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Strontium and Transuranic Precipitation and Crossflow Filtration of a Large Hanford Tank 241-AN-102 Sample[#]

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ABSTRACT

This work provides an important confirmation of the strontium/permanganate precipitation process to achieve both acceptable filterability and decontamination for Envelope C (Tanks 241-AN-102 and 241-AN-107) complexant wastes to be treated by the Hanford River Protection Project. This bench-scale demonstration contained a series of seven precipitation batches and crossflow filtration campaigns to decontaminate filtrate of Sr-90 and transuranics from 16.5 L of Tank 241-AN-102 supernatant liquid with entrained solids. Batches were caustic adjusted, strontium and permanganate precipitated, and crossflow filtered with entrained solids using a 2-ft long, 3/8″-internal diameter, 0.1-micron pore size Mott

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crossflow filter tube. Test ranges for the transmembrane pressures and crossflow velocities were in the range of 30 to 70 psid (2.07 to 4.83 bar) and 9 to 15 ft/s (2.7 to 4.6 m/s), respectively.

INTRODUCTION

The Department of Energy (DOE) is sponsoring the River Protection Project (RPP) at the Hanford site to pretreat and vitrify nuclear waste. Processing of Hanford complexant-bearing aqueous waste requires pretreatment to remove specific radionuclides from a liquid stream to be vitrified as low-activity waste (LAW) glass. This removal will be accomplished by a strontium nitrate/sodium permanganate precipitation and filtration process. Decontamination, chemical, and filtration measurements that were made with actual Hanford Tank 241-AN-102 supernate waste are presented in this article.

A scoping study by Herting[1] showed the efficacy of a strontium nitrate-ferric nitrate strike on the removal of Sr-90 and transuranics from caustic adjusted Hanford wastes. However, the ferric hydroxide precipitate resulting from this chemistry was difficult or impossible to filter. This led to the discovery of a filterable calcium nitrate-strontium nitrate-sodium permanganate strike during an investigation of alternate chemistries with simulated waste at the Savannah River Technology Center (SRTC).[2] The process was then optimized.[3] Work following this at the Pacific Northwest National Laboratory (PNNL) also demonstrated sufficient removal efficiencies and filterability with the strontium nitrate-sodium permanganate strike.[4] Based on these initial works, a 1.5-L scale study with radioactive Hanford 241-AN-102 (Envelope C) waste was conducted at SRTC using lower strontium and permanganate quantities. It demonstrated acceptable filterability and Sr/TRU removal.[5] This new process reduces soluble Sr-90 by isotopic dilution. Reagent strontium nitrate solution, 1 molar in strontium, is added, resulting in precipitation of strontium carbonate. Sodium permanganate addition results in precipitate as manganese dioxide, and this has been found to effect high lanthanide and transuranic decontamination. A detailed background supporting the new process is given.[2] The work presented in this article is documented in detail in a publicly available full report.[6]

The purpose for this work was to demonstrate the efficacy of this new process on a bench-scale in semicontinuous operation. This included observation of longer term filtration performance at insoluble solids loadings above that of a single precipitation strike. This work served as a confirmation of the filterability and decontamination of the AN-102 supernatant liquid after precipitation without prefiltration to remove entrained solids. SRTC and PNNL have found that the entrained solids in Envelope C have been very difficult to filter alone. The entrained solids have activities sufficiently high for classification as high-level waste.

EXPERIMENTAL

History of Supernate Feed

The Hanford site contractor obtained approximately 14.25-L of waste solution from Tank 241-AN-102 during 1998. The waste samples were obtained by lowering sample bottles into the liquid phase of the waste and are denoted as "grab samples" since the contents of Tank 241-AN-102 were not agitated prior to or during the sampling event. The Hanford site contractor then packaged these samples for shipment, which the SRTC received in four separate deliveries from October through December 1998. The deliveries were mixed in a single container, diluted to 7-M sodium, and split into seven portions to be diluted to 6-M sodium for this work. Hay also performed a detailed characterization of the sample.[7]

Precipitation

The following steps were taken to prepare a precipitation batch for filtration. The 50°C temperature is typical of the plant process as specified by British Nuclear Fuels, Ltd.

1. Measure 1.2 or 2.4 L of 241-AN-102 supernate (preadjusted to 6-M sodium) into a large Erlenmeyer flask.
2. Heat and stir the liquid, target temperature being 50 ± 5°C.
3. Reagents, per Table 1, had been provided for the steps below.
4. Slowly add a premeasured amount of 17-M NaOH solution to boost the caustic level.
5. After 50°C is reached, slowly add 1-M strontium nitrate. Actual addition time was approximately 3 minutes for each of the 7 batches. 1-M Calcium nitrate was also added at this point for the first batch.
6. Stir for 10 minutes at the 50°C temperature.
7. The premeasured amount of 1-M sodium permanganate solution was added over a period of 3 minutes.
8. Stir with a magnetic stir bar for 4 hours while maintaining 50°C.
9. Precipitate slurry was added to the cells unit filter (CUF, described as follows) very slowly while the CUF heat exchanger was on to provide cooling. The material was cooled to room temperature in a single pass because of the slow addition. Filtration did not commence until after cooling was complete.

Table 1. Sr/TRU precipitation recipes—calculated volumes of solution addition per L 6.0-M Na + AN-102 feed.

	Milliliters of premeasured reagent per liter of feed	
Solution/recipe	Batch 1 Ca/Sr/MnO_4	Batches 2–7 Sr/MnO_4
17-M NaOH	64.1	73.3
1-M $Sr(NO_3)_2$	22.6	92.0
1-M $NaMnO_4$	33.9	61.3
1-M $Ca(NO_3)_2$	10.0	None added

As reagents cannot easily be quantified and poured in the remote shielded cells where the work was done, precipitation solutions were premeasured and placed into individual bottles for one-time use. The premeasured quantities were calculated based on the original experimental design volumes of 1.2-L and 2.4-L batch sizes, rather than the actual volumes. As the dilutions to the 6-M sodium level made the total amount of feed actually received larger than the $(1.2 + 6{*}2.4 = 15.6\,L)$ plan (Fig. 1), calculated final target ion concentrations (Table 2) through addition of the precipitating agents was slightly lower than planned. The process of adding these precipitation solutions and slurry wash solutions raised the volume to be filtered from the approximately 16.5 L of 6.0-M Na Tank AN-102 supernatant liquid to nearly 19.8 L total precipitated slurry. The measured sodium levels at the bottom of Table 2 show that final dilutions to the desired 6-M sodium level were within the ± 10% analytical error for sodium measurement.

