SRNS-STI-2008-00081
Revision 0

Sludge Mass Reduction: Primary Compositional Factors that Influence Melt Rate for Future Sludge Batch Projections

J.D. Newell
D.H. Miller
M.E. Stone
B.R. Pickenheim

August 2008

Environmental & Chemical Process Technology
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-08SR22470

SRNL
SAVANNAH RIVER NATIONAL LABORATORY
TM

DISCLAIMER

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

SRNS-STI-2008-00081
Revision 0

Keywords: *sludge mass reduction, DWPF, Al Dissolution, melt rate, MRF*

Retention: *permanent*

Factors that Influence Melt Rate for Future Sludge Batch Projections

J.D. Newell
D.H. Miller
M.E. Stone
B.R. Pickenheim

August 2008

Environmental & Chemical Process Technology
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-08SR22470

REVIEWS AND APPROVALS

AUTHORS:

J.D. Newell, Process Engineering Technology Date

D.H. Miller, Process Engineering Technology Date

M.E. Stone, Process Engineering Technology Date

B.R. Pickenheim, Process Engineering Technology Date

TECHNICAL REVIEWER:

D.K. Peeler, Process Engineering Technology Date

APPROVERS:

C.C. Herman, Manager, Process Engineering Technology Group Date

J.C. Griffin, Manager, E&CPT Research Programs Date

M.T. Keefer, Project Owner – Sludge Mass Reduction Program Date
Technology Development and Tank Closure – Liquid Waste Organization

P.C. Suggs, DOE – SRS/AMWDP Date
Technology Development Lead

EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) was tasked to provide an assessment of the downstream impacts to the Defense Waste Processing Facility (DWPF) of decisions regarding the implementation of Al-dissolution to support sludge mass reduction and processing. Based on future sludge batch compositional projections from the Liquid Waste Organization's (LWO) sludge batch plan, assessments have been made with respect to the ability to maintain comparable projected operating windows for sludges with and without Al-dissolution. As part of that previous assessment, candidate frits were identified to provide insight into melt rate for average sludge batches representing with and without Al-dissolution flowsheets.

Initial melt rate studies using the melt rate furnace (MRF) were performed using five frits each for Cluster 2 and Cluster 4 compositions representing average without and with Al-dissolution. It was determined, however, that the REDOX endpoint ($Fe^{2+}/\Sigma Fe$ for the glass) for Clusters 2 and 4 resulted in an overly oxidized feed which negatively affected the initial melt rate tests. After the sludge was adjusted to a more reduced state, additional testing was performed with frits that contained both high and low concentrations of sodium and boron oxides. These frits were selected strictly based on the ability to ascertain compositional trends in melt rate and did not necessarily apply to any acceptability criteria for DWPF processing. The melt rate data are in general agreement with historical trends observed at SRNL and during processing of SB3 (Sludge Batch 3)and SB4 in DWPF. When MAR acceptability criteria were applied, Frit 510 was seen to have the highest melt rate at 0.67 in/hr for Cluster 2 (without Al-dissolution), which is compositionally similar to SB4. For Cluster 4 (with Al-dissolution), which is compositionally similar to SB3, Frit 418 had the highest melt rate at 0.63 in/hr. Based on this data, there appears to be a slight advantage of the Frit 510 based system without Al-dissolution relative to the Frit 418 based system with Al-dissolution.

Though the without aluminum dissolution scenario suggests a slightly higher melt rate with frit 510, several points must be taken into consideration:

1. The MRF does not have the ability to assess liquid feeds and, thus, rheology impacts. Instead, the MRF is a "static" test bed in which a mass of dried melter feed (SRAT product plus frit) is placed in an "isothermal" furnace for a period of time to assess melt rate. These conditions, although historically effective in terms of identifying candidate frits for specific sludge batches and mapping out melt rate versus waste loading trends, do not allow for assessments of the potential impact of feed rheology on melt rate. That is, if the rheological properties of the slurried melter feed resulted in the mounding of the feed in the melter (i.e., the melter feed was thick and did not flow across the cold cap), melt rate and/or melter operations (i.e., surges) could be negatively impacted. This could affect one or both flowsheets.
2. Waste throughput factors were not determined for Frit 510 and Frit 418 over multiple waste loadings. In order to provide insight into the mission life versus canister count question, one needs to define the maximum waste throughput for both flowsheets. Due to funding limitations, the melt rate testing only evaluated melt rate at a fixed waste loading.
3. DWPF will be processing SB5 through their facility in mid-November 2008. Insight into the over arching questions of melt rate, waste throughput, and mission life can be obtained directly from the facility. It is recommended that processing of SB5 through the facility be monitored closely and that data be used as input into the

decision making process on whether to implement Al-dissolution for future sludge batches.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

Al	Aluminum
CPC	Chemical Process Cell
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EM	Environmental Management
LMR	Linear Melt Rate
LTAD	Low Temperature Aluminum Dissolution
LWO	Liquid Waste Organization
MAR	Measurement Acceptability Region
MRF	Melt Rate Furnace
PCCS	Product Composition Control System
QA	Quality Assurance
SB	Sludge Batch
SMR	Sludge Mass Reduction
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
T_L	Liquidus Temperature
η	Viscosity
WALD	With Al-Dissolution
WL	Waste Loading (weight percent)
WOALD	Without Al-Dissolution
WT	Waste Throughput

