PNNL-18701
WTP-RPT-201, Rev 0

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

Simulated Waste for Leaching and Filtration Studies—Laboratory Preparation Procedure

HD Smith
RL Russell
RA Peterson

October 2009

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

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

PNNL-18701
WTP-RPT-201, Rev 0

Simulated Waste for Leaching and Filtration Studies—Laboratory Preparation Procedure

HD Smith
RL Russell
RA Peterson

October 2009

Test Specification: 24590-PTF-TSP-RT-06-006, Rev 0
Test Plan: TP-RPP-WTP-469, Rev 0.2
Test Exceptions: 24590-WTP-TEF-RT-07-00008
R&T focus area: Pretreatment
Test Scoping Statement: None

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-06-006, Rev 0 and Test Plan TP-RPP-WTP-469, Rev. 0.2. The work followed the quality assurance requirements outlined in the Test Specification and Test Plan. The descriptions provided in this 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 has been reviewed and verified.

Approved:

DE Kurath for GHB — 10/27/09

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

Contents

Figures

Tables

Abbreviations and Acronyms

AV	axial velocity
BNI	Bechtel National Inc.
COA	certificate of analysis
CUF	cells unit filter
DIW	de-ionized water
DOE	U.S. Department of Energy
EFRT	External Flowsheet Review Team
HLW	high-level waste
IC	ion chromatography
ICP	inductively coupled plasma
IRP	issue response plan
LAW	low-activity waste
OES	optical emission spectroscopy
PEP	Pretreatment Engineering Platform
PNNL	Pacific Northwest National Laboratory
PSD	particle-size distribution
PTF	Pretreatment Facility
QA	quality assurance
QAM	Quality Assurance Manual
QAP	quality assurance program
QARD	Quality Assurance Requirements and Description (document)
REDOX	reduction-oxidation
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project

R&T	research and technology
SBMS	Standards-Based Management System
SIPP	Semi-Integrated Pilot Plant
SOW	statement of work
SWRI	Southwest Research Institute
TEM	transmission electron microscopy
UDS	undissolved solids
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray diffraction
TMP	transmembrane pressure—psid
TS	total solids

Testing Summary

This report discusses the simulant preparation procedure for producing multi-component simulants for leaching and filtration studies, including development and comparison activities in accordance with the Test Plan[a] prepared and approved in response to the Test Specification 24590-WTP-TSP-RT-06-006, Rev 0 (Smith 2006). A fundamental premise is that this approach would allow blending of the different components to simulate a wide variety of feeds to be treated in the Hanford Tank Waste Treatment and Immobilization Plant (WTP). For example, a given feed from the planned feed vector could be selected, and the appropriate components would then be blended to achieve a representation of that particular feed. Using the blending of component simulants allows the representation of a much broader spectrum of potential feeds to the Pretreatment Engineering Platform (PEP).

Objectives

The test objectives for the work addressed in TP-RPP-WTP-469, Rev 0.2 are summarized in Table S.1 along with a discussion of how the objectives were met. The overall objective of the work from the Test Plan described in this report was to develop, validate, and prepare a simulant preparation procedure.

Table S.1. Test Objectives from TP-RPP-WTP-469, Rev 0.2

Test Objective	Objective Met? (Y/N)	Discussion
1) Develop and characterize a gibbsite component simulant for testing aluminum leaching and provide a basis for the selected simulant.	Y	This objective was addressed in report WTP-RPT-176, Rev 0 and is briefly summarized in Section 3.4 of this report.
2) Develop and characterize a boehmite component simulant for testing aluminum leaching and provide a basis for the selected simulant.	Y	This objective was addressed in report WTP-RPT-184, Rev 1 and is summarized in this report.

(a) RL Russell and HD Smith. 2007. "Test Plan for the Development and Demonstration of Leaching and Ultrafiltration Simulants." TP-RPP-WTP-469, Rev 0.2, Pacific Northwest National Laboratory, Richland, Washington.

Table S.1. Test Objectives from TP-RPP-WTP-469, Rev 0.2

Test Objective	Objective Met? (Y/N)	Discussion
3) Develop and characterize inert ultrafiltration component simulant(s) for testing the ultrafiltration system and provide a basis for the selected simulant(s), which may include high and low viscosity simulants. Also, methods to adjust the filtration behavior will be tested in an attempt to develop simulants with various compositions to accurately show the variation in filter flux.	Y	This objective was addressed in report WTP-RPT-183, Rev 0 and is summarized in this report.
4) Provide a blended simulant procedure for use in Phase 1 integrated demonstration unit testing and demonstrate that the behavior of the blended components is equivalent (or correlated) with the behavior of the individual components. The Phase 1 integrated demonstration waste simulant will possess characteristic chemical components and physical properties of a representative waste that would be processed in the WTP as identified from the External Flowsheet Review Team (EFRT) issue M4 resolution team.	Y	This objective was addressed in report WTP-RPT-183, Rev 0 and is summarized in this report.
5) Evaluate available data to identify other potential candidate simulants that may be necessary to be developed during Stage 2 of the simulant development work for full evaluation of the leaching/ultrafiltration performance. This would be due to the identification of an additional physical or chemical property that was found to be fundamental to the process.	N	Insufficient information is available at this time to complete this activity. WTP has evaluated some potential additional simulants for testing, but this information has not been developed to the point where a recommendation regarding potential candidate simulants could be made.

Test Exceptions

The Test Exception is described in Table S.2.

Table S.2. Test Exceptions

Test Exception Number	Description of Test Exception
24590-WTP-TEF-RT-07-00008	This Test Exception was received from Bechtel National Inc. (BNI) on November 12, 2007. The Test Plan[(a)] only allowed for a single test to validate the performance of a blended simulant composition for use in the PEP for process demonstration. This test was carried out at a filtration temperature of 45°C, as was the oxidative leaching operation. However, the filtration temperature in the PEP during process demonstration remained undecided between 45°C and 25°C. Filtration at 45°C could potentially lead to post-precipitation of phosphates and other soluble salts if the solution is cooled to 25°C before being transferred to the permeate collection vessels UFP-62A/B/C and the subsequent ion-exchange feed vessel CXP-01. Therefore, a second test to validate the blended simulant composition for the PEP process demonstration was performed at 25°C with the results of these tests discussed in report WTP-RPT-183, Rev 0 (Russell et al. 2009c).

ICN-TP-RPP-WTP-469_R0.01 - The concentrations in Tables 6.3 and 6.4 were found to be incorrect due to an error in the SRNL report that these amounts were taken from. These two tables were updated to contain the correct concentrations of these chemicals.

Results and Performance Against Success Criteria

This work meets the first of the Success Criteria described in the Test Plan. How this success criterion was met is listed in Table S.3.

(a) RL Russell and HD Smith. 2007. “Test Plan for the Development and Demonstration of Leaching and Ultrafiltration Simulants.” TP-RPP-WTP-469, Rev 0.2, Pacific Northwest National Laboratory, Richland, Washington.

Table S.3. Results and Performance Against Success Criteria of the Test Plan

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
1. Develop proceduralized recipes that document each simulant (boehmite, gibbsite, and ultrafiltration) per “Guideline for R&T Simulant Development, Approval, Validation, and Documentation.”	Suitable commercial products were identified for a gibbsite simulant component based on the physical properties and a boehmite simulant component based on the dissolution rate. These are described in Appendices B and C. The ultrafiltration simulant preparation procedure was modeled after that of Zamecnik et al. (2004) for the Hanford Tank Waste AY-102/C-106 waste and then modified to fit the needs of the PEP. The preparation procedure for this component is given in Appendix A.
2. Develop a gibbsite simulant that has physical properties—in particular crystal size and habit—similar to that observed in prior actual waste samples and develop a correlation that predicts gibbsite simulant dissolution rate as a function of gibbsite properties such as crystal size and habit, as well as other physical properties.	This criterion is addressed in report WTP-RPT-176, Rev 0. and commented on in Section 3.4 this report.
3. Development of a boehmite simulant that has dissolution rate – in particular at 100ºC – similar to that observed in prior actual waste samples [13, 14] and the development of a correlation that predicts boehmite simulant dissolution rate as a function of system properties of crystal size, crystal habit, operating temperature, hydroxide concentration and mixing conditions.	This criterion is addressed in report WTP-RPT-184, Rev 1.
4. Development of inert (with respect to caustic and oxidative leaching) ultrafiltration simulant(s) that have filtration behavior that can be related to prior simulant testing [28] and actual waste testing [13, 14] where appropriate. The impact of simulant parameters – such as particle size, aging and preparation method – on filtration performance will be documented. In addition, correlation of filtration performance with other measured physical parameters – such as centrifuged solids and fines concentration will be developed. In particular, data will be obtained to allow adjustment of the centrifuged solids from 10 to 40-wt%. A laboratory scale crossflow ultrafiltration (CUF) system will be used for this performance assessment. The system will have technical specifications and operating conditions as nearly identical as experimentally practical to the system used in the actual waste filtration experiments.	This criterion is addressed in report WTP-RPT-183, Rev 0.

Table S.3. Results and Performance Against Success Criteria of the Test Plan

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
5. Provide Phase 1 integrated demonstration simulant makeup procedure.	This report describes the make up of the Phase 1 simulant that was processed in cold CUF runs and compares it with an actual waste that was also processed in identical CUF runs in RPL.
6. Documentation of the review of other potential candidate simulants that may be necessary to be developed during Stage 2 of the simulant development work and a recommendation with respect to which additional component simulants should be developed for a full evaluation of the leaching/ultrafiltration performance. This would be due to the identification of an additional physical or chemical property that was found to be fundamental to the process.	This criterion is not addressed in this report. To date, the only feature of concern is fouling, which has been flagged under follow-on testing and would be part of the Stage 2 work if considered serious enough when Stage 2 work is begun.

Quality Requirements

Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy (DOE) by Battelle under Contract DE-AC05-76RL01830. PNNL implements a quality assurance (QA) program that is based upon the requirements as defined in DOE Order 414.1C, “Quality Assurance,” and 10 CFR 830, “Energy/Nuclear Safety Management,” Subpart A—“Quality Assurance Requirements.” PNNL has chosen to implement the requirements of DOE Order 414.1C and 10 CFR 830, Subpart A by integrating them into the laboratory’s management systems and daily operating processes. The procedures necessary to implement the requirements are documented through the laboratory’s Standards-Based Management System (SBMS).

PNNL implemented the River Protection Project (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)*. These quality requirements were implemented through the River Protection Project–Waste Treatment Plant Support Program (RPP-WTP) Quality Assurance Manual (RPP-WTP-QA-003, QAM). All analytical services were provided by Southwest Research Institute (SWRI). The requirements of DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions (QARD),* were not required for this work.

A matrix that cross-references the NQA-1 and NQA-2a requirements with RPP-WTP’s procedures for this work is given in TP-RPP-WTP-509. It includes justification for those requirements not implemented. Experiments that were not method-specific were performed in accordance with RPP-WTP’s procedures QA-RPP-WTP-1101 “Scientific Investigations” and QA-RPP-WTP-1201 “Calibration and Control of Measuring and Testing Equipment” so that sufficient data were taken with properly calibrated measuring and test equipment to obtain quality results.

RPP-WTP addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNNL's procedure QA-RPP-WTP-604. This review verifies that the reported results were traceable, inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. This review procedure is part of PNNL's RPP-WTP QAM.

R&T Test Conditions

Please note that this report addresses only the procedure for preparing a small batch of the blended simulant in the laboratory as required by Section 7, Item 5, in the Test Specification 24590-PTF-TSP-RT-06-006, Rev 0.

The development and characterization of the individual simulant components were covered in a series of reports that have been published earlier and therefore are cited in Table S.4.

The various test conditions in Table S.4 have been included to provide the context and completion to the current report.

Table S.4. R&T Test Conditions from 24590-PTF-TSP-RT-06-006, Rev 0

List R&T Test Conditions	Were Test Conditions Followed?
1) Gibbsite Simulant Development— • Review the available literature and actual waste testing and characterization data. • Based on this review, target parameters for the proposed simulant will be developed. Note that the development of these criteria must also consider the requirements for scaled testing. It will likely be necessary to develop simulants with a range of parameters that can be adjusted to provide a scaled simulant for use in the integrated test platform. • Search available vendors and preparation methods to identify available sources of gibbsite materials. This review will include identifying available characterization data associated with each source material and will recommend which boehmite source materials should be obtained and tested. This recommendation should consider the diversity of both particle size and morphology in identifying candidate samples for additional testing. • Prepare and test the identified gibbsite source materials. It is anticipated that testing will involve multiple samples over a range of material properties, including particle size and morphology. At a minimum, the following properties will be measured for each gibbsite source material:	The simulant was developed and tested as a mixture of different components. Specific results for the gibbsite simulant component are discussed in WTP-RPT-176, Rev 0. A brief summary is given in Section 3.4 of this report.

