Process Testing Results and Scaling for the Hanford Waste Treatment and Immobilization Plant (WTP) Pretreatment Engineering Platform - 10173

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ABSTRACT

The U.S. Department of Energy-Office of River Protection's Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being designed and built to pretreat and then vitrify a large portion of the wastes in Hanford's 177 underground waste storage tanks at Richland, Washington. In support of this effort, engineering-scale tests at the Pretreatment Engineering Platform (PEP) have been completed to confirm the process design and provide improved projections of system capacity. The PEP is a $1/4.5$-scale facility designed, constructed, and operated to test the integrated leaching and ultrafiltration processes being deployed at the WTP. The PEP replicates the WTP leaching processes with prototypic equipment and control strategies and non-prototypic ancillary equipment to support the core processing. The testing approach used a nonradioactive aqueous slurry simulant to demonstrate the unit operations of caustic and oxidative leaching, cross-flow ultrafiltration solids concentration, and solids washing. Parallel tests conducted at the laboratory scale with identical simulants provided results that allow scale-up factors to be developed between the laboratory and PEP performance. This paper presents the scale-up factors determined between the laboratory and engineering-scale results and presents arguments that extend these results to the full-scale process.

INTRODUCTION

In 2005, The U.S. Department of Energy's Office of River Protection and Hanford Tank Waste Treatment and Immobilization Plant (WTP) prime contractor Bechtel National, Inc. commissioned an External Flowsheet Review Team (EFRT) to provide an extensive and critical review of design bases and flowsheets to be deployed at the WTP. One issue identified by the EFRT was that although the pretreatment leaching and filtration processes had been demonstrated at a laboratory scale with actual and simulated wastes, they had not been demonstrated at an engineering scale. Testing at engineering scale was considered necessary to confirm the process design and provide improved projections of system capacity [1].

The Pretreatment Engineering Platform (PEP) project was implemented to address this issue. The PEP is a $1/4.5$-scale facility designed, constructed, and operated to test the integrated leaching and ultrafiltration processes (UFPs) being deployed at the WTP. The PEP replicates the WTP leaching processes using prototypic equipment and control strategies and non-prototypic ancillary equipment to support the core processing. The testing approach used a nonradioactive aqueous slurry simulant to demonstrate the unit operations of caustic and oxidative leaching, cross-flow ultrafiltration solids concentration, and solids washing [2].

Ultimately, a link is needed between the laboratory-scale radioactive tests conducted with liter quantities of actual waste and the WTP projected performance. A large body of previous work provides a correlation between the results of actual waste and simulants at the laboratory scale. The PEP tests provide results at the engineering scale. Parallel tests conducted at the laboratory scale with identical simulants provide results that allow the development of scale-up factors between the laboratory and PEP

performance. A combination of PEP operational and equipment design features provides PEP performance that is expected to be similar to the WTP performance.

ULTRAFILTRATION AND LEACHING PROCESS DESCRIPTION

The purpose of the UFP is to concentrate radioactive waste solids from various blended feeds, leach specific nonradioactive solids that limit high-level waste (HLW) glass loading, and separate soluble species from the solids by washing. The integrated processes produce a concentrated solids slurry (the HLW stream), high-sodium solutions that are sent forward to the cesium ion-exchange process (the low activity waste, LAW stream), and low-sodium wash solutions that are sent to a process evaporator for concentration. The UFP includes caustic leaching (to dissolve aluminum solids), oxidative leaching (to dissolve chromium solids), solids washing (to remove soluble salts), and all ultrafiltration operations.

Two process flowsheets are currently being evaluated for the UFP. The baseline flowsheet performs caustic leaching on blended waste feed in the ultrafiltration feed preparation vessels (UFP-1A/B). The alternative flowsheet performs caustic leaching in the ultrafiltration feed vessels (UFP-2A/B) after the solids have been concentrated using cross-flow ultrafiltration. With both flow sheets, a 19-M sodium hydroxide solution (NaOH, caustic) is added to the waste slurry to leach aluminum solids (i.e., gibbsite, boehmite). In the baseline flowsheet, the 19 M NaOH is added to un-concentrated waste slurry (3 to 8 wt% solids), while for the alternative flowsheet, the slurry is concentrated to nominally 20 wt% solids using cross-flow ultrafiltration before adding caustic. Caustic addition is followed by direct injection of steam to heat the slurry and accelerate the leaching process. Following the caustic leach, the slurry is cooled using vessel cooling jackets and/or external heat exchangers. After cooling, the leached slurry is concentrated and washed with an aqueous solution of 0.01 M NaOH to remove soluble salts. If the resulting waste solids remain high in chromium, sodium permanganate reagent is added, and the slurry is circulated to oxidize and dissolve the chromium solids. Following the oxidative leaching of chromium-containing solids, the slurry is washed to remove the dissolved chromium and concentrated.

DESCRIPTION OF TESTING CONFIGURATIONS

The PEP and the laboratory-scale test systems are described below. The laboratory-scale systems, which include a small cross flow filtration system and small leaching vessels, were used to provide scale-up data by testing slurry samples obtained directly from the PEP.

Pretreatment Engineering Platform

The PEP is a $^1/_{4.5}$-scale facility that replicates the UFP processes using prototypic equipment and control strategies and non-prototypic ancillary equipment to support the core processing. Figure 1 depicts the major components of the PEP, excluding reagent supply and utility systems. Prototypic equipment is shown in red, functionally prototypic equipment (including transfer lines) is shown in black, and non-prototypic equipment (i.e., not in WTP) is shown in blue.