1.0 Introduction

Savannah River National Laboratory (SRNL) was tasked to provide an assessment of the potential downstream impacts to the Defense Waste Processing Facility (DWPF) of decisions concerning the implementation of Al-dissolution to support Sludge Mass Reduction (SMR). The primary intent of SMR is to minimize the mass of sludge that must be treated in DWPF via vitrification. Implementation of Al-dissolution is one means for accomplishing this objective since it should translate into a decrease in the number of high-level waste canisters produced assuming similar waste loadings can be achieved (as compared to the same sludge batch without Al-dissolution). However, there may be other technical issues that impact the effectiveness of the Al-dissolution process and decisions to implement. These include (but are not limited to):

(1) the effectiveness of the Al-dissolution process (i.e., the amount of Al that will be removed)[1],
(2) possible rheological issues associated with the sludge after Al-removal [2], which could hamper sludge transfer and/or melter processing and preparation in the Tank Farm,
(3) impacts to downstream processes [3] such as Saltstone (which will process the Al-rich supernate) and DWPF,
(4) impacts to glass formulation efforts (in particular, the ability of frit development efforts to compensate for the sludge compositional changes), and
(5) impacts to melt rate or waste throughput (i.e., the amount of waste being processed per unit time) for the DWPF.

If Al-dissolution is not implemented or less effective Al-dissolution is realized, glass formulation efforts will have to accommodate higher Al_2O_3 concentrations (assuming similar waste loadings are targeted). Although projected Al_2O_3 concentrations in glass do not appear to approach solubility limits for DWPF-type glasses [4], higher targeted waste loadings or significant improvements in melt rate would be required to off-set the increased sludge mass. It is possible that significant melt rate differences could exist between a sludge composition having undergone Al-dissolution relative to one that has not. A primary driver in defining that possible difference is the ability of frit development efforts to compensate for the higher or lower Al_2O_3 content while maintaining access to waste loadings of interest and meeting related process control criteria. As previously mentioned, the ability to target similar waste loadings for a sludge resulting from the Al-dissolution process, as compared to the same sludge without Al-dissolution, is the primary driver to support assessment of canister count differences.

Recently, the SRNL formulated a relatively high Al-based glass system for DWPF in support of Sludge Batch 4 (SB4) implementation.* As a result of that research, Frit 510 (a high B_2O_3-based frit) was recommended to DWPF. DWPF has been able to target a nominal waste loading of 34% for SB4 and, in general, glass production rates have not been limited by melt rate but by the ability to keep feed to the melter. SRNL has also been able to eliminate the formation of nepheline brought on by the high levels of both aluminum and sodium associated with HM feeds through the implementation of a nepheline discriminator and the use of the high B_2O_3-based Frit 510.

Although processing of the relatively high Al_2O_3 based SB4 has been successful in DWPF, there is the potential to improve upon that flowsheet with the introduction of the Al-dissolution process

* It should be noted that even though SB4 was an HM based sludge (high Al_2O_3) without Al-dissolution, the Al_2O_3 concentrations are lower than those projected for SB5 with al-dissolution due to the SB3 PUREX (high Fe_2O_3) based heel blending affects.

for future sludge batches. More specifically, if the Al-dissolution process can remove mass and minimize possible rheological effects on sludge transfer capabilities, while maintaining both waste loading targets and relatively high melt rates, not only will this have a direct impact on reducing canister count but will also maximize waste throughputs which lead to a positive impact of the overall mission life for DWPF.

Previous assessments have indicated that through strategic frit development efforts, it appears that similar projected operating windows can be achieved for sludges both with and without Al-dissolution. Although this result suggests or supports the concept of minimizing canister counts for a specific sludge batch, the assessments did not evaluate or provide any insight into potential melt rate difference. The previous assessments did indicate that there may be more compositional flexibility in frit space for the without Al-dissolution flowsheet which raised a question on whether this would translate into higher melt rates for this flowsheet, which could lead to enhanced waste throughputs for DWPF [5].

The Department of Energy (DOE) – Office of Environmental Management (EM) has funded SRNL to assess the impacts of the Al-dissolution process on DWPF operations. As outlined in the Task Technical and Quality Assurance (QA) Plan [6], there are three major task activities associated with this program: (1) assessing projected operating windows for future sludge batches with and without high temperature Al-dissolution (which includes frit development efforts for higher Al_2O_3 based glasses), (2) evaluating melt rate for specific frit – sludge combinations of interest, and (3) addressing CPC (Chemical Process Cell) impacts. This report focuses on the impacts of the Al-dissolution process relative to melt rate. The impact on the projected operating windows and CPC processing were previously documented[5].

2.0 Objective

The objective of this task is to evaluate if significant melt rate differences could be realized for these two flowsheets (with and without Al-dissolution) based on strategic frit development selection. To support this task, “average” sludge compositions (referred to as Cluster 2 and Cluster 4) were developed based on future projections as defined in the current High Level Waste Systems plan [5].