Table S.4. R&T Test Conditions from 24590-PTF-TSP-RT-06-006, Rev 0

List R&T Test Conditions	Were Test Conditions Followed?
o Particle size. o Surface area. o Crystal pattern by X-ray diffraction (XRD). o Dissolution rate under a variety of fixed testing conditions measured under multiple conditions. Note that sufficient data must be obtained for selected samples to provide an adequate description of the reaction-rate equation. Further note that the temperature range should be sufficient to provide a range of behaviors. In addition, sufficient information, including density and water content, should be obtained to provide meaningful correlation to actual waste samples. o Equilibrium solubility under various test conditions. • A correlation will be developed to predict the dissolution rate as a function of other physical characteristics. In addition, a boehmite source—or blend of boehmite sources—will be selected to best meet the criteria defined in 1). These results will be compared against the simulant basis criteria, and an appropriate method to correlate simulant performance to actual waste performance will be documented.	
2) Boehmite Simulant Development— • Review the available literature and actual waste testing and characterization data. • Based on this review, target parameters for the proposed simulant that will be developed. Note that the development of these criteria must also consider the requirements for scaled testing. It will likely be necessary to develop simulants with a range of parameters that can be adjusted to provide a scaled simulant for use in the integrated test platform. • Search available vendors and preparation methods to identify available sources of boehmite materials. This review will include identifying available characterization data associated with each source material and will recommend which boehmite source materials should be obtained and tested. This recommendation should consider the diversity of both particle size and morphology in	The simulant was developed and tested as a mixture of different components. Specific results for the boehmite simulant component are discussed in WTP-RPT-184, Rev 1.

Table S.4. R&T Test Conditions from 24590-PTF-TSP-RT-06-006, Rev 0

List R&T Test Conditions	Were Test Conditions Followed?
identifying candidate samples for additional testing. - Prepare and test the identified boehmite source materials. It is anticipated that testing will involve multiple samples over a range of material properties, including particle size and morphology. At a minimum, the following properties will be measured for each boehmite source material: o Particle size. o Surface area. o Crystal pattern by XRD. o Dissolution rate under a variety of fixed testing conditions measured under multiple conditions. Note that sufficient data must be obtained for selected samples to provide an adequate description of the reaction-rate equation. Further note that the temperature range should be sufficient to provide a range of behaviors. In addition, sufficient information, including density and water content, should be obtained to provide meaningful correlation to actual waste samples. o Equilibrium solubility under various test conditions. - A correlation will be developed to predict the dissolution rate as a function of other physical characteristics. In addition, a boehmite source—or blend of boehmite sources—will be selected to best meet the criteria defined in 1). These results will be compared against the simulant basis criteria, and an appropriate method to correlate simulant performance to actual waste performance will be documented.	
3) Filtration Simulant Development— - Review the available literature and actual waste testing and characterization data. Based on this review, target parameters for the proposed simulant will be developed. - Search available preparation methods to identify available sources of filtration simulant materials. This review includes identifying available characterization data associated with each source material and will provide recommendations for which filtration source materials should be obtained and tested. This task also evaluates whether existing preparation methods should be	Results of filtration properties specific to the combination of the different simulant components are discussed in WTP-RPT-183, Rev 0.

Table S.4. R&T Test Conditions from 24590-PTF-TSP-RT-06-006, Rev 0

List R&T Test Conditions	Were Test Conditions Followed?
modified to meet the target parameters and whether selected components from various vendors/preparation methods should be blended for evaluation. • Prepare and test the identified filtration simulant source materials. It is anticipated that testing will involve multiple samples over a range of material properties.	

Simulant Use

Use of actual waste in PNNL's PEP is not possible due to safety, cost, and volume. Therefore, a simulant that was simple and chemically benign enough to assemble needed to be developed for use in the PEP testing. This simulant would be capable of covering a wide range of waste compositions and could be disposed of at a reasonable cost yet still be a realistic test material for PEP evaluation. The simulant that has been developed and is discussed in this report consists of a simplified version of actual waste sludge, which includes elements found in most wastes with additions of aluminum compounds, chromium oxide, phosphate, and sulfate as needed to match a given waste type. Hence, this waste simulant contains some of each of the waste components (i.e., aluminum compounds) that WTP is planning to remove from the high-level waste stream. As such, the simulant can be readily shimmed to target compositions needed for PEP testing while maintaining similar chemical and physical properties to the actual waste to be treated in the plant.

Discrepancies and Follow-on Tests

No discrepancies were observed in the simulant behavior from the requirements for its use in the PEP and as specified in Test Plan TP-RPP-WTP-469, Rev 0.2. However, additional studies are recommended in the following areas:

- Develop a better understanding of the mechanism for filter fouling so that future simulant formulations could appropriately mimic the fouling and cleaning behavior in the ultrafilter,
- Understanding of the causes for the differences in boehmite dissolution kinetics between the simulant and the actual waste, and
- Identification and development of a chromium simulant component that can mimic the behavior of chromium in the actual waste during caustic leaching operation.

1.0 Introduction

After separating the high-level waste (HLW) from the low activity waste (LAW) liquid stream by ultrafiltration in the Pretreatment Facility (PTF), the concentrated HLW will undergo caustic and oxidative leaching processes to dissolve and wash out materials that would otherwise limit HLW loading in the immobilized waste glass (aluminum, chromium, phosphates, and sulfates). The current design calls for the leaching processes to be carried out in the ultrafiltration process vessels (UFP-1A, UFP-1B, UFP-2A and UFP-2B). The concentrated HLW solids are sequentially caustic leached, washed, and oxidatively leached, if required, and then washed once more during pretreatment. The caustic leaching dissolves the aluminum in the HLW solids, while the oxidative leaching oxidizes the chromium with sodium permanganate ($NaMnO_4$) in a mild caustic solution. The HLW solids are concentrated after each leach and wash using the crossflow ultrafiltration system.

In October 2005, a team of experts from industry, national laboratories, and universities (referred to as the External Flowsheet Review Team or EFRT) was assembled by Bechtel National Inc. (BNI) to conduct a thorough and critical review of the process flowsheet for the design of the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Among the issues the EFRT identified from the critical review of the process flowsheet (Lucas 2006; CCN 132846 2006; CCN 132847 2006), the following is considered relevant to work reported here.

Issue M12: Neither the caustic leaching nor the oxidative leaching process has been demonstrated at greater than bench-scale size. The small-scale experiments are capable of defining the leaching chemistry. However, they are limited in their capability to predict the effectiveness of these processes without a scale-up demonstration.

Issue M13: For wastes requiring leaching, a combination of inadequate filter flux and area will likely limit throughput to the HLW or LAW vitrification facilities.

This report addresses a portion of the work required for the resolution of Issue M12. Filtration and leaching simulants were developed that can be used in the laboratory and in the integrated demonstration testing portion in Tasks 4 and 5 of the M-12 EFRT issue response plan (IRP) (Barnes and Voke 2006.) The requirements to define the simulant are specified in Section 3.3.3 of the IRP. This report provides important data needed to prepare a blended simulant to meet those performance targets.

2.0 Quality Assurance

The PNNL QA 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 Standards-Based Management System (SBMS).

PNNL implements the RPP-WTP quality requirements by performing work in accordance with the *River Protection Project—Hanford Tank Waste Treatment and Immobilization 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.

The 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) were plotted over time to look for anomalies. In general, the plots of concentrations associated with the inductively coupled plasma (ICP) and ion chromatography (IC) analysis of solutions show recovery within limits of 80% to 120%.

Additional equipment that may be used includes a thermometer, clock, and balances. The thermometer for monitoring the batch-contact temperature and the timepiece are standard laboratory equipment for use as indicators only. Balances are calibrated annually by a certified contractor, QC Services, Portland, Oregon.

NCR 44384.1, Rev 0 was written to describe correction of some data reported WTP-RPT-184, Rev 0 resulting in WTP-RPT-184, Rev 1. The changes made had no effect on this report.

3.0 Simulant Designation

The simulant development approach described here is based on the development of component simulants that can be blended to form a wide variety of filtration and leaching simulants. The simulant components are shown in Figure 3.1. Note that the "inert solids component" is principally iron oxyhydroxide slurry with other metal hydroxides also present and is also referred to as the filtration slurry component. The selection and preparation of these components are described in the reports identified.

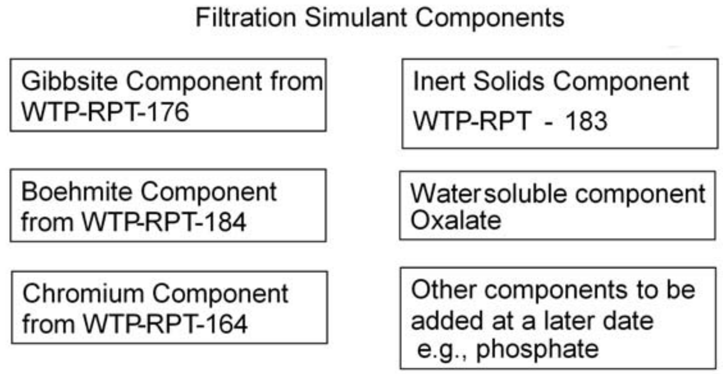


Figure 3.1. Components of Blended Simulant

A fundamental premise is that this approach would allow blending of the different components to simulate the leaching and filtration behavior of a wide variety of feeds to be treated in the WTP. For example, a given feed from the planned feed vector could be selected, and the appropriate components would then be blended to achieve a representation of the leaching and filtration behavior that particular feed. Using the blending of component simulants could allow the representation of a much broader spectrum of behaviors of potential feeds to the Pretreatment Engineering Platform (PEP).

WTP carried out process development and scale-up testing using the PEP to demonstrate the design effectiveness of both the caustic and the oxidative leaching processes. Therefore, the simulant composition was dictated by the needs of PEP and defined by the specifications on mass loss, batch size, and treatment time in Task 3.3 of the M12-IRP (Barnes and Voke, 2006). The leaching and filtration performance data obtained from actual waste testing were used as benchmarks for defining simulant characteristics and behaviors and as a basis for revising the parameters used in evaluating WTP process performance using the appropriate process models.

The simulant discussed in this report is designated as the PEP simulant and consists of four main components [gibbsite, boehmite, chromium oxyhydroxide (CrOOH) slurry, and filtration slurry] blended together with sodium oxalate in a caustic supernate containing various sodium salts. These four main components are discussed individually in the following section.

4.0 Filtration Slurry Simulant Waste Stream Components, Unit Operation Usage, and Requirements

4.1 Introduction

The PEP simulant is prepared as separate components so that the components can be mixed together in different proportions to simulate different tank waste compositions. The simulant waste stream components are the filtration slurry iron rich simulant, boehmite simulant, gibbsite simulant, and CrOOH slurry simulant. Sodium oxalate is also added to the simulant as a component to represent all of the water soluble solids such as the sulfates, phosphates, oxalates and fluorine-phosphates. All of the simulant components are blended together in an alkaline supernatant solution containing the various soluble salts.

The intent of these simulant components is to be able to adjust the behavior of the PEP simulant by combining these components in the desired ratios. After selecting a ratio of the filtration slurry simulant components, several other simulant component combinations were also examined. The final step in the process was to test the filtration behavior of the chosen integrated simulant (chosen component ratio) and compare it with the specifications for use in the PEP.

4.2 Filtration Slurry Iron Rich Simulant Component

The filtration slurry simulant (iron rich) component was based on a previous simulant developed for Hanford Waste Tanks AY-102/C-106 (Zamecnik et al. 2004). This simulant is sometimes referred to as the Semi-Integrated Pilot Plant (SIPP) simulant and was developed for use in the crossflow filtration operation. The iron rich simulant component was simplified from the SIPP simulant by reducing the number of chemicals present. The chemicals removed from this component are present in the actual waste in low quantities, however. They are considered to exert negligible chemical influence on filtration and leaching reactions aimed at removing certain major components. Radioactive isotopes are not included, so there are no radiological hazards associated with the simulant. Though radiolysis can affect chemical reaction rates, there is no evidence to indicate that it has a major effect on the leaching reactions being investigated by PEP. In addition, trace heavy metals are not included to reduce the toxicity of this component. Some trace elements, such as the noble metals (rhodium, palladium, and ruthenium), make this component quite expensive and were therefore not included. These elements are known catalysts for a number of organic reactions, but are not believed to have a significant effect on the leaching reactions being investigated by PEP. These simplifications resulted in an iron rich simulant component that is nonradioactive, minimally toxic, and comparatively inexpensive in terms of purchase and disposal costs.

