

Examination of Sodium Titanate Applicability in the In-Tank Precipitation Process

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**Examination of Sodium Titanate Applicability in the In-
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Summary

The In-Tank Precipitation (ITP) process decontaminates radioactive waste by precipitating radioactive cesium with tetraphenylborate (TPB⁻) and adsorbing strontium and actinides on monosodium titanate (MST). An alternative strontium absorbent material, sodium titanate (ST), has been developed by AlliedSignal, Inc. as part of the Efficient Separations and Processing Crosscutting Program of the Department of Energy Office of Science and Technology. An examination using simulated and radioactive waste indicates this material is effective for Savannah River Site High Level Waste (HLW), although the particle size of the material must be optimized to reduce the impact on filtration. The highest average decontamination factors after 48 hours was 260 (± 100). This performance is higher than the specified decontamination factor of 150 for MST used in ITP. Progress has been made by the vendor in formulating improvements in the material since the preliminary examination of this material.¹

The AlliedSignal material is being examined because of three potential benefits over the conventional MST:

- potential for higher ITP filter performance due to a larger particle size while retaining decontamination effectiveness,
- absence of residual alcohols in the material, and
- potential for increasing the ratio of plutonium to uranium selectivity, thereby reducing the alpha-emitting radionuclide content in Saltstone.

This study concluded that, compared to MST, the AlliedSignal material:

- exhibits a higher Sr decontamination factor
- has similar Pu and U loading
- produces a 35% decrease in filter flux, relative to MST
- has no negative influence on chemical cleaning of the Mott filters

Introduction

The ITP Process decontaminates radioactive waste in Tank 48H by precipitating cesium with TPB⁻ and adsorbing strontium on MST. The radioactive solids are separated from the salt solution by cross flow filters. Alternate strontium sorbents are being examined due to several factors. Principal among these are the potential for increased filter performance and improved selectivity of plutonium to uranium absorption. Increasing the plutonium absorption and decreasing the uranium absorption would reduce the alpha-emitting radionuclide (primarily Pu and Np) content in the treated waste while using the same amount of ion exchange material. The limit on alpha-emitting radionuclides in treated material is based on the Waste Acceptance Criteria for the Saltstone facility at SRS.

The supplier of material tested in this study, sodium titanate (ST), is AlliedSignal, Inc. The materials are reported by the vendor to be within the current particle size specification for MST (<1 wt % less than 1 micron, <1 wt % greater than 35.5 microns).²

These tests allow determination of the decontamination factor (DF) for any radionuclide:

$$DF = [C]_i / [C]_f$$

where $[C]_i$ = initial radionuclide concentration and $[C]_f$ = final concentration.

Prior to proposing use of this compound as a replacement for MST, the compatibility and effectiveness of it must be examined. Comparisons of the absorption of uranium, plutonium, neptunium, americium, and curium are also needed if the absorption of strontium proves effective.

The development of this material was funded by the Department of Energy, Office of Science and Technology, Efficient Separations and Processing Crosscutting Program. Testing of this material at SRS was also funded by the Efficient Separations and Processing Crosscutting Program (Technical Task Plan SR1-3-20-07); John Mathur, DOE Headquarters Program Manager.

Experimental

Standard Decontamination Factor Measurements

Three replicate salt solution samples were prepared for each sample of ST received from AlliedSignal (lot numbers: 8212-79, 8212-89-1, 8212-91, 8212-123, and 8212-107 [slurry of 8212-89-1]). The standard simulant salt solutions (SSS-95-3 or SSS-96-1, Table 1) were prepared from reagent grade chemicals.

The salt solutions remained slightly turbid after 12 hours and were filtered to remove any insoluble solids. The solid (or slurry) samples of ST (~50 mg) were contacted with 100 mL of the filtered simulated salt solution. The mixtures of salt solution and ST were stirred at room temperature (~23 °C). Contact time for these measurements was 48 hours. After the contact time elapsed, the samples were then filtered through a 0.2 micron Nalgene® disposable filter apparatus and analyzed by gamma counting for Sr-85. Blank solutions were also filtered through an identical filter and the filtrate analyzed.

