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ABSTRACT

Bechtel National, Inc. has been contracted by the Department of Energy to design a Waste Treatment and Immobilization Plant (WTP) to stabilize liquid radioactive waste that is stored at the Hanford Site as part of the River Protection Project (RPP). Because of its experience with radioactive waste stabilization, the Savannah River National Laboratory (SRNL) of the Westinghouse Savannah River Company is working with Bechtel and Washington Group International, to help design and test certain parts of the waste treatment facility.

One part of the process is the separation of radioactive solids from the liquid wastes by cross-flow ultrafiltration. To test this process a cross-flow filter was used that was prototypic in porosity, length, and diameter, along with a simulated radioactive waste slurry, made to prototypically represent the chemical and physical characteristics of a Hanford waste in tank 241-AY-102/C-106.

To mimic the filtration process the waste slurry undergoes several steps, including dewatering and washing. During dewatering the concentration of undissolved solids (UDS) of the simulated AY102/C106 waste is increased from 12 wt% to at least 20 wt%. Once at the higher concentration the waste must be washed to prepare for its eventual receipt in a High Level Radioactive Waste Melter to be vitrified.

This paper describes the process of washing and filtering a batch of concentrated simulated waste in two cycles, which each containing 22 washing steps that used approximately 7.7 liters of a solution of 0.01 M NaOH per step. This will be the method used by the full-scale WTP to prepare the waste for vitrification.

The first washing cycle started with the simulated waste that had a solids concentration of 20 wt% UDS. This cycle began with a permeate filter flux of 0.015 gpm/ft² (3.68 cm/hr) at 19.6 wt% UDS with a density of 1.33 kg/L, consistency of 19.1 mPa•s, and yield stress of 8.5 Pa. At the end of the 22 washing steps the permeate filter flux increased to 0.023 gpm/ft² (5.64 cm/hr) at 20.1 wt% UDS with a density of 1.17 kg/L, consistency of 12.6 mPa•s, and yield stress of 10.4 Pa. The average permeate filter flux during the 7 hours of Cycle 1 washing was 0.018 gpm/ft² (4.41 cm/hr).

During Cycle 2 the simulated waste started at a permeate filter flux of 0.025 gpm/ft² (6.13 cm/hr). Note that the starting flux for Cycle 2 was greater than the ending flux for Cycle 1. The period between the cycles was approximately 12 hours. While no filtering occurred during that period either solids dissolution continued and/or the filter cake was dislodged somewhat with the stopping and starting of filter operation. At the end of the second set of 22 washing steps, the permeate filter flux increased to 0.032 gpm/ft² (7.84 cm/hr) at 20.6 wt% UDS with a density of 1.16 kg/L, consistency of 9.0 mPa•s, and yield stress of 8.2 Pa. The average permeate filter flux during the 4 hours of Cycle 2 washing was 0.029 gpm/ft² (7.11 cm/hr).

Keywords: filtration, experiment, radioactive-waste-treatment plant, slurry washing, pilot-scale

INTRODUCTION

The goal of this work was to demonstrate the filter performance that WTP could expect in processing the Hanford wastes. The waste that WTP plans to use on start-up is a mixture from tanks 241-AY-102 and 241-C-106. Herein, this mixture is referred to as AY102/C106. Before running this filter test it was necessary to have a simulant that accurately matched the radioactive tank waste in filter performance and filter unit prototypic in key features.

After making a cold simulated waste [1] it was verified against the real radioactive waste at a bench-top scale [2,3]. When the simulant was found to have the same filter performance as the actual waste, pilot-scale testing was done with the simulant to determine full-scale filter performance data. The chosen filter was manufactured by the Mott
Metallurgical Corporation to meet RPP-WTP specifications as follows:

- 7 filter tubes with each having an inside diameter of 0.5-inch.
- 90-inch porous length for each filter tube and made of 316L stainless steel
- Nominal rated 0.1 micron filter element (Nominal mean that 95% of particles greater than 0.1 μm will not pass the filter.)

and the pilot test rig was designed to operate prototypically with:

- Maximum axial velocity (V) through filter tubes of 15 ft/s (4.6 m/s)
- Maximum transmembrane pressure (TMP) of 60 psid (414 M Pa)
- Maximum V to be achievable at the maximum TMP
- Instrumentation to monitor V, TMP, the permeate flow rate, and the slurry temperature

NOMENCLATURE
AY102/C106 DOE Hanford Site Combined Tanks 241-AY-102 and 241-C-106
CUF Cells Unit Filter (bench-top cross-flow filter for non-radioactive simulants and radioactive wastes)
°C Degree Centigrade (or Celsius)
cp Centipoise
D Diameter
DOE US Department of Energy
dP Differential Pressure
ft Foot
ICPES Inductively coupled plasma emission spectroscopy
in. Inch
hr Hour
kg Kilogram
L Liter
m Meter
M Molar
mg Milligram
min Minute
mL Milliliter
mm Millimeter
mPa*s MilliPascal Second
NTU Nephelometric Turbidity Unit
Pa Pascal
PSD Particle Size Distribution
psi Pounds Per Square Inch [psig for gauge and psid for differential]
RPP River Protection Project (at the DOE Hanford Site)
s Second
SRNL Savannah River National Laboratory (part of the Westinghouse Savannah River Company)
std dev Standard Deviation
TS Total Solids
TMP Transmembrane Pressure (the average pressure drop across the thickness of the filter medium – perpendicular to the slurry flow.)
UDS Undissolved Solids
V Velocity of the slurry flow along the length of the filter tubes
WTP Waste & Immobilization Treatment Plant
YS Yield Stress (Pa)

SIMULANT
To verify the AY102/C106 simulant [1] an actual waste sample was obtained from Hanford and cross-flow filter tested at a bench-top scale [2]. A simulant recipe was developed and within measurement uncertainty† matched the chemical breakdown of the actual waste shown in Table 1.

The simulant was then tested at the bench-top scale to evaluate its performance (CUF Run 1) against the actual waste. Within measurement uncertainty the two filter results were the same [3] as is shown in Fig. 1.

Table 1. Actual Waste Composition

<table>
<thead>
<tr>
<th>Species</th>
<th>mg/kg</th>
<th>Species</th>
<th>mg/kg</th>
<th>Species</th>
<th>mg/kg</th>
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<tr>
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<td>Mg</td>
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<td>Mn</td>
<td>4889</td>
<td>Zn</td>
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<td>13.9</td>
<td>Mo</td>
<td>47.3</td>
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<tr>
<td>Bi</td>
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<td>NO2-</td>
<td>4077</td>
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<td>693</td>
<td>Nd</td>
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<tr>
<td>Cd</td>
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<td>P</td>
<td>1670</td>
<td>SO4=</td>
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<tr>
<td>Ce</td>
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<tr>
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<td>548</td>
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<tr>
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<td>V</td>
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<tr>
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<td>92.6</td>
<td>W</td>
<td>125</td>
<td>CO3=</td>
<td>58474</td>
</tr>
</tbody>
</table>

Unfortunately, when both the actual waste and simulants were evaporated to attain a sodium molarity of 5 M, a significant amount of solids, basically calcium carbonate, precipitated causing pluggages throughout the filter test apparatus. This is the reason why the actual waste and CUF Run 1 curves in Fig. 1 fluctuate so much.

A decision was made not to boil the simulant, but to leave it at the 3 M sodium concentration that the actual waste had when it was first received. Another bench-top filter test, CUF Run 2, was done with a second simulant batch that was left at 3 M sodium. There was not another actual waste sample to repeat that test, but since permeate flux is strongly dependent upon the permeate viscosity all the data were adjusted, with the equation

† The analytical measurement uncertainty is ±25% for measurements of less than 10,000 mg/kg and ±10% for measurements equal to and above that value.
show in Fig. 1, to that of the actual waste, i.e., 2.9 cp, thus a better comparison can be made. Even with the viscosity adjustment, the 3 M sodium simulant, from 11 to 15 wt% UDS, had a higher permeate flux. A relatively smooth descent in flux for CUF Run 2 indicated a significant reduction in precipitated solids in the feed. The bench-top studies were accepted by WTP as sufficient to verify that the AY102/C106 simulant properties matched the actual waste.