The chemicals used to produce the iron rich simulant component are listed in Table 4.1 and Table 4.2. Table 4.1 shows the chemicals of the slurry solids consisting primarily of iron. The insoluble hydroxide solids are produced when NaOH is added to the metal nitrate solution to a pH of 10 to 11. The $KMnO_4$ and $Mn(NO_3)_2$ are pre-reacted to produce insoluble MnO_2 before the nitrate salts are added by mixing them together in deionized water (DIW). The excess nitrate is then washed from the slurry using the simple supernate that only contains the major salt anions (hydroxide, phosphate, oxalate, carbonate, and nitrite) described in Appendix A. The final simulant recipe for material used in the PEP was modified to remove selected chemical constituents such as barium, cadmium, copper, lead, and ruthenium from the filtration slurry component and formate, acetate, tungstate, and metasilicate from the supernate. The hazardous ingredients were removed to reduce disposal costs for the spent simulant and to minimize the safety/environmental hazards associated with the simulant. Removing these components also reduced the procurement and fabrication costs. In addition, washing the filtration slurry to remove nitrate was replaced with a cost-effective "shimming" strategy to adjust the liquid portion of the filtration slurry to that of the Specific Supernate[a].

Table 4.2 shows the chemicals used to produce the iron rich simulant supernate component. This includes both the nitrate and non-nitrate anions present.

Figure 4.1 illustrates how the iron rich simulant component is produced. Appendix A provides the preparation procedure for the filtration slurry iron rich simulant component along with the iron rich simulant supernate component. This process is discussed in further detail in WTP-RPT-183, Rev 0 (Russell et al. 2009c).

Table 4.1. Chemicals Used to Produce Sludge Solids for Filtration Slurry Iron Rich Simulant Component

Chemicals Used to Produce Sludge Solids	Composition
Zirconyl nitrate	$ZrO(NO_3)_2$-xH_2O x~6
Sodium hydroxide	$NaOH$
Sodium phosphate	Na_3PO_4-$12H_2O$
Sodium oxalate	$Na_2C_2O_4$
Potassium permanganate	$KMnO_4$
Manganous nitrate (50 wt% soln)	$Mn(NO_3)_2$
Calcium nitrate	$Ca(NO_3)_2$-$4H_2O$
Ferric nitrate	$Fe(NO_3)_3$-$9H_2O$
Magnesium nitrate	$Mg(NO_3)_2$-$6H_2O$
Neodymium nitrate	$Nd(NO_3)_3$-$6H_2O$
Nickel nitrate	$Ni(NO_3)_2$-$6H_2O$
Cerium nitrate	$Ce(NO_3)_3$-$6H_2O$
Lead nitrate	$Pb(NO_3)_2$

Table 4.2. Chemicals Used to Produce the Iron Rich Supernate Simulant Component

Chemicals Used to Produce Supernate	Composition
Potassium nitrate	KNO_3
Sodium phosphate	Na_3PO_4-$12H_2O$
Sodium metasilicate	Na_2SiO_3-$9H_2O$
Sodium sulfate	Na_2SO_4
Sodium hydroxide	$NaOH$
Sodium acetate	$NaCH_3COO$-$3H_2O$
Sodium oxalate	$Na_2C_2O_4$
Sodium nitrite	$NaNO_2$

---

[a] Scheele RD, GN Brown, and DE Kurath. 2009. *Scale-up, Production, and Procurement of PEP Simulants*. WTP-RPT-204, Rev 0, Pacific Northwest National Laboratory, Richland, Washington.

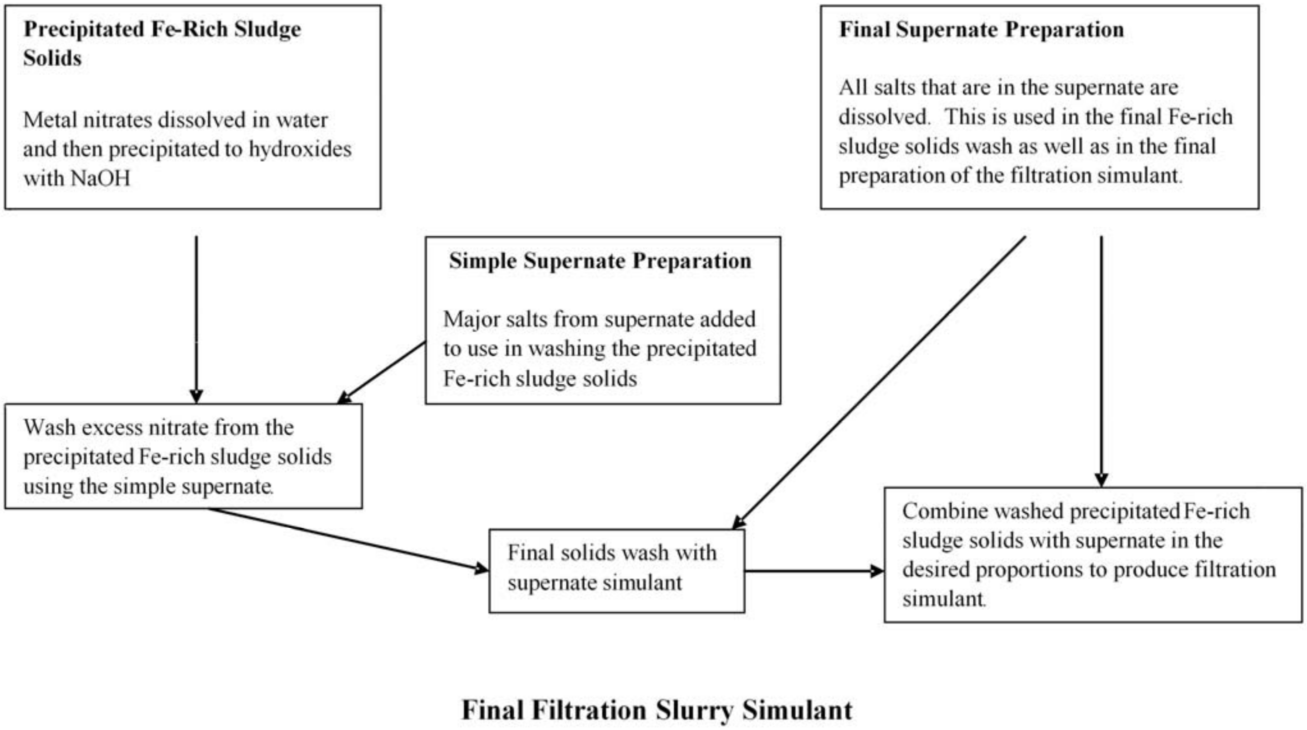


Figure 4.1. Flowsheet of Filtration Slurry Simulant Component Preparation

4.3 Filtration Slurry Boehmite Simulant Component

The boehmite simulant component selected was to be used in testing for caustic leaching of aluminum as boehmite. The boehmite material chosen (APRYAL AOH 20) was based on its leaching rate that was similar to that found for the actual waste (Fiskum et al. 2008). The product description is given in Appendix B. The mineral powder described in Appendix B is added to the actively mixing slurry in the amount specified in the recipe. Further details of the boehmite simulant component are discussed in WTP-RPT-184, Rev 1 (Russell et al. 2009b).

4.4 Filtration Slurry Gibbsite Simulant Component

The gibbsite simulant component selected was also to be used in testing for caustic leach of aluminum as gibbsite and to determine the effects of the presence of gibbsite on the boehmite dissolution. The gibbsite material chosen for testing (Almatis C333) was initially selected primarily on the basis of crystal size and shape in comparison to the actual waste gibbsite particles as no leaching behavior was available from actual waste at that time (Snow et al. 2008). The aluminum leaching rate for this gibbsite material was later found to be consistent with that for the actual waste when leaching behavior results became available. The product description is given in Appendix C. The mineral powder described in Appendix C is added to the actively mixing slurry in the amount specified in the recipe. Further details of the gibbsite simulant component are discussed in WTP-RPT-176, Rev 0 (Russell et al 2009a).

4.5 Filtration Slurry Chromium Oxyhydroxide Simulant Component

It is planned to leach the chromium component of the waste in the WTP using an oxidative leaching process with sodium permanganate. Chromium in the actual waste appears to be an amorphous compound, so it has not been possible to conclude with certainty what chemical phase includes the chromium in the actual waste. Oxidative leaching of actual waste brings the chromium into solution and also some aluminum, suggesting that the chromium perhaps is part of a more complex aluminum-chromium compound structure. Transmission electron microscopy (TEM) work on some chromium-containing wastes has identified nano-crystals of Cr_2O_3 that are much too small to be identified by X-ray diffraction (XRD). Subsequent efforts to make such a fine-grained chromium oxide were unsuccessful, and no vendors for such a material were identified. In screening tests with freshly prepared Cr2O3, CrOOH and Cr(OH)3 as candidate chromium simulant component, it was decided that the leaching behavior of CrOOH was an acceptable approximation of the leaching behavior of the actual waste compound under oxidative leaching conditions. Therefore, a vendor was contracted to produce a slurry of CrOOH for use in the PEP simulant as the chromium (oxyhydroxide) slurry component. However, the vendor-produced CrOOH slurry leached under caustic leaching conditions (about 5N NaOH and 100 C) whereas the actual waste chromium compound did not. However, this CrOOH slurry in a 2 M NaOH supernate was continued to be used as the chromium simulant component because no better simulant component could be found. More detailed information about the selection of this simulant component is discussed in WTP-RPT-164, Rev 0 (Rapko 2007). The preparation procedure for this CrOOH slurry component is given in Appendix D.

4.6 Filtration Slurry Simulant Sodium Oxalate Addition

Sodium oxalate was included in the solids phase of the simulant for several reasons. It is one of the principal organic salts in the Hanford wastes. Oxalates have a low solubility and are temperature sensitive compared to other salts in the waste. Oxalate complexes with ferric iron to form a soluble iron complex. In the simulant, it also represented all of the water soluble constituents of the solids phase such as the carbonates, sulfates, phosphates, oxalates and fluorine-phosphates.

5.0 Actual Filtration Slurry Simulant Preparation Procedure

Basic simulant component preparations are described in Appendix A and D, and product descriptions are provided in Appendix B and C. From these different blended simulants can be prepared by mixing the simulant components in different ratios. The M-12 issue requires the project to develop a simulant that "shall be based upon an 80% confidence level that the composition is bounded based upon projected sludge mass loss, batch size and treatment time" (Barnes and Voke 2006). To meet the requirements for mass loss, the WTP project has specified that the PEP simulant will be a blend of the simulant components in the ratios shown in Table 5.1.[(a)]

Table 5.1. PEP Simulant Component Ratios

Component	Wt Fraction
Boehmite	0.346
Gibbsite	0.346
Chromium as CrO(OH)	0.026
Sodium Oxalate	0.100
Iron Rich	0.181

The PEP simulant of blended simulant components used in the laboratory testing discussed in this report is composed of the simulant components as shown in Table 5.2 and Table 5.3. Note that the recipes in these tables give the weights of each simulant component in the final PEP simulant. A vendor prepared the supernate component and the filtration simulant component according to the recipe described in Appendix A. The gibbsite and boehmite components were commercially purchased (see Appendices B and C). The chromium oxyhydroxide slurry was vendor produced according to the recipe provided by PNNL and detailed in Appendix D. The simulant created according to Table 5.2 was used for the first two laboratory filtration tests (CBM and CBM25), which are described WTP-RPT-184, Rev 1 (Russell et al. 2009b). (Note that CBM25 ≡ CBM-2, so the series of five tests is CBM, CBM-2, CBM-3, CBM-4, and CBM-5. Test CBM is also known as CBM45. The 45 and 25 refer to temperatures at which a leaching process was carried out during these two tests. Other parameters were changed in the remaining three tests.) The simulant created according to Table 5.3, without the chromium oxyhydroxide slurry added initially, was used for the last three laboratory filtration tests (CBM-3, CBM-4, and CBM-5). In these tests, the chromium oxyhydroxide slurry was added after the caustic leaching step of testing. The CrOOH slurry needed to be added after the caustic leaching step because the CrOOH was found to also leach during the caustic leaching step. This left only a fraction of the initial chromium remaining for the oxidative leach step. By adding the CrOOH slurry after the simulant had been caustically leached and washed, a known amount of CrOOH was present so that the oxidative leach process could be quantitatively tested. This is again described WTP-RPT-184, Rev 1 (Russell et al. 2009b).

(a) PS Sundar. 2007. "Simulant Testing in Support of Phase I Demonstration of the Ultrafiltration and Leaching Processes in the Integrated Test Facility." WTP Project Doc. No. 24590-WTP-TSP-RT-07-004, Rev. 0., Bechtel National Inc., Richland, Washington.

