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EVALUATION OF FOAMING AND ANTIFOAM EFFECTIVENESS DURING THE WTP OXIDATIVE LEACHING PROCESS

SEPTEMBER 2005

SAVANNAH RIVER NATIONAL LABORATORY

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PRETREATMENT

EVALUATION OF FOAMING AND ANTIFOAM EFFECTIVENESS DURING THE WTP OXIDATIVE LEACHING PROCESS

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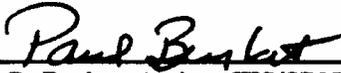
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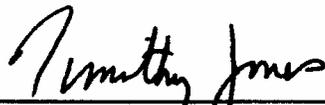
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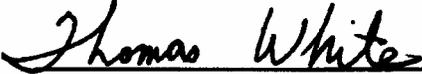
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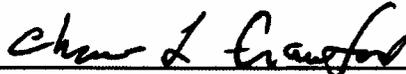
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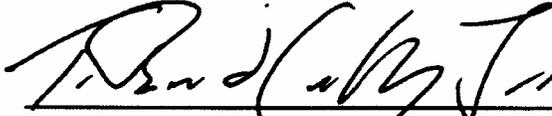
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TABLE OF CONTENTS

LIST OF FIGURES	iv
LIST OF TABLES	iv
LIST OF ACRONYMS	iv
EXECUTIVE SUMMARY	1
1.0 TESTING SUMMARY	4
1.1 OBJECTIVES.....	4
1.2 TEST EXCEPTIONS.....	4
1.3 RESULTS AND PERFORMANCE AGAINST SUCCESS CRITERIA	4
1.4 QUALITY REQUIREMENTS.....	4
1.5 R&T TEST CONDITIONS	5
1.6 SIMULANT USE.....	5
1.7 DISCREPANCIES AND FOLLOW-ON TESTS	5
2.0 INTRODUCTION.....	6
3.0 EXPERIMENTAL.....	7
3.1 EXPERIMENTAL APPARATUS AND METHODOLOGY	7
3.2 BASE SIMULANT FORMULATION	11
3.3 SIMULANT FOAMING VS. Q2-3183A ANTIFOAM CONCENTRATION	14
3.4 FOAMING VS. CAUSTIC LEACHING AND WASHING	16
3.5 FOAMING VS. OXIDATIVE LEACHING & WASHING VS. ppm Q2-3183A ..	16
3.6 FOAMING VS. WT% UDS IN HIGH CHROME SLURRY	22
3.7 FOAMING VS. CAUSTIC LEACH & OXIDATIVE LEACH AT BASELINE & IDLE SPARGER FLUXES.....	23
3.8 EFFECTIVENESS OF ANTIFOAMS Q2-3183A, Q2-3315, 1520US, AND IIT-747 DURING OXIDATIVE LEACHING	26
4.0 DISCUSSION / CONCLUSIONS.....	29
5.0 REFERENCES.....	32
APPENDIX A. HIGH CHROMIUM ADDITION TO SIMULANT FOR OXIDATIVE LEACH	33
APPENDIX B. PERMANGANATE ADDITION TO SIMULANT FOR OXIDATIVE LEACH	34
APPENDIX C. FOAMING PICTURES.....	35

LIST OF FIGURES

Figure 1. Foam Column Schematic	7
Figure 2. Foaminess Calculation Example	8
Figure 3. Caustic Leach Apparatus Schematic	9
Figure 4. %Foaminess vs. Permeate Dilution with Deionized Water.....	12
Figure 5. Foaminess vs. Wt% UDS in 50/50 SIPP Wash 1 Permeate.....	13
Figure 6. Foaminess of 12.9 wt% UDS Slurry vs. Q2-3183A Concentration.....	15
Figure 7. Foaminess vs. Caustic Leach and Washing at Air Flux of 2.2 ft ³ /min/ft ²	16
Figure 8. Oxidative Leaching and Washing of High Cr Slurry with No Antifoam.....	17
Figure 9. Oxidative Leaching and Washing of High Cr Slurry with Antifoam.....	18
Figure 10. Oxidative Leaching and Washing of High Cr Slurry at Various Air Fluxes.....	19
Figure 11. Oxidative Leaching and Washing of Low Cr Slurry with No Antifoam	20
Figure 12. Oxidative Leaching and Washing of Low Cr Slurry with 350 ppm Antifoam	21
Figure 13. Wt% UDS vs Foaminess vs Q2-3183A.....	22
Figure 14. Wt% UDS vs Foaminess vs Q2-3183A, Zero Point Removed	22
Figure 15. Foaminess After Caustic Leach and Washes.....	24
Figure 16. Foaminess During Oxidative Leach at 2.2 ft ³ /min/ft ²	25
Figure 17. Foaminess During Oxidative Leach at 0.22 ft ³ /min/ft ²	25
Figure 18. Difference in AY-102 Simulant Batches.....	26
Figure 19. Foam Column with Recirculation Loop.....	27
Figure 20. Foaminess During Oxidative Leach for Various Antifoams at 0.22 Sparger Flux	28
Figure 21. Foaminess During Oxidative Leach for Various Antifoams at 2.2 Sparger Flux	28

LIST OF TABLES

Table 1. Wash Supernate Appearance After Oxidative Leach	3
Table 2. Final Simulant Components.....	14
Table 3. Simulant Foaminess	14
Table 4. Wash Supernate Appearance After Oxidative Leach	30

LIST OF ACRONYMS

DOE	Department of Energy
HLW	High Level Waste
QA	Quality Assurance
PJM	Pulse Jet Mixers
RPP	River Protection Project
SIPP	Semi-Integrated Pilot Plant
SRNL	Savannah River National Laboratory
UDS	Undissolved Solids
WTP	Waste Treatment Plant

EXECUTIVE SUMMARY

The River Protection Project-Waste Treatment Plant (RPP-WTP) requested Savannah River National Laboratory (SRNL) to conduct small-scale foaming and antifoam testing using a Hanford waste simulant subjected to air sparging during the oxidative leaching process¹. The foaminess of Hanford tank waste solutions was previously demonstrated by SRNL during WTP evaporator foaming studies² and commercial antifoam Dow Corning Q2-3183A was recommended to mitigate the foam in the evaporators and in WTP vessels equipped with pulse jets and air spargers³. Currently, WTP is planning to use air spargers in the HLW Lag Storage Vessels (HLP-VSL-00027A/B), the Ultrafiltration Vessels (UFP-VSL-00002A&B), and the HLW Feed Blend Vessel (HLP-VSL-00028) to assist the performance of the Pulse Jet Mixers (PJM)¹.

Objectives of this test are:

- Evaluate effectiveness of the recommended antifoam (Q2-3183A) under the oxidative leaching process.
- Develop an antifoam addition strategy for the oxidative leaching process if it is effective under certain conditions.
- Evaluate effectiveness of three other antifoams and compare performances to the baseline antifoam.

This report covers test 3 of the three antifoam tests per Test Specification 24590-WTP-TSP-05-0001 to support WTP process design. Test #1 focused on degradation products and rates for this antifoam and the test results are covered by WSRC report WRSC-TR-2004-00387 rev. 1. Test #2 focused on the hydrogen generation rate from the baseline antifoam and the results are presented in WSRC report WRSC-TR-2005-00281.

The initial oxidative leaching tests were performed for the following conditions:

1. High^a Insoluble Cr, No Antifoam
2. High Insoluble Cr, with Antifoam.
3. Low Insoluble Cr, No Antifoam
4. Low Insoluble Cr, with Antifoam

Oxidative leaching of Cr is accomplished with the addition of 1M NaMnO₄ at ambient temperature (~25°C). Tests 1 and 3 (no antifoam added, see Figures 8 and 11) both showed an increase in foaminess over slurry with no NaMnO₄ added. Test 1, high insoluble Cr simulant with no antifoam showed considerably more foaminess (>1000% vs. a baseline simulant foaminess of 283%) due to the 6X larger addition of NaMnO₄. The maximum foam height occurred more than five hours after the addition of NaMnO₄. Tests 2 and 4 (High and Low Insoluble Cr, antifoam added, Figures 9 and 12) showed a rapid degradation in the effectiveness of the antifoam, possibly due to reaction with the NaMnO₄ solution. The amount of foam produced by the oxidative leaching process is a strong function of the total NaMnO₄ added to the vessel. While not completely understood at this time, the mechanism

^a Low Cr = 3.17 mg Cr/g washed solids and High Cr = 12 mg Cr/g washed solids.

causing the formation of foam during the oxidative leaching process is believed to be caused by insoluble Mn particles. A secondary cause for foaming in this process is believed to be caused by an unknown surfactant that is present in the base simulant.

The Q2-3183A antifoam was not very effective at reducing the foam during the oxidative leaching process at the baseline sparger air flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$. The antifoam reduced the foaminess to a maximum of 180% and 90% for the high and low insoluble Cr simulants, respectively. Previous SRNL foam column experiments, that were conducted to simulate air sparge tank systems, showed that an initial charge of 345 ppm antifoam reduced the foaminess of a Hanford tank waste sample AN-104, with 9 wt% undissolved solids, to 13% foam³. Therefore, Q2-3183A is not recommended for use during the oxidative leaching process at the baseline sparger air flow of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$. *Based on the results of this test, WSRC recommends WTP engineering to evaluate alternative mixing strategy, such as recirculation pumping, during the oxidative leaching process. This will mitigate the need of adding excessive antifoam during normal leaching operation.*

Further testing was performed with Q2-3183A as well as three other antifoams at the idle sparger air flux of $0.22 \text{ ft}^3/\text{min}/\text{ft}^2$ during the oxidative leaching process. As discussed in section 4.7 of this report, ***the performance of the antifoam Q2-3183A was satisfactory during the oxidative leaching process when the sparger air flux was controlled to $0.22 \text{ ft}^3/\text{min}/\text{ft}^2$*** . With no additional Q2-3183A added just prior to the oxidative leach, the foaminess remained under 7%. By adding 350 ppm Q2-3183A just prior to oxidative leaching, the foaminess remained under 2%.

By running with the sparger flux at the baseline flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$, the foaminess rose to 57% and 44% during oxidative leaching for the cases of no additional Q2-3183A added just prior to the oxidative leach and 350 ppm Q2-3183A added just prior to oxidative leaching. Note that these foaminess values are lowered by the addition of 350 ppm Q2-3183A to the slurry just prior to an initial caustic leach and washing procedure that was performed on the slurry prior to the oxidative leach. *This test further documents that mixing should not be performed with the sparger during the oxidative leaching process.*

Additional bench scale studies were also performed to test other antifoams for the oxidative leaching process. Section 4.8 of this report investigated the use of Dow Corning Q2-3315, DeBourg 747, and Dow Corning 1520US antifoams during the oxidative leaching process. In all cases, the Q2-3183A antifoam outperformed the other antifoams tested.

Washing of the oxidative leached slurry was performed with six successive dilutions of 2.7 ml 0.01M NaOH to 30 ml of slurry. Between dilutions, the wash and slurry was centrifuged, and an equivalent amount of supernate was drawn off. The appearance of the supernate from the washes provides some clues to the oxidative leaching process as illustrated in Table 1.

Table 1. Wash Supernate Appearance After Oxidative Leach

Test	Supernate Appearance
High Cr, No Antifoam	Clear purple, then green, then yellow
High Cr, with Antifoam	Cloudy yellow
Low Cr, No Antifoam	Clear yellow
Low Cr, with Antifoam	Clear yellow

For the high Cr, no antifoam case, the purple color of the supernate indicates that there was still some reactive NaMnO_4 left over after the leaching process. This NaMnO_4 could damage the ion exchange columns downstream in the WTP process. One possible reason for the remaining NaMnO_4 is mixing of the slurry only occurred for about 5 minutes per hour for the first seven hours of the leach process and then 5 more minutes at the end of the process.

For the high Cr, with antifoam case, the cloudiness of the supernate is an indication of the antifoam degradation due to reaction with the NaMnO_4 . The low Cr, with antifoam runs did not create a cloudy wash permeate. Two reasons why the high Cr runs may have had more antifoam degradation whereas the low Cr runs did not are: 1) the high Cr runs had a 6X greater concentration of NaMnO_4 than the low Cr runs, 2) the high Cr runs used 2X and 4X the amount of antifoam as the low Cr runs used.

