



U.S. DEPARTMENT OF
ENERGY

WTP-RPT-188, Rev 1
PNNL-18500, Rev 1

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

EFRT M-12 Issue Resolution: Comparison of PEP and Bench-Scale Oxidative Leaching Results

| | |
|---------------|-------------|
| BM Rapko | TS Hausmann |
| PP Schonewill | JL Huckaby |
| CF Brown | BD Hanson |
| PW Eslinger | DE Kurath |
| MS Fountain | MJ Minette |

January 2010



Pacific Northwest
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;

ph: (865) 576-8401

fax: (865) 576 5728

email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

ph: (800) 553-6847

fax: (703) 605-6900

email: orders@nits.fedworld.gov

online ordering: <http://www.ntis.gov/ordering.htm>

EFRT Issue Resolution: Comparison of PEP and Bench-Scale Oxidative Leaching Results

| | |
|---------------|-------------|
| BM Rapko | TS Hausmann |
| PP Schonewill | JL Huckaby |
| CF Brown | BD Hanson |
| PW Eslinger | DE Kurath |
| MS Fountain | MJ Minette |

January 2010

Test Specification: 24590-PTF-TSP-RT-07-001 Rev 2
Work Authorization: WA# 2007-024
Test Plan: TP-RPP-WTP-506, Rev. 0.4, TP-WTP-PEP-044, Rev 0.2
Test Exceptions: 24590-PTF-TEF-RT-08-00002
24590-WTP-TEF-RT-09-00003
24590-PTF-TEF-RT-09-00001
24590-WTP-TEF-RT-09-00002, Rev 0
24590-WTP-TEF-RT-09-00001 Rev 1

R&T focus area: Pretreatment
Test Scoping Statement(s): NA

Prepared for
the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-PTF-TSP-RT-07-001 Rev 2 "Pretreatment Engineering Platform (PEP) Testing (Phase 1)" and Test Plans TP-RPP-WTP-506 Rev 0.4 "Pretreatment Engineering Platform (PEP) Testing (Phase 1) and TP-WTP-PEP-044 Rev 0.2" Test Plan for the PEP Parallel Laboratory Testing." The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test Plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager
WTP R&T Support Project

1/29/10
Date

REVISION HISTORY

| Revision Number | Interim Change No. | Effective Date | Description of Change |
|-----------------|--------------------|----------------|--|
| 0 | 0 | 8/14/09 | Initial issue. |
| 1 | 0 | When issued. | <p>Throughout: References to the primary process vessel UFP-VSL-T02A and the Integrated Tests (Integrated Test A and Integrated Test B) were updated to improve consistency in their use. UFP-VSL-T02A was sometimes referred to as "T02A;" this was updated to "Tank T02A." Cases where Integrated Test A and B were referred to as simply "A" and "B" were updated to include "Integrated Test." A few editorial changes were made at places in the text to improve clarity.</p> <p>Executive Summary: Updated QA section to reference HDI instead of SBMS.</p> <p>Section 2: Updated to reference HDI instead of SBMS.</p> <p>Table 4.1: Values were replaced with new values which incorporated triplicate sample data and a corrected approach to the uncertainty calculations. Note that hydroxide is now presented in units of molarity in order to agree with the text on page 4.2.</p> <p>Figure 4.1: Updated for clarity of presentation and appropriate start and end times for the oxidative leach. There were no changes to the data values themselves.</p> <p>Page 4.4: The bench-scale vessel was incorrectly referred to as "T02A," this was replaced with "the reaction vessel."</p> <p>Figure 4.2: Updated for clarity of presentation. There were no changes to the data values themselves.</p> <p>Table 4.4: Updated with corrections to the Mn:Cr ratios. Also affects one number in the text on page 4.6.</p> <p>Section 4.3.1: Completely rewritten to reflect small changes in the calculation method and improve the use of nomenclature. The section is similar to section 11.3.3.1 in WTP-RPT-197 Rev 0.</p> <p>Section 4.3.2: Changed the leach factors from "0.90 or greater" to "0.85 or greater" since it is Method 2 being used.</p> <p>Figure 4.3: Removed in this revision. This figure was deemed redundant and non-informative. Accompanying text was rewritten to update figure and table references and to point to data in Table 4.5 which gives the same information was Figure 4.3.</p> <p>Figure 4.4: Became Figure 4.3 in this revision. The figure was updated to reflect the new leach factors based on the calculation method outlined in section 4.3.1. The changes in the leach factors are very small.</p> <p>Table 4.5: Updated with the leach factor values that were changed when the new calculation method was used.</p> <p>Table 4.6: Updated with new mass balance values due to the new calculation method. The impact on the mass balance is very small.</p> |

Contents

| | |
|---|-------|
| Acknowledgments..... | ix |
| Acronyms..... | xi |
| Testing Summary..... | xiii |
| Objectives..... | xiv |
| Test Exceptions..... | xv |
| Results and Performance Against Success Criteria..... | xix |
| Quality Requirements..... | xxiii |
| R&T Test Conditions..... | xxiv |
| Simulant Use..... | xxvi |
| Discrepancies and Follow-On Tests..... | xxvii |
| 1.0 Introduction..... | 1.1 |
| 2.0 Quality Assurance..... | 2.1 |
| 3.0 Experimental Approach..... | 3.1 |
| 3.1 PEP Process Description..... | 3.1 |
| 3.2 PEP Oxidative-Leach..... | 3.3 |
| 3.3 Bench-Scale Oxidative-Leach..... | 3.5 |
| 3.4 Relationship of PEP to Plant Performance..... | 3.5 |
| 4.0 Results..... | 4.1 |
| 4.1 Starting Slurry Composition..... | 4.1 |
| 4.2 PEP Experimental Process Conditions..... | 4.2 |
| 4.2.1 Temperatures During PEP Oxidative Leaching..... | 4.3 |
| 4.2.2 Temperatures During Oxidative Leaching Bench-Scale Testing A and B..... | 4.4 |
| 4.2.3 Initial Permanganate to Chromium Ratios..... | 4.5 |
| 4.3 Results – Cr Leach Factors..... | 4.6 |
| 4.3.1 Methods for Calculating Cr Oxidative-Leach Factors..... | 4.6 |
| 4.3.2 Results from Cr Oxidative-Leach Factor Calculations..... | 4.8 |
| 5.0 Summary and Conclusions..... | 5.1 |
| 6.0 References..... | 6.1 |

Figures

| | |
|---|-----|
| 3.1. PEP Simplified Flow Diagram | 3.2 |
| 3.2. Caustic- and Oxidative-Leach and Ultrafilter Operations | 3.3 |
| 3.3. In-Tank Sampling, Showing the Three Radial Positions at Three Heights and Sampling Flow Loop..... | 3.4 |
| 4.1. Prototypic Temperatures in Tank T02A During Oxidative Leaching of Integrated Tests A and B..... | 4.4 |
| 4.2. Bench-Scale Test Temperatures During Oxidative Leaching of Integrated Tests A and B..... | 4.5 |
| 4.3. Cr Leach Factors as a Function of Time (hours) for the PEP and Bench-Scale Integrated Tests A and B as Calculated by Method 2 | 4.9 |

Tables

| | |
|---|------|
| S.1. Summary of Test Objectives and Results..... | xv |
| S.2. Test Exceptions..... | xvi |
| S.3. Deviations from Test Specification | xix |
| S.4. Success Criteria | xx |
| S.5. R&T Test Conditions..... | xxiv |
| 4.1. Key Analytes in Initial Slurry Composition (uncertainty equals 1 standard deviation) | 4.1 |
| 4.2. Integrated Test A PEP Experimental Parameters | 4.2 |
| 4.3. Integrated Test B PEP Experimental Parameters (UFP-VSL-T02 leaching)..... | 4.3 |
| 4.4. Mn:Cr Experimental Ratio..... | 4.6 |
| 4.5. Final Cr Leach Factors for the PEP (6-hr contact time) and Bench-Scale Integrated Tests A and B (8-hr contact time) as Calculated by Methods 1 and 2 (95% confidence range in parenthesis) | 4.9 |
| 4.6. Mass Summary of Cr for Oxidative Leaching in Integrated Tests A and B..... | 4.10 |

Acknowledgments

The authors would like to thank Wayne Cosby for valuable editorial support, Dave MacPherson and Kirsten Meier for Quality Assurance support throughout the project, Gregg Lumetta for his technical review, and Andrew Felmy for helpful discussions.

In addition to the authors, this report was supported by many dedicated staff involved in laboratory experiments, sampling, data acquisition, data processing, data-quality confirmation, technical reviews, and data analysis.

| | | |
|-----------------|-----------------|--------------|
| JM Alzheimer | CA Burns | SV Shoemaker |
| C Arimescu | JM Cuta | DM Smith |
| DD Bachand | CE Guzman-Leong | PS Sundar |
| EBK Baer | RE Hohimer | JJ Toth |
| S Barnes | ML Kimura | JC Tucker |
| AW Baumann | WL Kuhn | MW Urie |
| GH Beeman | WE Lawrence | BE Wells |
| DL Blanchard Jr | RP Pires | JK Young |
| JC Bower | DE Rinehart | |
| OP Bredt | RL Russell | |
| GN Brown | RD Scheele | |
| SA Bryan | GJ Sevigny | |

These individuals and the rest of the operations and sampling crew are especially recognized for supporting the Pretreatment Engineering Platform Project by working unpredictable, long, and off-hour shifts for the better part of a year. The tests and reports could not have gotten this far without their extraordinary effort.

Acronyms

| | |
|------|---|
| AFA | antifoam agent |
| ASME | American Society of Mechanical Engineers |
| ASO | Analytical Support Operations |
| BNI | Bechtel National Inc. |
| CD | Coriolis densitometer |
| CUF | Cells Unit Filter |
| DOE | U.S. Department of Energy |
| EFRT | External Flowsheet Review Team |
| FEP | Feed Evaporation Process |
| HDI | “How Do I ...?” |
| HLW | high-level waste |
| IC | ion chromatography |
| ICP | inductively coupled plasma |
| JTG | Joint Task Group |
| LAW | low-activity waste |
| LCS | laboratory control sample |
| M&TE | measuring and test equipment |
| OES | optical emission spectroscopy |
| PEP | Pretreatment Engineering Platform |
| PJM | pulse jet mixer |
| PLM | polarized light microscopy |
| PMP | polymethylpentene |
| PNNL | Pacific Northwest National Laboratory |
| PTF | Pretreatment Facility |
| QA | quality assurance |
| QAP | Quality Assurance Program |
| QARD | Quality Assurance Requirements and Descriptions |
| RPL | Radiochemical Processing Laboratory |
| RPP | River Protection Project |
| R&T | research and technology |
| SwRI | Southwest Research Institute |
| UDS | undissolved solids |
| UFP | ultrafiltration process |
| WTP | Hanford Tank Waste Treatment and Immobilization Plant |

Testing Summary

Pacific Northwest National Laboratory (PNNL) has been tasked by Bechtel National Inc. (BNI) on the River Protection Project-Hanford Tank Waste Treatment and Immobilization Plant (RPP-WTP) project to perform research and development activities to resolve technical issues identified for the Pretreatment Facility (PTF). The Pretreatment Engineering Platform (PEP) was designed, constructed, and operated as part of a plan to respond to issue M12, “Undemonstrated Leaching Processes” of the External Flowsheet Review Team (EFRT) issue response plan.^(a) The PEP is a 1/4.5-scale test platform designed to simulate the WTP pretreatment caustic leaching, oxidative leaching, ultrafiltration solids concentration, and slurry washing processes. The PEP replicates the WTP leaching processes using prototypic equipment and control strategies. The PEP also includes non-prototypic ancillary equipment to support the core processing.

Two operating scenarios are currently being evaluated for the ultrafiltration process (UFP) and leaching operations. The first scenario has caustic leaching performed in the UFP-2 ultrafiltration feed vessels (i.e., vessel UFP-VSL-T02A in the PEP; and vessels UFP-VSL-00002A and B in the WTP PTF). The second scenario has caustic leaching conducted in the UFP-1 ultrafiltration feed preparation vessels (i.e., vessels UFP-VSL-T01A and B in the PEP; vessels UFP-VSL-00001A and B in the WTP PTF).

In both scenarios, 19-M sodium hydroxide solution (NaOH, caustic) is added to the waste slurry in the vessels to dissolve solid aluminum compounds (e.g., gibbsite, boehmite). Caustic addition is followed by a heating step that uses direct steam injection to accelerate the leaching process. Following the caustic-leach, the vessel contents are cooled using vessel cooling jackets and/or external heat exchangers. The main difference between the two scenarios is that for leaching in UFP-1, the 19-M NaOH is added to unconcentrated waste slurry (3- to 8-wt% solids), while for leaching in UFP-2, the slurry is concentrated to nominally 20-wt% solids using cross-flow ultrafiltration before the addition of caustic.

For wastes that have significantly high chromium content, the caustic leaching and slurry dewatering is followed by adding sodium permanganate to UFP-VSL-T02A, and the slurry is subjected to oxidative leaching at nominally ambient temperature. The purpose of the oxidative leaching is to selectively oxidize the poorly alkaline-soluble Cr(III) believed to be the insoluble form in Hanford tank sludge to the much more alkaline-soluble Cr(VI), e.g., chromate.

The PEP testing program was conducted under Test Plan TP-RPP-WTP-506^(b) using a waste simulant that was developed in response to Task 5 from the M-12 External Flowsheet Review Team (EFRT) issue response plan.^(a) The testing included the following tests with simulated Hanford tank waste:

- Shakedown/Functional testing: Tested process operations (e.g., slurry transfers, steam heating of the vessels and the accumulation of condensate, filter backpulsing and flushing), process controls (e.g., transmembrane pressure and axial flow velocity in the filter-loop), and certain test functions (e.g., in-line slurry sampling accuracy and precision).