Table 5.2. Initial PEP Blended Simulant Components (Target of 45 kg of Simulant)

	Ingredients	Preparation
1	Weigh out 31700 g of supernate (pre-shimmed to correct Na concentration).	Appendix A.2
2	Add 7910 g of 5 M NaOH with mixing.	Commercially available laboratory grade
3	Add 779 g gibbsite with mixing.	Commercially available (Almatis C333)
4	Add 779 g boehmite with mixing.	Commercially available (APYRAL AOH 20)
5	Add 91.4 g Cr oxyhydroxide slurry with mixing.	Purchased from Noah Chemical
6	Add 225 g sodium oxalate with mixing.	Commercially available laboratory grade
7	Add 3560g iron rich sludge simulant with mixing.	Appendix A.3
8	Add another 638 g of 5M NaOH with mixing.	Commercially available
9	Actively mix for 1 hour.	

Table 5.3. PEP Blended Simulant Components with CrOOH Slurry Added Later (Target of 28.5 kg Simulant)

	Ingredients	Preparation
1	Weigh out 24800 g of supernate (pre-shimmed to correct Na concentration).	Appendix A.2
2	Add 458 g gibbsite with mixing.	Commercially available (Almatis C333)
3	Add 458 g boehmite with mixing.	Commercially available (APYRAL AOH 20)
4	Add 131 g sodium oxalate with mixing.	Commercially available laboratory grade
5	Add 2150 g iron rich sludge simulant with mixing.	Appendix A.3
6	Add another 379 g of 5 M NaOH with mixing.	Commercially available laboratory grade
7	Actively mix for 1 hour.	

6.0 Key Characteristics and Limitations of a Simulant to be Used for Filtration and Chemical Leaching Confirmation

Time, cost, and safety considerations limit the extent to which all possible interactions can be considered in testing a HLW simulant. Note that this PEP simulant was being used both as a filtration simulant and a chemical leaching simulant.

6.1 Key Characteristics of a Filtration Simulant

The approach was to evaluate the properties believed to be the most important to the filtration behavior and assume that if they were close enough to those of the actual waste, this would be close enough to give reasonable engineering data. Therefore, the approach taken can be described as "close as reasonably achievable" for simulant properties based on our knowledge of actual wastes. The properties that appear to be important to filtration behavior are solids properties (particle type and size distribution) and slurry rheology, which were tested each time.

6.2 Key Characteristics of a Chemical Leaching Simulant

A chemical leaching simulant needs to contain the elements that are to be leached, but not necessarily the toxic minor components (safety consideration) that exist in an actual waste unless there is good reason to believe that the trace component can have a significant effect on a leaching rate, i.e., as a catalyst or other interaction. Also, the solid phases should be similar to those in the actual waste, both in terms of particle size and shape and in terms of chemical reactivity.

The PEP simulant used for filtration in this case is also used for chemical leaching by adding the appropriate components in the proper ratios. For example, to make a simulant for a high-aluminum waste, one adds boehmite and gibbsite in a known ratio to the other waste components to give a waste simulant with an aluminum level equivalent to the real waste.

6.3 Evaluation Method via Bench Scale CUF (Cell Unit Filter)

Because time, cost, and safety considerations result in empirical simplifications of the PEP simulant, the best comparison of the blended PEP simulant is an empirical comparison of leaching and filtration results obtained using the simulant with those obtained with the actual waste. In this case, a bench scale CUF system was used on actual waste (Shimskey et al. 2009) in the Radiochemical Processing Laboratory (RPL), and a virtually identical CUF system was used with the simulant (Russell et al. 2009c, WTP-RPT-183, Rev 0). In such a comparison, reasons for differences or similarity may not be certain, so they are not a logical topic of analysis. They are only qualitative to determine if they are good enough so that their use provides useful engineering results. Therefore, the comparison approach is to document simulant results in filtration and leaching experiments and compare these with results using actual wastes under the same (or similar) conditions. This comparison is discussed in the following section.

7.0 Property Comparison of Actual and Simulated Waste

7.1 Introduction

Ideally, simulant is developed to have similar physical and chemical properties as the actual waste material, but in this case the simulant composition was dictated by the needs of PEP and defined by the specifications on mass loss, batch size and treatment time in Task 3.3 of the M12-IRP (Barnes and Voke, 2006) and does not represent one specific tank waste. However, the actual waste mixture of group of 5 and 6 wastes was chosen to compare with the simulant due to its high iron hydroxide concentration along with its presence of both boehmite and gibbsite which is similar to the simulant composition.

7.2 Filtration Simulant Chemistry, Physical Properties, and Leaching Characteristics Compared to that of Actual Filtration Waste

The blended PEP simulant and the actual waste characteristics are compared in Table 7.1 on the basis of physical properties, particle size distribution (PSD), chemical composition, leaching characteristics, and rheology at the similar solids concentration.

Table 7.1. A Comparison of Physical and Chemical Properties between the Actual Waste and Blended Simulant

Property		Blended Simulant	Blended Simulant Reference	Actual Waste	Actual Waste Reference
Waste Type		Modified AY-102/C-106 Simulant	See Appendix A	Mixture of Group 5 and 6 Wastes[(a)]	WTP-RPT-172, Sec.4.1
Slurry Density @ % total solids		1.36 g/mL @ 44-wt% TS	WTP-RPT-183 Table 6.7	1.25 g/mL @ 37-wt% TS	WTP-RPT-172, Sec. 4.2, Table 4.3
Density Supernate @ % diss. solids		1.23 g/mL @ 30-wt% DS	WTP-RPT-183 Table 6.7	1.25 g/mL @ 35-wt% DS	WTP-RPT-172, Sec. 4.2, Table 4.3
Low Solids UDS (wt%)		4	WTP-RPT-183 Table 6.3	3	WTP-RPT-172, Sec. 4.2, Table 4.3
High Solids UDS (wt%)		21	WTP-RPT-183 Table 6.7	13	WTP-RPT-172, Sec. 4.3.4, Table 4.8
PSD	D_{10}	1.6 µm	WTP-RPT-183 Fig. 6.3	0.6 µm	WTP-RPT-172, App. H, Table 7
	D_{50}	4.3 µm	WTP-RPT-183 Fig. 6.3	2.5 µm	WTP-RPT-172, App. H, Table 7

Table 7.1. A Comparison of Physical and Chemical Properties between the Actual Waste and Blended Simulant

Property		Blended Simulant	Blended Simulant Reference	Actual Waste	Actual Waste Reference
	D_{90}	10.9 µm	WTP-RPT-183 Fig. 6.3	12 µm	WTP-RPT-172, App. H, Table 7
Rheology	η	0.008 Pa-s	WTP-RPT-183 Table 6.8	0.013 Pa-s	WTP-RPT-172 App. J, Table 23
	τ	1.4 Pa	WTP-RPT-183 Table 6.8	7.4 Pa	WTP-RPT-172 App. J, Table 23
Chemical composition of solids (µg/g-solids)	Fe	74,000	WTP-RPT-183 Table 6.7, SWRI analytical data	8,740	WTP-RPT-172 Table 4.10
	Al	263,000	WTP-RPT-183 Table 6.7, SWRI analytical data	267,000	WTP-RPT-172 Table 4.10
	Mn	16,000	WTP-RPT-183 Table 6.7, SWRI analytical data	4,610	WTP-RPT-172 Table 4.10
	Cr	7,000	WTP-RPT-183 Table 6.7, SWRI analytical data	24,300	WTP-RPT-172 Table 4.10
	Na	33,000	WTP-RPT-183 Table 6.7, SWRI analytical data	42,500	WTP-RPT-172 Table 4.10
Chemical composition of supernate (µg/mL)	Na	107,000	WTP-RPT-183 Table 6.7, SWRI analytical data	119,000	WTP-RPT-172 Table 4.10
	K	2,079	WTP-RPT-183 Table 6.7, SWRI analytical data	1,040	WTP-RPT-172 Table 4.10
	NO_3	32,040	WTP-RPT-183 Table 6.7, SWRI analytical data	130,000	WTP-RPT-172 Table 4.9
	NO_2	9,420	WTP-RPT-183 Table 6.7, SWRI analytical data	37,000	WTP-RPT-172 Table 4.9
	Oxalate	907	WTP-RPT-183 Table 6.7, SWRI analytical data	890	WTP-RPT-172 Table 4.9

Table 7.1. A Comparison of Physical and Chemical Properties between the Actual Waste and Blended Simulant

Property		Blended Simulant	Blended Simulant Reference	Actual Waste	Actual Waste Reference
	P_2O_5	511	WTP-RPT-183 Table 6.7, SWRI analytical data	8,300 as PO_4	WTP-RPT-172 Table 4.9
	SO_4	1,140	WTP-RPT-183 Table 6.7, SWRI analytical data	6,700	WTP-RPT-172 Table 4.9
Leaching Characteristics	Al	56.8-wt% of the original Al leaches during caustic leaching	WTP-RPT-184, Table 6.5	52-wt% of original Al leaches during caustic leaching	WTP-RPT-172, Figure 4.39
	Cr	9.7-wt% of the original Cr remains in UDS	WTP-RPT-184, Table 6.5	0-wt% of original Cr remains in UDS	WTP-RPT-172, Figure 4.48

(a) The low solids test was performed using only Group 6, but Group 5 was added during dewatering to increase the undissolved solids (UDS).

Figure 7.1 through Figure 7.3 show the filtration behavior comparisons of the actual waste slurry and the blended PEP simulant slurry. In Figure 7.1 and Figure 7.2, each flux curve is accompanied by a pair of numbers that give the test conditions under which the data were collected. The first number is the transmembrane pressure—psid (TMP), which is the pressure gradient across the filter media, and the second is the axial velocity (AV) in feet per second, i.e., the rate at which the slurry is moving parallel to the surface of the filter.

The data indicate that the PEP simulant filters faster under all conditions tested than the actual waste (a mixture of reduction-oxidation (REDOX) sludge [Group 5] and S-Saltcake [Group 6] for the high solids waste and just S-Saltcake [Group 6] for low solids testing [Shimskey et al. 2009]). There are at least two possible reasons for the behavior observed. The first and most probable reason is that the simulant waste (see Appendix A, Russell et al. 2009c [WTP-RPT-183, Rev. 0]) and the actual wastes (see above) are somewhat different in their chemical composition, and second, the data for each slurry were collected using different (but very similar) filtration systems. In addition, the rheological properties for both slurries differ, particularly in shear strength as shown in Table 7.1. Hence, it is possible that the observed shift in the filtration response is consistent with differences in the properties of the PEP simulant and the actual waste. A similar shift is also observed in the dewatering curves (Figure 7.3), which also shows that the PEP simulant filters faster than the actual waste.

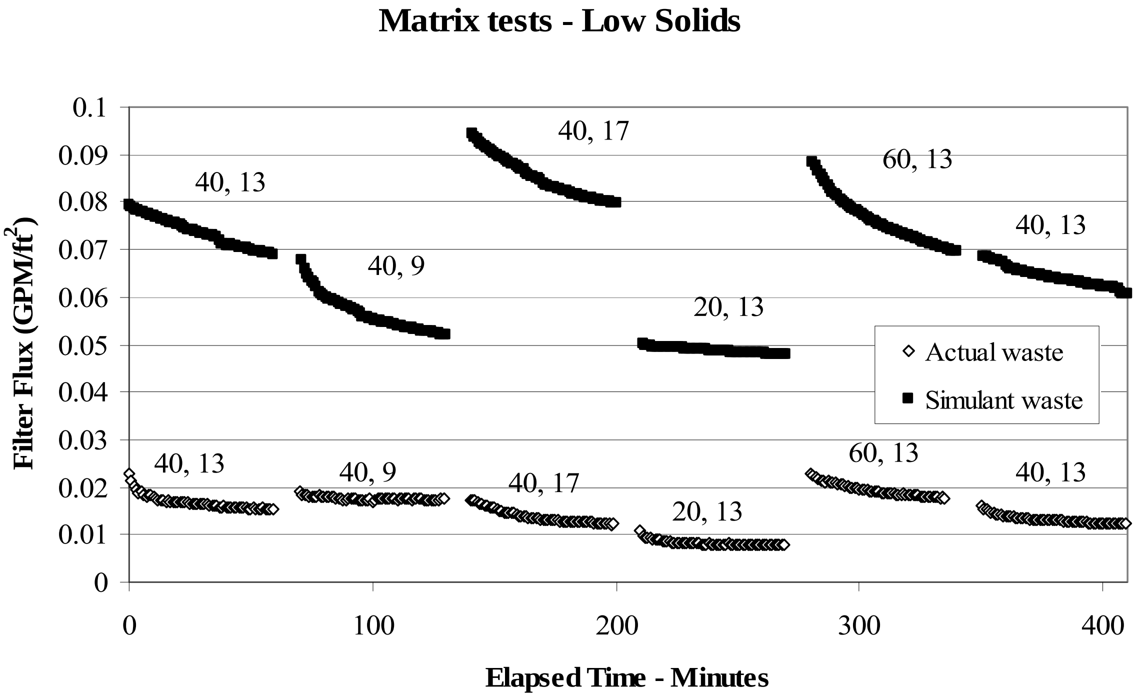


Figure 7.1. Low Solids Matrix Test Profiles for both Actual Tank Waste (S-Saltcake [Group 6]) and PEP Simulant. The first number is the transmembrane pressure—psid (TMP) and the second is the axial velocity (AV) in feet per second.