Table 1. 5.2 M [Na+] Standard Simulated Aqueous Salt Solution

<u>Component</u>	<u>Concentration (M)</u>
Na ₂ SO ₄	0.14
NaNO ₂	0.73
NaNO ₃	1.07
NaOH	2.66
NaCl	0.022
NaF	0.015
Na ₂ SiO ₃ ·9H ₂ O	0.0039
Na ₃ PO ₄ ·12H ₂ O	0.0083
Na ₂ CO ₃ ·H ₂ O	0.17
Al(NO ₃) ₃ ·9H ₂ O	0.31
Na ₂ C ₂ O ₄	0.014
Sr (non-rad.)	<0.18 mg/L
Sr-85	0.06 mCi/L

Actinide Loading Measurements

A simulated salt solution³ (4.27 M Na⁺, Table 2) was spiked with Sr-85, commercial depleted uranyl nitrate hexahydrate (Mallinckrodt, lot 8640, 200 g/L U solution), and weapons grade plutonium (Kyser CR#99, 30.7 g/L Pu-239). The ratio of ST to salt solution varied from 0.9 to 0.05 g/L. Three replicate salt solution samples were prepared for each concentration of ST. The ST was from samples obtained from AlliedSignal (lot numbers: 8212-89-1, 8212-123) and Boulder Scientific (BSC2650005). The 4.27 M Na⁺ simulant salt solutions (Table 2) were prepared from reagent grade chemicals.

Table 2. 4.27 M [Na+] Simulated Aqueous Salt Solution for Actinide Loading Studies

<u>Component</u>	<u>Concentration (M)</u>
SO ₄ ⁻	0.40
NO ₂ ⁻	0.10
NO ₃ ⁻	1.00
OH ⁻	2.00
CO ₃ ⁻	0.02
AlO ₂ ⁻	0.33
U-238	10.6 mg/L
Pu-239	0.150 mg/L

The salt solution was spiked with non-radioactive strontium, filtered, Sr-85 added, filtered, uranium and plutonium added, stirred for 5 days, and filtered. The mixtures of salt solution and ST were stirred at room temperature (~23 °C). Contact time for these measurements was 48 hours. After the contact time elapsed, the samples were filtered through a 0.2 micron Nalgene® disposable filter apparatus and analyzed by gamma counting for Sr-

85, and by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) for actinides. Blank solutions (no ST) were also filtered through an identical filter and the filtrate analyzed.

Radioactive Waste Decontamination Factor Measurements

Radioactive waste salt solution samples were received from Tanks 43H (7/94) and 46H (8/94) and adjusted to a density of 1.24 g/mL with deionized water. The samples were stirred for over 10 hours at room temperature, and filtered with a 0.2 micron Nalgene® filter. The ST (~10 mg, lot #8212-89-1) was mixed with a 20 mL aliquot of the salt solution, and the slurry stirred at room temperature (~25 °C) for 48 hours. The samples were then filtered with a 0.2 micron Nalgene® filter. The samples were next acidified by mixing with an equal volume of 8 M nitric acid and mixed with Bio-Rad AMP-1 resin (0.1 g/mL) to remove radioactive cesium. The resin was then removed by filtration (0.45 micron) and washed with water. The aqueous samples were then analyzed. The initial untreated sample was also acidified and treated with AMP-1 resin prior to analysis. An initial untreated sample was also diluted (~1000:1) with deionized water and analyzed. The samples were analyzed by counting the radioactive Sr-90 and Sr-85 decay energy, and by measuring the Sr-88 and actinide concentrations using ICP-MS.

Simulated Tanks 43H and 46F Waste Decontamination Factor Measurements

Simulants designed to mimic the major constituents in the Tank 43H and Tank 46F samples were prepared from reagent grade chemicals (Table 3). These simulants were spiked with Sr-85. Decontamination factor experiments, identical to those described above for standard salt solution, were performed with AlliedSignal ST (lot #8212-89-1).