(a) SM Barnes, and R Voke. 2006. “Issue Response Plan for Implementation of External Flowsheet Review Team (EFRT) Recommendations - M12: Undemonstrated Leaching Process.” 24590-WTP-PL-ENG-06-0024 Rev. 0, Bechtel National Inc., Richland, Washington.

(b) GB Josephson, OP Bredt, JK Young, and DE Kurath. 2009. *Test Plan for Pretreatment Engineering Platform (PEP) Testing (Phase I)*. TP-RPP-WTP-506, Rev. 0.4, Pacific Northwest National Laboratory, Richland, Washington.

- Integrated Test A: Demonstrated integrated processing when caustic leaching (98°C) is performed in UFP-VSL-00001A/B (PEP equivalent: UFP-VSL-T01A&B) with the Cr simulant component added after the post-caustic-leach washing step.
- Integrated Test B: Demonstrated integrated processing when the caustic leaching (98°C) was performed in UFP-VSL-00002A (PEP equivalent: UFP-VSL-T02A) with the Cr simulant component added after the post-caustic-leach washing step.
- Integrated Test D: Demonstrated integrated processing when the caustic leaching is performed at a lower temperature (85°C) in UFP-VSL-00002A (PEP equivalent: UFP-VSL-T02A) and with the Cr simulant component added to the initial batch of simulant.

Integrated Test C was deleted from the scope of the testing (ICN-TP-RPP-WTP-506_R0.2).

The work described in this report examines the test results that are related to the efficiency of the oxidative leaching process to support process modeling based on tests performed with a Hanford waste simulant. The tests were completed both at the laboratory-bench scale and in the PEP. This report summarizes the results from both scales that are related to oxidative leaching chemistry to support the development of a scale factor for the submodels to be used in the G2 model, which predicts WTP operating performance. The PEP test data to be included in this report are limited to those from Integrated Tests A (Tank T01A/B caustic leaching) and B (Tank T02A caustic leaching). Whether caustic leaching is carried out in UFP-VSL-T01A/B (Integrated Test A) or UFP-VSL-T02A (also referred to as UFP-2) (Integrated Test B), all oxidative leaching processes occur in vessel UFP-2.

In the Results section, two methods were used to calculate leach factors: one method was based on comparison between the initial and final mass of Cr in the residual solids, and a second method compares the amount of Cr dissolved in the leachate with the total mass of Cr present in the initial solids.

From this information, the fraction of Cr removed by oxidative leaching gives a leach factor of approximately 0.9 regardless of the test and regardless of test scale. This allows a key conclusion to be made—namely, that the scale-up factor from bench-scale oxidative leaching to PEP scale testing is 1.

Objectives

Table S.1 summarizes the objectives and results of this testing and discusses how the objectives were met. The objectives for the entire PEP testing program are provided with discussion limited to those objectives met by the scope of this report (those that are not applicable to this report are shaded in gray).

Table S.1. Summary of Test Objectives and Results

| Test Objective | Objective Met? | Discussion |
|--|----------------|--|
| Caustic-leach process: Compare engineering- and laboratory-scale results to determine impact of scale-up. | NA | Results to meet this objective are discussed in report WTP-RPT-186 and WTP-RPT-197. |
| Oxidative-leach process: Compare engineering- and laboratory-scale results to determine impact of scale-up. | Y | Chromium concentrations and leach factors obtained during the PEP and laboratory-scale testing are compared in Section 4.3. |
| Cross-flow ultrafiltration: Monitor cross-flow filter performance at engineering- and laboratory-scale to determine scale-up. | NA | Results to meet this objective are discussed in report WTP-RPT-185 and WTP-RPT-197. |
| Slurry wash process: Determine the post-caustic and oxidative leaching slurry wash efficiencies. | NA | Results to meet this objective are discussed in report WTP-RPT-187 and WTP-RPT-197. |
| Process integration: Evaluate the chemical addition, filter operation cycle performance, and pressure pot operations. Also perform mass balances for aluminum, chromium, manganese, sodium, hydroxide, oxalate, phosphate, sulfate, and water and monitor permeates for post filtration precipitation. | NA | Results to meet this objective are discussed in report WTP-RPT-197. |
| Monitor the performance of the recirculation system pumps, filters, and heat exchanger to support Engineering fabrication decisions for these components. | NA | The data required to meet this objective were provided on Compact Disks transmitted in the following reference: Letter from GH Beeman to H Hazen, "Subcontract No. 24590-QL-HC9-WA49-00001, Project No. 53569 (WA-024) Engineering Ties Data Transmittal: The Electronic File Enclosed With This letter Has Been Reviewed For Technical Accuracy Per the quality assurance (QA) Program," WTP/RPP-MOA-PNNL-00392, dated 4/10/09. |

Test Exceptions

A summary description of the Test Exceptions applied to these tests is shown in Table S.2.

Table S.2. Test Exceptions

| Test Exceptions | Description of Test Exceptions |
|--|---|
| <p>1) 24590-PTF-TEF-RT-08-00002, incorporated into ICN1 to Test Plan TP-RPP-WTP-506.</p> | <p>This Test Exception:</p> <ol style="list-style-type: none"> 1) Added a stage during the filter conditioning section of the Functional Test where the simulant slurry is concentrated from approximately 5-wt% solids to 20-wt% solids in one operation. This is in addition to the previously specified low-solids filter and high-solids filter testing. 2) Documented the Joint Task Group's (JTG) decision regarding the number of replicate samples to be collected at various processing times. 3) Revised the terminology specifying the Coriolis densitometer (CD) sample locations changed to be consistent with PEP operating procedures. Renamed the "center" array to "inner." 4) The sampling specified in the low-solids filtration test over-specifies the sample collection timing required. The technical requirement is to get 30 unique samples. The sampling schedule specified is not required to achieve this test objective. |
| <p>2) 24590-PTF-TEF-RT-09-00001 incorporated into ICN-2 and ICN-3 to Test Plan TP-RPP-WTP-506.</p> | <ol style="list-style-type: none"> 1) In several steps the sampling location was changed from the filter-loop in-line location to a middle-low CD sample loop location in the UFP-VSL-T02A vessel. This change impacted sampling in the Functional and all Integrated tests (ref CCN 187749). 2) Added a step to the Shakedown/Functional Test (step A.1.31) to add sodium permanganate to UFP-VSL-T02A to assess possible foaming issue (ref CCN 187749). 3) Changed location of second sample for parallel Cells Unit Filter (CUF) testing from the in-line filter-loop to the middle-low CD port in the UFP-VSL-T02A (step A.1.10; Functional Test) (ref CCN 187749). 4) Collected samples for parallel laboratory leaching test before and after caustic addition in UFP-VSL-T01A (A.1.20; Functional Test) and UFP-VSL-T02A (step A.1.15; Functional Test), and in the Integrated Test steps (B.1.2; Integrated Test A, B.2.6; Integrated Tests B/D) (ref CCN 192734). 5) Deleted reconfiguration of the filter-loop to bypass UFP-VSL-T02A and circulate flush water with UFP-PMP-T02A and/or UFP-PMP-43A to allow collection of a representative in-line sample. This step (step A.1.17; Functional Test) could not be done under the operating restrictions in place on the operation of the filter-loop (ref CCN 192734). 6) Eliminated step A.1.25 (filter-loop bypass test with tracer) from the Functional Test. This test was conducted after the completion of Integrated Test B (ref CCN 187753). 7) Modified step A.1.29 (Functional Test) to eliminate the removal of solids from UFP-VSL-T02A prior to the high-solids filter test. This step was not needed as the amount of solids is less than anticipated (ref CCN 187752). 8) Modified step A.1.30 (Functional Test) to include 5 filter backpulses prior to starting the high-solids filter test (ref CCN 187752). 9) Modify step B.1.8 (Integrated Test A) to allow 80% of caustic to be added during in-line simulant transfers to UFP-VSL-T01B and 20% to be added directly to UFP-VSL-T01B (ref CCN 187748). 10) Added a high-solids filter test to the end of Integrated Test B to replace the high-solids filter test from the simulant Shakedown/Functional Test. The test conducted during the Functional Test was hampered by pump cavitation and the target solids concentration was not met (ref CCN 192734). 11) Eliminated Integrated Test C from the Test Plan (ref CCN 192735). 12) The requirement to record density using the CDs on the samplers in UFP-VSL-T02A was eliminated. The density function was not useable due to entrained air in the simulant. |

Table S.2. Test Exceptions

| Test Exceptions | Description of Test Exceptions |
|--|---|
| | <p>13) Modified step B.2.6 (caustic addition in Integrated Test B/D)) temperature limit to change from 60°C to "as specified in run sheet". This temperature is calculated based on various other run parameters and specified in the run sheet.</p> <p>14) Eliminated the monitoring of Integrated Test D permeate samples for 30 days to look for precipitation. This scope was deleted and a revised scope incorporated into Test Plan (TP-WTP-PEP-044, Rev. 0.2;^(a) Test Plan for PEP parallel Laboratory testing).</p> <p>15) Step B.2.20 (Integrated Tests B and D) sampling of the heel in UFP-VSL-T01A was deleted. This sample was not needed since the heels were removed prior to follow-on testing.</p> <p>16) Step B.1.26 (Integrated Test A) sampling of heel in UFP-VSL-T01B was deleted. This sample was not needed since the heels were removed prior to follow-on testing.</p> <p>17) Steps B.1.25 (Integrated Test A) and B.2.19 (Integrated test B/D) were modified from “transfer slurry from UFP-VSL-T02A to HLP-VSL-T27” to “transfer slurry from UFP-VSL-T02A to UFP-VSL-62A/B or to totes for storage as directed by the WTP test director”. The HLP-VSL-T27 vessel was no longer available for use since it served as the receipt vessel for the filter-loop pressure safety valves.</p> <p>18) Added a second batch of leaching to Integrated Tests B/D in UFP-VSL-T02A. This additional leaching batch was needed to provide a sufficient quantity of solids to operate the UFP-VSL-T02A at prototypic levels for the steps following caustic leaching.</p> <p>19) Added a filter bypass tracer test following the post-caustic-leach dewatering step in Integrated Test B. This test replaced the filter bypass tracer test that could not be conducted during the simulant Shakedown/Functional testing.</p> <p>20) Deleted instructions to route permeate to a specific tank (i.e., UFP-VSL-T62A/B). There was no need to segregate various permeate streams.</p> <p>21) Minor changes were made to make the Test Plan consistent with the approved run sheets.</p> |
| <p>3) 24590-WTP-TEF-RT-09-00003 incorporated into ICN-1 to Test Plan TP-WTP-PEP-044.</p> | <p>This Test Exception specified activities to be performed with permeate samples obtained from Integrated Test D. The Integrated Test D permeate samples were originally stored in a temperature-controlled environment and then moved to a location with a reduced temperature where precipitation was likely to occur. The Test Exception requested that the approximate size distribution of the solids be measured in several (3 or 4) selected PEP samples from Integrated Test D using polarized light microscopy (PLM). Size-calibrated photographs should be provided along with the analysis. If possible, record the mineral identification of the solids phase(s) along with the particle-size distribution. The samples will be selected by WTP personnel in consultation with the subcontractor and will be based in part on observation of which samples contain the most solids or appear to contain different types of solids. Repeat the size-distribution analysis approximately 1 week after the initial measurements to determine whether there was a significant change in crystal size, habit, or composition.</p> <p>Perform each size-distribution analysis by measuring the diameter (or length and</p> |

(a) RL Russell. 2008. “Test Plan for the PEP Parallel Laboratory Testing.” TP-WTP-PEP-044, Rev. 0.2, Pacific Northwest National Laboratory, Richland, Washington.

Table S.2. Test Exceptions

| Test Exceptions | Description of Test Exceptions |
|---|---|
| | width for elongated crystals) of approximately 100 individual particles in each sample. The size may be measured either on the microscope slide, using a calibrated ocular scale, or on the size-calibrated photographs. The program recognizes the limitations of the statistical significance of a size-distribution measurement based on such a small population. This Test Exception did not affect any of the existing Test Plan objectives. |
| 4) 24590-PTF-TEF-RT-09-00002, incorporated into ICN-4 to Test Plan TP-RPP-WTP-506. | <p>This Test Exception:</p> <ol style="list-style-type: none"> 1) Requests a report summarizing the lessons learned during scale-up, manufacture, and transport of the PEP simulant. 2) Specifies the sampling and analysis scope to be performed to complete the prototypic nitric acid PEP filter cleaning process. 3) Deletes the Engineering Ties report scope. 4) Specifies additional experimental and analytical work required to estimate the amount of excess caustic in caustic leachate samples and post-caustic-leach wash solutions containing ≈ 3.5 M Na. |
| 5) 24590-WTP-TEF-RT-09-00001 Rev 1 incorporated into ICN-2 to Test Plan TP-WTP-PEP-044. | <p>This Test Exception specifies additional work to be conducted with caustic-leach solutions and post-caustic-leach washing permeate samples obtained from PEP Integrated Tests A, B, and D. It contains the following tasks:</p> <ol style="list-style-type: none"> 1) Determination of precipitate mineralogy, precipitate phase compositions and solution saturation composition. 2) Determination of rate of approach to saturation concentrations. 3) Identification and characterization of precipitates formed in post-caustic-leach filtrate. 4) Determination of the dilution required to redissolve the precipitate. 5) Determination of super-saturation in post-caustic-leach filtrates from Integrated Test B in the PEP. 6) Determine the effects of blending during the post-caustic-leach dewatering and wash cycle. |

As documented in the PEP Test Plan, the deviations from the Test Specification are provided in Table S.3.