Figure 1. A bench-top scale comparison of actual to simulated waste

**TEST EQUIPMENT**

Details on the bench-top and the pilot-scale equipment are well documented and will not be repeated here [4, bench-top test apparatus; 5-7, pilot-scale test apparatus]. However, the key piece of test equipment is the filter itself, shown in Figs. 2 and 3, and a simple schematic of the overall pilot-scale test apparatus is shown in Fig. 4. The following is a short description of that equipment:

The test rig is made up of two basic flow loops:

*Slurry loop*

This loop contains the filter and its housing and serves as the primary flow path for circulating slurries. The filter unit contains seven tubes, which are welded in a 60° triangular pitch geometry with a center-to-center pitch distance of 22.2 mm to match the WTP filters, Figs. 2 and 3. The slurry loop has an internal volume of approximately 26 liters, excluding the filter feed tank. It is made of primarily 1.5-inch sch 40 pipe, which has an inside diameter of 1.6 inches.

*Permeate loop*

This loop (the Permeate lines) begins at the filter housing, allows the separated permeate liquid to flow through the backpulse pulse pot before circulating back to the filter feed tank to close the circuit. The loop has an internal volume of approximately 15 liters. It is made of primarily 0.375-inch tubing.

The facility shown in Fig. 4 stands approximately 25-feet tall and is serviced by a two-level mezzanine. The test rig is taller than the seven 90-inch tall filter elements because it originally had other uses. The entire test rig is made of 300 series stainless steel with the majority being of 304 stainless steel.

**MEASUREMENT UNCERTAINTY**

The uncertainties listed here are based on past work, which was done on the same equipment under similar circumstances and similar individual instrument uncertainties [7]. These uncertainties illustrate the expected magnitude of principal parameters measured throughout this test. The measurement uncertainties (at the 95% confidence level) for the important calculated quantities are:

- Slurry Velocity = ± 6 %
- Transmembrane Pressure = ± 2 %
- Temperature Adjusted† Flux = ± 6 %

For analytical results included herein the measurement uncertainty vary and sometimes can be large. Uncertainties for analytical data generally assumed to be no larger than ± 20% of any result shown. For properties measured in the Engineering Development Laboratory, the following uncertainties on a reading were obtained through calibration:

- Slurry or Liquid Density = ± 0.5%
- Liquid Viscosity = ± 0.5%
- Turbidity = ± 0.1 NTU

† This temperature adjustment is discussed in the next section.
Figure 3. Seven-tube pilot scale filter unit outside of its housing

*** INSTRUMENTATION ***

Flow
- Q₁ = slurry
- Q₂ = low permeate
- Q₃ = high permeate
- QBP = backpulse

Pressure
- P₁ = slurry at filter
- P₂ = permeate at filter
- P₃ = permeate at pulsepot
- dP₁ = axial slurry drop
- dP₂ = slurry-to-permeate drop at bottom of filter
- dP₃ = slurry-to-permeate drop at top of filter
- TMP = (dP₂ + dP₃)/2

Temperature
- T₁ = slurry loop
- T₂ = permeate loop
- T₃ = not used
- T₄ = ambient at top
- T₅ = ambient at bottom

Figure 4. Cross-flow Ultrafilter
DEWATERING

While the intention for this paper is to limit the discussion to the washing aspects of the filtering process, washing it is better understood in the context of dewatering, which prepares the waste for washing. In general, filter performance data from the pilot test rig are assumed to well represent those that will be obtained in the full-scale unit. Differences in filter operation that will ultimately be realized during plant operation will likely result from differences between the simulant used and several very complex waste streams to be filtered. Little is known on how either gross or subtle differences in the many waste-stream properties will affect filtration. However, this study proved useful to improve the understanding of filter operation and will be very useful for plant operation.

Figure 5 shows the temporal permeate flux data with the ordinate adjusted for temperature to account for the effect of viscosity and surface tension. The adjustment equation is:

\[
\text{Flux@ } 25^\circ\text{C} = \text{Flux@ } T \times \exp \left[ \frac{2500}{T+273} - \frac{1}{298} \right]
\]

where \( T \) = slurry/permeate temperature in degrees Celsius.