3.0 Background: Historical Trends of Melt Rate and Waste Loading

Prior to a detailed discussion on the specific test and results of this study, a high level overview of the historical trends between melt rate and waste loading is warranted. The maximum waste throughput, amount of sludge processed per unit time, at DWPF is a function of several factors but two of the most critical are: waste loading and melt rate. The historical general trend between melt rate and WL indicates that as WL increases, melt rate gradually decreases, Figure 3-1. This trend leads to a situation in which the maximum waste throughput is not found at the maximum WL allowed by PCCS but at some intermediate WL determined experimentally or during DWPF operations. Therefore, if one were solely interested in minimizing the number of canisters produced, DWPF should target the maximum WL allowed by PCCS model predictions (with uncertainties accounted for). This would yield a minimum canister count. But based on previous operational metrics, this strategy could lead to a significant increase in canister pour times (or production rates), which ultimately could increase the overall mission life of both the tank farm and DWPF.

As noted in Section 1.0, assuming mission life is a critical aspect or input into the Al-dissolution implementation decision, sole use of the MAR assessment results and the general comments about "comparable" operating windows with and without Al-dissolution could lead one to make a sub-optimal decision. More specifically, the MAR assessments provide no insight into melt rate and/or waste throughput. The MAR assessments provide the projected operating windows (as defined by PCCS acceptable waste loadings) over which the specific glass forming system could be processed. That being the case, if one were to take the projected operating windows from the previous report[5], an assessment of canister reduction counts could be made, however; no insight into the possible impacts on mission life would result.

Consider the two scenarios shown in Figure 3-2 and Figure 3-3 in which mission life is dependent upon the quantity of waste vitrified and waste throughput, which is a function of the melt rate versus waste loading curve. In Figure 3-2, the blue line represents a nominal waste throughput (lb/hr) for the without Al-dissolution flowsheet. The red line represents the with Al-dissolution flowsheet waste throughput. The difference in the amount of waste to be immobilized is strictly a function of the efficiency of the Al-dissolution process and the sludge batches to which it is applied. In this example, the waste throughput for the without Al-dissolution flowsheet is higher than the with Al-dissolution flowsheet (based on the slope) but not high enough to overcome the increased mass. Therefore, one could conclude that Al-dissolution would ultimately reduce overall mission life even though it has a lower waste throughput. This is an ideal situation given it could lead not only to a reduced mission life but a significant reduction in canister count.

Alternatively, consider the case in which the waste throughput for the without Al-dissolution flowsheet is substantially higher, Figure 3-3. Under this scenario, it could be possible that the higher waste throughput would overcome the mass differences between the two flowsheets resulting in a shorter mission life. Could this be the case given the MAR assessments (in general) provide more flexibility for frit development efforts to improve melt rate based strictly on the number of frits available to provide comparable operating windows? Another possible scenario could be if the Al-dissolution flowsheet had a negative impact on the rheology of the sludge which translated into significantly lower melt rates. These general type questions are a primary focus of the experimental melt rate portion of this program.

Figure 3-1: Historical Trend Between Melt Rate and Waste Loading.

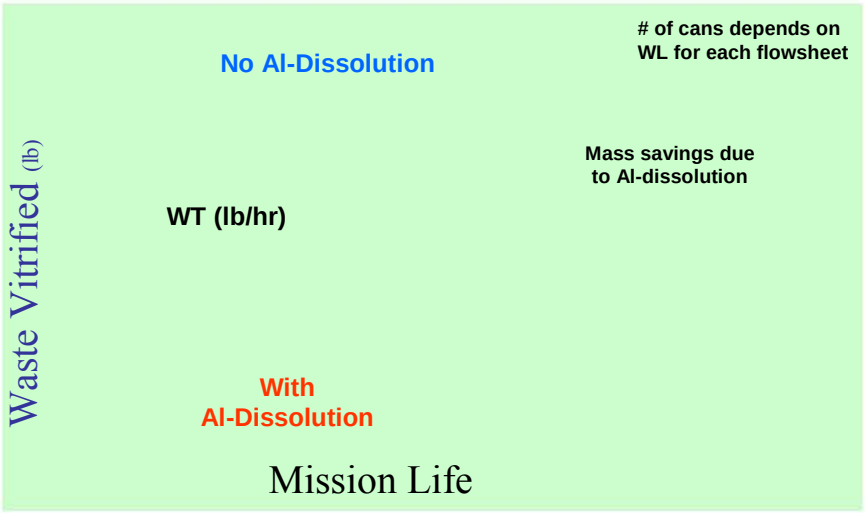


Figure 3-2. Schematic in which Higher WT for "Without Al-Dissolution" Does Not Overcome Mass Reduction in Terms of Mission Life.