The run data summary (see Fig. 1) lists in graphical form the information in Table 2, as well as the product filtrate bottles produced from each precipitation and filtration batch. The crossflow filter unit was emptied of high-insoluble solids content slurry when filtration fluxes became excessively low, and other relevant operation and experiment material balance information was recorded.

Generally, the cells unit filter (CUF) was operated by semicontinuously adding precipitated slurry as filtrate (or permeate) was produced continuously, allowing insoluble solids to accumulate in the filter loop. When pump and filter performance seriously deteriorated, concentrated slurry was removed (during Batch 3, before Batch 5, and during Batch 6) before precipitated feed material was added and filtration operations resumed. At the end of Batch 7, the accumulated solids were washed in four batches by semicontinuously feeding 600-mL aliquots of inhibited water (0.01-M NaOH) as filtrate was produced continuously.

After the fourth wash campaign, the washed solids/slurry was drained from the CUF rig as much as possible through the drain valves and brief pump

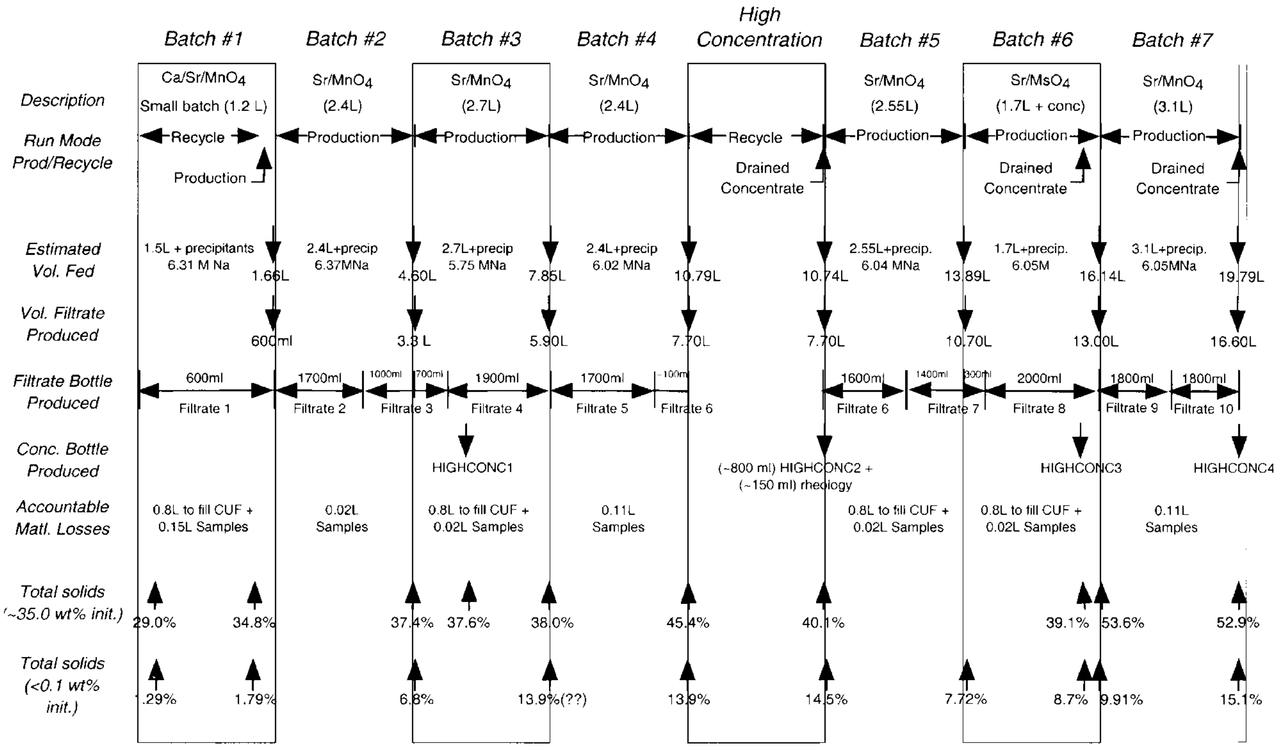

Figure 1. Run data summary.

Table 2. Sodium level adjustment in Tank 241-AN-102 samples.

Precipitation batch #	1	2	3	4	5	6	7
∽ 6.0 M Na AN-102 volume (L)	1.5	2.4	2.7	2.4	2.55	1.7 (+0.7 L CUF conc.)	3.1 (0.6 + 2.5)
AN-102 + precipitants volume (L)	1.66	2.94	3.24	2.94	3.09	2.2	3.64
Calculated Na+ , M	6.50	6.21	5.71	5.92	5.94	5.93	5.96
Calculated free OH^-, M	0.88	1.10	1.00	1.10	1.05	1.32	0.90
Calculated Sr^{2+}, M	0.016	0.075	0.068	0.075	0.071	0.040	0.061
Calculated Mn^{x+}, M	0.025	0.050	0.045	0.050	0.048	0.041	0.040
Calculated Ca^{2+}, M	0.014	—-	—-	—-	—-	—-	—-
Bottle Na+ molarity	6.31	6.37	5.75	6.02	6.04	6.06	6.03

operation. The CUF was then flushed out using deionized (DI) water, then 1-M nitric acid, and DI water rinses. Then postexperiment clean water fluxes were taken. Caustic cleaning solution was not used.

Apparatus

Crossflow filtration is a process where a slurry concentrate passes down a porous tube or channel under pressure, forcing permeate through the walls of the channel and, at the same time, sweeping concentrated solid cake off the filter medium. The process stands in contrast to deadend filtration, where the cake continues to build on the porous medium. Backpulsing of a crossflow filter (short reversal of the pressure across the medium) reverses the filtrate flow momentarily for extended cake removal so that filter flux is boosted.