Table 3. Simulated Tank 43H and 46F Salt Solutions

Component	Concentration (M)	
	Tank 43H	Tank 46F
Na ⁺	7.46	7.63
NO ₂ ⁻	0.73	0.40
NO ₃ ⁻	0.87	1.87
OH ⁻	6.03	5.5
AlO ₂ ⁻	0.27	0.23

In-Tank Precipitation Simulant Filter Performance

A sample of AlliedSignal ST (lot #8212-123) was mixed with a simulated ITP slurry of potassium tetraphenylborate and salt solution. The formulation for the 1 wt % insoluble solids simulant has been described.⁴ A sample of MST (Optima Drum #4) was mixed with a second sample of simulated ITP slurry. Both samples

used a final ST (or MST) concentration of 0.21 g/L. The slurries were then tested using the Parallel Rheology Experimental Filter (PREF). The PREF was equipped with 0.5 micron Mott sintered-metal filters. The tests used a standard statistically designed test matrix.⁴ At the conclusion of each experiment, the filters were chemically cleaned with 2.0 wt % oxalic acid for 1 hour. To verify that the filter was clean, the filtrate flow rate with deionized water was determined. In both cases, the filtrate clean water flux was restored after the chemical cleaning.

Particle size distribution data were collected on the AlliedSignal ST sample (lot #8212-123). The sample was analyzed using a Microtrac II, Series 7998 Particle Size Analyzer. The range of this instrument is 0.7 to 700 microns. The instrument operates via low-angle forward scattering of diode laser light.

Results and Discussion

Standard Decontamination Factor Measurements

The calculated decontamination factors (DFs) for the samples of ST are presented in Table 4 as corrected for slight changes in the weight of ST used in each experiment. The variability in the DF was calculated by a propagation of errors. The reported variability is the 95% confidence interval for the measurement.

Table 4. Standard DF measurements

Lot #	DF (48 hour)	Kd (mL/g)
8212-79 ¹	47 ± 22	9.2E4
8212-89-1 ¹	73 ± 24	1.4E5
8212-107	69 ± 16	1.4E5
8212-91 ¹	101 ± 26	2.0E5
8212-123	260 ± 100	5.2E5

During the test program, AlliedSignal improved the formulation of the material to increase the strontium absorption. The results in Table 4 are in chronological order of manufacture. The efforts to improve the strontium absorption capacity have been highly successful. The characteristic that causes the difference between these samples is not known to SRTC personnel due to proprietary concerns. All samples were reported by the vendor to be within the particle size specification for MST.

Actinide Loading Measurements

The best available (at the time of the experiment) AlliedSignal material (8212-89-1) was used in actinide loading experiments to evaluate the absorption of uranium and plutonium. A sample of 8212-123 was also included in the study when it became available. Comparison tests were completed using a sample of the Boulder

Scientific Co. (BSC2650005) manufactured material. This material was used by D.T. Hobbs in earlier actinide loading experiments.⁶

Table 5. Actinide Simulant Measurements

Lot #	Loading	Decontamination Factors		
		Sr	U	Pu
8212-89-1	0.053 g/L	3.8 \pm 1.4	0.98 \pm 0.05	1.64 \pm 0.58
"	0.17	30 \pm 6.8	1.03*	3.43*
"	0.31	97 \pm 10	1.02 \pm 0.06	5.45 \pm 1.97
"	0.89	720 \pm 293	1.20 \pm 0.07	12.8 \pm 7.2
8212-123	0.30	231 \pm 116	1.25 \pm 0.14	24.3 \pm 15.8
BSC "standard"	0.30	84 \pm 11	1.18 \pm 0.05	24.9 \pm 19.4

* only two samples used for DF determination due to apparent analytical problems

The results indicate that the decontamination factors of plutonium are lower with 8212-89-1 AlliedSignal material than with the BSC material, although uncertainty in the plutonium absorption is large for the BSC material. The uranium decontamination factor is also marginally lower for this material. The actinide absorption of the AlliedSignal 8212-123 material is comparable to that for the BSC material. The strontium decontamination factor for the BSC material is much higher than previously reported for solutions doped with strontium, uranium, and plutonium, but this may result from the lower sodium concentration in this simulant. Overall, the 8212-123 material shows good removal of Sr, U, and Pu.