The entire run time can be seen as approximately 12.5 hours. However, in an attempt to match plant operation, the dewatering was stopped at the one-half batch mark and allowed to sit for a minimum of 12 hours; it turned out to be 14.5 hours. This hold period was done to mimic the much longer time needed to filter in the plant during which some waste instabilities may cause changes, e.g., precipitation. The entire dewatering process took 27 hours but Fig. 5 only shows the actual filtering time. The data scatter in Fig. 5 was caused by two actions: sampling and backpulsing. The two larger disturbances were caused by backpulsing. The criterion was backpulse when the flux dropped below 0.015 gpm/ft\(^2\) (3.68 cm/hr). However, as is evident, the flux started very close to the criterion, therefore, it was changed to backpulse when the flux dropped below 0.010 gpm/ft\(^2\) (2.45 cm/hr). At 2.5 hours into the run, the flux dropped to 0.0095 gpm/ft\(^2\) (2.33 cm/hr) and a backpulse was initiated, but within 30 minutes the flux returned to what it had been before the backpulse. Because of the poor recovery, a backpulse was not repeated during the first one-half batch of dewatering. On the next day, which is shown as the 6.5-hour point, the dewatering began once again and it was started with a backpulse. Once again, it only took a few minutes for the flux to return to the main flux curve. The further instability at the beginning of the second day was probably caused by the settling of the viscous slurry and it seems that between 60 to 90 minutes were needed to fully mix and bring the dewatering to steady state again.

Another way to understand the dewatering process is to see how the undissolved solids changed. Figure 6 repeats the data of Fig. 5, but the corresponding solids concentration has been substituted for time. These concentration data were obtained by the samples taken during the test and then extrapolation between the sample points by knowing how much permeate mass was removed with time.

The use of this adjustment was a customer requirement. It was applied to the data in Figs. 5, 6, 7, and 8.
As can be seen from the table, the consistency of the slurry simulant almost doubled from 13 to 24 mPa•s, which coincidentally matched the concentration of undissolved solids. During the same time period, the yield stress increased a factor of 7 (i.e., 5 to 35 Pa), while the density increase was 7% (i.e., 1.27 to 1.36 g/mL). The fact that there was a finite yield stress means the waste stream is rheologically non-Newtonian. More specifically the waste is shear thinning. The solids particle behavior makes sense in that there was very little change to the bulk of the particle sizes. The mean size of both number distributions reduced insignificantly, while the range of sizes became more uniform as seen be the small standard deviations after dewatering. The permeate rheology showed that the density and the viscosity did not change throughout the process. Finally, the turbidity measurements of the permeate indicated it to be free of solids.

WASHING

The current plant operation plan is to concentrate the waste in the ultrafilter to only approximately 17 wt% UDS before washing begins. For this test after the simulant was dewatered to above 20 wt% it was then diluted back to 20 wt% UDS.

Once all the waste is fed through the filter and concentrated in the 18,000-gallon filter feed tank of WTP it will be washed twice with 21,770 gallons. The WTP will transfer the wash water (0.01 M NaOH) in approximately 1,000-gallon batches. To mimic plant operation, the wash water was transferred to the pilot test rig in 22 mini-batches. Since the batch size was 140 liters, batch of wash water was 140 L x 21,770/18,000 = 169.3 L, making each mini-batch of wash water 7.7 liters. That is, to the concentrated slurry 7.7 L of 0.01 M NaOH were added and then dewatered until 7.7 L of permeate was removed. This was repeated 22 times. This was one complete wash cycle, which was repeated, for a total of 44 mini-batches of wash water. Figure 7 shows the first washing cycle results.

As water was added to the concentrated simulant the permeate flux slowly increased from 0.015 to 0.023 gpm/ft² (3.68 cm/hr to 5.64 cm/hr) during the first wash cycle. Figure 8 shows during the second washing cycle the flux continued to increase but at a much slower rate, from approximately 0.025 to 0.031 gpm/ft². (6.13 to 7.60 cm/hr).