Crossflow filtration was performed with a CUF rig that was set up in Cell 16, B-Block, at SRTC. The unit was designed to provide plant-typical flow and pressure to a single crossflow filter tube using less than a liter of liquid inventory. Figure 2 shows the unit without cooling tubes connected to the heat exchanger for clarity. Feed from the reservoir at the left went to a progressive cavity pump. The pump was operated at variable speed by controlling air

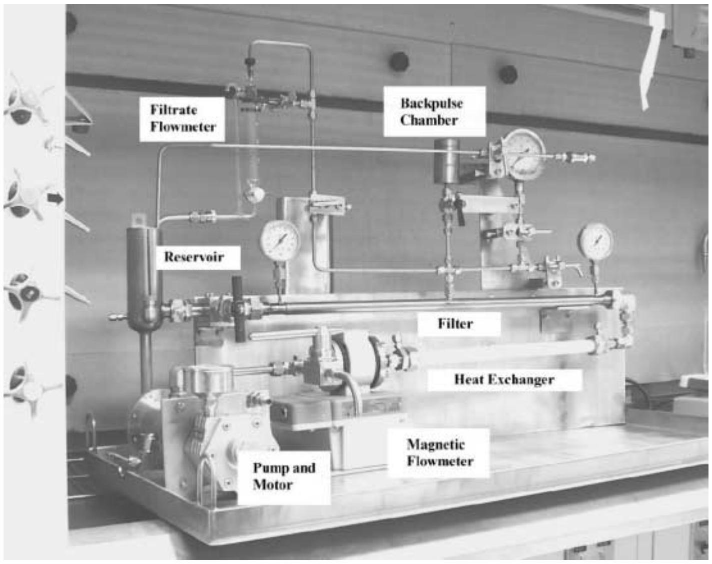

Figure 2. Cells unit filter in a nonradioactive laboratory.

pressure to its air motor. Slurry concentrate flowed from the pump through a magnetic flowmeter, a heat exchanger that removed pump heat, then down the center of a crossflow filter of 2-ft porous length. A throttle valve downstream of the filter dropped fluid pressure back to atmospheric pressure. Filtrate production was measured with a graduated sightglass and stopwatch. A simple backpulse system could be charged with filtrate and pressurized with air. The backpulse was accomplished using a manual toggle valve.

A 0.1-micron-pore, stainless steel, Mott filter tube was used in this work. The filter had a 2-ft active length, 3/8″-ID bore, and 1/16″-wall thickness. The filter elements planned for use in the River Protection Project Waste Treatment Plant (RPP-WTP) will also be 0.1-micron-pore size Mott filter tubes. However, the plant filter elements are expected to be over 80 inches in length.

Filter Operation

The CUF rig was first cleaned by circulation of 1-M nitric acid, 1-M sodium hydroxide, or deionized water. These filter cleaning fluids were prefiltered with 0.22-micron nylon filters before use. 1-M Sodium hydroxide was not used in the current work; only 1-M nitric acid with DI water flushes before and after were used for cleaning.

Clean water fluxes were taken after the rig was flushed with cleaning fluids. Transmembrane pressures were between 5 and 20 psid and fluxes were measured for periods of 20 minutes or more per the TTP, after initial backpulsing.

Operation of the CUF involved the following routine:

1. Filtrate was generated to fill the backpulse chamber. The chamber was air pressurized to provide 45-psid overpressure with respect to the filter tubeside. Filter concentrate (tubeside) pressure was reduced as low as possible for best backpulse effectiveness.
2. Two backpulses were performed before each set of conditions was run.
3. Conditions were set after the second backpulse while the filtrate valve was kept closed.
4. Start time for each run was recorded when the filtrate needle valve was opened completely. The needle valve was opened gradually to reduce pressure on the filtrate side in a smooth manner over 10 to 20 seconds.

5. Samples of concentrate and filtrate were taken at the beginning, middle, and end of the campaign.
6. The valve at the bottom of a graduated glass column in the filtrate flow path was closed momentarily to allow flow measurement. Level increase and corresponding time were recorded periodically to determine filter flux.

Solution Analyses for Sr-90 and Actinides

Filtrate and digested solids samples were analyzed for Sr-90 content using an Eichrom Sr-spectroscopy-based extraction procedure. Sample blanks were run concurrently to determine counting efficiencies and chemical recoveries. Samples were counted using a liquid scintillation procedure after Sr-90/Y-90 equilibrium was reached.

Analyses for the actinides Pu-238 and 239/240, Am-241, and Cm-244 were performed by a thenoyltrifluoroacetone (TTA) separation followed by alpha spectroscopy. A sample spiking method was used to resolve the plutonium isotopes.

RESULTS AND DISCUSSION

Precipitation Chemistry Results

Decontamination—Desired Targets for the Process

The purpose of the precipitation/filtration process is to decontaminate the waste entering the plant so the bulk of the mass, a liquid stream, will produce immobilized low-activity waste (ILAW) glass when vitrified. Transuranic (TRU) and Sr-90 limits must both be met. The transuranic limit here is 100 ηCi/g of glass.

The waste sodium oxide loading in the ILAW glass depends on glass chemistry that results in a product that meets certain disposal requirements. Glass sodium oxide loading from the pretreated AN-102 sample was revised to 11.8 wt% subsequent to conducting these tests. The waste sodium oxide loading was reduced to avoid the formation of a separate sulfur-bearing phase during the vitrification of the pretreated AN-102 waste.

The Sr-90 target is 20 Ci/cubic m of glass. This translates to an upper strontium level of 9.8 ηCi/mL for the same basis of 7-M sodium in solution.

The limits are reduced proportionally for dilution to lower sodium levels. The final filtrate product from this campaign therefore, has a Sr-90 limit of 6.7-ηCi/mL. It also translates to a TRU level of 88 ηCi/mL for 4.8-M sodium in solution.

