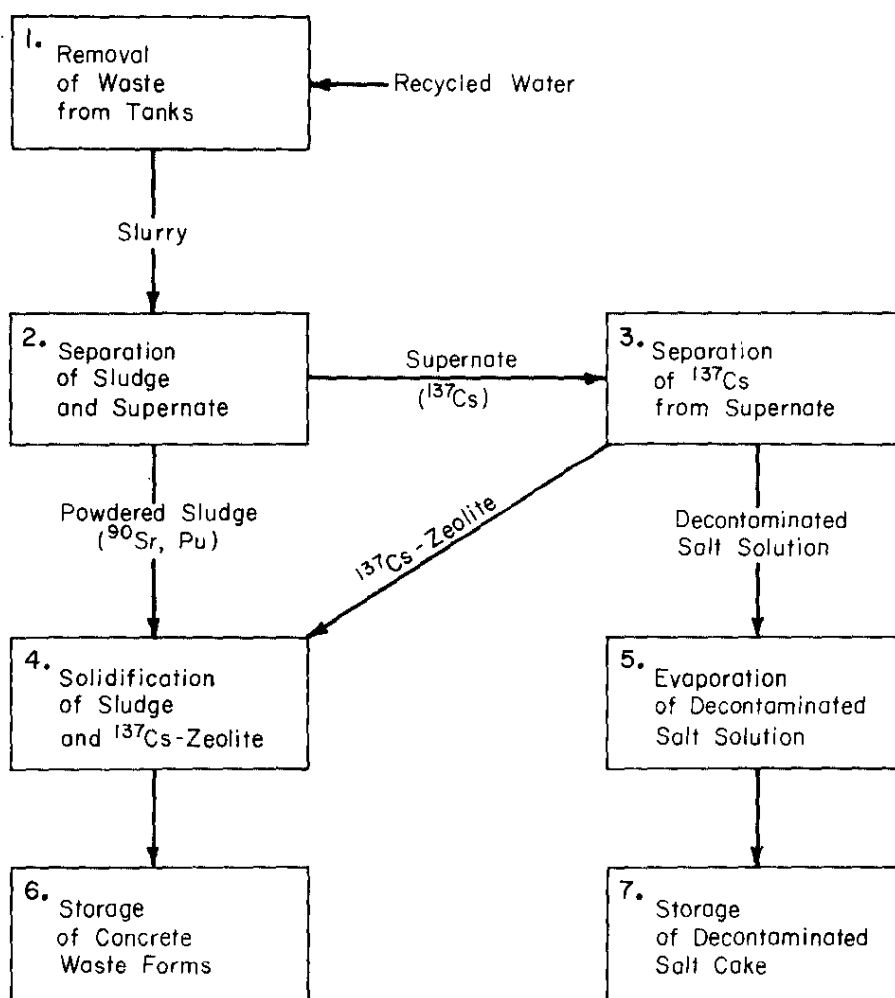
FIGURE 1. Conceptual Process for Solidification of SRP High-Level Waste

SLUDGE-SUPERNATE PARTITIONING

Steps in the sludge-supernate separation module of the conceptual process are shown in more detail in Figure 2. The primary separation is made by centrifugation, which removes ∿95 vol % of the solids from the feed slurry. The remaining solids in the centrate are removed by sand filtration, which produces a clarified salt solution suitable for ion-exchange feed in the cesium removal module. Centrifuged sludge is dried, washed, and redried, to yield a powdered product for fixation in the solidification module. The conceptual process for large-scale operations is described below. Small-scale studies simulated parts of the process.

Waste
Slurry

| Centrifugation | Centrate | Sand Filtration |

Sludge

Salt
Solution

First Drying

To
Cesium Removal
Process
(Module 3)

Washes

Second Drying

Washed, Dried
Sludge

To
Solidification
Process
(Module 4)

FIGURE 2. Sludge-Supernate Partitioning Module

The conceptual process requires two stages of centrifugation for initial partitioning of the sludge and supernate. The first centrifuge, operating at a relatively fast feed rate, removes the bulk of the solids. The centrate from the first centrifuge feeds the second centrifuge at a slower rate to remove most of the remaining solids. Small streams of flocculating agent are fed concurrently with slurries to promote agglomeration of sludge particles and thereby increase separation efficiency. Centrifugation is done batchwise. After each batch is centrifuged the small amount of centrate liquid remaining in a centrifuge is skimmed off.

For final clarification, the centrate is passed through a dual-media filter, usually referred to as a sand filter. Feed to the sand filter contains ∿5% of the solids in the original slurry. A small stream of flocculant is mixed with the feed near the top of the sand filter. At the end of each batch, the sand filter is backwashed to remove accumulated sludge particles, and the backwashes are returned t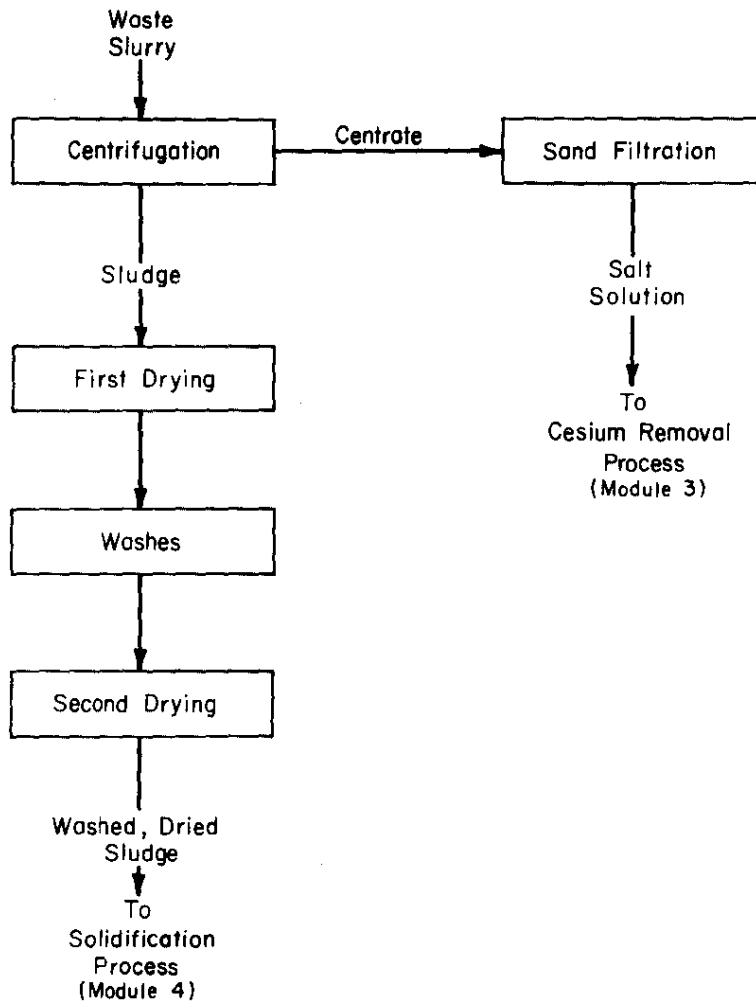o the first centrifuge feed for recycle. The filtrate from normal operation of the sand filter is clarified supernate containing soluble salts, ^{137}Cs, and residual (minor) amounts of ^{90}Sr and plutonium.