The baseline leaching flowsheet test was conducted in the Ultrafiltration Feed Preparation vessels. The caustic was added either in-line during the transfer of the simulant from the HLW receipt vessel or added directly to the vessel. Mixing was provided by an array of eight pulse jet mixers (PJMs). Steam was supplied via an in-vessel steam sparge ring for heating and maintaining the vessel temperature during the caustic-leaching process.
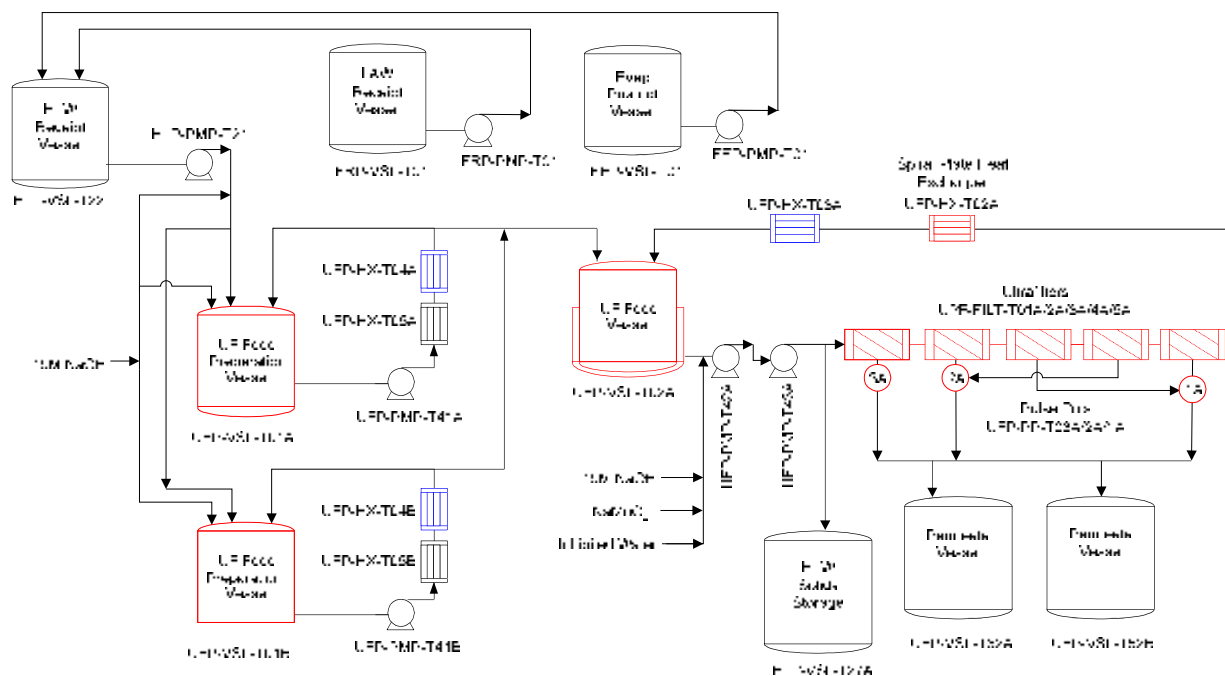
Fig. 1. PEP simplified flow diagram.

Solids were concentrated and washed with cross-flow ultrafiltration, a process that uses flowing slurry to limit the formation of filter cake. In the PEP, as in the WTP, two centrifugal pumps were used to flow slurry through the five ultrafilters and back to the Ultrafiltration Feed vessel. Each ultrafilter was composed of 12 microporous filter tubes (supplied by Mott with a nominal pore size of 0.1μm), arranged in parallel, through which the slurry flowed. The pressure difference between the inside and shell-side of the filter tubes drove filtrate radially through the filters, while axial slurry flow through the tubes minimized cake formation. The PEP filter tubes were the same diameter (1.27 cm), length (three 3.0 m and two 2.4 m) and type as planned for the WTP. The filtration loop was operated such that flow passed either through all five bundles in series, through filter bundle 1 only, or through filter bundles 2 to 5. A spiral plate heat exchanger was used to remove excess pump heat from the circulating slurry.

The Ultrafiltration Feed vessels served as the feed tank for the filtration system. The alternative caustic leaching, solids washing, and oxidative leaching process steps were also performed using this vessel. Caustic, wash water, and sodium permanganate reagent were added in-line to promote blending. Mixing in the Ultrafiltration Feed vessel was provided by an array of six PJMs, air spargers, and jet mixing by the filter-loop return nozzle. Steam was supplied via an in-vessel steam sparge ring.

The PEP contained approximately 1500 instruments, including 400 nuclear quality assurance (NQA)-1 qualified instruments to monitor the process and record test data. These instruments provided data on flow rates, vessel levels, pressures, temperatures, and filter-loop pump speed and power. Additional details on the PEP equipment and operation are provided by Kurath et al. [3].

Laboratory-Scale Filtration System

The Cell Unit Filter (CUF) was used to perform laboratory-scale cross-flow ultrafiltration tests with a single 0.61-m section of the WTP filter tubes. The CUF filtration system is composed of a slurry reservoir

3

tank, a positive displacement pump, a single-pass heat exchanger to remove pump heat, a filter assembly, and a filtrate flow loop with a backpulse chamber. The process parameters that were measured include slurry and filtrate flow rate, axial and transmembrane pressure (TMP) drops, and temperature. The slurry in the baffled feed tank was agitated with an overhead mixer using two impellers. Details of the CUF and its operation are provided by Daniel et al. [4].