Table S.3. Deviations from Test Specification

| Test Specification Reference | Exception Taken |
|--|--|
| <p>Section 6.4.4 “Analytical measurements will be made in conformance to the <i>Guidelines for Performing Chemical Physical, and Rheological Properties Measurements</i>^(a) as applicable.”</p> | <p>Three method exceptions are required under this Test Plan:</p> <ol style="list-style-type: none"> <li data-bbox="760 344 1419 674">1. Caustic-leach and oxidative-leach samples taken during this testing must be separated more quickly than the standard method using syringes. This testing will use a modified method with a shorter centrifuge time, and higher <i>g</i> forces will be applied (e.g., 4000 <i>g</i> vs. 1000 <i>g</i>). <i>Impact on results:</i> If the standard method were used, the longer time could very well lead to greater precipitation and inaccurate results. Laboratory testing will be conducted with simulants to confirm that this method of sample handling is adequate. <li data-bbox="760 684 1419 982">2. Densities of samples smaller than 10-mL can only be established within two significant figures of accuracy. Density measurements for this Test Plan require greater accuracy. Therefore, a more accurate method employing a pycnometer will be used. <i>Impact on results:</i> The change to a pycnometer will generate more precise results than the standard method. The main impact is expected to be on analysis time. The pycnometer method will be slower. <li data-bbox="760 993 1419 1178">3. The process for determining the wt% undissolved solids (UDS) content of the slurries will in some cases be determined with the use of a moisture analyzer. In addition, the method of drying samples will be modified to allow the use of glass fiber filters to aid in drying the samples. <i>Impact on results:</i> Both modifications are intended to decrease the time required to obtain results. |

Results and Performance Against Success Criteria

The PEP system tests were designed to generate the data necessary to:

- Provide engineering-scale system performance data. This information is used to support the WTP computer process models projections of the waste processing campaign
- Confirm the operability and functionality of UFP system components.

The research and technology (R&T) success criteria for achieving these objectives are discussed in Table S.4. The success criteria for the entire PEP testing program are provided with discussion limited to the success criteria covered by the scope of this report (those criteria not relevant to this report are shaded in gray).

(a) GL Smith and K Prindiville. May 20, 2002. *Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements*. 24590-WTP-GPG-RTD-001, Rev 0, Bechtel National, Inc., Richland, Washington.

Table S.4. Success Criteria

| Success Criteria | How Testing Did or Did Not Meet Success Criteria |
|--|---|
| UFP System Process Performance | |
| Measure the aluminum leaching performance of the PEP and laboratory systems as a function of time under WTP UFP-1 and UFP-2 projected leaching conditions at bounding high and low process temperatures (nominally 100°C and 80°C). | Results to meet this success criterion are discussed in report WTP-RPT-186 and WTP-RPT-197. |
| Compare aluminum leach performance in UFP-1 where all of the NaOH is added in-line to the case where a fraction of the total NaOH is added directly to the tank. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Measure chromium leaching performance in the PEP and laboratory systems as a function of time at the WTP projected conditions in UFP-2 for both the UFP-1 and UFP-2 aluminum leaching flowsheets. | Cr leach factors for both bench-scale and PEP studies are provided in the Results section of this report for Integrated Tests A (Tank T01A/B caustic leaching) and B (Tank T02A caustic leaching). Additional discussion and results for Integrated Test D are provided in WTP-RPT-197. |
| Evaluate the process control strategy for specification of required reagent additions including NaOH, NaMnO ₄ , and wash solutions provided in the Pretreatment Engineering Platform (PEP) Phase 1 Testing Process Description. | A comparison of targeted and delivered reagent additions is provided in the Results section of this report for Integrated Tests A (Tank T01A/B caustic leaching) and B (Tank T02A caustic leaching). Additional discussion and results for Integrated Test D are provided in WTP-RPT-197. |
| Measure the filter system performance at the nominal flow velocity and transmembrane pressures for the solids concentration and washing stages for the UFP-1 and UFP-2 aluminum leaching flowsheets. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Evaluate the control strategy for make-up additions from UFP-VSL-00001A/B to UFP-VSL-00002A/B during initial dewatering process. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Measure the wash water volumes required to remove or reduce the free hydroxide following the aluminum leaching stage and dissolved chromium after the oxidative leaching process to the specified concentrations. | Results to meet this success criterion are discussed in report WTP-RPT-187 and WTP-RPT-197. |

Table S.4. Success Criteria

| Success Criteria | How Testing Did or Did Not Meet Success Criteria |
|---|--|
| Perform mass balances for selected constituents including aluminum, chromium, manganese, sodium, hydroxide, oxalate, phosphate, sulfate, and water to evaluate leaching and washing process performance. | Chromium mass balances are provided in the Results section of this report. Mass balances for the entire PEP process are discussed in report WTP-RPT-197. |
| Measure solids distribution under scaled mixing conditions before and after caustic leaching evolutions. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Measure the rheology of the slurry simulat and shear strength of the settled solids before and after each leaching and washing unit operation and following final concentration. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Estimate the quantity of excess hydroxide added in the process that may not be needed to keep aluminate in solution following filtration. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Collect and retain permeate samples for extended precipitation studies (including permeate/simulated supernatant blended cases) from each concentration cycle. | Samples were collected and retained for extended precipitation studies. The results of the precipitation studies are discussed in WTP-RPT-197, WTP-RPT-200, and WTP-RPT-205. |
| UFP System Operability and Functionality | |
| Verify that the dual, in-series pump configuration is controllable and maintains the required slurry velocity and pressures for ultrafilter operation. | The data required to meet this success criterion were provided on Compact Disks transmitted in the following reference: Letter from GH Beeman to H Hazen, "Subcontract No. 24590-QL-HC9-WA49-00001, Project No. 53569 (WA-024) Engineering Ties Data Transmittal: The Electronic File Enclosed With This letter Has Been Reviewed For Technical Accuracy Per the QA Program", WTP/RPP-MOA-PNNL-00392, dated 4/10/09. |
| Measure the operating characteristics for the cooling heat exchanger for the UFP-VSL-00002 filter recirculation loop (temperature changes as a function of flow to determine how to achieve the desired performance in the PTF analog). | The data required to meet this success criterion were provided on Compact Disks transmitted in the following reference: Letter from GH Beeman to H Hazen, "Subcontract No. 24590-QL-HC9-WA49-00001, Project No. 53569 (WA-024) Engineering Ties Data Transmittal: The Electronic File Enclosed With This letter Has Been Reviewed For Technical Accuracy Per the QA Program", WTP/RPP-MOA-PNNL-00392, dated 4/10/09. |

Table S.4. Success Criteria

| Success Criteria | How Testing Did or Did Not Meet Success Criteria |
|--|--|
| Confirm whether the WTP process control strategies for ultrafilter system filling, operating, backpulsing, draining, flushing, and cleaning are adequate for stable operation. Provide to WTP data to determine whether backpulsing is a required and effective means of restoring the filter permeate rates to confirm that production throughput is maintained and determine whether operation of the backpulse system induces any process or equipment operations issues. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Use only the process information and data available to the WTP PTF operating staff during WTP operations (e.g., caustic and permanganate addition volumes, permeate mass balances for solids concentration, etc.) to operate the PEP. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Confirm whether the elevated temperature PJM operating strategy is adequate for stable PEP and WTP operation. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Measure the heat-up rate and controllability of the PEP UFP-VSL-00001 and UFP-VSL-00002 vessels and the cooling performance for UFP vessels. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Measure the performance of the in-line addition of process chemicals into the simulated wastes and determine the extent of blending in the process vessels. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Monitor ultrafilter performance (to include visual inspection of the filter tubes, tube sheets, and heads from an ultrafilter for any evidence of flow mal-distribution and/or solids buildup at least once during Phase 1). | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Measure, record, and control ultrafiltration temperature, transmembrane pressure, and slurry flow during filter-loop operations. | Data to meet this success criterion are discussed in WTP-RPT-185 for the low- and high-solids tests and are discussed for the remaining tests in the run reports for each of the Integrated Tests. |

Table S.4. Success Criteria

| Success Criteria | How Testing Did or Did Not Meet Success Criteria |
|--|---|
| Record any solids accumulations observed during any operating stage or maintenance evolution. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Monitor the permeate production rate of each ultrafilter assembly in operation. | Results to meet this success criterion are discussed in WTP-RPT-185 for the low- and high-solids tests and are discussed for the remaining tests in report WTP-RPT-197. |
| Record operating time of each ultrafilter assembly. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Record each ultrafilter assembly cleaning event (backpulse, flush, chemical cleaning, etc.). | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Evaluation of the pulse-pot operation and backpulse operation strategies contained in PEP Phase 1 Testing Process Description. | Results to meet this success criterion are discussed in report WTP-RPT-197. |
| Evaluate permeate and permeate blends for precipitation of solids, particularly aluminum and oxalate solids. | Results to meet this success criterion are discussed in reports WTP-RPT-197, WTP-RPT-200, and WTP-RPT-205. |

Quality Requirements

The PNNL Quality Assurance Program is based upon the requirements as defined in the U.S. Department of Energy (DOE) Order 414.1C, *Quality Assurance* and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A—*Quality Assurance Requirements* (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, *Requirements for Quality Assurance Programs for Nuclear Facilities*.
- ASME NQA-1-2000, Part II, Subpart 2.7, *Quality Assurance Requirements for Computer Software for Nuclear Facility Applications*.
- ASME NQA-1-2000, Part IV, Subpart 4.2, *Graded Approach Application of Quality Assurance Requirements for Research and Development*.

The procedures necessary to implement the requirements are documented in PNNL’s “How Do I ...?” (HDI) system.^(a)

PNNL implements the RPP-WTP quality requirements by performing work in accordance with the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Plan (RPP-WTP-QA-001, QAP)*. Work was performed to the quality requirements of NQA-1-1989 Part I, *Basic and Supplementary Requirements*, NQA-2a-1990, Part 2.7 and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD)* as applicable. These quality requirements are implemented through the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Manual (RPP-WTP-QA-003, QAM)*. The requirements of

^(a) HDI is PNNL’s system for managing the delivery of laboratory-level policies, requirements, and procedures.

DOE/RW-0333P Rev 13, *Quality Assurance Requirements and Descriptions (QARD)* and 10 CFR 830 Subpart A were not required for this work.

RPP-WTP addresses internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with RPP-WTP's procedure QA-RPP-WTP-604. This review procedure is part of PNNL's *RPP-WTP Quality Assurance Manual* (RPP-WTP-QA-003). Following this procedure, a technical review would verify that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the objectives.

Key analytes in the laboratory control sample (LCS) and PEP control sample were plotted over time to look for anomalies. The PEP control sample is a project-provided material generated from material very similar to the initial simulant feed. In general, the plots constructed to date associated with the inductively coupled plasma (ICP) and ion chromatography (IC) analyses of solutions show recoveries within limits of 80% to 120%.

R&T Test Conditions

The R&T test conditions as defined in the Test Specification, are summarized in Table S.5. The R&T test conditions for the entire PEP testing program are provided with discussion limited to the R&T test conditions covered by the scope of this report (those conditions not relevant to this report are shaded in gray).

Table S.5. R&T Test Conditions

| List R&T Test Conditions | Were Test Conditions Followed? |
|---|---|
| General Requirements | |
| Perform mass balances for selected constituents; including aluminum, chromium, manganese, sodium, hydroxide, oxalate, phosphate, sulfate, and water to evaluate leaching and washing process performance. | Yes. Chromium mass balance is discussed in the Results section for Integrated Tests A (Tank T01A/B caustic leaching and B (Tank T02A caustic leaching). Mass balances for the remaining components are discussed in report WTP-RPT-197. |
| Evaluate ultrafilter performance (to include visual inspection of the filter tubes, tube sheets, and heads from an ultrafilter for any evidence of flow mal-distribution and/or solids buildup or evidence of potential failure). | This R&T test condition is discussed in report WTP-RPT-197. |
| Assess the blending achieved during in-line additions of leaching and washing solutions. | In-line addition of wash water during Integrated Tests A and B are assessed in report WTP-RPT-187 and are fully discussed in report WTP-RPT-197. |
| Record any solids accumulations observed during any operating stage or maintenance evolution (e.g., photography, particle size distribution). | This R&T test condition is discussed in report WTP-RPT-197. |
| Leaching Operations | |
| Maintain caustic leaching temperature at the required setpoint and record steam usage to remain in the temperature range. | This R&T test condition is discussed in report WTP-RPT-186 and WTP-RPT-197. |

