

Investigation of Varied Strontium-Transuranic Precipitation Chemistries for Crossflow

by

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April 24, 2000

BNF-003-98-0171

Mr. Mike Johnson
BNFL, Inc.
2940 George Washington Way
Richland, WA 99352

Dear Mike:

**RPP-WTP PRIVATIZATION PART B, SRTC WFO-98-003, SUBMITTAL OF
INVESTIGATION OF VARIED STRONTIUM-TRANSURANIC PRECIPITATION
CHEMISTRIES FOR CROSSFLOW FILTRATION REPORT, BNF-003-98-0171.**

Attached please find the "Investigation of Varied Strontium-Transuranic Precipitation
Chemistries for Crossflow Filtration" Report.

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Please contact Charles Nash (803-725-2615) if you have any questions.

Sincerely,

A handwritten signature in cursive script that reads 'H. F. Sturm, Jr.'.

Harold F. Sturm, Jr.
BNFL RPP-WTP Project Manager
Savannah River Technology Center

hfs/sgm

Att.

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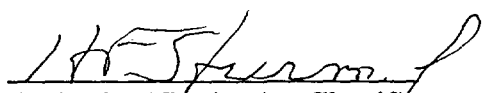
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**Investigation of Varied Strontium-Transuranic Precipitation
Chemistries for Crossflow Filtration**

April 18, 2000

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SUMMARY

Precipitation chemistries for strontium and transuranic (TRU) removal have been tested for crossflow filterability and lanthanide removal with simulants of Hanford tank 241-AN-107 supernate. This is the initial work indicating the usefulness of a strontium and permanganate precipitation process as applied to the Hanford River Protection Project. Precipitations with both ferric and ferrous iron were shown to be at least two orders of magnitude less filterable than a 0.1 gpm/ft² target average flux that was desired at the time. A precipitate from a strontium nitrate strike alone was found to filter easily and to make the desired average flux. Other chemistries tested included precipitants of lanthanum(III), nickel(II), calcium(II), and a redox chemistry using sodium permanganate. Of these chemistries a strontium and permanganate strike including calcium provided the highest filter flux compared to the other chemistries. It showed the most promise in lanthanide removal as well. This work provides a promising direction for further work to achieve both acceptable filterability and decontamination for Envelope C wastes to be treated by the Hanford River Protection Project.

INTRODUCTION

The work reported here was originally intended to satisfy needs for crossflow filter testing of a strontium and ferric precipitation method for treating Envelope C using a 241-AN-107 simulant. All Hanford tanks have the prefix "241", which has been dropped for convenience in the remaining text. However, extreme filtration difficulties with the ferric hydroxide precipitation led to investigations of other chemistries. Most notable is a permanganate strike to replace ferric reagents. This report covers the chemistries, filterabilities, and lanthanide decontaminations for the chemistries tested with a Mott crossflow filter. The initial ferric hydroxide work followed a Technical Task Plan.¹ Failure of the material to demonstrate practical filtration led BNFL to direct testing of alternate chemistries also being explored with small "beaker" tests.² This work is an initial investigation into transuranic removal treatment for the Hanford River Protection Project with permanganate. Further work is beyond this is required as shown in the Recommendations section.

Background on Ferric Hydroxide Precipitation Problems

Filtration of caustic simulants containing aqueous soluble complexants have in the past shown great difficulty in both deadend and crossflow filtration. Original test planning by McCabe³ considered deadend filtration for strontium-ferric precipitations of aliquots of both simulants and active supernates. Plans were revised to use centrifugation as testing commenced.^{4,5}

Part A crossflow testing of a "worst case" Envelope C simulant with strontium and ferric precipitation found no filtrate production despite trials with both Mott 0.5 micron and a Graver precoated (effective 0.07 micron) filter tubes.⁶ The simulant was high in aluminum but also high in organics similar to AN-107 supernate. The test matrices were

cancelled because of the difficulties. It was thought that filter fouling was not the problem but that the precipitate slurry formed impermeable cakes.

Similar crossflow filtration problems were found at the BNFL plc operated site in Sellafield, England using a simulant of AN-107 and ferric nitrate / strontium nitrate reagents.⁷ It was thought that the presence of organic materials in the feed caused the low to zero filterability. The Enhanced Actinide Removal Plant at Sellafield finds ferric precipitation practical for high caustic feeds that do not have organic complexants.

Background on Precipitation

Flocculation and precipitation are widely used for clarification in municipal water treatment. Iron (III) and aluminum salts are the most common in use, with lime being used to raise pH as needed. The LANL Liquid Waste Processing Plant also used such a process for decontamination.⁸ Water was treated with about 2000 mg/L ferric sulfate followed by precipitation with 8000 mg/L lime. Rotary drum filters required a filter aid precoat, either diatomaceous earth or Perlite, to operate efficiently.

Co-precipitation of Np, Am, and Pu with ferric hydroxide is used within an analytical method for the sum of those analytes.⁹ The two-stage method on average extracts 98% of the actinides in aqueous samples adjusted to high pH with strong ammonium hydroxide. The work separated these actinides from samples containing Cs-137 and Sr-90 as well, but it did not address special problems that complexant-containing samples might pose.

Use of hydrated ferric hydroxide and manganese dioxide precipitates to remove radionuclides from aqueous streams received extensive study in the 1950's. Two Ph. D. (doctoral) theses review the voluminous literature.^{10,11} Many methods exist to produce manganese oxide precipitates including the Guyard reaction (reaction of Mn(II) and permanganate to create manganese dioxide) and oxygenation of Mn(II) under basic conditions (pH approximately 10). Products were often not pure manganese dioxide but a mixture of the +2, +3, and +4 oxidation states of manganese. Other metal ions that were present would be incorporated or adsorbed into the solids. The most highly charged metal ions were generally favored in adsorption.

The ability of manganese oxides to adsorb plutonium has been shown to be greater than that of iron oxides in naturally occurring minerals.¹² Plutonium was found to be in the +5 and +6 oxidation states which are generally more water-soluble at high pH than the +3 and +4 states. The +5 state is most common in neutral to basic groundwaters where oxygen is present.

The association of manganese and calcium for synergistic adsorption of water contaminants is prevalent in the literature. Aziz and Smith found that limestone was better for treating manganese-containing water than gravel or crushed brick at the same pH.¹³ Goel and Chaudhuri also demonstrated the special ability of calcium plus manganese to remove organic (humic) acids from water.¹⁴

Bostick et. al. studied a strontium removal process whereby strontium chloride was added to caustic low-level waste (LLW) to precipitate SrCO₃.¹⁵ It is to be noted that the wastes

and simulants in those cases do not contain complexants. After the solids were separated from the waste sulfuric acid was used to drop the pH to 8, leading to further decontamination effected by the precipitation of aluminum hydroxide. At least 50 ppm strontium was needed to be added to the waste to obtain maximum decontamination. Good and efficient mixing during this precipitation was needed because of the rapid precipitation process. Mixing was also needed to effect the desired isotopic dilution. Ferric ion was found to be a useful additive to the strontium strike solution (added at a 25 ppm level of ferric sulfate) because it made the resulting precipitate easier to filter.

Decontamination factor (DF) for the above work was defined as the ratio of strontium activity in each input sample to that of the product liquid. Dilution caused by reagent addition thus contributed to stated DF along with the decontaminating action of the process. The DF of Sr-90 removal was found to exceed 100 in the first step. The second step removed additional Sr-90, resulting in an overall DF of about 350. Increasing the initial concentration of aluminum in the incoming waste was found to increase DF linearly in the range of aluminum concentrations 300 to 1300 mg/L.

In the same study Bostick et. al. used two successive 80 mg/L calcium chloride additions instead of strontium chloride additions to find that the DF of the first step was about 10 after the second strike. The DF of the pH reduction step, however, was increased so that a process DF of 164 was realized.

D. L. Herting attempted to precipitate Sr-90 from Tank AN-107 waste using 0.1 M strontium nitrate.¹⁶ The complexant concentration in the waste was too high to allow precipitation. Herting then increased the strontium nitrate concentration by a factor of ten and studied a mixture of 101-AW, 106-AP, and 102-AP to find that this reagent solution removed 99.4% of the Sr-90.¹⁷ It must be noted here that this mixture of 101-AW, 106-AP, and 102-AP is not an Envelope C (complexant) liquid in contrast to AN-107 supernate. Higher strontium decontaminations are to be expected in cases like this where complexation is not impacting the process. Nickel (II) nitrate was also effective, removing 98.5% of the Sr. Manganese (II) nitrate and calcium nitrate were marginally effective under the same conditions. Carbonate, phosphate, sulfate, and sulfide ions had no effect. Herting extended the work to include ferric precipitation for Am-241 and Pu removal.¹⁸ Ferric precipitation removed 97% of the Am-241 at 3 M hydroxide, though that level of hydroxide alone removed 72%. Ferric nitrate was much less effective at removing plutonium, taking 57 to 78% out regardless of iron or hydroxide level.