The flux data in Fig. 7 start steady but becomes a more erratic, with the transition somewhere between 150 and 200 minutes. The 150-minute mark is when approximately 35% of the first entire washing batch is processed (at around the 8th mini-batch). This instability may always occur when reducing the supernatant density with water, but some of it was a systematic problem of air in small permeate lines that will not occur in the full-size plant operation.

Another characteristic of the data is what appears to be outliers, the data points far above and below the main filter flux data. Those for the most part indicate when a sample was taken. To take a sample of permeate that stream is temporarily redirected to a sampling station, which stops the flow for a very short period of time. Then when the sample is taken, there is a very short surge as permeate pressure reestablishes steady state flow.

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especially oxalate, Fig. 11. The oxalate dissolution is also the reason the total organic carbon peaked approximately midway through washing, see Fig. 12. A measure of the insoluble solids before and after washing indicated that approximately 7% of the solids did dissolve.

The next sixteen figures (i.e., Figs. 10 to 25) show analytical results of the analyte concentrations in the slurry being washed. To obtain these concentrations the appropriate concentration was measured in each one of the thirteen permeate samples during washing (i.e., twelve were taken during the washing process and the first one, before the washing began). Then with the measured concentrations from the initial slurry sample, the intermediary slurry concentration could be calculated.

The trends in the rheological data in Fig. 9 were generally as expected. As the number of washes increased, the consistency of the simulated waste slurry was cut in half; it decreased from a high of 19 mPa·s at 19.6 wt% UDS then dropped to 9 mPa·s at 20.6 wt% UDS. However, the yield stress stayed the same (i.e., 8.5 to 8.2 Pa), which was unexpected since a past test [7] showed that the yield stress doubled for similar slurry washing. However, this is good news for plant operation since avoiding a higher yield stress would not challenge the pumps more. Finally, the density of the slurry dropped from 1.33 g/mL before washing to 1.16 g/mL after the first washing cycle. During the second washing cycle (mini-washes 23 to 44) the slurry density remained basically constant, indicating that the majority of the soluble solids were removed during the first 22 mini-washes.

Throughout washing, permeate samples were taken at approximately every 4th washing. (The washing number sampling points were: 1, 5, 9, 13, 17, 22). These numbers are important because while both slurry and permeate samples were taken at the same time, they are not matched samples. Since the permeate flux is very low it takes approximately 30 minutes for permeate created at the filter to flow to the sampling point. With this knowledge, it is easy to relate slurry and permeate samples by matching the time difference. The following figures show the effect of washing on particular analytes from the slurry. However, it is important to realize that the very first sample of permeate does not reflect the result of washed slurry, it is actually permeate of unwashed slurry, since the washed slurry permeate was in the permeate line at that time.
Figure 13. Soluble Na in the slurry during washing

Figure 14. Soluble Al in the slurry during washing

Figure 15. Soluble P in the slurry during washing

Figure 16. Soluble Cr in the slurry during washing

Figure 17. Soluble S in the slurry during washing

Figure 18. Soluble Cl in the slurry during washing
Figure 19. Soluble Cs in the slurry during washing

Figure 20. Soluble formate in the slurry during washing

Figure 21. Soluble phosphate in the slurry during washing

Figure 22. Soluble sulfate in the slurry during washing

Figure 23. Soluble nitrate in the slurry during washing

Figure 24. Soluble nitrite in the slurry during washing
PILOT VS. BENCH-TOP TESTING

As a check on the overall filter operation, dewatering results are compared to bench-top (CUF) work. While the comparison is not exact due to differences in scale, it is instructive to contrast differences. Figure 26 is a repeat of CUF Run 2 data, seen in Fig. 1, with the data from Fig. 6 superimposed.

Note, that like the bench-top data, the pilot data were adjusted for differences in permeate viscosity. As has been seen in the past [7], the bench-top data are above the pilot data. Past estimates on scale differences have indicated differences of at least 30%, which would bring the two curves very close to each other. The bench-top data had to be stopped at 16 wt% UDS due to system limitations. However, as the slurry becomes more concentrated the two curves would expect to be even closer when the filter cake becomes very thick and differences in scale become smaller.

REFERENCES


