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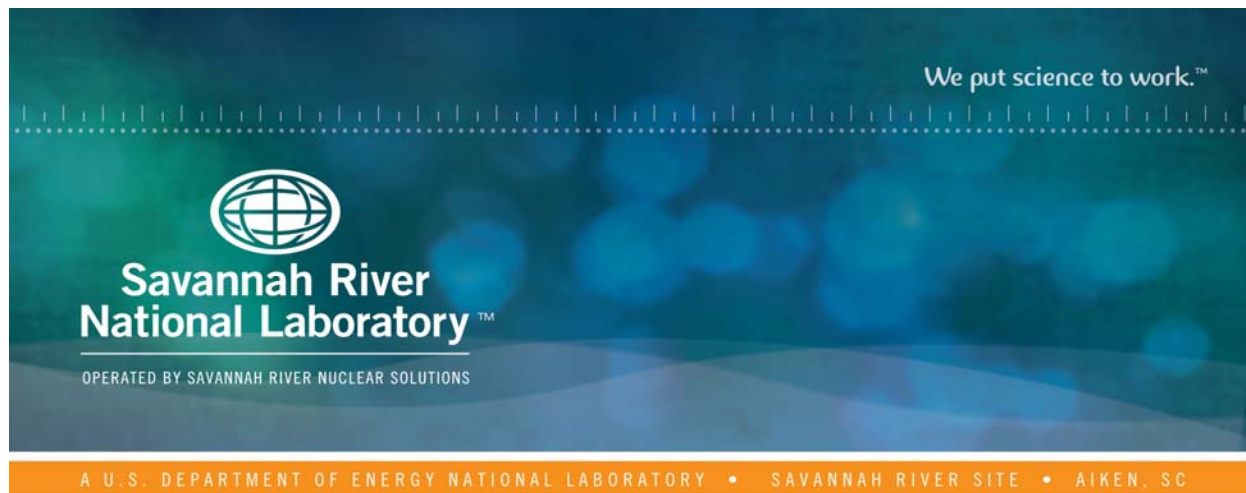
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# **Solid-liquid Separation Testing for the Remediation of Hanford Waste Treatment Plant Low Activity Waste Melter Off-Gas Condensate**

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May 9, 2019

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## EXECUTIVE SUMMARY

The Low Activity Waste (LAW) vitrification facility at the Hanford Waste Treatment and Immobilization Plant (WTP) will generate an aqueous condensate stream (LAW Off-Gas Condensate) from the off-gas system. The plan for disposition of this stream during Direct Feed LAW operations is to transfer it to the Effluent Management Facility (EMF), where it will be concentrated by evaporation and recycled to the LAW vitrification facility again. The primary reason to recycle this stream is so that the semi-volatile  $^{99}\text{Tc}$  isotope eventually becomes incorporated into the glass. However, this stream also contains non-radioactive salt components that are problematic in the melter, so diversion of this stream to another process would eliminate recycling of these salts and would enable simplified operation of the LAW melter and the Pretreatment Facilities. This diversion from recycling this stream within WTP would have the effect of decreasing the quantity of glass waste produced by allowing further increases in waste loading, resulting in a shortened LAW vitrification mission duration. The concept being tested here involves selectively removing the  $^{99}\text{Tc}$  so that the decontaminated aqueous stream, with the problematic salts, can be disposed as a different waste form and avoid reprocessing through vitrification.

There are no plans to remove technetium from the aqueous tank waste during pretreatment in the Hanford WTP, so it will be sent to the LAW melter. It is intended that  $^{99}\text{Tc}$  will be immobilized in the LAW glass. Because it is semi-volatile at melter temperatures and roughly 65% vaporizes, it will be repeatedly recycled into the LAW melter to improve retention in the glass. Although other radionuclides are expected to be present in very low concentration in the LAW Off-Gas Condensate, it is the long-lived and environmentally mobile  $^{99}\text{Tc}$  that is the primary component of concern.

The LAW Off-Gas Condensate stream originates from two subsystems; the Submerged Bed Scrubber (SBS) and the Wet Electrostatic Precipitator (WESP) in the LAW melter off-gas process. Pilot simulant tests indicate that this stream is expected to be a dilute salt solution with near neutral pH and will likely contain some insoluble solids from melter carryover. The soluble salt components are expected to be mostly sodium and ammonium salts of nitrate, chloride, fluoride, and sulfate. Although this stream has not yet been generated and will not be available until the WTP begins operation, a simulant has been produced based on models, calculations, and comparison with non-radioactive pilot-scale tests using simulants of the LAW waste.

The components in the LAW Off-Gas Condensate that are problematic for recycling to the glass waste form are halides and sulfate, which are volatile at melter temperatures. Recycling to incorporate the  $^{99}\text{Tc}$  in the glass causes these components to accumulate in the Condensate stream, exacerbating their impact on the number of LAW glass containers that must be produced. Diverting the stream to an alternate disposal path reduces the halides and sulfate in the melter and is a key goal of this work. This project examines the potential treatment of this stream to precipitate radioactive  $^{99}\text{Tc}$  and subsequently disposition the decontaminated aqueous stream elsewhere, perhaps through an altered EMF where the concentrated stream is immobilized as a low temperature waste form. The envisioned treatment process focuses on using mature technologies that are also compatible with long-term tank storage and immobilization methods. For this process, testing is needed to demonstrate acceptable precipitation agents and solid-liquid separation techniques to remove the  $^{99}\text{Tc}$  from this waste stream.

Previous work has shown  $\text{SnCl}_2$  to be an effective agent for the  $^{99}\text{Tc}$  removal from this stream through reductive precipitation. The removal is believed to work by reducing the  $\text{Tc(VII)}$  ion in the soluble pertechnetate ( $\text{TcO}_4^-$ ) to  $\text{Tc(IV)}$ , leading to its precipitation as technetium dioxide ( $\text{TcO}_2$ ). The present work focused on experiments needed to begin to mature the technology readiness of this process. A key component of that readiness is the scale-up of the reaction and the solid-liquid separation method. These two are related because the mixing of the chemicals during the reaction affects the particle size of the solids,

thereby impacting the solid-liquid separation method. Prior kinetics testing has been performed to determine the speed of the Tc removal reaction so that appropriate equipment for mixing scale-up tests could be selected. It was found previously that at small scale, the Tc is removed to below the detection limit within 5 minutes of the addition of stannous chloride at a pH of 7.5. To perform the bench scale experiment as a non-radioactive test, the precipitation of chromium was studied. Chromium is present in the tank waste and SBS/WESP condensate and is the predominant species that reacts with the stannous reductant. Based on previous small-scale testing, the kinetics of the chromium reduction will serve as a reasonable and conservative surrogate for the Tc reduction kinetics. Results from the bench scale mixing experiment indicated that the Cr precipitation is complete within 5 minutes of the addition of stannous chloride. The solid-liquid separation test can be done non-radioactive because the mass of  $\text{TcO}_2$  that forms is a tiny fraction (~1%) of the total amount of solids, which are overwhelmingly chromium and tin oxyhydroxides which dominate the morphology and physical properties of the precipitate and so would dominate the settling and filtration rates.

This report provides results from a solid-liquid separation test using a clarifier followed by a polymeric filter. A total of four tests were performed. Two of these tests were performed to mimic an actual process facility as closely as feasible, with fresh precipitation of the solids followed by a settling time and then clarification and filtration. The other two tests were performed using a previously-prepared simulant slurry and were intended to evaluate a lower shear mixer, temperature differences, and to better quantify the initial settling period. The filter fouled more quickly than expected in the first test with the freshly prepared simulant slurry at elevated temperature, requiring modifications to the equipment and experimental conditions. The pressure drop across the filter increased from 6 psi at the start of the test to 22 psi after only 11 minutes. The pressure drop continued to increase, even after decreasing the filter flow rate to reduce fouling. The permeance (filter flow rate divided by differential pressure) decreased by 95% within an hour. This indicated that a longer clarifier residence time and equipment changes to reduce particle shearing were needed. Typical settling (detention) time was only ~30 minutes in this first test, based on earlier bench-scale tests that indicated rapid settling.

After the first test, a mixer with a larger blade size was used for all subsequent testing. The second and third tests, which used a previously-prepared batch of simulant slurry, indicated that a longer initial settling time to ~two hours was beneficial. (This initial settling time is the time between filling the clarifier and turning on the slurry pump to the time when filtration of the clarified liquid begins.) This allowed for a clearer layer to form in the clarifier so that less solids were sent to the filter. Similarly, the feed flow rate to the filter was decreased so that the slurry had a longer residence time in the clarifier, which averaged about a two hour turnover time.

The fourth test, which used a second batch of the freshly precipitated slurry, had lower filter fouling rates. The improved performance is attributed to lower shear mixing and a longer initial settling time. The pressure drop across the filter increased from 5 psi at start up to 26 psi after 134 minutes, and the permeance decreased by ~80% over 134 minutes, which is significantly improved versus Test 1. Further, there was minimal filter fouling for the first 40 minutes, indicating that the initial settling and clarifying period was sufficient, but increased agitation in the clarifier due to the increased rate of flow from the feed tank caused filter fouling after this period. This provides a basis to estimate the settling period needed to allow filtration with minimal fouling. The initial settling time in this test, ~2 hours, is closer to the minimum duration typically used with industrial clarifiers of 2-5 hours. Once filtration began, the turn-over rate in the clarifier was approximately 136 minutes, but some filter fouling occurred. Clarifier turn-over rates of 4-5 hours are evidently needed to minimize filter fouling or incorporation of a design that reduces agitation.

Measurements of the particle size distribution of the precipitated solids were also performed. The solids from Test 1 had a mean particle size of 7.52 microns (volume distribution), with a distribution of sizes from 2.58 microns at the 10<sup>th</sup> percentile to 22.5 microns at the 95<sup>th</sup> percentile. The particle size distributions

measured in Tests 2 and 3 were significantly narrower, ranging from 3.22 to 8.46 microns and 3.95 to 12.7 for the 10<sup>th</sup> and 95<sup>th</sup> percentiles, respectively. Test 4 exhibited a bimodal distribution with a small population of particles centered around 90 microns, along with the larger fraction centered around 3-4 microns. These are smaller particles than those observed in prior bench-scale tests, and suggests that scale-up, mixing, and slower stannous chloride addition rates may have played a role. It is also possible that some of the solids may have settled in the feed tank and not been fully suspended by the mixer and so were not in the sample used for particle size analysis.

Production of hydrogen during this process is electrochemically possible because of the redox chemistry of the stannous chloride in this solution. To ensure safety of the experiment and of the potential future facility, it was prudent to examine if hydrogen is actually generated. The hydrogen generation rate was found to be below detection levels during measurement, corresponding to maximum hydrogen generation rates less than 1/50<sup>th</sup> of the action limit for LAW feed in WTP.

Additional tasks related to equipment design needed to further develop this technology include slurry rheology measurements, corrosion and erosion studies, and slurry storage.

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## LIST OF ABBREVIATIONS

avg	Average
°C	Degrees Celsius
cm	centimeter
DF	Decontamination Factor
DOE	Department of Energy
eq	Equivalents
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
FM	Flow Meter
g	grams
GFC	Glass Forming Chemical
hr	Hour
HGR	Hydrogen Generation Rate
HLW	High-Level Waste
HTWOS	Hanford Tank Waste Operations Simulator
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IDF	Integrated Disposal Facility
L	Liter
LAW	Low-Activity Waste
M	Molarity
min	minute
mg	milligram
mmole	millimole
psi	Pounds per square inch
rpm	Revolutions per minute
sccm	Standard cubic centimeters per minute
SBS	Submerged Bed Scrubber
SRNL	Savannah River National Laboratory
WESP	Wet Electrostatic Precipitator
wt%	Weight percent
WTP	Waste Treatment and Immobilization Plant
XRD	X-Ray Diffraction

## 1.0 Introduction

### 1.1 Background

The Hanford LAW Off-Gas Condensate stream will be generated in the WTP by condensation and scrubbing of the LAW melter off-gas system by an SBS and WESP, as shown in Figure 1-1. This stream, which will contain substantial amounts of chloride, fluoride, ammonia, and sulfate ions, will get recycled within the WTP baseline process by return to the Pretreatment Facility where it will be combined with LAW and evaporated. Although the SBS and WESP streams are generated separately, they are routed to a single tank within WTP, so they are combined for purposes of this study. The SBS and WESP streams each contain a substantial portion of the  $^{99}\text{Tc}$ , so separating them would not be beneficial. The halide and sulfate components in the stream are only marginally soluble in glass, and often dictate glass waste loading and thereby impact LAW waste glass volume. Additionally, long-lived  $^{99}\text{Tc}$  and  $^{129}\text{I}$  are volatile radionuclides that accumulate in the LAW system and are challenging to incorporate in glass under the Hanford LAW melter operating conditions. Because  $^{99}\text{Tc}$  has a very long half-life and is highly mobile, it is the largest dose contributor to the Performance Assessment of the Integrated Disposal Facility (IDF)<sup>1</sup>, although the glass waste form has been shown to meet the leaching requirements of the IDF waste acceptance criteria. Diverting this LAW Off-Gas Condensate stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP because it would reduce the halides and sulfate in the melter feed and would permit further improvements to the glass waste loading, decreasing glass product volume.

The only chemical form of  $^{99}\text{Tc}$  expected in the off-gas condensate stream is pertechnetate anion ( $\text{TcO}_4^-$ ) with a +7 Tc oxidation state because the high melter temperature should decompose any other form, although this has not been proven experimentally. The volatility of Tc under oxidizing melter conditions is well known to be high, with ~65% vaporized<sup>2</sup>, where the potential volatile species are the heptoxide ( $\text{Tc}_2\text{O}_7$ ) (because of its boiling point of 311 °C) and an alkali metal pertechnetate, ammonium pertechnetate, or perhaps  $\text{TcO}_2$ .<sup>3</sup> A recent review concluded that the primary volatile species is an alkali pertechnetate, preferentially vaporizing as the potassium salt.<sup>4</sup> Regardless, the species used in this test program is the pertechnetate because even if the volatile species is the heptoxide, once it contacts water, it would disproportionate to the pertechnetate.<sup>5</sup> However, Tc was not used in this test because the solids generated in these experiments are overwhelmingly Cr and Sn oxide and hydroxy-oxide species, which will make up the majority of the precipitate in the actual process. The Tc is present at such a relatively small concentration (~3 mg/L) that the amount of technetium oxide precipitate will not affect the bulk characteristics of the precipitate (~1000 mg/L). The objective of this test was to examine the preparation and physical separation of the slurry, so  $^{99}\text{Tc}$  was omitted from the testing to avoid generating a radioactive waste unnecessarily.

It has been found in prior experiments that the quantity of stannous needed for good removal of Tc is 1.5 times the stoichiometric number of electrons needed to reduce the  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  plus the number needed to reduce Tc from +7 to +4, i.e., 50% more than the theoretical equivalents of electrons.<sup>6</sup> The reason for the need of this excess has not been determined but is likely related to water hydrolysis and precipitation of some portion of the stannous ion as  $\text{Sn}(\text{OH})_2$ , along with a need for some excess  $\text{Sn}^{2+}$  dissolved in solution.

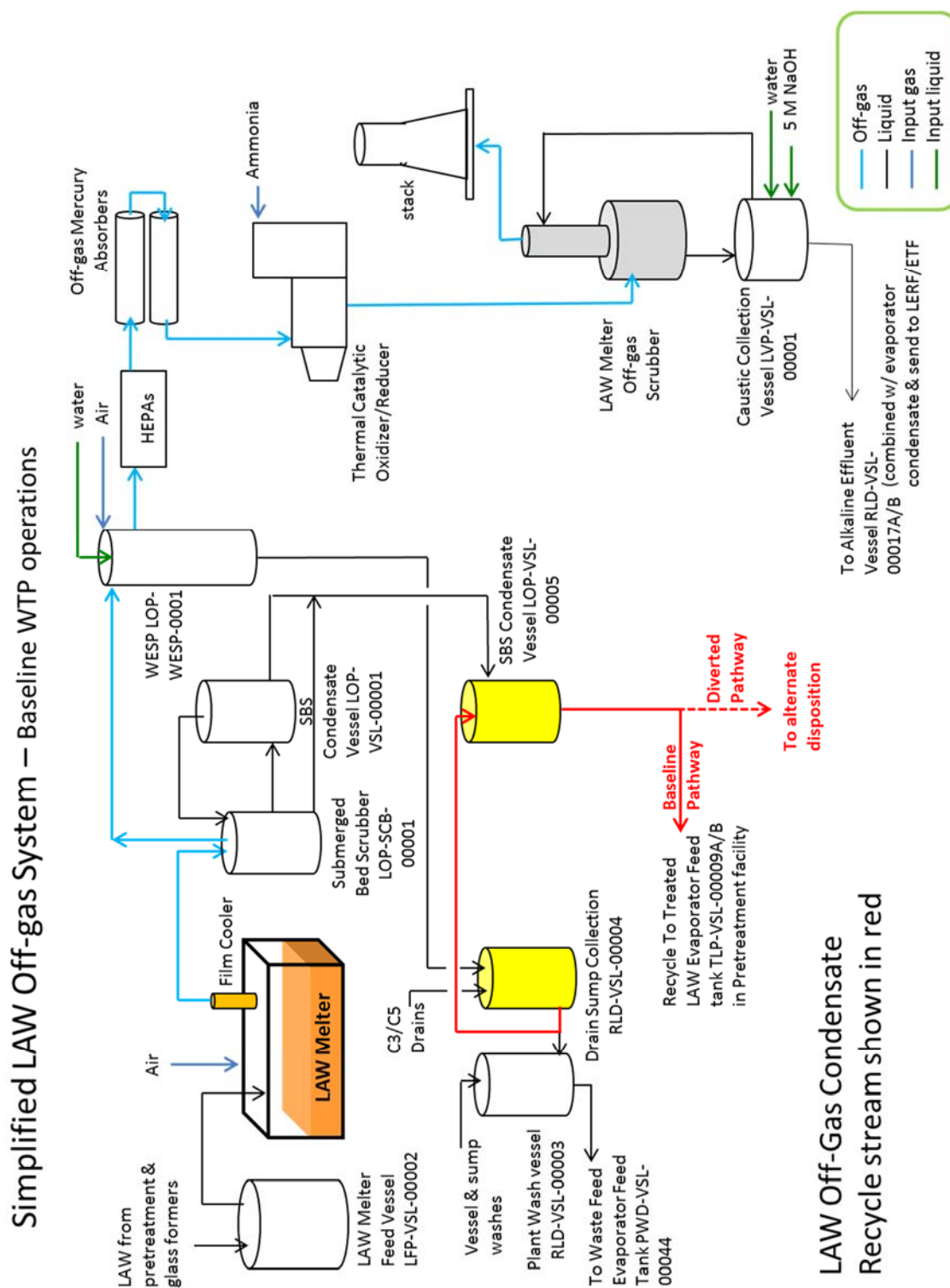
### 1.2 Test Objective

The overall objective of this development task is to evaluate decontamination of the stream using sorbents and/or precipitation agents so that it can be diverted for immobilization and disposal elsewhere (Figure 1-2). The facility that is envisioned to be needed for this process would utilize common industrial chemicals and equipment. Stannous chloride is a readily available chemical. The solid-liquid separation equipment is expected to be commonly available products as well, since the radiation dose rate for this stream is low,

enabling “hands-on” maintenance and inexpensive containment methods. The objective of this specific test was to mature the process design by examining a solid-liquid separation method at a bench scale to establish feasibility and enable preliminary estimates of the equipment size and throughput. This involves (1) demonstrating the precipitation process at increasingly larger scale, (2) measuring the clarifier and filter flow rate and transmembrane pressure, to project process parameters, and (3) measuring the decontamination factor for removal of contaminants of concern. The objective of the hydrogen generation rate test was to identify if there is an important process safety parameter that must be addressed.