Washing of the low Cr, with antifoam runs caused an increase in the slurry foaminess which is probably due to the dilution and removal of the antifoam from the slurry during washing. Washing of the runs which had no antifoam caused a decrease in slurry foaminess which is probably due to the reduction of dissolved solids.

Recommendations from this study are:

- The Dow Q2-3183A antifoam is not effective during the oxidative leaching process at the existing sparging flow and is not recommended for use in this condition. WSRC would recommend WTP to consider alternate mixing strategy, such as recirculation pumping, during the oxidative leaching operation.
- The Dow Q2-3183A antifoam is effective at idle sparging flow and should be used to control foaming post Design Basis Event condition. 350 ppm of Q2-3183A antifoam is recommended to use to reduce foaming as long as the spargers are controlled at idle flow.
- Based on the four antifoams tested, Dow Q2-3183A out performs other antifoams and is recommended for WTP use.
- Based on the results of these tests, no additional antifoam test work is recommended. However, preliminary data generated by SRNL in support of the Office of Science indicated that slurries generated in the Sr/TRU precipitation process also foam. WTP may consider performing tests to minimize foaming during the precipitation operation.

1.0 TESTING SUMMARY

1.1 OBJECTIVES

Test Objective	Objective Met (Y/N)	Discussion
1. Evaluate degradation of antifoam effectiveness during oxidative leaching	Y	The foaminess of the Hanford simulant was determined without oxidative leaching, with oxidative leaching at 3.17 mg Cr/g slurry, and with oxidative leaching at 12 mg Cr/g slurry. See section 3.3.
2. Develop an addition strategy for the oxidative leaching process.	Y	350 ppm of Q2-3183A antifoam was effective at reducing the foam in the oxidative leaching process as long as the sparger air flux was controlled to 0.22 ft ³ /min/ft ² .
3. Test three alternate antifoams during the oxidative leaching process.	Y	The Q2-3183A out performs the other three antifoams tested.

1.2 TEST EXCEPTIONS

List Test Exceptions	Describe Test Exceptions
1. None	

1.3 RESULTS AND PERFORMANCE AGAINST SUCCESS CRITERIA

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
1. Accurate assessment and evaluation of effectiveness of the antifoam during oxidative leaching operations.	Test results met success criteria by measuring foam height with and without antifoam. See sections 4.5 and 4.6.

1.4 QUALITY REQUIREMENTS

This work was requested by Hanford per test specification 24590-WTP-TSP-05-0001¹. The technical task plan, WSRC-TR-2005-00127⁴, provides the matrices to WTP demonstrating compliance of the SRNL QA program with the requirements specified by WTP.

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRNL as identified in DOE IWO MOSRLE60. SRNL has provided matrices to WTP demonstrating compliance of the SRNL QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRNL QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices.

1.5 R&T TEST CONDITIONS

List R&T Test Conditions	Were Test Conditions Followed?
1. Study of Make up Slurry with no Treatment	YES. See section 4.3.
2. Study with Minimum Cr Treatment without Antifoam	YES. See section 3.5.
3. Study with Minimum Cr Treatment with Antifoam	YES. See section 3.5.
4. Study with Maximum Cr Treatment without Antifoam	YES. See section 3.5.
5. Study with Maximum Cr Treatment with Antifoam	YES. See section 3.5.
6. Study with varying solids levels with Antifoam	YES. See section 4.6.
7. Perform oxidative leach per WTP-RPT-117 Rev.0 (DRAFT)	YES. The procedure was followed with some minor exceptions. See section 4.1.
8. Perform oxidative leach of high Cr Slurry with sparger flux at idle	YES. See section 4.7.
9. Test alternate antifoams at both idle and baseline sparger fluxes during the oxidative leaching process.	YES. See section 4.8.

1.6 SIMULANT USE

The Semi-Integrated Pilot Plant (SIPP) AY102/C106 simulant created during the SIPP filtration of this simulant was used for these experiments⁵. This simulant was diluted with SIPP filter caustic wash solutions and deionized water to increase foaminess of the slurry. In previous testing by Hassan et al.³, slurries were diluted to study the effect of insoluble solids concentrations on foaming.

Refer to section 3.2 for a description of the simulant formulation.

1.7 DISCREPANCIES AND FOLLOW-ON TESTS

None

2.0 INTRODUCTION

The River Protection Project-Waste Treatment Plant (RPP-WTP) requested Savannah River National Laboratory (SRNL) to conduct small-scale foaming and antifoam testing using a Hanford waste simulant subjected to air sparging during oxidative leaching¹. The foaminess of Hanford tank waste solutions was previously demonstrated by SRNL during WTP evaporator foaming studies and in small scale air sparger studies^{2,3}. The commercial antifoam, Dow Corning Q2-3183A was recommended to mitigate the foam in the evaporators and in vessel equipped with pulse jet mixers and air spargers. Currently, WTP is planning to use air spargers in the HLW Lag Storage Vessels (HLP-VSL-00027A/B), the Ultrafiltration Vessels (UFP-VSL-00002A&B), and the HLW Feed Blend Vessel (HLP-VSL-00028) to assist the performance of the Pulse Jet Mixers (PJM). The previous air sparger antifoam studies conducted by SRNL researchers³ did not evaluate the hydrogen generation rate expected from antifoam additions or the effectiveness of the antifoam during caustic leaching or oxidative leaching. The fate of the various antifoam components and breakdown products in the WTP process under prototypic process conditions (temperature & radiation) was also not investigated. The effectiveness of the antifoam during caustic leaching, expected hydrogen generation rate associated with antifoam addition, and the fate of various antifoam components are being conducted under separate SRNL research tasks^{4,6}.

3.0 EXPERIMENTAL

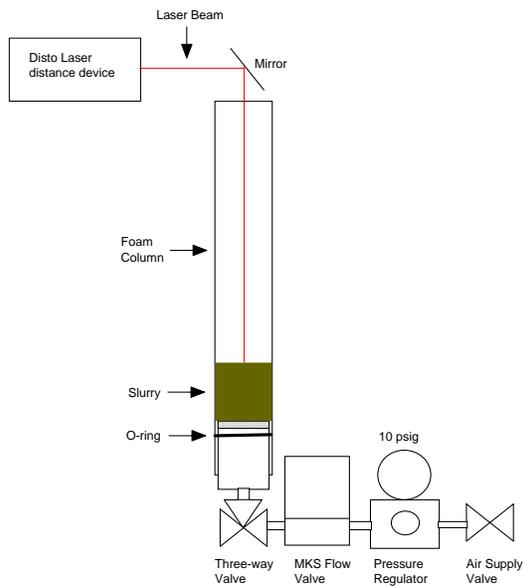
3.1 EXPERIMENTAL APPARATUS AND METHODOLOGY

The apparatus used to perform the foaming tests is the exact same apparatus used and described in “Evaluation of Foaming/Antifoaming In WTP Tanks Equipped With Pulse Jet Mixers And Air Spargers,” WSRC-TR-2004-00387³. Many details regarding bubble size, wall effects, etc. are described in that report which will not be discussed in this report.

The apparatus used to perform the foaming and antifoam experiments consisted of a glass column (3.1 cm diameter x 60 cm height) with graduations along the column wall, an air flow metering device with a three-way valve, a Disto™ Pro4 laser measuring device, and a Sony™ Mini-DV video recording camera. The foam column had a coarse fritted disk with 75-100 micron holes fitted into its base. The small bubbles created by the fritted disk were used to simulate a larger air sparger bubble broken up by introduction into a recirculation pump or sheared by some other means.

To provide the air sparging, air was introduced into the column through a 0.6 cm (1/4-inch) i.d. tube directly below the fritted disk. The flow of air was controlled by a mass flow meter (MKS Instruments, Inc.) to attain air flow rates of 0.25, 0.5, 0.75, and 1.0 L/min. These flows correspond to air fluxes of 1.1, 2.2, 3.3, 4.4 ft³/min/ft². A three-way valve below the column air-supply tube was utilized to divert air away from the column during intermittent air flux changes between tests. Figure 1 shows a schematic of the foam column.

Figure 1. Foam Column Schematic



The foam height was measured by using a Disto Pro4™ laser height detector or by visual inspection versus a centimeter/millimeter scale along the glass wall of the foaming column.

The percent foaminess was calculated per the following equations which were used and described in “Evaluation of Foaming/Antifoaming In WTP Tanks Equipped With Pulse Jet Mixers And Air Spargers”, WSRC-TR-2004-00387³.

H1 = height of liquid at rest

H2 = height of liquid at known air flux

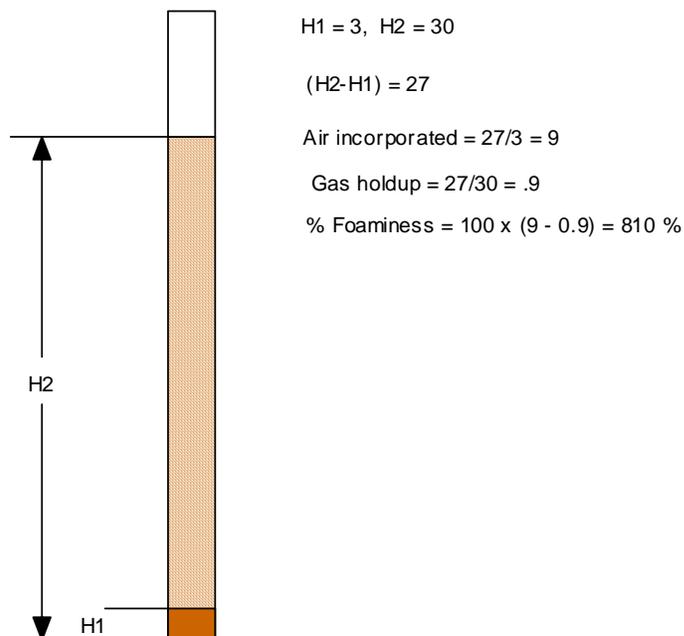
Degree of air incorporated = $(H2-H1)/H1$

Gas holdup = $(H2-H1)/H2^b$

% Foaminess = 100 x (Degree of air incorporated – gas holdup)

Figure 2 shows an example of this calculation.

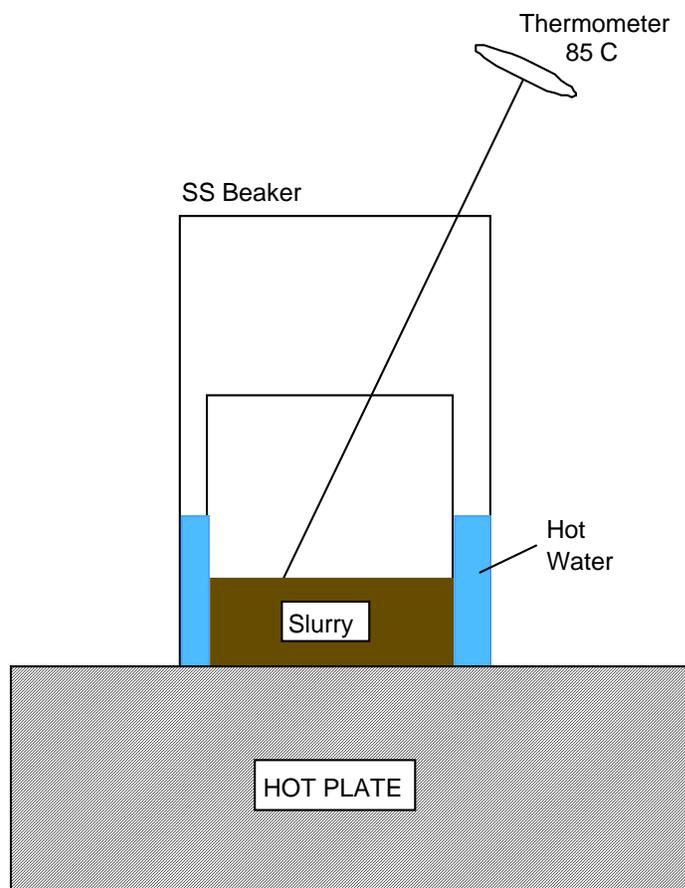
Figure 2. Foaminess Calculation Example



^b Euzen, J. P., P. Trambouzer & J. P. Wauguier, “Scale-up Methodology for Chemical Processes”, Gulf Publishing Co., New York, p. 130(1993)

Caustic leaching was performed in a 250 ml Pyrex beaker, covered with aluminum foil, which was partially submerged in a water bath which was heated by a hot plate so that the temperature of the slurry in the 250 ml beaker was 85°C. A separate heater kept standby bath water at 85°C for addition to the caustic leach bath (due to evaporative losses) to avoid a temperature disturbance. Figure 3 shows a schematic of the caustic leach apparatus.