Kupfer et. al. reported work by Herting where strontium nitrate strikes and ferric nitrate strikes were applied to separate samples of AN-107 complexant waste.¹⁹ Samples were first NaOH-adjusted to 1.5 or 3.0 M NaOH. The strontium strike (final concentration range 0.1 to 0.3 M) removed 95% of the Sr-90. A similar process applied to a composite of three non-complexant tank wastes removed 99% of the Sr-90. No significant TRU removal was observed in this step.

Peretrukhin et. al. used the method of appearing agents to create metal oxide precipitates in caustic simulants.²⁰ This method is as close as one can get to a perfectly homogeneous addition because the precipitating agent is produced in solution from the breakdown of carrier complexes. The presence of complexants severely reduced the DF. In 0.1 and 0.3

M NaOH, with 0.02 M added iron as a nitroprusside appearing agent, 0.1M EDTA reduced the DF for Pu(IV) to 8, while HEDTA eliminated all precipitates and prevented any separation at all. Glycolate and citrate reduced DF to between 32 and 93. Addition of 0.1 M calcium ion improved DF by 1 to 2 orders of magnitude by masking the EDTA and HEDTA. "Masking" refers to reducing the chemical activity of complexants by providing a metal that they readily chelate. In this case the metal is calcium. The Ca (II)/EDTA ratio must be at least 1 for efficient masking.

Reference 20 above lists in its "Objectives Section" summarized results for Direct Coprecipitation using ferrous ion in the presence of oxygen. Plutonium decontaminations of 100 were reported for both 0.5M to 4 M NaOH solutions and 0.2 M added iron, and 3.2 M NaOH with 0.075 M added iron.^{21, 22}

Krot et. al. studied the removal of Pu and Np from NaOH solution using various metals and ligands as appearing agents.²³ Agents that produced ferric hydroxide effected Pu (VI) and Pu(V) DF's exceeding 210 for NaOH levels 0.5 to 4 M. The concentration of the Fe(III) appearing agent was typically 0.01 M Fe(III) during reaction in the waste. Hydroxide levels of 7 M and above significantly reduced DF. Ferric hydroxide was much less effective at removing Neptunium (VI) and (V), DF's typically being less than 10. They exceeded 14 only in the 0.5 M NaOH solution.

The work that follows applies chemistries found in the background references to determine not only decontamination in a simulant of a Hanford waste of interest (AN-107) but also to observe filterability. The motivator in modifying the strontium-iron process in the SRTC Part A work is that the resulting slurry could not be filtered. The background can be summarized by the following: (1) Metal oxide precipitates such as those of iron, cobalt, manganese, and nickel can decontaminate actinides in high-sodium caustic waste, (2) isotopic dilution of strontium has been effective in removing Sr-90 from filtrates, (3) the presence of organic complexants can prevent both actinide and Sr-90 removal, and (4) addition of easily complexed metals can recover process efficiency when complexants are present. The following work addresses both decontamination and filterability as an initial effort to establish a process that meets the needs of the Hanford River Protection Project.

EXPERIMENTAL

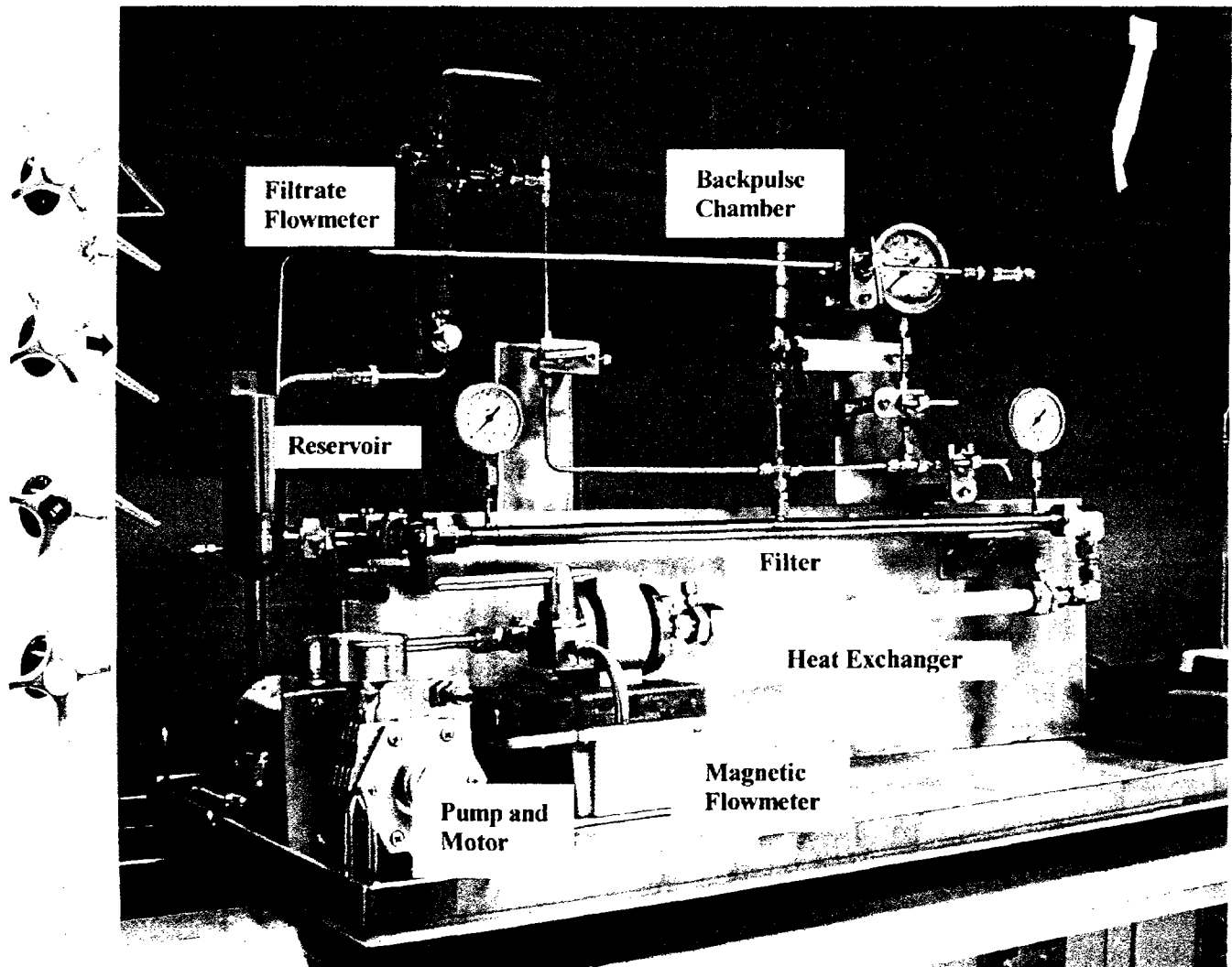
Apparatus

Crossflow filtration was performed with a Cells Unit Filter (CUF) portable rig that was set up in a nonradioactive laboratory hood. Figure 1 shows the unit without cooling tubes connected to the heat exchanger for clarity. Feed from the reservoir at the left goes to a progressive cavity pump. The pump is operated at variable speed by controlling air pressure to the air motor that drives it. Liquid is pumped through a magnetic flowmeter and heat exchanger that removes pump heat. It then passes down the center of a crossflow filter of 2 foot porous length. A throttle valve downstream drops fluid pressure back to near atmospheric.

Filtrate flowrate is measured with a sightglass and stopwatch. A simple backpulse system can be charged with filtrate and compressed air stored in the filtrate chamber forces

reverse flow upon the filter medium. Standard Bourdon-type pressure gauges indicate pressure. A thermocouple mounted near the bottom of the reservoir measures slurry temperature directly. Details of the CUF are documented on six approved engineering drawings.²⁴

**FIGURE 1. PHOTOGRAPH OF THE CELLS FILTER UNIT
IN A NONRADIOACTIVE LABORATORY**



Operations

General operation of the CUF follows an SRTC procedure.²⁵ The rig is first cleaned by circulation of 1 M nitric acid, 1 M sodium hydroxide, or deionized water. These reagents are prefiltered to 0.22 micron with a nylon filter.

Initial work to obtain clean water flux with a 0.1 micron, 3/8-inch ID, Mott filter tube ran into difficulty when very low fluxes were obtained. Discussions with Mott personnel and comparisons with similar experience at the Pacific Northwest National Laboratory

(PNNL) revealed that the filter was a "gas" service and not a "liquid" service, 0.1 micron Mott filter. The "gas" versus "liquid" distinction is made by Mott despite the same nominal pore size for both media. Since the delivery time to obtain a "liquid" service filter was so long the BNFL pretreatment technical manager directed SRTC personnel to use an available Mott, 0.2 micron, 0.5-inch ID filter tube. This resulted in lower crossflow velocities than would be seen in a 3/8-inch ID, 0.1 micron filter tube, but still allowed comparison of the filterability of different precipitation chemistries.