Batches of wet sludge cake from centrifugation are washed and dried in typical large-scale process equipment, to remove the large mass (60-80%) of soluble salts retained in the sludge. An initial drying is necessary to destroy the gelatinous properties of wet sludge. Two stages of washing are provided, in each of which the sludge is reslurried with water to dissolve soluble salts. Each stage consists of a washer and a centrifuge to remove spent wash-water for recycle. The washed sludge is dried in a second dryer, yielding a product containing nearly all of the ^{90}Sr and plutonium, and a residual amount of ^{137}Cs.

For the small-scale studies described in this report, emphasis was placed on obtaining process information on the centrifugation and sand filtration steps. Secondary goals were to provide clarified supernate for cesium-removal tests (Module 3), and to prepare washed, dried sludges for characterization and future solidification. Because these studies were not intended as a full demonstration of the entire module, several departures from conceptual process conditions were made. For example, the primary sludge-supernate separation was performed by two passes through a single small-scale centrifuge, rather than using two centrifuges in series. Sludge washing and drying operations were by methods that were convenient on the small scale, and did not simulate the large-scale unit operations.

A number of process effects and parameters were investigated in the tests. These included:

- Sludges from different waste tanks and areas

- Various flow rates for slurry and flocculant

- Elimination of flocculant

- Various batch sizes

- Sand filter efficiency

- Various drying techniques

- Ruthenium volatility during sludge drying

- Sludge washing efficiency

- Yields of sludge products

The tests were performed with small-scale process equipment described in the following section.

SMALL-SCALE PROCESS EQUIPMENT

Several pieces of equipment for small-scale sludge-supernate separations were modified for remote operation and assembled into an operating system in the shielded cell facilities at the Savannah River Laboratory (SRL). The system included a basket-type centrifuge and a sand filter similar to those proposed for large-scale operation. In addition, two types of dryers were tested. Various auxiliary equipment, such as pumps, flowmeters, and tanks, completed the system.

Centrifuge

A top view of the small-scale centrifuge (De Laval Separator Co., Hyde Park, Mass.) is shown in Figure 3. The basket-type stainless-steel bowl is 12 in. (30.5 cm) in diameter by 5.5 in. (14 cm) high. The solid bowl is mounted on a resilient spindle that is belt-driven by an electric motor. The speed of rotation may be adjusted by varying the tension on the drive belt. For the tests described in this report the centrifuge was operated at 2750 rpm or about 1300 G, to simulate the centrifugal force in a production-size machine. Bowls are interchangeable and are attached by a single nut for ease of removal. Other features of the centrifuge, not shown in Figure 3, are a cover plate, a linear skimmer, and a brake.

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During centrifugation, a slurry is fed into the rotating centrifuge bowl at a point about midway between the center and outer rim. Solids are forced to the inner wall of the bowl. Liquid is also thrown uniformly to the wall, eventually filling the bowl, overflowing into the stainless-steel curb, and emerging as centrate from an outlet pipe. After the startup period during which the bowl fills, sludge-supernate separation depends upon residence time in the bowl, and thus upon the feed rate. In principle the separation could continue until the thickness of the solids cake reached the lip of the bowl. However, solids contents of batches used in the present tests were much below this limiting value. To terminate a separation, the excess liquid between the bowl lip and the cake is skimmed from the rotating bowl.
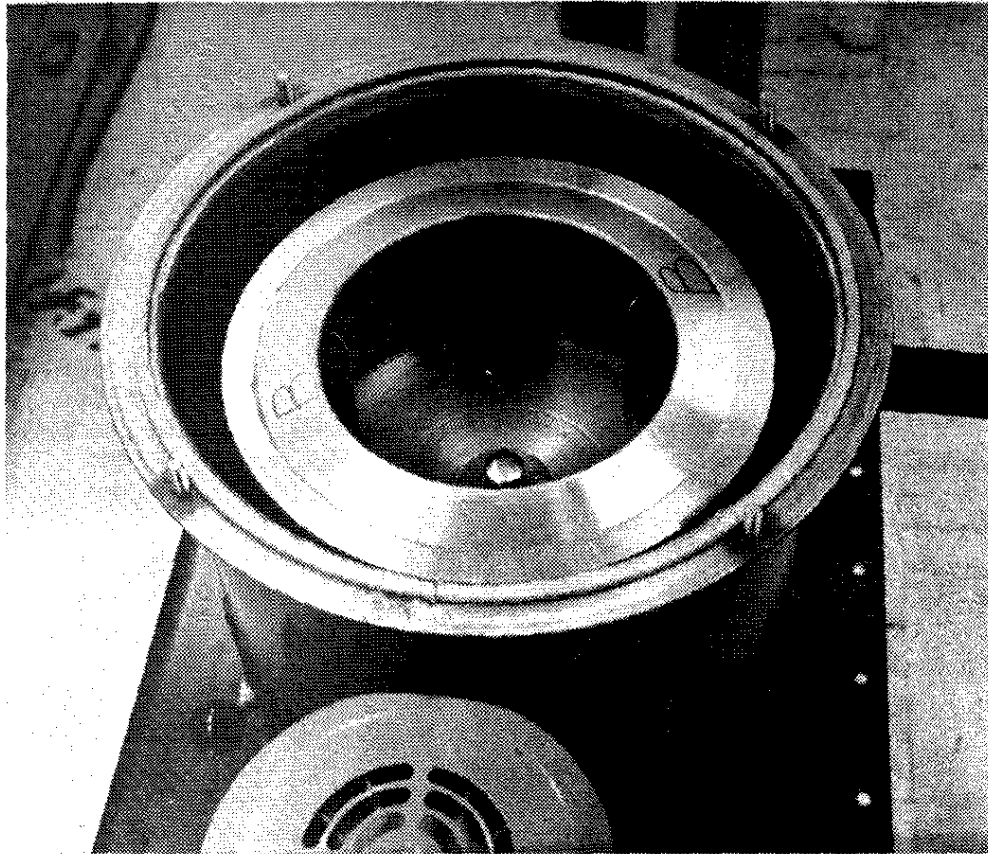
FIGURE 3. Top View of 12-in. (30.5 cm) Basket Centrifuge

The centrifuge and bowl were also useful for washing and drying sludge. In one method of drying, the bowl containing wet sludge cake was placed in a heater to dry, eliminating a difficult sludge unloading step. The sludge was also washed in the centrifuge bowl. With the bowl stationary in the centrifuge, wash water was added, and the cake was reslurried with a stirrer; after the slurry was stirred for one hour, the centrifuge was started to separate the washed solids from the liquid, which was removed by skimming.