Laboratory-Scale Leaching Apparatus

The laboratory-scale caustic and oxidative leaching tests were conducted in 1-L polymethylpentene (PMP) reaction vessels. The contents of the baffled vessels were agitated with a rotating blade mixer. Heating tape controlled by a temperature sensor allowed ramped heating and temperature control above room temperature. Details of the laboratory-scale leaching apparatus are provided by Russell et al. [5].

SCALING CONSIDERATIONS

The PEP is not capable of simultaneously matching all aspects of the full-scale WTP processes. The relationships between the PEP and WTP follow different scaling relationships for different phenomena of interest. This means, for example, that the PEP can be operated to maximize the similarity of its ultrafiltration behavior to that of the WTP, but when this is done, the similarity of its mixing behavior to that of the WTP is not maximized. Though different scaling relationships may have prevented the PEP from behaving exactly like the WTP, PEP operating parameters were selected so that the most important aspects of the WTP processes were preserved in the PEP.

One consequence of adjusting operating parameters to maximize similarities between the PEP and WTP is that some process steps were conducted at a rate that was 4.5 times that of the WTP (referred to as scale-time), and some required the same amount of time in the PEP as in the WTP (referred to as plant-time). For example, most transfers, including the reagent additions, were conducted to maintain a fluid velocity similar to that of the WTP but in piping with diameters approximately $^1/_{4.5}$ that of the WTP. The result was that the transfer of a prototypic volume (i.e., $^1/_{4.5}{}^3$ that of the WTP) took only $^1/_{4.5}$ as much time (i.e., scale-time) as it would have in the WTP . Whether a given process operation was conducted at scale- or plant-time was based on the identification of which process parameters were most important to that operation.

The PJM operating parameters depended on the anticipated rheology of the slurry. When a process step involved Newtonian slurry, the PJMs were operated to match the mixing power per unit volume of the WTP, and when it involved non-Newtonian slurry, the PJMs were operated to match the PJM nozzle velocity of the WTP [6]. While there was not a clear transition in the rheology of the slurry, PJM mixing was operated to match the (mixing power)/volume ratio of the plant until the end of the solids concentration after the caustic leaching, and then the Ultrafiltration Feed vessel PJMs were adjusted to match the plant velocity. They were operated in that manner for the remainder of each test.

Prototypic air sparge mixing from the air sparge tubes and the steam ring air purge were set to match the power/volume ratio of the WTP [6]. Because air sparge mixing scales differently at different heights within a vessel, and because its most important impact is to mix the upper regions of the leaching vessel, the air flow rate was chosen to match the power/volume ratio of the WTP at an intermediate vessel level. Regions below this level received somewhat less mixing than in the WTP; regions above this received somewhat more mixing than in the WTP.

The kinetics of aluminum dissolution required that the duration of the caustic-leaching process be the same in the PEP and full-scale facilities (plant-time) [6]. The heat-up and cool-down of the caustic-leach slurry was also controlled to mimic that expected in the WTP (plant-time), so the PEP exhibited approximately the same extent of aluminum dissolution during the heat-up and cool-down. An additional

reason to conduct the cool-down at plant-time was to allow a prototypic time for the sodium oxalate that had dissolved at the elevated leaching temperature to reprecipitate.

An important aspect of slurry washing is the mixing of added wash water with slurry in the Ultrafiltration Feed vessel. It was therefore considered important that this mixing be similar between PEP and WTP. Because the mixing in the Ultrafiltration Feed vessel was inherently a scale-time phenomenon during any ultrafiltration operation (due to the PEP design of the filter loop and its return nozzle in the Ultrafiltration Feed vessel), the objective of matching the mixing of the WTP vessel to the PEP was best done by conducting the washing operations at scale-time also.

The oxidative leaching process steps were provided the same duration in the PEP as in the WTP (plant-time). The bases for this approach are essentially the same as the bases for conducting caustic leaching at plant-time—the rates of chemical reactions in the PEP are inherently plant-time.

PEP TEST CAMPAIGN STRATEGY

Testing was designed to address the two primary objectives—demonstrate the integrated process flowsheets and improve specific WTP performance predictions—with as few tests as possible. Three integrated tests were conducted in the PEP to qualitatively demonstrate the processes, equipment design, and process control strategies. The tests were conducted with a single chemical waste simulant, which was processed through each step of the baseline process flowsheet and an alternative flowsheet.

The strategy to improve model projections of plant leaching and ultrafiltration performance was based on testing under idealized conditions (i.e., in a laboratory), testing under plant-simulated conditions in the engineering-scale PEP, and analyses that relate the results of laboratory and PEP results to the full-scale WTP performance. Laboratory testing included characterization and parametric testing of both actual waste samples and simulants conducted in advance of, and apart from, the PEP testing as well as laboratory-scale performance testing conducted in parallel with PEP testing using slurry samples taken from the PEP. The laboratory and PEP tests were designed to provide complementary data so that WTP performance projections can be based on actual waste analyses without having to run the PEP with actual waste.

At a minimum, separate integrated process tests for the baseline and alternative process flowsheets were required. Additional testing was also needed for the scale-up of laboratory-to-PEP filter performance. The main portion of the test campaign included three integrated tests briefly described below.