Table S.5. R&T Test Conditions

| List R&T Test Conditions | Were Test Conditions Followed? |
|--|---|
| Maintain oxidative leaching temperature at the required setpoint. | Yes. The average temperature during oxidative leaching in the PEP was maintained at the required setpoint although the temperature deviated during the first hour due to heat generated with the addition of the permanganate. The temperature during oxidative leaching in the bench-scale tests exceeded 25°C and ranged from 26°C (end of test) to 31.5°C (beginning) but an acceptable range was not provided. The initial temperature increase is due to heat generated with the addition of the permanganate. Cooling capability at the bench-scale was not available. Additional discussion on this R&T test condition is provided in WTP-RPT-197. |
| Obtain periodic samples during the leaching operations to monitor the amount of aluminum or chromium that has dissolved and concentrations of the reactants and products in the liquid fraction in the vessel. | Yes. The required samples for Cr leaching were obtained and are discussed in the Results section for Integrated Tests A (Tank T01A/B caustic leaching) and B (Tank T02A caustic leaching). Additional information on this R&T test condition is discussed in reports WTP-RPT-186 and WTP-RPT-197. |
| Provide data to demonstrate the WTP process control strategy for the caustic and permanganate addition. | This R&T test condition is discussed in report WTP-RPT-197. |
| Measure the rheology of the slurry simulant and shear strength of the settled solids prior to and following each leaching unit operation. | This R&T test condition is discussed in report WTP-RPT-197. |
| Concentration Operations | |
| Monitor the permeate production rate of each ultrafilter assembly in operation. | This R&T test condition is discussed in reports WTP-RPT-185, the individual run reports, and report WTP-RPT-197. |
| Record operating time of each ultrafilter assembly. | This R&T test condition is discussed in report WTP-RPT-197. |
| Record each ultrafilter assembly ‘cleaning’ event (backpulse, flush, chemical cleaning, etc.). | This R&T test condition is discussed in report WTP-RPT-197. |
| Confirm pulse-pot operation and backpulse operation strategies. | This R&T test condition is discussed in report WTP-RPT-197. |
| Control ultrafiltration temperature, transmembrane pressure, and slurry flow as specified in test specific run sheets. | This R&T test condition is discussed in report WTP-RPT-185, the run reports for each individual tests, and WTP-RPT-197. |
| Collect and retain permeate samples for extended precipitation studies (including permeate/simulated supernatant blended cases) from each concentration cycle. | Samples were collected and retained for extended precipitation studies. The results of the precipitation studies are discussed in WTP-RPT-197, WTP-RPT-200, and WTP-RPT-205. |
| Demonstrate WTP ultrafiltration system control scheme in normal operating modes (e.g., fill and startup, operation, backpulsing, flush and drain, cleaning and return to service). | This R&T test condition is discussed in report WTP-RPT-197. |
| Washing Operations | |

Table S.5. R&T Test Conditions

| List R&T Test Conditions | Were Test Conditions Followed? |
|---|---|
| Wash slurries using a washing protocol to be specified in test specific run sheets. | This R&T test condition is discussed in report WTP-RPT-187 and WTP-RPT-197. |
| Sample permeate immediately before each wash solution addition to monitor washing performance/efficiency. | This R&T test condition is discussed in report WTP-RPT-187 and WTP-RPT-197. |
| Measure rheology of the washed solids. | This R&T test condition is discussed in report WTP-RPT-187 and WTP-RPT-197. |

Simulant Use

PEP process testing was performed with a nonradioactive aqueous slurry of simulant waste chemicals and solids. The simulant composition and make-up recipe were provided by WTP as documented in *Simulant Recommendation for Phase 1 Testing in the Pretreatment Engineering Platform*.^(a) Aqueous chemical concentrations were within ranges expected for waste feeds to the PTF except for the hydroxide, oxalate, and phosphate anions. The hydroxide concentration was approximately one standard deviation from the average concentration expected in the feeds to the plant. The oxalate and phosphate components were at their respective solubility limits. The solids components and blend were selected to obtain targeted solids mass loss (aluminum and chromium leaching and oxalate washing) and treatment time. The simulant was not selected to represent any particular Hanford tank waste type.

The simulant was blended from the components listed below. The basis for selecting the individual components and comparison to actual waste behavior is provided where applicable in the indicated references:

- Boehmite (for Al) (Russell et al. 2009a)
- Gibbsite (for Al) (Russell et al. 2009b)
- Chrome oxyhydroxide (CrOOH) slurry (Rapko 2007)
- Sodium oxalate
- Filtration simulant (Russell et. al. 2009c)
- Supernate.

Because the high-temperature caustic leaching was found to dissolve significant amounts of the CrOOH solids, a separate chromium solids simulant was prepared and added to the PEP process after post-caustic-leach washing (a non-prototypic addition) in Integrated Tests A and B. In Integrated Test D the chromium solids component of the simulant was added to the feed to demonstrate the PTF permanganate addition strategy.

Simulant was procured from NOAH Technologies Corporation (San Antonio, TX). Samples of each simulant batch were characterized to make certain that chemical and physical properties requirements were met. Batches of the simulant were procured as follows:

(a) PS Sundar. 2008. *Simulant Recommendation for Phase 1 Testing in the Pretreatment Engineering Platform*. 24590-PTF-RT-08-006 Rev. 0, Bechtel National, Inc., Richland, Washington.

- A 15-gallon trial batch of the blended simulant for laboratory testing to demonstrate the efficacy of the simulant fabrication procedure.
- A 250-gallon scale-up batch of the blended simulant to demonstrate scale-up of the simulant fabrication procedure to an intermediate scale.
- Batches 0, 1, and 2, each nominally 3500 gallons, of blended simulant for the PEP Shakedown/Functional tests and PEP Integrated Tests A and B. These batches did not contain the CrOOH component.
- Batch 3, nominally 1200 gal, for Integrated Test D. This batch contained the CrOOH solids component.
- The CrOOH solids slurry for the Shakedown/Functional Test and Integrated Tests A and B was obtained in two separate batches containing nominally 18 and 36 kg of Cr as CrOOH.

Discrepancies and Follow-On Tests

Follow-on testing has occurred in the PEP Integrated Test D, where the Cr portion of the simulant was added at the beginning of the test and so experienced both caustic-leach and oxidative-leach conditions. These results are analyzed and reported in WTP-RPT-197 (PEP testing summary report).

1.0 Introduction

Pacific Northwest National Laboratory (PNNL) has been tasked by Bechtel National Inc. (BNI) on the River Protection Project-Hanford Tank Waste Treatment and Immobilization Plant (RPP-WTP) project to perform research and development activities to resolve technical issues identified for the Pretreatment Facility (PTF). The Pretreatment Engineering Platform (PEP) was designed, constructed, and operated as part of a plan to respond to issue M12, “Undemonstrated Leaching Processes.”^(a) The PEP is a ¹/_{4.5}-scale test platform designed to simulate the WTP pretreatment caustic leaching, oxidative leaching, ultrafiltration solids concentration, and slurry washing processes. The PEP replicates the WTP leaching processes using prototypic equipment and control strategies. The PEP also includes non-prototypic ancillary equipment to support the core processing.

Two operating scenarios are currently being evaluated for the ultrafiltration process (UFP) and leaching operations. The first scenario has caustic leaching performed in the UFP-2 ultrafiltration feed vessels (i.e., vessel UFP-VSL-T02A in the PEP; and vessels UFP-VSL-00002A and B in the WTP PTF). The second scenario has caustic leaching conducted in the UFP-1 ultrafiltration feed preparation vessels (i.e., vessels UFP-VSL-T01A and B in the PEP; vessels UFP-VSL-00001A and B in the WTP PTF).

In both scenarios, 19-M sodium hydroxide solution (NaOH, caustic) is added to the waste slurry in the vessels to dissolve solid aluminum compounds (e.g., gibbsite, boehmite). Caustic addition is followed by a heating step that uses direct steam injection to accelerate the leaching process. Following the caustic-leach, the vessel contents are cooled using vessel cooling jackets and/or external heat exchangers. The main difference between the two scenarios is that for leaching in UFP-1, the 19-M NaOH is added to unconcentrated waste slurry (3- to 8-wt% solids), while for leaching in UFP-2, the slurry is concentrated to nominally 20-wt% solids using cross-flow ultrafiltration before adding caustic.

For wastes that have significantly high chromium content, the caustic leaching and slurry dewatering is followed by adding sodium permanganate to UFP-VSL-T02A, and the slurry is subjected to oxidative leaching at nominally ambient temperature. The purpose of the oxidative leaching is to selectively oxidize the poorly alkaline-soluble Cr(III) believed to be the insoluble form in Hanford tank sludge to the much more alkaline-soluble Cr(VI), e.g., chromate.

The PEP testing program was conducted under Test Plan TP-RPP-WTP-506, Rev. 0.4^(b) with a waste simulant that was developed in response to Task 5 from the M-12 External Flowsheet Review Team (EFRT) issue response plan.^(a) The testing included the following tests with simulated Hanford tank waste:

- Shakedown/Functional testing: Tested process operations (e.g., slurry transfers, steam heating of the vessels and the accumulation of condensate, filter backpulsing and flushing), process controls (e.g., transmembrane pressure and axial flow velocity in the filter-loop), certain test functions (e.g., in-line slurry sampling accuracy and precision).

(a) SM Barnes and R Voke. 2006. “Issue Response Plan for Implementation of External Flowsheet Review Team (EFRT) Recommendations - M12: Undemonstrated Leaching Process.” 24590-WTP-PL-ENG-06-0024 Rev. 0, Bechtel National Inc., Richland, Washington.

(b) GB Josephson, OP Bredt, JK Young, and DE Kurath. 2009. *Test Plan for Pretreatment Engineering Platform (PEP) Testing (Phase I)*. TP-RPP-WTP-506, Rev. 0.4, Pacific Northwest National Laboratory, Richland, Washington.

- Integrated Test A: Demonstrated integrated processing when caustic leaching (98°C) is performed in UFP-VSL-00001A/B (PEP equivalent: UFP-VSL-T01A&B) with the Cr simulant component added after the post-caustic-leach washing step.
- Integrated Test B: Demonstrated integrated processing when the caustic leaching (98°C) is performed in UFP-VSL-00002A (PEP equivalent: UFP-VSL-T02A) with the Cr simulant component added after the post-caustic-leach washing step.
- Integrated Test D: Demonstrated integrated processing when the caustic leaching is performed at a lower temperature (85°C) in UFP-VSL-00002A (PEP equivalent: UFP-VSL-T02A) and with the Cr simulant component added to the initial batch of simulant.

Integrated Test C was deleted from the scope of the testing (ICN-TP-RPP-WTP-506_R0.2).

The work described in this report provides the test results that are related to the efficiency of the oxidative leaching process to support process modeling based on tests performed with a Hanford waste simulant. The tests were completed both at the laboratory-bench scale and in the PEP. The purpose of this report is to summarize the results from both scales that are related to oxidative leaching chemistry to support the development of a scale factor for the submodels to be used in the G2 model, which predicts WTP operating performance. The PEP test data to be included in this report are limited to those from Integrated Tests A (Tank T01A/B caustic leaching) and B (Tank T02A caustic leaching). Whether caustic leaching is carried out in UFP-VSL-T01A/B (Integrated Test A) or UFP-VSL-T02A (also referred to as Tank T02A) (Integrated Test B), all oxidative leaching processes occur in Tank T02A.

2.0 Quality Assurance

The PNNL Quality Assurance Program is based upon the requirements as defined in the U.S. Department of Energy (DOE) Order 414.1C, *Quality Assurance* and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A—*Quality Assurance Requirements* (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, *Requirements for Quality Assurance Programs for Nuclear Facilities*.
- ASME NQA-1-2000, Part II, Subpart 2.7, *Quality Assurance Requirements for Computer Software for Nuclear Facility Applications*.
- ASME NQA-1-2000, Part IV, Subpart 4.2, *Graded Approach Application of Quality Assurance Requirements for Research and Development*.

The procedures necessary to implement the requirements are documented through PNNL’s “How Do I ...?” (HDI) system.^(a)

PNNL implements the RPP-WTP quality requirements by performing work in accordance with the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Plan (RPP-WTP-QA-001, QAP)*. Work was performed to the quality requirements of NQA-1-1989 Part I, *Basic and Supplementary Requirements*, NQA-2a-1990, Part 2.7 and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD)* as applicable. These quality requirements are implemented through the *River Protection Project – Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Manual (RPP-WTP-QA-003, QAM)*. The requirements of DOE/RW-0333P Rev 13, *Quality Assurance Requirements and Descriptions (QARD)* and 10 CFR 830 Subpart A were not required for this work.

RPP-WTP addresses internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with RPP-WTP’s procedure QA-RPP-WTP-604. This review procedure is part of PNNL’s *RPP-WTP Quality Assurance Manual (RPP-WTP-QA-003)*. Following this procedure, a technical review would verify that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the objectives.

Key analytes in the laboratory control sample (LCS) and PEP control sample were plotted over time to look for anomalies. The PEP control sample is a project-provided material generated from material very similar to the initial simulant feed. In general, the plots constructed to date associated with the inductively coupled plasma (ICP) and ion chromatography (IC) analyses of solutions show recoveries within limits of 80% to 120%.

^(a) HDI is PNNL’s system for managing the delivery of laboratory-level policies, requirements, and procedures.

3.0 Experimental Approach

This section provides an overview of the PEP process description as well as the experimental approach for the oxidative leaching tests conducted in the PEP and bench-scale equipment.

3.1 PEP Process Description

The pretreatment processes of interest include caustic leaching, oxidative leaching, and all ultrafiltration processes. The purpose of these processes is to concentrate radioactive waste solids from various blended feeds, leach (dissolve) specific nonradioactive components (i.e., Na, Al, Cr, P, S, C₂O₄) that limit high-level waste glass loading, and separate soluble species from the high-level waste (HLW) solids by washing. Feed can include HLW, low-activity waste (LAW), and Feed Evaporation Process (FEP) concentrates. The integrated processes produce concentrated high-level radioactive solids, low-sodium wash solutions that are returned to the FEP, and high-sodium solutions that are sent forward to the cesium ion-exchange process.

The PEP was designed to perform an engineering-scale demonstration of the WTP slurry wash, caustic leaching, oxidative leaching and ultrafiltration processes. The unit operations tested included solids washing, chemical reagent addition and blending, heating, cooling, leaching, cross-flow filtration, and filter cleaning. A simplified flow diagram of the PEP system is shown in Figure 3.1.