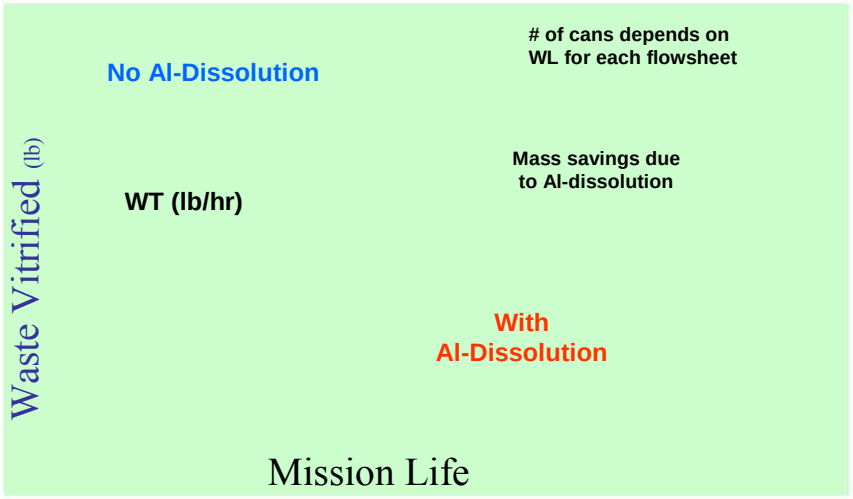


Figure 3-3. Schematic in which Higher WT for "Without Al-Dissolution" Does Overcome Mass Reduction in Terms of Mission Life.

Recent DWPF processing could provide some insight into the potential throughput trends for high and low Al-based sludges. For example, consider DWPF operations for SB3 (Purex based feed, low Al_2O_3 and high Na_2O) and SB4 (HM based feed, high Al_2O_3). Frit 418 was used as the primary frit to process SB3, which ultimately yielded a maximum waste throughput value of ~ 55 lb/hr when targeting 38% WL. Note the projected operating window for the Frit 418 – SB3 system was ~ 25 - 45% WL, but lower melt rates were experienced at WLs greater than 38%. Frit development for SB3 (leading to the Frit 418 recommendation) was primarily based on increasing the Na_2O content of the frit to reduce liquidus temperature predictions and improve melt rate. Other frit components, B_2O_3 and Li_2O, did not have a significant impact on melt rate for that system.

Current processing of SB4 (HM based feed) is utilizing Frit 510 which is a high B_2O_3 based frit (14 wt% relative to 8 wt% in Frit 418). Higher B_2O_3 concentrations were found during frit development efforts [7] to improve melt rate – with Na_2O having less influence on melt rate than observed in the Frit 418 development for SB3. Although the current targeted WL for SB4 is 34%, and the wt% solids in the feed is relatively low due to pump in-leakage, waste throughputs are approximately 60 – 65 lb/hr with the CPC operations limiting production (prior to the decant of Tank 40). With indications that higher feed rates and/or higher WLs could be targeted, even greater waste throughputs could be achieved for this relatively high Al_2O_3 feed. Not knowing what WL will yield the maximum waste throughput for this system, the question one should ask is: Could the higher throughputs for this system overcome the same sludge (SB4) having undergone Al-dissolution, which may ultimately result in a sludge batch similar to SB3 (higher Fe_2O_3, lower Al_2O_3)? More specifically, assume the maximum waste throughput for the Frit 510 – SB4 system was determined to be on the order of 80 lb/hr. If LWO had implemented Al-dissolution for SB4 (reducing the overall mass to be immobilized) but maximum waste throughput was similar to that observed for SB3 (~55 lb/hr), which flowsheet would be completed first by DWPF (i.e., which flowsheet would have the minimum mission life impact)? Which flowsheet would yield the minimum number of canisters? Are the answers to these two questions the same? Even if the "without Al-dissolution" flowsheet did not fully reduce the overall mission life, are there other factors (e.g., implementation cost of Al-dissolution or rheology impacts) that would play a role in the decision making process?

Although experimentally determining the waste loading versus melt rate trends for each of the 26 future sludge batches provided by LWO would be of great value, time and budget constraints ultimately place restrictions on that possibility. Therefore, developing a defensible strategy that could be used to provide general insights into the advantages or impacts of Al-dissolution to overall mission life is paramount for this task. That is, how does one select a "worst case" or "best case" scenario for each flowsheet with respect to melt rate or waste throughput? Even if successful on that issue, how does one select the optimal frit to use in that melt rate assessment to provide each flowsheet with the best probability/possibility to show its optimal behavior? The frit selection strategy used to support initial melt rate testing for this program were discussed in detail in a previous report[5].

4.0 Experimental

In this section, specifics regarding the feed preparation for Cluster 2 and Cluster 4 Sludge Receipt and Adjustment Tank (SRAT) product are provided, fabrication and characterization of the frits used to support melt rate testing are discussed, and the experimental set-up and procedures used during the Melt Rate Furnace (MRF) tests summarized.

4.1 Feed Preparation for SMR Melt Rate Testing

SRAT products for Cluster 2 (without Al-dissolution) and Cluster 4 (with Al-dissolution) were prepared from the compositions outlined in the initial Al-dissolution paper study[5] and represent average composition of future sludge batches for the without and with Al-dissolution flowsheet, respectively. Simulants were prepared and processed through the DWPF SRAT process to prepare SRAT product for melt rate testing.† Compositions of the sludge simulants were renormalized after removal of radioactive species (U_3O_8 and ThO_2) from the elemental compositions and adjusted for charge balance as required. Elemental composition targets for each cluster simulant are shown in Table 4-1.