Sand Filter

The sand filter consists of two stainless-steel columns in series (Figure 4), filled with finely graded sand and anthracite coal. Each column is 4 in. (10.2 cm) in diameter by 51 in. (129.5 cm) long, with the filter bed composed of 24 in. (61 cm) of sand and 8 in. (20.3 cm) of coal. Piping, valves, and pressure gauges are provided for operating and for backwashing the sand filter in various ways.
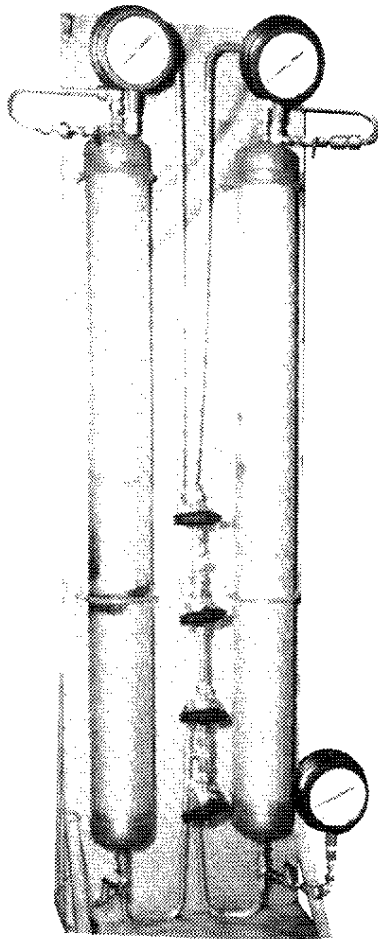
FIGURE 4.
Sand Filter Columns

For the small-scale studies, the sand filter was operated batchwise. Centrate was pumped through the sand filter at 400 ml/min, and flocculant was fed at 20 ml/min. The filtrate was stored for subsequent use in cesium-removal studies. After each batch, the sand filter was backwashed with water at 10 l/min for 4 minutes to remove accumulated sludge particles.

Dryers

Two types of sludge dryers were tested for small-scale batch operations. An oven-like heater for direct drying of sludges in a centrifuge bowl was used in most tests. A semi-continuous rotary dryer was also developed.

Figure 5 shows the centrifuge bowl dryer. A simple container holds a band heater and insulation around the wall, and the floor is covered with firebrick material. Evaporated water and other gases flow through a lid to the offgas system. Temperature is measured by metal thermometers inserted through the lid and in the air gap between heater and bowl. With this arrangement, a batch of sludge typically can be dried in 16 to 24 hours at 140°C. After sludge and bowl cool, they can be returned to the centrifuge for washing, or dried product can be scraped from the bowl.

Figure 6 shows the rotary dryer, which consists of heated rotating drums fed with wet sludge forced from a hydraulic chamber. The sludge is spread uniformly into a thin film by being squeezed between the two drums. The film of sludge dries quickly and is scraped off the slowly rotating drum after a half rotation. A batch of sludge can be dried in about two hours. With the rotary dryer, wet sludge must be transferred from the centrifuge bowl to the hydraulic chamber.

Auxiliary Equipment

Other equipment used in the small-scale separations of sludge and supernate included four pumps to handle various liquid streams, a magnetic flowmeter for measuring slurry flow rates to the centrifuge, two 70-liter tanks for feed and centrate, and a high-speed test-tube centrifuge for measuring solids content of slurry samples.

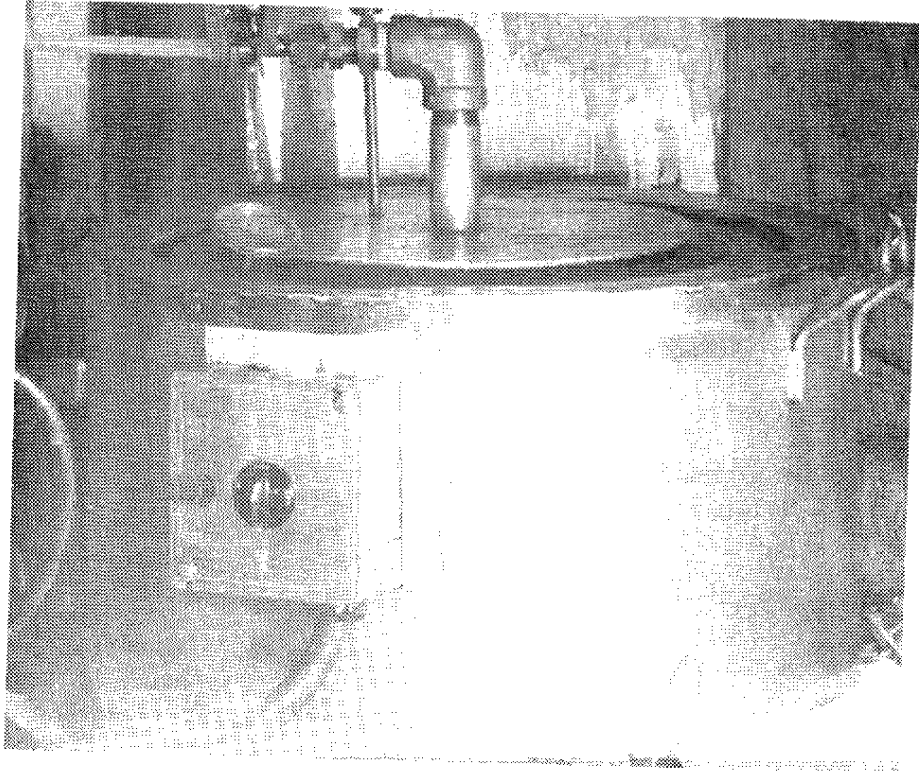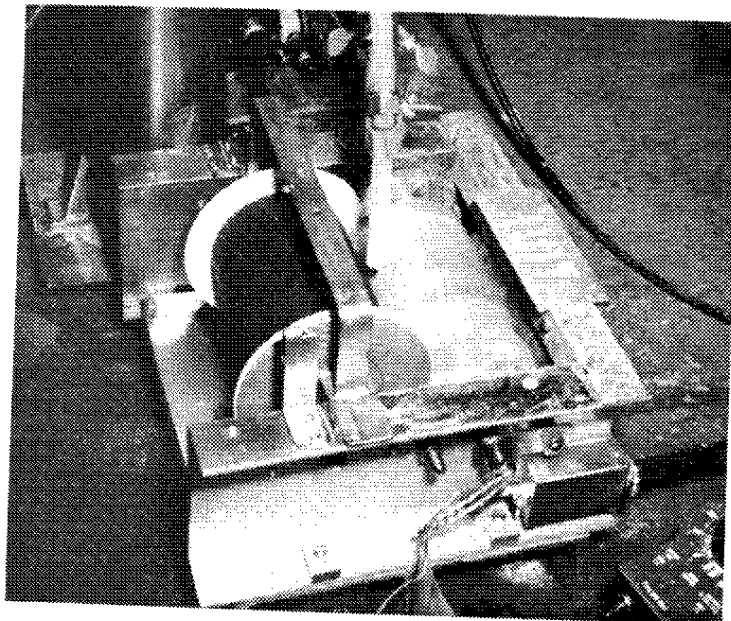FIGURE 5. Centrifuge Bowl Dryer