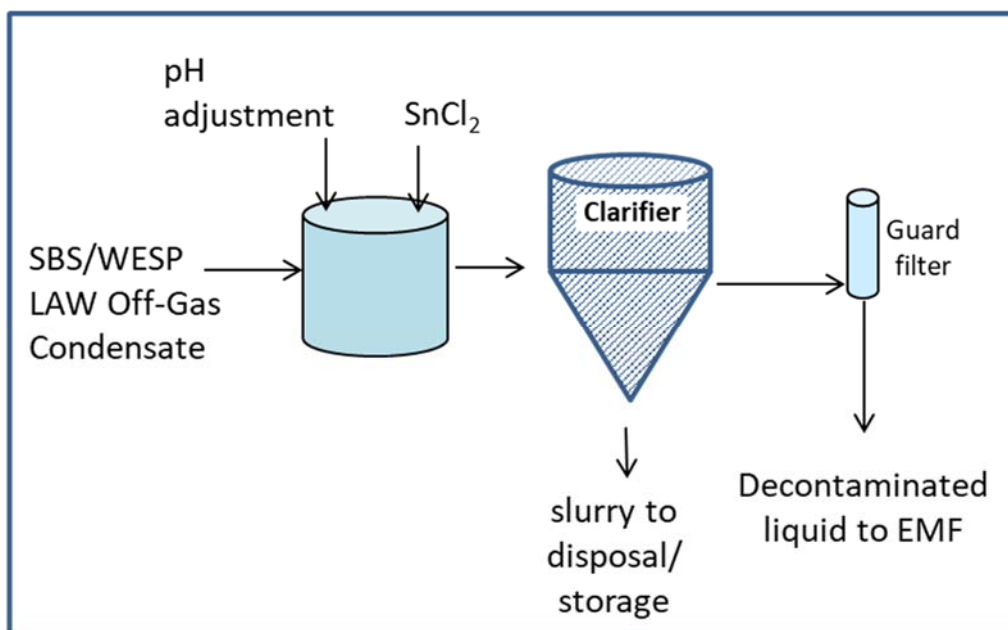
Although the chloride salt was used in testing, it is expected that other soluble stannous salts, such as sulfate, would be equally effective since the anion is not involved in the redox or the precipitation. Implementation of this process at WTP would make available both a short-term disposition path if the LAW facility commences operation prior to operation of the Pretreatment Facility and in the long term to divert the stream from recycling. Although Figure 1-2 indicates sending the decontaminated liquid to the EMF, other paths may also be viable options, since the stream would be very low in radioactivity. The core processing equipment in EMF is a filter and an evaporator<sup>7</sup>, and it would likely still be beneficial to concentrate this stream, even after the Tc is removed, to minimize the volume of the waste form. The most feasible disposal path for the Tc-containing slurry would be to recycle it to the LAW melter, because it would have no impact on the LAW glass volume and would be immediately available with minimal additional cost.<sup>8</sup> Other options for disposal or storage could be considered as well.

The overall plan for technology development of this process, along with options for disposal has been documented.<sup>9</sup> The laboratory testing of Tc removal and slurry characterization of this process has also been completed, including examination of optimized conditions, competitors, and settling.<sup>6,10,11,12</sup>



(simplified/adapted from 24590-WTP-RPT-PT-02-005, Rev. 8); (yellow indicates SBS/WESP LAW Off-Gas Condensate collection tanks, red lines indicate the collected off-gas condensate pathway)

### Figure 1-1. Simplified LAW Off-gas System



**Figure 1-2. Schematic of a Proposed Decontamination Process and Disposition Path of LAW Off-Gas Condensate**

### 1.3 Simulant Formulation Basis

Because this stream is not yet available for characterization, the simulant formulation was based on input from two sources. The projected solution chemistry was based on version 7.4 of the Hanford Tank Waste Operations Simulator (HTWOS) modeling of the flow sheet<sup>13</sup> performed by Washington River Protection Solutions.<sup>14</sup> This model run was for the average composition of this stream for the entire WTP mission (all 177 tanks) and with full integration of all WTP pretreatment processes, such as caustic leaching, oxidative leaching, and cesium ion exchange. Additional information on composition was obtained from analysis of samples obtained from pilot-scale melter testing using simulated LAW feed. More detail on the basis for and synthesis of the simulant has been documented.<sup>9,15,16</sup> Although the simulant is based on the projected composition during the entire WTP mission, there is no reason to expect that it would not also be applicable to the Direct Feed LAW scenario; albeit with a different composition. Prior work has shown that no soluble non-metal anions or insoluble glass formers impact the technetium precipitation, only soluble transition metals compete for the available reducing electrons, dominated by chromium.<sup>17,11</sup> Varying the Cr(VI) concentration was shown to directly and stoichiometrically impact the quantity of Sn(II) needed, as expected. Mercury (II) ion is also known to compete for electrons from Sn(II), requiring a slight increase in the amount of stannous chloride added. The lack of competition from major components and low concentration of soluble redox-sensitive transition metals in this stream is expected to make this process broadly applicable to the entire WTP mission.

### 1.4 Solid-Liquid Separation Method Selection

There are many methods available for solid-liquid separation, such as settling, centrifugation, hydrocyclone, and froth flotation, along with a myriad number of different types of filters. To narrow the possible options to those most feasible and economical for this application, a review of options was performed by a subject matter expert in solid-liquid separation applications in radioactive service for the DOE Complex. The review concluded with selection of a recommended priority for testing. A summary of that review is attached as Appendix A.

The concept for this test was to prepare a batch of simulant, add the stannous chloride at a scaled rate to cause the precipitation, and transfer the slurry to a clarifier, followed by a polishing filter. The filtrate and the underflow from the clarifier were returned to the feed tank to enable a continuous flow. The batch of simulant was large enough (20-25 L) to be able to use a reasonably sized clarifier. Because the off-gas condensate from the melter is hot, the apparatus was outfitted with a heater to be able to operate at ~40 °C (which is roughly the expected temperature for the process effluent from the LAW facility). The temperature would also be expected to impact the precipitated particle size and morphology, so this was an important detail. Similarly, the addition rate of stannous chloride can impact the particle size and morphology, so it was added over a period comparable to a scaled down processing rate. The processing rate of the full scale system is expected to be 9.25 gallons per minute (555 gallons per hour).<sup>18</sup> Prior work had estimated the reaction tank for this process would need to be about 2000 gallons.<sup>12</sup> The feed tank (modified carboy) used in the test contains about 6 gallons (23 L) of simulant, or ~1/333<sup>rd</sup> scale (on a volume basis). A 30-minute settling time in the clarifier was initially targeted for testing, although this is shorter than the typical 2-5 hour detention times in industrial clarifiers.<sup>19,20</sup> However, because of the rapid settling of the precipitate observed in previous testing, the 30 minutes was selected to attempt to reduce the size of the clarifier needed. The filter feed rate was originally estimated at 0.35 L/min, which means that the feed tank volume would turn over in 65 minutes. To achieve a comparable pseudo-continuous precipitation, the stannous chloride was added over a period of about one hour. The resulting solids are composed of chromium and tin oxyhydroxides. The stannous ion causes precipitation of the chromium by reducing it from +6 to +3 oxidation state, and the accompanying oxidation of the stannous ion converts it to stannic ion (+4), which precipitates as tin(IV) oxide/hydroxide. Some of the stannous is expected to also precipitate as the +2 hydroxide due to hydrolysis with the water. This ~0.08 wt% slurry was then slowly transferred to the clarifier, where the clarified liquid was pumped to a polishing filter and the underflow was pumped back to the feed tank.

The initial concept for the test was to demonstrate the processing rates under a single set of conditions. However, the initial test indicated faster than expected filter fouling. It was suspected that the mixer was shearing the particles, so a larger blade was installed. The larger impeller was able to suspend the solid particles at a lower rotational speed, while not excessively shearing them. Subsequent testing was then performed re-using the same batch of simulant at 40 and 25 °C to compare processing rates, and with a longer initial settling time. A follow-up test was then performed with a fresh batch of simulant, but with the liquid at 25 °C instead of 40 °C, and with a longer initial settling period prior to beginning filtration.

## 2.0 Experimental Procedure

### 2.1 Simulant Preparation

Detail on the basis and synthesis of the simulant has been documented elsewhere, and is repeated here for completeness and to describe details for these two batches.<sup>15</sup> The target concentrations of chemicals were derived from the output from the HTWOS calculation, documented in SVF-2732.<sup>14</sup> Because the HTWOS model is not constrained to generate a charge-balanced composition, no formulation can match all component concentrations simultaneously, and the chemical formulation must balance between cations and anions to create a mixture that can actually be synthesized. Previous simulant preparations have included the addition of glass forming chemicals (GFCs), which were allowed to come to equilibrium with the aqueous phase before the insoluble portion was removed by filtration. Based upon previous simulant analyses, the completely insoluble GFCs were excluded from this preparation, and only the soluble GFCs were added. That included borax, boric acid, lithium carbonate, and sodium carbonate; which were completely soluble at the amounts added. The semi-soluble silica and zinc oxide are added in the amounts shown to be soluble in previous simulant preparations. The insoluble GFCs were omitted from this test, even though it is recognized that they could impact the solid-liquid separation performance. In the melter,

the GFCs will react with the caustic liquid and other chemicals in the cold cap and melter plenum to produce entrained solids that will be captured by the SBS and WESP. Without a melter system it is not possible at this time to create a simulant that can replicate the speciation, morphology, or particle size of the entrained solids. Testing of a melter system indicated that the entrained solids will pass a 5-micron filter but will be captured on a 1-micron filter.<sup>21</sup> Particle size analysis indicated that the entrained solids were 1.2  $\mu\text{m}$  median diameter. This particle size would be expected to impact the solid-liquid separation method. However, the stannous ion precipitation process tested here is likely to flocculate these entrained solids, similar to how common precipitate flocculation processing in water treatment works, which typically improves the settling and filtration properties of fine solids. The quantity of solids from this stannous ion precipitation process are in much higher concentration at  $\sim 800$  mg/L, compared to the entrained solids in the SBS/WESP in that melter test at 148 mg/L so should dominate the settling properties. Future maturation of this process will involve obtaining a sample of SBS/WESP condensate from the WTP LAW melter during cold commissioning, where the detailed results of a solid-liquid separation process with a simulant containing entrained solids produced in a large melter can be finalized.

These experiments utilized one 24-L batch of non-radioactive simulant and a second 23-L batch. The non-radioactive simulant was prepared from dissolution of laboratory chemicals in deionized water, in the order shown in Table 2-1. After preparing the simulant, the solutions were mixed for several days at ambient temperature. The resulting solutions were measured to have a pH range of 8.1 – 8.2. The pH of each batch was then adjusted to 7.5 – 7.7 with the addition of an average of 4.30 g of 1 M nitric acid per L of simulant. Duplicate samples from each preparation were analyzed for elemental composition by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES), anions and ammonium by Ion Chromatography (IC).

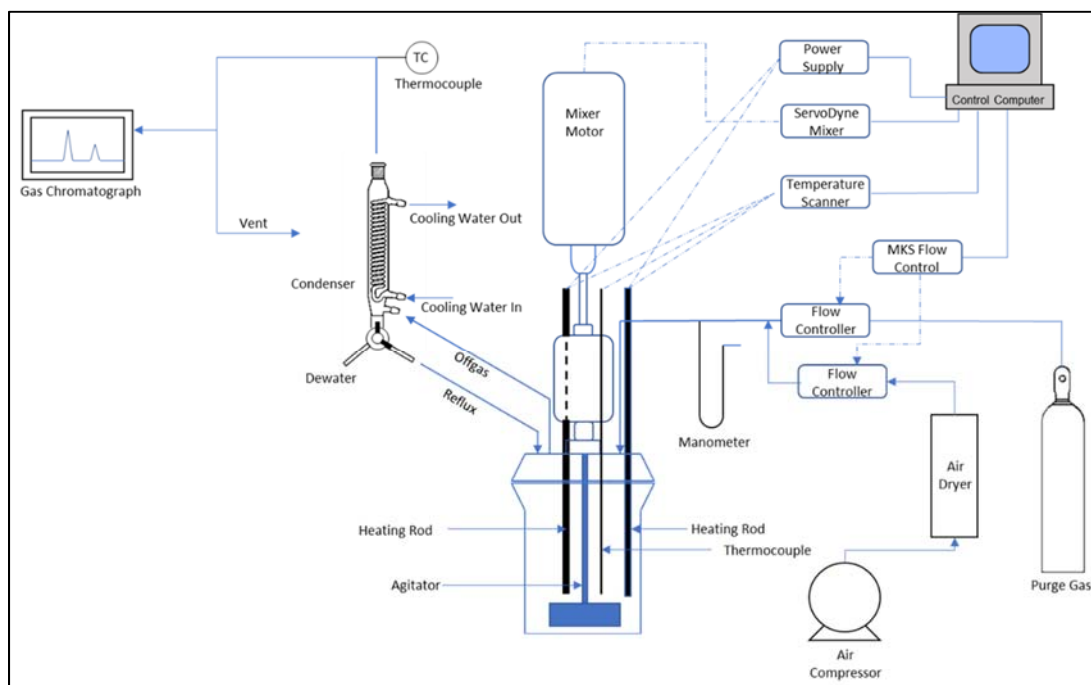
**Table 2-1. Non-Radioactive Simulant Formulation Targets**

Chemical	Formula	Target Mass (g)/L simulant	Target Molarity
Sodium fluoride	NaF	3.209	0.0764
Potassium chloride	KCl	0.219	0.0029
Sodium chloride	NaCl	1.395	0.0239
Sodium chromate	Na <sub>2</sub> CrO <sub>4</sub>	0.283	0.0017
Sodium nitrite	NaNO <sub>2</sub>	0.016	0.0002
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	3.220	0.0244
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	2.820	0.0352
Borax	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.0123	0.00003
Boric acid	H <sub>3</sub> BO <sub>3</sub>	1.430	0.0231
lithium carbonate	Li <sub>2</sub> CO <sub>3</sub>	0.392	0.0053
sodium carbonate monohydrate	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	0.0035	0.00003
zinc oxide	ZnO	0.018	0.0002
silica	SiO <sub>2</sub>	0.026	0.0004
Sodium nitrate	NaNO <sub>3</sub>	0	0*
calculated total dissolved solids		13.04	

\*note that nitrate ion is added later as nitric acid during pH adjustment

## 2.2 Hydrogen Generation Rate Measurement

The Hydrogen Generation Rate (HGR) was measured using a system previously described.<sup>22</sup> A schematic of the apparatus is shown in Figure 2-1.



**Figure 2-1. Schematic of the HGR Apparatus Employed in Simulant Testing**

The 1.2 L reactor system and HGR apparatus was charged with 1.0 L (~997.7 g) of SBS/WESP simulant. Next, the HGR apparatus was sealed and agitation was initiated at a rate of 200 revolutions per minute (rpm). A purge gas of 0.5% Kr and 20% O<sub>2</sub> in N<sub>2</sub> was applied at a rate of 10 standard cubic centimeters per minute (sccm) (21 °C, 1 atmosphere (atm.)). The outlet gas concentration was allowed to equilibrate (determined by an outlet Kr concentration of 0.5% ± 0.05%) before beginning the experiment.

The first HGR experiment was performed to determine the HGR from the simulant in the absence of stannous chloride to provide a “blank” measurement. The mixture was heated from room temperature (~20 °C) to 45 °C over a period of 38 minutes. The apparatus was held at 45 °C for > 1 hr to ensure that a steady-state HGR could be measured. Afterward, heating was turned off and the apparatus was allowed to cool overnight.

Following the blank test, 0.85073 g of stannous chloride dihydrate (equivalent to 1.5 equivalents of the number of electrons needed to reduce the Cr from +6 to +3) was charged to the simulant mixture. Agitation was restarted at 200 rpm and a purge rate of 3 sccm was applied to the apparatus. The simulant and stannous chloride mixture were then heated to 45 °C and held for >3.3 hours to observe if there was any hydrogen generation.

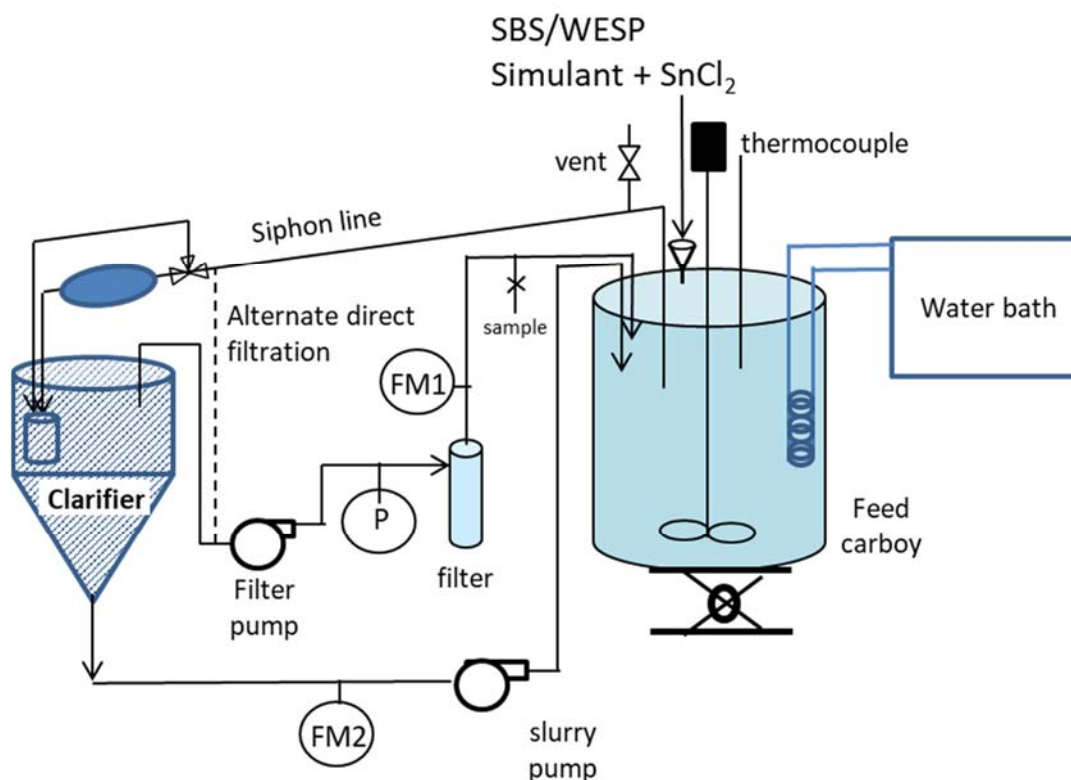
Concentrations of Kr, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> were measured with an Inficon 3000 MicroGC installed downstream of the HGR apparatus. The Gas Chromatograph (GC) was calibrated with a gas blend consisting of 52 ppm H<sub>2</sub> diluted in 0.5% N<sub>2</sub>O, 1% CO<sub>2</sub>, 20% O<sub>2</sub>, and a balance of N<sub>2</sub>.