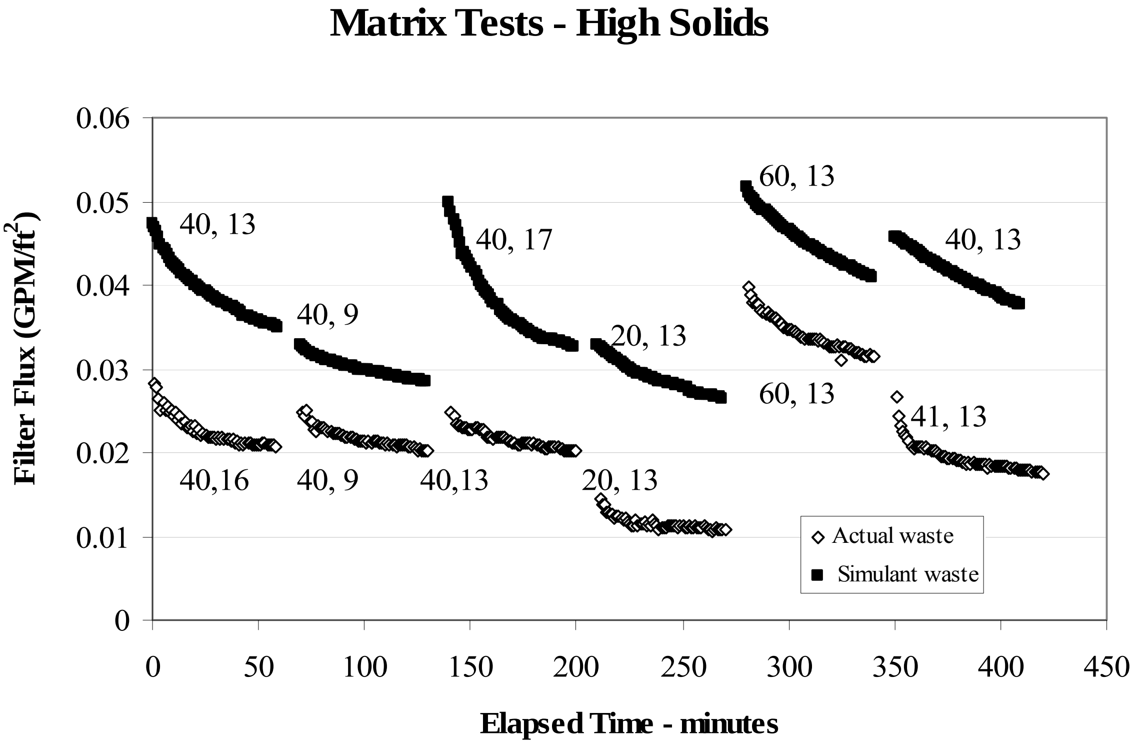


Figure 7.2. High Solids Matrix Test Profiles for both Actual Tank Wastes (REDOX sludge [Group 5] and S-Saltcake [Group 6] composite) and PEP Simulant. The first number is the transmembrane pressure—psid (TMP) and the second is the axial velocity (AV) in feet per second.

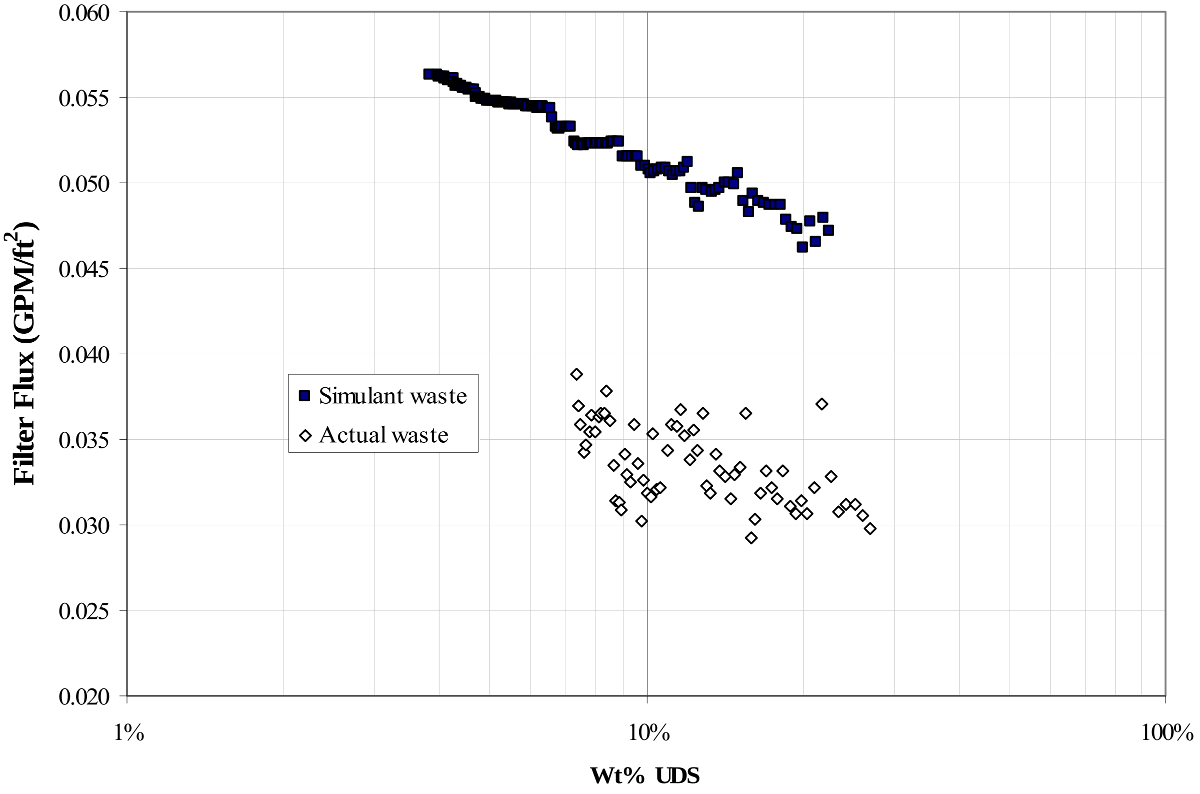


Figure 7.3. Dewatering Curves for the Actual Tank Wastes (REDOX sludge [Group 5] and S-Saltcake [Group 6] composite) and PEP Simulant

8.0 Concluding Comments

Historically, the process of simulation (Hanford Tank waste in particular) has been a balancing act between producing a material that really acts like the actual material for specified physical and chemical properties and producing a material that is cost effective and minimally toxic. The blended PEP simulant is a good example of this balancing act. On the one hand, it represents a large range of waste types (i.e., the Hanford Waste Tank compositions), and on the other hand, it is similar in behavior to a specific example of Hanford Tank Waste. The Test Objectives and Success Criteria given in the Summary of this report reflect this philosophy. Five out of the six objectives were met and criteria attained, and the sixth point covering additional specific waste elements will be performed in Phase 2 work. Hence, it is concluded that the PEP simulant blends are acceptable for application to current PEP testing of filtration and leaching and have the compositional flexibility necessary to determine the optimal chemical management of individual chemical species as well as to simulate various types of Hanford Tank Wastes with respect to aluminum and chromium.

Comments on the similarity of the PEP simulant to the actual waste in terms of chemical and physical properties are summarized in Table 8.1. The table comments on the similarity of the simulated and actual wastes based on comparable measurements that were made.

Table 8.1. Comments Relating to the Waste Simulant as a Suitable Surrogate for the Actual Waste

Property	Comments
Waste Type	They are different in levels of specific chemical components but overall provide a similar chemical matrix of HLW.
Slurry Density	This is expected when the combination of UDS and dissolved solids is about the same for both materials.
Density Supernate	This is expected when the amount of dissolved solids is about the same for both materials.
PSD	This is expected because the same compounds are produced using the same types of reactions and similar ambient conditions. Differences could be due to different amounts of the same compound and different aging times.
Rheology	A large difference in yield strength has been observed before for different wastes at the same wt% total solids. (See WTP-RPT-112, Rev 0, [Poloski et al. 2006], Figures 4.13 and 4.14.].) It is not unexpected.
Chemical composition (Solids)	Simulants were put together with the objective that they would be shimmed with certain elements to bring their percentage into line with particular waste compositions for leaching studies. In this case, both aluminum and chromium were added to bring them to the levels of the actual waste for leaching studies. The client concurred with the levels actually used.
Chemical composition (Supernate)	Salt composition is in significantly different proportions reflecting the differences in the model simulant and the actual waste samples that were mixed together. However, they are similar in terms of total sodium concentration.
CUF Filtration Characteristics Test Matrix	In general, the simulant was observed to filter about twice as fast as the actual waste. The same behavior was observed in the dewatering test where they displayed offset trends but showed the same slope. This may be because the Group 6 waste displayed strong fouling properties (Shimskey et al. 2009).
Leaching Characteristics	In the simulant, 43-wt% of the alumina remained while 48-wt% of the alumina remained in the actual waste after caustic leaching. For chromium, 9-wt% remained in the simulant while 0-wt% remained in the actual waste after oxidative leaching.

9.0 References

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

CCN 132846. 2006. "Comprehensive Review of the Hanford Waste Treatment Plant Flowsheet and Throughput - Assessment Conducted by an Independent Team of External Experts." Chartered by the Hanford Waste Treatment and Immobilization Plant Project at the Direction of the U.S. Department of Energy, Office of Environmental Management, Washington DC.

CCN 132847. 2006. "Background Information and Interim Reports for the Comprehensive Review of the Hanford Waste Treatment Plant Flowsheet and Throughput - Assessment Conducted by an Independent Team of External Experts." Chartered by the Hanford Waste Treatment and Immobilization Plant Project at the Direction of the U.S. Department of Energy, Office of Environmental Management, Washington DC.

Fiskum SK, EC Buck, RC Daniel, K Draper, MK Edwards, TL Hubler , LK Jagoda, ED Jenson, GJ Lumetta, BK McNamara, RA Peterson, SI Sinkov, and LA Snow. 2008. *Characterization and Leach Testing for REDOX Sludge and S-Saltcake Actual Waste Sample Composites.* PNNL-17368 (WTP-RPT-157, Rev 0), Pacific Northwest National Laboratory, Richland, Washington.

Lucas L. 2006. *Hanford Waste Treatment and Immobilization Plant (WTP) Project Response Plan for Resolution of Issues Identified by the Comprehensive Review of the WTP Flowsheet and Throughput.* 24590-WTP-PL-ENG-06-0008, Rev 0, Bechtel National, Inc., Richland, Washington.

Poloski AP, ST Arm, OP Bredt, TB Calloway, Y Onishi, RA Peterson, GL Smith, and HD Smith. 2006. Final Report: *Technical Basis for HLW Vitrification Stream Physical and Rheological Property Bounding Conditions*. PNWD-3675 (WTP-RPT-112, Rev 0.), Battelle - Pacific Northwest Laboratories, Richland, Washington.

Rapko BM. 2007. *Process Development for Permanganate Addition During Oxidative Leaching of Hanford Tank Sludge Simulants.* PNNL-16794 (WTP-RPT-164), Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, DE Rinehart, HD Smith, and RA Peterson. 2009a. *Development and Characterization of Gibbsite Component Simulant.* PNNL–18013 (WTP-RPT-176 Rev. 0), Pacific Northwest National Laboratory Richland, Washington.

Russell RL, DE Rinehart, RA Peterson, PM Aker, HD Smith, and EC Buck. 2009b. *Development and Characterization of Boehmite Component Simulant.* PNNL-18176 (WTP-RPT-184, Rev 1), Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, DE Rinehart, JM Billing, HD Smith and RA Peterson. 2009c. *Development and Demonstration of Ultrafiltration Simulants.* PNL-18090 (WTP-RPT-183, Rev 0), Pacific Northwest National Laboratory, Richland, Washington.

Snow LA, EC Buck, JV Crum, RC Daniel, K Draper, MK Edwards, SK Fiskum, LK Jagoda, ED Jenson, AE Kozelisky, PJ MacFarlan, RA Peterson, and RG Swoboda. 2008. *Characterization and Leach Testing for PUREX Cladding Waste Sludge (Group 3) and REDOX Cladding Waste Sludge (Group 4) Actual Waste Sample Composites.* PNNL-18054 (WTP-RPT-167, Rev 0), Pacific Northwest National Laboratory, Richland, Washington.