Decontamination—Strontium

Sr-90 was tracked throughout the campaign. Figure 3 summarizes the results with respect to the limits given previously. Instantaneous samples of filtrate were taken at the completion of each batch of precipitate. They are grab samples taken from the filtrate outlet. In contrast, "Bottle" samples are taken at the end of the filling of each filtrate collection bottle. They are more representative of a composite because the filtrate bottle has from 600 to 2000 mL of filtrate product when "Bottle" samples are taken.

It is seen that the process is robust in removing Sr-90 from the filtrate stream. In Batch 1, the target added concentration of Sr was only 0.02 M. Calcium has previously been shown not to affect the removal of Sr-90 from Envelope C solutions. Even with this nonconservative level of strontium, addition the process output was less than half of the tolerable limit.

A decontamination factor calculated from total strontium (not Sr-90) is shown on the *y* axis in Fig. 4. This is calculated by dividing 0.075 M, the bulk strontium level after precipitation, by the total strontium measured in the filtrate. The bulk strontium level is the slurry is thus compared to the soluble fraction of strontium. It would be comparable to the active decontamination factor in the case where isotopic mixing is good during the precipitation and

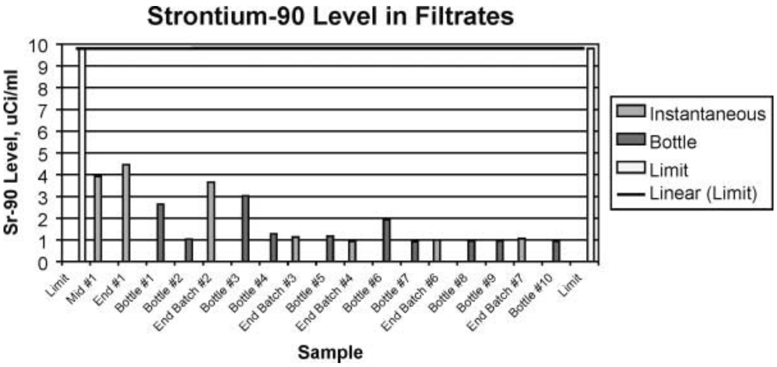

Figure 3. Strontium-90 level in filtrates.

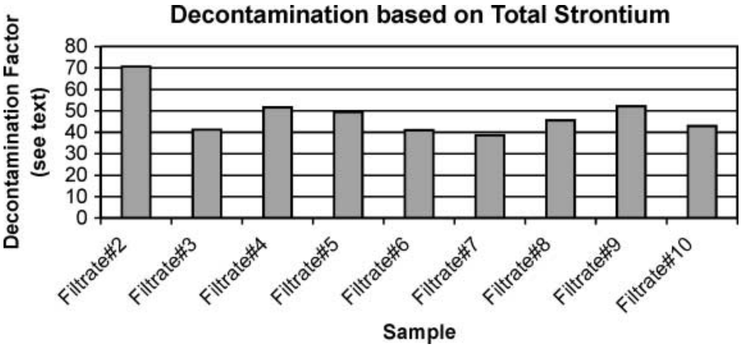

Figure 4. Decontamination based on total strontium.

mixing. The typical values of 40 to 50 during the campaign (average of 48) agree with the active data of Fig. 4 because the feed Sr-90 activity was 50 ηCi/mL. The typical activities of 1 ηCi/mL, shown in Fig. 3, indicate a decontamination factor of approximately 50.

If incoming waste contains negligible total strontium on a molar basis and if the saturation level of soluble strontium in the liquid is known, then decontamination can be expressed by the following equation for perfect isotopic dilution.

$$\text{DF based on total strontium} = (\text{Ret} + \text{Sol})/(\text{Sol} \times \text{MDil})$$

where Sol = (sample volume + 1-M SrNO3 added volume) × (final total Sr concentration measured in filtrate), and Ret = Sr retained in precipitate, which is [(1 Molar × 1-M SrNO3 added volume)—Sol], and MDil is the mass dilution ratio.

Decontamination—Transuranics

Figure 5 shows the activities of five transuranic species that were measured and their relative contribution to the total. All filtrate product bottles were below the limit of 0.109 ηCi/mL, except for filtrate #8, which appears to have excess curium-244 contamination. The curium was an artifact of the work location and is not present to significant levels in 241-AN-102 waste.[7]

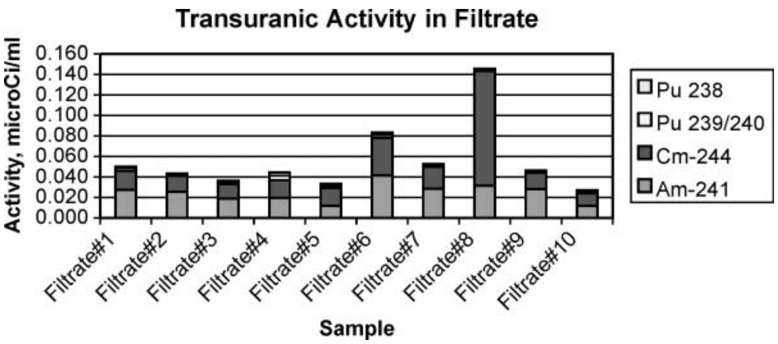

Figure 5. Transuranic activity in large C (AN102) filtrates.

Removal of the curium contamination from the total activity would show that the product was well below the limit in all cases. The Large C campaign demonstrated robust and ample removal of transuranics from the feed.

Decontamination factor based on 6-M sodium feed is provided in Table 3. Filtrate samples are from the 1- or 2-L collection bottles after each had been filled during the Large C filtration campaign. Feed activity levels used in the calculations were as found by Hay.[7] Removal of curium contamination was not calculated because of uncertainties in levels of that element in the input samples. The table shows a simple average and standard deviation for the ten decontaminations with equal weighting, then a volume-based weighted

Table 3. Decontamination factor for transuranics in large C filtrate samples.

Filtrate number	Am-241	Pu 239/240
1	4.4	5.5
2	4.7	12.4
3	6.3	7.2
4	6.0	3.3
5	10.1	6.4
6	2.9	5.2
7	4.2	10.1
8	3.8	10.7
9	4.2	11.3
10	10.0	8.2
Average	5.7 ± 2.5	8.0 ± 3.0

average is shown at the bottom. The volume weighted average was calculated by multiplying each filtrate bottle by its final volume, summing all ten, and dividing by a total product volume of 16.6 L of filtrate product (wash solutions are excluded).