### 2.3 Clarifier-Filter Rig

A schematic of the clarifier-filter rig that was constructed for this test is shown below. The simulant was added into a 25-L carboy adapted for this rig as a feed tank. The clarifier was a clear acrylic cylinder, 29 cm internal diameter, 34-cm tall, with a conical bottom that was 6-cm deep. The pumps were peristaltic

metering pumps. The feed tank was equipped with an overhead mixer with a 4-blade, 4.2-inch diameter pitch-blade turbine impeller with 1.25-inch-wide blades for the first test, and a 3-blade high shear impeller with a 5.75-inch diameter and 2.6-inch-wide blades, and for the subsequent tests. The impeller rotated at 100 - 120 rpm for tests 2 - 4. The filter was a Pall Mini Profile™ II Capsule filter, 1.0  $\mu\text{m}$  absolute pore size. The polypropylene filter surface area for these filters is 46  $\text{cm}^2$ .<sup>a</sup> The feed tank/carboy was equipped with an internal heating coil connected to a recirculating water bath, thermocouple, chemical addition port, and mixer. The feed tank was connected to the clarifier by a siphon tube instead of a pump to minimize shearing of the solids as the liquid transfers to the clarifier and to ease maintaining liquid level. The end of the siphon tube in the clarifier was placed inside a glass container submerged in the liquid to minimize agitation in the clarifier by the incoming flow of liquid. The glass container was approximately 300 mL in volume and had a conical bottom with a hole to allow solids to flow out while the liquid overflowed the top. The feed carboy was on a jack stand to allow adjustment of the liquid level between the carboy and the clarifier using the siphon line.

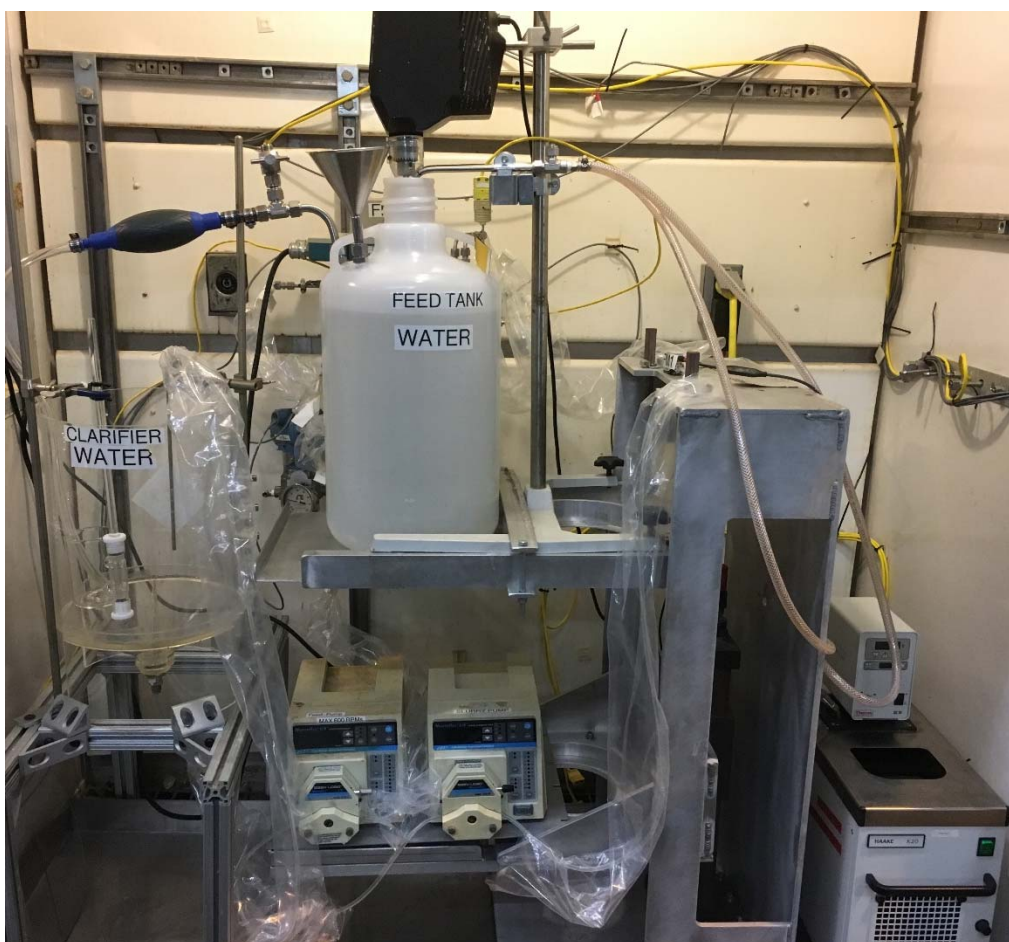
The filter and concentrated slurry flows were produced with Masterflex model 7518-10 peristaltic pumps. The filtrate flow rate was measured with a Fischer Porter Model 10D1475 flow meter, and the concentrated slurry flow rate was measured with a Sensirion Model SLQ-QT 500 flow meter. The filter feed pressure was measured with a Rosemount Model 3051CD pressure transducer. The temperature of the feed was controlled with a HAAKE Model K20 chiller bath and a HAAKE Model DC-10 controller.



<sup>a</sup> <https://shop.pall.com/us/en/biotech/filtration/particulate-filters/mini-profile-capsules-zidgri781ea>

**Figure 2-2. Schematic of Clarifier-Filter Rig<sup>b</sup>**

An image of the clarifier-filter rig is shown in Figure 2-3. The filter housing is not visible in this image because it is behind the feed tank.<sup>c</sup> An image of the filter is shown in Figure 2-4.



**Figure 2-3. Image of Clarifier-Filter Rig**

<sup>b</sup> “P” indicates a pressure measurement device; “FM” indicates a flow meter.

<sup>c</sup> The siphon bypass line is not shown in Figure 2-3 because it was added just prior to beginning tests



**Figure 2-4 Image of Pall Mini Profile™ II Capsule filter**

## 2.4 Precipitation

For the first precipitation process, one liter had been removed from the 24-L batch for the hydrogen generation test, so the remainder, 22.952 L of simulant, was added to the feed carboy. Mixing was initiated by turning on the stirrer and the heating water bath was set to achieve the target  $40 \pm 2$  °C in the feed carboy. After reaching temperature, the stannous chloride dihydrate ( $19.5322 \text{ g}^d$ ) was added to the feed carboy over a period of 63 minutes by adding a small aliquot every few minutes. The solution was originally bright yellow due to the soluble Cr(VI) chromate ion, but blue-green solids indicative of Cr(III) oxide began to appear almost immediately after the first aliquot of stannous chloride was added. No yellow color was visible in the final liquid.

For the precipitation of the second batch of simulant (fourth test), the feed carboy was loaded with 22.954 L of simulant. Mixing was initiated by turning on the stirrer and the heating water bath was set to achieve the target  $25 \pm 2$  °C in the feed carboy. After reaching temperature, the stannous chloride dihydrate ( $20.3980 \text{ g}^d$ ) was added to the feed carboy over a period of 60 minutes by adding a small aliquot every few minutes. The blue-green solids began to appear almost immediately after the first aliquot of stannous chloride was added. A sample of the solids was filtered and air dried for crystal analysis by X-ray diffraction (XRD).

## 2.5 Clarifier-filter Testing

A total of four tests were performed. They are described in more detail individually below, but briefly described here in approximate temperatures and durations to explain the differences. The first test was performed at  $\sim 40$  °C with fresh precipitation of the solids, transfer of liquid into the clarifier, and  $\sim 30$  minutes of initial settling in the clarifier before initiating filtration. The liquid level in the clarifier was  $\sim 17$  cm for all tests (not including the conical bottom), which corresponds to  $\sim 12.5$  L of liquid. The feed tank mixer blade was removed after the first test and replaced with a larger mixer blade used for all subsequent tests. The second test was performed re-using the slurry from the first test, and operating at 25 °C, but the initial settling time in the clarifier was extended to  $\sim 120$  minutes before initiating filtration to

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<sup>d</sup> The amount of stannous chloride dihydrate added for each experiment was calculated based on the Cr concentration in the simulant. For the first experiment the measured Cr concentration ( $87.2 \text{ mg/L}$ ) was utilized for the calculation. Characterization results for the second batch of simulant were not available prior to testing, and therefore the target Cr concentration of  $91 \text{ mg/L}$  was utilized for this calculation.

decrease solids loading to the filter. The third test also re-used the slurry from the first test and used the same filter that was partially fouled, but the system was operated at 40 °C, and similarly allowed ~90 minutes of settling before initiating filtration. The fourth test was performed at 25 °C, with fresh precipitation of the solids, transfer of liquid into the clarifier, and ~120 minutes of settling in the clarifier before initiating filtration.

The testing was to demonstrate the clarifier effectiveness at removing the solids and to monitor the rate of pressure increase of the filter. Clarification and filtration continued until the pressure in the filter approached the maximum set point, 30 psi. Samples were collected to measure the concentration of solids and the effectiveness of removing Cr. Since this test was performed using non-radioactive equipment, the Cr removal was a surrogate for Tc removal.

### Test 1

The first test was performed by heating the stirred simulant to  $40 \pm 2$  °C and adding stannous chloride to produce a fresh precipitate of the solids. After the 63-minute addition of stannous chloride was complete, the simulant was mixed for an additional ten minutes and then siphon transfer of slurry into the clarifier began. After 9 minutes the liquid level in the clarifier was increasing, and the slurry pump was turned on with a flow rate set to 62.3 mL/min but was reduced to 40.0 mL/min after 34 minutes to increase settling time in the clarifier. Forty-one minutes after turning on the slurry pump, the filter suction line was set approximately one inch below the top of the liquid in the clarifier and the filter feed pump was turned on, initiating filtration. For the beginning of the first test, the flow rate to the filter was initially set to 287 mL/minute and the filter pressure was initially 6.7 psi. This corresponds to a clarifier turn-over time of 40 minutes (i.e., volume of clarifier/liquid flow rate out). The pressure on the filter began to increase quickly, so after 12 minutes, the flow rate was reduced, initially to 220 mL/minute, and then decreased in several increments, ending at 50 mL/minute, twenty minutes after beginning filtration. The test was ended after a total of 57 minutes of filtration time when the filter pressure was approximately 22 psi.

### Test 2

Prior to the second test, the mixer blade was removed and replaced with a larger mixer blade used for all subsequent tests. The filter was replaced with a new cartridge for this test. The second test was performed re-using the slurry from the first test (i.e., a fresh precipitation was not performed), and the process was operated at  $25 \pm 2$  °C with a mixer rotation speed of 104 rpm, later raised to 120 rpm. For the second test, the slurry was siphoned into the clarifier, which filled in 17 minutes and the slurry pump was turned on at ~28 mL/min. 113 minutes after the slurry pump was turned on, a visually clear layer had formed at the top of the clarifier, so the filter pump was turned on and set to 82 mL/min with an initial pressure of 5.4 psi. Although still moderate duration, the 113 minutes is closer to typical detention times in industrial clarifiers (2 – 5 hours).<sup>19,20</sup> The clarifier turn-over duration was approximately 124 minutes. These flow rate settings were maintained for the duration of the test, and the filter feed pressure slowly rose over a period of about 2 ½ hours to 9.0 psi.

### Test 3

The third test also re-used the slurry from the first test and used the same filter that was partially fouled, but the system was operated at  $40 \pm 2$  °C. The warm slurry was mixed at 115 rpm and then siphoned into the clarifier, which continued to fill for 22 minutes and then the slurry pump was turned on at ~39 mL/min. 81 minutes after the slurry pump was turned on, the filter pump was turned on and set to 83 mL/min and had an initial pressure of 8.5 psi. The clarifier turn-over duration was approximately 118 minutes. These flow rate settings were maintained for the duration of the test, and the filter backpressure slowly rose over a period of 2 hours to 23 psi.

#### Test 4

The fourth test was performed with a fresh batch of simulant. The simulant was mixed at 100 rpm at  $25 \pm 2$  °C during the addition of stannous chloride over a period of 60 minutes. After addition of all the stannous chloride, the slurry was mixed for an additional fifteen minutes and then the siphon transfer of the fresh slurry into the clarifier was initiated. After filling the clarifier for ten minutes, the slurry pump was turned on at ~16 mL/min. 126 minutes after starting the slurry pump, the suction line for the filter was set to approximately one inch below the liquid level in the clarifier, and the filter feed pump was turned on, initiating filtration. For this fourth test, the flow rate to the filter was set to 84 mL/min. This corresponds to a clarifier turn-over duration of about 136 minutes. The flow rate settings were maintained for the duration of the test, which was terminated after 2 ¼ hours when the filter pressure reached 25 psi.

#### 2.6 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This test program is described in the Task Technical and Quality Assurance Plan for Developing a Flowsheet for Off-Gas Process Liquids from the Hanford Low Activity Waste Vitrification Process.<sup>23</sup> Results are recorded in Electronic Laboratory Notebook #E7518-00211.<sup>24</sup>

### 3.0 Results and Discussion

#### 3.1 Simulant Preparation

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized SBS/WESP simulant are shown in Table 3-1. These match the target compositions reasonably well, with the exception of nitrate which was low. Note that the HTWOS model output that was used to develop this formulation is not charge balanced, so it is not possible to create a solution that is chemically identical to the model outputs, and nitrate is adjusted to account for the imbalance. The small variations are not expected to impact results obtained here because the concentrations of these constituents are sufficient to indicate if an interfering or detrimental reaction occurs.

**Table 3-1. Neutralized SBS/WESP Simulant Composition**

Component	Average Concentration Batch 1 (24 L) (mg/L)	Std. Dev.	Average Concentration Batch 1 (24 L) (M)	Average Concentration Batch 2 (23 L) (mg/L)	Std. Dev.	Average Concentration Batch 2 (23 L) (M)
B	252	2.83	0.023	252	7.07	0.023
Cr	87.2	0.35	0.0017	87.9	0.42	0.0017
K	115	0.71	0.0029	115	0.71	0.0029
Li	70.9	0.07	0.010	74.9	0.42	0.011
Na	2.49E3	21.2	0.11	2.49E3	14.1	0.11
S	836	15.6	0.026	806	29.0	0.025
Si*	3.93	0.25	1.4E-4	< 4	n/a	< 1.4E-4
Zn*	12.3	0.21	1.9E-4	0.8	1.41E-3	1.2E-5
F <sup>-</sup>	1.39E3	7.07	0.073	1.71E3	35.4	0.090
Cl <sup>-</sup>	950	2.83	0.027	958	6.36	0.027
NO <sub>2</sub> <sup>-</sup>	< 50	n/a	< 0.0011	10.2	0.141	2.2E-4
NO <sub>3</sub> <sup>-</sup>	2.46E3	7.07	0.040	2.48E3	7.07	0.040
SO <sub>4</sub> <sup>2-</sup>	2.37E3	42.4	0.025	2.36E3	14.1	0.025
NH <sub>4</sub> <sup>+</sup>	1.53E3	21.2	0.085	1.49E3	7.07	0.082

\*Added in reduced amounts compared to previous preparations. Only the expected soluble amount was added.

### 3.2 Hydrogen Gas Generation

A key objective of this test program was to identify if there is an important process safety parameter that must be addressed, particularly if any flammable gas is produced in the redox reaction. Hydrogen concentration in the “blank” test was not detectable (<1.0 ppm), indicating a blank (tin-free) HGR of  $<2.48 \times 10^{-8} \text{ gmol H}_2 \text{ hr}^{-1} \text{ L}^{-1}$ .

Testing with stannous chloride and simulant was performed at a lower purge rate (3 sccm vs. the 10 sccm purge rate used in blank testing), and therefore was capable of more sensitive HGR measurements. Stannous chloride testing also resulted in hydrogen concentration below detectable limits, indicating an HGR of  $<7.45 \times 10^{-9} \text{ gmol H}_2 \text{ hr}^{-1} \text{ L}^{-1}$ . These results suggest that hydrogen generation due to the addition of stannous chloride is approximately 50 times smaller than the actionable limit for incoming LAW to WTP of  $3.7 \times 10^{-7} \text{ gmol H}_2 \text{ hr}^{-1} \text{ L}^{-1}$ .

### 3.3 Clarifier-Filter Testing

Testing was performed using a bench-scale clarifier-filter apparatus set up for this experiment. One objective was to demonstrate the precipitation process at increasingly larger scale. This testing was done using >20 L of simulant, significantly larger than previous testing. Performing this test at larger scale demonstrated formation of solids under more realistic conditions than in small laboratory tests, and hence should exhibit more realistic results for solid-liquid separation performance and decontamination factor. Those results are discussed below. The initial tests were done with the simulant at ~40 °C, although the actual temperature of this stream will not be known until WTP operates. This temperature was an initial estimate based on the design for the SBS which controls the recirculation loop to 50 °C, which would blend with the cooler WESP stream, which is not temperature controlled but uses a single pass water spray and periodic deluge with process water.

Another key objective of this testing was to measure the clarifier and filter flow rates to project process parameters. This scale of testing is viewed as an intermediate step, where the information provides a basis for testing at an engineering scale. As mentioned in Section 1.4, this test is ~1/333 scale (on a volume basis) of what is envisioned to be the full-scale system for WTP. Importantly, the results show proof-of-principle of the utility of a clarifier-filter system to remove Tc in this conceptualized process.

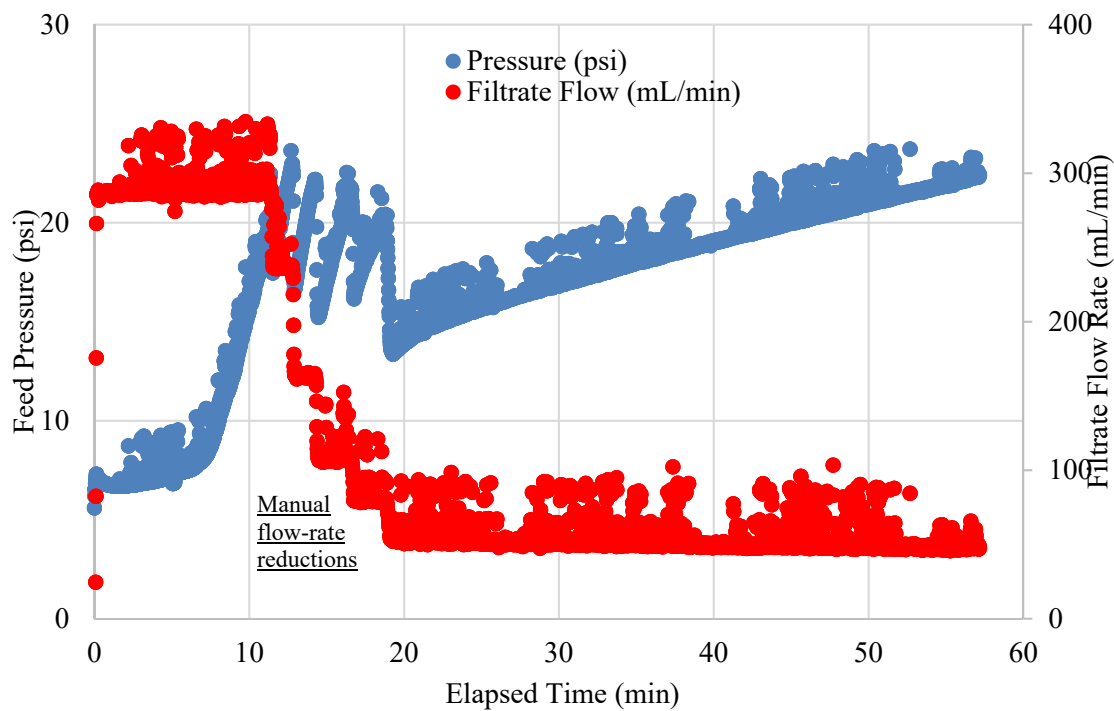
The test rig was designed to primarily focus on the clarification and filtration processing rates, and less so for quantifying the conditions for the under-flow from the clarifier (i.e., the concentrated slurry). It was not practical to construct an apparatus at this scale that would accurately recreate the wt% solids that would be achievable in an industrial-scale system. To do so would take considerably longer clarifier residence time and liquid depth to reach a good approximation of the solids compaction behavior at full scale. Since the slurry in this process is only ~0.08 wt% insoluble solids, and typical metal hydroxide precipitate sludges can be concentrated by settling to 10-20 wt%,<sup>19</sup> it was not practical to scale up this aspect of the process and simultaneously measure the filtration of the clarified liquid. Even a 23-liter batch of simulant only yields ~20 g of insoluble solids, which is <0.25 L of slurry at 10 wt% solids. An engineering scale rig would be needed to measure the achievable slurry concentration and physical properties accurately.