FIGURE 6. Rotary Dryer

Slurries of waste were fed to the centrifuge and transferred between the two tanks by a stainless-steel centrifugal pump (Sethco Manufacturing Co., Freeport, NY). The slurry pump has a double stuffing box with graphite asbestos packing. The seals are cooled by an external water line arranged to permit small leakage into the seals, rather than outward. The pump provides flow rates up to 8 l/min in the test system, while simultaneously recirculating the remaining slurry to prevent settling.

Flocculant was fed to the centrifuge with a variable-speed tubing pump (Cole-Parmer Instrument Co., Chicago, Ill.). Flow rates from 70 to 490 ml/min were measured by precalibrating the pump speed control with the solution to be pumped.

Centrate and flocculant were fed to the sand filter with two small bellows pumps (Gorman-Rupp Industries, Bellville, Ohio). Centrate was fed at 400 ml/min by a pump incorporating a 1.5-in. (3.8 cm) bellows, and flocculant was fed at 20 ml/min by a pump with a 0.5-in. (1.3 cm) bellows.

A magnetic flowmeter with stainless steel tube, flanges, and float (Wallace & Tiernan, Belleville, NJ) measured slurry feed rates to the centrifuge. An ordinary rotameter-type flow-meter would have been undesirable for this application because of difficulty in reading with the darkly colored slurries. The magnetic flowmeter was precalibrated with slurries over the range 0 to 7.6 l/min.

Tanks for feed slurry and centrate were cylindrical 70-liter stainless steel vessels, open at the top. Volume of liquid in a tank was indicated by a calibrated wooden rod attached to a float.

Figure 7 shows the centrifuge and some of the auxiliary equipment in a mock-up cell, with the same arrangement later used in a shielded cell. The slurry pump, magnetic flowmeter, and 70-liter tanks are shown. Movable inlet and outlet lines for the slurry pump provided operating flexibility with a single pump.

Solids in samples of feed slurries and centrate streams were measured with a small high-speed centrifuge (De Laval Separator Co., Poughkeepsie, N.Y.). Calibrated centrifuge cones with capillary tips were used to measure solids contents down to 0.01 volume %. With only minor modifications, this centrifuge was operated remotely for routine solids determinations in a shielded cell.
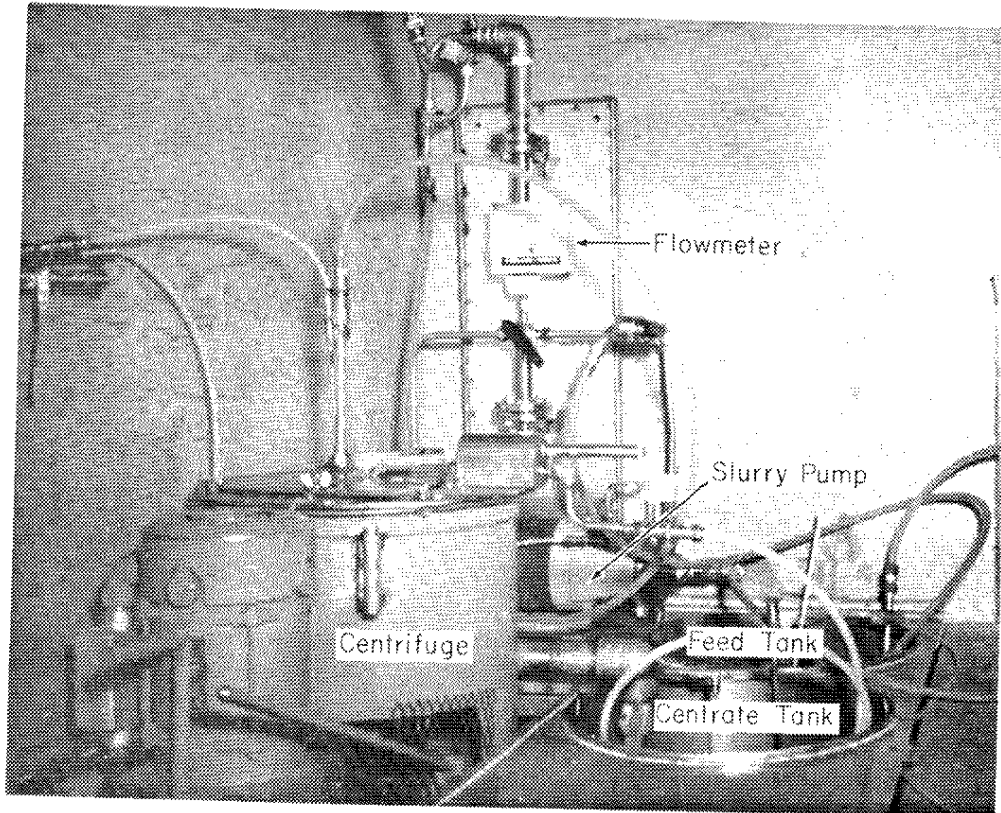
FIGURE 7. Equipment Arrangement for Operation in a
Shielded Cell

TESTS WITH SIMULATED SRP WASTES

Several components and operations of the sludge-supernate
partitioning module were tested with simulated (nonradioactive)
wastes before remote operations were performed in a shielded
cell. Centrifuge tests with simulated waste slurries provided
data for comparison with results for actual wastes. Washing
and drying procedures were developed with the simulated-sludge
products from some of the tests.

About 200 liters of each of three types of slurries were
prepared for tests on simulated waste. The sludge components
simulated the chemical compositions of sludges in three SRP
waste tanks.[8] Each sludge contained the hydrous oxides of five
principal elements of the actual sludge, as shown in Table 1.
Procedures for preparing simulated sludges have been given
previously.[4] The sludges were slurried with a simulated super-
nate[9] (Table 2) to give ~5 vol % solids in each.