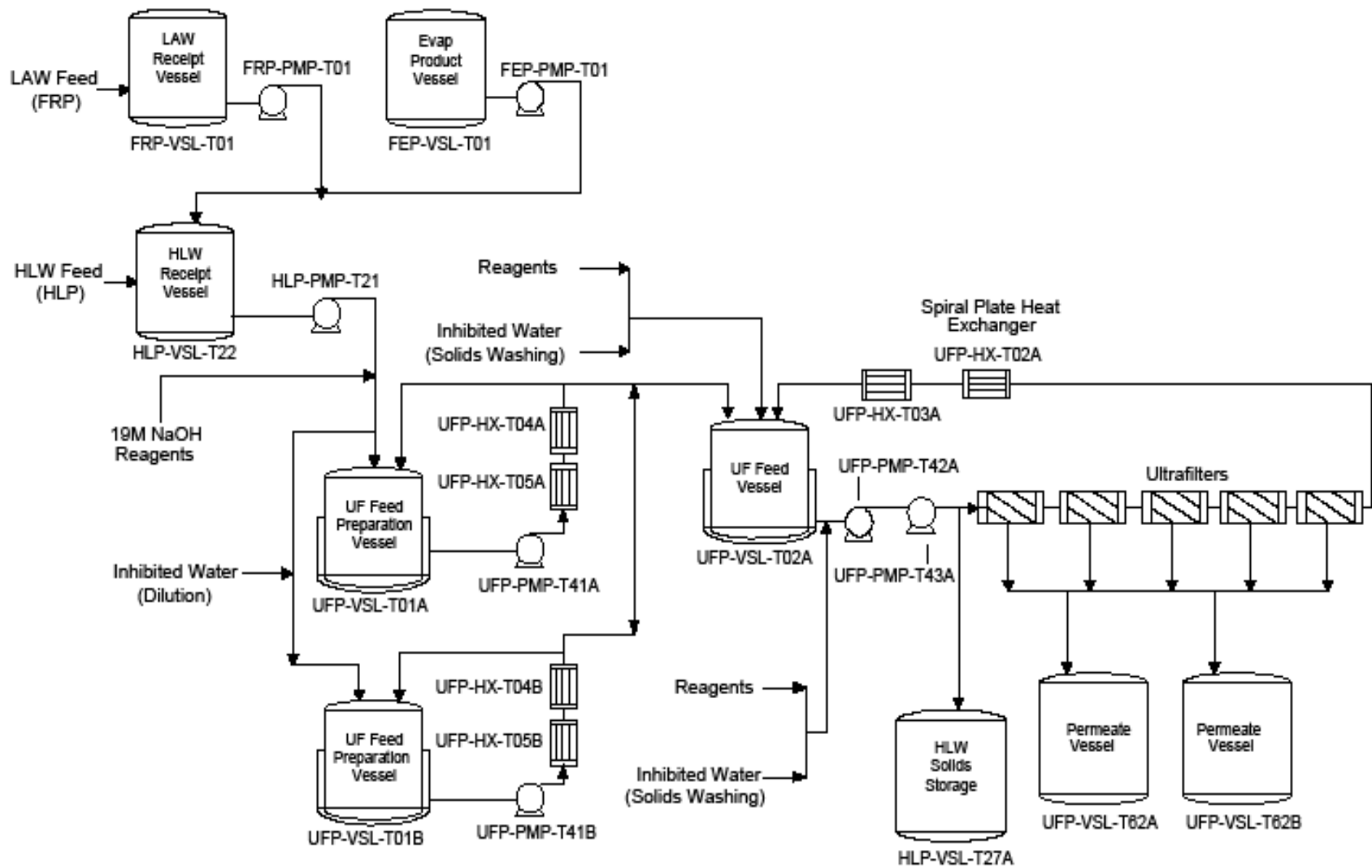


Figure 3.1. PEP Simplified Flow Diagram

Two operating scenarios are currently being evaluated for the UFP system. The first scenario has the caustic leaching performed in the ultrafiltration feed vessel (UFP-VSL-T02A). The second scenario has caustic leaching conducted in the ultrafiltration feed preparation vessels (UFP-VSL-T01A/B). The different flowsheets for these two scenarios are shown in Figure 3.2. The effects of oxidative alkaline leaching in both scenarios were evaluated by the testing covered in this report.

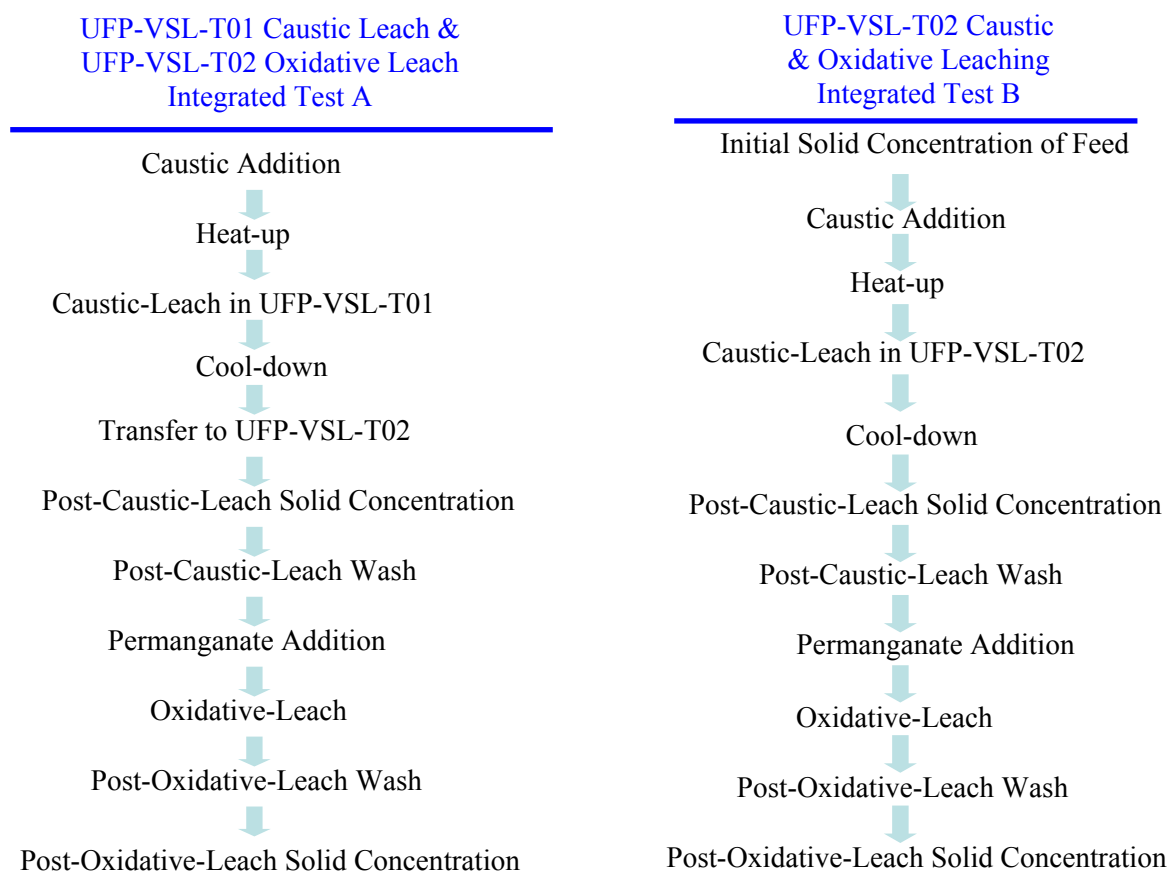


Figure 3.2. Caustic- and Oxidative-Leach and Ultrafilter Operations

3.2 PEP Oxidative-Leach

Following the post-caustic-leach wash shown in Figure 3.2, oxidative-leach process in Integrated Tests A and B proceeded similarly.

First, a chromium oxyhydroxide slurry was added in-line. The slurry was then dewatered, and the slurry was washed to reduce the OH^- to a targeted concentration of ≈ 0.25 M. During these washing steps, antifoam agent (AFA) was added periodically. Following washing of the Cr-containing slurry, a sample of the slurry was taken for use in the bench-scale oxidative leaching tests (described below). Then, the oxidative-leach was begun by adding nominally 1 M NaMnO_4 upstream of the filter-loop pumps at the prototypic ratio of $(\text{NaMnO}_4 \text{ addition rate})/(\text{filter-loop flow rate})$, until the target of approximately 1 mole of permanganate/mole of chromium had been added to the system. To complete the oxidative leaching, the slurry was continuously pumped through the filter-loop at approximately the

prototypic flow rate and mixed with the pulse jet mixers for 6 hr at a targeted temperature of 25°C. PJMs were operated to match the planned PTF nozzle velocities and cycled at 4.5 times the rate as planned in the PTF. The specific PEP experimental test conditions for oxidative leaching during Integrated Tests A and B are summarized in the Results section.

Slurry samples (typically 40- to 45-mL) for oxidative leaching were collected every hour or 6 hours using the in-tank sampling system shown in Figure 3.3. Samples were obtained with the sample loop in recirculation mode with slurry returned to the vessel. To obtain a sample, a valve was used to divert the entire flow to the sample bottle. The sampling valve and line were purged before each sample to confirm that there was no cross contamination with previous sampling events. Samples for this test were taken at the lowest height at the outer position, 16.4 inches from the center (88% of total radius) and 11 inches from the center-bottom of the dished tank bottom. The slurry samples were quickly (≈ 10 min) separated in a centrifuge into liquid and wet solids fractions for analysis.

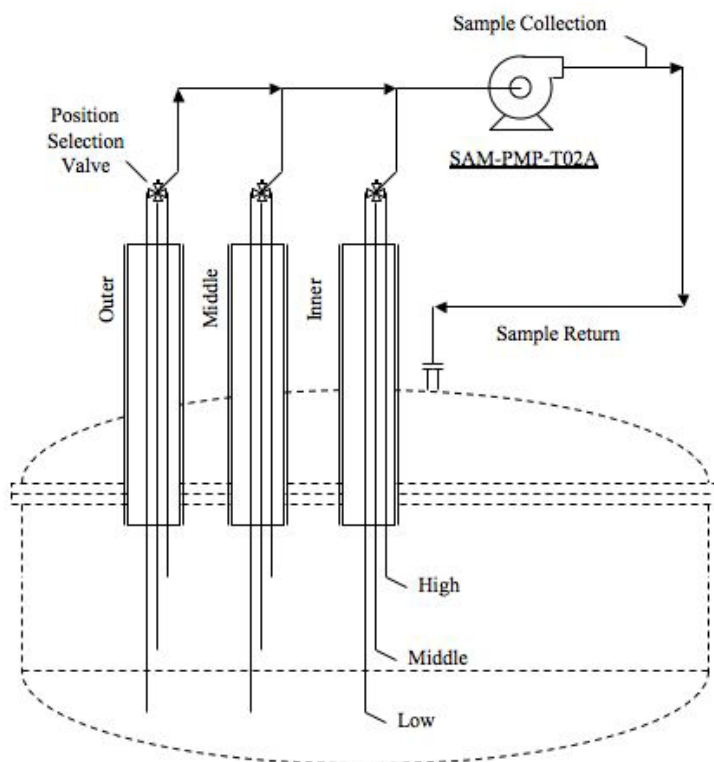


Figure 3.3. In-Tank Sampling, Showing the Three Radial Positions at Three Heights and Sampling Flow Loop. Oxidative leaching samples were obtained from the outer-low position.

Analyses were performed at Southwest Research Institute (SwRI) unless otherwise indicated. Solids samples were submitted for metals analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Slurry samples were submitted for analysis of density, metals content, and wt% undissolved solids (UDS). Supernatant samples were submitted for metals content, anions content, and free hydroxide concentration (the last performed by PNNL's Analytical Support Operations [ASO]).

3.3 Bench-Scale Oxidative-Leach

For the purposes of scale-up, the bench-scale testing was performed once under Integrated Test A (Tank T01A/B caustic leaching) conditions and using Integrated Test A simulant and once under Integrated Test B (Tank T02A caustic leaching) conditions using Integrated Test B simulant. Slurry was sampled from UFP-VSL-T02A (as described above) immediately before the permanganate reagent was used.

The bench-scale oxidative leaching tests were carried out with roughly 700-g batches of the PEP simulant within a covered 1-L reaction vessel made of polymethylpentene (PMP). The system's temperature was controlled by electrical resistance wrap heaters to maintain $25 \pm 1^\circ\text{C}$ and was continuously mixed at 120 rpm with an overhead stir motor. Approximately 90 grams of 1 M NaMnO_4 was added to the stirred reaction vessel during each test.

Before and immediately after adding 1 M NaMnO_4 , two 30-mL analytical samples of the initial slurry were obtained, with one sample being washed and the other sample remaining unaltered. The slurry sample washing was completed using three equal volumes of 0.01 M NaOH; mixing and centrifuging were performed each time to separate and decant the wash solution. In addition, a third sample was recovered to obtain an initial supernate sample. This 6-mL slurry sample was filtered through a 0.45- μm syringe filter to separate the solids from the desired supernate.

Additional 6-mL analytical samples were taken and filtered using a 0.45- μm filter each hour over the 8 hours of reaction, timed from the initial addition of 1 M NaMnO_4 . At the end of the test, two more 30-mL slurry analytical samples were obtained. Again, one sample was washed and the other remained unaltered.

Analyses were performed at SwRI unless otherwise indicated. Solids samples were submitted for metals analysis by ICP-OES. Slurry samples were submitted for analysis of density, metals content, and wt% UDS. Supernatant samples were submitted for metals content, anions content, and free hydroxide concentration (the last performed by PNNL's ASO).