#### 3.3.1 Test 1

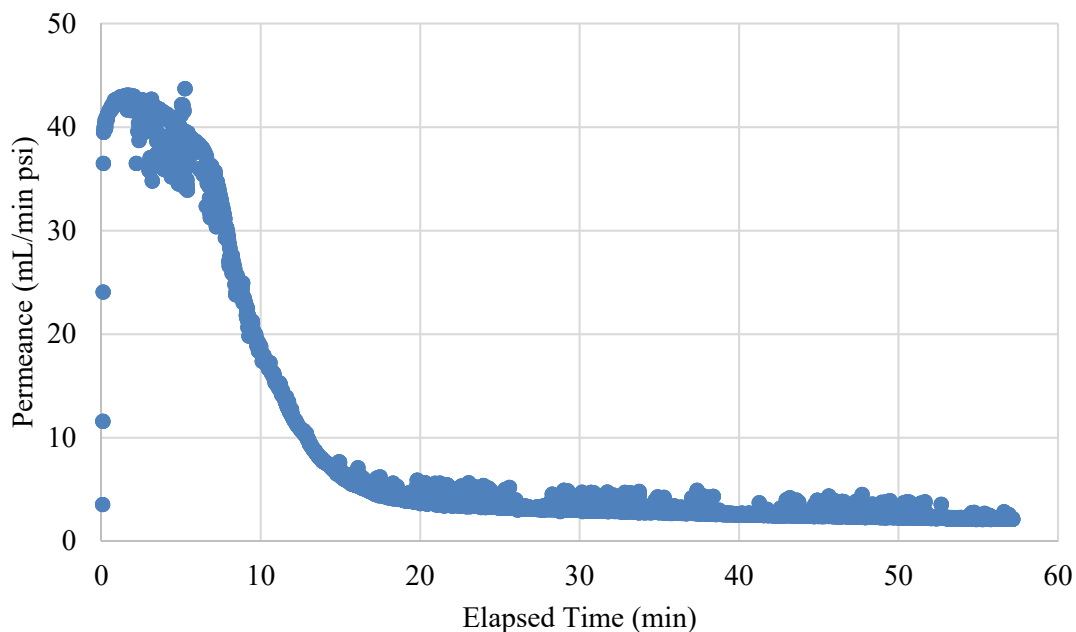
Test 1 was the initial trial of using a clarifier-filter arrangement to remove the insoluble solids from the simulant to get an indication of the process flow rates that could be achieved. As such, the target flow rates were initially set high in an attempt to bound the maximum throughput conditions. The flow rate and filter pressure measurement results are shown in Figure 3-1, and the filter permeance (permeance = flow rate/pressure) is shown in Figure 3-2. Additional results are shown in Appendix B.

The initial filtrate flow rate and feed pressure were 285 mL/min and 6 psi, respectively. The feed pressure increased to 22 psi after 11 minutes. The flow rate was manually decreased to 236 mL/min. The feed pressure decreased initially to 18 psi, and then increased to 23 psi within about one minute. The filtrate flow rate was further decreased to 162 mL/min. The feed pressure decreased initially to 17 psi, and then increased to 22 psi within two minutes. Additional decreases in the filtrate flow rate led to initial decreases in the feed pressure followed by rapid increases. Eventually, the filtrate flow rate was decreased to 50 mL/min at nineteen minutes after starting filtration. The feed pressure initially decreased to ~14 psi, and then increased to 22 psi over the next 40 minutes.

At the start of the test, the permeance was ~ 40 mL/min psi. It increased to ~ 43 mL/min psi over 2 minutes, before decreasing to 2 mL/min psi over the next 55 minutes. Integrating the area under the filtrate curve indicates that a total of 6.46 L of liquid was filtered during the test.



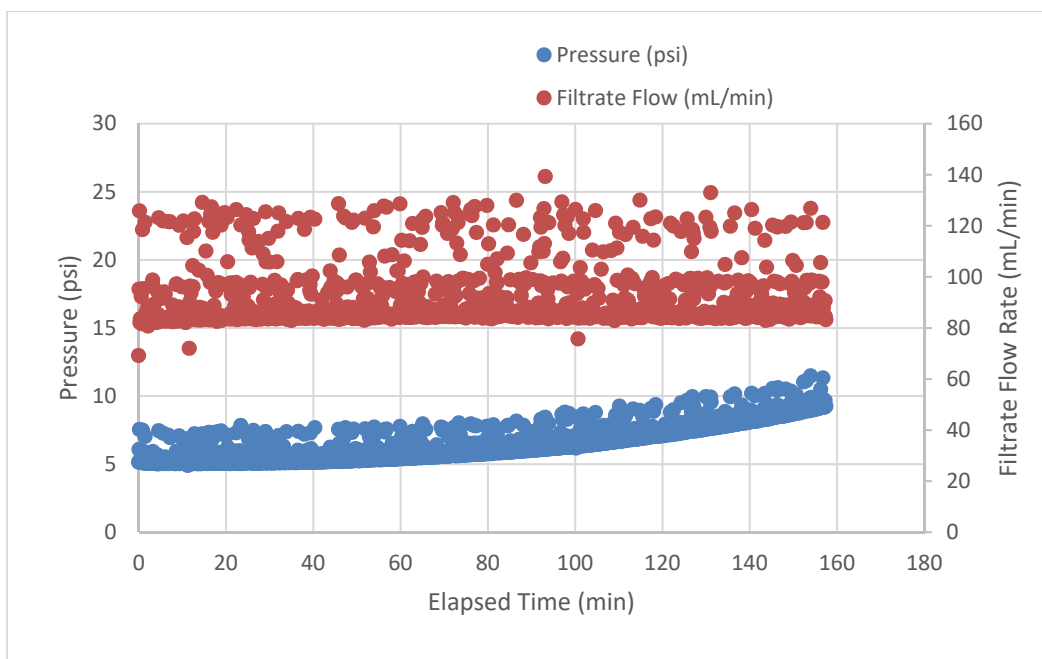
**Figure 3-1 Test 1 Flow Rates and Filter Pressure**



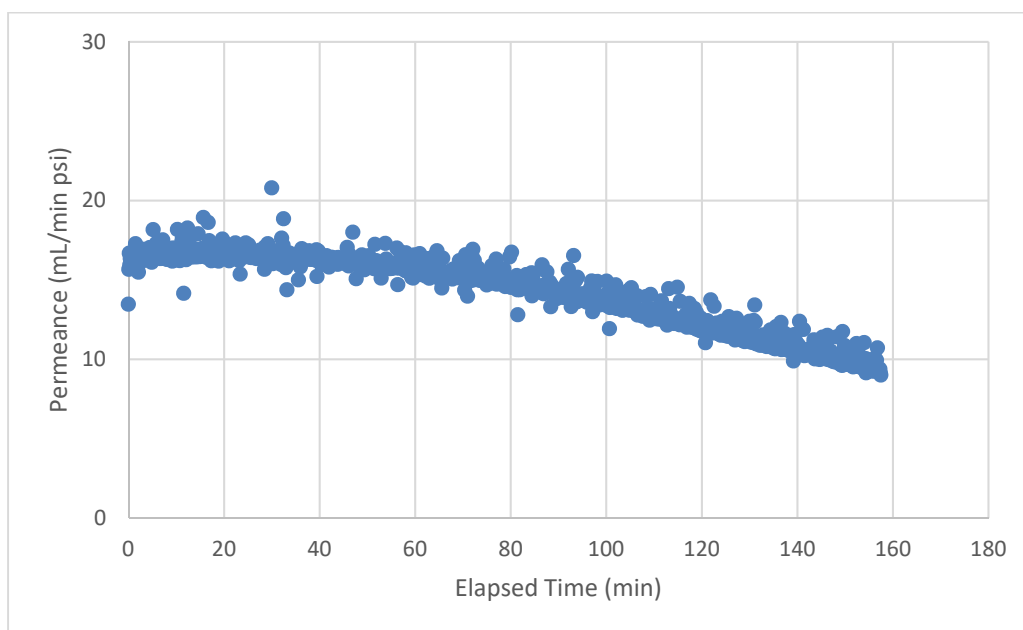
**Figure 3-2 Test 1 Filter Permeance**

### 3.3.2 Test 2

Test 2 was performed at ~25 °C using the batch of simulant from Test 1 that had been stored for a few weeks. The flow rate and filter pressure measurement results are shown in Figure 3-3, and the filter permeance (permeance = flow rate/pressure) is shown in Figure 3-4. Additional results are shown in Appendix B. The initial filtrate flow rate and feed pressure were 83 mL/min and 5 psi, respectively. The feed pressure increased to 9 - 11 psi after 157 minutes. The initial permeance was 16 mL/min psi, and the permeance after 157 minutes was 9 mL/min psi. At the lower filtrate flow rate and lower temperature, the filter fouling was much less than in the first test. Integration of the curve indicated that the total amount of filtrate produced was much higher than in Test 1, at 14.1 L.



**Figure 3-3 Test 2 Flow Rates and Filter Pressure**



**Figure 3-4 Test 2 Filter Permeance**

Analysis results of wt% of the solids in the slurry samples collected from Test 2 are shown in Table 3-2. The calculated insoluble solids range from 0.07 wt% if the Cr and Sn completely precipitate as the oxides to 0.09 wt% if they precipitate as the hydroxides. The mass of solids could also be even higher if the solids contain waters of hydration not removed in the analysis method or if other metals (e.g. Zn) co-precipitate. So, the approximate calculated solids content is 0.08 wt%. The measured values are in the range of the expected 0.08 wt% solids but with high variability, indicating that the slurry is not homogeneously mixed.

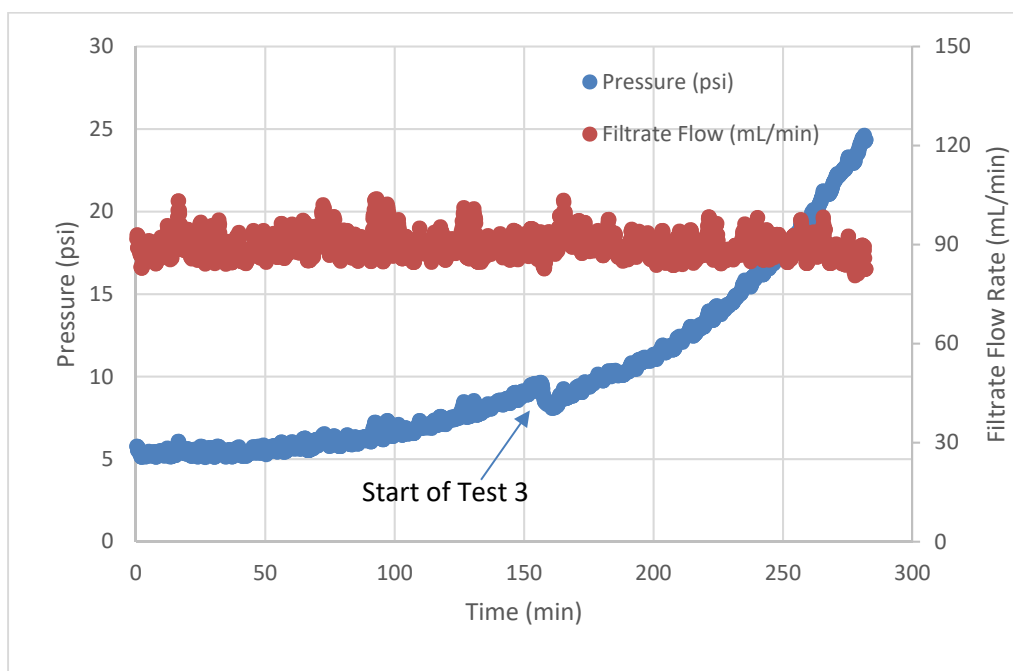
**Table 3-2 Test 2 Slurry Sample Weight Percent Solids Analysis Results**

Date/Time Sample Pulled	wt % Solids
11/5/18 12:37	0.124
11/5/18 14:00	0.069

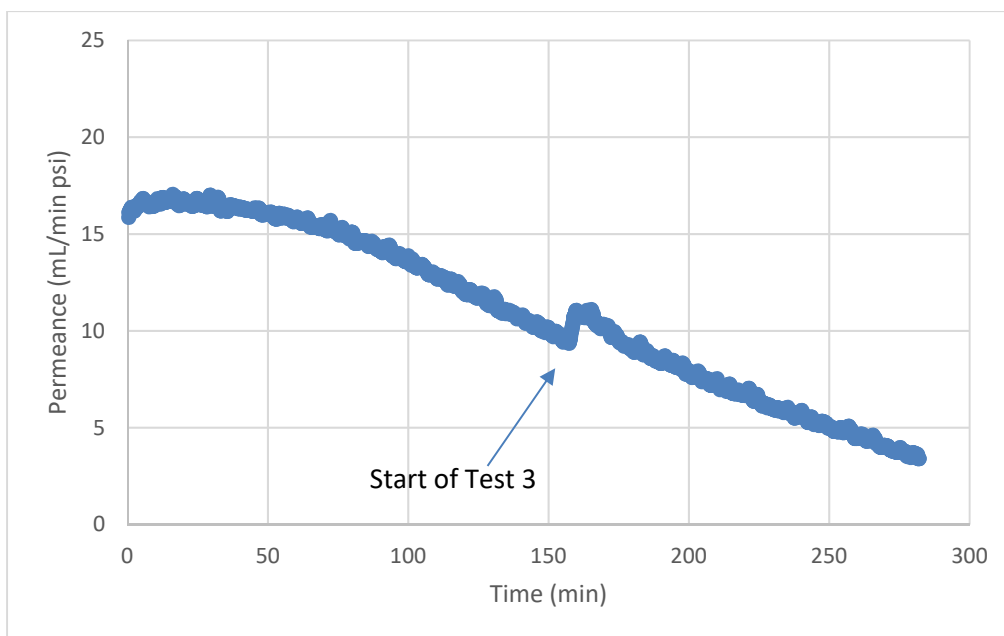
### 3.3.3 Test 3

Test 3 was performed again using the batch of simulant from Tests 1 and 2, but the temperature of the simulant was ~40 °C. The flow rate and filter pressure measurement results from both Tests 2 and 3 are combined and shown in Figure 3-5. Additional results are shown in Appendix B.

The initial filtrate flow rate and feed pressure during Test 3 (beginning after 160 minutes in Figure 3-5) were 84 mL/min and 8 psi, respectively. The feed pressure increased to 25 psi after 124 minutes. The initial permeance was 11 mL/min psi, and the permeance after 124 minutes was 3 mL/min psi. Test 3 showed more filter fouling than Test 2, but Test 3 did not use a new filter and was conducted at a higher temperature. The permeance plot with the combined results from Test 2 and 3 illustrates how the filtrate permeance decreased at comparable or perhaps slightly faster rates during Test 3 compared with Test 2, as indicated by the upward curve in the pressure. The total volume of filtrate produced in Test 3 was 11.2 L.



**Figure 3-5 Tests 2 and 3 Flow Rates and Filter Pressure**



**Figure 3-6 Test 2 and 3 Filter Permeance**

A single slurry sample pulled from the clarifier during test 3 indicated a weight percent solids concentration of 0.096 wt %, which is just above the range of calculated solids concentration.

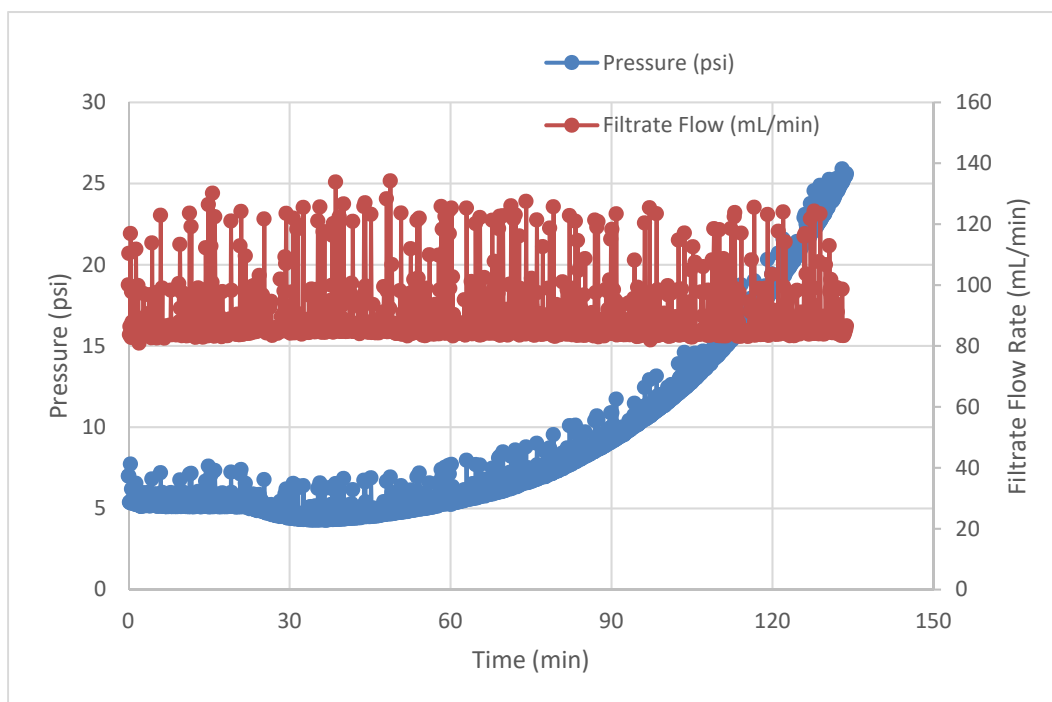
The clarity of the liquid in the clarifier during Test 3 is shown in Figure 3-7. At the time that the filtration was initiated (left image), the liquid was almost completely clear, with just a slight bluish haze near the top of the clarifier. Increased agitation in the clarifier due to the increase flow of liquid out to the filter, and thus in-flow from the feed tank, caused the mixture to become increasingly cloudy within 85 minutes (right image). Presumably, this is what caused the increased filter fouling rate. Although it is not easily seen in the image, in all tests, solids that had settled in the glass container inside the clarifier would continuously flow out the hole in the bottom and downward into the bottom of the clarifier.