The loading of Pu observed by Hobbs⁶ for the BSC material at 0.066 wt % Pu (calculated) at 0.3 g/L MST was higher than that observed here (Table 6). However, this work indicates that the 8212-123 material is comparable to the BSC material, and the 8212-89-1 is only slightly lower. The plutonium loading for the three materials tested are shown in Figure 1. The curve for the 8212-89-1 material appears logarithmic, as opposed to the previous work which indicated linear behavior.⁶ The plutonium loading is comparable to that previously observed.

Table 6. Actinide Simulant Loading Calculations

Lot #	Loading	wt % U	wt % Pu
8212-89-1	0.053 g/L	<d.l.	0.123
"	0.17	0.36*	0.063*
"	0.31	0.17	0.039
"	0.89	0.23	0.015
8212-123	0.30	0.788	0.047
BSC "standard"	0.30	0.62	0.047

<d.l. = less than detection limit

* only two samples used for DF determination due to apparent analytical problems

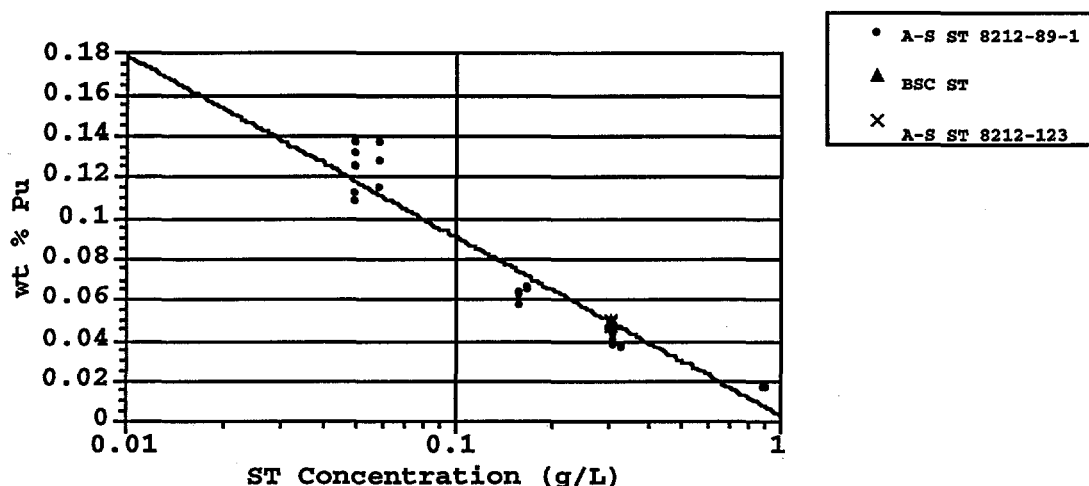


Figure 1. Plutonium loading on sodium titanates

$$\text{wt \% Pu} = -3.825700\text{E-}2 * \ln(\text{ST concentration}) + 3.002941\text{E-}3$$

$$R^2 = 9.357302\text{E-}1$$

The uranium loading in the previous work⁶ was 0.64 wt % U (calculated) at 0.3 g/L MST. This loading exceeds that for the 8212-89-1 material, but is lower than the 8212-123 material. The BSC and 8212-123 materials both had higher uranium loading than the 8212-89-1 material. The uranium loading for all three materials is shown in Figure 2. Results from several tests with the 8212-89-1 material, primarily at 0.05 g/L ST, were deleted from Figure 2. The deletions were necessary because the differences between initial and final uranium concentrations were within the scatter of the data and the calculated decontamination factors were less than unity. These are shown in Table 6 as less than the detection limit. The loading of uranium vs. ST concentration (Figure 2) appears linear, although the data is scattered. The linear behavior of uranium loading agrees with previous work with MST manufactured by Boulder Scientific.