TABLE 1

Composition of Simulated Sludges, mole %

	Tank 5F	*Tank 13H*	*Tank 15H*
Fe	58	50	4
Mn	23	16	3
Al	7	27	92
Ca	2	6	0.5
Ni	10	1	0.5

TABLE 2

Composition of Simulated Supernate

Salt	*Concentration, M*
$NaNO_3$	2.60
$NaNO_2$	1.45
Na_2SO_4	0.40
Na_2CO_3	0.40

Three centrifuge tests with each type of slurry were made with procedures to be used for actual wastes. Some refinement of the procedures (given in the following section) was possible as the tests progressed. In a centrifuge test, 50 liters of slurry were passed through the centrifuge two or three times under different conditions of feed rate and flocculant usage. With each sludge, the first test was without flocculant; a relatively slow feed rate of 2.2 l/min was used for three passes (two with Tank 15H sludge). The second test also had slurry feed rates of 2.2 l/min for two passes, but with flocculant (Betz 1100) fed at 140 ml/min for the first pass and 70 ml/min for the second pass. In the third test, the slurry feed rate for the first pass was increased to 6.2 l/min with flocculant at 470 ml/min; conditions for the second pass were the same as for the preceding test, 2.2 l/min for slurry and 70 ml/min for flocculant.

The separations achieved in the nine centrifuge tests with simulated waste slurries are shown in Table 3. For each test the cumulative solids removal for each pass is shown. In all tests but one, >95 vol % of the solids were removed from the final centrates. Comparison of tests with and without flocculant shows that good separations were achieved either way; these data give little evidence of beneficial effects from flocculant. Slurries of simulated Tank 5F and Tank 15H wastes were separated better than were slurries of simulated Tank 13H waste. A third pass improved the separation of Tank 13H slurry, but not the other two separations. As expected, the high feed rate for the first pass removed fewer solids than did the slow feed rate; however, the second pass at the slow feed rate gave satisfactory cumulative results.

Mechanical effects in the centrifuge strongly affected the degree of separation. Experiments prior to installation in the shielded cell showed that spindle type, bowl balance, and leveling of the centrifuge were important for proper operation. A rigid spindle originally installed in the centrifuge caused excessive vibration above 1800 rpm, but substitution of a resilient spindle produced satisfactory operation. Centrifuge bowls, although interchangeable, were not identical in balance, thus affecting performance at the operating speed. If the centrifuge was not sufficiently level, two effects occurred: a) liquid-solid separation would cease because of an oscillatory motion of the bowl, and b) excessive forces on the spindle would cause bearings to wear out prematurely. With proper leveling and balancing, the centrifuge separated slurries satisfactorily.

TABLE 3

Centrifuge Tests with Simulated Waste Slurries

Test	Centrifuge Pass	Flow Rate, 1/min		Cumulative Solids Removal, vol %		
		Slurry	Flocculant	Tank 5F	Tank 13H	Tank 15H
A	1	2.2	0	98	80	98
	2	2.2	0	98	93	98
	3	2.2	0	99	96	-
B	1	2.2	0.14	98	87	96
	2	2.2	0.07	98	95	98
C	1	6.2	0.47	75	75	92
	2	2.2	0.07	95	93	97

Sludge drying methods were investigated in preliminary experiments with nonradioactive sludges separated during the centrifuge tests. In-bowl drying was tested by heating a centrifuge bowl containing wet sludge cake at 140°C overnight in a laboratory oven. The sludge dried satisfactorily, and heating did not harm the bowl. These drying tests led to development of the bowl dryer shown in Figure 5.

For convenience in remote operations, a method of washing sludge in the bowl, while it is mounted in the centrifuge, was developed using sludges from four centrifuge tests. Samples of the sludge and washes were analyzed[10] for Na^+, NO_3^-, NO_2^-, and SO_4^{2-}, to determine washing efficiency. The washes also were analyzed for CO_3^{2-} and $Al(OH)_4^-$. Some typical results are given in Table 4, where material balances reflect analytical uncertainties. Three washes of $\sim$4 liters each were judged satisfactory for the simulated sludges.

The sand filter was tested once with centrate from a centrifuge test with simulated waste slurry. Filtration and backwashing behavior were satisfactory. Most of the development was done with earlier models of the sand filter.

TABLE 4

Typical Analyses of Tank 15H Simulated Sludges and Washes

	Quantity	Na^+ Conc	Moles	Grams	NO_3^- Conc	Moles	Grams
Unwashed Sludge	762 g	24.0 wt %	7.95	183	33.8 wt %	4.16	258
Washes:							
First	3.34	1.45M	4.84	111	0.742M	2.48	154
Second	3.60	0.39M	1.40	32	0.189M	0.68	42
Third	3.68	0.10M	0.36	8	0.050M	0.18	11
Total	10.62 liters		6.60	151		3.34	207
Product Sludge	97 g	11.1 wt %	0.47	11	2.7 wt %	0.04	3

TESTS WITH ACTUAL SRP WASTES

Procedure

Sixteen 3-liter batches of high-level waste sludges were collected from seven SRP waste tanks, by methods developed in an earlier sampling campaign.[8] Sludges were obtained from Tanks 4, 5, and 6 in F Area, and Tanks 12, 13, 15, and 16 in H Area. Waste supernates were obtained in 40-liter batches[3] from Tanks 15H and 34F. Waste slurries were reconstituted from sludge, supernate, and nonradioactive chemicals added to adjust concentrations to conditions specified in the conceptual process. The supernate concentrations after adjustment are given in Table 5; generally, the supernates were diluted to reduce OH^- concentration to the desired value, and appropriate quantities of the other salts were added.[3] From these sludge and supernate batches, 13 centrifuge tests were made, and the liquids and solids from the tests were further processed to yield clarified salt solution and washed, dried sludge powder. Conditions for the 13 tests are given in Table 6. A general procedure, used with occasional variations in all the tests, is given below. All operations with radioactive waste slurries were performed in shielded cells.

TABLE 5

Adjusted Composition of Actual Supernates

	Concentration, M
$NaAlO_2$	0.50
NaOH	0.75
$NaNO_3$	2.2
$NaNO_2$	1.1
Na_2SO_4	0.3
Na_2CO_3	0.3
$CsNO_3$	0.0002

TABLE 6

Centrifuge Test Conditions with Actual Waste Slurries

Test	Tank	*Flow Rate, 1/min*				*Carrier Precipitant*
		First Pass		*Second Pass*		
		Slurry	*Flocculant*	*Slurry*	*Flocculant*	
1	13H	1.9	0	1.9	0	None
2	13H	1.9	0.14	1.9	0.07	$Sr_3(PO_4)_2$
3	13H	6.6	0.49	1.9	0.07	$Sr_3(PO_4)_2$
4	5F	1.9	0	1.9	0	$Sr_3(PO_4)_2$
5	5F	1.9	0.14	1.9	0.07	$Sr_3(PO_4)_2$
6	5F	6.6	0.49	1.9	0.07	$Sr_3(PO_4)_2$
7	4F,6F[a]	4.7	0.35	1.9	0.07	$Sr_3(PO_4)_2$
8	15H	3.8	0.28	1.9	0.07	None
9	15H	3.8	0[b]			
		3.8	0.28	1.9	0.07	$Sr_3(PO_4)_2$
10	16H	5.7	0.42	1.9	0.07	$FeCl_3$
11	16H	5.7	0[b]			
		5.7	0.42	1.9	0.07	$ZrO_2 \cdot xH_2O$
12	12H	7.6	0.49	1.9	0.07	$CaCO_3 + FeCl_3$
13	12H	1.9	0.07	1.9	0.07	None

a. Double batch.

b. Reslurried after preliminary pass with no flocculant.