Shimskey RW, JM Billing, EC Buck, RC Daniel, K Draper, MK Edwards, JGH Geeting, RT Hallen, ED Jenson, AE Kozelisky, PJ MacFarlan, RA Peterson, LA Snow, and RG Swoboda. 2009. *Filtration and Leach Testing for REDOX Sludge and S-Saltcake Actual Waste Sample Composites.* PNNL-17965 (WTP-RPT-172, Rev 0), Pacific Northwest National Laboratory, Richland, Washington.

Smith GL. 2006. *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*. WTP Project Doc. No. 24590-PTF-TSP-RT-06-006, Rev. 0, Bechtel National Inc., Richland, Washington.

Zamecnik JR, PR Burket, RE Eibling, and MR Poirier. 2004. *Tank 241-AY-102 Simulant Development, Ultrafiltration, and Washing*. WSRC-TR-2003-00547, Rev. 0 (or SRT-RPP-2003-00240, Rev. 0). Westinghouse Savannah River Company, Aiken, South Carolina.

Appendix A

Recipe for Simulant Preparation

Appendix A: Recipe for Simulant Preparation

The following is a step-by-step recipe for preparing the filtration simulant component of the simulant described in this report and chosen to be used in the Pretreatment Engineering Platform (PEP) testing. This is the recipe that was used by Pacific Northwest National Laboratory (PNNL) and a vendor to prepare the simulant. **Note:** The component make up procedures (A.1, A.2, and A.3) are for a specified target volume (A.1 and A.2) or weight UDS (A.3) so multiples of the target values are generally made up when the wt% UDS and volume of the simulant batch is known. The final simulant recipe for material used in the PEP was modified to remove selected chemical constituents such as barium, cadmium, copper, lead, and ruthenium from the filtration slurry component and formate, acetate, tungstate, and metasilicate from the supernate. The hazardous ingredients were removed to reduce disposal costs for the spent simulant and to minimize the safety/environmental hazards associated with the simulant. Removing these components also reduced the procurement and fabrication costs. In addition, washing the filtration slurry to remove nitrate was replaced with a cost-effective "shimming" strategy to adjust the liquid portion of the filtration slurry to that of the Specific Supernate[a].

A.1 - PREPARATION OF SIMPLE SUPERNATE

This preparation is for a "simple" version of the Supernate Simulant that is used for the initial washes of the Precipitated Sludge Solids. This simple simulant contains the most abundant species found in the Supernate Simulant, but does not contain the minor species. Perform at ambient temperature unless indicated otherwise.

Note: ≤±0.5% is sufficient accuracy on masses.

The following recipe should be carried out in a plastic or stainless steel vessel. **No glass shall be used.** All additions are based on mass.

Note: The target volume is 1-L.

Tare weight of 2-L vessel:_________________

1- Add to the 2-L vessel:

	Mass Needed (g)	Actual Mass (g)	Resistivity of water
Water (deionized, DI)	*~ 200.0*		

2 Add:

Compounds	Formula	Target Mass (g)	Actual Mass (g)

---

[a] Scheele RD, GN Brown, and DE Kurath. 2009. *Scale-up, Production, and Procurement of PEP Simulants*. WTP-RPT-204, Rev 0, Pacific Northwest National Laboratory, Richland, Washington.

Sodium Sulfate	Na_2SO_4	2.67±0.013	

3 In separate 10-L container, mix the following:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Water (deionized)		*~ 200.0*	
Sodium Hydroxide	NaOH	15.38±0.077	
Sodium Phosphate	$Na_3PO_4 \cdot 12H_2O$	15.38±0.077	
Sodium Oxalate	$Na_2C_2O_4$	5.30±0.027	

4 Mix vigorously for ~15 minutes. Then add the above solution to the 2-L vessel.

5 Add to the 2-L vessel:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Sodium Carbonate	Na_2CO_3	102.3±0.51	

6 Mix vigorously for ~15 minutes.

7 In separate 250-mL container, mix the following:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Sodium Nitrite	$NaNO_2$	6.49±0.032	
Water (deionized)		*~ 100*	

8 Add to the 2-L vessel and mix vigorously for ~15 minutes.

9 Add to the 2-L vessel:

	Total Mass Target (g)	Added	*Mass of Water to Add (g)*
DI Water to a total mass of:	1,000		*~350*

Record Final Mass of Vessel + solution:_________________
Record Final Mass of solution:_________________

A.2 - PREPARATION OF SUPERNATE SIMULANT

This simulant is used for final washing of the Precipitated Sludge Solids and for makeup of the final overall simulant.

Note: ≤±0.5% is sufficient accuracy on masses.

The following recipe should be carried out in a plastic or stainless steel vessel. **No glass shall be used.** All additions are based on mass.

Note: The target volume is 1-L.

Tare weight of 2-L vessel: _________________

1- To a 2-L vessel, add:

	Target Mass (g)	Actual Mass (g)	Resistivity of water
Water (deionized, DI)	*~ 200.0*		

2- Add the Transition Metals, Complexing Agents, Halides, Sulfate, and Potassium to the 2-L vessel:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Potassium Nitrate	KNO_3	0.4325±0.0022	
Sodium Chloride	$NaCl$	0.2007±0.001	
Sodium Fluoride	NaF	0.1345±0.0007	
Sodium Sulfate	Na_2SO_4	2.671±0.013	

3- In separate 250-mL container, mix the following:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Water (deionized)		*~ 200*	
Sodium Hydroxide	$NaOH$	15.380±0.077	
Potassium Hydroxide	KOH	0.2691±0.0013	
Sodium Phosphate	$Na_3PO_4 \cdot 12H_2O$	15.380±0.077	
Sodium Tungstate	$Na_2WO_4 \cdot 2H_2O$	0.1577±0.0008	
Sodium Metasilicate	$Na_2SiO_3 \cdot 9H_2O$	0.5455±0.0027	
Sodium Formate	$NaHCOO$	0.2062±0.0010	
Sodium Acetate	$NaCH_3COO \cdot 3H_2O$	1.034±0.005	
Sodium Oxalate	$Na_2C_2O_4$	5.303±0.027	

4- Mix vigorously for ~15 minutes. Then add this solution to the 2-L vessel. Add:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Sodium Carbonate	Na_2CO_3	102.30±0.51	

Mix vigorously for ~15 minutes.

5- In separate 250-mL container, mix the following:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Sodium Nitrite	$NaNO_2$	6.494±0.032	
Water (deionized)		*~ 100*	

6- Add to the 2-L vessel and mix vigorously for ~15 minutes. Add:

	Total Target Mass (g)	Added	*Mass of Water to Add (g)*
DI Water to a total mass of:	1,000		*~300*

7 Analyze the Supernate Simulant for wt% total solids by drying 10-mL at 110°C until a stable weight is obtained.

Wt% total solids:_________________

8 Collect a 5- to 10-mL sample for ICP/IC analysis in a tared vial.
Sample wt:_________________

A.3 - PREPARATION OF PRECIPITATED Fe-Rich SLUDGE SOLIDS

This recipe details the steps to make Precipitated Fe-Rich Sludge Solids. The general steps involved are to dissolve metal nitrates, neutralize these nitrates to form the metal hydroxides, add trim chemicals (phosphate, oxalate, carbonate), then wash the solids with the Simple Supernate for Washing and then with the Supernate.

Note: ≤±0.5% is sufficient accuracy on masses.

The following preparation should be carried out in a plastic or stainless steel vessel. **No glass shall be used.** All additions are based on mass.

Note: The target weight of precipitated solids is ~60 g.

Tare weight of 2-L vessel:_________________

1- Add to the 2-L vessel:

	Target Mass (g)	Actual Mass (g)
Deionized Water	~ *300*	

A.3.1 - MANGANESE DIOXIDE PRODUCTION

2- Add to the 2-L vessel:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Potassium Permanganate	$KMnO_4$	4.37±0.022	

Compound should completely dissolve.

3- Add to the 2-L vessel:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Manganous Nitrate Solution	$Mn(NO_3)_2$, 50-Wt % solution	14.85±0.074	

Mix vigorously for ~15 minutes. It will produce fine black solids which will remain suspended while being agitated.

A.3.2 - PREPARATION OF METAL HYDROXIDES

4 Add to the 2L vessel the following transition and other metals compounds with mixing to ensure complete dissolution (order not of addition not believed important):

Compounds	**Formula**	**Target Mass (g)**	**Actual Mass (g)**
Barium Nitrate	$Ba(NO_3)_2$	0.213±0.001	
Calcium Nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	2.425±0.012	
Cadmium Nitrate	$Cd(NO_3)$	0.06±0.0003	
Cerium Nitrate	$Ce(NO_3)_3 \cdot 6H_2O$	0.65±0.003	
Copper Nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	0.157±0.0008	
Ferric Nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	128.1±0.64	
Lanthanum Nitrate	$La(NO_3)_3 \cdot 6H_2O$	0.482±0.002	
Lead Nitrate	$Pb(NO_3)_2$	1.295±0.006	
Magnesium Nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	1.72±0.009	
Neodymium Nitrate	$Nd(NO_3)_3 \cdot 6H_2O$	1.32±0.007	
Nickel Nitrate	$Ni(NO_3)_2 \cdot 6H_2O$	2.87±0.014	
Praseodymium Nitrate	$Pr(NO_3)_3 \cdot xH_2O$ x~6	0.33±0.002	
Ruthenium Trichloride	$RuCl_3$	0.11±0.0005	
Silver Nitrate	$AgNO_3$	0.486±0.002	
Strontium Nitrate	$Sr(NO_3)_2$	0.347±0.002	
Yttrium Nitrate	$Y(NO_3)_3 \cdot 6H_2O$	0.14±0.0007	
Zinc Nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	0.169±0.0008	
Zirconyl Nitrate	$ZrO(NO_3)_2 \cdot xH_2O$ x~6	1.73±0.009	
Mercuric Nitrate	$Hg(NO_3)_2$	0.052±0.0003	

5 Mix vigorously in order to completely dissolve everything except the fine black solids of MnO_2. A little DIW may be added if necessary in order for complete dissolution to occur.

DIW water added:_________________

A.3.3 - NEUTRALIZATION OF NITRATE SOLUTION

6 Standardize a pH electrode with pH 4, 7 and 10 buffers.

pH 4 buffer:
Manufacturer: _________________ Lot#:_________________ Exp Date: _________________

pH 7 buffer:
Manufacturer: _________________ Lot#:_________________ Exp Date: _________________

pH 10 buffer:
Manufacturer: _________________ Lot#:_________________ Exp Date: _________________

7 Place the pH electrode in the precipitation vessel with the metal nitrates and measure the pH.

pH: _________________ Note: pH should be <1.

With the nitrate solution agitating, slowly add 8 M NaOH, until the pH reaches 10 to 11. Estimated amount of 8M NaOH needed is 190 g.

8 Measure the pH.

pH:_________________

9 Continue mixing for 1 hour and then recheck pH.

pH:_________________

10 Add additional 8 M NaOH to return the pH to 10 if it is lower.

Total 8M NaOH added:_________________
Final pH:_________________

A.3.4 - ADDITION OF ADDITIONAL REAGENTS

11 Add to the 2-L vessel:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Calcium Fluoride	CaF_2	0.205±0.001	
Sodium Phosphate	$Na_3PO_4 \cdot 12H_2O$	5.05±0.03	

12 Combine the following in a separate 250-mL container while stirring:

Compound	Formula	Target Mass (g)	Actual Mass (g)
Water (deionized)		*~ 100*	
Sodium Oxalate	$Na_2C_2O_4$	6.7±0.03	

Add this sodium oxalate solution to the 2-L vessel while stirring.

13 Combine the following in a separate 250-mL container while stirring:

Compound	Formula	Target Mass (g)	Actual Mass (g)
Water (deionized)		*~100*	
Sodium Carbonate	Na_2CO_3	9.50±0.05	

Add this sodium carbonate solution to the 2-L vessel with stirring. Approximate volume at this point should be about 0.9 L.

14 Mix (vigorously) the slurry to ensure good mixing. Mix the slurry for at least 1 hour.

A.3.5 - WASH PRECIPITATED SLUDGE SOLIDS TO REMOVE NITRATE

Four washes are performed to reduce the nitrate concentration to below about 500 mg/kg. The slurry is centrifuged between each wash. The total solids content of the centrifuged solids needs to be at least 25-wt% for sufficient washing to be completed in four washes. If less wash solution is removed during centrifuging, additional washing steps must be added. However, excessive washing is to be avoided so that the nitrate and trace compounds are not reduced in concentration too far.