Figure 3. Caustic Leach Apparatus Schematic



Fifty ml of slurry was treated with 19M caustic to attain a 3 M caustic solution per 24590-PTF-3YD-UFP-00001, Rev. A, page 13⁷. The solution was mixed, and then heated to 80 – 90 °C for 8 hours. The solution was allowed to cool overnight. Washing was performed per the modified wash procedure of WSRC-TR-2003-00240 rev 0, page 10⁸. Six washes were performed using 4.5 ml inhibited water per 50 ml of leached slurry.

Oxidative leaching occurred in the foam column shown in Figure 1. One molar NaMnO₄ solution or 10000 ppm Q2-3183A antifoam solution were added to the column via a calibrated auto-pipette. The pipettes were calibrated prior to each use using a calibrated scale and de-ionized water.

With WTP Engineering concurrence approval, the lower and upper Cr levels to be leached from the washed slurry were 3.17 mg Cr/g UDS and 12 mg Cr/g UDS in the slurry respectively. The chromium in the base slurry was determined and additional chromium was added in the form of Cr_2O_3 , a green non-water-soluble solid, to simulate higher chromium slurries for oxidative leaching. The calculations for the amount added for the high Cr concentration are shown in Appendix A. The calculations for the amount of 1M NaMnO_4 solution required for the high Cr content slurry are shown in Appendix B.

The oxidative leaching procedure as referenced from WTP-RPT-117 Rev. 0 is shown in the numbered instructions below.

1. Caustic leach as currently designed.
2. Cool to 25 °C.
3. Re-concentrate to original batch volume.
4. Wash as currently designed.
5. Add caustic to make the slurry 0.1 M free OH^- .
6. Add 1M NaMnO_4 at 1.1:1 ratio with Cr in unwashed solids.
7. Allow 16 hours for reaction.
8. Concentrate solids to 20 wt%.
9. Wash solids as currently designed.

Minor exceptions to this procedure are:

Step 1: Caustic leach was not performed in order to preserve the foaminess of simulant prior to the oxidative leach.

Step 3: Used 12.9 wt% UDS slurry for greatest initial foaminess.

Step 4: Not applicable since there was no caustic leach and the slurry was made up with wash solutions and undissolved AY102 slurry. The slurry was therefore partially washed to a pH of 13.6.

Step 5: The slurry had a measured pH of 13.6 so no caustic was added since the free OH^- was assumed to be greater than 0.1 M OH^- (pH=13).

Step 7: Final slurry foaminess testing didn't occur until about 22 hours after addition of NaMnO_4 solution.

Step 9: Performed using a modified six step wash procedure as described in steps 9-16 below. Note that sample size for all leaches was 30 ml.

Performance of an oxidative leach and wash was as follows:

1. Transfer 50 grams of 12.9 wt% AY-102/C-106 slurry into a beaker.
2. Add appropriate amount of Cr_2O_3 and mix well.
3. Transfer 35.4 grams of slurry into the foam column.
4. Add antifoam (if called for).
5. Turn ON air sparge at 0.50 L/min for 1 minute to mix antifoam into slurry.
6. Add appropriate amount of NaMnO_4 solution.

7. Start clock and perform foaming tests at least once per hour until quitting time.
8. Perform foaming test at start of work on next day.

WASHING

9. Pour slurry from foam column into 50 ml centrifuge tube.
10. Add 2.7 ml of 0.01M NaOH solution. (NOTE: no antifoam agent was in the wash solutions)
11. Shake well.
12. Centrifuge at setting 4 for 10 minutes.
13. Remove 2.7 ml of supernate with a slurry pipette. Put supernate into a sample bottle.
14. Shake well and visually insure homogeneous slurry is obtained.
15. Pour slurry back into foam column after wash 1, wash 3, and wash 6 for foam test.
16. After wash 6 foam test, pour slurry into sample bottle for storage.

3.2 BASE SIMULANT FORMULATION

The objective of this experiment was to study changes in simulant foaminess and antifoam effectiveness due to the oxidative leaching process. Therefore, a simulant based upon the composition of Hanford tank AY102/C106 was formulated since this simulant was shown to foam previously by Hassan³. This simulant was derived from solutions created during the processing simulant AY-102/C-106⁵ through the Semi-Integrated Pilot Plant (SIPP). Wash solutions (“Wash 1 Permeate and Wash 2 Permeate”) created during the washing of AY102/C106 were combined with AY102/C106 undissolved solids to form the simulant. Wash 1 Permeate was created during the first cycle (22 washes) of washing the AY102/C106 simulant. Wash 2 Permeate was created during the second cycle (22 washes) of washing the AY102/C106 simulant. AY102/C106 simulant foams primarily due to the presence of an unknown surfactant. The undissolved solids present in AY102/C106 simulant also help stabilize the foam to some degree. Thus, for the purposes of this testing, the AY102/C106 simulant formulated provides a reasonable model of Hanford tank waste AN104 (contains foaming surfactant & AY102/C106 solids simulant tested previously by Hassan et. al.)

SIPP wash solutions were further modified by diluting with water. Tests used the “Wash 1 Permeate” from the Hanford waste simulant AY-102/C-106 (campaign IV of the SIPP operation)⁵. Figure 4 shows the results of diluting the SIPP Wash 1 Permeate with deionized water.

Figure 4. %Foaminess vs. Permeate Dilution with Deionized Water

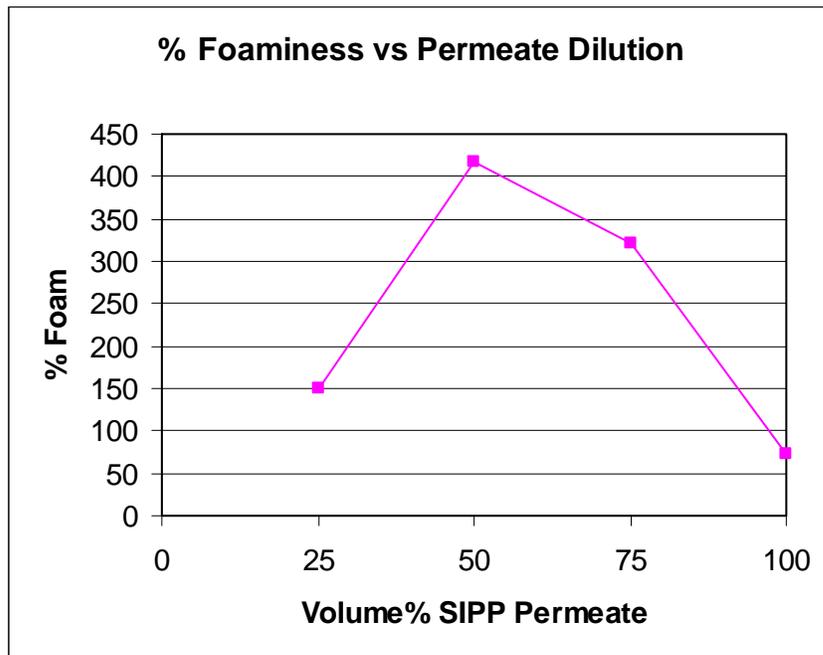


Figure 4 shows that the dilution of the permeate has a great effect on foaminess and that the peak foaminess is at or near the 50% dilution point of the wash 1 permeate. Diluting the electrolyte concentration in aqueous solutions containing surfactants is known to increase the effectiveness (& in this case the foaminess) of the surfactant. Increasing salt concentration inhibits ordering of the surfactant micelles because the added ions compress the electric double layer surrounding the micelles resulting in a dramatic decrease in the effective volume (& effectiveness) of the surfactant micelles⁹. Since the Wash 1 Permeate contained 20.78 wt% dissolved solids, a dissolved solids content near 11 wt% represents the worst case foaminess for this solution.

A second parameter that affects foaminess is the wt% undissolved solids (UDS). The starting material for the solids is the 20 wt% UDS slurry product from campaign IV product of the SIPP operation⁵. These solids were diluted to 15.3, 12.9, and 8.4 wt% UDS with Wash 1 Permeate that was diluted by 50% with de-ionized water. Therefore, this simulant represents AY102/C106 slurries that are expected to be encountered during the washing of AY102/C106 Hanford tank waste. Figure 5 shows the results of this experiment.

Figure 5. Foaminess vs. Wt% UDS in 50/50 SIPP Wash 1 Permeate

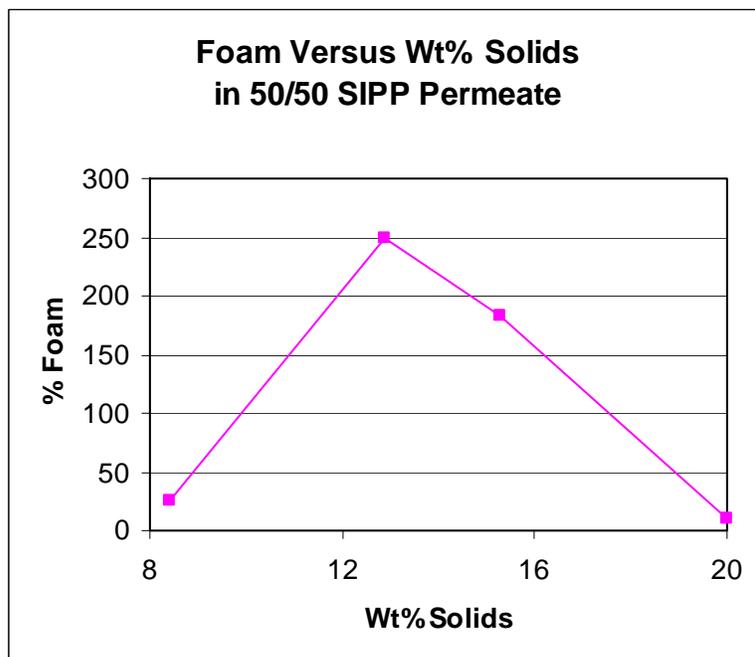


Figure 5 shows that the wt% UDS of the slurry has a great effect on foaminess and that the peak foaminess is at or near 12.9 wt% UDS slurry.

Thus, for these experiments a single batch of 12.9 wt% UDS AY102/C106 slurry was made by mixing 50/50 diluted Wash 1 Permeate with 20 wt% UDS AY102/C106 slurry. Analysis of the experiments and simulant volume required determined that about 1 liter of simulant was required. However, there was only enough of the wash 1 permeate to make-up 500 ml of 12.9 wt% UDS slurry.

Thus in an effort to find more wash 1 permeate, only wash 2 permeate could be obtained. A foaming test of the SIPP Wash 2 Permeate showed 594% foaminess at $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$ compared to 417% for the 50/50 Wash 1 Permeate at the same flux. Wash 2 Permeate was generated during the second cycle of washing AY102/C106 in the SIPP. Wash 2 Permeate foams more than Wash 1 Permeate because the electrolyte concentration is higher in the Wash 1 Permeate. The dissolved solids of the wash 2 permeate was $8.96\%⁵$ which is close to the 11 wt% obtained by diluting the wash 1 permeate by 50%.

The simulant was actually made as two batches. The first batch was 500 ml made from 50/50 wash 1 permeate plus water mixed with 20 wt% UDS slurry. The second batch was 650 ml made from wash 2 permeate mixed with 20 wt% UDS slurry. The final slurry was the mixture of the two batches together.

The final simulant components are as follows in Table 2.

Table 2. Final Simulant Components

Component	Milliliters
DI Water	93.75
Wash 1 permeate of SIPP Campaign IV	93.75
Wash 2 permeate of SIPP Campaign IV	243.75
20 wt% UDS SIPP Campaign IV product	719

The foaminess of each batch and of the combined batches is shown in Table 3.