Feed Preparation

Waste slurry for centrifuge feed was prepared by mixing measured quantities of actual sludge, simulated supernate, and actual supernate in the feed tank. The mixture was allowed to stand overnight to permit additional solids to precipitate. Typically, ∿3 liters of SRP sludge was mixed with supernate to give 50 liters of slurry. Prior to a centrifuge test the slurry was agitated for one hour with the slurry pump operating in the recirculation mode, to simulate the shearing action of waste tank slurry pumps. The slurry was then sampled and measured for solids content.

Flocculant Preparation

Flocculant solution (1000 ppm) was prepared in 10-liter batches, no earlier than one day before a centrifuge test. 10.0 g of solid flocculant (Betz 1100) was slurried in a small volume of isopropyl alcohol and added to ∿3.5 liters of water in a beaker. The mixture was heated at ∿50°C with gentle stirring for 4 hours, to give a clear solution. After cooling, the solution was transferred to a bottle and diluted to 10 liters. Flocculant solution was fed to the centrifuge with a tubing pump, from outside the shielded cell.

Centrifugation

A centrifuge test started with the bowl empty and rotating at full speed. The flocculant flow was started, immediately followed by feed (slurry) flow, at measured flow rates. Centrate was collected in the centrate tank. A sample was taken from the centrate stream after each 10 liters of centrate was collected, as determined by timed intervals. When the feed tank was empty, the flocculant flow was stopped. Residual liquid in the centrifuge bowl was removed by skimming into a calibrated glass bottle; typically, 2 to 4 liters were collected. The skimmed liquid and bottle rinsings were blended with the centrate in the centrate tank. The volume of centrate was measured, the centrate was thoroughly mixed by recirculation with the slurry pump, and a sample was taken for measurement of solids content.

For the second pass through the centrifuge, the centrate was pumped back to the unrinsed feed tank; the centrate tank was rinsed with ∿2 liters of water, and the rinsings were added to the feed tank. In those tests in which carrier precipitation[3] of ^{90}Sr was tested, 250 ml of a precipitant solution (identified in Table 6) was poured into the feed tank. Volume measurement, agitation, sampling, and measurement of the solids content were repeated for the slurry in the feed tank. The centrifugation operations then were repeated, typically with slower feed and flocculant flow rates than for the first pass. When the feed tank was empty, it was rinsed with ∿2 liters of water, and the rinsings were fed to the centrifuge. After the second-pass skimming, the centrifuge was stopped.

First Drying

Drying operations were done in the centrifuge bowl dryer for most of the tests. After removing any excess liquid from the bowl and sampling the wet cake for analysis, the bowl was removed from the centrifuge and placed in the dryer. For the first drying, the sludge was heated at ∿140°C with a good off-gas

sweep until the cake was dry, typically overnight. In a few tests the off-gases were bubbled through a trap containing 2M NaOH to measure possible ruthenium evolution. When drying was complete, the bowl was removed from the oven and cooled.

Washes

To wash the sludge, the bowl containing dried sludge was placed into the centrifuge, and the cake was broken up mechanically. Then, 4 liters of water were jetted into the bowl to further break up the cake and wash down the inner wall. The contents of the bowl were agitated for 1 hour with an electric stirrer to reslurry the cake. With the stirrer removed, the centrifuge was started carefully, to ensure good balance with the full bowl. The cake was centrifuged for 10 minutes, and then the wash liquid was skimmed out of the bowl into a glass bottle. After skimming was completed, the centrifuge was stopped. The volume of the wash liquid was measured, a sample was taken for analysis, and the excess wash was discarded. For second and subsequent washes, the operations were repeated with 4 liters of fresh wash water. Typically, 3 washings were performed. Excess liquid was removed from the bowl after the final wash.

Second Drying

For the second drying, the bowl containing washed sludge was removed from the centrifuge, placed in the dryer, and heated as before, until the cake was dry. After cooling, the washed, dried cake (product) was removed from the bowl mechanically. The product was pulverized, weighed, sampled for analysis, and stored for possible future use. The centrifuge bowl was cleaned in preparation for another test.

Sand Filtration

Centrate from centrifugation operations was stored in the centrate tank and/or in 50-liter polyethylene bottles, until needed for cesium-removal process steps[3] (Module 3). Then, batches of 50 to 150 liters of centrate were passed through the sand filter for clarification. During sand filtration, the centrate was agitated with the slurry pump and transferred to the sand filter at 400 ml/min with a bellows pump. Dilute flocculant solution (1 ppm) was pumped to the sand filter at 20 ml/min with another bellows pump. Filtrate was collected in the feed bottle for the cesium-removal process. When the centrate container was

empty, it was rinsed with 2 liters of water, the rinsings were fed to the sand filter, and then the flocculant flow was stopped. At the end of the filtration, the filtrate was sampled for measurement of solids content. The sand filter was backwashed after each use.

Process Variations

In a few tests, parts of the procedure were altered to accommodate special conditions. For example, in Test 7, 100 liters of slurry were processed to study the effects of increased cake volume on the separation. The larger slurry volume required extra 50-liter storage bottles and additional manipulations; each centrifuge pass was divided into two parts to permit changing feed and centrate containers.

In Tests 9 and 11, an extra pass through the centrifuge was made to evaluate a proposal to operate normally without flocculant and to recycle with flocculant any centrate with high solids content. During these tests, in a preliminary pass, slurry was fed to the centrifuge without flocculant, residual liquid was skimmed, and the centrifuge was stopped. The centrate was pumped back into the bowl to reslurry the cake, and the reslurried material was transferred to the feed tank. Then, centrifugation operations were resumed with flocculant as with other tests.

Sludge was washed three times in all tests except Tests 3 and 7. In Test 3 the sludge was washed five times to study the effect of additional washes. In Test 7 the double batch of sludge was washed six times because of the larger volume of sludge.