Table 4-1: Projected and Normalized Elemental Compositions

	Cluster 2 Projection	Cluster 2 Normalized	Cluster 4 Projection	Cluster 4 Normalized
	Oxide Wt %	Oxide Wt %	Oxide Wt %	Oxide Wt %
Al_2O_3	23.10	25.23	14.62	15.89
BaO	0.21	0.23	0.25	0.27
CaO	2.63	2.87	3.26	3.54
Ce_2O_3	0.55	0.60	0.58	0.63
Cr_2O_3	0.27	0.29	0.34	0.37
CuO	0.08	0.09	0.11	0.11
Fe_2O_3	30.81	33.66	35.17	38.24
K2O	0.18	0.19	0.23	0.24
La_2O_3	0.20	0.22	0.22	0.24
MgO	0.41	0.45	0.47	0.51
MnO_2	4.00	4.37	5.17	5.62
Na_2O	20.25	22.13	21.21	23.06
NiO	1.16	1.27	1.28	1.39
PbO	0.24	0.26	0.25	0.28
SiO_2	3.35	3.66	5.09	5.54
ThO_2	1.00	-	1.20	-
TiO_2	3.29	3.60	2.77	3.01
U_3O_8	7.44	-	6.76	-
ZnO	0.13	0.14	0.16	0.18
ZrO_2	0.50	0.52	0.61	0.62

Elemental compositions of each simulant were measured after preparation was complete. The compositions matched the targets for all major species, as shown in Table 4-2. The anion composition and solids results for each simulant are shown in Table 4-3.

† As will be mentioned in a following section, the MRF testing utilizes a dry SRAT product mixed with frit at some targeted WL for assessments of melt rate.

Table 4-2: Simulant Elemental Composition Results

	Cluster 2			Cluster 4		
	Normalized Oxide Wt %	**Result Oxide Wt %**	**% Difference**	**Normalized Oxide Wt %**	**Result Oxide Wt %**	**% Difference**
Al_2O_3	25.23	27.88	10.49	15.89	18.03	13.47
BaO	0.23	0.19	-16.97	0.27	0.26	-3.97
CaO	2.87	3.09	7.56	3.54	3.96	11.72
Ce_2O_3	0.6	0.60	0.14	0.63	0.65	2.99
Cr_2O_3	0.29	0.24	-16.93	0.37	0.33	-9.84
CuO	0.09	0.09	2.78	0.11	0.12	8.52
Fe_2O_3	33.66	33.82	0.47	38.24	39.11	2.28
K_2O	0.19	0.11	-43.47	0.24	0.11	-52.25
La_2O_3	0.22	0.00	-	0.24	0.00	-
MgO	0.45	0.45	-0.22	0.51	0.48	-6.10
MnO_2	4.37	4.25	-2.74	5.62	5.44	-3.15
Na_2O	22.13	18.29	-17.34	23.06	18.63	-19.21
NiO	1.27	1.19	-6.05	1.39	1.36	-2.24
PbO	0.26	0.19	-25.02	0.28	0.20	-27.49
SiO_2	3.66	3.92	7.00	5.54	5.91	6.61
TiO_2	3.6	3.82	6.00	3.01	3.15	4.58
ZnO	0.14	0.13	-6.11	0.18	0.18	-1.49
ZrO_2	0.52	0.30	-41.46	0.62	0.27	-55.80

Table 4-3: Simulant Anion Composition and Solids Results

	Cluster 2	**Cluster 4**	**Units**
F	<100	<100	mg/kg slurry
Cl	<100	<100	mg/kg slurry
NO_2	16700	14000	mg/kg slurry
NO_3	9870	9205	mg/kg slurry
SO_4	314	314	mg/kg slurry
PO_4	<100	<100	mg/kg slurry
HCO_2	<100	<100	mg/kg slurry
C_2O_4	879	2845	mg/kg slurry
TIC	923	872	mg/kg slurry
Base Eq.	0.55	0.69	molar
Total Solids	22.85	22.55	wt%
Soluble Solids	6.65	6.61	wt%
Insoluble Solids	16.19	15.94	wt%
Calcine Solids	16.97	17.40	wt%

Four SRAT runs in the 22L SRAT vessels were performed to provide enough SRAT product to support the MRF tests - two SRAT runs with Cluster 2 and two SRAT runs with Cluster 4. The repeat runs were performed in the same vessels and no cleaning was performed between batches. The laboratory testing was conducted in accordance with procedure ITS-0094 of the L29 manual: "Laboratory Scale Chemical Process Cell Simulations". The experimental apparatus was set up using the guidance of SRNL-PSE-2006-00074 utilizing a 22L SRAT vessel. At the conclusion of the SRAT cycles, the SRAT products from the duplicate runs were blended and one 125 ml sample was pulled from each of the blended SRAT products for analyses. All data was recorded in laboratory notebooks‡.