Integrated Process Test A demonstrated the baseline process flowsheet with caustic leaching conducted in the Ultrafiltration Feed Preparation vessels on unconcentrated simulant at the target temperature of 98ºC. Six caustic-leach batches were conducted: three with 100% of the caustic added in-line during the transfer of simulant from HLP-VSL-T22 and three with 80% in-line and 20% in-tank caustic addition. Because the chromium solids simulant was extensively oxidized during the high-temperature caustic-leach step, it was omitted from the feed simulant and added (non-prototypically) after the post-caustic-leach wash step.

Integrated Test B demonstrated the alternative process flowsheet, with caustic leaching conducted in the Ultrafiltration Feed vessel after the simulant had been concentrated to 20 wt% solids. As with Integrated Test A, caustic leaching was conducted at 98ºC, and the chromium solids were added after post-caustic-leach washing. Because the PEP filter loop volume was much larger than would be prototypic (i.e., about 0.31 m^3 instead of the prototypic 0.074 m^3), the alternative process flowsheet could not be run with the selected simulant without some adjustment of slurry volumes after caustic leaching. The chosen resolution of this problem was to conduct two separate caustic-leach batches, storing the product of the first batch temporarily until the second batch had been completed.

Integrated Test D demonstrated the alternative process flowsheet like Integrated Test B, but with caustic leaching conducted at a target temperature of 85ºC. In this test, the chromium solids component of the simulant was added to the initial simulant.

SIMULANT

The PEP testing program was conducted with a non-radioactive aqueous slurry of simulant waste chemicals and solids. The aqueous phase consisted of an ≈5-M Na solution of sodium salts at concentrations within the ranges expected for waste feeds to the WTP. The solids phase, which represented ~5 wt% of the neat simulant, consisted of the components in Table I. The median particle size based on a volume distribution d(0.50) ranged from 6.4 to 8.6 µm [7,8]. The solids components and blend composition were selected to obtain targeted solids mass loss (aluminum and chromium leaching and oxalate washing) and treatment time. The simulant did not represent any particular Hanford tank waste type.

Table I. PEP Simulant Solids Component Ratios.

Component	Wt Fraction of Solids
Boehmite	0.346
Gibbsite	0.346
Chromium as CrOOH	0.026
Sodium Oxalate	0.100
Iron Rich	0.181

FILTRATION

The scale-up factors for filtration were determined based on filtration tests conducted at low and high solids concentrations [4]:

- Low-Solids Tests #1 and #2: Each low-solids scaling test consisted of an initial 12-hr run-in period, a 12-hr period during which the filters were backpulsed every 30 minutes, and a final 12-hr period. The filtrate was recycled back to the Ultrafiltration Feed vessel throughout these tests to maintain a constant solids concentration.

- High-Solids Test: This test involved dewatering a high-solids slurry. The goal of this test was to assess scaling effects that exist between the PEP and CUF filtration operations in the solids-cake-limited filtration regime.

The scale-up factor for filtration at low-solids concentrations is presented as a ratio of the corrected filter flux (adjusted to standard temperatures and TMPs) of the PEP to the laboratory scale. Scale-up factors for filtration at high-solids concentrations are applied to the dewatering mass transfer coefficient and the slurry-limiting gel concentration.

For each low- and high-solids test run at the PEP, a parallel test was conducted with the CUF system. The parallel PEP and CUF tests were performed at similar slurry solids-to-filter surface area ratios.

A summary of results for the low-solids scaling tests (and key operational parameters) is included in Table II. The low-solids scaling tests indicate that for similarly conditioned filters, the CUF flux is comparable to, but slightly lower than, the total (area averaged) flux obtained at PEP. The final filter scaling factors based on total (area-averaged) PEP flux for low-solids tests #1 and #2 were both 1.1 ± 0.1. To provide a conservative estimate for process scaling, a scaling factor of 1.0 is recommended for scaling low-solids filtration operations.

Table II. Results for Low-Solids Scaling Tests.

Item	CUF	PEP	CUF	PEP
Test Description	Low-Solids Test #1		Low-Solids Test #2	
Target axial velocity (AV) (m/s)	4.57	4.57 ± 0.4	4.57	4.57 ± 0.4
Actual Average AV (m/s)	4.54 ± 0.2	4.52	4.56 ± 0.2	4.51
Target TMP (kPa)	276	276 ± 28	276	276 ± 28
Actual TMP (kPa)	277 ± 6	274	277 ± 3	275
Filtration Area (m²)	0.0243	6.71	0.0243	6.71
Solids-To-Filter Area Ratio (kg/m²)	16.5	12.2	15.0	15.0
Flux Scaling Factor Range (S)	1.1 to 1.4		1.1 to 1.2	
Recommended Scaling Factor	1.0		1.0	