Decontamination—Technetium-99

Technetium is clearly not removed from the waste by this precipitation process. Though technetium is a congener of manganese, Tc(VII) is not as strong an oxidant as Mn(VII). Technetium levels were measured by mass spectroscopy, which was found to be more reliable than counting methods for this sample matrix. The technetium-99 level was consistent over all the filtrate samples and its average value compared well with that of the feed. Hay reported 6.28 mg/L ± 1.4% at 6.42-M sodium.[7] At 6-M sodium that would be 5.85 mg/L, which compares well with the average and standard deviation of 5.5 ± 1.4 mg/L for eight filtrate measurements measured across the campaign.

Components Showing Little Removal

The strontium-permanganate process leaves many components in the filtrate product with insignificant removal efficiency. It is desired that aluminum and sulfate remain in the filtrate because they are better handled in the low-level waste melter as opposed to the much smaller high-level waste melter. It would be a benefit if other components, like cesium and technetium, were removed during precipitation, but they are handled by ion-exchange columns just downstream of the precipitation process.

Table 4 shows splits of stable elements with concentrations that were measured in both the concentrate and filtrate during the campaign. Concentration ratios near unity show elements that are not separated very well. Strontium and manganese levels are artificially high because of the addition of these elements for precipitation.

It is interesting to note that barium, copper, iron, lead, tin, zirconium, and cadmium to some extent were separated more efficiently in the first batch than in the following six batches. This is despite the lower addition of strontium (0.02 M vs 0.075 M after mixing) and lower permanganate level (0.03 vs 0.05 M addition) for the first batch. Since this batch had added calcium these elemental levels provide evidence of the efficacy of calcium to increase removal of elements targeted by the process. This effect observed in Batch 1 was verified with two sets of samples.

Table 4. Table of slurry-based concentration ratios for metallic elements.

Element	Batch 1-mid	Batch 1-end	Batch 2	Batch 3	Batch 4	Batch 5	Batch 7
Al	1.0	1.1	0.3	0.7	1.2	0.6	0.1
B			1.2	0.9	1.1	1.1	1.1
Ba	21.6	25.6	7.6	0.3	5.5	4.8	9.6
Ca	2.4	2.5	2.6	1.5	1.9	1.6	1.8
Cd	1.4	1.6	1.0	0.9	0.8	0.8	0.8
Cr	2.0	2.2	1.8	1.3	1.1	1.5	1.9
Cu	2.6	3.0	0.7	0.4	0.5	0.5	0.5
Fe	48.0	80.1	3.7	2.5	10.2	7.6	5.1
Mn	3579.1	1841.5	2384.8	247.6	345.3	705.5	285.1
Mo	1.9	1.8	0.9	0.8	0.7	0.7	0.7
Na	1.0	1.1	1.0	1.0	0.9	0.9	0.7
Ni	1.2	1.4	1.3	0.9	0.9	1.0	0.9
P	1.2	1.2	1.1	0.9	0.8	0.9	0.8
Pb	4.1	5.7	1.9	0.7	1.1	1.1	1.2
Sn	4.6	4.2	0.2	0.4	0.6	0.4	0.2
Sr	35.0	34.8	110[a]	8.0[a]	38.9	36.2	49.5
Tc	bd	bd	0.5	0.5	bd	bd	bd
Zn	3.3	2.4	3.0	0.6	4.1	3.8	6.2
Zr	15.0	18.6	0.0	0.2	0.0	0.0	0.1

bd = Below detection.

[a] Sampling error of slurry is the suspected cause of this variation.

Table 4 data from Batches 2 to 7 were averaged because they all used the same precipitation recipe. Results are tabulated in Table 5 for the leftmost data column under "This Work." The results of other works are also shown for comparison where data are available.

These works were compared partly to draw general conclusions on precipitation process performance across the variation represented by Tank 241-AN-102 and Tank 241-AN-107 materials. Elements not removed in either case are, for example, easily modeled in the process flowsheet without further effort.

Aluminum, boron, cadmium, molybdenum, sodium, nickel, and phosphorus are clearly not removed by this process and remain in the filtrate whether the feed is from Tank AN-102 or from Tank 241-AN-107. Approximately half of calcium, chromium, lead, zinc are removed. The process always has a strong interaction with iron, and removes at least 80% of it.

Decontamination of strontium based on elemental totals compares well with decontaminations based on Sr-90 activity. The data from this set of

Table 5. Elemental split across the filter, ICP-ES data, several works.

	AN-102 (this work)				
Sample	Average	St dev	AN-102 small C Ref.[5]	Sim. AN-107 cold CUF Ref.[2]	AN-107 PNNL Ref.[4]
Al	0.6	0.37	0.9	0.9	1.1
B	1.1	0.09	1.0		
Ba	5.5	3.11			
Ca	1.9	0.40	1.5	2.4	1.6
Cd	0.9	0.09	1.0		1.0
Cr	1.5	0.30	1.4		2.0
Cu	0.5	0.12	1.0	>10	
Fe	5.8	2.76	8.7	5.3	100
Mo	0.8	0.09	0.9		
Na	0.9	0.10	1	1.0	1.0
Ni	1.0	0.16	1	1.0	1.0
P	0.9	0.11	0.9	1.1	1.0
Pb	1.2	0.41	1.4		2.5
Sn	0.4	0.16	0.4		
Sr	48.3	33.21	39.3	91	120
Zn	3.5	1.81	2.4	1.3	
Zr	0.1	0.05	0.3		
Added Mn, M	0.05		0.044	0.04	0.05
Added Sr, M	0.075		0.066	0.075	0.075

samples support the data shown in the "Strontium Decontamination" section, which used total and Sr-90 data from other sample sets. This equality indicates that isotopic mixing in the process is complete. While this affirms the goal of activity reduction by isotopic dilution, it also gives some credibility to the use of nonradioactive simulants to report a strontium decontamination where only data from total strontium measurements are available.