The AN-107 simulant used in this work was developed by Russ Eibling of the Savannah River Technology Center. Development of the simulant is currently being documented. The constituents and concentrations are provided in Appendix A of this report.

The routine for testing a precipitation chemistry was as follows:

1. Measure 1 liter of Envelope C AN107 simulant into a large Erlenmeyer flask.
2. Heat and stir the liquid, target temperature being 50 °C.
3. Slowly add 266 mL dilution water.
4. Slowly add 85 mL of 17 M NaOH solution. The sodium target level is 7 M and it is desired to arrive at 1 M added free hydroxide at the end of the precipitation. The sodium level tested here is considered to be the high end – levels of 6 or 5 M sodium may be favored in further process work.
5. After 50 °C is reached, slowly add 2 M strontium nitrate, typically 55 mL to obtain 0.075 M added strontium.
6. Wait 15 minutes during stirring at the 50 °C temperature.
7. Slowly add the desired amount of metal nitrate solution, typically 2 M in the metal being studied.
8. Stir with a magnetic stir bar for four hours while maintaining 50 °C.
9. Cool to room temperature. The flask was swirled in ice water to accomplish this.
10. Archive some material and use the rest in the CUF.

Operation of the CUF involved the following routine:

1. The unit had been chemically cleaned and drained previously. The feed from above is introduced into the reservoir.
2. Two conditions were typically used, with runs lasting for an hour after initial backpulses. The first run was often at 5 ft/sec and 20 psid transmembrane, and the second was at 6.9 ft/sec and 55 to 60 psid transmembrane. Original plans were for 9 and 12 ft/sec velocity, but the use of the filter with the larger ID (1/2" versus 3/8" ID) resulted in these lower velocities.
3. Temperature was controlled to 25 +/-5 °C by turning the cooling exchanger on or off as needed. Water from a bucket of ice water was circulated to provide the cooling.
4. Both concentrate and filtrate samples were collected during the runs.
5. After runs were completed the rig was drained.
6. Cleaning consisted of a water flush, a 1 M nitric acid flush, and a final water flush.
7. Clean water flux was measured to show that cleaning was effective.
8. The rig was drained of the water and thus ready for the next slurry. The filter loop was always wet within because air drying was not desired.

Two conditions for filter operation had been chosen to cover a relatively wide range of crossflow filter conditions in an abbreviated test matrix. The conditions of low and high combinations of pressure and velocity are extremes in the Ultrafiltration Specification.²⁶ The filter testing was abbreviated to two points for each chemistry because the nature of this work was to test different precipitation chemistries quickly. This would maximize the chances that a successful modified process would be found in a short time.

RESULTS AND DISCUSSION

Filtration – Precipitate Slurries

Results of filtration of precipitate slurries follow a description plus significant observations for each of the chemistries. Molarities of precipitants are summarized in Table 1 following the descriptions.

Run 1: Standard strontium and ferric nitrate precipitation. This first test was a control and also an initial attempt to see if any filtrate could be produced at all. The experimental routine above was followed with strontium added to 0.075 M and ferric nitrate added to 0.075 M iron. No filtrate was seen when the filter was started at 20 psid transmembrane and 5.1 ft/s (1.6 m/s) and run for an hour. Conditions were increased to 55 psid and 6.9 ft/s (2.1 m/s) and held for half an hour. No filtrate was seen and there was none available for backpulse.

Run 2: Strontium only. The purpose was to see if the strontium precipitation alone was filterable. Simulant was caustic adjusted per the experimental routine and precipitated to 0.075 M strontium. No further precipitants were added. Four hours later filter fluxes were found to be relatively high, with averages exceeding 0.1 gpm/ft²*ft. This run was also designed to test “split processing” where filtrate was to be further processed with iron in a following run.

Run 3: Ferric addition only, of a previously strontium-treated material. The filtrate from Run 2 was precipitated with 0.075 M ferric nitrate. No filtrate flux was seen in a 40 minute period at 55 psid transmembrane and 6.9 ft/s (2.1 m/s). The cooling exchanger was turned off and temperature allowed to rise to 42 °C. 50 ppm of polyethylene oxide polymer (PEO, a general flocculating filter aid) was also added when the temperature alone did not produce filtrate. The polymer did nothing to promote flocculation under these alkaline conditions.

Run 4: Ferric addition only, treating fresh simulant. This repeat of Run 3 used fresh simulant with standard caustic adjustment and ferric addition to 0.075 M. Extremely small fluxes were found.

Run 5: Ferrous treatment. The Run 4 concentrate had been removed from the CUF. The purpose of this run was to treat it with 0.05 M ferrous sulfate (Fe (II)). Ferrous ion is known to react with ferric ion under precipitating conditions to produce Magnetite, a granular and magnetic material that should show improved filterability.

4.02 g of NaOH solids was first dissolved into a liter of the precipitate to compensate for the addition of more acidic precipitating agent. The ferrous precipitant was added over 5 minutes at 50 °C. Black (not the typical dark brown) precipitate was noted to form, though a cloudy brown phase was always present. The brown phase settled little if at all. The stirrer was turned off temporarily. A magnet held next to the flask attracted black granular particles, indicating that the goal to form magnetite was likely met.

Run 6: Precipitation with strontium and lanthanum(III). The purpose was to try lanthanum as a new sequestering agent. Lanthanum, being trivalent, might perform as a good substitute for other lanthanides and actinides. It has also been investigated in drinking water treatment.²⁷

Run 7: Precipitation with strontium and iron(II). Iron(II) was used alone to see if a more filterable form of iron precipitate could be created after standard strontium addition. While filter fluxes looked favorable in the first few minutes it quickly degenerated with time and shear. It is likely that air oxidation of ferrous ion created some of the difficulty filterable ferric floc that has plagued this process.

Run 8: Precipitation with strontium and nickel(II). Nickel(II) as nitrate was used as a substitute for iron because of the known affinity of nickel for complexants.²⁸ The high concentration of nickel in the filtrate showed that this is the case, but filterability and lanthanide decontamination did not indicate that nickel(II) chemistry was attractive overall.

Run 9: Precipitation with strontium and cobalt (II). Cobalt(II) nitrate was used as a substitute for iron because of the known affinity of cobalt (II) and (III) for complexants.²⁸ The affinity of cobalt (III) is so high with EDTA that it may act as a strong reductant in order to form the cobalt(III) complex. Again the goal was to displace lanthanides (simulating actinides) from complexation in order to remove them.

Run 10: Precipitation with strontium and calcium. The goal was to test the effect of calcium on filterability. Small-scale precipitation studies with AN-107 simulant² was finding that calcium and permanganate might be of interest as a new chemical process.

Run 11: Calcium – strontium – sodium permanganate precipitation. This chemistry was run to try to get the best combination of filterability and decontamination based on developing small-scale precipitation studies with AN-107 simulant² that showed the advantages of this chemistry over iron precipitation chemistry.

Table 1. Summary of Chemistries Tested

Run Number	Sr Molarity or starting material	Other precipitant	Filtrate flux seen	Date Run
1	0.075	0.075 M Fe(III)	No	3/2/99
2	0.075	none	~ 0.1 gpm/ft ²	3/3/99
3	Run 2 filtrate	0.075 M Fe(III)	No	3/4/99
4	0	0.075 M Fe(III)	<0.01 gpm/ft ²	3/8/99

Run Number	Sr Molarity or starting material	Other precipitant	Filtrate flux seen	Date Run
5	Run 4 concentrate	0.05 M Fe(II)	<0.004 gpm/ft ²	3/9/99
6	0.075	0.075 M La(III)	<0.005 gpm/ft ²	3/17/99
7	0.075	0.05 M Fe(II)	<0.007 gpm/ft ²	3/23/99
8	0.075	0.03 M Ni(II)	<0.015 gpm/ft ²	3/25/99
9	0.075	0.03 M Co(II)	~0.02 gpm/ft ²	3/26/99
10	0.075	0.075 M Ca(II) added before Sr	~0.013 gpm/ft ²	4/13/99
11	0.075	0.02 M Ca(II), then Sr, then 0.04 M NaMnO ₄	~ 0.017 gpm/ft ²	4/27/99

Figure 2 below shows the one-hour average fluxes for the 11 runs. Note that:

Series 1 data are at 20 psid and 5.1 ft/s (1.6 m/s) and run for an hour.
Series 2 data are at 55 psid and 6.9 ft/s (2.1 m/s) and held for an hour.

Figure 3 (following) shows the respective permeabilities for the runs.