The CUF and PEP dewatering curves for the high-solids filter test are shown in Fig. 2. The filter flux has been corrected to a standard 25°C and a TMP of 276 kPa (40 psi) and is plotted against the mass fraction of undissolved solids (UDS). The parameters used to characterize the high-solids filter test are the dewatering mass transfer coefficient, k, and the slurry-limiting gel concentration, C_g, which are the key parameters in the following high-solids filter flux model:

$$J_c = k \ln\left(\frac{x}{C_g}\right)$$

(Eq. 1)

where J_c is the filtrate flux, and x is the mass fraction of solids in the slurry. Two separate scaling factors were defined—the first is the ratio of PEP k to CUF k, and the second is the ratio of PEP C_g to CUF C_g. The high-solids dewatering curves are analyzed using Eq. 1 to determine the best-fit values of k and C_g. The results of this analysis are shown in the upper-right-hand corner of Fig. 2. These results provide the basis of the scaling factor analysis for high-solids dewatering operations.
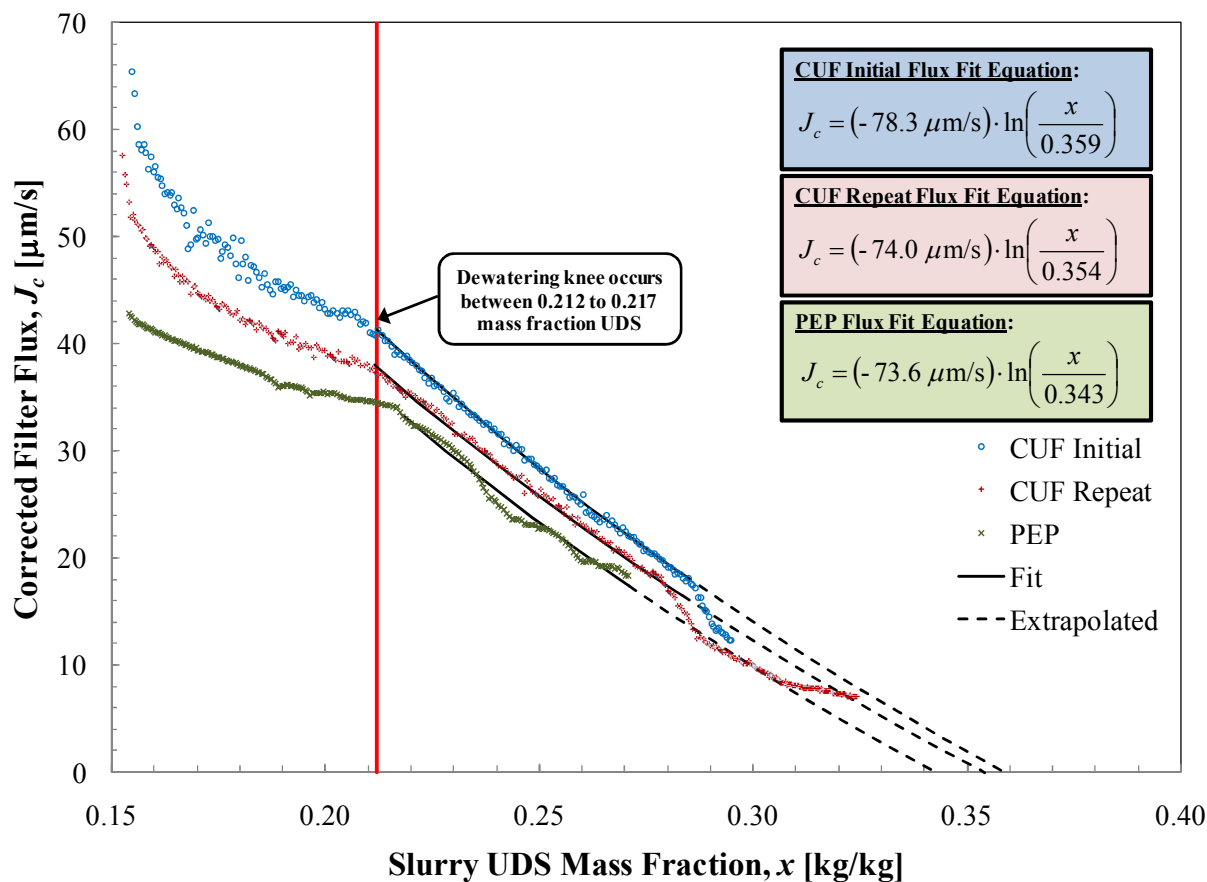
Fig. 2. Summary of PEP and CUF dewatering curves for the high-solids filter tests.

Analysis of PEP and CUF high-solids dewatering curves indicates scaling factors of 0.97 ± 0.03 and 0.96 ± 0.05 for both k and C_g, respectively. Given the uncertainty in the results, the scaling factor for high-solids dewatering operations can be taken as one, and the CUF provides an accurate representation of PEP filter flux performance during high-solids dewatering operations approaching the gel point. A summary of results for the high-solids scaling test (and key operational parameters) is included in Table III.

Table III. Results for High-Solids Scaling Test.

Item	CUF	PEP
Test Description	High Solids Test	
Target AV (m/s)	4.57	4.57 ± 0.4
Actual Average AV (m/s)	4.57 ± 0.03	4.48
Target TMP (kPa)	276	276 ± 28
Actual TMP (kPa)	283 ± 9	274
Filtration Area (m²)	0.0243	1.46
Solids-To-Filter Area Ratio (kg/m²)	156	150
Dewatering Mass Transfer Coefficient (μm/s)	-76.2 ± 0.6	-73.6 ± 2.3
Limiting Gel Concentration (kg/kg)	0.357 ± 0.005	0.343 ± 0.019
Mass Transfer Scaling Factor (S_k)	0.97 ± 0.03	
Limit Gel Concentration Scaling Factor (S_g)	0.96 ± 0.05	
Recommended Scaling Factor	1.0	

CAUSTIC LEACHING

Scale-up factors for caustic leaching were developed from experimental rate constants for boehmite dissolution [9]. A kinetic model was fitted to the time history of dissolved aluminum concentrations measured in samples taken over the course of leaching with the kinetic rate constant being determined as the adjustable fitting parameter. The rate constants were developed from a single batch in each Integrated Test and from six laboratory-scale tests (two for each of the three integrated tests). The rate constants from the PEP were divided by those from the laboratory-scale tests to give PEP/laboratory scale-up factors. Because the PEP was designed and operated to be prototypic of the WTP, and its operation reasonably satisfied prototypic operational criteria, the PEP/laboratory scale-up factor is assumed to be the same as the plant/laboratory scale-up factor.