Analyses of Final Filtrate Products

All 6-M sodium and slurry wash filtrates were combined and mixed for delivery to the cesium ion-exchange process. Table 6 shows how the composite greatly exceeds the decontamination for both Sr-90 and transuranics. Decontamination numbers from this data set show the material met decontamination requirements.

Table 6. Radiochemical data for final product composite.

Radiochem	Dilution-corrected dpm/mL	μCi/mL	Limit for 4.8 M Na +
Sr-90	2.03E + 06	0.9144	6.7 ηCi/mL
Pu-238	2.06E + 03	0.9	
Pu-239-240	1.64E + 03	0.7	
Am-241	2.31E + 04	10.4	Transuranic total must be
Cm-244	2.51E + 04	11.3	Less than 88 ηCi/mL
Cs-137	3.34E + 08	150.5 ηCi/mL	Not removed by this process

Chemical Analysis of Slurry Washing

The slurry concentrate in the CUF at the end of Batch 7 filtration was washed with inhibited water (0.01-M NaOH). Four 600-mL portions of washwater were used to generate four 600-mL samples of spent washwater. Slurry being washed was left in the rig between each 600-mL wash and was only removed at the end. Data from the four washwater analyses are presented below to show impacts of the washing sequence on chemistry and radioactive elements.

Elements that could be detected by ICP-ES in all four of the 600-mL "Wash-1" to "Wash-4" samples are shown in Fig. 6. Two types of washout behaviors are clearly shown. These are separated in the figure by use of large vs smaller plot symbols.

Sodium, nickel, phosphorus, and cadmium appear to wash out by a dilution effect only, as if they have insignificant association with the solids in the slurry. These are shown with small plot symbols in Fig. 6. The filtration rig inventory volume is estimated to be 800 mL, but the 600 mL of washwater passed through it for each "Wash-#" sample appears to reduce soluble concentration by half. This higher efficiency would be expected because the washwater was pumped in semicontinuously rather than all at once; the rig would not have been able to hold all 600 mL in a one-time addition. The permanganate process in all previous work did not remove these elements.

Calcium, strontium, and lead washed out with apparent bleed from the slurry solids. These are plotted with the larger symbols. The curves are higher than those of purely soluble elements, indicating that they are bleeding from the solids to some extent. Strontium is an important part of the slurry and would have this expected behavior. Calcium, as well, associates in some way with the manganese oxide-hydroxide solids in the slurry and thus washes out

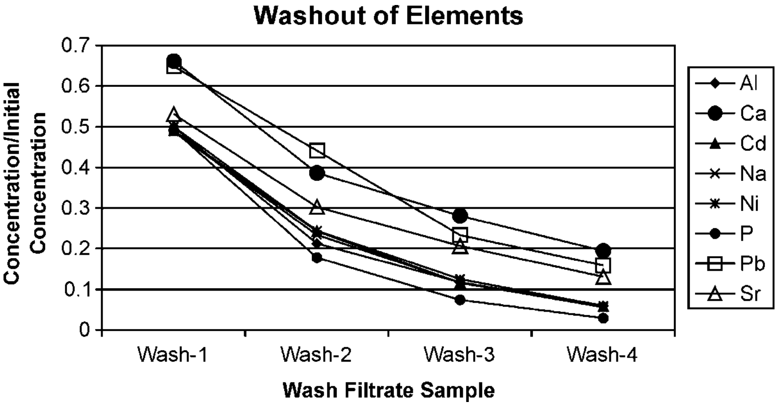

Figure 6. Washout of elements.

slowly. Lead has a removal factor of slightly above unity and is removed by the caustic wash solution as shown.

Manganese was below detection in the Wash-3 and -4 samples and was only 10 mg/L and 1.6 mg/L in the Wash-1 and Wash-2 samples, respectively. The form of manganese in the slurry was insoluble with respect to the washing operation. It did not bleed out significantly.

Figure 7 shows that sodium and Cs-137 wash out as totally soluble components. These are plotted with heavy lines and both follow the same trend of halved concentration with each 600-mL wash. Americium-241,

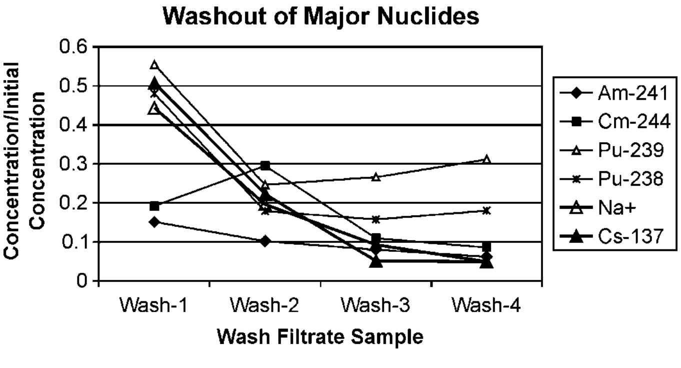

Figure 7. Washout of major nuclides.

the most prevalent source of transuranic activity, is retained by the slurry solids and shows no significant bleed.

Plutonium behavior initially follows the trend of diluted soluble elements, but then seems to begin to wash out of the solids in the latter two washes. This is seen by its departure from the normal downward trend in Washes 3 and 4. Sodium and cesium follow a downward trend where concentrations are roughly halved with each new wash. The lower ionic strength of the slurry might have promoted this bleeding for plutonium. Oxidation of plutonium to the $+5$ or $+6$ state might produce a similar result.

It is fortunate that plutonium contributes no more than about 10% of the total transuranic activity; the permanganate process thus retains the most important element (Am-241) during washing. Curium-244 behavior is uncertain at the first data point but follows the soluble components beyond the first data point (average of two measurements). It shows little evidence of accelerated bleeding during slurry washing. This curium is not a normal part of complexant waste and contributes an insignificant amount of transuranic activity. Curium-244 has been found in higher levels alone in the sample used here due to inadvertent contamination of the 241-AN-102 sample within the SRTC hot cells.