FIGURE 2. ONE-HOUR AVERAGE CROSSFLOW FILTER FLUXES FOR THE SLURRIES

Data are at 25 +/- 5 C

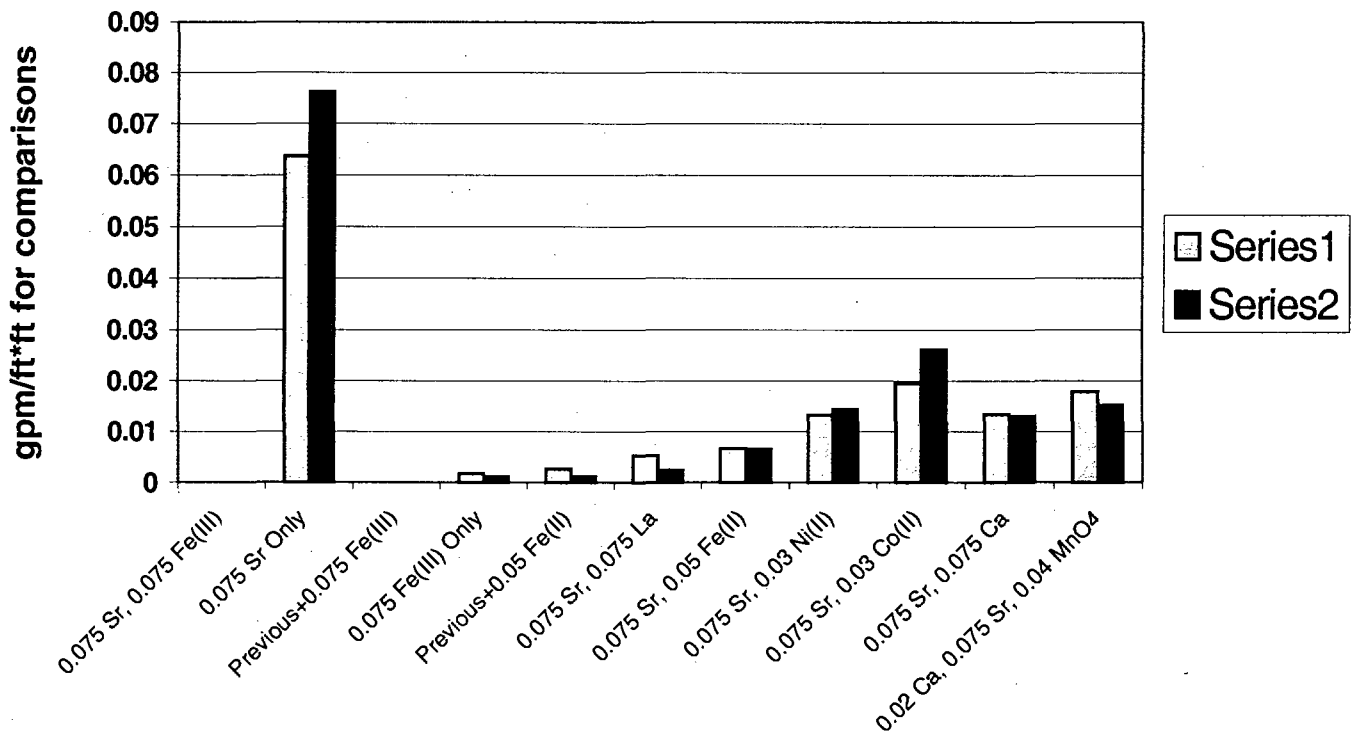
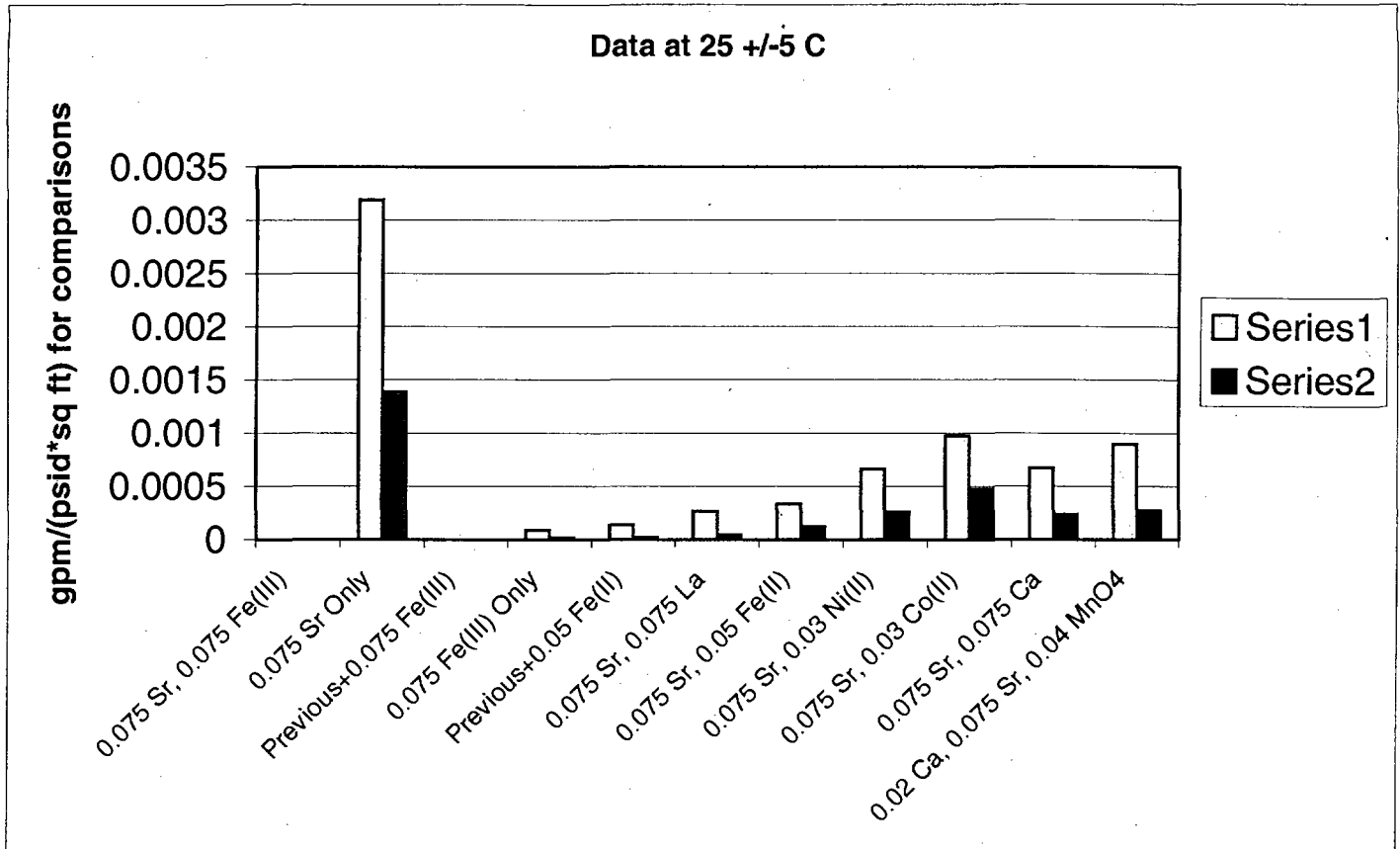


FIGURE 3. ONE-HOUR AVERAGE CROSSFLOW FILTER PERMEABILITIES



The run order of the two series conditions was meant to show the relative effect of conditions applied to the filter (transmembrane pressure and velocity) versus run time effect (filter fouling). In cases where series 2 average flux exceeded series 1 flux the applied conditions are more significant than filter fouling on a one-hour time basis.