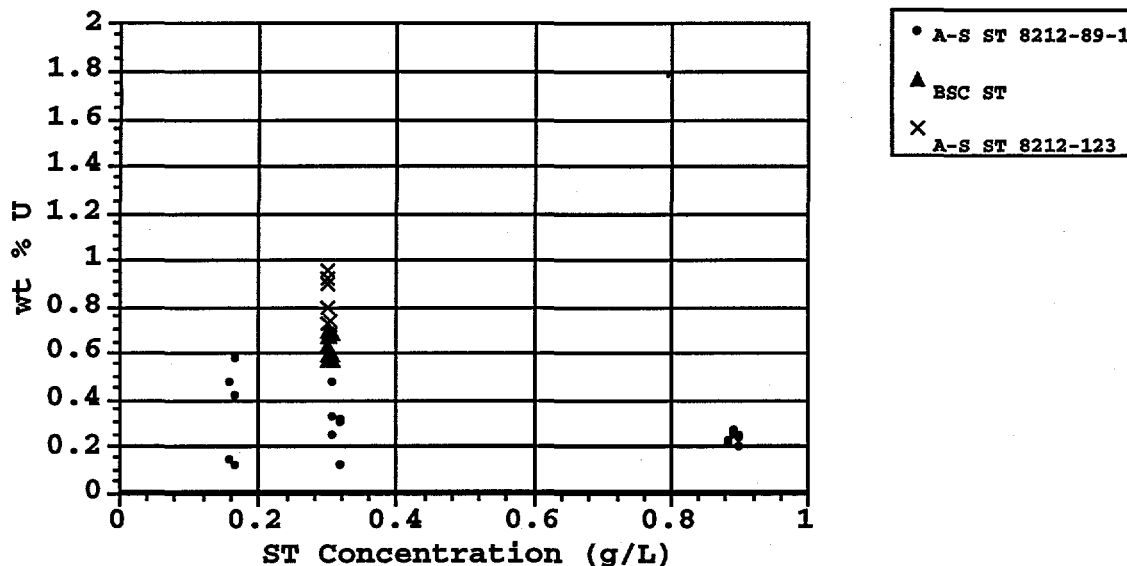


Figure 2. Uranium Loading on Sodium Titanates

Radioactive Waste Decontamination Factor Measurements

Radioactive waste samples were used in standard decontamination factor tests in the SRTC Shielded Cells. The results (Table 7) indicate that strontium removal was not very effective. Also, the removal of actinides proved inconsistent. The U-235 analysis indicated more uranium in the treated sample than in the untreated sample (i.e., DF < 1). These observations were attributed to cross contamination of samples or contamination from the Shielded Cells environment.

Table 7. Standard DF measurements with Radioactive Waste Samples

Radionuclide	DF Tank 43H	DF Tank 46F
Sr-90	<1*	1.6*
Sr-88	3.4	1.9
Th-230	n.d.	>11
U-235	1.4	0.6
Np-237	2.8	>20
Pu-239	3.6	1.6
Am-243	n.d.	>11
Cm-245	>36	n.d.

* significant interference from H-3 or Ru-106
n.d. = none detected

To further evaluate the possibility that the samples were contaminated through manipulation in the Shielded Cells or that interference from other radionuclides was impeding the analysis,

the samples from Tanks 43H and 46F were reused in a decontamination factor test. The samples were spiked with Sr-85 to allow comparison of Sr-85 with Sr-90 analyses. Replicate tests were not feasible due to the lack of sample volume.

Table 8. Standard DF Measurements with Reused Radioactive Waste Samples

Lot #	DF Tank 43H	DF Tank 46F
Sr-85	5.1*	n.d.
Sr-90	39*	<1
U-234	3.4	n.d.