Table 3. Simulant Foaminess

Permeate Type	Volume 12.9 wt% Slurry	Foaminess at 2.2 Flux
50/50 Wash 1	500 ml	293 %
Wash 2	650 ml	265 %
Combined Slurries Above	1150 ml	283%

The final simulant with a foaminess of 283% at the design basis plant air flux was used for these tests.

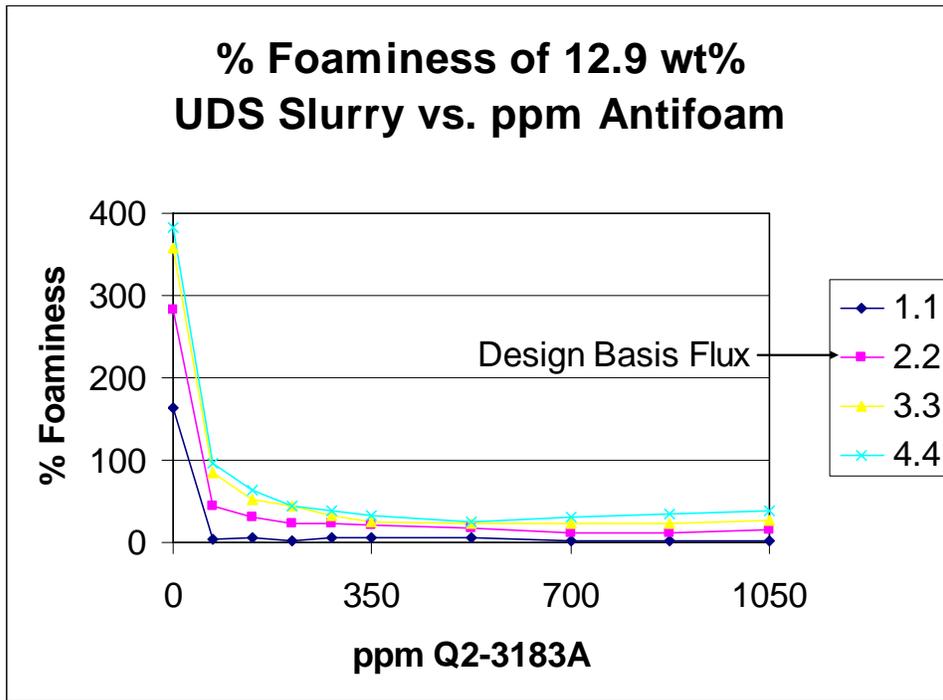
The specific gravity of the 12.9 wt% UDS simulant was 1.18 g/ml. All foam column tests using the 12.9 wt% slurry started with 30 ml of simulant which was added as 35.4 grams slurry.

3.3 SIMULANT FOAMING VS. Q2-3183A ANTIFOAM CONCENTRATION

An antifoam solution containing 10,000 ppm Dow Corning Q2-3183A in water was made. This same solution was used for all experiments in this report. The antifoam solution was added to the slurry contained in the foam column (slurry volume was controlled at 30 mL) prior to onset of foaming. In addition, the antifoam was added to existing foam in a foaming solution subjected to air sparging, and the foam collapse was followed.

The baseline performance of the simulant and how its foaming was affected by various concentrations of the Q2-3183A antifoam in the slurry was established. Foaming was measured at four air flowrates as described in section 4.1. After measuring the foaming of the slurry without antifoam, 70 ppm increments of antifoam were added to the slurry, and the foaming was measured at each increment, up to 350 ppm antifoam. From 350 ppm antifoam on, 175 ppm increments of antifoam were added to the slurry, and the foaming was measured at each increment, up to 1050 ppm antifoam. Figure 6 shows the results of this experiment.

Figure 6. Foaming of 12.9 wt% UDS Slurry vs. Q2-3183A Concentration



These results show the simulant foams in a manner that is consistent with the AY102 simulant used previously by SRNL researchers³. However, the magnitude of the foam is not as high as the AY102 simulant used previously. While the origin (both used materials from the SIPP) of both simulants is the same, the age and exact make-up of the simulants is different. However for the purposes of this study, the foaming of the simulant turned out to be somewhat insignificant compared to the foam caused by the oxidative leaching process (See Section 4.5)

3.4 FOAMING VS. CAUSTIC LEACHING AND WASHING

Caustic leaching and washing of 50 ml of slurry was performed as discussed in section 4.1 using the apparatus shown in Figure 3". Upon completion of these processes, 30 ml of the treated slurry were added to the foam column (shown in Figure 1) to measure foaming. Figure 7 shows the effect that caustic leaching and washing has on foaming at the design basis plant air flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$.

Figure 7. Foaming vs. Caustic Leach and Washing at Air Flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$

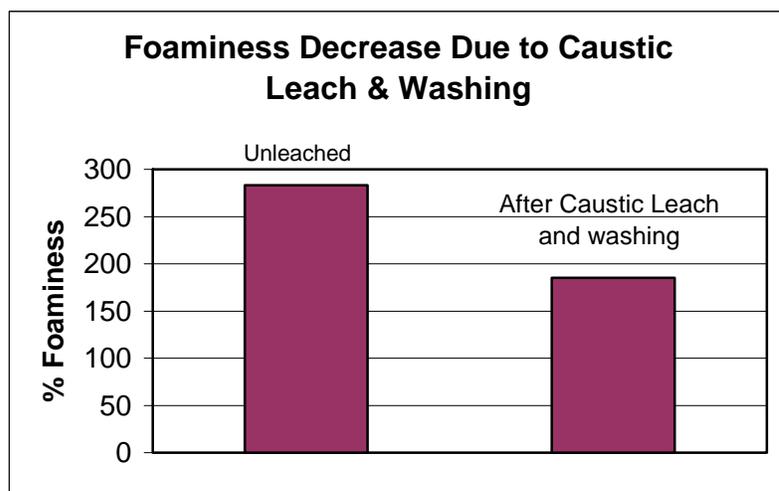


Figure 7 shows that the foaminess of the slurry is reduced from 283% down to 185%. The 283% foaminess comes from Figure 6 where the condition is $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$ flux and no antifoam. The reduction in foaminess is probably due to a reduction in the dissolved solids content of the supernate fraction along with a reduction in the undissolved solids content (see Figure 4 and Figure 5). The reduction could also be due to a dilution of the surfactant concentration in the simulant.

3.5 FOAMING VS. OXIDATIVE LEACHING & WASHING VS. ppm Q2-3183A

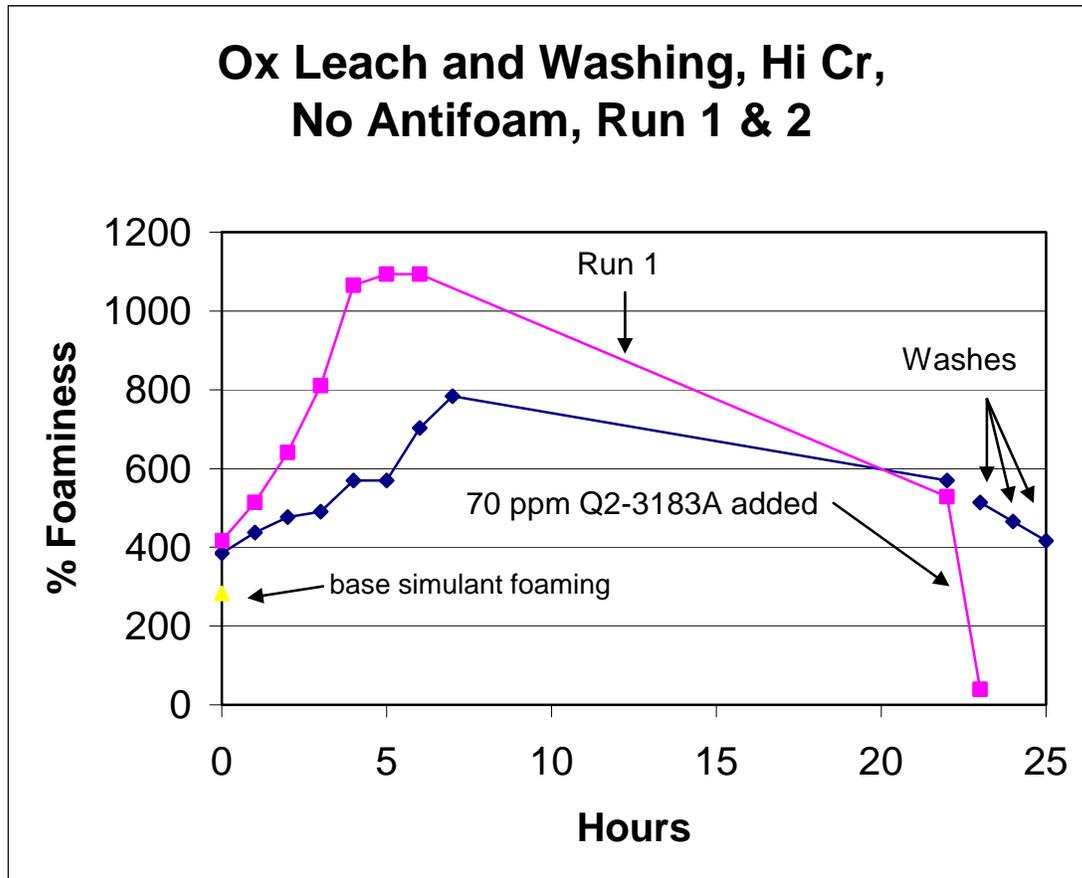
The oxidative leach test results will be described in the following order:

1. High Insoluble Cr, No Antifoam
2. High Insoluble Cr, with Antifoam.
3. Low Insoluble Cr, No Antifoam
4. Low Insoluble Cr, with Antifoam

Oxidative Leaching and Washing of High Cr Slurry with No Antifoam

Two runs were performed as described in section 4.1 of this report. The oxidative leach with high Cr used 1.8 ml of 1M NaMnO₄ solution. Run 1 had 70 ppm Q2-3183A added at the end of the oxidative leach, but did not undergo washing. Figure 8 shows the results for the design basis plant air flux of 2.2 ft³/min/ft².

Figure 8. Oxidative Leaching and Washing of High Cr Slurry with No Antifoam

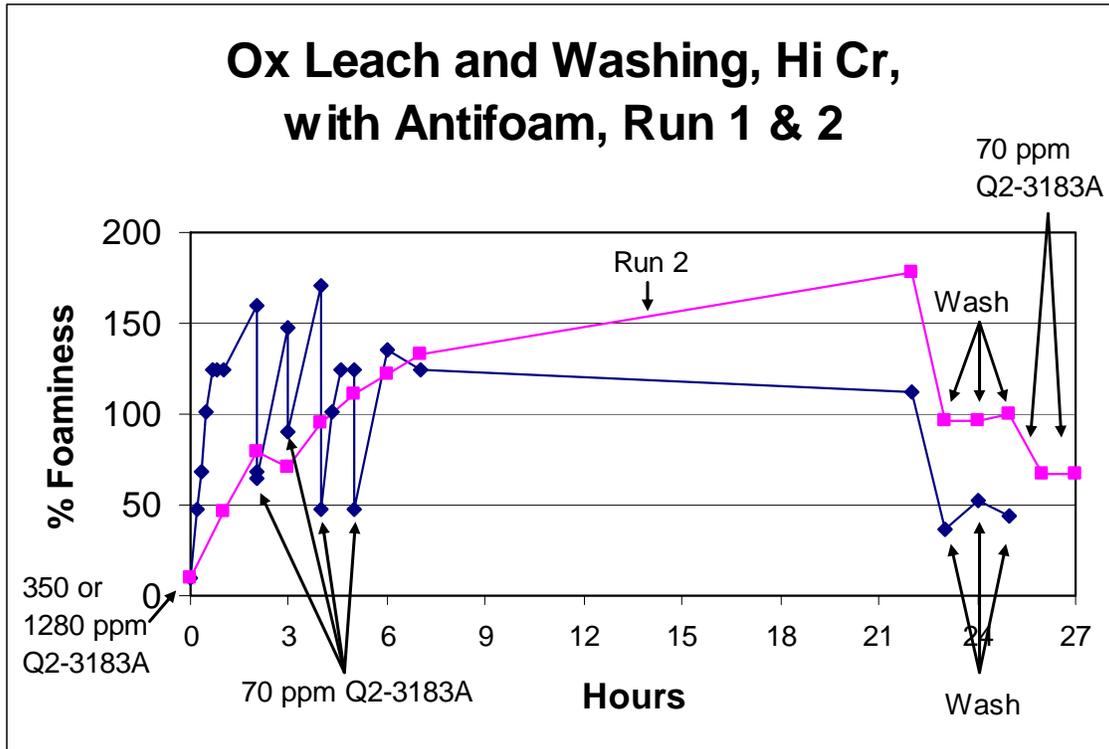


Though there is a significant difference in maximum foaminess between the two runs it is notable that they both began the oxidative leach near 400% and ended the oxidative leach near 550%. Compare to 283% foaminess for basic slurry. Washing lowered run 2 foaminess down to 400% and a 70 ppm addition of antifoam lowered run 1 foaminess down to 40%. The run 2 wash 1 supernate initially appeared a clear dark purple. After sitting for an hour undisturbed, it turned to a clear dark green. The run 2 wash 2 supernate appeared a clear light green. The remainder of the wash supernates were clear yellow.