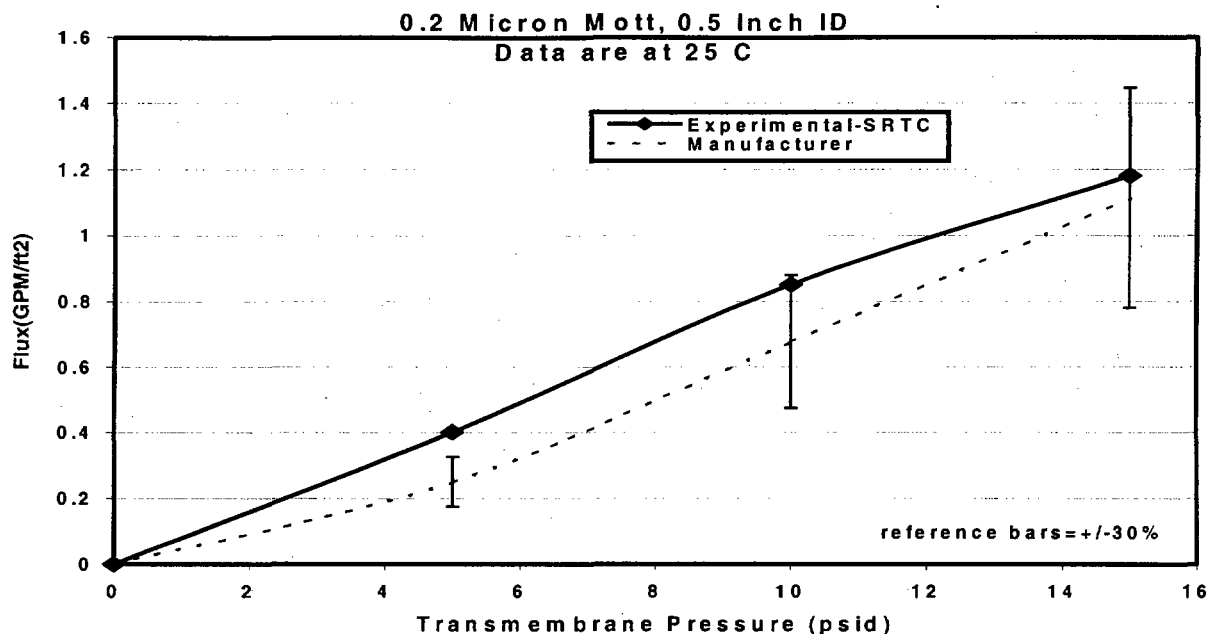
Fluxes are for data comparison only because this work was done with a larger diameter filter and lower concomitant velocity than originally planned. Problems with Mott 0.1-micron gas versus liquid filters led to the use of the larger filter here (as previously mentioned).

The data were taken at 25 +/- 5 °C. This range of temperature causes a change in water viscosity of +/- 14% when the viscosity formula provided by BNFL is applied.¹

Filtration - Clean Water Flux

Clean water flux for the 0.2 micron Mott 1/2-inch ID filter agree well with data found in the Mott standard product literature as shown in Figure 4.

FIGURE 4. CUF CLEAN WATER FLUX



Decontamination of Strontium, Lanthanides, and Transition Metals

The AN107 simulant contained lanthanum, neodymium, and cerium along with a very small quantity of strontium to simulate strontium and actinides. Filtrate compositions were compared with initial feed measurements to produce “decontaminations”. For strontium the decontamination was defined as:

$$\text{Sr DF} = \text{Strontium concentration in filter feed (concentrate)} / (\text{Sr concentration in filtrate})$$

Note that the concentrate in most cases contained about 0.075 M Sr. The “Sr DF” above therefore would approximate the process Sr decontamination assuming good isotopic dilution.

Decontaminations for other elements were defined similarly. This is the most conservative definition of DF because filter feed levels were measured after process dilutions were made. Results are in Table 2. Note that when lanthanum was used as a precipitating agent the La decontamination is calculated to be unusually high; there is no ability to obtain the true decontamination with an inactive experiment in that case. The removal of manganese, iron, and other transition metals was also of interest during the precipitations since these analytes may also affect the HLW glass formulation.

Table 2. Decontaminations for Lanthanides and Strontium

SLURRY PRECIPITATE	Decontaminations			
	La	Nd	Ce	Sr
0.075M Sr, 0.075M Fe(III)	2.8	1.8	2	17
0.075M Sr	1.2	1.0	1.0	15
0.075M Sr, 0.075M La(III)	6.7*	1.3	1.3	41
0.075M Fe(III), 0.05M Fe(II)	2	2	1.6	NA
0.075M Sr, 0.05M Fe(II)	7.4	1.2	1.3	31
0.075M Sr, 0.03M Ni(II)	4.8	1.1	1.3	79
0.075M Sr, 0.075M Co(II)	2	1.1	1.2	87
0.075M Ca(II), 0.075M Sr	1.8	1.3	1.4	87
0.02M Ca(II), 0.075M Sr, 0.04 MnO ₄	>4.2	3.4	2.8	91

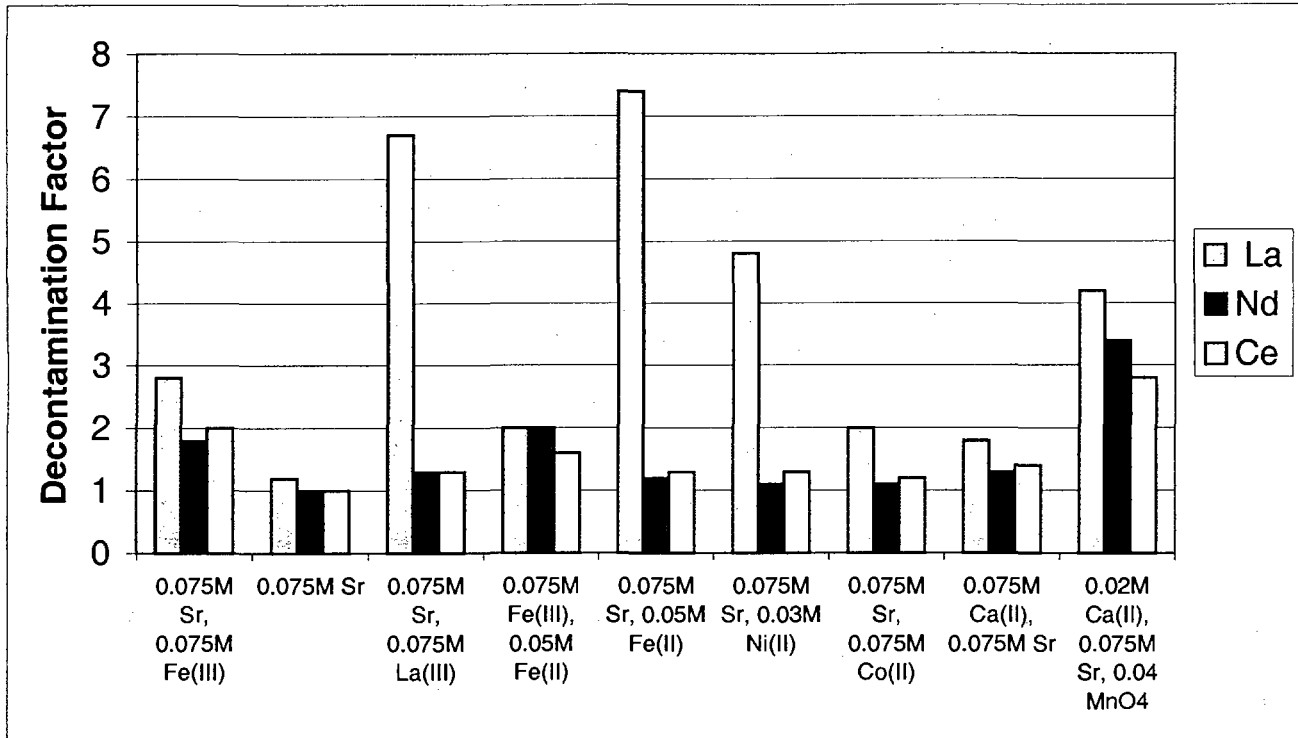
*Artificially high because the element was used as a precipitant

It is clear that the permanganate chemistry is uniquely better than are the others in removing the lanthanides while maintaining good strontium removal. The fact that this chemistry was practical in a crossflow filter makes it worthy of further study. It is also clear that a strontium strike alone does little to remove the lanthanides; co-precipitation by a transition metal provided the additional effect. The data are found in Figure 5.

Removal of other simulant waste constituents is examined in Table 3. Overall there is little significant removal of the nine elements shown except where permanganate is concerned. Note that calcium, nickel, and manganese DF's are artificially high in cases where they are added as precipitants.

The permanganate treatment removed significant amounts of iron, copper, and manganese. Note that the manganese level here is calculated for Mn(II) in the waste only (pre-strike); it would be artificially high if the added manganese from the precipitant was added to the total. It is believed that these metals are easily incorporated into the manganese oxide or hydroxide solid that forms from the permanganate reaction. Evidence for this is given by the existence of many manganese-transition metal minerals like Franklinite, Romanchite, Psilomelane, and Androsite. Strontium doped rare earth manganites have been studied extensively because of their useful role in electrical fuel cells.²⁹ The extremely large number of known manganese mixed metal oxides as well as mixtures containing only manganese in the +2, +3, and +4 states indicates that the resulting solid precipitate composition from the permanganate process will be waste dependent.