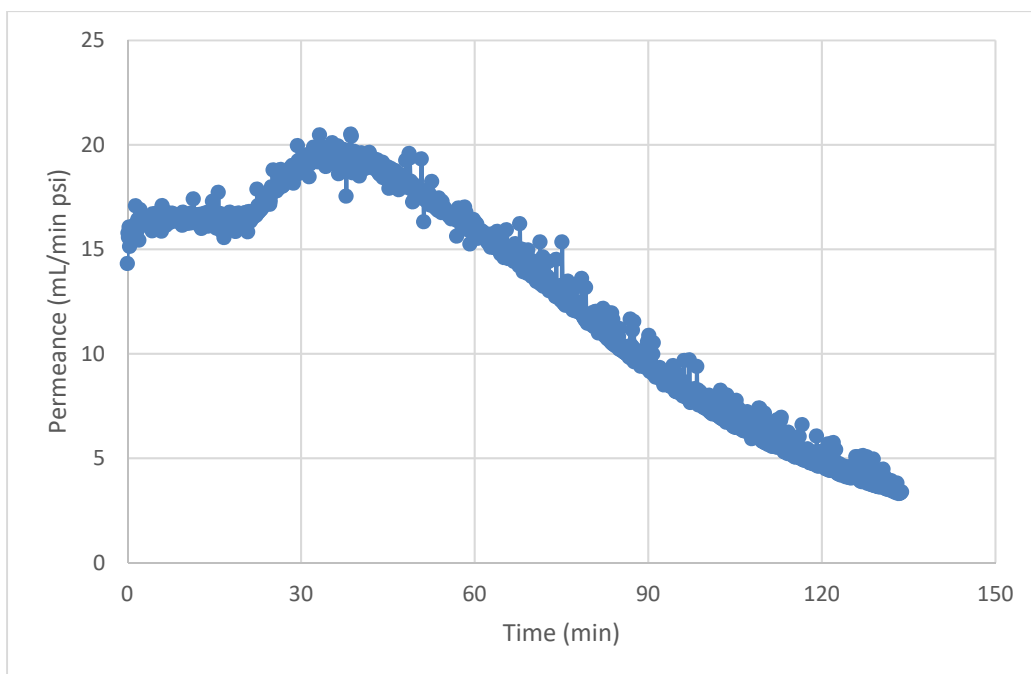
**Figure 3-7. Test 3 Clarifier Images (at beginning of filtration (left) and 85 minutes later (right))**

### 3.3.4 Test 4

Test 4 was performed using a fresh batch of simulant, and the precipitation and solid-liquid separation was performed at 25 °C. The flow rate and filter pressure measurement results are shown in Figure 3-8, and the filter permeance (permeance = flow rate/pressure) is shown in Figure 3-9. Additional results are shown in Appendix B. The initial filtrate flow rate and feed pressure were 83 mL/min and 5 psi, respectively. The feed pressure increased to 26 psi after 134 minutes. The initial permeance was 14 mL/min psi, and the permeance after 134 minutes was 3 mL/min psi. The increase in permeance after ~20 minutes is attributed to pushing the air out of the new filter housing and fully wetting the filter surface area. Test 4 showed higher filter fouling than Test 2. However, this test used fresh feed rather than previously used feed that had been allowed to sit undisturbed for a few weeks. How this storage contributed to the differences in performance is not known. Integrating the area reveals that the total amount of filtrate produced in this test was 12.0 L.



**Figure 3-8 Test 4 Flow Rates and Filter Pressure**



**Figure 3-9 Test 4 Filter Permeance**

Analysis results of wt% of the solids in the slurry samples collected from Test 4 are shown in Table 3-3. Results indicate significant inhomogeneity in samples. The first and third samples are somewhat above the expected value of 0.08 wt% solids, but the second sample is well below, indicating a sampling or mixing inhomogeneity.

**Table 3-3 Test 4 Slurry Sample Weight Percent Solids Analysis Results**

Date/Time Sample Pulled	wt % Solids
11/13/18 09:10	0.147
11/13/18 11:35	0.010
11/13/18 12:35	0.118
11/13/18 13:35	0.065

The clarity of the liquid in the clarifier is shown in Figure 3-10. As the filtration was initiated (left image), the liquid was almost completely clear, with just a slight bluish haze near the top of the clarifier. Increased agitation in the clarifier due to the increase flow of liquid out to the filter, and thus in-flow from the feed tank, caused the solution to become considerably more cloudy within 71 minutes (right image). Presumably, this caused the filter to foul, increasing the back pressure.



**Figure 3-10 Test 4 Clarifier Images (at beginning of filtration (left) and 71 minutes later (right))**

### 3.4 Clarifier-Filter Filtrate Analysis

Another objective of this testing was measuring the decontamination factor<sup>e</sup> (DF) for removal of contaminants of concern. Although Tc was not used for this test, it has been shown by experiment that the removal of Cr is a conservative comparison value to the removal of Tc.<sup>11</sup> Testing has shown that the measured DF for Tc exceeds that measured for Cr and the removal of Tc is more rapid than Cr. This comparison is only valid in this limited case, where the specific chemical compositions and conditions have been thoroughly tested to demonstrate the comparability of Tc and Cr removal. Note, however, that although the testing has shown that the DF and precipitation kinetics are comparable, the removal efficiency of the specific filter used in this testing has not been shown equally effective for both Tc and Cr. Testing with the Tc precipitation had been done using a 0.1- $\mu\text{m}$  laboratory syringe filter, and the current testing used a different filter media with a 1.0- $\mu\text{m}$  filter, but the difference in removal of Cr and Tc is expected to be insignificant. The trace amount of Tc solids would likely co-precipitate or be flocculated with the bulk of the Cr/Sn solids and would not likely form a separate phase with a different particle size. The DF of Cr measured in this testing can thus be used as a conservative value for the DF expected for Tc in the process. The original target DF for Tc was 100, but this is essentially an arbitrary value since this is a conceptual process with no documented acceptance criteria for the product at this time.

**The results of the Cr analysis of feed and filtrate samples for the testing are shown in**

Table 3-4. All filtrate samples were visually clear and colorless. The Cr concentrations in the feed are from the original simulant compositions prior to the addition of stannous chloride.

<sup>e</sup> DF is the initial concentration ( $C_0$ ) divided by the concentration at time  $t$  ( $C_t$ ),  $DF = C_0/C_t$

**Table 3-4 Measured Chromium Decontamination Factors**

Test Sample	Cr Feed Concentration (mg/L)	Cr Filtrate Concentration (mg/L)	DF	Test Temperature (°C)
Test 1 Sample 1	87.2	0.877	99	40
Test 1 Sample 2		0.736	118	
Test 1 Sample 3		0.820	106	
Test 2 Sample 1		< 0.06	> 1453	25
Test 2 Sample 2		< 0.06	> 1453	
Test 3 Sample 1	87.9	< 0.06	> 1453	40
Test 4 Sample 1		0.517	170	25
Test 4 Sample 2		0.427	206	
Test 4 Sample 3		0.30	293	

### The results in

Table 3-4 show that Cr continued to precipitate after the initial experiment during the time the slurry was stored between Tests 1 and 2. The impact of temperature, seen when comparing Tests 1 and 4, illustrates the higher solubility of Cr at elevated temperature, which decreases the DF. This is also expected to translate to a lower DF for Tc if the process is performed at elevated temperature. These DF values for Cr are comparable to those observed in previous testing that also contained Tc. In those previous tests, the DF for Tc was significantly higher than for Cr under comparable conditions,<sup>9,10</sup> so the values in Table 3-4 should be bounding. The target DF for Tc in this program is 100, and these results indicate that this is achievable with the equipment selected under the conditions and scale tested.

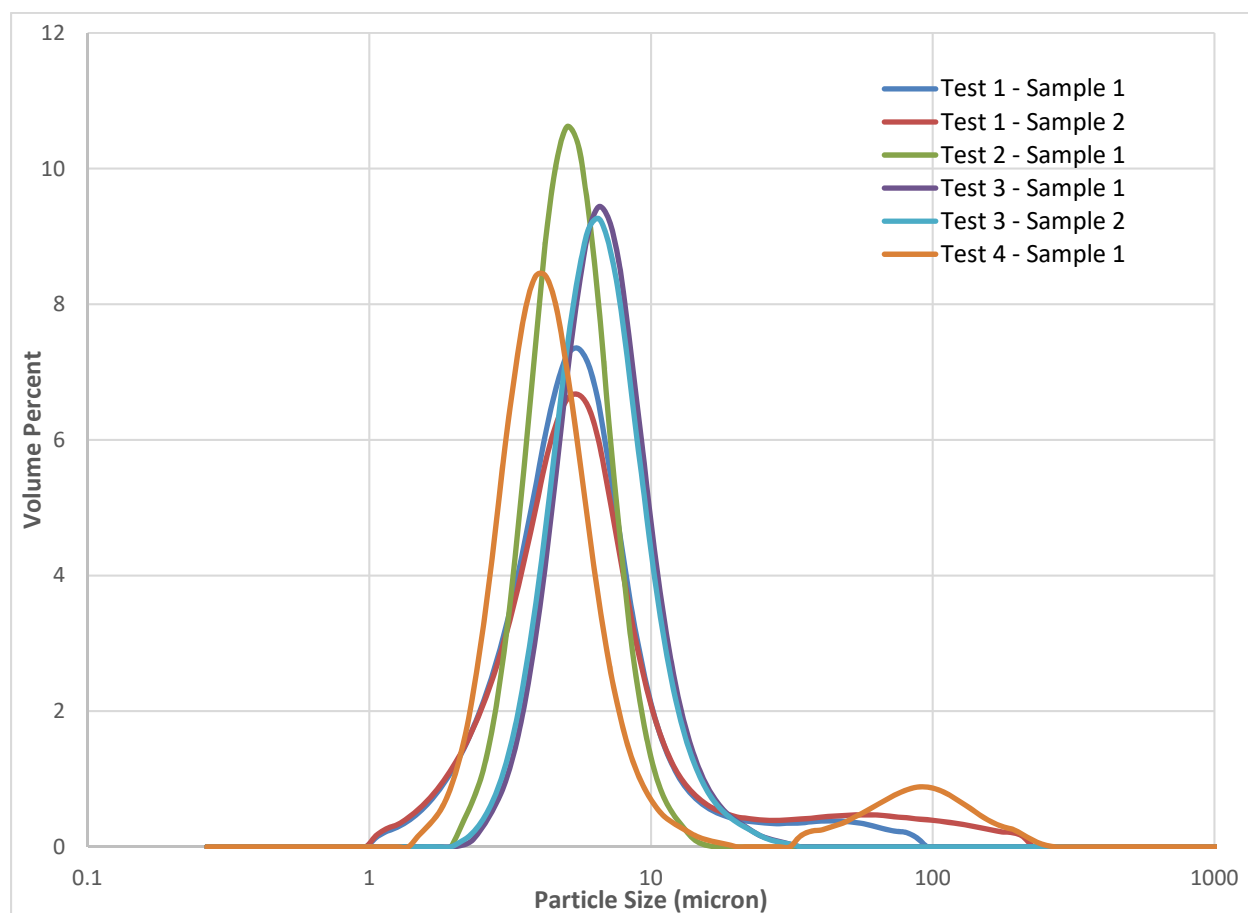
Additional compositional analyses were also performed on the filtrate samples, including additional metal ions, ammonia, carbonate, pH, and anions. Results were roughly comparable to the expected values. The detailed results are shown in Appendix C. Comparison of the results of the filtrate analysis to the simulant composition indicates the Zn is also removed during the precipitation; although the mechanism for Zn removal is not known. It is conceivable that the marginally soluble Zn is simply flocculated by the Sn/Cr solids and removed by physical separation without being reduced to a lower oxidation state.

#### 3.4.1 Solids Characterization

Results of particle size analysis of the slurry samples collected from testing are shown in Table 3-5 and Figure 3-11. Additional information on the particle size measurements is included in Appendix D. Inspection of Figure 3-11 indicates that the particle sizes did not vary much, with most of the peaks at about 6  $\mu\text{m}$ . The data in Table 3-5 indicate a larger size for two samples from Tests 1 and 4, but this is because the mean values are skewed by a small amount of large particles, as shown by a bimodal distribution of particles shown in Figure 3-11.

**Table 3-5 Slurry Sample Particle Size Analysis Results**

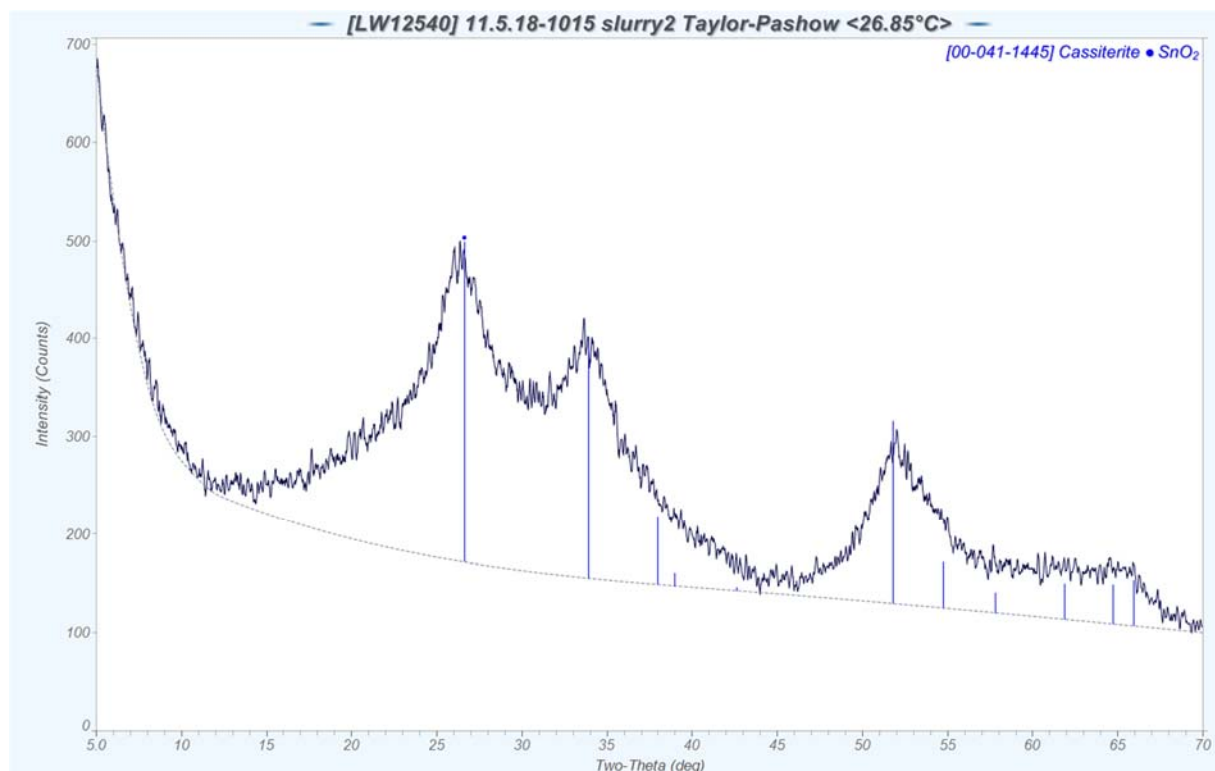
Sample ID	Mean Particle Size (µm) (Volume)	10 <sup>th</sup> Percentile by volume (µm)	95 <sup>th</sup> Percentile by volume (µm)
Test 1 – Sample 1	7.52	2.582	22.48
Test 1 – Sample 2	12.17	2.554	58.22
Test 2	5.18	3.22	8.46
Test 3 – Sample 1	7.07	4.02	12.79
Test 3 – Sample 2	6.87	3.87	12.55
Test 4	14.49	2.598	91.71



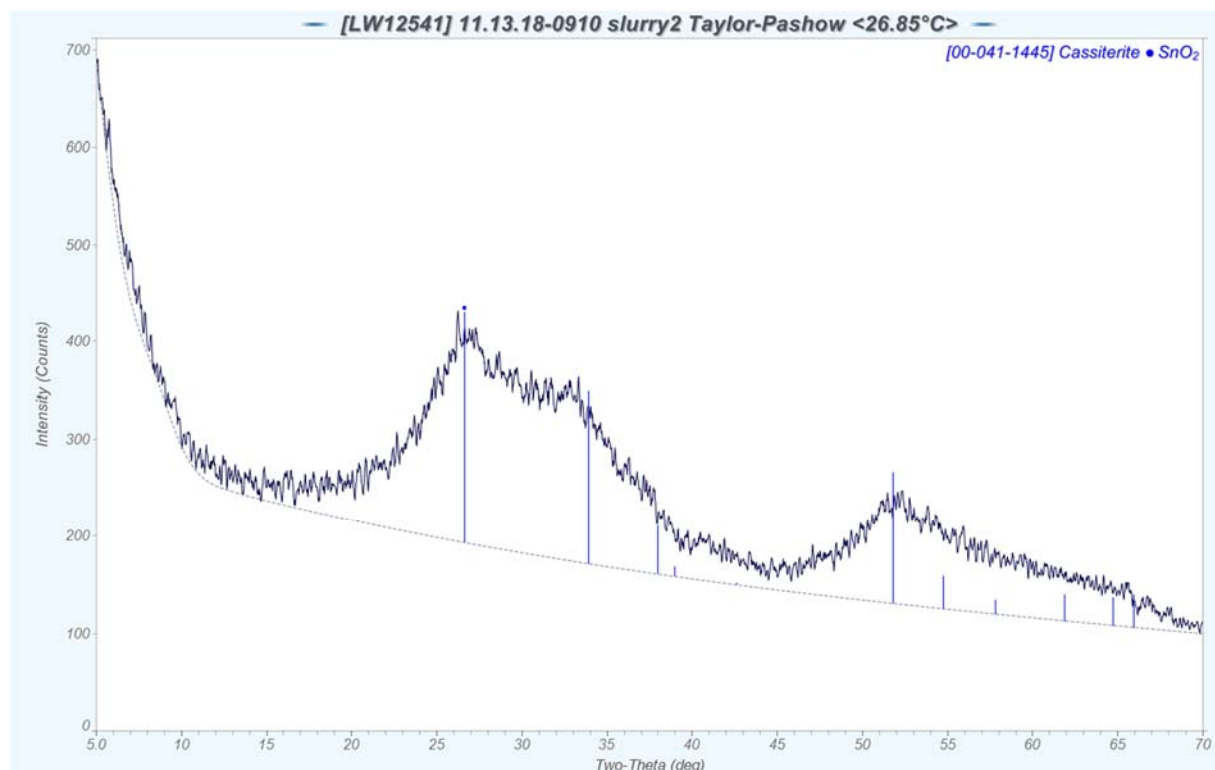
**Figure 3-11 Particle Size Distributions of Slurry Samples from Tests 1 through 4 (by Volume)**

Results in Table 3-5 indicate that the two batches of freshly prepared simulant had roughly the same average particle size by volume (Tests 1 and 4). After the simulant had set for a period of time (Tests 2 and 3) and was re-used in testing, the particle size distributions were narrower. The freshly precipitated solids (Tests 1 and 4) had a wider distribution of particles as evidenced by the lower and higher numbers at the 10<sup>th</sup> and 95<sup>th</sup> percentiles, respectively. The 10<sup>th</sup> percentile portion was small, at only ~2.5 µm. It is this small particle size portion that likely dominated the filter fouling because it would have been the slowest to settle in the clarifier.

Samples of the slurry were also filtered, dried at ambient temperature, and characterized for crystalline species by X-ray Diffraction (XRD). Results of the analysis are shown in Figure 3-12 and Figure 3-13. The only crystalline species identified was a tin(IV) oxide (cassiterite) indicating that the precipitated chromium oxides are amorphous. The lack of sharp peaks indicates that the cassiterite is poorly crystalline. Most of the Sn(II) is expected to be oxidized to Sn(IV) when it reduces the Cr(VI) and precipitate as the stannic oxide or hydroxide, which is consistent with the XRD results. These two metals, Sn and Cr, have previously been shown to dominate the composition of the solids.<sup>25</sup>



**Figure 3-12 XRD Analysis Results Test 2 Sample**



**Figure 3-13 XRD Analysis Results Test 4 Sample**

## 4.0 Conclusions

Overall, the test program successfully demonstrated the solid-liquid separation step for this Tc-removal process at bench scale for this waste stream. Precipitation of the solids at larger scale, settling, and filtration were all shown effective, and the process performed as expected. No measurable amounts of hydrogen were observed to form, indicating this stannous chloride precipitation does not cause flammable gas process safety issues.