The rotary dryer (Figure 6) was evaluated with the second drying step in Test 11, and with both drying steps in Tests 12 and 13. Wet sludge cake was scraped from the centrifuge bowl and placed in the hydraulic chamber of the dryer. After the sludge was dried, it was returned to the centrifuge bowl for reslurrying with wash water. After a second drying the product was pulverized and stored.

Results

Solids contents and specific gravities were determined for samples of the feed slurry, centrate, and centrate stream in each of the 13 tests. Typical data for a test are given in Table 7. Specific gravities, calculated from volume and weight measurements, ranged from 1.18 to 1.30 and were correlated with solids contents of the liquids.

TABLE 7

Typical Centrifuge Test Data (Test 6)

	Centrate Volume, liters	First Pass		Second Pass	
		Sp G	Solids, vol %	Sp G	Solids, vol %
Feed Slurry		1.27	3.0	1.21	0.2
Centrate Stream	10	1.22	0.2	1.19	0.05
	20	1.23	0.3	1.19	0.05
	30	1.24	0.3	1.19	0.05
	40	1.24	0.2	1.19	0.05
	50	1.09	0.1	1.18	0.04
Centrate Tank		1.22	0.1	1.18	0.05

Solids removal in the first centrifuge pass depended on the feed rate, the type of sludge, and the use of flocculant, as shown in Figure 8. In the centrifuge tests, 50 to 97.5 vol % of solids in the feed slurries were separated in the first pass. For sludges from Tanks 12H and 13H, the solids removal decreased with increasing feed rate; the solids removal was nearly independent of feed rate for Tank 5F sludge. Tests without flocculant gave better separations than the tests with flocculant in two of the three comparisons made. In general, the first-pass separations behavior of the actual sludges was similar to that of simulated sludges (Table 3).

Cumulative solids removal after the second centrifuge pass is given in Table 8 for each of the 13 tests. In every test, the feed rate was 1.9 l/min for the second pass. The cumulative solids removal ranged from 90.0 to 99.2 vol %. Solids contents of the centrates after two passes through the centrifuge ranged from 0.05 to 0.2 vol % and averaged 0.11 vol %. These centrates were fed to the sand filter for further reduction of solids content.

For every batch of centrate passed through the sand filter, the filtrate had <0.01 vol % solids (the minimum detectable level). The sand-filter product was suitable for further processing to remove cesium by ion exchange.[3] The sand-filter columns operated very reliably during the small-scale process studies.

Results of Test 7 showed that batch-size effects were unimportant. In this test the quantity of supernate was doubled, and four batches of sludge were blended to give a slurry with high solids content. 97.5 vol % solids removal was achieved in two passes. Measurements of solids in centrate stream samples

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showed no reduction in degree of separation as the cake increased
in depth. Presumably, adequate centrifugal separation could have
continued until the cake filled the bowl entirely; 200 to 300
liters of slurry could have been processed before the bowl would
be full of sludge cake.

Tests 9 and 11 showed that material that has passed through
the centrifuge can be reslurried and recycled. By adding flocculant
during the recycle operation, good separations were obtained.
Because other tests suggested that operating without flocculant
would be satisfactory in most cases, Tests 9 and 11 demonstrated
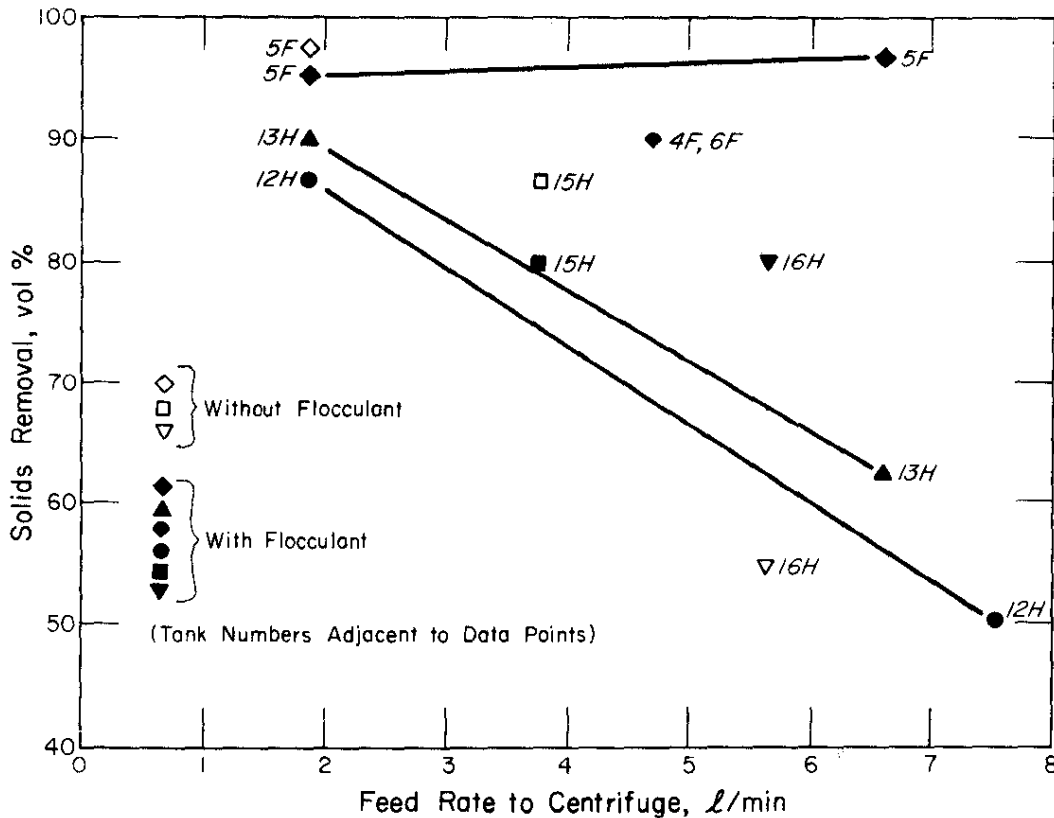a method to handle the exceptions.

FIGURE 8. Solids Removal in First-Pass Centrifugation
of SRP Waste Slurries

TABLE 8

Centrifuge Test Results with Actual Waste Slurries, vol %

Test	Solids in Feed Slurry to		Cumulative Solids Removal	
	Centrifuge	Sand Filter	First Pass	Second Pass
1	1.5	0.15	a	90.0
2	3	0.06	90	98.0
3	4	0.15	62.5	96.3
4	2	0.07	97.5	96.5
5	2	0.07	95.5	96.5
6	3	0.05	96.7	98.3
7	4	0.10	90	97.5
8	4	0.08	80	98.0
9	6		86.7[b]	
	5	0.05	96.7	99.2
10	4	0.20	80	95.0
11	4		55[b]	
	2	0.08	82	98.2
12	4	0.20	50	95.0
13	3	0.15	86.7	95.0
Average		0.11		96.4

a. Not measured.

b. Reslurried after preliminary pass.