The amount of wash solution required per wash is approximately 3X the mass of the centrifuged solids. Three washes with the "Simple Supernate for Washing" are used, followed by a wash with the actual "Supernate Simulant". Use this information to calculate the amount of wash and Supernate Simulant needed.

15 Centrifuge the slurry for 30 minutes at ~4500 G.

Time started:_________________ Time finished:_________________
Centrifuge speed:_________________

16 Decant the supernate. (The supernate is waste.)

Amount of supernate decanted:_________________

17 Combine all centrifuged slurry fractions.

Weight of centrifuged solids:_________________

18 Measure the nitrate concentration of the slurry using the nitrate probe for indication.

NO_3^- concentration:_________________

19 Add “AY-102Simple Simulant for Washing” at approximately 3 times the mass of the slurry and mix thoroughly (for ~1 hour).

Amount of wash solution added:_________________

20 Centrifuge the slurry for 30 minutes at ~4500 G.

Time started:_________________ Time finished:_________________
Centrifuge speed:_________________

21 Decant the supernate. (The supernate is waste.) **<u>End of Wash 1</u>**

Amount of supernate decanted:_________________

22 Combine all centrifuged slurry fractions.

Weight of centrifuged solids:_________________

23 Measure the nitrate concentration of the slurry using the nitrate probe for indication.

NO_3^- concentration:_________________

24 Add "AY-102 Simple Simulant for Washing" at approximately 3 times the mass of the slurry and mix thoroughly (for ~1 hour).

Amount of wash solution added:_________________

25 Centrifuge the slurry for 30 minutes at ~4500 G.

Time started:_________________ Time finished:_________________
Centrifuge speed:_________________

26 Decant the supernate. (The supernate is waste.) **<u>End of Wash 2</u>**

Amount of supernate decanted:_________________

27 Combine all centrifuged slurry fractions.

Weight of centrifuged solids:_________________

28 Measure the nitrate concentration of the slurry using the nitrate probe for indication.

NO_3^- concentration:_________________

29 Add "AY-102 Simple Simulant for Washing" at approximately 3 times the mass of the slurry and mix thoroughly (for ~1 hour).

Amount of wash solution added:_________________

30 Centrifuge the slurry for 30 minutes at ~4500 G.

Time started:_________________ Time finished:_________________
Centrifuge speed:_________________

31 Decant the supernate. (The supernate is waste.) **<u>End of Wash 3</u>**

Amount of supernate decanted:_________________

32 Combine all centrifuged slurry fractions.

Weight of centrifuged solids:_________________

33 Measure the nitrate concentration of the slurry using the nitrate probe for indication.

NO_3^- concentration:_________________

34 Add **<u>ACTUAL</u>** Supernate Simulant (the batch to be used for the final combined simulant) at approximately 3 times the mass of the slurry and mix thoroughly (for ~1 hour).

Amount of wash solution added:_________________

35 Centrifuge the slurry for 30 minutes at ~4500 G.

Time started:_________________ Time finished:_________________
Centrifuge speed:_________________

36 Decant the supernate. (The supernate is waste.) **<u>End of Wash 4</u>**

Amount of supernate decanted:_________________

37 Combine all centrifuged slurry fractions.

Weight of centrifuged solids:_________________

38 Measure the nitrate concentration of the slurry using the nitrate probe for indication.

NO_3^- concentration:_________________

39 Add **<u>ACTUAL</u>** Supernate Simulant (the batch to be used for the final combined simulant) at approximately 3 times the mass of the slurry and mix thoroughly (for ~1 hour).

Amount of wash solution added:_________________

40 Add to the 2L vessel with agitation:

Compounds	Formula	Target Mass (g)	Actual Mass (g)
Sodium Carbonate	Na_2CO_3	156.0±0.78	

41 Centrifuge the slurry for 30 minutes at ~4500 G.

Time started:_________________ Time finished:_________________
Centrifuge speed:_________________

42 Decant the supernate. (The supernate is waste.) **End of Wash 5**

Amount of supernate decanted:_________________

43 Measure the nitrate concentration of the slurry using the nitrate probe for indication. If <500 mg/kg, continue to next step. If not, then perform another washing step.

NO_3^- concentration:_________________

44 Analyze the slurry for wt% total solids and wt% supernate solids (wt% solids of supernate separated from the slurry) by drying at 110°C.

Wt% total solids:_________________

Wt% supernate solids:_________________

Acceptance Criteria

The acceptance criteria below apply to the PEP simulant. This is a good example of the criteria that might be required of a simulant vendor. These criteria are chosen to control the important features of the simulant which are based on the application of the simulant. Hence for another simulant there could be an adjusted set of criteria that reflects another application.

Specific Supernate (i.e., step 7 of Section A.2)

- Shall be 5.0±0.5 M sodium, e.g., 5.0±10% (0.5M Na).
- Anion concentrations in final supernate shall be ±10% of target calculated from amounts added and final volume.

Fe-rich Solids Slurry (step 14 of Section A.3)

- Concentrations in the liquid phase of the slurry shall match the specific supernate acceptance criteria within ±10% in all categories or as determined by Technical Administrator.
- The mass ratio of iron to other elements in the UDS shall be as given in Table 2 within ±10% for the elements whose mass ratio to iron is greater than 0.01 and within ±20% for the elements whose mass ratio to iron is less than 0.01 or as determined by Technical Administrator. Because of the very, very low solubility of zirconium phosphate analysis of Zr is difficult in this high phosphate medium and it might not be observed without sophisticated analytical methods; we have successfully observed 80% of added Zr for this material.

Simulant (as shipped, not including the specific supernate set aside for rinsing)

- Shall contain ≥ 5.8-wt% UDS.
- Liquid phase shall be 5.0±0.5 <u>M</u> Na.
- Concentrations in the liquid phase of the slurry (as defined at the beginning of Section 4) shall match the specific supernate acceptance criteria within ±10% in all categories.
- The mass ratio of iron to other elements in the simulant slurry shall be as given in Table 1 within ±10% for the elements whose mass ratio to iron is greater than 0.01 and within ±20% for the elements whose mass ratio to iron is less than 0.01. Because of the very, very low solubility of zirconium phosphate analysis of Zr is difficult in this high phosphate medium and it might not be observed without sophisticated analytical methods; we have successfully observed 80% of added Zr for this material.

Table 1. Expected Mass Batching Ratios for the UDS in Fe-Rich Slurry Simulant

Element	Mass Element / Mass Fe
Mn	0.214
Ca	0.029
Ce	0.012
Fe	1.000
La	0.0087
Pb	0.046
Mg	0.0092
Nd	0.024
Ni	0.033
Sr	0.0081
Zr	0.026

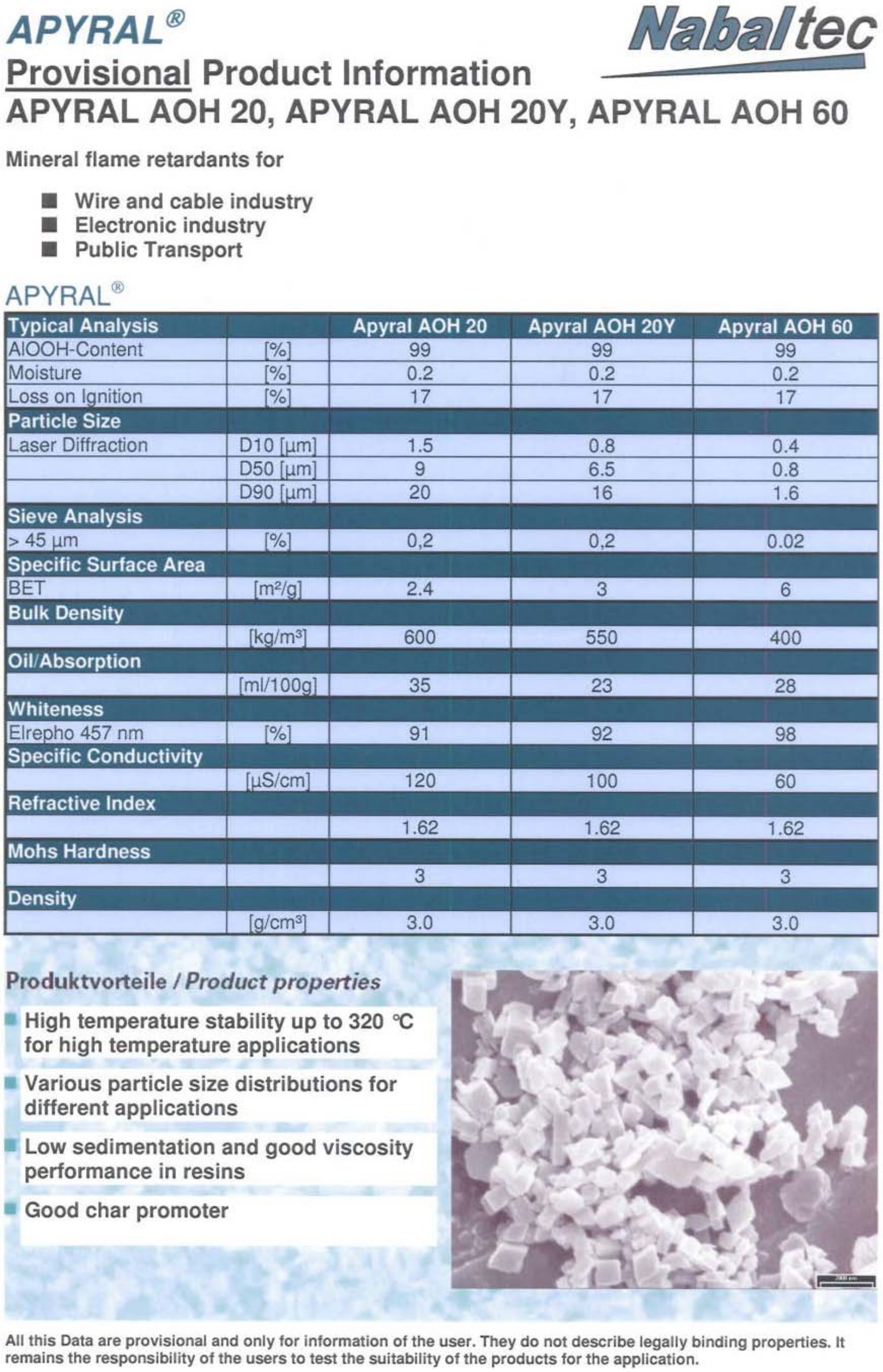
Use 24590-WTP-GPG-RTD-001, Revision 0, Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements, Effective Date: 05/20/02 which describes the measurements and calculation method to be used to determine the wt% UDS.

Appendix B

APYRAL Boehmite Product Description

Appendix B: APYRAL Boehmite Product Description

The mineral powder described below is added to the actively mixing slurry in the amount specified in the recipe.