Conditions used for Test 1, with only a ~30-minute settling period and high flow rate to the filter were clearly inadequate to achieve a good process flow. Longer settling periods and lower filter flow rates were selected for subsequent testing.

Tests 2 and 3 were aimed at quantifying conditions that would yield lower filter fouling rates. It was concluded that longer settling times in the clarifier are beneficial. It is not clear if temperature makes a significant difference in the process flow rates. The filter fouling rate in Test 3 may have been somewhat accelerated versus Test 2, but the results are not definitive.

Test 4 demonstrated successful precipitation and solid-liquid separation of the slurry. Although the filter gradually fouled, the rate was lower than in earlier tests. The results indicate that the process can be made to function as envisioned, albeit with settling rates more typical of industrial processes. The ~2 hour settling used here was evidently long enough to initially yield a clear fluid for filtration. However, as the process continued, the flow rate into the clarifier increased, leading to additional turbulence that caused suspended solids to gradually foul the filter. With the shorter settling time used in Test 1, the filter was able to process only ~6.5 L. With the longer settling time used in Test 4, the filter treated ~12 L, nearly doubling the volume processed in Test 1. It appears necessary to further extend the settling period and clarifier turn-

over duration to 4-5 hours or incorporate design elements to reduce agitation in the clarifier, to further reduce filter fouling.

Earlier work had examined the size of the reactor vessel needed to perform the stannous chloride precipitation step.<sup>12</sup> At the process flow rate of 555 gallons per hour (9.25 gpm), it was estimated that the reactor working volume should be 1980 gallons (~2,000 gallons). This work indicates that a 4-5 hour settling time is needed to facilitate solid-liquid separation, which would translate to a ~2500-gallon clarifier. Even doubling this to get a conservative target of a 5000-gallon clarifier would fit into a relatively reasonable facility footprint to process this waste stream. Since dose rates are expected to be low, this would be a contact-maintained facility. This indicates that continued development of this process is likely to result in a system that could be constructed and operated for relatively low cost. This would be beneficial to the WTP mission by diverting troublesome glass components away from the melters, while retaining Tc that could be recycled to the melters.

As expected, the solids contained oxidized tin, present as a poorly crystalline cassiterite ( $\text{SnO}_2$ ). The solid chromium species was not identified by XRD, indicating that it was amorphous or microcrystalline.

Another observation is that a better DF can be achieved by lowering the temperature, as would be expected due to the lower solubility of the metals. However, for the full-scale system, this may require a heat exchanger to cool the process liquid prior to the precipitation. Whether this is sufficiently beneficial to justify the cost would need to be determined when the acceptance criteria for the decontaminated liquid is determined, which is beyond the scope of what can currently be addressed.

## 5.0 Future Work

Additional tasks needed to further develop this technology include examination of scale-up behavior to a pilot-scale clarifier-filter system. As mentioned above, future maturation of this process will involve obtaining a sample of SBS/WESP condensate from the WTP LAW melter during cold commissioning, where the detailed results of a solid-liquid separation process with a simulant containing entrained solids produced in a large melter can be finalized. Also needed are slurry rheology measurements, corrosion and erosion studies. It has previously been evaluated and found that the concentrated slurry with minimal liquid can be added to the LAW melter feed for immobilization with no expected impact,<sup>7</sup> so no testing of vitrification is planned. Unrelated to solid-liquid separation method development, additional radioactive testing is needed to demonstrate kinetics of a larger scale removal of Tc.

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**Appendix A.**  
**Evaluation of Solid-Liquid Separation Technologies for Tc Removal**  
**M.R. Poirier, SRNL-L3300-2018-00057**




**INTEROFFICE MEMORANDUM**


September 26, 2018

SRNL-L3300-2018-00057, Rev. 0

TO: D. J. MCCABE

FROM: M.R. POIRIER

Approval:   
C. C. Herman, Director

Technical Review per E7 2.60:   
D. T. Herman

**Evaluation of Solid-Liquid Separation Technologies for Tc Removal**

**Introduction**

The Low Activity Waste (LAW) vitrification facility at the Hanford Waste Treatment and Immobilization Plant (WTP) will generate an aqueous condensate recycle stream (LAW Off-Gas Condensate) from the off-gas system. The plan for disposition of this stream during baseline operations is to send it to the WTP Pretreatment Facility, where it will be blended with LAW, concentrated by evaporation, and recycled to the LAW vitrification facility again. The primary reason to recycle this stream is so that the semi-volatile <sup>99</sup>Tc isotope eventually becomes incorporated into the glass.

This stream also contains non-radioactive salt components (e.g., halides and sulfate) that are problematic in the melter. Halides and sulfate limit the waste loading in the glass. Diversion of this stream to another process would eliminate recycling of these salts and remove them from the LAW melter feed. Reducing the amount of halides and sulfate in the LAW melter feed would allow higher waste loading in the glass, decrease the LAW vitrification mission duration, and decrease the quantity of glass waste produced. The concept being tested involves removing the <sup>99</sup>Tc so that the decontaminated aqueous stream can be disposed elsewhere.<sup>1</sup>

Pilot-scale simulant tests indicate that the LAW Off-Gas Condensate stream is expected to be a dilute salt solution with near neutral pH, and will likely contain some insoluble solids from melter carryover.<sup>1</sup>

This project examines the potential treatment of this stream to precipitate radioactive <sup>99</sup>Tc and subsequently disposition the decontaminated aqueous stream elsewhere, such as the Effluent Treatment Facility (ETF) or through an altered Effluent Management Facility (EMF) where the Tc-decontaminated and concentrated stream is immobilized as a low temperature waste form. The treatment process envisioned focuses on using mature radionuclide removal technologies that are also compatible with long-term tank storage and immobilization methods.

Previous work has shown SnCl<sub>2</sub> to be an effective agent for reacting with pertechnetate and forming a technetium dioxide precipitate.<sup>1</sup> Once the precipitation process is complete, the precipitated solids must be removed from the condensate stream.

The objective of this task was to examine potential solid-liquid separation techniques and recommend techniques to be investigated and tested for this project.

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### Analysis

The evaluation was conducted by reviewing previous SRNL studies of solid-liquid separation processes, the technical literature, and the author's previous experience evaluating, developing, and troubleshooting solid-liquid separation processes for the Savannah River Site (SRS) and Hanford.<sup>2,3,4</sup>

The author identified the following potential technologies:

- Settling/Clarification
- Centrifugation
- Hydrocyclone
- Filtration
  - Crossflow
  - Dead-End
  - Rotary Microfilter
- Dissolved Air Flotation
- Clarification followed by polishing filtration

The requirements for the solid-liquid separation method are to achieve a high decontamination factor, such as >99% removal of insoluble solids, have a small footprint, and have continuous processing with minimal maintenance requirements. Since this stream has low radioactivity, contact maintenance is feasible. The insoluble solids produced from the precipitation process are approximately 1 g/L (0.1 wt. %), and the aqueous stream is near neutral pH and moderate ionic strength with about 1.3 wt. % total dissolved solids. The particle size based on previous testing has a range of 0.75 – 176  $\mu$  and a median size of ~5  $\mu$ .<sup>1</sup>

### Settling

Clarifiers are settling tanks built with mechanical means to remove the solids deposited by settling. The solid particles settle by gravity and are removed from the tank bottom by a device, such as a scraper or a conveyor belt. Clarifiers work best when separating large, dense (i.e., fast settling) particles from liquids. Flocculants are often added to the feed to increase particle size and settling rate. The hold-up time in the clarifier must be long enough for the solid particles to settle to the bottom. Inlet and outlet velocities to the tank must be minimized to prevent turbulence, which would reduce the settling rate. The advantage of clarifiers is their simplicity. The disadvantage is that with slow settling particles, the required tanks can be very large, and they often require flocculants, which may not be compatible with down-stream processes.

SRNL testing of the tin-technetium precipitate from the condensate indicated rapid settling, suggesting that these particles settle quickly and could be removed with clarifiers. Figure 1 (from a previous test report<sup>1</sup>) shows settling of the precipitate produced. The figure shows particles settling ~12 inches in 7 – 10 minutes. Figure 2 shows the measured settling rate from the precipitation test as a function of time. Initially, the settling rate is approximately 60 in/hr. After ~10 minutes, the settling rate decreased to approximately 10 in/hr. After ~30 minutes, the settling rate decreased to ~1 in/hr, but this settling rate may be impacted by hindered settling and the particles concentrating at the bottom of the vessel. With a settling rate of 60 in/hr, the required clarifier would be of reasonable size, but with a settling rate of 1 in/hr, the required clarifier size would not be practical for this application. Figure 3 shows the measured particle size of the precipitate formed. Figure 4 shows the time calculated for the precipitated particles to settle 8 feet based on the measured particle size, the density of SnO<sub>2</sub>, and settling rate equations such as Stoke's Law.<sup>5</sup> The results show very fast settling particles and very slow settling particles. Additional testing should be conducted to better quantify the settling rate and to assess the potential for a clarifier to provide the solid particle removal needed.

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Larger scale testing of clarification of the precipitate should be conducted to estimate the potential size of a clarifier to remove the precipitated technetium. Although circular clarifiers are typically very large, the footprint can be significantly smaller by utilizing engineered designs, such as inclined plate or tube settler systems.

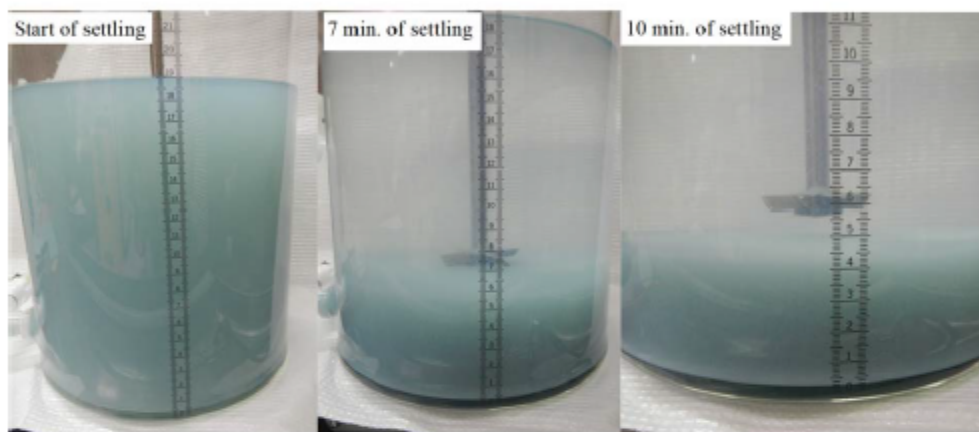


Figure 1. Particle Settling in Precipitation Test

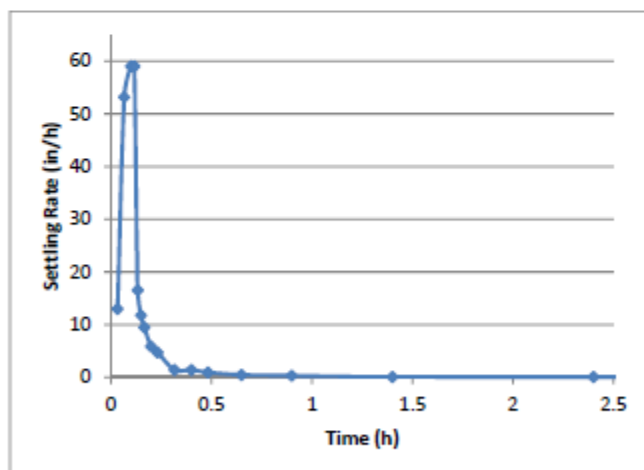


Figure 2. Measured Settling Rate from Precipitation Test

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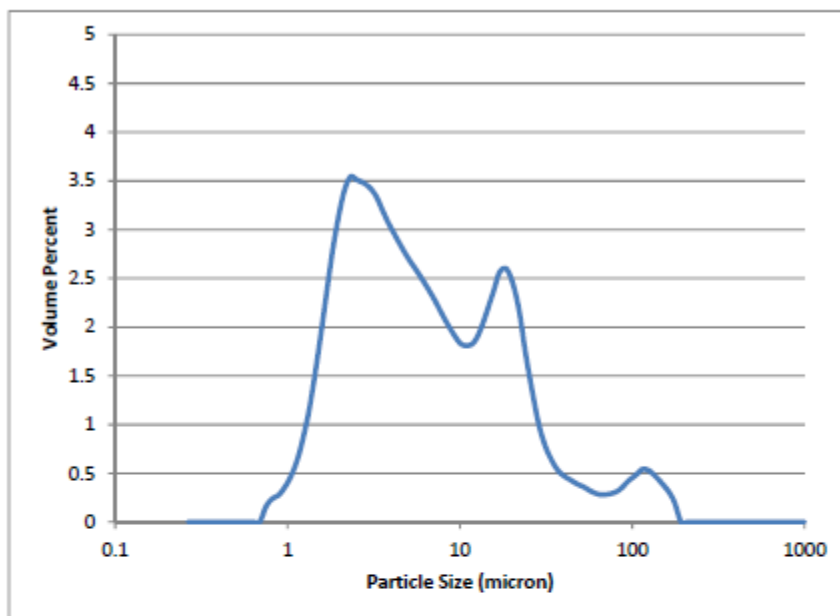


Figure 3. Measured Particle Size from Precipitation Tests

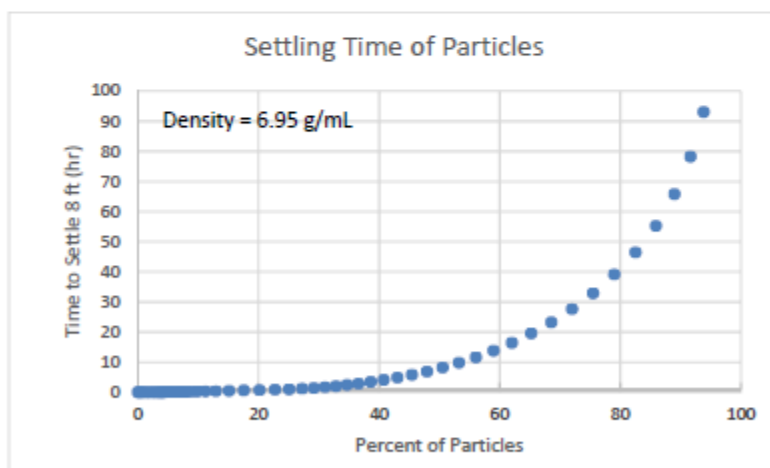


Figure 4. Time for Stannic Oxide to Settle in 8 foot High Clarifier

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### *Centrifugation*

The centrifuge relies on centrifugal force to exaggerate the density difference between the particles and a liquid, so the particles will "settle" more quickly. Thus, the centrifuge can theoretically be expected to completely remove even small, colloidal solids, given a large G-force and a long holdup time. There is no separation by a barrier, and therefore, no place for solids to become trapped. Centrifuges work best with fast settling solids. However, adhesive particles could be difficult to remove from the centrifuge bowl.

Hanford evaluated centrifuges for separating solids in Purex sludge, Redox sludge, Cladding removal waste, and Neutralized Current Acid Waste (NCAW) streams. In simulant testing performed, the centrifuge was ineffective unless polymeric flocculants were added to the waste. In a test performed with actual NCAW, large volumes of water were required to remove the separated solids from the centrifuge bowl.<sup>2</sup>

Centrifuges have been used successfully in the SRS Separations canyons. The centrifuges used there are standard milk centrifuges. The motors are remotored from the bowls so they can receive periodic maintenance. The bowls have not required replacement.

SRNL performed testing with a decanter centrifuge using simulated SRS sludge and monosodium titanate (MST). The centrifuge generated 4100Gs, but did not remove sufficient solid particles to meet the 5 – 10 NTU target for the clarified liquid.<sup>6</sup>

SRNL performed additional testing to investigate a centrifuge as an alternative to the ceramic microfilters at the SRS Effluent Treatment Facility (ETF). The testing showed the centrifuge to be ineffective at meeting the solid-liquid separation requirements for the ETF.<sup>4</sup>

The clarifier is a much simpler design and should be evaluated before a centrifuge.

### *Hydrocyclone*

A hydrocyclone is a static device that applies centrifugal force to a flowing liquid mixture to promote the separation of solid particles from a liquid. They are often used to separate large particles from small particles. A hydrocyclone converts incoming liquid velocity into rotary motion by directing inlet flow tangentially near the top of the vessel. The tangential flow creates centrifugal force in the liquid. Heavy components move outward toward the wall of the vessel where they agglomerate and spiral down the wall to the outlet at the bottom of the vessel. Light components (i.e., the liquid or small, slow settling particles) move toward the center axis of the hydrocyclone where they move up toward the overflow at the top of the vessel. Hydrocyclones work well in separating large, dense (i.e., fast settling), rigid particles from liquids, such as in mining applications. The advantages of hydrocyclones are the small size and the lack of moving parts. The disadvantage is that they are not suitable to separate small, light (i.e., slow settling), soft particles from liquids.

A hydrocyclone is not recommended for this application because the solids are not sufficiently large, dense, or rigid.

### *Filtration*

Filters separate solids from liquids with a semi-permeable barrier. The barrier contains pores which allow liquids and dissolved solids to pass, but which block insoluble solids that are larger than the pores. The filter could be dead-end or crossflow. The advantages of filters are that they can remove small, slow settling particles with high efficiency. The filter pore size should be selected to remove the expected particles in the feed. A filter system would be smaller than a clarifier. The disadvantages of a filter are that it will foul from the particles present in the feed and it will require a method such as chemical cleaning, backpulsing, and/or replacement to recover from the fouling.

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While important, the median particle size is not the best parameter for selecting the filter pore size. The smaller particles provide the largest contribution to filter fouling. Tartleton and Wakeman recommend comparing the 10<sup>th</sup> percentile particle size to the 90<sup>th</sup> percentile pore size (for crossflow filtration).<sup>8</sup> When this ratio is significantly greater than 1, they observed much less pore fouling. An alternative approach is to select the filter pore size equal to or smaller than the smallest particle in the feed. Pall Corporation, a major supplier of filtration, separation, and purification equipment, recommends a filter pore size lower than the size of the smallest particle to be retained (for crossflow filtration).<sup>9</sup> However, this approach can be overly conservative and lead to very low filter flux and a large filter unit to meet throughput requirements. In the previous testing, the minimum particle size of the precipitate was 0.75 micron, and the 10<sup>th</sup> percentile particle size was ~ 1.7 micron. In selecting a filter pore size, a pore size between 0.75 and 1.7 microns is recommended.

Filters for SRS and Hanford radioactive liquid tank waste treatment processes are typically constructed of porous metal because of the high radiation dose, harsh chemicals, and lack of feasible contact maintenance. Conversely, because of the expected low radioactivity and moderate chemistry of the condensate stream, polymeric or ceramic filters could be used. Previous SRNL testing and the authors experience have shown polymeric filters to produce higher flux than ceramic filters, and ceramic filters to produce higher flux than porous metal filters. The author recommends testing polymeric filters prior to testing ceramic or porous metal filters. Any potential polymeric filters that look promising should be evaluated for compatibility with the expected feed streams and radiological dose.

#### Dead-End

One filtration technology for removing particles from the condensate stream is dead-end filters. The dead-end filter would either be replaced when it becomes loaded with solids or backwashed to remove the collected solids and extend its life. A typical dead-end filter system would be composed of multiple filter elements, which are cylindrical tubes, that are capped on one end and open on the other. The filter media would be the outside surface of the cylinder, which is approximately 2 inches in diameter and 10 – 50 inches long.