*significant interference from Ru-106

n.d. = not detected

The initial Sr-90 concentration in the Tank 43H sample was only slightly above the Saltstone Waste Acceptance criteria (0.04 uCi/g) and the initial Tank 46F sample is below the limit. The transuranic actinides were removed in the first decontamination test, and were below the detection limit after the second. The analyses of the U-234 isotope was in the proximity of the detection limits for the ICP-MS analyses, reducing the confidence in the analyses. The Sr-88 analyses indicated that the concentration of strontium was also near the detection limit. A significant interference from Ru-106 was noted in the Sr-90 and Sr-85 analyses. These data suggest that the widely varying results are due to scatter in the data near the detection limit. Use of samples containing higher initial concentrations of Sr-90 are recommended for further testing. The poor decontamination factors observed in the radioactive samples are probably not due to an attribute of the AlliedSignal material.

Simulated Tanks 43H and 46F Waste Decontamination Factor Measurements

Simulants were prepared that contained the major constituents of the Tank 43H and 46F waste. The solutions were spiked with Sr-85, and comparison tests were performed (Table 9) with the same batch of ST as the radioactive waste tests (AS 8212-89-1). Although the results indicate lower decontamination factors when compared with standard salt solution, the higher sodium concentration of these simulants is expected to reduce strontium removal.³

Table 9. Simulated Tank 43H and 46F Sr-85 Decontamination Factor Measurements

Simulant	Sr-85 DF
Tank 43H	39 ± 8
Tank 46F	54 ± 12

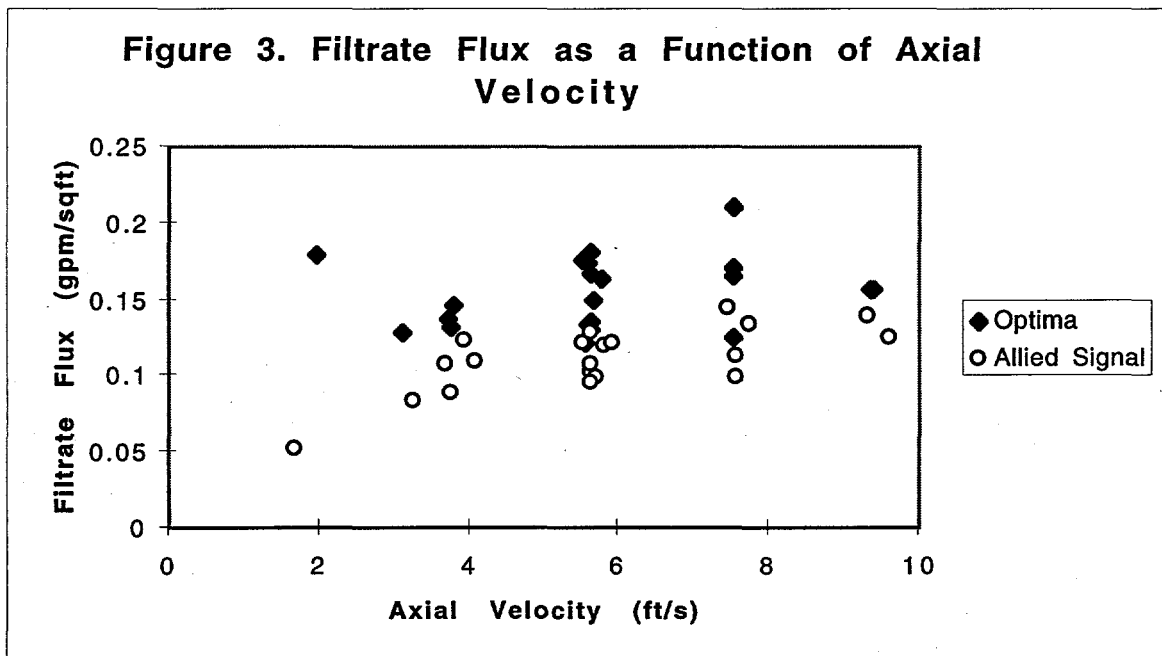
In-Tank Precipitation Simulant Filter Performance