The development of the equation for the rate of boehmite dissolution is described by Russell et al. [5], and details about the application of the rate equation to scale-up factors are given by Mahoney et al. [9]. The equation is consistent with a shrinking-core model of boehmite dissolution, which gives an exponent of $^2/_3$ on the moles of boehmite. The dissolution mechanism matches the stoichiometry of the reaction, giving a linear dependence of rate on total hydroxide concentration and a decreasing reaction rate as the dissolved aluminum approaches equilibrium.

The rate constants and scale-up factors were calculated as the median of the population for the integrated tests and for both laboratory-scale tests and are presented in Table IV. The uncertainties are expressed as the 95% confidence interval around the median values and were calculated with a Monte Carlo approach based on uncertainties derived from sample handling and analytical techniques. Much of the uncertainty comes from uncertainty in the initial-condition concentrations used as inputs to the kinetic model. Given the broad overlapping confidence intervals, the rate constants from the six PEP and laboratory-scale tests are not statistically distinguishable from each other at a 95% confidence level.

Table IV. Median Scale-up Factors and Kinetic Rate Constants for PEP and Laboratory-Scale Tests (95% confidence intervals in parentheses).

Test	Rate constant k (hr^{-1}*[mol total OH/L]$^{-1}$)	Scale-up factor, k_{PEP}/k_{lab}
PEP Test A Batch 1 (Caustic Leach in Ultrafiltration Feed Preparation Vessel at 98°C)	0.019 (0.013–0.025)	---
Combined Laboratory-Scale Test A Results	0.021 (0.013–0.035)	0.88 (0.47–1.56)
PEP Test B Batch 2 (Caustic Leach in Ultrafiltration Feed Vessel at 98°C)	0.025 (0.018–0.034)	---
Combined Laboratory-Scale Test B Results	0.018 (0.012–0.028)	1.38 (0.80–2.41)
PEP Test D Batch 2 (Caustic Leach in Ultrafiltration Feed Vessel at 85°C)	0.014 (0.010–0.019)	---
Combined Laboratory-Scale Test D Results	0.013 (0.0078–0.019)	1.10 (0.64–2.02)

The results suggest that the conditions present during caustic leach at 98°C in Tank T02A (Integrated Test B) might produce higher scale-up factors than the other tested conditions. The reasons for scale-up factors significantly less than or greater than one are not completely clear, but could include temperature and solids-concentration variation within the vessel. However, the Integrated Test B scale-up factors are within the 95% confidence intervals of the factors from other tests, and so are not conclusively different from them.

SOLIDS WASHING

The performance of the solids washing process was assessed by comparing the solute concentrations measured in the PEP to the solute concentrations expected if wash water were instantaneously mixed throughout the slurry [10]. The washing efficiency w_{eff} is defined by Eq. 2

$$\frac{C_n}{C_0} = \left(1 + \frac{V_w}{V_L} w_{eff}\right)^{-n}$$
(Eq. 2)

where n = wash step number, where each step adds an increment of V_w volume (targeted at 11 gallons) of wash liquid and removes V_w volume of filtrate
C_{n-1} = molar concentration of a species at the end of the preceding wash step
C_n = molar concentration of a species at the current wash step
V_w = volume of IW added at each wash step (targeted at 11 gallons)
V_L = volume of liquid in the slurry before wash liquid is added.

Overall washing efficiencies for each solute were determined with a weighted least squares fit. Weighting was based on the magnitude of the analytical measurements.

An example of the concentration data is shown in Fig. 3 for soluble aluminum (present as $Al(OH)_4^-$) obtained during the wash after caustic leaching. The concentration data at each wash step (C_n) are normalized to the initial concentration (C_o). The expected ideal concentration ratio is provided for reference; by definition, ideal behavior has a wash efficiency equal to one. Any deviation from log-linearity may indicate slow dissolution or precipitation of analytes or an approach to the analytical method detection limit. In each case, the ideal wash efficiency curve, $W_{eff} = 1$, is included for comparison to the actual data. Plots for the remaining analytes may be found [10 and 3].