3.4 Relationship of PEP to Plant Performance

The PEP was designed to achieve prototypic oxidative leaching performance in Tank T02A by employing the following design features:^(a)

1. The PEP ultrafiltration feed vessel Tank T02A is dimensionally prototypic, with inlet and outlet nozzles and primary internal structures (e.g., PJMs) also sized and located prototypically.
2. Mixing equipment in Tank T02A is prototypic: PJMs and PJM nozzles, the filter-loop return nozzle, and the air sparge mixing tubes are scaled and located to achieve prototypic mixing.
3. The in-line NaMnO_4 reagent addition inlet is prototypically located at the inlet of PMP-T42A.

PEP design limitations, such as Tank T01A/B internal support structures that were not prototypic, are assumed here to be of minor importance to prototypic performance.

The operation of the PEP to achieve prototypic oxidative leaching is based on guidelines given in *Technical Basis for Scaling Relationships for the Pretreatment Engineering Platform* (Kuhn et al. 2008)

(a) B Stiver. 2007. *Functional Requirements for Pretreatment Engineering Platform (PEP)*, 24590-PTF-3YD-UFP-00002 Rev. 1, Bechtel National Incorporated, Richland, Washington.

and *PEP Process Description*,^(a) and specific directions are given in the Test Plan *Pretreatment Engineering Platform (PEP) Testing (Phase I)*.^(b) Key elements are:

1. The location of NaMnO_4 reagent addition and the ratio of (in-line reagent addition rate)/(slurry feed rate) should match that of the PTF. Reagent should be added to the filter-loop upstream of PMP-T42A to achieve similar blending to the PTF.
2. Prototypic mixing for the non-Newtonian slurry during the leach is best achieved by adjusting PJM parameters and the filter-loop flow rate to match the planned nozzle velocities of the PTF. This results in greater mixing of the slurry than in the PTF, but was deemed necessary to maintain the prototypic PJM mixing cavity in the non-Newtonian slurry.
3. Prototypic air sparge mixing from the air sparge tubes and steam-ring air purge should match the power/volume ratio of the PTF. 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 steam-ring air sparge flow rate was chosen to match the power/volume ratio of the PTF at about 39 in. or 60% of the normal batch depth in Tank T02A. Regions below this will receive somewhat less mixing than in the PTF, and regions above this will receive somewhat more mixing than the PTF.
4. Slurry levels in Tank T02A should be prototypic of the PTF because mixing can be a function of fluid depth.

Provided these operational parameters are generally satisfied, the oxidative leaching results should be reasonably prototypic of the PTF.

(a) S Lehrman. 2008. *Pretreatment Engineering Platform (PEP) Phase I Testing Process Description*. 24590-WTP-RPT-PET-07-002, Rev. 1, Bechtel National Incorporated, Richland, Washington.

(b) G Josephson, O Bredt, J Young, and D Kurath. 2008. *Pretreatment Engineering Platform (PEP) Testing (Phase I)*. TP-RPP-WTP-506 Rev 0.4, Pacific Northwest National Laboratory, Richland, Washington.

4.0 Results

4.1 Starting Slurry Composition

Table 4.1 shows the composition of the slurry in UFP-VSL-T02A just before permanganate was added.^(a)

Table 4.1. Key Analytes in Initial Slurry Composition (uncertainty equals 1 standard deviation)

| Analyte | Integrated Test A | | Integrated Test B | |
|----------------------|-------------------|--------------------------------|-------------------|--------------------------------|
| | Slurry | Liquid Phase | Slurry | Liquid Phase |
| | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ |
| Al | 42870 \pm 836 | 71.7 \pm 1.3 | 42881 \pm 834 | 189 \pm 3 |
| Ca | 1068 \pm 23 | 2.9 \pm 0.3 ^(a) | 1279 \pm 25 | 2.5 \pm 0.3 ^(a) |
| Cr | 7429 \pm 144 | 23.2 \pm 0.3 | 7394 \pm 144 | 17.8 \pm 0.2 |
| Fe | 34592 \pm 676 | 14.7 \pm 1.0 | 37365 \pm 728 | 6.8 \pm 0.5 |
| Mg | 734 \pm 15 | 5.5 \pm 0.6 ^(a) | 767 \pm 15 | 5.0 \pm 0.5 ^(a) |
| Mn | 7416 \pm 145 | 0.74 \pm 0.03 | 8235 \pm 905 | 0.61 \pm 0.03 |
| Na | 9843 \pm 122 | 9674 \pm 148 | 10966 \pm 137 | 10856 \pm 148 |
| Nd | 859 \pm 17 | 0.248 \pm 0.004 | 889 \pm 17 | 0.112 \pm 0.002 |
| Sr | 415 \pm 8 | 0.32 \pm 0.03 ^(a) | 320 \pm 6 | 0.25 \pm 0.03 ^(a) |
| Cs | 0.68 \pm 0.05 | 0.53 \pm 0.01 | 1.09 \pm 0.06 | 0.68 \pm 0.01 |
| Nitrite | n/a | 70 \pm 9 | n/a | 93 \pm 9 |
| Nitrate | n/a | 3617 \pm 64 | n/a | 3757 \pm 66 |
| Phosphate | n/a | 201 \pm 9 | n/a | 81 \pm 8 |
| Sulfate | n/a | 33 \pm 3 | n/a | 55 \pm 3 |
| Free Hydroxide (M) | n/a | 0.26 \pm 0.01 | n/a | 0.28 \pm 0.01 |
| wt% UDS | 18.7 \pm 0.1 | n/a | 17.0 \pm 0.1 | n/a |
| Density (g/mL) | 1.147 \pm 0.005 | 1.035 \pm 0.007 | 1.071 \pm 0.005 | 1.015 \pm 0.005 |
| Wt% H ₂ O | 79.4 \pm 0.1 | 98.1 \pm 0.1 | 80.8 \pm 0.1 | 97.8 \pm 0.1 |

(a) At least one of the triplicate values contained in this average value was at or below the detection limit.

The Cr shown in Table 4.1 was not exposed to caustic leaching in PEP Integrated Test A (Tank T01A/B caustic leaching) and Integrated Test B (Tank T02A caustic leaching), but rather came from an in-line addition of a chromium oxyhydroxide slurry to Tank T02A.

As summarized in Table 4.1, the major components of the slurry are Al, Fe, Na, Mn, and Cr, with Al and Fe being the major constituents. It is also clear from Table 4.1 that, as expected, given that these solids were well washed before sampling, that the bulk of these major components (with the exception of Na) are present in the solid phase, as their corresponding liquid phase concentrations are orders of magnitude lower than that in the solid phase. Excluding the target of oxidative leaching, Cr, these major components, with the possible exception of Mn and hydroxide, all would be expected to be inert to the presence of permanganate.

As with the slurry, most of the major components in the liquid phase—Na, nitrate and hydroxide--also should be inert with respect to the presence of permanganate. It also should be noted that

(a) A complete reporting of the analytical results will be provided in the PEP run reports: WTP-RPT-191 (Integrated Test A run report) and WTP-RPT-192 (Integrated Test B run report).

the initial free hydroxide concentrations for oxidative leaching in both Integrated Tests A (0.26 M) and B (0.28 M) are close to their targeted initial concentration of 0.25 M.

4.2 PEP Experimental Process Conditions

A summary and comparison of the process conditions used in PEP Integrated Tests A and B is presented below in Table 4.2 (Integrated Test A) and Table 4.3 (Integrated Test B).

Table 4.2. Integrated Test A PEP Experimental Parameters

| Process Step | Quantity | Target Value UFP-2 Leach | Range of Measured Values Integrated Test A | Value in Range? |
|------------------------------|--|--------------------------|--|-----------------|
| Sodium Permanganate Addition | Gallons of Cr simulant to add after washing | 144 ± 1 | 145 | yes |
| | Permanganate reagent concentration (M) | 1 | 1.06 | n/a |
| | Permanganate reagent volume (endpoint) gal | 38.1 ± 0.3 | 37.2 | no |
| | Permanganate reagent addition rate (gpm) | 5.0 ± 3 | 5.09 | yes |
| | Filter-loop flow rate (gpm) | 109 ± 10 | 114 ^(b) | yes |
| | Tank T02A pulse jet mixer (PJM) jet velocities (m/sec) | 12 ± 0.6 | 12.1 | yes |
| | Tank T02A PJM stroke length (%) | 80 ± 5 | 83 | yes |
| | Tank T02A PJM cycle time (sec) | 20 ± 1 | 20.8 | yes |
| | Upper sparger trickle flow rate (scfm) | 0.30 (0 ^(a)) | 0 | n/a |
| | Lower spargers trickle flow rate (scfm) | 1.19 (0 ^(a)) | 1.13 to 1.25 | n/a |
| | Steam ring purge air flow rate (scfm) | 4.17 (0 ^(a)) | 0 | n/a |
| | System temperature (°C) | 25 ± 2 | 24.9 to 27.7 | no |
| Oxidative-Leach | Leach temperature (°C) | 25 ± 2 | 24.4 to 27.8 | no |
| | Leaching duration (endpoint) (hr) | 6(-0.1,+0.5) | 6 | yes |
| | Final Tank T02A slurry volume (estimate) gal | 227 | 228 | n/a |
| | Filter-loop slurry volume (gal) | 82 | 82 | n/a |
| | Filter-loop flow rate (gpm) | 109 ± 10 | 89 ^(b) | no |
| | Tank T02A PJM jet velocities (m/sec) | 12 ± 0.6 | 12.1 | yes |
| | Tank T02A PJM stroke length (%) | 80 ± 5 | 82 | yes |
| | Tank T02A PJM cycle time (sec) | 20 ± 1 | 20.8 | yes |
| | Upper sparger trickle flow rate (scfm) | 0.30 (0 ^(a)) | 0 | n/a |
| | Lower spargers trickle flow rate (scfm) | 1.19 | 1.18 | n/a |
| | Steam ring purge air flow rate (scfm) | 4.17 (0 ^(a)) | 0 | n/a |
| | System temperature (°C) | 25 ± 2 | 24.9 to 27.4 | no |

(a) Reduced due to air entrainment issues.

(b) All filter-loop flow rates taken from flowmeter FT-0635.

Table 4.3. Integrated Test B PEP Experimental Parameters (UFP-VSL-T02 leaching)

| | | Target Value | Range of Measured Values | Value in Range? | |
|---|---|-----------------------------------|--------------------------|---------------------|-----|
| | | UFP-2 Leach | Integrated Test B | | |
| Sodium | Gallons of Cr simulant to add after washing | 81.2 | 82.7 | n/a | |
| Permanganate Addition | Permanganate reagent concentration (M) | 1 | 1.06 | n/a | |
| | Permanganate reagent volume (endpoint) gal | 20.9 ± 0.3 | 20.9 | yes | |
| | Permanganate reagent addition rate (gpm) | 5 ± 3 | 5.22 | yes | |
| | Filter-loop flow rate (gpm) | 88 ± 10 | 86 to 89 ^(b) | yes | |
| | Tank T02A PJM jet velocities (m/sec) | 12 ± 0.4 | 11.7 | yes | |
| | Tank T02A PJM stroke length (%) | 80 ± 5 | 70 | no | |
| | Tank T02A PJM cycle time (sec) | 20 ± 1 | 20.2 | yes | |
| | Upper sparger trickle flow rate (scfm) | 0.30 (0 ^(a)) | 0 | n/a | |
| | Lower spargers trickle flow rate (scfm) | 1.19 (0 ^(a)) | 0 | n/a | |
| | Steam ring purge air flow rate (scfm) | 4.17 (0 ^(a)) | 0 | n/a | |
| | System temperature (°C) | 25 ± 2 | 22.6 to 26.0 | no | |
| | Oxidative-Leach | Leach temperature | 25 ± 2 | 21.6 to 26.0 | no |
| | | Leaching duration (endpoint) (hr) | 6(-0.1, +0.5) | 6 | yes |
| | | Filter-loop flow rate (gpm) | 88 ± 10 | 92.4 ^(b) | yes |
| Tank T02A PJM jet velocities (m/sec) | | 12 ± 0.4 | 12.1 | yes | |
| Tank T02A PJM stroke length (%) | | 80 ± 5 | 83 | yes | |
| Tank T02A PJM cycle time (sec) | | 20 ± 1 | 20.8 | yes | |
| Upper sparger trickle flow rate (scfm) | | 0.30 (0 ^(a)) | 0 | n/a | |
| Lower spargers trickle flow rate (scfm) | | 1.19 (0 ^(a)) | 0 | n/a | |
| | Steam ring purge air flow rate (scfm) | 4.17 (0 ^(a)) | 0 | n/a | |

(a) Reduced due to air entrainment issues.

(b) All filter-loop flow rates taken from flowmeter FT-0635.

Neither the PEP nor the bench-scale testing documentation revealed any operational issues. The lower-than-targeted filter-loop flow rates in both Integrated Tests A and B should reduce the amount of jet mixing in Tank T02A and potentially reduce oxidation reaction rates. However, the rapid and complete oxidation of chromium (as described below) indicates that these deviations do not interfere with the goals of oxidative leaching. The lack of air sparging during Integrated Test B would not be expected to be significant because air sparging is conducted only to mix the upper region of Tank T02A, and the slurry level in Tank T02A during Integrated Test B was quite low. At the corresponding slurry level, the PTF would use air sparge and steam-ring purge flow rates just sufficient to keep waste from filling up the spargers and steam ring.