Oxidative Leaching and Washing of High Cr Slurry with Antifoam

Two runs were performed as described in section 4.1 of this report. The oxidative leach with high Cr used 1.8 ml of 1M NaMnO₄ solution. Run 1 began with 350 ppm Q2-3183A and run 2 began with 1280 ppm Q2-3183A. Run 1 received five additional 70 ppm Q2-3183A additions during the first five hours of the oxidative leaching. Both runs received the standard wash. Run 2 received two additional 70 ppm Q2-3183A additions after the washes. Figure 9 shows the results for the design basis plant air flux of 2.2 ft³/min/ft².

Figure 9. Oxidative Leaching and Washing of High Cr Slurry with Antifoam

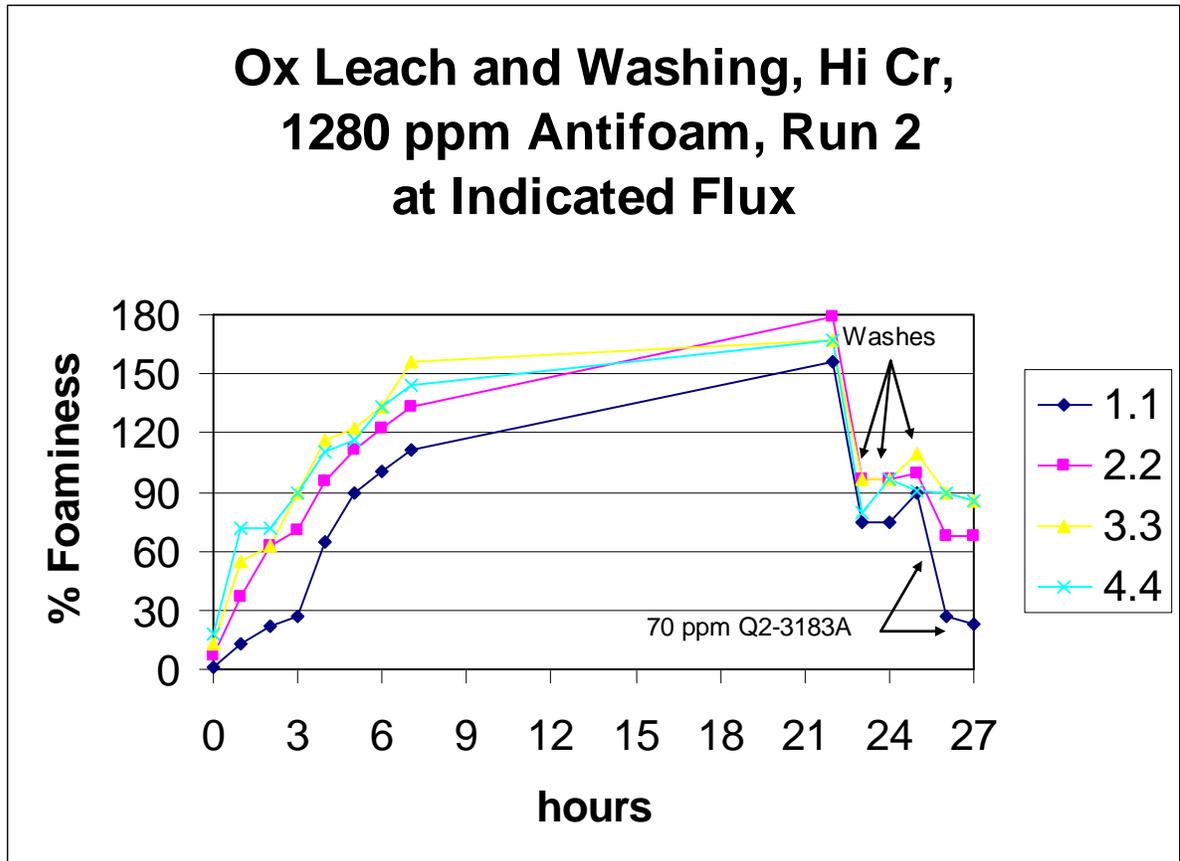


The NaMnO₄ impaired the antifoam’s effectiveness in both runs, possibly due to degradation of the antifoam by the highly oxidizing permanganate. Less of the Q2-3183A was used in run 1 (2 ml of 10000 ppm Q2-3183A) than in run 2 (4.2 ml of 10000 ppm Q2-3183A). The washes reduced foaminess in both runs. A cloudy yellow supernate was observed after the first wash and all subsequent washes. The two additional 70 ppm Q2-3183A additions after the washes to run 2 only provided a marginal reduction in foaminess.

Oxidative Leaching and Washing of High Cr Slurry at Various Air Fluxes

Figure 10 is run 2 from Figure 9 on “Oxidative Leaching and Washing of High Cr Slurry with Antifoam” shown as a function of air sparge rate. The air fluxes range from 1.1 to 4.4 ft³/min/ft².

Figure 10. Oxidative Leaching and Washing of High Cr Slurry at Various Air Fluxes

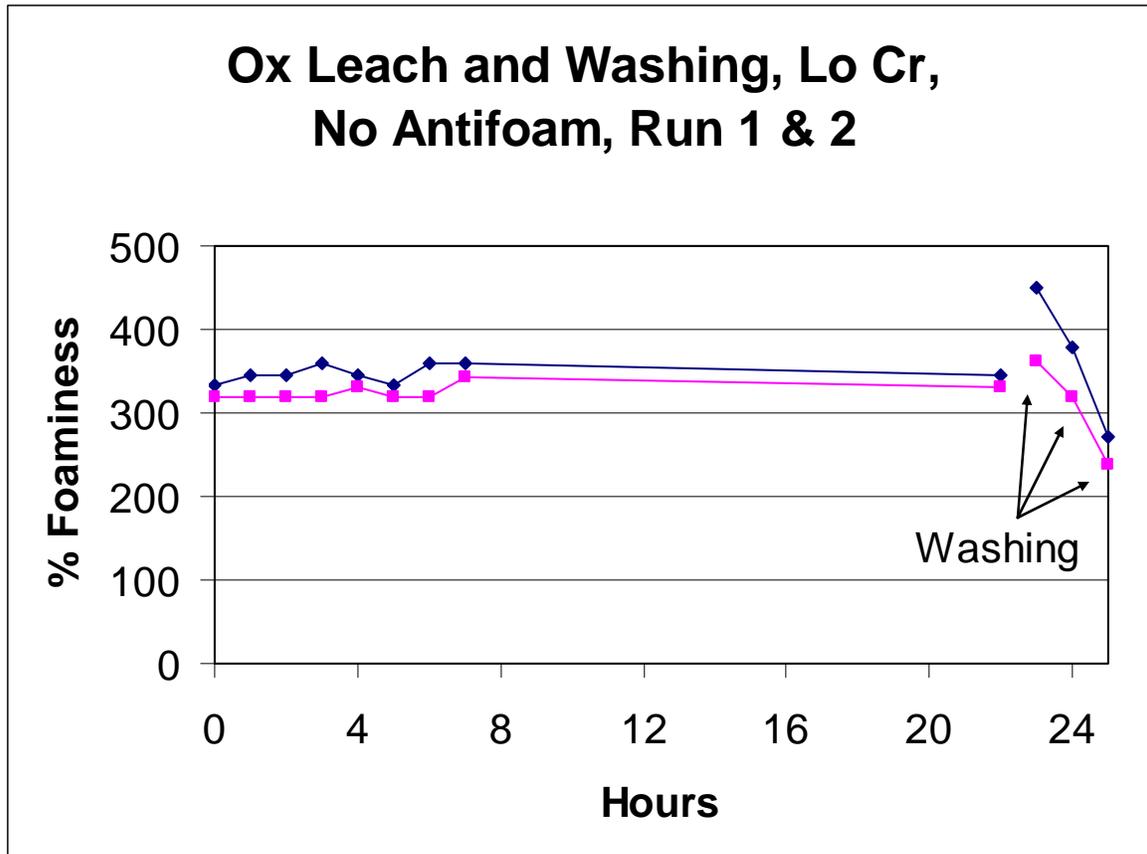


In general, more air bubbled through the slurry produces a higher foam height. This same phenomenon can also be observed in Figure 6.

Oxidative Leaching and Washing of Low Cr Slurry with No Antifoam

Two runs were performed simultaneously in two adjoining foam columns and were performed as described in section 4.1 of this report. Due to a calculation error performed in the lab, only 0.3 ml of 1M NaMnO₄ solution was added to the slurry instead of the required 0.47 ml. Thus, enough permanganate was added to treat 2 mg Cr/g solids rather than 3.17 mg Cr/g solids actually in the slurry. Figure 11 shows the results for the design basis plant air flux of 2.2 ft³/min/ft².

Figure 11. Oxidative Leaching and Washing of Low Cr Slurry with No Antifoam

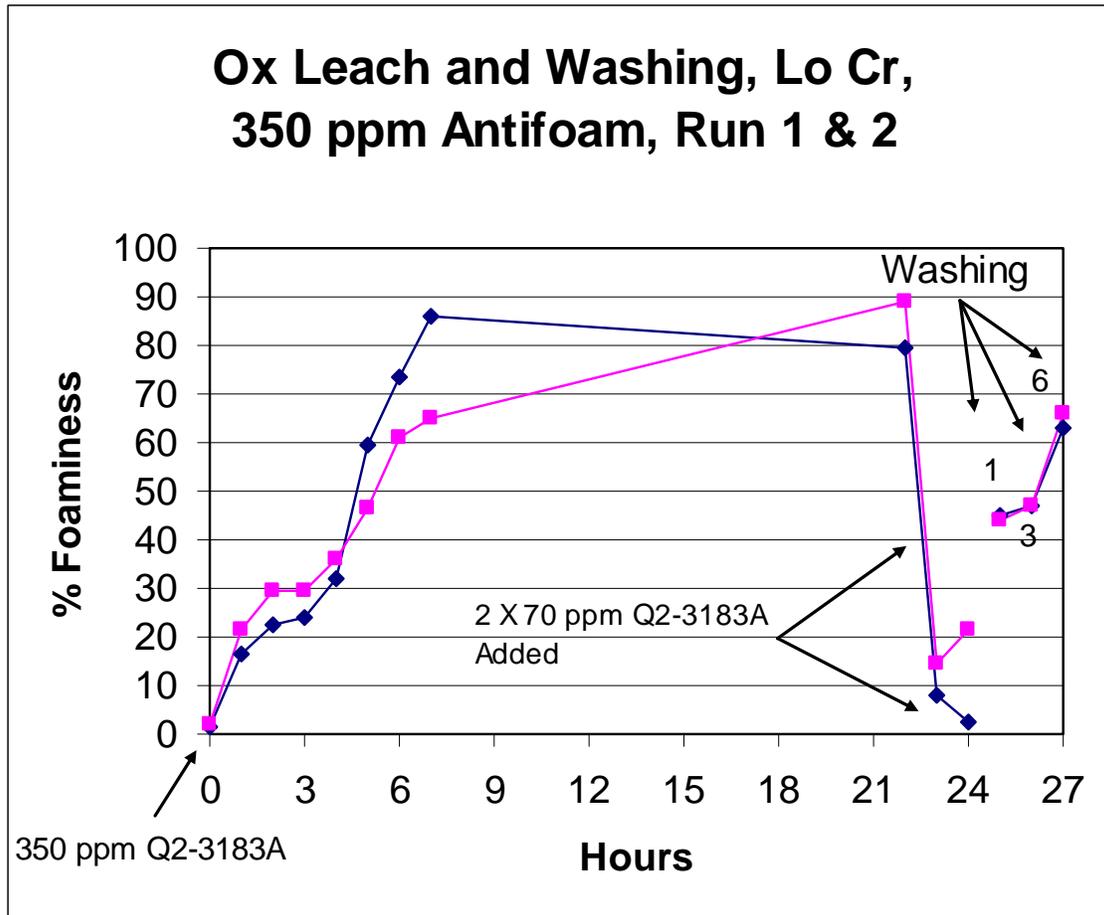


An average foaming of 336% shows a slight increase in foaming versus the 283% for untreated slurry shown in Figure 7. A clear yellow supernate was observed after the first wash and all subsequent washes. Foaming first increased due to washing, then decreased from further washing.