Mercury is not typically added to feed intended for use in melt rate testing to eliminate personnel exposure and avoid complicating the MRF testing set-up. Therefore, mercury was not added to either the Cluster 2 or Cluster 4 sludges. Noble metals were also excluded from these runs, a change from past protocols. Higher rates of formic acid destruction have been noted during melt rate testing without mercury than comparable runs with mercury during flowsheet evaluations. These higher destruction rates lead to melter feed with higher yield stress and less formate than comparable flowsheet runs. However, increased yield stress is not an issue here, as the SRAT product will be dried. Given the higher hydrogen generation rates seen with the higher formic acid destruction, adjusting the acid calculation to add more formic acid to account for the differences between the flowsheet runs and melt rate feed preparation runs was deemed less practical than eliminating the noble metals and adjusting the acid calculation for less formic acid destruction. The gas chromatograph analysis of the offgas is not needed for runs without noble metals, therefore the elimination of noble metals also represents a reduction in cost and complexity of the runs.

The standard acid calculations for CPC process simulations were completed based on the sample results from each run. The input assumptions, sample results utilized, and calculation results are shown in Appendix A. A summary of key assumptions and results is shown in Table 4-4.

Table 4-4: Acid Calculation Summary

Results of Acid Calculation	Cluster 2	Cluster4	Units
Stoichiometric factor	130	130	%
Nitrite to Nitrate Conversion	25	25	% of nitrite in feed
Formic Acid Destruction	10	10	% of formic acid added
Acid Addition Amount	1.61	1.85	g/mol per liter
Ratio of Formic Acid to total Acid	0.891	0.867	mol formic/mol acid

The target versus measured elemental compositions for Cluster 2 and Cluster 4 SRAT products are shown in Table 4-5.

‡ Sludge Mass Reduction Notebook, WSRC-NB-2007-00173

Table 4-5: Target versus Measured SRAT Product Elemental Oxides

	Cluster 2 Target Oxide Wt %	Cluster 2 SRAT Oxide Wt %	Cluster 4 Target Oxide Wt %	Cluster 4 SRAT Oxide Wt %
Al_2O_3	25.23	25.99	15.89	14.64
BaO	0.23	0.19	0.27	0.23
CaO	2.87	3.32	3.54	4.42
Ce_2O_3	0.60	0.58	0.63	0.56
Cr_2O_3	0.29	0.25	0.37	0.30
CuO	0.09	0.09	0.11	0.10
Fe_2O_3	33.66	34.46	38.24	35.61
K_2O	0.19	0.14	0.24	0.16
La_2O_3	0.22	nm	0.24	nm
MgO	0.45	0.49	0.51	0.60
MnO_2	4.37	4.61	5.62	6.56
Na_2O[§]	22.13	21.26	23.06	25.99
NiO	1.27	1.12	1.39	1.16
PbO	0.26	0.17	0.28	0.08
SiO_2	3.66	3.88	5.54	5.17
ThO_2	-	-	-	-
TiO_2	3.60	3.67	3.01	2.68
U_3O_8	-	-	-	-
ZnO	0.14	0.13	0.18	0.16
ZrO_2	0.52	0.31	0.62	0.23

[§] Na is likely biased high for Cluster 4 due to the low solids in the sample, as shown in the Table 4-6.

Table 4-6: SRAT Product Anion Results

	Cluster 2	Cluster 4	Units
F	<100	<100	mg/kg slurry
Cl	262	275	mg/kg slurry
NO_2	1310	531	mg/kg slurry
NO_3	22,250	24,350	mg/kg slurry
SO_4	175	185.5	mg/kg slurry
PO_4	<100	<100	mg/kg slurry
HCO_2	41,450	46,200	mg/kg slurry
C_2O_4	<100	<100	mg/kg slurry
Total Solids**	21.88	19.66	wt%
Soluble Solids	8.84	10.07	wt%
Insoluble Solids	13.04	9.59	wt%
Calcine Solids	14.03	12.11	wt%
pH	6.01	5.74	
Density	1.13	1.14	g/ml

The results indicate the feed preparation process produced feed that matched the desired elemental composition within measurement uncertainty. Nitrite destruction was not complete for some runs, but either met or was close to the DWPF limit of 1,000 ppm. See Appendix A for acid equation inputs and results.

4.2 Frit Compositions

Measurement Acceptability Region (MAR) assessments were completed for the Cluster 2 and Cluster 4 systems and were previously reported [5]. Glass compositional regions of interest were defined and evaluated against existing Product Composition Control System (PCCS) criteria to establish projected operating windows for each glass system.

With the end result being the investigation of melt rate on sludges containing either high or low concentrations of aluminum, frits were identified with compositions that would provide the best opportunities for influencing melt rate. Previous studies have shown that increasing Na_2O content for SB3-type sludges (PUREX, high Fe_2O_3) provided an increase in melt rate[8]. For SB4-types (HM, high Al_2O_3), Na_2O and B_2O_3 increases produced a positive effect on melt rate[9]. With this being considered, five frits were selected for each cluster, Table 4-7 and Table 4-8. All frits maintained a constant lithium concentration of 8 wt%. Na_2O and B_2O_3 were varied from lower to higher concentrations in order to observe the effect in melt rates for each cluster.