4.2.1 Temperatures During PEP Oxidative Leaching

The PEP temperature profile in Tank T02A during oxidative leaching is summarized in Figure 4.1.

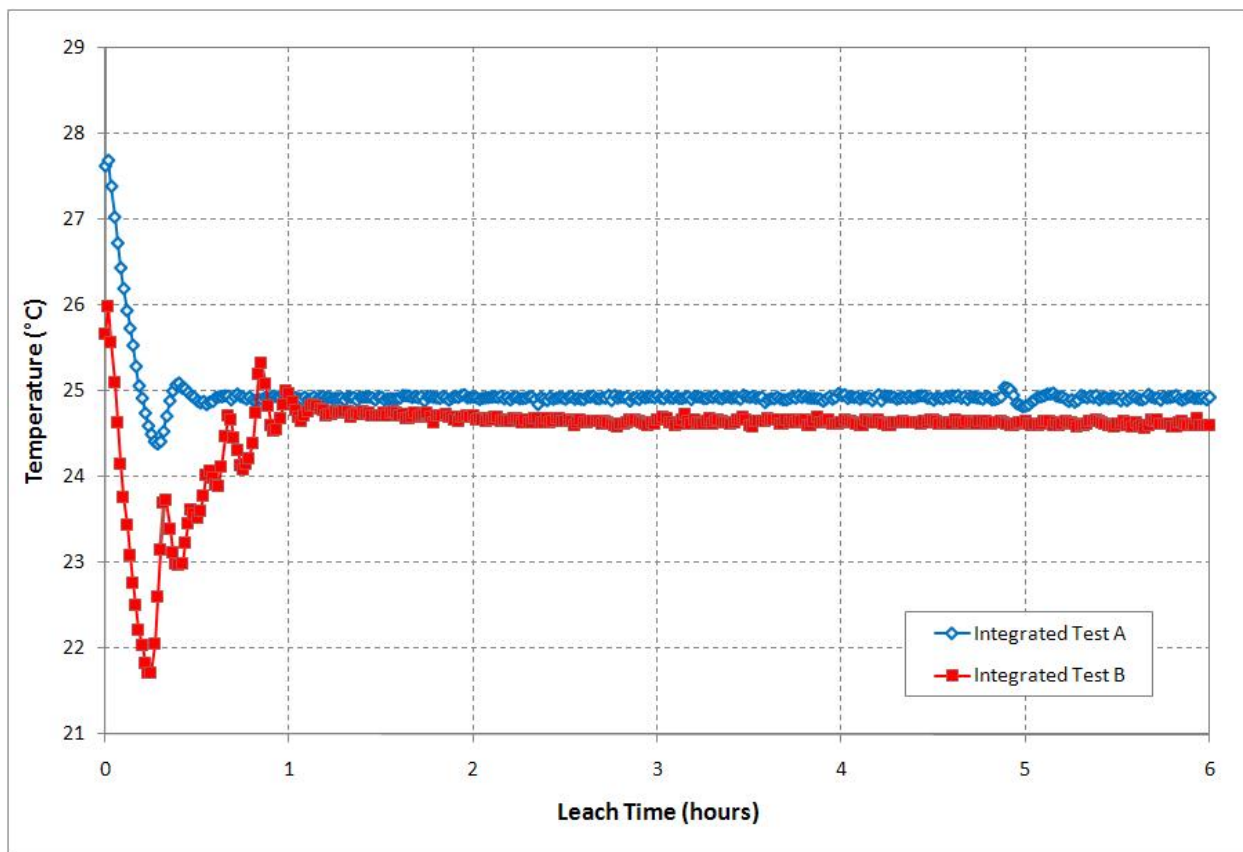


Figure 4.1. Prototypic Temperatures in Tank T02A During Oxidative Leaching of Integrated Tests A and B

The temperature behavior in Tank T02A is similar in both Integrated Tests A and B. An initial temperature increase of several degrees C is observed, presumably because of the heat of mixing of 1 M permanganate with the slurry and/or, more likely, the heat of reaction of permanganate with the Cr in the slurry (see section 4.2.3). Then a decrease in temperature occurs, which overshoots the targeted temperature of 25°C, followed by an increase in temperature to the targeted 25°C, which then remains essentially constant for the remainder of the 6-hour reaction time. Most of the temperature oscillations that occur do so over the first hour of reaction time.

4.2.2 Temperatures During Oxidative Leaching Bench-Scale Testing A and B

The bench-scale temperature profile in the reaction vessel during oxidative leaching is summarized in Figure 4.2.

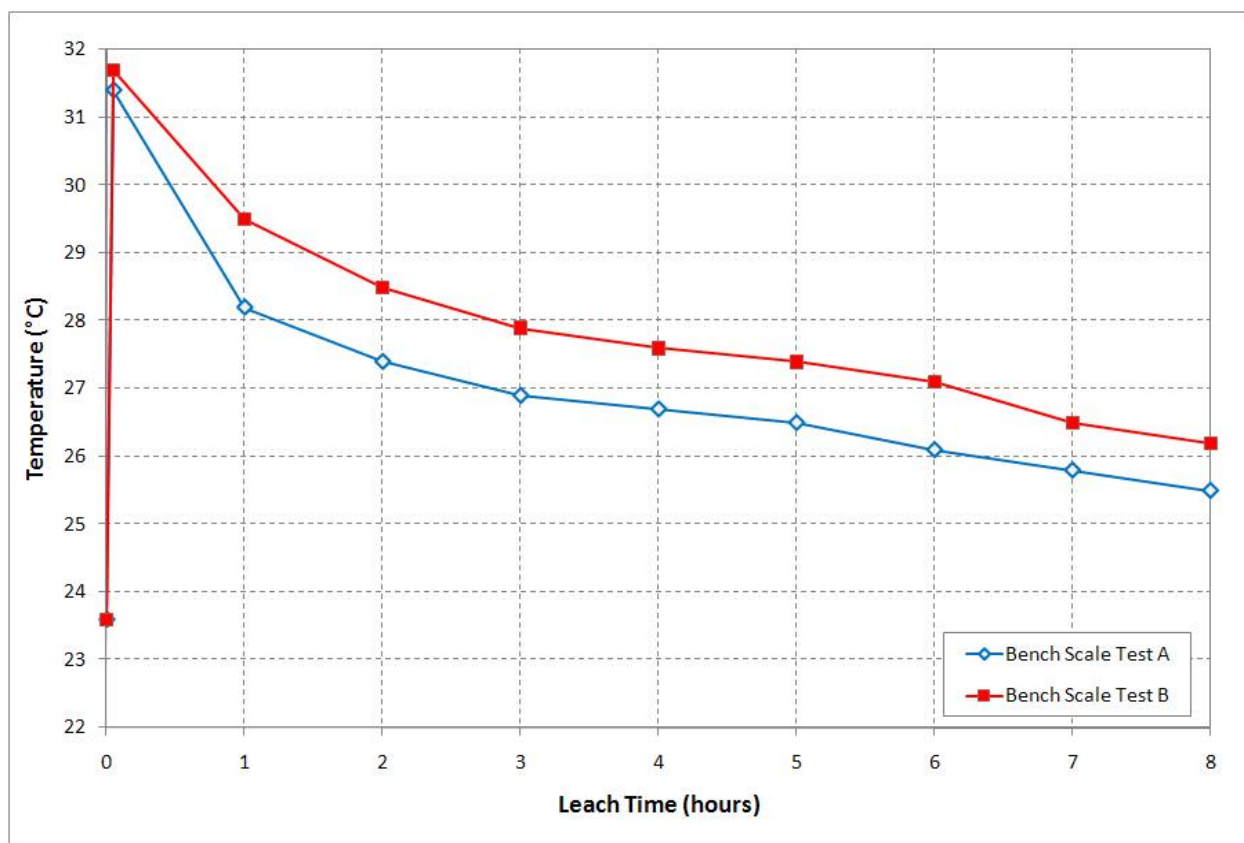


Figure 4.2. Bench-Scale Test Temperatures During Oxidative Leaching of Integrated Tests A and B

The temperature profile for the bench-scale tests shows the same initial temperature spike of several degrees that was observed during the Integrated testing, presumably for the same reasons as noted above. What differs from the Integrated testing is that in the bench-scale tests, after the initial temperature spike, the temperature slowly decays towards, but never reaches, ambient temperature over the 6-hour reaction time for oxidative leaching. This difference between PEP and bench-scale testing temperature behavior is presumably caused by the differences in cooling between the two experiments—active cooling being available in PEP, with only passive cooling available in the bench-scale tests.

4.2.3 Initial Permanganate to Chromium Ratios

The reaction of permanganate with Cr(III) can be expressed in the following equation:



The molar stoichiometry for permanganate to oxidize all of the Cr(III) is 1. The reaction is exothermic,^(a) with a standard state reaction enthalpy, ΔH , of -119.9 KJ/mol, which may have led to difficulties in maintaining temperature control at the targeted 25°C as noted in Section 4.2.1. Table 4.4 summarizes the stoichiometry of permanganate to Cr based on the total mass of Cr in the test and the amount of

(a) Data for enthalpy calculation taken from: DD Wagman, WH Evans, VB Parker, RH Schumm, I Halow, SM Bailey, KL Churney, and RL Nuttall. 1982. "The NBS Tables of Chemical Thermodynamic Properties." *Journal of Physical and Chemical Reference Data*. Volume 11, Supplement 2.

permanganate added. Using the stoichiometry in Equation 4.1, we should expect maximum Cr leach factors of 0.97 for Integrated Test A (Tank T01A/B caustic leaching) oxidative leaching and 0.98 for Integrated Test B (Tank T02A caustic leaching) oxidative leaching.

Table 4.4. Mn:Cr Experimental Ratio

| Experiment | Moles MnO_4^- | Moles Cr | MnO_4^-/Cr |
|--------------------|------------------------|----------|----------------------------|
| Integrated Test A | 149.6 | 153.7 | 0.97 |
| Bench-Scale Test A | 0.084 | 0.083 | 1.01 |
| Integrated Test B | 83.5 | 84.9 | 0.98 |
| Bench-Scale Test B | 0.087 | 0.093 | 0.93 |

4.3 Results – Cr Leach Factors

4.3.1 Methods for Calculating Cr Oxidative-Leach Factors

Oxidative-leach factors for Cr were calculated using two different methods: total Cr mass changes in the initial and final solids (see Equation [4.2] and [4.3]) and an implied mass balance based on the measured Cr inventory in the supernatant as compared to the initial amount of Cr present (Equation [4.4] and [4.5]).

The specific data needed for leach factor calculations are identified in the equations below. Each method has two equations. The first describes how the leach factor was calculated using information from the PEP tests, and the second describes how the leach factor was calculated using information from the bench-scale tests.

Method 1 calculates the Cr leach factor based on change in inventory of Cr in the solid phase. For the PEP tests,

$$f_{Cr,1} = 1 - \frac{m_{CrS}}{m_{CrS,0}} = 1 - \frac{V_B \rho_B f_{cs} c_{Cr,cs}}{V_{B,0} \rho_{B,0} f_{cs,0} c_{Cr,cs,0}} \quad (4.2)$$

and for the bench-scale tests,

$$f_{Cr,1} = 1 - \frac{m_{CrS}}{m_{CrS,0}} = 1 - \frac{m_s \left(\frac{\omega_s}{\omega_{rs}} \right) c_{Cr,rs} \left(\frac{m_{s,0}}{m_s} \right)}{m_{s,0} \left(\frac{\omega_{s,0}}{\omega_{rs,0}} \right) c_{Cr,rs,0}} = 1 - \frac{\left(\frac{\omega_s}{\omega_{rs}} \right) c_{Cr,rs}}{\left(\frac{\omega_{s,0}}{\omega_{rs,0}} \right) c_{Cr,rs,0}} \quad (4.3)$$

where

- $f_{Cr,1}$ = Cr leach factor using Method 1
- m_{CrS} = mass of Cr in the solid phase at time t
- $m_{CrS,0}$ = initial mass of Cr in the solid phase
- V_B = volume of the process slurry at time t
- $V_{B,0}$ = initial volume of the process slurry
- ρ_B = density of process slurry at time t
- $\rho_{B,0}$ = initial density of the process slurry

- ω_{cs} = weight fraction of centrifuged solids (mass of centrifuged solids/mass of slurry) at time t
- $\omega_{cs,0}$ = initial weight fraction of centrifuged solids
- $c_{Cr,cs}$ = concentration of Cr in the centrifuged solids at time t
- $c_{Cr,cs,0}$ = initial concentration of Cr in the centrifuged solids
- m_s = mass of the slurry at time t
- $m_{s,0}$ = initial mass of the slurry
- ω_s = weight fraction of undissolved solids in the slurry
- $\omega_{s,0}$ = initial weight fraction of undissolved solids in the slurry
- ω_{rs} = weight fraction of undissolved solids in the rinsed wet solids
- $\omega_{rs,0}$ = initial weight fraction of undissolved solids in the rinsed wet solids
- $c_{Cr,rs}$ = concentration of Cr in the rinsed solids at time t
- $c_{Cr,rs,0}$ = initial concentration of Cr in the rinsed solids

Differences in equation 4.2 and 4.3 occur because different quantities were measured in each test configuration. Note that the quantities $c_{Cr,cs}$ and $c_{Cr,rs}$ listed above are measuring the same thing. They had been given different subscripts to associate them with corresponding weight fractions, which are measuring different quantities (ω_{cs} vs. ω_{rs}). The mass of slurry in PEP is calculated using the volume and density of the process slurry, whereas in the bench-scale tests it was measured directly. In the PEP testing, the concentration of Cr is scaled to a slurry basis using the fraction of the sample that was centrifuged solids. In the bench-scale tests, the UDS of the slurry and the rinsed wet solids are used to scale the Cr concentration. An additional correction is necessary in the bench-scale test expression to account for removal of sample mass, which cannot be neglected. A simple ratio is used to place the mass of slurry at time t on the same basis as the original slurry (at t = 0). The use of a ratio is a simplification that is justified because the Cr is leached almost completely within the first few minutes.