Oxidative Leaching and Washing of Low Cr Slurry with Antifoam

Two runs were performed simultaneously in two adjoining foam columns and were performed as described in section 4.1 of this report. Since the oxidative leach with low Cr and no antifoam used 0.3 ml of 1M NaMnO₄ solution, the same was added in these experiments for comparative results. Antifoam (350 ppm) was added at the start of the runs. Two successive additions of 70 ppm antifoam were added at the end of the oxidative leach, but prior to washing. Figure 12 shows the results for the design basis plant air flux of 2.2 ft³/min/ft².

Figure 12. Oxidative Leaching and Washing of Low Cr Slurry with 350 ppm Antifoam



The average peak foaminess at the end of the oxidative leach was 85% which compares favorably to the average foaminess of 336% for treated slurry without antifoam shown in Figure 11. A clear yellow supernate was observed after the first wash and all subsequent washes. Foaminess increased due to washing probably due to the dilution and removal of the antifoam.

3.6 FOAMING VS. WT% UDS IN HIGH CHROME SLURRY

Foaminess of the high chrome slurry was tested at three different concentrations of undissolved solids (UDS). These concentrations were 8, 15, and 20 wt% UDS. The effectiveness of the Q2-3183A antifoam was tested for each of these cases. Figure 13 and Figure 14 show the results of these tests for the design basis air flux of 2.2 ft³/min/ft².

Figure 13. Wt% UDS vs Foaminess vs Q2-3183A

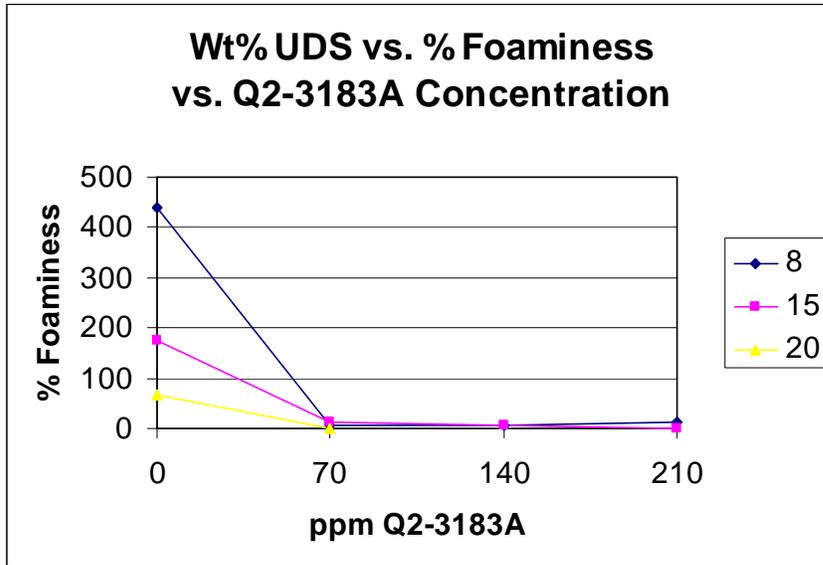
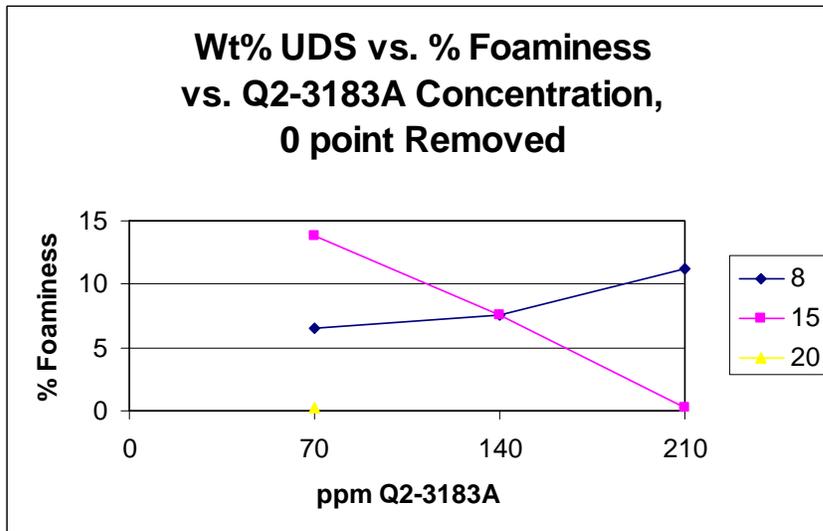


Figure 14. Wt% UDS vs Foaminess vs Q2-3183A, Zero Point Removed



The much reduced foaminess in the higher solids concentrations are corroborated by these tests versus those shown in Figure 5. The antifoam was quite effective at reducing the foaming at all three solids concentrations. At 70 ppm Q2-3183A, the 20 wt% UDS slurry foam's percent foaminess was reduced to 0%. At 210 ppm Q2-3183A, the 15 wt% UDS slurry foam's percent foaminess was reduced to 0%. At 70 ppm Q2-3183A, the 8 wt% UDS slurry foam's percent foaminess was reduced to 6%. The 8 wt% UDS slurry exhibited an odd behavior of increasing foaminess after 70 ppm Q2-3183A.

The high initial result for the 8 wt% UDS condition contradicts the result for the nearly same condition shown in Figure 5. The odd behavior of the 8 wt% slurry is probably due to a difference in how it was made. It was expected that a mixture of the 12.9 wt% slurry mixed with wash 2 permeate to form an 8 wt% slurry would act nearly the same as if supernate from the 12.9 wt% slurry itself was used. However, the slurry foamed much more than expected and does not compare favorably with similar results for the nearly same condition shown in Figure 5.

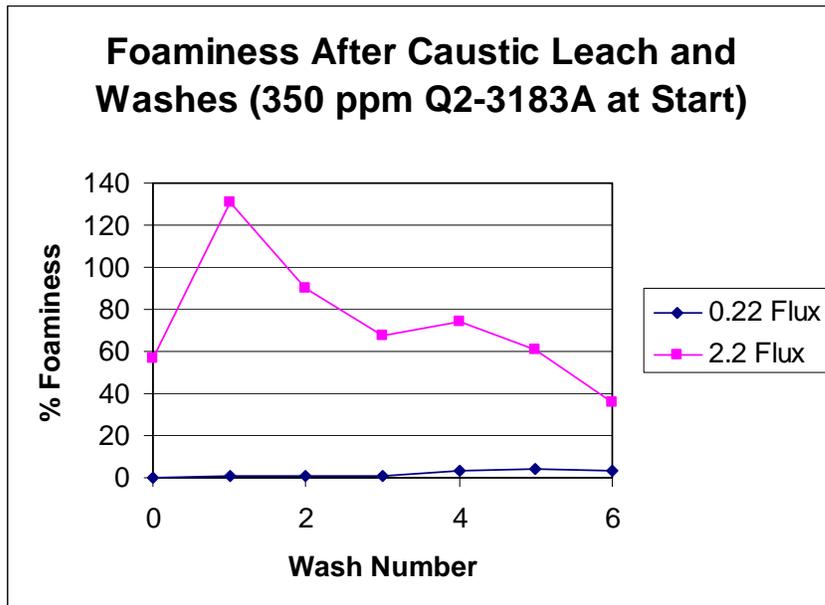
Thus 12 ml of the wash 2 permeate was mixed into 18 ml of the 12.9 wt% base solution to form an 8 wt% UDS solution. The 8 wt% data point should be ignored with relation to all other data in this report. This result does show that foaminess can be affected by differences in simulant make-up.

3.7 FOAMING VS. CAUSTIC LEACH & OXIDATIVE LEACH AT BASELINE & IDLE SPARGER FLUXES

If the oxidative leach is performed at ambient temperature, then the process pump can be used for agitation of the tank material and the sparger can be left at an idle flowrate to prevent pluggage in the sparger tube. These tests measured percent foaminess at the idle sparger air flux of $0.22 \text{ ft}^3/\text{min}/\text{ft}^2$ and at the baseline sparger air flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$. To simulate pump mixing, a peristaltic pump recirculated the slurry through the foam column at a rate of approximately one total slurry volume per ten minutes.

The 12.9 wt% UDS simulant had Cr_2O_3 added so that the simulant had 12 mg Cr / g slurry, which is considered the highest expected Cr concentration for Hanford waste. Q2-3183A antifoam was added just prior to the caustic leaching such that there was 350 ppm antifoam in the slurry. After performing the caustic leach and cooling the material down to ambient temperature, the 100 ml of caustic leached slurry was washed six times with 9 ml of 0.01M NaOH. A centrifuge was used to separate and remove supernate for each wash. The % foaminess was measured at the idle flux ($0.22 \text{ ft}^3/\text{min}/\text{ft}^2$) and at the baseline flux ($2.2 \text{ ft}^3/\text{min}/\text{ft}^2$) after the caustic leach and each wash. The results are shown in Figure 15.

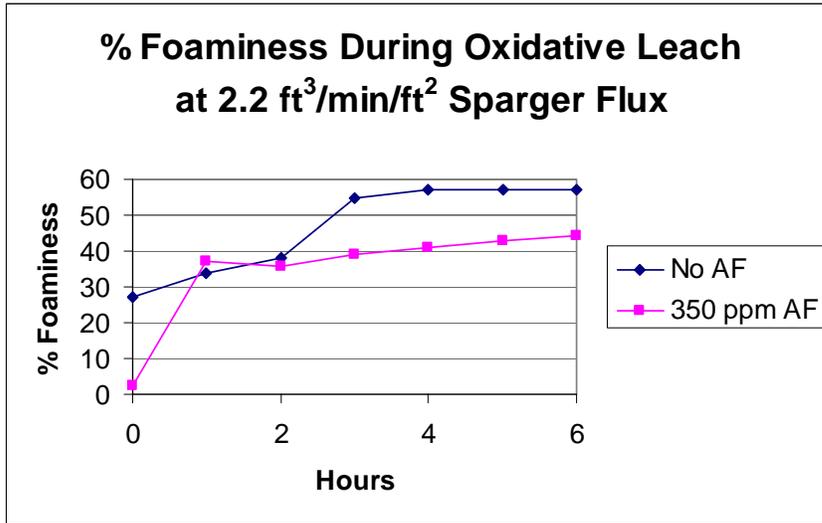
Figure 15. Foaminess After Caustic Leach and Washes



As seen in Figure 15, the caustic leach and washing reduces the foaminess of the slurry. In this case it went from 56% down to 36% foaminess. Figure 7 showed a reduction from 283% down to 185% foaminess with no antifoam. The percentage of drop in percentage foaminess is very close between the two runs (35% versus 34% respectively). The difference in magnitude is due to the addition of antifoam in this latest run.