Observations on Post-filtration Precipitation

Various researchers working on this process have noted that the filtrate from permanganate precipitation appears to drop small amounts of black solid on standing. One hypothesis being tested in follow-on work is that the boosted hydroxide level in the process leads to slow decomplexation and hydroxide precipitation of some transition metals. While no systematic study of this has been published, it was planned to watch the bottles of filtrate product from this campaign for such post-filtration precipitation solids.

In summary, some bottle discoloration, but no solids, was seen with the bottles of high-sodium filtrate product. Free solid formation was seen with the lower sodium filtrate from washing. All bottles of filtrate were checked after sitting in the shielded cells for 2 weeks after they were produced. No solids were seen in the bottles, but some discoloration of the polyethylene that was in contact with the solution in each bottle was observed. The filtrates were clear and straw colored, while the discoloration was gray-black. Bottles containing filtrate from the first two of four washes formed visible solids within 2 days of standing. It was noted that the solutions in the bottles were light brown-yellow and clear. No post-filtration precipitation solids were captured or analyzed in this work.

Filtration Flux Data Summary

Table 7 summarizes the average filter fluxes obtained for each batch of precipitated Hanford AN-102 Large C waste, filter conditions and settings, and insoluble solids concentration average and range. The average flux and insoluble solids concentrations were calculated by integral average over the volume of filtrate produced. The remaining filtration discussion focuses on comparing specific conditions [e.g., different transmembrane pressures (TMP) and fluid axial velocity at constant insoluble solids contents, different insoluble solids contents for the same TMP and axial velocity, etc.] summarized in Table 7.

Batch 1 had the lowest solids loadings, these being 1.3 wt% insoluble solids and 35 wt% total solids (includes soluble salts). Figure 8 shows how fluxes increased with increasing TMP (low cake buildup) and axial velocity (shearing off of cake). Despite the added calcium nitrate addition, this batch did not present detectable differences in filtration difficulty over past work without the calcium. Calcium addition might be of interest because of its enhancement of decontamination chemistry.[3]

In addition to the effects shown in Fig. 8, a stopping and restart of flow in the crossflow filter was found to be equivalent to a backpulse in improving flux. This effect was found to disappear between 4.5 and 6.8 wt% insoluble solids, suggesting this range as the “transition” point between low- and high-insoluble solids filtration behavior.

High-Insoluble Solids Concentration Flux Data

Permeate flux data under high-insoluble solids loads were collected during crossflow filter operation. The purpose of these runs was to test the effect of changing conditions around the “standard” operating conditions of TMP = 3.45 bar (50 psi) and 3.72 m/s (12 ft/s) axial velocity. To produce a fluid with high-insoluble solids content, freshly prepared feed material was semicontinuously pumped into the CUF reservoir to produce filtrate without concentrate being removed from the system, except for small samples. The ramping up of insoluble solids level ran from the beginning of the campaign to the end of Batch 4 to produce a fluid with a measured 45.4 wt% total solids and 13.9 wt% insoluble solids.

Upon comparison of the matrix operating conditions with the flux at “standard” conditions obtained just prior (Fig. 9), raising the TMP from 3.45 to 4.83 bar (50 to 70 psi) has no effect on permeate flux and lowering the axial velocity only reduced the permeate production. Permeate flux and

Table 7. Summary of filtration flux data.

Batch number	Precipitation chemistry	TMP	Axial velocity	Average flux	Measurement time (min)	Average IS (wt%)	Insoluble solids (IS) range (wt%)
1	Ca/Sr/Mn	**70 psid** **4.8 bar**	**13.5 ft/s** **4.1 m/s**	**0.074 gpm/ft^2** **4.3 m^3/(m^{2}day)**	60	1.3	1.3
2	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.045 gpm/ft^2 2.7 m^3/(m^{2}day)	73	3.9	1.8–6.8
3	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.034 gpm/ft^2 2.0 m^3/(m^{2}day)	23	7.3	6.8–8.2
	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.030 gpm/ft^2 1.8 m^3/(m^{2}day)	59	8.2	7.1–9.4
4	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.021 gpm/ft^2 1.2 m^3/(m^{2}day)	110	11.0	9.4–13.0
	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.022 gpm/ft^2 1.3 m^3/(m^{2}day)	30	13.5	13.0–13.9
	Sr/Mn	**30 psid** **2.1 bar**	**15.2 ft/s** **4.6 m/s**	**0.016 gpm/ft^2** **0.94 m^3/(m^{2}day)**	30	14.5	14.5
5	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.023 gpm/ft^2 1.3 m^3/(m^{2}day)	48	4.3	3.6–5.0

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	Sr/Mn	30 psid 2.1 bar	15.2 ft/s 4.6 m/s	0.025 gpm/ft^2 1.5 m^3/(m^{2}day)	30	5.5	5.0–6.0
	Sr/Mn	40 psid 2.8 bar	15.2 ft/s 4.6 m/s	0.027 gpm/ft^2 1.6 m^3/(m^{2}day)	43	6.8	6.0–7.7
6	Sr/Mn	30 psid 2.1 bar	9.1 ft/s 2.8 m/s	0.015 gpm/ft^2 0.9 m^3/(m^{2}day)	33	8.1	7.7–8.5
	Sr/Mn	30 psid 2.1 bar	15.2 ft/s 4.6 m/s	0.022 gpm/ft^2 1.3 m^3/(m^{2}day)	15	8.9	8.6–9.1
	Sr/Mn	50 psid 3.5 bar	12.2 ft/s 3.7 m/s	0.018 gpm/ft^2 1.1 m^3/(m^{2}day)	29	9.5	9.1–9.9
7	Sr/Mn	25 psid 1.7 bar	15.2 ft/s 4.6 m/s	0.021 gpm/ft^2 1.2 m^3/(m^{2}day)	30	10.3	9.9–10.6
	Sr/Mn	30 psid 2.1 bar	15.2 ft/s 4.6 m/s	0.023 gpm/ft^2 1.3 m^3/(m^{2}day)	30	11.0	10.6–11.4
	Sr/Mn	30 psid 2.1 bar	15.2 ft/s 4.6 m/s	0.019 gpm/ft^2 1.1 m^3/(m^{2}day)	156	13.1	11.4–14.7
	Sr/Mn	30 psid 2.1 bar	15.2 ft/s 4.6 m/s	0.015 gpm/ft^2 0.9 m^3/(m^{2}day)	34	14.7	14.5–15.0

[a] Bold signifies maximum flux observed during test matrix.