The analytes selected for determining wash efficiency were those analytes that were fully soluble throughout the entire washing procedure and presented log-linear concentration curves. These were dissolved aluminum, free hydroxide, nitrate, nitrite, and sulfate for the wash after caustic leaching. Other analytes (e.g., sodium, oxalate, phosphate) were not suitable for determining a wash efficiency because their concentrations were affected by the dissolution of soluble solids during the wash after caustic leaching. The analytes selected for determining the wash efficiency were dissolved chromium and oxalate for the wash after oxidative leaching. Sodium was eliminated from consideration because the wash water contained 0.01 M NaOH, and the sodium concentration was approaching this value. Other analytes, such as aluminum, phosphate, sulfate, and nitrite, were at low concentrations approaching or below the analytical reporting limit for most or all of the wash steps.
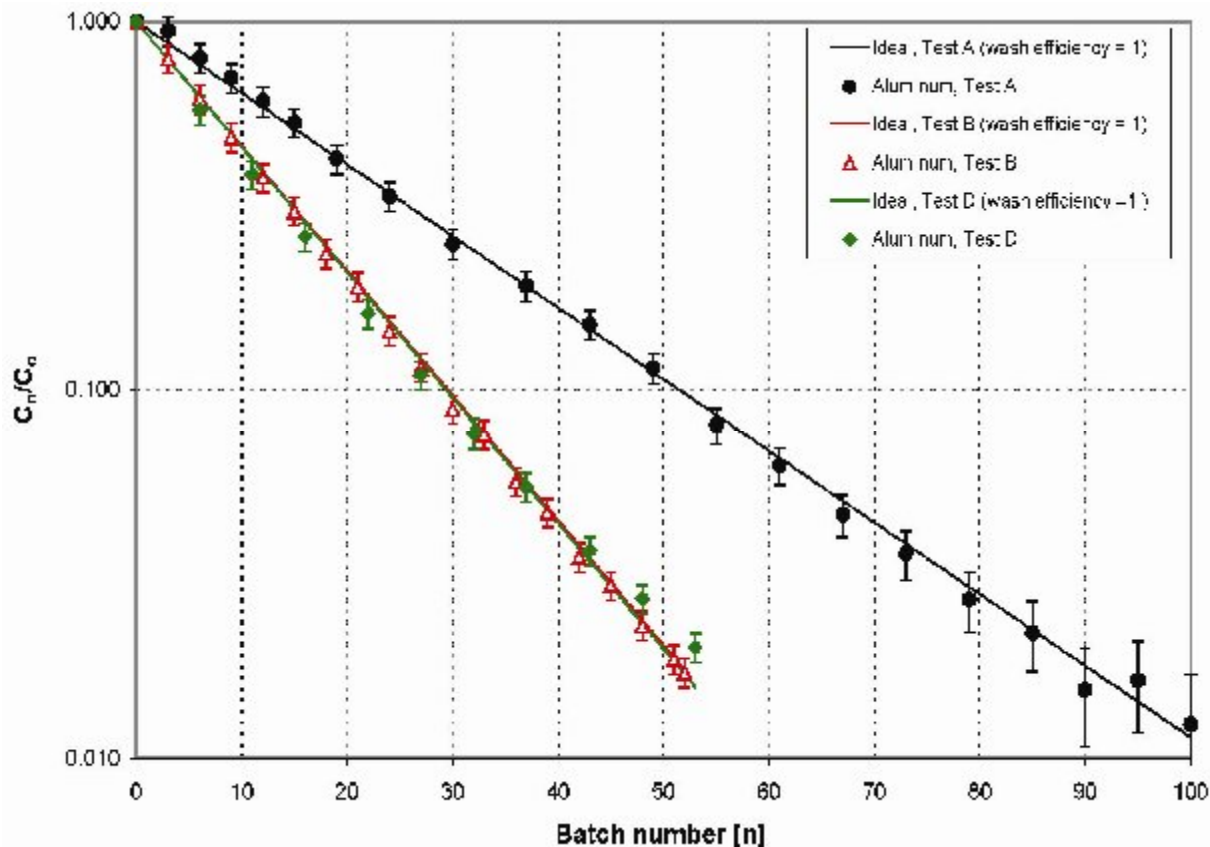
Fig. 3. Concentration ratio (C_n/C_o) for aluminum during the post-caustic leach wash.

A summary of the washing efficiencies determined for all selected analytes is shown in Table V. The uncertainties are expressed as the 95% confidence interval and were estimated with a Monte Carlo approach. The results are generally consistent with the assumption of instantaneous mixing of the wash water additions.

The overall wash efficiency for the wash after caustic leaching, averaged over all analytes for all of the Integrated Tests, is 1.00 ± 0.01. The overall wash efficiency for the wash after oxidative leaching, averaged over all analytes for all of the Integrated Tests A, B, and D is 0.98 ± 0.01. The overall conclusion is that all three integrated tests show consistent wash efficiency values that are effectively one.

Table V. Summary of W_{eff} results (Weighted Least Squares) for all Analytes.

Post-Caustic Leach Wash W_{eff}			
Analyte	Integrated Test A	Integrated Test B	Integrated Test D
Aluminum	1.00±0.03	1.01±0.03	0.98±0.02
Sulfate	1.00±0.03	1.02±0.03	1.04±0.02
Nitrate	1.00±0.02	1.01±0.03	1.05±0.03
Nitrite	1.01±0.03	1.02±0.04	1.02±0.03
OH	0.93±0.05	0.99±0.06	1.01±0.05
Average	0.99±0.01	1.01±0.02	1.02±0.02
Post-Oxidative Leach Wash W_{eff}			
Analyte	Integrated Test A	Integrated Test B	Integrated Test D
Cr	0.98±0.02	1.01±0.02	0.93±0.03
Oxalate	1.00±0.04	0.99±0.03	0.98±0.03
Average	0.99±0.02	1.00±0.02	0.96±0.02

OXIDATIVE LEACHING

The oxidative leaching scale-up factors are based on the results of three oxidative leaching tests conducted during the integrated tests [11]. The scale-up factor is determined as the ratio of the chromium leach factor obtained from the PEP results to the leach factor determined from the laboratory-scale tests. The leach factors were determined using two methods. Method 1 uses the total Cr mass changes in the initial and final solids (see Eq. 3). Method 2 uses an implied mass balance based on the measured Cr inventory in the supernatant as compared to the initial amount of Cr present (Eq. 4).