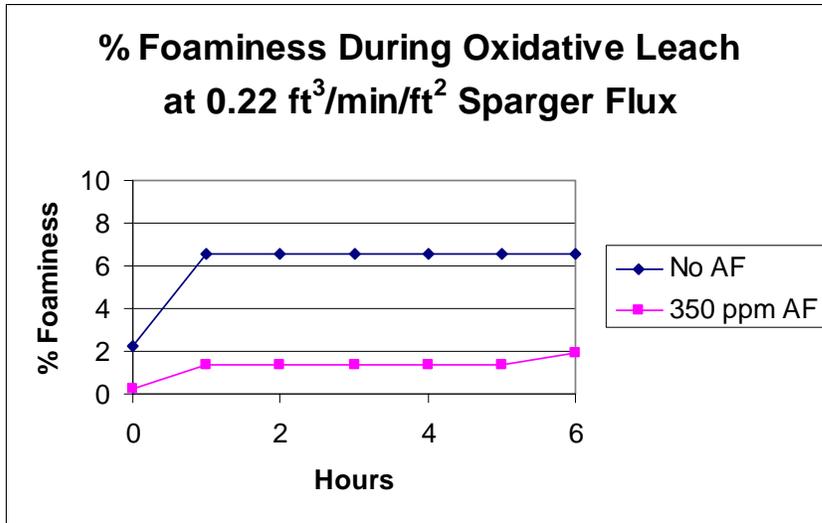
Two comparative runs using the slurry from the caustic leach and washing were then run through an oxidative leach. The first run was performed without further antifoam added. The second run had an additional 350 ppm of Q2-3183A added just prior to the start of the oxidative leaching. Each reaction ran for 6 hours at ambient temperature. Each 32 ml of slurry was constantly being recirculated at 4 ml/min to mimic plant recirculation. The sparger air was set at 0.22 ft³/min/ft² throughout each run. It was raised to 2.2 ft³/min/ft² once per hour to get a baseline foaminess reading. The results from these runs are shown in Figure 16 and Figure 17.

Figure 16. Foaminess During Oxidative Leach at 2.2 ft³/min/ft²



At the baseline sparger air flux, the added 350 ppm of Q2-3183A antifoam, (in addition to the 350 ppm Q2-3183A added at the start of the caustic leach), only reduced the percentage foam height by an average of 14.75% from the third hour to the sixth hour of the reaction.

Figure 17. Foaminess During Oxidative Leach at 0.22 ft³/min/ft²

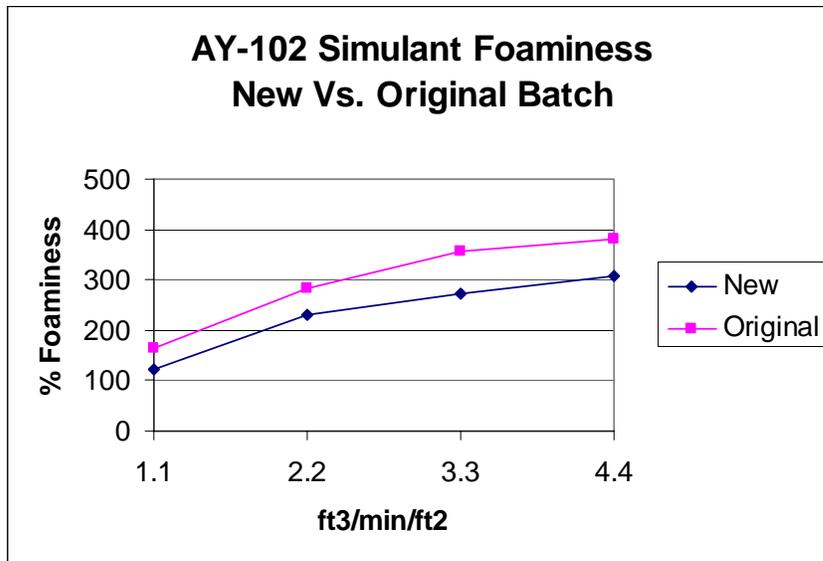


The added 350 ppm of Q2-3183A had a minimal effect on reducing the percentage foam at the idle sparger air flow rate because there was so little foam formed at that condition.

3.8 EFFECTIVENESS OF ANTIFOAMS Q2-3183A, Q2-3315, 1520US, AND IIT-747 DURING OXIDATIVE LEACHING

These tests were performed to determine if other antifoams might prove to be more effective at reducing the foam during the oxidative leaching process. Unfortunately, the supply of slurry simulant, used for all previous tests discussed in this report, was consumed. Therefore, another batch of simulant was made using the same base materials as the original simulant. However, the new batch of simulant did not exhibit the same foaming as the original batch of simulant. Therefore, all data in this section of the report is not comparable to the data in the rest of the report. A comparison of the new 12.9 wt% AY-102 slurry versus the original 12.9 wt% AY-102 slurry is shown in Figure 18.

Figure 18. Difference in AY-102 Simulant Batches



Since the new simulant was different (less foamy) than the original simulant, a run was performed with the Q2-3183A and the new simulant for comparison with the other antifoams in this section.

The foam column had a recirculating peristaltic pump connected up to it as shown in Figure 19. This was added to simulate pump mixing in the process tank while the sparger air is at idle flow.

Figure 19. Foam Column with Recirculation Loop



The process for these tests was performed as follows:

1. Add 41.5 ml of AY-102 slurry to the foam column. Note that this volume gives the same starting liquid level in the foam column as 30 ml did with a foam column that did not have a recirculating pump loop.
2. Add Q2-3183A antifoam to reach 70 ppm concentration in slurry.
3. Add (antifoam under investigation) to reach 350 ppm concentration in slurry.
4. Run pump on prime (high speed) until all air is out of pump lines (no bubbles appear from line discharge).
5. RECORD liquid level.
6. Set air flux to $0.22 \text{ ft}^3/\text{min}/\text{ft}^2$.
7. RECORD FOAM height.
8. STOP air flow.
9. ADD 1M NaMnO_4 solution.
10. RECORD liquid level.
11. Run pump on prime (high speed) for 1 minute to thoroughly mix permanganate into slurry.
12. Set pump flow to 5 ml/min.
13. Set air flux to $0.22 \text{ ft}^3/\text{min}/\text{ft}^2$.
14. RECORD FOAM height.
15. RECORD FOAM height every hour for remainder of shift (at least 6 hours). Also measure foam height at air flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$ once per hour.
16. ADD 70 ppm of antifoam after the 6th hour. RECORD FOAM height after antifoam addition. Also measure foam height at air flux of $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$.

The results of performing this test for antifoams Q2-3183A, 1520US, Bourgman 747, and Q23315 are shown in Figure 20.

Figure 20. Foaminess During Oxidative Leach for Various Antifoams at 0.22 Sparger Flux

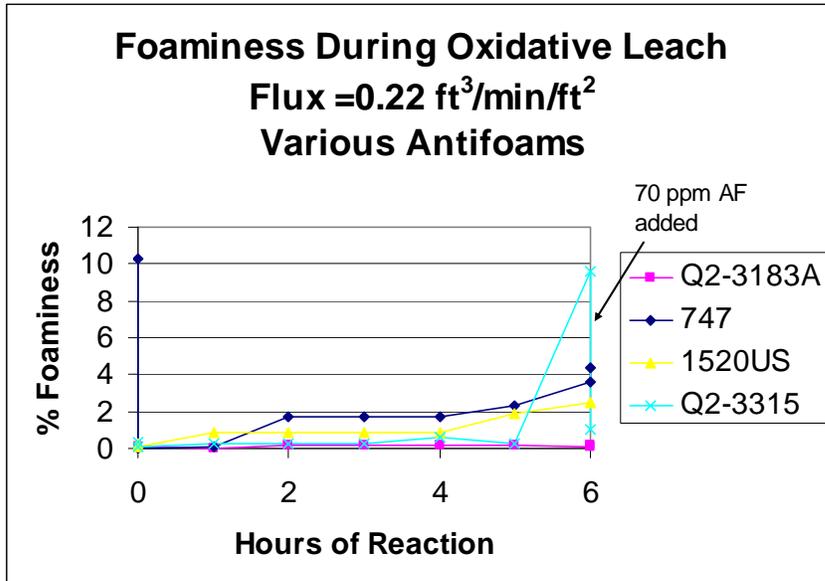
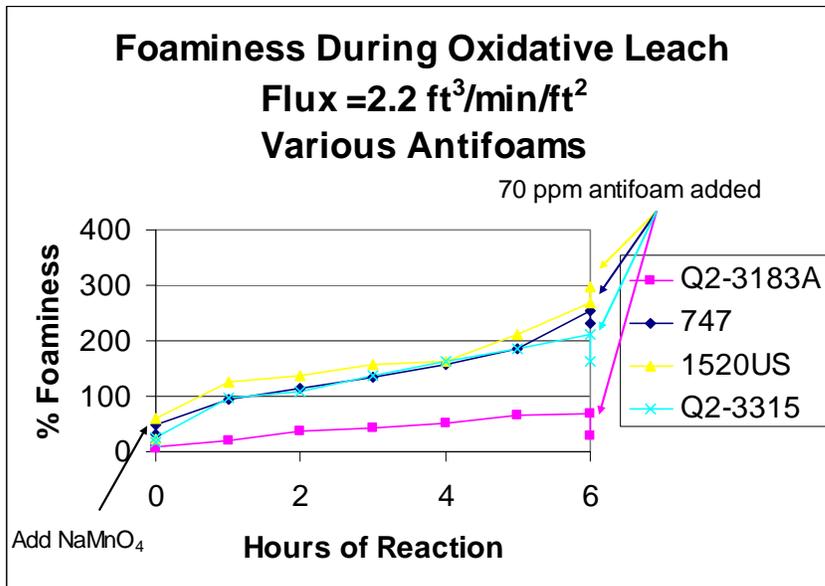


Figure 21. Foaminess During Oxidative Leach for Various Antifoams at 2.2 Sparger Flux



Though the difference in foaming was insignificant between the four antifoams at the idle sparger rate of 0.22 ft³/min/ft², once the sparger rate was increased to the baseline rate of 2.2 ft³/min/ft², the Q2-3383A antifoam showed much better performance than the other three antifoams tested.

4.0 DISCUSSION / CONCLUSIONS

The Dow Corning Q2-3183A antifoam was effective at reducing the foaminess of the simulant as shown in Figure 6 when the spargers are either at idling or sparging condition, but not when oxidative leaching and full sparging are in progress.

Caustic leaching and washing of the simulant reduced the foaminess of the simulant from 283% down to 185%. This is probably due to a reduction in both the undissolved solids (due to the caustic leach) and dissolved solids (due to the washing). Thus the caustic leach and wash was not performed on the simulant used for the oxidative foaming tests.

The oxidative leaching tests were performed for the following conditions:

1. High insoluble Cr, No Antifoam
2. High insoluble Cr, with Antifoam
3. Low insoluble Cr, No Antifoam
4. Low insoluble Cr, with Antifoam.

Oxidative leaching of Cr is accomplished with the addition of 1M NaMnO₄ at ambient temperature. Tests 1 and 3 (no antifoam added, see Figure 8 and Figure 11) both showed an increase in foaminess over slurry with no NaMnO₄ added. Test 1, high insoluble Cr simulant with no antifoam showed considerably more foaminess (>1000% vs. a baseline simulant foaminess of 283%) due to the 6X larger addition of NaMnO₄. The maximum foam height occurred more than five hours after the addition of NaMnO₄. Tests 2 and 4 (High and Low Insoluble Cr, antifoam added, Figure 9 and Figure 12) showed a rapid degradation in the effectiveness of the antifoam, possibly due to reaction with the NaMnO₄ solution. The amount of foam produced by the oxidative leaching process is a strong function of the total NaMnO₄ added to the vessel. While not completely understood at this time, the mechanism causing the formation of foam during the oxidative leaching process is believed to be caused by insoluble Mn particles. A secondary cause for foaming in this process is believed to be caused by an unknown surfactant that is present in the base simulant.

The antifoam was not very effective at reducing the foam during the baseline oxidative leaching process. The antifoam reduced the foaminess to a maximum of 180% and 90% for the high and low insoluble Cr simulants, respectively. Previous SRNL foam column experiments, that were conducted to simulant air sparge tank systems, showed an initial charge of 345 ppm antifoam reduced the foaminess of a Hanford tank waste sample, AN-104 with 9 wt% simulant solids, to 13%³ foam. Therefore, Q2-3183A is not recommended for use during the oxidative leaching process at the baseline sparger air flow of 2.2 ft³/min/ft².

Further testing was performed with Q2-3183A as well as three other antifoams at the idle sparger air flux of 0.22 ft³/min/ft² during the oxidative leaching process. As discussed in section 4.7 of this report, ***the performance of the antifoam Q2-3183A was satisfactory during the oxidative leaching process when the sparger air flux was controlled to 0.22 ft³/min/ft².*** With no additional Q2-3183A added just prior to the oxidative leach, the foaminess remained under 7%. By adding 350 ppm Q2-3183A just prior to oxidative leaching, the foaminess remained under 2%.