Initially, five frits for each cluster were selected for testing. The frit selection was primarily based on the ability of the frit to satisfy all of the PCCS criteria at the MAR over a waste loading interval of interest to DWPF. Although this strategy identified specific frits of interest for Cluster 2 and Cluster 4, it did restrict the opportunity to increase certain frit oxide components to provide a more thorough assessment of historical trends. The five frits selected provided reasonable operating windows, were MAR acceptable, and to the extent possible provided primary frit

** Total and calcine solids were significantly low for the Cluster 4 samples. Repeat analysis was conducted that indicated total solids were 24.5 wt% for these samples and calcine solids was 16.4 wt%. Cluster 2 also had lower solids, but the 23.9 and 16.0 values were closer to the original sample results.

components to be tested over some range (albeit it rather limited). Based on the frit compositions, the melt rate data will provide little, if any, insight into the impacts of specific frit components on melt rate. More specifically, more than one component changes among the different frits selected for a specific cluster. Again, the initial strategy was to define the "optimal" frit available for use at DWPF – not to gain insight into specific compositional trends within each cluster.

Each frit was tested with its respective cluster at a fixed waste loading of 36% to identify a single frit for each cluster that yielded the maximum melt rate. Based on the results of the initial 36% WL MRF tests, it was postulated that a primary frit for each cluster would be identified and could be used to assess the impact of waste loading on melt rate. This would lead to or provide data to assess or at least get insight into the waste throughput curves for each cluster. This information could then be used to gage not only the impact on canister counts but also mission life for DWPF. Previous experience has shown if a frit performs better than another at one waste loading, it should do so at any given waste loading (i.e., the melt rate versus waste loading curves do not cross but are essentially parallel).

Table 4-7: Frit Compositions for Cluster 2.

Oxide	B_2O_3	Na_2O	Li_2O	SiO_2
SMR-1	8	11	8	73
SMR-2	11	9	8	72
SMR-3	14	7	8	71
SMR-4	17	5	8	70
SMR-5	9	8	8	75

Table 4-8: Frit Compositions for Cluster 4.

Oxide	B_2O_3	Na_2O	Li_2O	SiO_2
SMR-6	10	7	8	75
SMR-7	11	6	8	75
SMR-8	8	6	8	78
Frit 418	8	8	8	72
Frit 503	14	4	8	74

4.3 MRF Testing

The dry-fed MRF has a cylindrical inner chamber that is approximately 0.5 cubic feet in size, with heating coils winding around the chamber walls. The diameter of the chamber is ~7", and an insulating sleeve and a 1200 mL stainless steel beaker (6" deep) were inserted from the top. The tests were conducted with the stainless steel beakers inserted with the sleeve so that the beaker bottom was approximately flush with the top of the uppermost chamber coil. An insulating block was used to cover the beaker. The furnace was heated to 1150°C with the top opening covered. Once the furnace reached the setpoint, the cover was removed and the beaker containing sufficient dried, sieved material to produce 525 grams of glass was inserted. After 50 minutes, the beaker was removed from the furnace and allowed to cool to room temperature. This residence time in the furnace was determined during testing in 2002 to establish a standard

test time for melt rate comparison for this dry-fed furnace. After cooling down, the beakers were sectioned.

The relative melt rate is determined by measuring the height of the glass layer in the bottom of each sectioned beaker at 0.25" intervals. The average height and duration in the furnace is used to yield a relative linear melt rate (LMR) number (inches/hour). General observations of the sectioned beaker are also used to describe differences between runs. Melt rate runs were performed under the auspices of a melt rate run plan [10]. MRF runs were performed at Aiken County Technology Laboratory for the selected frits for both clusters at a waste loading of 36%. The results of all runs were recorded in notebook WSCR-NB-2003-00213.

5.0 Results and Discussion

5.1 Cluster 2 and Cluster 4 MRF Run

The results of the Cluster 2 (w/o Al-dissolution) MRF runs are summarized in Table 5-1. The melt rates are reported as LMR, inches of glass height produced per hour of melt time. As is common practice, a standard run was also made with Frit 418 without sludge. The standard melt rate was 1.33 in/hr, which is consistent with the acceptable range of 1.3-1.6 in/hr.

Table 5-1: MRF Test Results for Cluster 2 (w/o Aluminum Dissolution)

Cluster	Frit	B_2O_3	Na_2O	$B_2O_3 + Na_2O$	LMR
2	SMR-1	8	11	19	0.60
2	SMR-2	11	9	20	0.63
2	SMR-3	14	7	21	0.48
2	SMR-4	17	5	22	0.37
2	SMR-5	9	8	17	0.65

With respect to composition, Cluster 2 (without Al-dissolution) is similar to SB4 (higher Al_2O_3 sludges). It was expected that the historical trends for HM feeds would hold true for Cluster 2, namely higher concentrations of B_2O_3 and Na_2O in the frit would result in higher melt rates. However, when the sum of the measured concentrations of the Na_2O and B_2O_3 are examined with respect to melt rate, the opposite is generally observed.

The results of the Cluster 4 (with Al-dissolution) MRF run are summarized in Table 5-2. In general, the Cluster 4 MRF data appears to follow the historical trend of higher melt rates for SB3-like systems (high Fe_2O_3 contents) by using frits with higher concentrations of Na_2O. The exception to the general trend is Frit 503 that targets a higher B_2O_3 content and relatively low Na_2O. It should be noted that the use of higher B_2O_3 based frit during the development of Frit 418 for SB3 was not extensive.