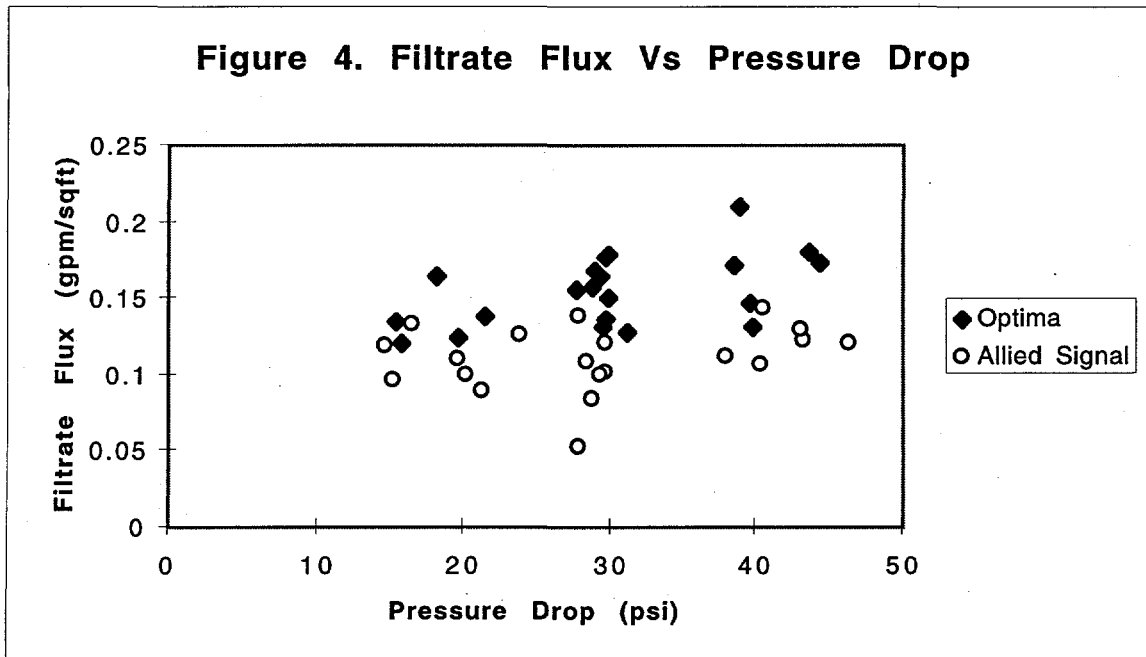
The performance of the filters with Optima MST and AlliedSignal ST are statistically different. The filter performance can be described by the following equation:

$$Q = 0.0489 + 0.0011dP + 0.0093V + 0.0444f(\text{type})$$

Where Q = the filtrate flux in gpm/ft^2 , dP is the differential pressure (transmembrane) in psi, V is the axial velocity in gpm , and $f = 1$ for Optima MST and $f = 0$ for AlliedSignal ST.

The Optima MST filtrate flux (Figure 3) is approximately 35% higher than the AlliedSignal material (8212-123). The difference in performance is likely due to the difference in particle size of the two materials. The average particle size of the AlliedSignal ST was 3.10 microns, and the Optima material was 17.2 microns. The AlliedSignal material has a much narrower size distribution of particles than the Optima material. Both materials exceeded the acceptance criteria for fines (<1 vol % less than 1 micron), with the AlliedSignal material at 3 vol % and the Optima material at 1.5 vol % less than 1 micron. The Optima material also exceeded the criteria for large particles with 20 vol % greater than 35.5 microns. Routine chemical cleaning with oxalic acid and sodium hydroxide was adequate to restore the filter to pristine conditions, based on the clean water flux.





Conclusions

The AlliedSignal sodium titanate material requires only slight modifications to be acceptable for use in ITP. Increasing the particle size is necessary to avoid impacting the filter performance. Increasing the particle size will decrease the surface area and is expected to decrease the strontium decontamination factor. Although the decontamination factor will be impacted, the newest formulation (8212-123) exceeds the acceptance criteria for strontium removal. The particle size and decontamination factor will need to be balanced to optimize performance of both the filter and the strontium removal.

The removal of strontium from radioactive samples was not clearly demonstrated due to experimental design limitations. The analytical results were not internally consistent, suggesting an interference in the counting method. The decontamination performance for simulated waste was relatively well behaved and consistent with previous results using ST from other vendors.

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Design Check

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