It is interesting to note that nickel is not removed by any of the chemistries. Above pH 9 nickel and gluconate have a very high stability constant (Base 10 log K of 29.4 for a 2:1 Ni:gluconate mole ratio complex).³⁰

Figure 5. Lanthanide Decontamination by Chemistry**Table 3. Decontaminations for Several Elements**

SLURRY PRECIPITATE	Decontaminations								
	Al	Ca	Cu	Fe	Ni	Mn	Zn	P	S
0.075M Sr, 0.075M Fe(III)	0.8	1.4	1.3	2.5	0.8		0.8	1.0	1.0
0.075M Sr	1.0	1.1	1.0	1.0	1.0		1.0	1.0	1.0
0.075M Sr, 0.075M La(III)	1.0	1.8	1.2	1.4	1.0	1.6	1.1	1.1	1.0
0.075M Fe(III), 0.05M Fe(II)	1.0	1.2	2.9	3.6	1.0			1.0	1.0
0.075M Sr, 0.05M Fe(II)	1.0	1.8	2.0	5.2	1.0	3.7	1.7	1.0	1.0
0.075M Sr, 0.03M Ni(II)	1.2	1.9	1.3	1.3	2.4	1.5	1.7	1.0	1.0
0.075M Sr, 0.075M Co(II)	1.1	2.2	1.0	2.0	1.1	2.1	0.9	1.0	1.0
0.075M Ca(II), 0.075M Sr	1.0	4.3	2.7	1.2	1.0	1.9	1.1	1.1	1.0
0.02M Ca(II), 0.075M Sr, 0.04 MnO4	0.9	2.4	>10	5.3	1.0	7.6	1.3	1.1	1.0

Values are +/- 10 percent.

Element not measured where there are blanks

Phosphate and sulfate were never seen to be removed by any of the chemistries. While this is good news for the high level melter it also shows that sulfate removal by the concentration of the many precipitants that were tried is not effective. These precipitants included calcium and strontium, which have relatively insoluble sulfates.

Table 4 below provides the metals-basis analysis of strontium-calcium and strontium-calcium-manganese oxide solids after gentle washing with deionized water. A single analysis was done for each of the two samples. The material composition falls in line with the removals seen above; the main constituents are manganese, strontium, calcium, and small detectable levels of some transition metals. Notably absent are sulfur, phosphorus, and nickel. The bulk of the precipitate mass (70 %) is not included below. That portion of the mass is assumed to be mostly water, oxygen as oxide, hydroxide, and waters of hydration.

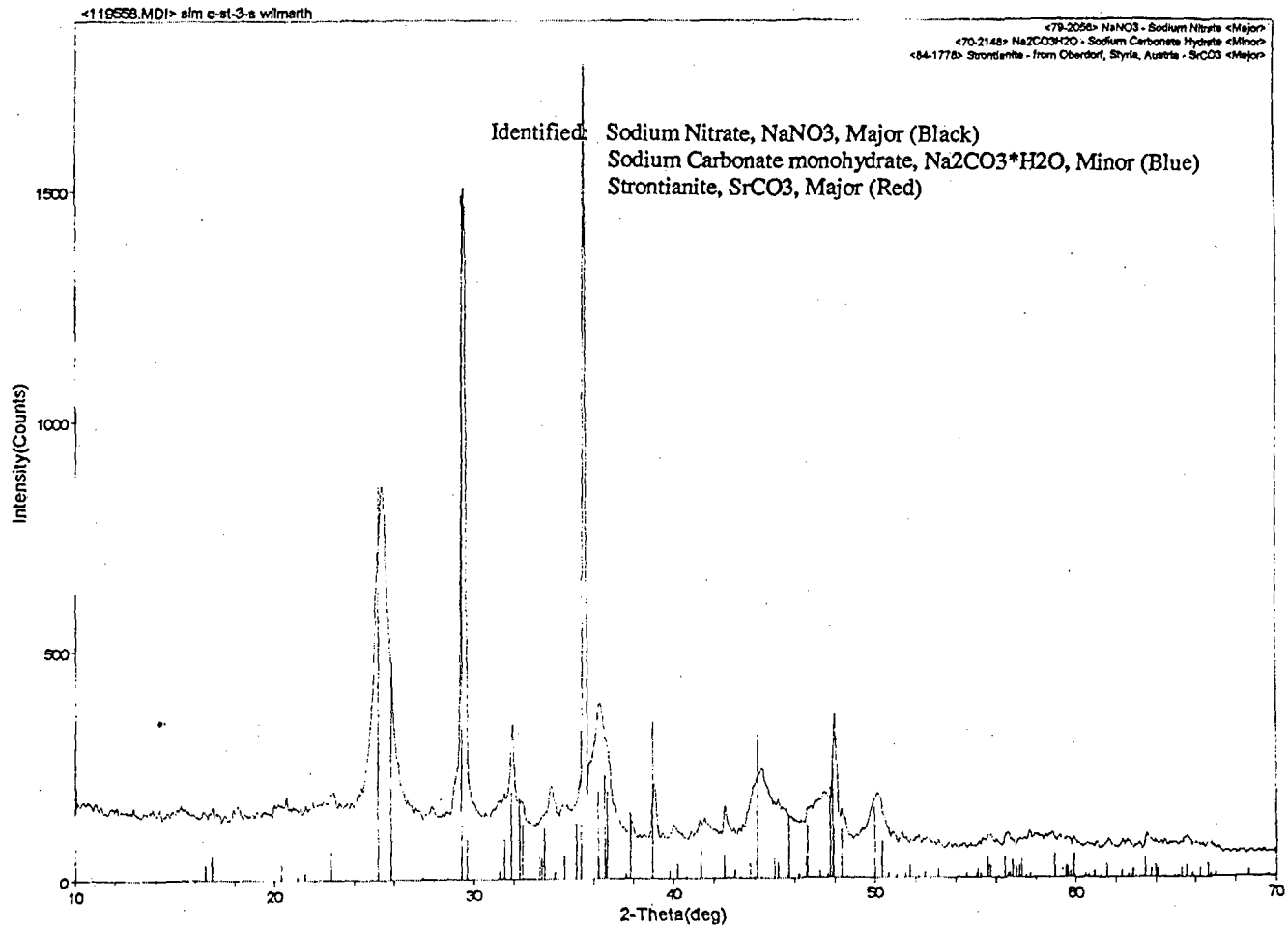
TABLE 4. COMPOSITION OF WASHED PERMANGANATE PRECIPITATE SOLIDS

Metals are wt %		
Element	Sr-Ca	Ca-Sr-Mn
Al	<0.04	<0.04
Ba	<0.005	<0.005
Ca	4.2	1.0
Cd	<0.005	<0.005
Ce	<0.08	<0.08
Co	<0.01	<0.01
Cr	<0.005	<0.005
Cu	<0.005	<0.005
Fe	0.4	1.9
La	<0.02	<0.02
Li	<0.07	<0.07
Mg	0.03	0.02
Mn	0.3	4.8

Metals are wt %		
Element	Sr-Ca	Ca-Sr-Mn
Mo	<0.01	<0.01
Na	12.5	11.3
Nd	<0.03	<0.03
Ni	<0.006	<0.006
P	<0.09	<0.09
Pb	<0.05	<0.05
Si	0.7	1.2
Sn	<0.04	<0.04
Sr	11	6.7
Ti	<0.01	<0.01
V	<0.01	<0.01
Zn	<0.01	<0.01
Zr	0.7	0.4

Solids collected when the AN-107 simulant was precipitated with strontium nitrate were submitted for X-ray diffraction. Figure 6 shows that strontium carbonate is the predominant product along with sodium nitrate from the supernate solution. No strontium sulfate was found. The X-ray diffraction peaks were identified using an International Center for Diffraction Data inorganic database. The database contains approximately 150,000 compounds.

Figure 6. X-ray Diffraction of Strontium Precipitate, showing Carbonate



Analytical Development Section

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Effect of Complexants on Metal Solubilities

Chemistry work on this AN-107 simulant naturally leads to questions about which complexant is chelating which metal. The current work is only able to address this by presenting levels of soluble metals – detailed electrochemical and spectroscopic work on this material has not been done. Table 5 shows the maximum levels of metals seen in filtrate using this simulant (all numbers are for 6.8 M sodium, where the gluconate level would be about 0.014 M, EDTA would be 0.015 M, and HEDTA would be 0.006 M). The levels seen below are adequately covered by the amounts of complexant in the simulant, though each filtrate also contained other metals. The amount of iron in the Run 5 filtrate is unusually high. While the table has averages of replicated measurements it is difficult to explain the ability to dissolve this much iron. This number should be viewed with caution. The initial precipitate was a mixture of Fe(II) and Fe(III) with a total molarity of 0.13 M iron.

TABLE 5. MAXIMUM SOLUBILITIES FOUND IN THE SIMULANT FILTRATE (6.8 M NA+)

Sr(II), Run 2	0.005 M
La(III), Run 6	0.0081 M
Fe(II) and (III), Run 5	0.075 M (Slurry contains a combination of added Fe(II) and (III))
Fe(II) only, Run 7	0.011 M (Not Sat'd; probable interaction with waste Fe(III))
Ni(II), Run 8	0.01 M
Co(II), Run 9	0.012 M
Ca(II), Run 10	0.02 M

The appendix to this report contains the recipe for the simulant. It presents component molarities from which batching steps are derived. Batching follows a specific order and produces two intermediate solutions (acid-complexant-metal and strong caustic).