Method 2 calculates the Cr leach factor using the initial amount of Cr in the solid phase and the change in the Cr liquid phase concentration. For the PEP tests,

$$f_{Cr,2} = \frac{m_{CrL} - m_{CrL,0}}{m_{CrS,0}} = \frac{V_B \rho_B (1 - \omega_s) c_{CrL} - V_{B,0} \rho_{B,0} (1 - \omega_{s,0}) c_{CrL,0}}{V_{B,0} \rho_{B,0} c_{Cr,cs,0} \omega_{cs,0}} \quad (4.4)$$

and for the bench-scale tests,

$$\begin{aligned} f_{Cr,2} &= \frac{m_{CrL} - m_{CrL,0}}{m_{CrS,0}} = \frac{\left(\frac{m_{s,0}}{m_s}\right) m_s (1 - \omega_s) c_{CrL} - m_{s,0} (1 - \omega_{s,0}) c_{CrL,0}}{m_{s,0} c_{Cr,rs,0} \left(\frac{\omega_{s,0}}{\omega_{rs,0}}\right)} \\ &= \frac{(1 - \omega_s) c_{CrL} - (1 - \omega_{s,0}) c_{CrL,0}}{c_{Cr,rs,0} \left(\frac{\omega_{s,0}}{\omega_{rs,0}}\right)} \end{aligned} \quad (4.5)$$

where

- $f_{Cr,2}$ = Cr leach factor using Method 2
- m_{CrL} = mass of Cr in the liquid phase at time t
- $m_{CrL,0}$ = initial mass of Cr in the liquid phase

$$\begin{aligned}
c_{CrL} &= \text{concentration of Cr in the liquid phase at time } t \\
c_{CrL,0} &= \text{initial concentration of Cr in the liquid phase}
\end{aligned}$$

The same differences observed in equations 4.2 and 4.3 also appear in equations 4.4 and 4.5. The liquid phase concentrations consist of both the supernate concentration and the rinsate concentration at the initial and final sample points. The liquid phase concentrations at intermediate leaching times are the supernate concentration only. Note that the leach factors are calculated with the same denominator, and since it is expected that $m_{CrL} - m_{CrL,0} = m_{CrS,0} - m_{CrS}$, the two leach factors are equivalent.

Each method has its own advantages. Method 1 is more straightforward and is similar to previous calculations of Cr leach factors; however, it requires sampling and analyzing the Cr solids every time the leach factor is calculated. Method 2 is more complex, but calculation of intermediate leach factors is simpler because only the liquid phase needs to be sampled and analyzed.

4.3.2 Results from Cr Oxidative-Leach Factor Calculations

The results from both the PEP and bench-scale testing are summarized in Figure 4.3 and Table 4.5, which shows the leach factor calculated by Method 2 as a function of leach time, readily suggest four conclusions that can be drawn about the oxidative-leach. First, the final Cr leach factors are all 0.85 or greater. Second, by the time the initial samples are collected, the reaction appears to be essentially over, with the final leach factors unchanged from those obtained after only a few minutes of reaction time. This factor implies that the mixing in both the PEP and bench-scale tests must allow for contact of the permanganate with the Cr solids almost immediately. Third, there is essentially no difference between the Cr leach factors obtained from PEP and bench-scale testing. Fourth, there is essentially no difference between the leach factors calculated from Integrated Test A (Tank T01A/B caustic leaching) and Integrated_Test B (Tank T02A caustic leaching). The Cr leach factor could only be calculated via Method 1 at 5 min and the end of the leach, so the Method 1 leach factors are not presently graphically.

The summarized data in Table 4.5 shows a comparison of all the final leach factors calculated by both methods. The leach factors evaluated by Method 2 are slightly lower, with broader 95% confidence bands, than the Method 1 leach factors. However, they are all in good agreement with one another.

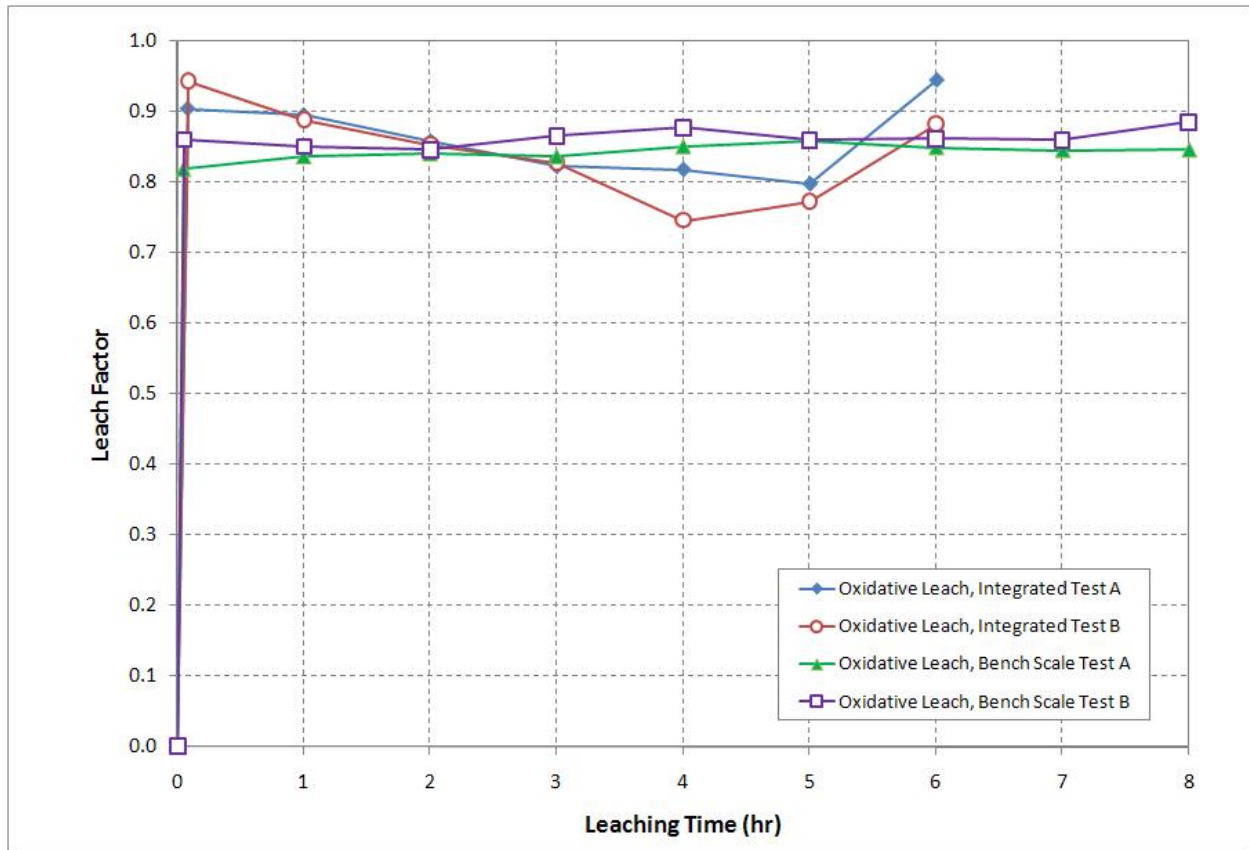


Figure 4.3. Cr Leach Factors as a Function of Time (hours) for the PEP and Bench-Scale Integrated Tests A and B as Calculated by Method 2

Table 4.5. Final Cr Leach Factors for the PEP (6-hr contact time) and Bench-Scale Integrated Tests A and B (8-hr contact time) as Calculated by Methods 1 and 2 (95% confidence range in parenthesis)

| Method # | Cr Leach Factor – Integrated Test A | Cr Leach Factor – Bench-Scale Integrated Test A | Cr Leach Factor – Integrated Test B | Cr Leach Factor – Bench-Scale Integrated Test B |
|----------|-------------------------------------|---|-------------------------------------|---|
| 1 | 0.94 (0.94 – 0.95) | 0.91 (0.90 – 0.92) | 0.91 (0.90 – 0.91) | 0.93 (0.92 – 0.94) |
| 2 | 0.95 (0.90 – 1.00) | 0.85 (0.73 – 0.97) | 0.88 (0.83 – 0.94) | 0.89 (0.77 – 1.01) |

A possible concern involves the leaching of Cr, with the corresponding consumption of permanganate from the Cr present in the stainless steel of the leach vessel. To address this concern, a mass-balance calculation was performed, comparing the total initial amount of Cr as determined by initial sample analysis with the amount of Cr present in the leach liquid and residual solids at the conclusion of oxidative leaching. The results of this comparison are summarized in Table 4.6. The good agreement in mass balance for both Integrated Tests A and B indicates that the added Cr is the sole source for leached Cr during oxidative leaching.

Table 4.6. Mass Summary of Cr for Oxidative Leaching in Integrated Tests A and B

| Test | Leach Time | Mass Cr in Solids (g) | Mass Cr in Liquids (g) | Total Mass Cr (g) ^(a) | % Difference |
|------|------------|-----------------------|------------------------|----------------------------------|--------------|
| A | 0 | 8798 | 22 | 8820 | -- |
| A | 6 | 495 | 8338 | 8833 | 0.15 |
| B | 0 | 4282 | 9 | 4290 | -- |
| B | 6 | 397 | 3789 | 4186 | -2.51 |

(a) Round-off errors may lead to slightly different values for sums versus individual components as written.

Based on the agreement between the leach factors from PEP testing and bench-scale testing for both Integrated Test A and Integrated Test B, the scale-up factor for bench-scale testing is unity.

5.0 Summary and Conclusions

A comparison was made between the Cr leach factors found for PEP Integrated Tests A and B and bench-scale testing using the same simulant and same permanganate-to-Cr ratios. The following observations were made:

- No significant operational issues were reported during any of the oxidative-leach testing.
- The actual permanganate:chromium ratios used in these tests were all close to the targeted ratio of 1.
- Two methods were used to calculate leach factors: one method was based on comparison between the initial and final mass of Cr in the residual solids, and a second method compares the amount of Cr dissolved in the leachate with the total mass of Cr present in the initial solids.
- The kinetic behavior observed with respect to the Cr leach factors indicates that the rate of Cr oxidative dissolution is extremely fast for the Cr(III) form used in the simulant. For both the bench-scale and PEP test, the fraction of dissolved Cr reached its final value within a few minutes of permanganate contact time.
- Consistent with a rapid, exothermic reaction, an initial increase in slurry temperature was observed upon permanganate addition to the Cr slurry. The superior temperature control in the PEP allows for more rapid cooling (returning to the target temperature within 1 hour of leaching) than with the bench-scale testing (return to the initial temperature not observed after conclusion [8 hours] of leaching).
- The fraction of Cr removed by oxidative leaching gives a leach factor of approximately 0.9 regardless of the test and regardless of test scale. This allows a key conclusion to be made—namely, that the scale-up factor from bench-scale oxidative leaching to PEP scale testing is 1.
- Test conditions specified to allow direct application of PEP results to PTF performance (i.e., prototypic performance) were met, so the scale-up of bench-scale results to the PTF is 1.

6.0 References

Kuhn WL, ST Arm, JL Huckaby, DE Kurath, and SD Rassat. 2008. *Technical Basis for Scaling Relationships for the Pretreatment Engineering Platform*. WTP-RPT-160, PNNL-16948, Pacific Northwest National Laboratory, Richland, Washington.

Rapko BM, GJ Lumetta, JR Deschane, and RA Peterson. 2007. *Process Development for Permanganate Addition During Oxidative Leaching of Hanford Tank Sludge Simulants*. WTP-RPT-164, PNNL-16794, Pacific Northwest National Laboratory, Richland, Washington.

Russell R, H Smith, R Peterson, D Rinehart, P Aker, and E Buck. 2009a. *Development and Characterization of Boehmite Component Simulant*. WTP-RPT-184, PNNL-18176, Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, RA Peterson, DE Rinehart, and HD Smith. 2009b. *Development and Characterization of Gibbsite Component Simulant*. WTP-RPT-176, PNNL-18013, Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, JM Billing, RA Peterson, DE Rinehart, and HD Smith. 2009c. *Development and Demonstration of Ultrafiltration Simulants*. WTP-RPT-183, PNNL-18090, Pacific Northwest National Laboratory, Richland, Washington.

Distribution

No. of
Copies

No. of
Copies

OFFSITE

ONSITE

1 Pacific Northwest National Laboratory
(authors will be notified electronically)

| | |
|---------------------------|--------|
| BM Rapko | P7-25 |
| PP Schonewill | P7-25 |
| CF Brown | P7-22 |
| PW Eslinger | K6-52 |
| MS Fountain | P7-27 |
| JL Huckaby | H4-02 |
| BD Hanson | P7-27 |
| TS Hausmann | Sequim |
| DE Kurath | K3-52 |
| MJ Minette | P7-25 |
| Information Release (pdf) | |

| | |
|------------------|-------|
| Project File (1) | K3-52 |
|------------------|-------|

2 Bechtel National Inc

| | |
|--------------|-------|
| WTP R&T Docs | H4-02 |
| SM Barnes | H4-02 |



Pacific Northwest
NATIONAL LABORATORY

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnl.gov



U.S. DEPARTMENT OF
ENERGY