The fluid would flow from the outside to the inside of the filter at a constant flow rate. The filter media would collect solid particles and allow the liquid to pass through. The liquid/filtrate would exit through the open end of the cylinder. As the solids are rejected by the filter, they form a filter cake and increase the pressure drop across the filter. When the pressure drop reaches a specified value, the filter is either replaced or back washed and the collected solids or concentrated solid slurry is sent on for further processing. If the time between filter replacement or back washes is long, this filter is a viable option. If the time between replacement or backwashes is short, the dead-end filter is not desirable. For this reason, dead-end filters are best suited for streams containing low concentrations of insoluble solids and insoluble solids that foul the filter media slowly. Dead-end filters are often used as polishing filters.

Previous SRTC (now SRNL) testing evaluated dead-end filters as a replacement for the ceramic crossflow filters at the ETF.<sup>4</sup> During testing, the filter fouled very rapidly and the time between back-washes was typically 5-6 minutes and about 50% of the filtrate was needed to back-wash the filter. The filter had a pore size of 5  $\mu$  and was fouled by small, colloidal particles. A smaller pore size filter may have processed more waste between back-washes.

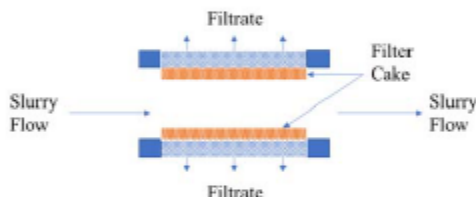
The performance of the dead-end filter might be improved with the addition of a filter aid.<sup>2</sup> Diatomaceous earth is commonly used as a filter aid, but it is not generally desirable to add solids to this waste stream because it increases the volume of material that must be disposed. Any filter aid would need to be evaluated for compatibility with the expected waste stream, as well as compatibility with down stream processes.

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In the previous investigation of solid-liquid separation technologies, it was found that dead-end filtration worked best with low concentrations of large particles. In a study to treat Hanford Cladding Removal Waste, researchers investigated crossflow and dead-end filtration. The simulated waste contained 1000 – 2100 ppm solids with a mean particle size of  $1.2 \mu^2$ .

#### Crossflow

An approach to improving filtration flow rates is to employ crossflow filtration. Crossflow filters can be implemented through a variety of designs. Common designs include plate and frame, hollow fibers, spiral wound, and tubular. Tubular is the most common design for DOE site radioactive waste treatment. The reasons for using the tubular design is that it can handle higher concentrations of insoluble solids, it can handle yield stress fluids, it operates in the turbulent flow regime, and it can be backpulsed. As shown in Figure 5, slurry flows through the center of cylindrical filter tubes. The filter media occupies the inner surface of the filter element. A pressure gradient forces slurry liquid through the filter-tube barrier, which blocks the solids. The rapid fluid motion through the filter tube sweeps the solid particles away from the surfaces, retarding cake buildup. The fluid containing the solids (i.e., the concentrated slurry) exits the other end of the tube. The filtrate liquid exits the cylinder through a separate outlet.



**Figure 5. Schematic of Crossflow Filtration**

As solid particles build up on the filter surface, they can be removed by backpulsing. In backpulsing, water is injected into the cylinder to increase the pressure on the filtrate side to displace the filter cake from the feed side of the filter tube. This reverse flow removes particles from the inner surface of the filter tube. Fine particles that are smaller than the pore opening can become trapped in the filter pores. These particles decrease the porosity of the filter resulting in reduced filter flux. Pore fouling is generally not alleviated by backpulsing. Filter flux can be restored by chemically cleaning particles from the filter pores, with compounds such as citric acid, hydrochloric acid, oxalic acid, or nitric acid. Oxalic and nitric acid are often used for DOE site applications.

The advantage of crossflow filters over dead-end filters is that the tangential flow of the feed stream creates a shear force at the filter surface which reduces the filter cake thickness and the axial velocity sweeps particles away from the filter surface, which increases filter flux. This allows a continuous process that can run for extended periods with minimal interruption in flow. It also allows processing of streams containing a higher concentration of solids that would typically foul dead-end filters quickly.

The disadvantages of the crossflow filter are that it requires a larger feed pump than the dead-end filter, crossflow hardware would typically be larger than a dead-end filter unit, crossflow filter systems typically have higher capital costs than dead-end filter systems, and the crossflow filter systems typically produce larger volumes of concentrated waste than dead-end systems.

Because of the low concentration of insoluble solids expected in this stream, and expected smaller footprint and cost, a dead-end filter should be tested first.

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#### Rotary Microfilter

A variation of crossflow filtration is the rotary microfilter (RMF). The SpinTek ST-II rotary microfilter is a compact filtration system that uses membrane filters mounted on rotating disks (Figure 6).<sup>3,10,11,12</sup> The flux advantage of the RMF compared to other membrane processes results from the high shear and centrifugal force acting on the boundary layer next to the membrane. This shear greatly reduces fouling of the membrane surface and increases fluid flow through the membrane.

The membranes rotate at a top speed of 60 ft/s, which effectively cleans and sweeps solids from the membrane surface with a stable filtrate throughput. For comparison, previous cross-flow filter testing used axial velocities ranging from 3 to 25 ft/s. The SpinTek RMF unit uses 1 to 25 eleven inch diameter disks covered with filter membranes. The disks are physically mounted and are hydraulically connected to a common hollow rotating shaft. The entire stack of membrane disks is enclosed within a vessel. The feed fluid enters the vessel and flows across the membrane surface, where permeate flows through the membrane and exits through the hollow shaft. The concentrated slurry is pumped from the chamber. Stationary surfaces, or turbulence promoters, oppose the rotating membrane disks, generating large fluid shear rates across the membrane surface. Figure 6 illustrates the flow paths during filtration.

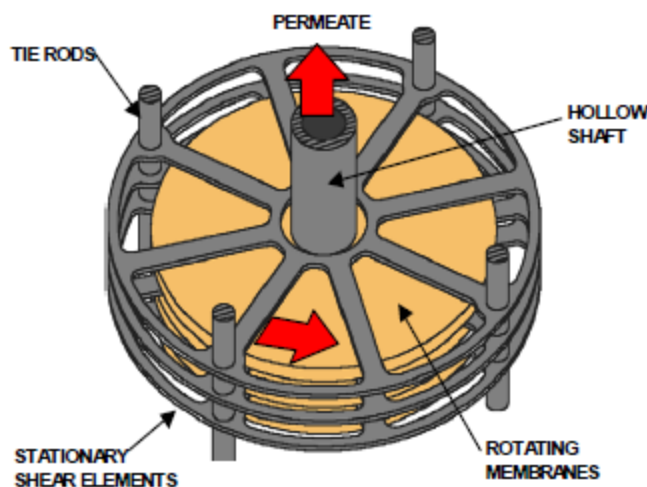


Figure 6. Schematic of Rotary Microfilter

SRNL performed rotary filter testing with a full-scale, 25-disk unit equipped with 0.5 micron filter media manufactured by Pall Corporation using a Hanford AN-105 simulant at solids loadings of 0.06, 0.29, and 1.29 wt %.<sup>13</sup> The rotary filter produced a flux that was 1 to 3 times higher than the flux produced with a crossflow filter using the AN-105 simulant. Filtrate turbidity measured  $< 4$  NTU in all samples collected.

The advantages of the rotary microfilter over a crossflow filter are higher filter flux, ability to handle feeds with higher concentrations of insoluble solids, smaller footprint, and smaller feed pump requirements.

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The disadvantage is the higher cost of the equipment. The rotary filter provides the most improvement in filtration of feeds with high concentrations of insoluble solids. Given the low concentration of insoluble solids expected in this stream, testing with a dead-end filter should be conducted prior to testing with a crossflow filter or a rotary microfilter.

#### *Dissolved Air Flotation*

Dissolved air flotation is a water treatment process that clarifies wastewater by dissolving air in the water under pressure, and then releasing the air at atmospheric pressure in a tank. The released air forms tiny bubbles which adhere to suspended matter causing the suspended matter to rise to the surface. At the surface, the suspended matter is removed with a skimming device. Air flotation is effective in removing light particles which are easy to suspend such as algae. It is capable of producing effluent with low turbidity.

Previous testing investigated dissolved air flotation to separate insoluble solids from simulated Hanford Redox and Purex sludge, and found the technology to be ineffective.<sup>2</sup>

Air flotation is not suited for wastewater with high density solids or high turbidities, and it is more complicated than clarification and therefore not recommended for this application.

#### *Clarification + Filtration*

While clarification is a technology that would likely remove most of the solid particles, there is a possibility that fine particles would not be removed. A properly sized filter should remove almost all of the precipitated particles, but the filter will be fouled by the particles in the waste stream. If the particles foul the filter rapidly, a large fraction of the processing time would be spent back-washing, chemically cleaning, or replacing filter elements.

Another approach would be to combine the technologies, taking advantage of their benefits, while minimizing their weaknesses. This approach would be to use a clarifier to remove most of the solid particles and combine it with a polishing filter to remove particles that pass through the clarifier. In this approach, the insoluble solids would settle in the clarifier, and the supernate would be decanted and filtered with a dead-end filter.

By using settling and decantation as a pretreatment step to the dead-end filter, the solids loading on the filter will be decreased which should lead to a longer operating time between back-pulses. If 90% of the solid particles could be removed by settling, the improvement in operating time could be as much as 10X, which would reduce the size of the filter unit required. If 99% of the solid particles could be removed by settling, the operating time between back-pulses could be as much as 100X, reducing the size of the filter unit required even more. Additionally, the process would need to be designed so the settled solids could be recovered and sent to a treatment or immobilization process.

#### **Recommendations**

The author recommends evaluating three technologies for removing the precipitate generated by the proposed process.

- Settling/Clarification
- Dead-End Filtration
- Settling/Clarification followed by a polishing dead-end filter

Previous testing showed very rapid settling of a large fraction of the solid particles. If the particles settle rapidly, a clarifier could provide the particle removal necessary for the proposed process. Since the

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expected radioactivity of the stream is low, the relatively large size of the clarifier would not be problematic, and can be minimized by using an engineered design such as an inclined plate clarifier.

If a clarifier alone will not provide the solid particle removal needed to achieve the high decontamination factor, an alternative technology would be a dead-end filter. If sized properly, the filter will remove > 99.9% of the particles. Because the concentration of insoluble particles is low, a dead-end filter is the recommended filtration technology. Because of the low concentration of particles, the time between backpulses, chemical cleaning, and/or filter replacement is expected to be long. The dead-end filter will require a smaller feed pump than a crossflow filter, and the dead-end filter system will be smaller than a crossflow filter system.

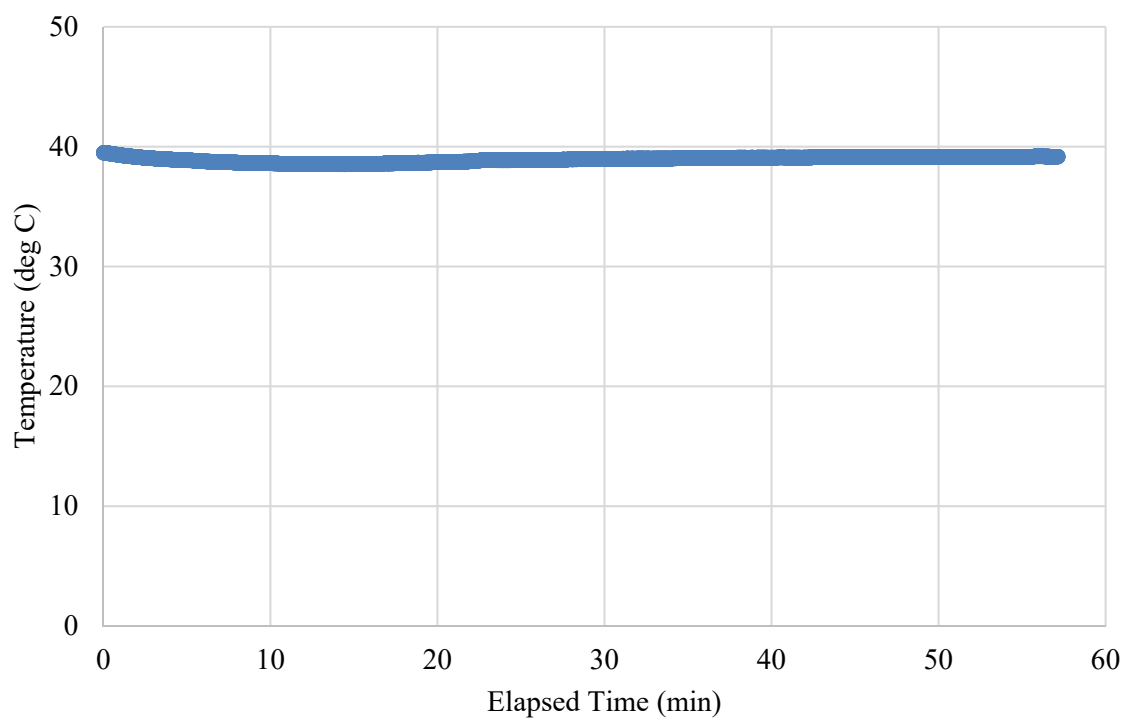
Because the radiation dose expected with this stream is low, polymeric filters should be evaluated before ceramic or porous metal filters.

A combination of a clarifier and a polishing filter should be evaluated as an optimized process. If the clarifier removed a large fraction of the solid particles (e.g., 90 -99%), it would reduce the solids load on the filter and increase the time between backpulses, chemical cleaning, or replacement (e.g., by 10 – 100X). The filter would remove the fine, slow settling particles that were not removed by the clarifier, allowing both nearly continuous processing, minimal maintenance, and a high decontamination factor.

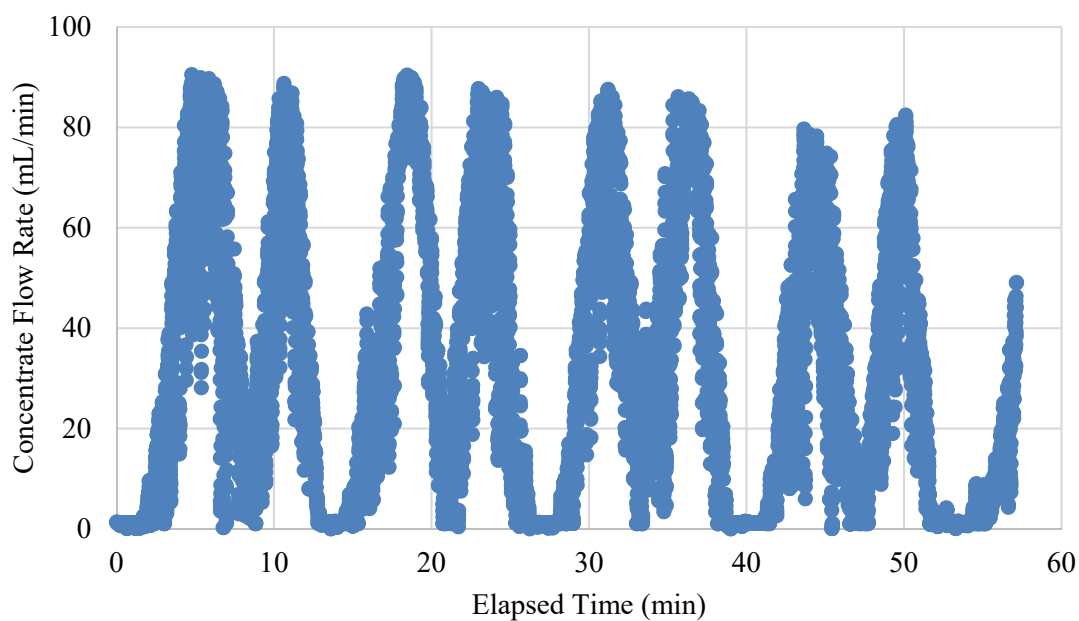
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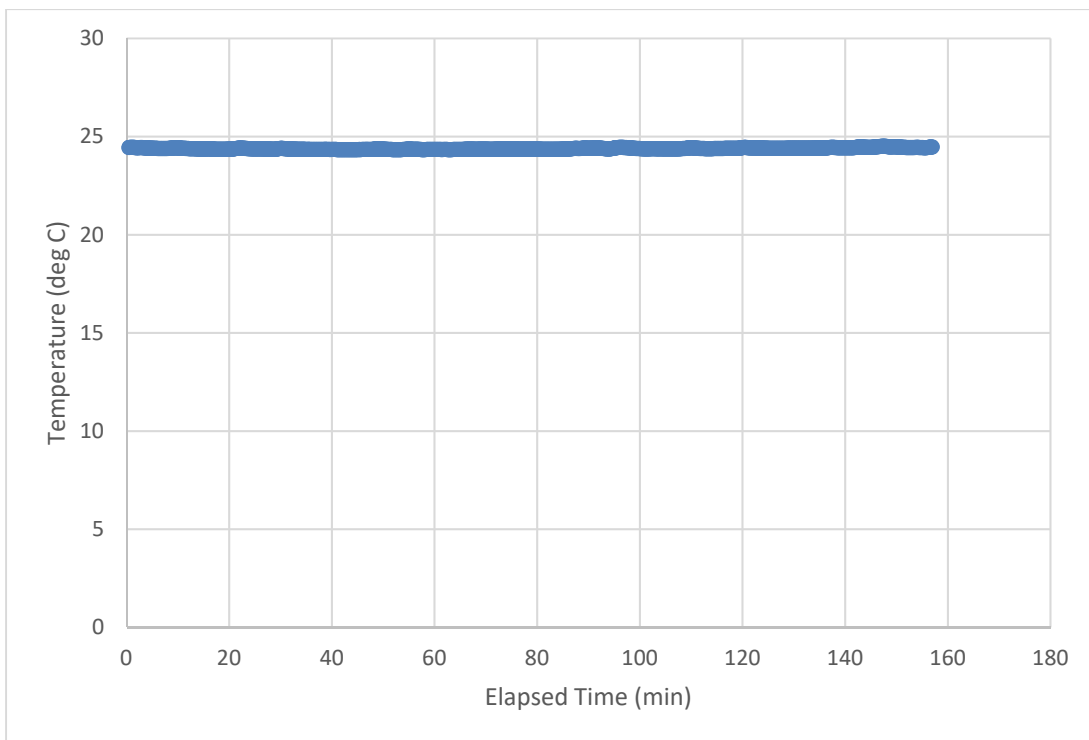
## Appendix B Flowrate and Temperature Detail