Preliminary work was therefore done to address which metal is dissolved by which complexant. Table 6 shows the compositions of filtrates where the AN107 simulant was made with single complexants or with mixtures of EDTA and HEDTA only. Complexants are always added to typical levels per the recipe rather than to equal levels. The net effect is to show the chelating impact with consideration of concentration included. In all cases the recipe left significant sludge in the mixing bottle because of the lack of the full set of seven complexants (the FULL recipe composition, sample 10, as measured is in the rightmost column). Significant amounts of metals are shaded.

It is clear that the glycolate in sample 1, the most prevalent organic in the mixture at 0.25M (see Appendix A recipe), does little to complex any of the metals. Nitrilotriacetic acid, citric acid, and iminodiacetic acid also play little role, though they have some chelating action with copper.

It should be noted that while boron, sulfur, phosphorus and molybdenum are reported they are not expected to be present in organic chelate groups. Respectively they are expected to exist as borate, sulfate, phosphate, and molybdate which do not participate in

Table 6. 241-AN-107 Simulant Soluble Metals found with Single Complexants

Sample:	1	2	3	4	5	6	7	8	9	10
	Glycolate	H/EDTA*1	H/EDTA/2	Gluconate	NTA	Citric	IDA	H/EDTA*1	H/EDTA*2	FULL
Al	215	282	291	325	214	215	213	304	321	83
B	39	37	53	42	38	34	41	41	42	39
Ca	1	406	303	206	1	<1	<1	448	490	126
Ce	<1	<1	<1	41	<1	<1	<1	<1	<1	36
Co	<0.5	<0.5	<0.5	4	<0.5	<0.5	<0.5	<0.5	6	4
Cr	0	0	89	0	0	0	0	86	79	130
Cu	144	311	16	349	19	54	74	24	26	26
Fe	8	<0.7	<0.7	1350	1	0	<0.7	20	<0.7	1289
La	<1.5	8	<1.5	31	<1.5	<1.5	<1.5	8	35	34
Mn	<1.2	4	<1.2	4	<1.2	<1.2	<1.2	5	<1.2	440
Mo	31	29	37	31	31	31	35	36	37	40
Nd	0	6	0	76	0	0	0	0	19	70
Ni	0	318	168	437	0	0	256	390	422	418
P	222	247	672	235	230	257	287	668	691	313
Sr	<1	3	2	1	<1	<1	<1	7	20	2
Zn	6	16	38	51	13	10	4	4	29	38
Zr	<1.5	<1.5	<1.5	40	<1.5	<1.5	<1.5	<1.5	<1.5	38
S	2552	2427	2409	2661	2413	2576	2261	2336	2504	2528

NOTES: Concentrations reported in mg/L
 Named complexants are at typical levels, FULL = all seven complexants included
 "H/EDTA" refers to the typical ratio of HEDTA and EDTA together in the mixture
 "/2", "*1", and "*2" refer to half, typical, or twice typical concentration of H+EDTA

complexation. Aluminum may exist as aluminate. It is also easily complexed by HEDTA or EDTA.

The gluconate in sample 4 shows extreme chelating action. Calcium, the lanthanides, nickel, zirconium, and iron all have high and significant levels of solubility. Summation of the metal molarities provides several times the 0.014 M gluconate concentration. Gluconate is clearly very active in dissolving metals at high pH. It is the only complexant considered here that dissolves ferric ion at high pH. It was also the only complexant to dissolve the small amounts of cerium and zirconium that were available. While the cerium was added to the simulant as the trivalent nitrate it is not clear whether its available (+4) oxidation state is playing a role in its complexation. Cerium is the only lanthanide to form a (+4) state and its chemistry in that state is similar to that of zirconium.³¹

It is curious that the soluble manganese(II) only exists in the full recipe. The gluconate may have been fully loaded by other metals in the gluconate-only sample. Competition with other metals might have prevented soluble manganese from forming in the gluconate-only sample. The samples with 0.5, 1, and 2 times the typical HEDTA and EDTA levels show some ability to solubilize lanthanum, neodymium, calcium, and nickel.

CONCLUSIONS

Iron precipitation chemistries in for the caustic complexant simulant (AN-107 simulant) reduce crossflow filterability to impractical levels. Addition of ferrous ion did not improve the filtration. Sr precipitation alone gave adequate filtration, with fluxes exceeding 0.1 gpm/ft² for non-optimized conditions.

Precipitation with the divalent transition metals that were tested improved Sr decontamination over ferric chemistries. It is suspected that divalent metals are able to replace strontium in the complexant system, reducing its apparent solubility in filtrate. This is consistent with results of Herting's work with a 101-AW composite sample and a variety of ions including divalent metals.¹⁷

A combination of strontium and permanganate precipitation, including some calcium, gave the best removal of lanthanides for all the tests. The material was filterable though no optimization of filter conditions was performed here. This precipitate material adsorbs other transition metals that are complexed except for nickel(II) and aluminum.

None of the precipitants at the tested concentrations in this work showed any promise of removing sulfate from the simulant. Sulfate and phosphate remained soluble during all the precipitations. No significant amounts of these compounds were found in the Sr-Ca and Ca-Sr-Mn precipitated solids removed from the filter rig.

A preliminary study of the role of individual complexants that are known to be in the waste provided evidence that most of them do not participate in significant metal complexation. EDTA, HEDTA, and most importantly gluconate demonstrated abilities to dissolve transition and alkaline earth metals in this caustic solution. The EDTA/HEDTA combination demonstrated an ability to dissolve calcium, copper, nickel, and lanthanum

and neodymium. Gluconate could in addition dissolve iron, cerium, and zirconium. Gluconate clearly is the component that is responsible for soluble iron in this simulant.

RECOMMENDATIONS

Precipitation involving strontium and permanganate reagent solutions with possible inclusion of calcium should be investigated for filterability, strontium-90, and transuranic removals. Testing with tank waste with small deadend filters followed by more crossflow filtration are important next steps.

The reaction rate of permanganate needs to be determined as a function of waste composition and temperature. One primary reason is to provide assurance that this step in the precipitation process is essentially complete before the slurry is filtered.

The permanganate reduction-oxidation chemistry in each tank supernate needs to be examined for reaction byproducts and their impact on the rest of the plant processes. Further study of the roles of complexants, both as reducing agents and as chelants for specific metals, is recommended. Additional efforts to identify the organic components in the envelope C wastes are important to support the follow-on work.

APPROVALS

Task Leader:	Signature:	Organization:	Date:
Technical Reviewer (if required):	Signature:	Organization:	Date:
Level 4 Manager:	Signature:	Organization:	Date:
Other Approval (if required):	Signature:	Organization:	Date:

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APPENDIX A

Recipe For AN-107 Supernate Simulant formulated by R. Eibling

Note: Barium, lead, and chromium compounds were omitted in the current work.

Compounds	Moles	Nitrate Moles	Sodium Moles
Aluminum Nitrate	1.43E-02	4.29E-02	5.72E-02
Ammonium Acetate	1.22E-03		
Barium Nitrate	5.42E-05	1.08E-04	
Boric acid	3.24E-03		9.71E-03
Calcium Nitrate	1.47E-02		
Cerium(III) Nitrate	3.77E-04	1.13E-03	
Cesium Nitrate	1.40E-04	1.40E-04	
Copper Nitrate	4.74E-04	9.47E-04	
EDTA	1.95E-02		3.90E-02
Ferric Nitrate	3.03E-02	9.08E-02	
HEDTA	7.78E-03		2.33E-02
Lanthanum Nitrate	3.28E-04	9.83E-04	
Magnesium Nitrate	1.03E-03	2.06E-03	
Manganous Chloride	1.02E-02		
Neodymium Nitrate	6.65E-04	1.99E-03	
Nickel Nitrate	9.03E-03	1.81E-02	
Potassium Nitrate	4.55E-02	4.55E-02	
Strontium Nitrate	7.54E-05	1.51E-04	
Zinc Nitrate	6.93E-04	1.39E-03	
Zirconyl Nitrate	7.67E-04	1.53E-03	
Glycolic Acid	2.48E-01		2.48E-01
Sodium Gluconate	1.80E-02		1.80E-02
Citric Acid	4.49E-02		1.35E-01
Nitilotriacetic Acid	2.98E-03		8.95E-03
Iminodiacetic Acid	4.54E-02		9.07E-02
Subtotal		2.11E-01	6.12E-01
		Sodium Moles	
Sodium Chloride	3.11E-02	3.11E-02	
Sodium Fluoride	7.00E-03	7.00E-03	
Sodium Chromate	3.38E-03	6.77E-03	
Sodium Carbonate	1.40E+00	2.80E+00	2.80E+00
Sodium Hydroxide	2.00E-02	2.00E-02	2.00E-02
Sodium Nitrite	1.33E+00	1.33E+00	1.33E+00
Sodium Phosphate	1.17E-02	3.51E-02	
Potassium Molybdate	3.73E-04		
Sodium Sulfate	8.59E-02	1.72E-01	
Sodium formate	2.31E-01	2.31E-01	
Sodium Acetate	1.74E-02	1.74E-02	
Sodium Oxalate	9.38E-03	1.88E-02	
Subtotal		4.66E+00	