Drying and washing operations for the centrifuged sludge cake from each test are described in Table 9, together with the yield of washed, dried sludge powder from each test. Samples of wet cakes, wash liquids, and dried products were analyzed[10] for Na^+, NO_3^-, NO_2^-, SO_4^{2-}, ^{90}Sr, and $^{134,137}Cs$. The solids also were analyzed for alpha emitters and for other gamma emitters. The wash liquids were analyzed for OH^-, CO_3^{2-}, and $Al(OH)_4^-$. Table 10 gives some typical analytical data showing the efficiency of the method of washing; as with the simulated sludges, the material balances are imperfect because of analytical uncertainties. One batch of washed, dried sludge product from each waste tank was analyzed for elemental composition. Chemical and radionuclide content of major species is given in Table 11.

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TABLE 9

Washed, Dried Sludges

Test	Dryer	Washes	Yield, grams
1	Bowl	3	265
2	Bowl	3	513
3	Bowl	5	471
4	Bowl	3	596
5	Bowl	3	931
6	Bowl	3	1,065
7	Bowl	6	1,335
8	Bowl	3	698
9	Bowl	3	914
10	Bowl	3	517
11	a	3	328
12	Rotary	3	264
13	Rotary	3	320

a. First Drying: Bowl
   Second Drying: Rotary

TABLE 10

Typical Analyses of Tank 15H Actual Sludges and Washes (Test 8)

	Quantity	Na^+ Conc	Moles	Grams	NO_3^- Conc	Moles	Grams	^{137}Cs Activity Conc[a]	Total, dis/min
Unwashed Sludge	~1800 g	11.58 wt %	9.08	209	19.1 wt %	5.54	343	1.75×10^9	3.15×10^{12}
Washes:									
First	3.25	2.01M	6.53	150	0.507M	1.65	102	3.78×10^8	1.23×10^{12}
Second	3.45	0.35M	1.21	28	0.148M	0.51	32	9.58×10^7	3.31×10^{11}
Third	3.80	0.09M	0.36	8	0.035M	0.13	8	2.08×10^7	7.90×10^{10}
Total	10.50 liters		8.10	186		2.29	142		1.64×10^{12}
Product Sludge	698 g	2.04 wt %	0.62	14	0.2 wt %	0.03	2	4.30×10^8	3.00×10^{11}

a. dis/(min)(g) for sludges; dis/(min)(ml) for washes

TABLE 11

Principal Components of Washed, Dried Sludges

		Tanks 4F,6F (Test 7)	Tank 5F (Test 6)	Tank 12H (Test 13)	Tank 13H (Test 3)	Tank 15H (Test 9)	Tank 16H (Test 11)
A.	Principal Metal Ions, wt %						
	Fe	32.77	28.90	4.49	25.57	5.29	13.91
	Al	2.28	1.57	30.16	8.70	18.75	16.61
	Mn	1.99	5.83	1.69	7.85	2.45	2.59
	U	9.22	10.81	a	4.18	3.77	4.49
	Na	2.95	5.66	1.03	2.58	2.45	2.19
	Sr	1.70^c	1.29^c	b	3.50^c	1.80^c	b
	Ca	2.28	0.90	2.13	1.76	0.52	2.87
	Hg	0.65	0.12	1.12	2.32	2.51	2.80
	Ni	6.29	6.34	0.46	0.45	0.73	0.30
B.	Principal Anions, wt %						
	NO_3^-	0.12	1.16	0.42	0.31	0.19	0.32
	NO_2^-	0.02	0.12	0.17	0.01	0.16	0.15
	SO_4^{2-}	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	PO_4^{3-}	0.69^c	0.32^c	b	2.15^c	2.87^c	b
C.	Principal Radionuclides, mCi/g						
	^{90}Sr	123.0	177.5	41.4	30.1	55.0	53.6
	^{144}Ce	30.5	1.5	17.4	0.3	5.4	0.6
	^{106}Ru	11.4	1.3	1.7	0.08	1.0	0.2
	^{137}Cs	0.7	0.9	0.05	0.3	0.1	0.2
	^{154}Eu	0.7	0.6	0.5	0.08	0.4	0.1
	^{125}Sb	1.4	0.9	0.3	0.06	0.3	0.04
	^{60}Co	1.1	1.1	<0.01	0.01	0.06	0.02
	Gross α	0.4	0.1	0.7	0.2	0.1	0.15

a. None detected.

b. Not determined.

c. $Sr_3(PO_4)_2$ carrier added.

Ruthenium volatility from sludge dried at 140°C was negligible. Traps for ruthenium evolved during drying were analyzed for ^{106}Ru, and none was detected. Also, the amount of ^{106}Ru measured in unwashed and washed sludges was approximately constant, showing that very little could have been lost by volatility.

Operation of the centrifuge bowl dryer was satisfactory for the 21 dryings for which it was used, although each drying required at least 16 hours. The rotary dryer was tested in 5 dryings, with mixed results. Dryings were rapid, in 2 hours or less, but in some cases difficulties were encountered with sludge adhering to rollers. This occurred only with some of the actual sludges and not with simulated sludges. Further development of the rotary dryer concept would be required for routine use.

CONCLUSIONS

The results of the small-scale process studies led to the following conclusions:

1. Slurries from SRP waste tanks can be separated adequately into sludge and supernate components by two stages of centrifugation. Further clarification of the supernate by sand filtration can remove almost all of the solids and provide salt solution suitable for cesium-removal process steps.

2. Centrifuge separations may be limited by mechanical effects such as improper balance or leveling of the centrifuge. Elimination of these effects may be more important to good separations than sludge properties or feed rate.

3. Solids removal in one stage of centrifugation was inversely proportional to slurry feed rate for sludges from Tanks 12H and 13H. However, the separation for Tank 5F sludge was nearly independent of feed rate.

4. After two stages of centrifugation, cumulative solids removal was large and nearly the same for all of the sludge types studied.

5. Batch size was not a significant factor in degree of separation attained.

6. Generally, good separations were obtained without flocculant. Flocculant proved to be only marginally useful in these tests. A method was demonstrated for recycling with flocculant, should poor separations without flocculant be encountered. On the basis of these results, routine use of flocculant in the conceptual process is not recommended.

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7. The washing and drying methods for sludges in the small-scale studies were generally satisfactory, although probably not suitable for a large-scale process.

8. The behavior of actual sludges in the centrifugation tests was quite similar to that of simulated sludges. Apparently both sludges have the same hydraulic and mechanical properties responsible for good separations. This similarity suggests that engineering development of the sludge-supernate separation module can proceed with simulated sludges, with a high degree of confidence that results will be appropriate for actual SRP waste.

ACKNOWLEDGMENTS

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