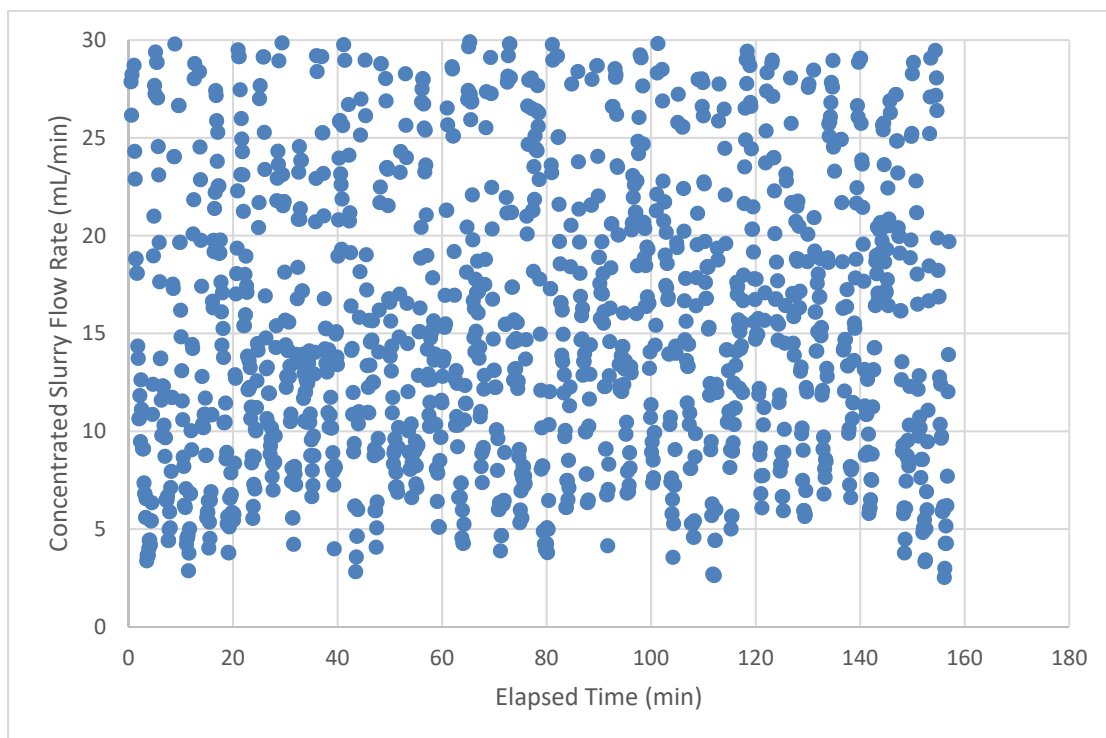
**Figure B-1. Feed Slurry Temperature during Test 1 (11-point rolling Average)**



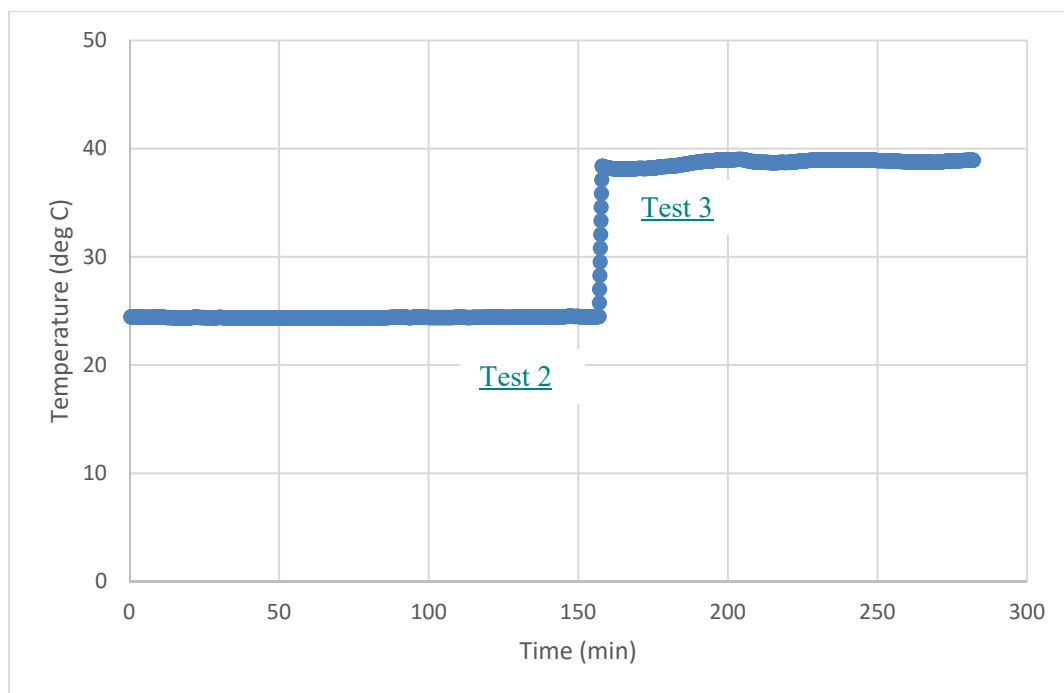
**Figure B-2. Concentrated Slurry Flow Rate during Test 1 (11-point rolling Average)**



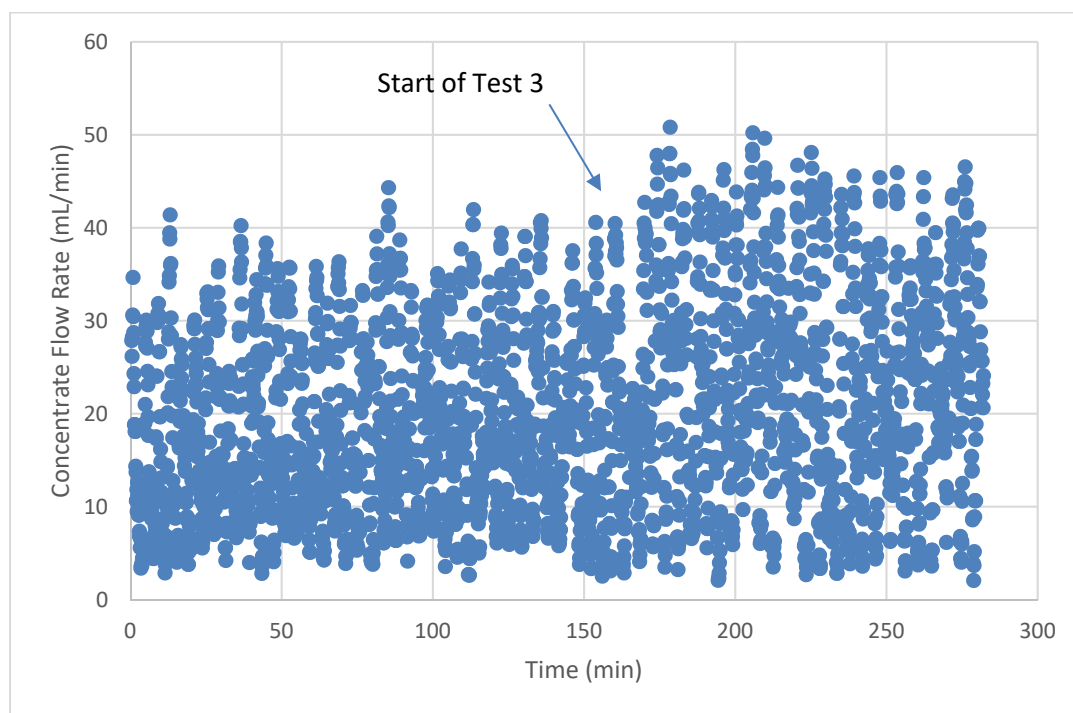
**Figure B-3. Feed Slurry Temperature during Test 2 (11-point rolling average)**



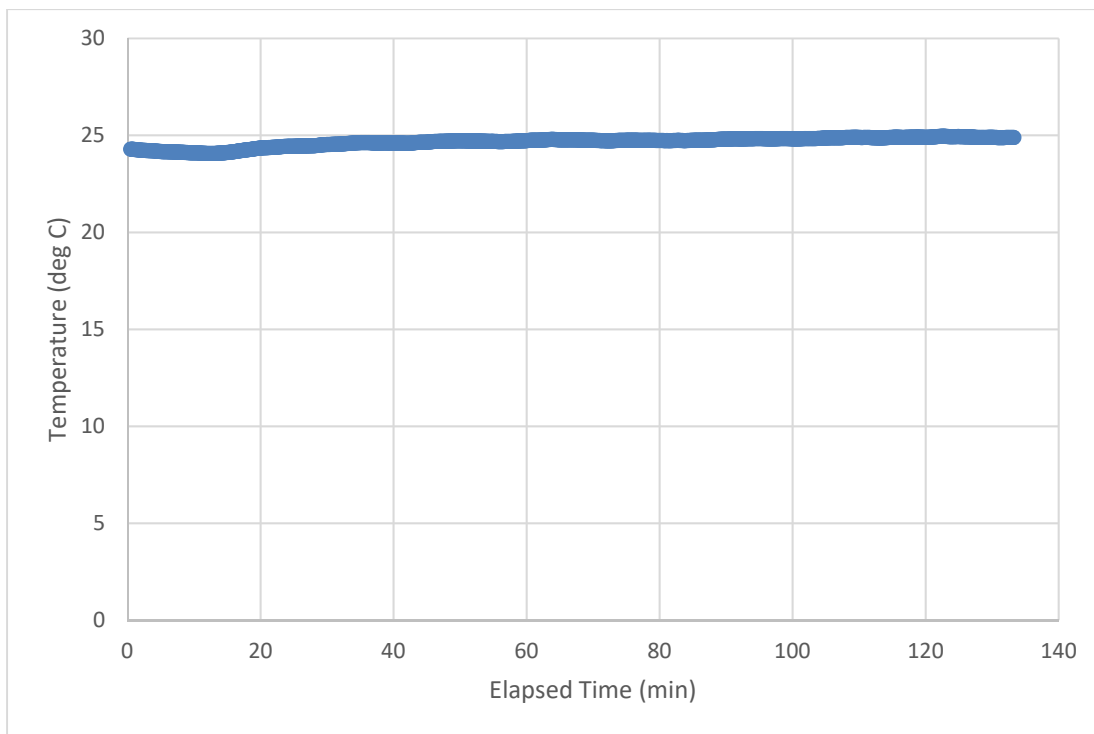
**Figure B-4. Concentrated Slurry Flow Rate during Test 2 (11-point rolling average)**



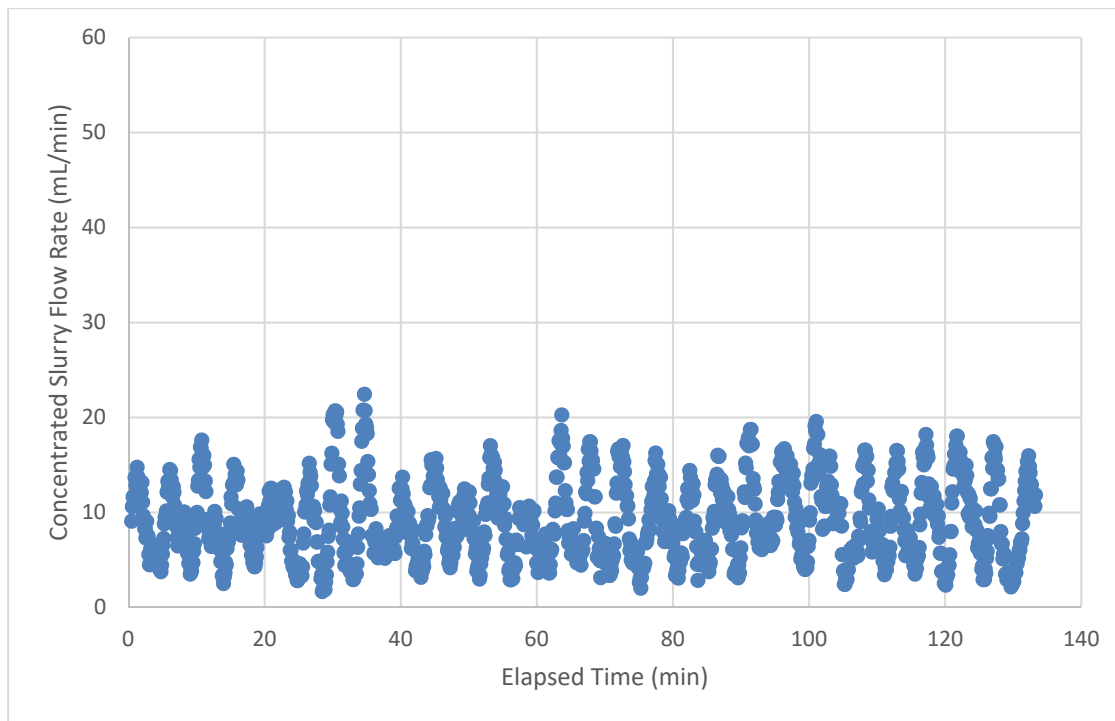
**Figure B-5. Feed Slurry Temperature during Tests 2 and 3 (11-point rolling average)**



**Figure B-6. Concentrated Slurry Flow Rate during Tests 2 and 3 (11-point rolling average)**



**Figure B-7. Feed Slurry Temperature during Test 4 (11-point rolling average)**



**Figure B-8. Concentrated Slurry Flow Rate during Test 4 (11-point rolling average)**

Discussion:

The oscillating and widely varying slurry flow rate measurements were not expected. Evidently, the slurry suction line at the bottom of the clarifier was becoming partially plugged with solids, starving the pump of fluid. This appears to have caused the oscillating flow observed in Test 1, which was run at a higher flow rate than the other tests. The subsequent tests had a lower slurry pump flow rate setting, which appears to have caused less oscillation but still wide scatter in the data. It is also important to note that the flow rate was at the lower end of the range for the flow rate meter, and the peristaltic pumps cause a pulsed flow instead of a steady rate. These could have further contributed to the scatter. In an attempt to reduce scatter, the plots are shown as 11-point rolling averages of the individual measurements, but the results still indicate wide scatter.

Table B-1 shows the concentrated slurry pump setting, the average measured concentrated slurry flow rate, and the standard deviation in the measured concentrated slurry flow rate. The data shows the relative standard deviation to be ~ 100%. This was evidently caused by the inability of the pump to maintain a homogeneous flow of slurry from the bottom of the clarifier.

**Table B-1. Target and Measured Concentrated Slurry Flow Rate**

<b>Test</b>	<b>Target Concentrated Slurry Flow Rate</b>	<b>Average Measured Concentrated Slurry Flow Rate</b>	<b>Standard Deviation</b>	<b>Relative Standard Deviation</b>
1	40 mL/min	31 mL/min	33 mL/min	106%
2	16 mL/min	18 mL/min	21 mL/min	117%
3	31 mL/min	22 mL/min	26 mL/min	118%
4	20 mL/min	9 mL/min	10 mL/min	111%

## Appendix C Filtrate Sample Analysis Results

**Table C-1. Test 1 Filtrate Sample Compositions**

Component	Sample 1 (mg/L)	%RSD	Sample 2 (mg/L)	%RSD	Sample 3 (mg/L)	%RSD
B	238	10	241	10	242	10
Cr	0.877	10.4	0.736	11.3	0.82	10.2
Cu	0.745	10.3	0.767	10.6	0.75	10.3
K	114	10	114	10	115	10
Li	70.1	10	70.8	10	71.1	10
Mg	0.022	10	< 0.01	n/a	< 0.01	n/a
Na	2.35E3	10	2.35E3	10	2.54E3	10
S	740	30	722	30	741	30
Si	6.44	15	3.04	15	2.55	15
Sn	8.63	10	6.81	10.2	7.83	10.4
Zn	0.447	10.1	0.452	10	0.469	10

**Table C-2. Tests 2 and 3 Filtrate Sample Compositions**

Component	Test 2, Sample 1 (mg/L)	%RSD	Test 2, Sample 2 (mg/L)	%RSD	Test 3, Sample 1 (mg/L)	%RSD
B	258	10	250	10	252	10
Cr	< 0.06	n/a	< 0.06	n/a	< 0.06	n/a
Cu	< 0.01	n/a	< 0.01	n/a	< 0.01	n/a
K	126	15	129	15	131	15
Li	69.2	10	67.1	10	69.1	10
Mg	0.026	10	0.033	10	0.029	10
Mn	0.0425	10	0.022	10	0.018	10
Na	2.44E3	10	2.41E3	10	2.44E3	10
S	844	15	840	15	832	15
Si	1.89	11	6.81	10	1.86	12
Sn	< 0.55	n/a	< 0.55	n/a	< 0.55	n/a
Zn	0.46	11	0.425	10	0.383	10
F <sup>-</sup>	1.26E3	10	NM	n/a	1.34E3	10
Cl <sup>-</sup>	1.21E3	10	NM	n/a	1.21E3	10
NO <sub>2</sub> <sup>-</sup>	14	10	NM	n/a	14	10
NO <sub>3</sub> <sup>-</sup>	2.51E3	10	NM	n/a	2.49E3	10
SO <sub>4</sub> <sup>2-</sup>	2.34E3	10	NM	n/a	2.36E3	10
NH <sub>4</sub> <sup>+</sup>	1.42E3	10	NM	n/a	1.46E3	10
pH	7.25	n/a	NM	n/a	NM	n/a

**Table C-3. Test 4 Filtrate Sample Compositions**

<b>Component</b>	<b>Sample 1 (mg/L)</b>	<b>%RSD</b>	<b>Sample 2 (mg/L)</b>	<b>%RSD</b>	<b>Sample 3 (mg/L)</b>	<b>%RSD</b>
B	239	10	235	10	232	10
Cr	0.517	10	0.427	10	0.3	11
Cu	< 0.01	n/a	< 0.01	n/a	< 0.01	n/a
K	121	15	124	15	127	15
Li	65.8	10	66.2	10	65.7	10
Mg	0.044	10	< 0.01	n/a	< 0.01	n/a
Mn	< 0.01	n/a	< 0.01	n/a	< 0.01	n/a
Na	2.51E3	10	2.47E3	10	2.44E3	10
S	838	15	801	15	794	15
Si	< 1.42	n/a	< 1.42	n/a	< 1.42	n/a
Sn	6.89	10	4.63	11	2.38	11
Zn	< 0.05	n/a	< 0.05	n/a	< 0.05	n/a
F <sup>-</sup>	1.34E3	10	NM	n/a	1.35E3	10
Cl <sup>-</sup>	1.21E3	10	NM	n/a	1.22E3	10
NO <sub>2</sub> <sup>-</sup>	15	10	NM	n/a	15	10
NO <sub>3</sub> <sup>-</sup>	2.41E3	10	NM	n/a	2.42E3	10
SO <sub>4</sub> <sup>2-</sup>	2.36E3	10	NM	n/a	2.36E3	10
NH <sub>4</sub> <sup>+</sup>	1.42E3	10	NM	n/a	1.43E3	10
pH	7.06	n/a	NM	n/a	NM	n/a

## Appendix D

### Slurry Solids Particle Size Analysis Results

**Table D-1 Slurry Sample Particle Size Mean Values**

<b>Sample ID</b>	<b>Mean Particle Size by Number (M<sub>N</sub>) (μm)</b>	<b>Mean Particle Size by Area (M<sub>A</sub>) (μm)</b>
Test 1 – Sample 1	2.45	4.48
Test 1 – Sample 2	2.356	4.64
Test 2	3.8	4.65
Test 3 – Sample 1	4.65	6.06
Test 3 – Sample 2	4.45	5.86
Test 4	2.934	4.24

**Table D-2. Slurry Sample Particle Size Analysis Results (by Volume)**

<b>Percentile</b>	<b>Size (μm)</b>					
	<b>Test 1 – Sample 1</b>	<b>Test 1 – Sample 2</b>	<b>Test 2</b>	<b>Test 3 – Sample 1</b>	<b>Test 3 – Sample 2</b>	<b>Test 4</b>
10 <sup>th</sup>	2.582	2.554	3.22	4.02	3.87	2.598
16 <sup>th</sup>	3.07	3.06	3.54	4.47	4.31	2.885
25 <sup>th</sup>	3.67	3.69	3.93	5.03	4.85	3.25
40 <sup>th</sup>	4.54	4.62	4.51	5.86	5.67	3.81
50 <sup>th</sup>	5.12	5.28	4.90	6.43	6.23	4.22
60 <sup>th</sup>	5.76	6.02	5.32	7.06	6.85	4.72
70 <sup>th</sup>	6.57	7.03	5.80	7.82	7.61	5.40
75 <sup>th</sup>	7.10	7.77	6.10	8.28	8.06	5.89
90 <sup>th</sup>	11.20	21.14	7.46	10.70	10.46	49.40
95 <sup>th</sup>	22.48	58.22	8.46	12.79	12.55	91.71

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