$$f_{Cr,1} = 1 - \frac{m_{CrS}}{m_{CrS,0}} \qquad \text{(Eq. 3)}$$

$$f_{Cr,2} = \frac{m_{CrL} - m_{CrL,0}}{m_{CrS,0}} \qquad \text{(Eq. 4)}$$

where
$m_{CrS,0}$ = mass of solid-phase Cr in the oxidative-leach vessel at the initial condition
m_{CrS} = mass of solid-phase Cr in the oxidative-leach vessel at the final condition
$m_{CrL,0}$ = mass of dissolved Cr in the oxidative-leach vessel at the initial condition
m_{CrL} = mass of dissolved Cr in the oxidative-leach vessel at the final condition.

The leach factors determined with equations 3 and 4 are shown in Table VI for all of the integrated tests and the associated laboratory-scale tests. The average leach factors are approximately 0.9 for Integrated Tests A and B, although the leach factors determined with Method 1 are slightly higher (0.91 to 0.94) than those determined with Method 2 (0.85 to 0.89). The presence of an unreactive chromium fraction is typical of the behavior of actual tank waste samples [12].

Table.VI. Final Cr Oxidative Leach Factors for the PEP and Laboratory-Scale Tests (95% confidence interval in parenthesis)

Test	Cr Leach Factor–Method 1	Cr Leach Factor–Method 2
Integrated Test A	0.94 (0.94–0.95)	0.89 (0.85–0.94)
Laboratory-scale Test A	0.91 (0.90–0.92)	0.85 (0.77–0.93)
Integrated Test B	0.91 (0.90–0.91)	0.88 (0.83–0.94)
Laboratory-scale Test B	0.93 (0.92–0.94)	0.89 (0.81–0.97)
Integrated Test D	0.39 (0.34–0.43)	0.94 (0.87–1.01)
Laboratory-scale Test D-1	0.46 (0.41–0.51)	0.49 (0.43–0.55)
Laboratory-scale Test D-2	0.49 (0.43–0.53)	0.47 (0.42–0.53)

The leach factors for Integrated Test D are approximately half that of the values found in Integrated Tests A and B. This is attributed to the fact that much of the chromium was dissolved during the caustic-leach step during Integrated Test D. This left a smaller amount of chromium available for leaching, some of which appears to be resistant to the oxidative leaching process. Note that the chromium component (i.e. CrOOH [13]) was added to the simulant after the post-caustic leach wash step in Integrated Tests A and B. When the considerable amount of chromium dissolved during the caustic leaching process is included, the value of the cumulative leach factors for Integrated Test D range from 0.91 to 0.93, in close agreement with the range of values of 0.91 to 0.94 found for Integrated Tests A and B.

For Integrated Test D, the Cr leach factor for PEP oxidative leaching based on Method 2 is more than twice as large as for the Laboratory Scale D Tests and for the PEP results obtained using Method 1. This difference is attributed to the possibility that there was a small amount of Cr added to the solution from corrosion of the PEP components. The quantity added was relatively small but was significant relative to the low amounts of chromium available for leaching.

As discussed by Kurath et al. [3] and [11], the oxidation process was essentially complete within about 10 minutes. This observation indicates that oxidation is rapid for the Cr(III) form (i.e. CrOOH) used in the simulant and that the permanganate reagent was rapidly mixed with the slurry.

There is essentially no difference between the Cr leach factors obtained from PEP and laboratory-scale testing. This indicates that the scale-up factor from laboratory-scale to PEP scale testing is one. Test conditions specified to allow direct application of PEP results to WTP performance (i.e., prototypic performance) were met, so the scale-up of laboratory-scale results to the WTP is one.

SUMMARY AND CONCLUSIONS

The successful completion of the PEP integrated tests demonstrated the baseline and alternative WTP flow sheets and provides scale-up factors to improve specific WTP performance predictions. Caustic leaching scale-up factors defined as a ratio of the kinetic rate constant for boehmite dissolution at the PEP scale to the laboratory scale ranged from a median of 0.88 for leaching in the Ultrafiltration Feed Preparation vessels to 1.38 for leaching in the Ultrafiltration Feed vessels. The scale-up factor for the low solids tests is presented as a ratio of the normalized filter flux (corrected to standard temperatures and TMPs) of the PEP to the laboratory scale. Scale-up factors for the high-solids filtration behavior are presented in terms of the parameters characterizing filtration dewatering performance at concentrations approaching the limiting gel concentration. These parameters include the dewatering mass transfer coefficient and the slurry-limiting gel concentration. For both sets of filtration tests, the recommended scale-up factor is one. Solids washing results are evaluated for soluble components by comparing the washing efficiencies determined in the PEP to those expected if wash water were instantaneously mixed throughout the slurry. This comparison indicates that the overall wash efficiency values are effectively one. Finally, scale-up factors for Chromium solids leaching are determined by comparing the leach

factors obtained at both scales. Since the leach factors are nearly the same at both scales, the recommended scaleup factor is one. Since key portions of the PEP equipment were scaled versions of the WTP equipment, and PEP operating parameters were selected to preserve the most important aspects of the WTP processes, these results may be applied to the WTP. These results provide a crucial tie between a large body of laboratory-scale tests conducted with simulants and actual waste and the WTP performance projections.

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