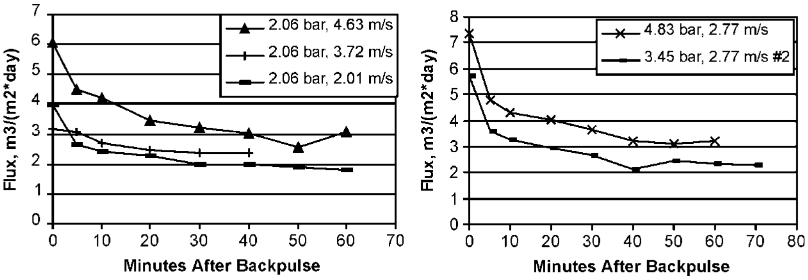

Figure 8. Effect of filtration parameters on flux at 1.3 wt% insoluble solids.

permeance increase when both the TMP is lowered to 2.06 bar (30 psi) and the axial velocity is increased from 3.72 to 4.63 m/s (12 to 15 ft/s).

The permeate fluxes and permeances obtained experimentally are almost identical to those obtained for a 14 wt% insoluble solids concentrate of precipitated AN-107 C-simulant filtered at TMP = 2.06 bar (30 psi), 4.63 m/s (15 ft/sec), and TMP = 3.45 bar (50 psi), 3.72 m/s (12 ft/sec) in the SRTC Thermal Fluids Laboratory.

Insoluble Solids Content and Effect of Backpulse

The filterability and the effect of the backpulse can be lessened as solids concentration rises. Some of these changes in filter performance and optimal filter operations observed were subtle. At low-insoluble solids concentration, the backpulse can approximately double the initial permeate flux and permeance over the steady-state values, independent of filter operating conditions. At high-insoluble solids concentrations, the doubling effect is seen

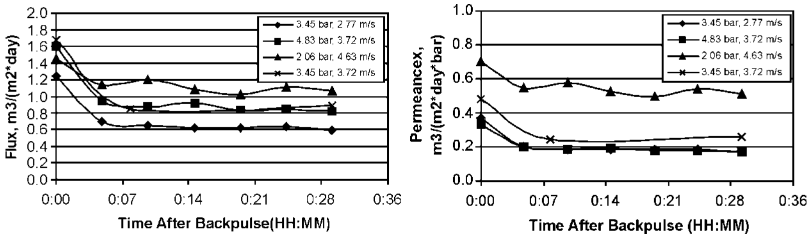

Figure 9. Permeate flux and permeance from filtration of 13.9 wt% insoluble solids fluid after successive $Sr(NO_3)_2/NaMnO_4$ precipitations.

only for the lowest fluxes and permeances (Fig. 9). At the "best" conditions (TMP = 2.06 bar [30 psi] and 4.63 m/s [15 ft/s]), the backpulse effect is lessened to ∽ 40 to 50% improvement, likely due to more rapid solids buildup on the filter at higher solids loading or thick higher consistency slurry being less easily removed from the filter surface.

As discussed earlier, "optimal" filtrate or permeate fluxes for low-insoluble solids loadings were observed with high-transmembrane pressure (TMP) and high-axial velocity. However for high-solids content, low TMP and high-axial velocity showed the best permeate fluxes. In the case of filter permeance, low TMP and high-axial velocity yielded the best values at both low and high solids concentration.

The results suggest two possible filtration strategies when concentrating insoluble solids: (1) initially begin with high TMP and high-axial velocity, lowering TMP as solids concentration increases or (2) filter continuously at low TMP and high-axial velocity over the entire solids concentration range while accepting a sacrifice in permeate flux at lower solids contents.

CONCLUSION

Precipitation Chemistry Study

The most significant observation on decontamination was that the level of reagent additions chosen here were found to be conservatively large. The low-level composite filtrate had about one-seventh the Sr-90 activity and one-quarter of the TRU activity permitted for low-level glass loading. This shows that reduced reagent addition will be permissible for the flowsheet.

Removal or passage of elements match past observations. Al, B, Cd, Mo, Na, Ni, S, and P were not removed. Very small amounts of Ca, Cr, Pb, and Zn were removed. About 80% of the Fe is removed. This process does not remove technetium-99 from the waste solution. Am-241 does not wash out of the slurry during washing; plutonium shows some washout behavior.

Filterability Study

At low-insoluble solids levels, high-transmembrane pressure and high-axial velocity favors filterability, although the effect of transmembrane pressure is smaller. Permeance data suggests highest energy usage efficiency at low transmembrane pressure and high axial velocity. At high-insoluble solids levels (∽ 14 wt%), low-transmembrane pressure (2.06 bar, 30 psi), and high-axial velocity (4.63 m/s, 15 ft/s) favors filterability. Stopping and restart of concentrate flow in the filter is equivalent to a backpulse up to ∽7 wt% insoluble solids, providing higher initial fluxes on restart. Washing of solids filterability is best at low-transmembrane pressure and high-axial velocity, with flux increasing with increased rinsing with inhibited water.

No significant difference in filterability was observed when the calcium nitrate-strontium nitrate-sodium permanganate strike data obtained was compared with previous literature for the strontium nitrate-sodium permanganate chemistry.

RECOMMENDATIONS

Future testing of the strontium and permanganate process should focus on reduction of added strontium and permanganate while still producing low level filtrate. Reduced levels of sodium hydroxide in the initial caustic adjustment would also provide a benefit of adding less sodium to the low-level glass. It is possible that the precipitation reagents do not consume free hydroxide, though some is needed to assure that aluminum does not precipitate.

Darkening of filtrate product bottles indicated some post-precipitation mechanism. This mechanism needs further study. Precipitation at lower temperatures need investigation for practicality. While not a focus of the current study, some room temperature precipitation has been tested in past "beaker" studies and would simplify the process. Backpulse frequency needs to be investigated to improve overall average filter fluxes.

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