By running with the sparger flux at the baseline flux of 2.2 ft³/min/ft², the foaminess rose to 57% and 44% during oxidative leaching for the cases of no additional Q2-3183A added just prior to the oxidative leach and 350 ppm Q2-3183A added just prior to oxidative leaching. Note that these foaminess values are lowered by the addition of 350 ppm Q2-3193A to the slurry just prior to an initial caustic leach and washing procedure that was performed on the slurry prior to the oxidative leach. *This test further documents that mixing should not be performed with the sparger during the oxidative leaching process.*

Additional bench scale studies were also performed to test other antifoams for the oxidative leaching process. Section 4.8 of this report investigated the use of Dow Corning Q2-3315, DeBourg 747, and Dow Corning 1520US antifoams during the oxidative leaching process. In all cases, the Q2-3183A antifoam outperformed the other antifoams tested.

Washing of the oxidative leached slurry was performed with six successive dilutions of 2.7 ml inhibited water to 30 ml of slurry. Between dilutions, the wash and slurry would be centrifuged, and an equivalent amount of supernate would be drawn off. The appearance of the supernate from the washes provides some clues to the oxidative leaching process. Table 4 summarizes the supernate appearance for the different runs.

Table 4. Wash Supernate Appearance After Oxidative Leach

Test	Supernate Appearance
High Cr, No Antifoam	Clear purple, then green, then yellow
High Cr, with Antifoam	Cloudy yellow
Low Cr, No Antifoam	Clear yellow
Low Cr, with Antifoam	Clear yellow

For the high Cr, no antifoam case, the purple color of the supernate indicates that there was still some reactive NaMnO₄ left over after the leaching process. This NaMnO₄ could damage the ion exchange columns downstream in the WTP process. One possible reason for the remaining NaMnO₄ is mixing of the slurry only occurred for about 5 minutes per hour for the first seven hours of the leach process and then 5 more minutes at the end of the process.

For the high Cr, with antifoam case, the cloudiness of the supernate is an indication of the antifoam degradation due to reaction with the NaMnO₄. The low Cr, with antifoam runs did not create a cloudy wash permeate. Two reasons why the high Cr runs showed antifoam degradation whereas the low Cr runs did not are: 1) the high Cr runs had a 6X greater concentration of NaMnO₄ than the low Cr runs, 2) the high Cr runs used 2X and 4X the amount of antifoam as the low Cr runs used.

Washing of the low Cr, with antifoam runs caused an increase in the slurry foaminess. This is probably due to the dilution and removal of the antifoam from the slurry during washing. Washing of the runs which had no antifoam caused a decrease in slurry foaminess. This is probably due to the reduction of dissolved solids.

The simulant for these experiments came from the SIPP operation⁵, campaign IV. This simulant was washed AY-102/C-106 simulant that did not have the caustic leach performed on it⁵.

In the process of making up a foamy simulant, two variables were found to have a major impact on the foaminess of the simulant. The first was the dissolved solids content of the permeate and the second was the undissolved solids content of the slurry. These observations are consistent with literature⁹. For both variables, there was a point of maximum foaminess where any increase or decrease in solids content would cause a decrease in foaminess. The final simulant was made at the solids concentrations of maximum foaminess and had a concentration of 12.9 wt% undissolved solids and ~11 wt% dissolved solids.

5.0 REFERENCES

1. Hani Abodishish, Test Specification - "*Evaluation Of Foaming/Antifoaming In WTP Tanks Equipped With Pulse Jet Mixers And Air Spargers.*" 24590-WTP-TSP-05-0001, Hanford, WA. March, 2005.
2. Baich, M. A., Stone, M. E., White, T. L., Calloway, T. B., "*Waste Treatment Plant Evaporation: Antifoam Performance,*" WSRC-TR-2003-00216, Rev. 0, Westinghouse Savannah River Company, August 2003.
3. Hassan, N. M., Jones, T. M., Daniel, W. E. Hansen, E. K., Eibling, R. E. Calloway, T. B., "*Evaluation of Foaming/Antifoaming In WTP Tanks Equipped With Pulse Jet Mixers And Air Spargers,*" WSRC-TR-2004-00387, Westinghouse Savannah River Company, September 2004.
4. Burket, P. R., Crawford, C. L., White, T. L., Duffey, C. E., Calloway, T. B., "*Task Technical and Quality Assurance Plan for Evaluation of Foaming/Antifoaming in the WTP Aluminum and Oxidative Leaching Processes,*" WSRC-TR-2005-00127, Westinghouse Savannah River Company, March 2005.
5. Duignan, M. R., Adamson, D. J., Calloway, T. B., Fowley, M. D., Qureshi, Z. H., Steimke, J. L., Williams, M. R., Zamecnik, J. R., "*Final Report: RPP-WTP Semi-Integrated Pilot Plant,*" WSRC-TR-2005-00105, Westinghouse Savannah River Company, February 2005.
6. Crawford, C. L., Duffey, C. E., Burket, P. R., Calloway, T. B., "*Task Technical and Quality Assurance Plan for H₂ Generation Rate Scoping Study of DOW Corning Antifoam Agent,*" WSRC-TR-2005-00144, Westinghouse Savannah River Company, March 2005.
7. Boh, G. L., "*System Description for Ultrafiltration Process System (10-UFP),*" 24590-PTF-3YD-UFP-00001, Rev. A, Bechtel, December 2001.
8. Poirier, M. R., Burket, P. R., Siler, J. L., Zamecnik, J. R., "*Filtration, Washing, and Leaching of a AY-102/C-106 Sample,*" WSRC-TR-2003-00240 rev. 0, Westinghouse Savannah River Company, June 2003.
9. Nikolov, A. D., D. T. Wasan, D. Hunge, A. D. Edwards, Presented at 61st Annual Technical Conference and Exhibition of Society of Petroleum Engineers, New Orleans, L. A. October 5-8, 1986; SPE Preprint 15443.
10. Titration of Oxalate with Permanganate,
<http://www.bgsu.edu/departments/chem/faculty/endres/ch128/oxalate.htm>, Bowling Green State University.

APPENDIX A. HIGH CHROMIUM ADDITION TO SIMULANT FOR OXIDATIVE LEACH

High Chromium in AY-102 Slurry for Oxidative Leach

RPP requested an upper limit of 12 mg Cr / g of washed solids for oxidative leaching. Though we are working with 12.9 wt% washed slurry, we are going to add Cr to it as if it were 20 wt% slurry.

The ADS analysis of the 12.9 wt% slurry reports 398 ug Cr / g slurry.

We will perform two 30 ml foam tests without antifoam and two 30 ml foam tests with antifoam for a total of 120 ml of slurry to be treated. An extra 40 ml of slurry will be made up to account for losses. Therefore 160 ml of slurry will be made up to have 12 mg Cr / g slurry.

$$\text{Total Slurry} = 160 \text{ ml slurry} \times \frac{1.18 \text{ g slurry}}{\text{ml slurry}} = 188.8 \text{ g slurry}$$

$$\text{Cr in Slurry} = 188.8 \text{ g slurry} \times \frac{.398 \text{ mg Cr}}{\text{g slurry}} = 75 \text{ mg Cr}$$

MW of Cr_2O_3 = 152 g / mol
 MW of Cr = 52 g / mol

$$\frac{\text{g Cr}_2\text{O}_3}{\text{g Cr}} = \frac{152 \text{ g Cr}_2\text{O}_3}{\text{mol Cr}_2\text{O}_3} \times \frac{\text{mol Cr}_2\text{O}_3}{2 \text{ mol Cr}} \times \frac{\text{mol Cr}}{52 \text{ g Cr}} = 1.4615$$

Chromium addition required:

$$\frac{75 \text{ mg Cr} + x \text{ mg Cr}}{188.8 \text{ g slurry} + (1.4615 \times \frac{x \text{ mg Cr}}{1000})} = \frac{12 \text{ mg Cr}}{\text{g solids}} \times \frac{.2 \text{ g solids}}{\text{g slurry}}$$

379 mg Cr needed.

$$\text{Cr}_2\text{O}_3 \text{ to add} = 0.379 \text{ g Cr} \times \frac{1.4615 \text{ g Cr}_2\text{O}_3}{\text{g Cr}} = 0.554 \text{ g Cr}_2\text{O}_3$$

Instruction:

Add 0.554 grams Cr_2O_3 to 188.8 g of slurry.

APPENDIX B. PERMANGANATE ADDITION TO SIMULANT FOR OXIDATIVE LEACH

Sodium Permanganate Addition for High Cr Leaching

Per WTP-RPT-117, 1M NaMnO₄ is added at a 1.1:1 ratio, based on the Cr in the unwashed slurry, to the washed slurry.

$$\frac{30 \text{ ml slurry}}{\text{column}} \times \frac{1.18 \text{ g}}{\text{ml slurry}} = \frac{35.4 \text{ g slurry}}{\text{column}}$$

Cr to treat per column

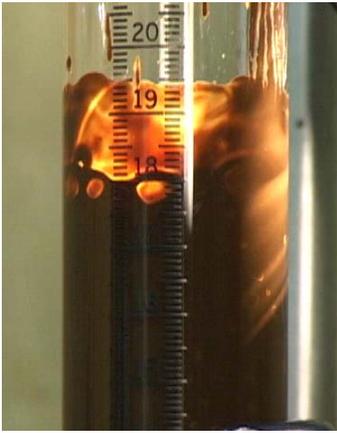
$$\frac{12 \text{ mg Cr}}{\text{g solids}} \times \frac{.2 \text{ g solids}}{\text{g slurry}} \times 35.4 \text{ g slurry} \times \frac{\text{g Cr}}{1000 \text{ mg Cr}} \times \frac{\text{mol Cr}}{52 \text{ g Cr}} = 0.00163 \text{ mol Cr}$$

ml of 1M NaMnO₄ to add per column

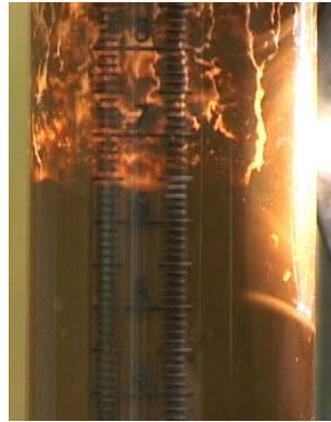
$$0.00163 \text{ mol Cr} \times \frac{1.1 \text{ mol MnO}_4}{\text{mol Cr}} \times \frac{1000 \text{ ml}}{\text{mol NaMnO}_4} = 1.8 \text{ ml 1M NaMnO}_4$$

For the Low Cr run, 0.3 ml of 1M NaMnO₄ was added. 0.48 ml of 1M NaMnO₄ should have been added, but a calculational error of using 12.5 wt% solids versus 20 wt% solids skewed the amount of NaMnO₄ added low.

APPENDIX C. FOAMING PICTURES



Baseline Simulant
Flux = $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$
Foam ht. = 18 cm
Foaminess = 283%

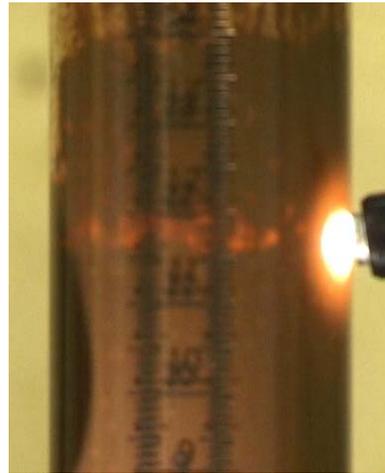


Baseline Simulant with 210 ppm
Antifoam, Flux = $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$
Foam ht. = 6.5 cm
Foaminess = 23%



Oxidative Leach of High Cr
Simulant at 4 hours after start of reaction,
Flux = $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$
Foam ht. = 44 cm
Foaminess = 1065%

No Antifoam



Oxidative Leach of High Cr
Simulant with 350 ppm Antifoam at
6 hours after start of reaction.
Flux = $2.2 \text{ ft}^3/\text{min}/\text{ft}^2$
Foam ht. = 11.5 cm
Foaminess = 203%

Antifoam Added