Compounds	Moles	Nitrate Moles	Sodium Moles
Sodium Nitrate	3.50E+00	3.50E+00	3.5
Sodium Hydroxide	6.12E-01		6.12E-01
Total			8.77E+00
		Grams	
Total Slurry Mass/Liter		1429	
Mass of Water to add		740.24	
Water		52.76 %	
TOC % Of Actual		48.46	

APPENDIX B

Experimental Uncertainties (All NIST Traceable)

1. CUF Slurry Flowmeter

The magnetic flowmeter was calibrated to $\pm 2\%$ of full scale (4.75 GPM). Actual one-sigma uncertainty found on 01/26/1999 was ± 0.09 GPM. Postcalibration of the instrument led to a question about span, 4.75 versus 8 gpm. Review of the pretest calibration paperwork showed that the zero to 4.75 gpm values (span no larger than 5 gpm maximum) are most consistent and are the reported values.

2. CUF Reservoir Thermocouple

The type K thermocouple was accurate to $\pm 2\%$ in its calibrated range of 0 to 80 °C.

3. CUF Pressure Gauges

Pressure gauges have the range 0 to 100 psig and are calibrated to an accuracy of ± 2 psig.

4. Analytical uncertainties were within 10% of stated values. The Analytical Development Section uses NIST traceable standards to provide this assurance.

APPENDIX C

Raw Filtration Data

Run Page	Vel. ft/s	Delta P PSID	Vol. mL	Seconds	GPM/ft2	m3/m2/day	GPM/ft2 Average	m3/m2/day Average
Batch 1	5.1	20	0	1800	0	0		
85								
Sr Only	5.1	20	35	8.68	0.244113	14.32394		
86			35	23.22	0.091253	5.354513		
			35	26.42	0.080201	4.705973		
			35	31.93	0.066361	3.893886		
			35	33.84	0.062615	3.674107		
			35	46.67	0.045402	2.664062		
			35	57.3	0.036979	2.169839	0.063802	3.743772
	5.1	55	35	6.71	0.315782	18.52933		
			35	7.92	0.267538	15.69846		
			35	14.41	0.147044	8.628161		
			35	25.34	0.083619	4.906543		
			35	34.58	0.061275	3.595483		
			35	44.03	0.048124	2.823797		
			35	51.41	0.041216	2.418436	0.108136	6.345218
	6.5	55	35	8.06	0.262891	15.42578		
			35	15.43	0.137323	8.057796		
			35	18.79	0.112767	6.616913		
			35	30.42	0.069655	4.087173		
			35	37.68	0.056234	3.299676		
			35	47.51	0.044599	2.616961		
			35	56.92	0.037226	2.184325	0.076301	4.477191
Sr+newFe	6.8	55	0	2400	0	0		
88								
Fe Only	5.1	20	15	98.84	0.009188	0.539104		
89			7	232.54	0.001822	0.106934		
			15	213.22	0.004259	0.249906		
			5	230.64	0.001312	0.07701		
			4	246.05	0.000984	0.05775		
			4	234.47	0.001033	0.060602		
			4	213.24	0.001136	0.066635	0.001758	0.103141
	6.5	55	5	88.47	0.003421	0.200765		
			3	125.44	0.001448	0.084957		
			3	172.85	0.001051	0.061655		
			3	164.92	0.001101	0.064619		
			2	96.08	0.00126	0.073945		
			3	149.05	0.001219	0.0715		
			2	130.44	0.000928	0.054467	0.001168	0.068525
89+Fe(II)	5.1	20	10	226.1	0.002678	0.157114		
90			5	111.6	0.002712	0.159155		
			5	114.8	0.002637	0.154719		
			3	72.34	0.002511	0.147318		
			3	71.85	0.002528	0.148323		
			4	69.23	0.003498	0.205248		
			4	93.22	0.002598	0.152428	0.002747	0.1612

	6.5	55	0	300	0	0		
			0	600	0	0		
			3	108.48	0.001674	0.098239		
			2	80.92	0.001496	0.087799		
			2	80.59	0.001502	0.088158		
			2	81.53	0.001485	0.087142		
			2	108.7	0.001114	0.06536	0.001212	0.071117
SrLa	5.1	20	20	60.33	0.02007	1.177635		
94			20	184.58	0.00656	0.38491		
			20	264.4	0.004579	0.268709		
			4	49.88	0.004855	0.284871		
			10	111.54	0.005428	0.318481		
			10	109.25	0.005541	0.325157		
			10	117.38	0.005158	0.302636	0.005353	0.314131
	6.5	55	0	300	0	0		
			0	600	0	0		
			5	95.39	0.003173	0.186201		
			10	169	0.003582	0.210197		
			4	91.28	0.002653	0.155668		
			4	91.35	0.002651	0.155548		
			5	116.89	0.00259	0.151952	0.002441	0.143263
SrFe(II)	5.1	20	20	53.4	0.022674	1.330463		
95			20	124.25	0.009745	0.571805		
			20	160.45	0.007546	0.442797		
			5	42.85	0.007064	0.414508		
			5	46.12	0.006563	0.385119		
			5	60.17	0.005031	0.295192		
			5	69.71	0.004342	0.254794	0.006715	0.39404
	6.5	55	5	26.43	0.011453	0.672027		
			5	32.96	0.009184	0.538886		
			5	40.76	0.007426	0.435763		
			5	53.21	0.005689	0.333804		
			5	48.35	0.006261	0.367356		
			5	53.38	0.005671	0.33274		
			5	57.38	0.005275	0.309545	0.006584	0.386353
SrNi(II)	5.1	20	20	39.59	0.030583	1.794563		
97			20	74.81	0.016185	0.949696		
			20	100.64	0.012031	0.705949		
			20	112.59	0.010754	0.631022		
			5	22.71	0.013329	0.782109		
			10	44.82	0.013507	0.792579		
			5	21.89	0.013828	0.811406	0.013272	0.778802
	6.5	55	10	18.17	0.033319	1.955056		
			5	13.64	0.022192	1.302176		
			10	36.48	0.016595	0.973777		
			10	42.69	0.014181	0.832124		
			5	28.53	0.01061	0.622562		
			5	25.15	0.012036	0.70623		
			5	28.16	0.010749	0.630742	0.014394	0.844611
SrCo(II)	5.1	20	20	20.18	0.06	3.520651		
99			20	49.74	0.024343	1.428362		
			20	65.8	0.018401	1.079738		
			20	65.08	0.018605	1.091683		

			20	66.23	0.018282	1.072727		
			20	65.21	0.018568	1.089507		
			20	64.29	0.018833	1.105098	0.019505	1.144532
	6.5	55	20	17.38	0.069666	4.087845		
			20	39.36	0.030762	1.805049		
			20	43.53	0.027815	1.632133		
			20	49.6	0.024411	1.432394		
			20	47.68	0.025394	1.490074		
			20	49.82	0.024303	1.426069		
			20	49.82	0.024303	1.426069	0.026165	1.535315
SrCa	5.1	20	15	27.17	0.033423	1.961172		
102			10	33.57	0.018034	1.058188		
			10	39.25	0.015424	0.905054		
			10	47.35	0.012786	0.75023		
			10	47.36	0.012783	0.750071		
			10	55.65	0.010879	0.638335		
			10	57.37	0.010553	0.619198	0.01341	0.786855
	6.5	55	10	18.44	0.032831	1.92643		
			10	29.94	0.02022	1.186485		
			10	40.68	0.014882	0.873239		
			10	47.71	0.012689	0.744569		
			10	55.26	0.010955	0.642841		
			10	59.46	0.010182	0.597433		
			10	64.61	0.00937	0.549812	0.01305	0.765738
CaSrMn	5.1	20	20	11.17	0.108397	6.360496		
104			20	45.41	0.026664	1.564562		
			10	32.12	0.018848	1.105958		
			10	34.8	0.017397	1.020786		
			10	38.21	0.015844	0.929688		
			10	36.63	0.016527	0.969789		
			10	48.93	0.012373	0.726004	0.017942	1.05281
	6.5	55	10	11.27	0.053718	3.152029		
			10	29.18	0.020747	1.217388		
			10	38.82	0.015595	0.915079		
			10	37.09	0.016322	0.957761		
			10	47.67	0.0127	0.745193		
			10	45.16	0.013406	0.786611		
			10	47.48	0.012751	0.748175	0.015253	0.895045

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