APYRAL®

Nabaltec

Provisional Product Information

APYRAL AOH 20, APYRAL AOH 20Y, APYRAL AOH 60

Mineral flame retardants for

- Wire and cable industry
- Electronic industry
- Public Transport

APYRAL®

Typical Analysis		Apyral AOH 20	Apyral AOH 20Y	Apyral AOH 60
AlOOH-Content	[%]	99	99	99
Moisture	[%]	0.2	0.2	0.2
Loss on Ignition	[%]	17	17	17
Particle Size				
Laser Diffraction	D10 [µm]	1.5	0.8	0.4
	D50 [µm]	9	6.5	0.8
	D90 [µm]	20	16	1.6
Sieve Analysis				
> 45 µm	[%]	0,2	0,2	0.02
Specific Surface Area				
BET	[m²/g]	2.4	3	6
Bulk Density				
	[kg/m³]	600	550	400
Oil/Absorption				
	[ml/100g]	35	23	28
Whiteness				
Elrepho 457 nm	[%]	91	92	98
Specific Conductivity				
	[µS/cm]	120	100	60
Refractive Index				
		1.62	1.62	1.62
Mohs Hardness				
		3	3	3
Density				
	[g/cm³]	3.0	3.0	3.0

Produktvorteile / *Product properties*

- High temperature stability up to 320 °C for high temperature applications
- Various particle size distributions for different applications
- Low sedimentation and good viscosity performance in resins
- Good char promoter

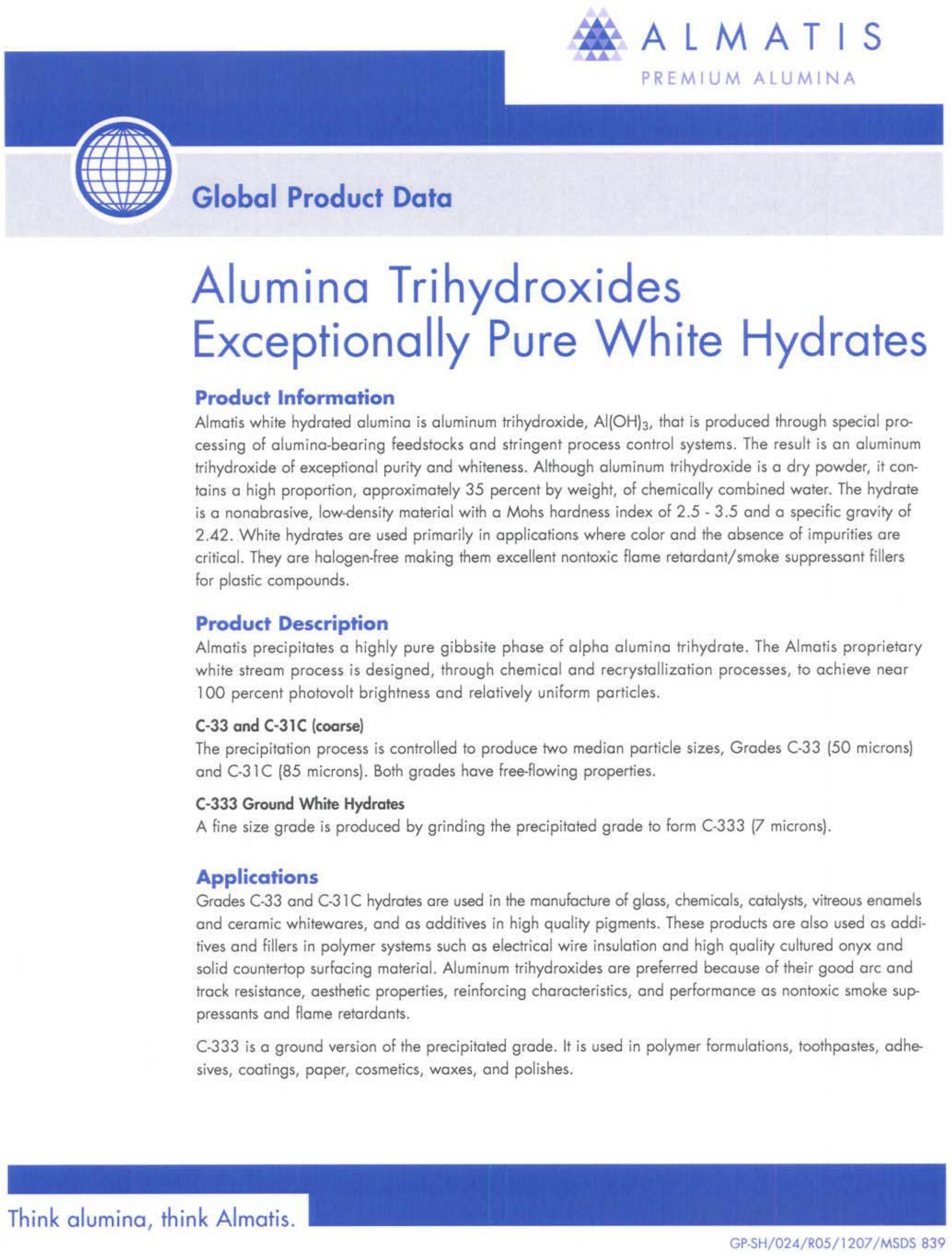
All this Data are provisional and only for information of the user. They do not describe legally binding properties. It remains the responsibility of the users to test the suitability of the products for the application.

Appendix C

Gibbsite Product Description

Appendix C: Gibbsite Product Description

The mineral powder described below is added to the actively mixing slurry in the amount specified in the recipe.



ALMATIS
PREMIUM ALUMINA

Global Product Data

Alumina Trihydroxides
Exceptionally Pure White Hydrates

Product Information

Almatis white hydrated alumina is aluminum trihydroxide, $Al(OH)_3$, that is produced through special processing of alumina-bearing feedstocks and stringent process control systems. The result is an aluminum trihydroxide of exceptional purity and whiteness. Although aluminum trihydroxide is a dry powder, it contains a high proportion, approximately 35 percent by weight, of chemically combined water. The hydrate is a nonabrasive, low-density material with a Mohs hardness index of 2.5 - 3.5 and a specific gravity of 2.42. White hydrates are used primarily in applications where color and the absence of impurities are critical. They are halogen-free making them excellent nontoxic flame retardant/smoke suppressant fillers for plastic compounds.

Product Description

Almatis precipitates a highly pure gibbsite phase of alpha alumina trihydrate. The Almatis proprietary white stream process is designed, through chemical and recrystallization processes, to achieve near 100 percent photovolt brightness and relatively uniform particles.

C-33 and C-31C (coarse)

The precipitation process is controlled to produce two median particle sizes, Grades C-33 (50 microns) and C-31C (85 microns). Both grades have free-flowing properties.

C-333 Ground White Hydrates

A fine size grade is produced by grinding the precipitated grade to form C-333 (7 microns).

Applications

Grades C-33 and C-31C hydrates are used in the manufacture of glass, chemicals, catalysts, vitreous enamels and ceramic whitewares, and as additives in high quality pigments. These products are also used as additives and fillers in polymer systems such as electrical wire insulation and high quality cultured onyx and solid countertop surfacing material. Aluminum trihydroxides are preferred because of their good arc and track resistance, aesthetic properties, reinforcing characteristics, and performance as nontoxic smoke suppressants and flame retardants.

C-333 is a ground version of the precipitated grade. It is used in polymer formulations, toothpastes, adhesives, coatings, paper, cosmetics, waxes, and polishes.

Think alumina, think Almatis.

GP-SH/024/R05/1207/MSDS 839

Alumina Trihydroxides
Exceptionally Pure White Hydrates

Product	Aluminum Trihydroxides			
	C-33	C-31C	C-333	Test Methods
Chemical Composition (%)				
$Al(OH)_3$ (min)	99.6	99.6	99.6	Difference
SiO_2	0.003	0.003	0.003	DC Arc Optical Emission Spectrometry
Fe_2O_3	0.009	0.009	0.009	
Na_2O (total)	0.20	0.26	0.17	
Na_2O (soluble)	0.008	0.008	0.026	Flame Emission Photometry
Moisture	0.08	0.08	0.26	Microwave
Physical Properties				
Loose bulk density (g/cm^3)	1.07	1.15	0.76	Modified ASTM B212-89
Packed bulk density (g/cm^3)	1.3	1.3	1.15	Modified ASTM B527-85
Refractive index	1.57	1.57	1.57	
Mohs hardness	2.5-3.5	2.5-3.5	2.5-3.5	
Density (g/cm^3)	2.42	2.42	2.42	
Surface area (m^2/g)	-	-	3.0	BET
LOI (%)	34.6	34.6	34.6	From 110-1100°C
Color	White	White	White	
Particle Size Distribution				
% on 100 Tyler mesh	0	0	-	
% on 200 Tyler mesh	8	45	0	
% on 325 Tyler mesh	60	90	1	
% through 325 Tyler mesh	40	10	99	Wet Screen
d50 (µ)	50	85	7	Sedigraph 5100 or Microtrac

2003 Data - All data are based upon Almatis standard test methods, and all test methods are available upon request.
Unless stated otherwise values are typical.

Appendix D

Preparation of Chromium Oxyhydroxide (CrOOH)

Appendix D: Preparation of Chromium Oxyhydroxide (CrOOH)

Preparation of CrOOH Slurry

General

The following recipe, which assumes 100% Cr solids yield, will provide 73.2 kg Cr as CrOOH in a nominal 2 M hydroxide slurry. Past characterizations suggest that the UDS is nominally CrOOH—H_2O.

Recipe

1) Completely dissolve 140.8 kg of $Cr(NO_3)_3$-$9H_2O$ in 1410 kg DIW with stirring. The DIW to $Cr(NO_3)_3$-$9H_2O$ mass ratio is 10:1 is critical. Use a saturated $Cr(NO_3)_3$-$9H_2O$ solution (77-wt% $Cr(NO_3)_3$-$9H_2O$) and dilute rather than beginning with a solid reagent to make certain that all the chromium is in solution.
2) Slowly add 203 kg of NaOH in the form of a 0.76 g NaOH/g DIW solution (estimated 15.8 M NaOH) with continued mixing of the solution while maintaining the temperature below 60°C.

Note: A precipitate should form during NaOH addition but should redissolve as more caustic is added.

3) After all the solids have redissolved, heat the mixture to 90°C within 1 to 2 h, while mixing.

Note: When the temperature reaches about 80°C, a precipitate should appear.

4) Maintain temperature at 90°C for 2 hours while mixing.
5) Actively cool the slurry slowly to ambient temperature in 8 to 16 hours while mixing. Monitor the temperature during cooling.
6) Measure the UDS and the $[OH^-]$ by titration to its first equivalence point.

Batch Characterization

1) Report the measured PSD, UDS, hydroxide, the common anions' (nitrate, nitrite, chloride, sulfate, phosphate, and oxalate) concentrations typically obtained using IC or an equivalent method and inorganic carbon.
2) Measure the metals content using ICP/OES or equivalent method. The elements to be reported include Al, B, Ba, Bi, Ca, Ce, Cr, Fe, K, La, Mg, Mn, Pb, Nd, Ni, P, Sr, S, Si, Sr, Zn, and Zr.

Acceptance Criteria for CrOOH Simulant Component

Based on the laboratory tests (Russell et al. 2009; Sundar 2008; Scheele 2009), the following acceptance criteria for the CrOOH simulant component are recommended for the acceptance of CrOOH simulants:

1. For each batch to be delivered, report the measured PSD, USD, hydroxide, the common anions' (nitrate, nitrite, chloride, sulfate, phosphate, and oxalate) concentrations typically obtained using ion chromatography (IC) or equivalent method approved by the Technical Administrator.

2. For each batch delivered, measure the metals content using inductively coupled plasma optical emission spectrometry (ICP/OES) or equivalent method approved by the Technical Administrator. The elements to be reported include Al, B, Ba, Bi, Ca, Ce, Cr, Fe, K, La, Mg, Mn, Pb, Nd, Ni, P, Sr, S, Si, Sr, Zn, and Zr.

3. Concentrations in the batch shall match the specific simulant acceptance criteria within ±10% for all measurable analytes except for trace constituents. Any measurable impurities detected shall be reported.

4. The CrOOH solids particle size distribution must meet the following values:
   $D_{10} \leq 5$ µm; $D_{50} \leq 25$ µm; $D_{90} \leq 60$ µm, and $D_{max} \leq 120$µm.

   $D_{10,}$ $D_{50,}$ and D_{90} represent the 10, 50 and 90 percentile size respectively of the cumulative particle size distribution by volume, and D_{max} is the maximum particle size based on volume.

5. The total amount of Cr remaining in the simulant after caustic leaching in 5M NaOH at 85°C for 8 hours should be ≥30% of the initial Cr content . The heat up period from ambient (18-20°C) to the reaction temperature of 85°C will be 4hrs. This criterion ensures availability of sufficient amount of reduced Cr for oxidative leaching.

References

Russell RL, DE Rinehart, RA Peterson, PM Aker, HD Smith, and EC Buck. 2009. *Development and Characterization of Boehmite Component Simulant.* PNNL-18176 (WTP-RPT-184), Pacific Northwest National Laboratory, Richland, Washington.

Scheele RD, GN Brown, and DE Kurath. 2009. *Scale-Up, Production, and Procurement of PEP Simulants.* PNNL-18678 (WTP-RPT-204, Rev 0), Pacific Northwest National Laboratory, Richland, Washington.

Smith GL. 2006. *Characterization and Small Scale Testing of Hanford Wastes to Support the Development and Demonstration of Leaching and Ultrafiltration Pretreatment Processes*. WTP Project Doc. No. 24590-PTF-TSP-RT-06-006, Rev 0.

Sundar PS. 2008. *Simulant Recommendation for Phase 1 Testing in the Pretreatment Engineering Platform.* WTP Project Doc. No. 24590-PTF-RPT-RT-08-006, Rev 0.

Zamecnik JR, PR Burket, and RE Eibling. 2004. *Tank 241-AY-102 Simulant Development, Ultrafiltration, and Washing.* WSRC-TR-203-00547, Rev 0, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC.

Distribution

No. of Copies	
OFFSITE	

No. of Copies		
ONSITE		
1	Pacific Northwest National Laboratory (authors will be notified electronically)	
	D.E. Kurath	K3-52
	R.A. Peterson	P7-22
	R.L. Russell	K6-24
	H.D. Smith	K6-24
	Information Release	
	Project File (1)	K3-52
4	Bechtel National Inc.	
	WTP R&T Docs (2)	H4-02
	S.M. Barnes	H4-02
	P.S. Sundar	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