Table 5-2: MRF Test Results for Cluster 4 (with Aluminum Dissolution)

Cluster	Frit	B_2O_3	Na_2O	$B_2O_3 + Na_2O$	LMR
4	SMR-6	10	7	17	0.52
4	SMR-7	11	6	17	0.39
4	SMR-8	8	6	14	0.43
4	418	8	8	16	0.54
4	503	14	4	18	0.57

The Cluster 4 MRF data appears to follow the historical trend of higher melt rates for SB3-like systems (high Fe_2O_3 contents) by using frits with higher concentrations of Na_2O.

From the data presented in Table 5-1 and Table 5-2, the best linear melt rate for Cluster 2 (w/o Aluminum Dissolution) was achieved with Frit SMR-5 at 0.65 inches/hour. For Cluster 4 (with Aluminum Dissolution), the best linear melt rate was realized with Frit 503 at 0.57 inches/hour. Although these two frits were not the expected best performers based on historical melt rate trends, they were advanced to the second phase of the melt rate study: multiple WL testing. The intent of the Phase 2 testing was to assess the impact of WL on melt rate in an effort to get insight to any differences in waste throughput for the two specific glass systems of interest.

5.2 MRF Multiple WL Testing for Clusters 2 and 4

Based on the results of the initial 36% waste loading tests, Frit SMR-5 and Frit 503 were chosen for multiple waste loading MRF tests for Cluster 2 and Cluster 4 respectively. Table 5-3 lists the compositions of the selected frits.

Table 5-3: SMR Frit Compositions (wt.%) for Each Sludge Batch Cluster

Cluster	Frit	B_2O_3	Na_2O	Li_2O	SiO_2
2	SMR-5	9	8	8	75
4	503	14	4	8	74

The results of the MRF multiple waste loading tests are presented in Table 5-4. Also shown in Table 5-4 is the waste throughput factor (WTF) which provides insight into the amount of waste processed per unit time – where WTF is determined by LMR x WL and is typically reported without units.

Table 5-4: SMR MRF Multiple Waste Loading Results for Clusters 2 and 4

Cluster	Frit	WL	LMR (in/hr)	WTF
2	SMR-5	32	0.65	20.8
2	SMR-5	34	0.70	23.8
2	SMR-5	36	0.71	25.6
2	SMR-5	38	0.67	25.5
2	SMR-5	40	0.59	23.6
2	SMR-5	42	0.61	25.6
4	503	32	0.56	17.9
4	503	34	0.59	20.1
4	503	36	0.49	17.6
4	503	38	0.50	19.0
4	503	40	0.57	22.8
4	503	42	0.53	22.3

Some scatter in the WTF calculations exists since trends between waste loading and melt rate are inconsistent with previous observations. This can be seen graphically in Figure 5-1 and Figure 5-2 as compared to the historical trends (refer to Figure 1-1). In Figure 5-1 and Figure 5-2, waste throughput factors are seen by following the blue data points, while melt rate can be seen with the

pink data points. Based on historical MRF data, waste throughput does not typically reverse trends as a function of increased waste loading (see Section 3.0 for more details), as seen in both figures. Historically, waste throughput typically is maximized at some intermediate waste loading. Having said that and based on the resulting data, the maximum WTF for the without Al-dissolution Cluster 2 / SMR-5 feed was 25.6. The maximum WTF for the Al-dissolution Cluster 4 / Frit 503 feed was 22.8. Therefore, for this set of MRF tests, without Al-dissolution Cluster 2 feed had a WTF that was about 12% higher than Cluster 4. This suggests that there is a possibility that the higher waste throughputs without Al-dissolution could off-set the lower mass to be vitrified with the Al-dissolution flowsheet.

Figure 5-1: Comparison of WTF and MR with respect to WL for Cluster 2

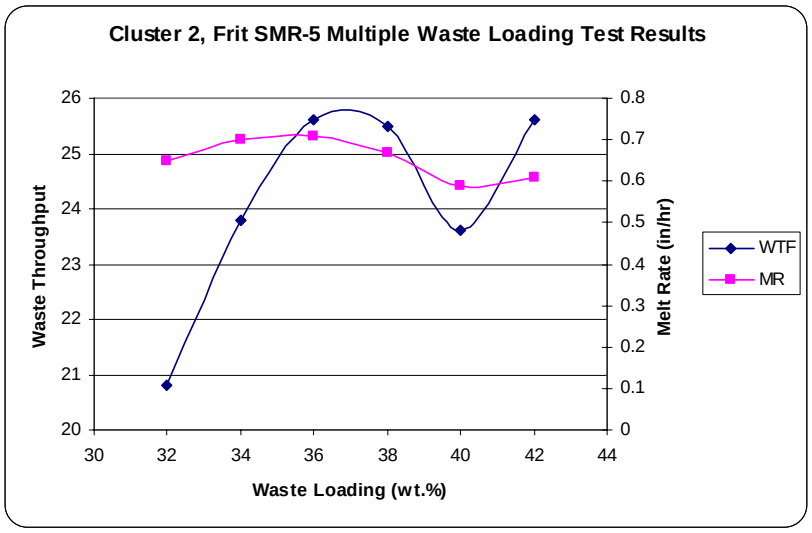
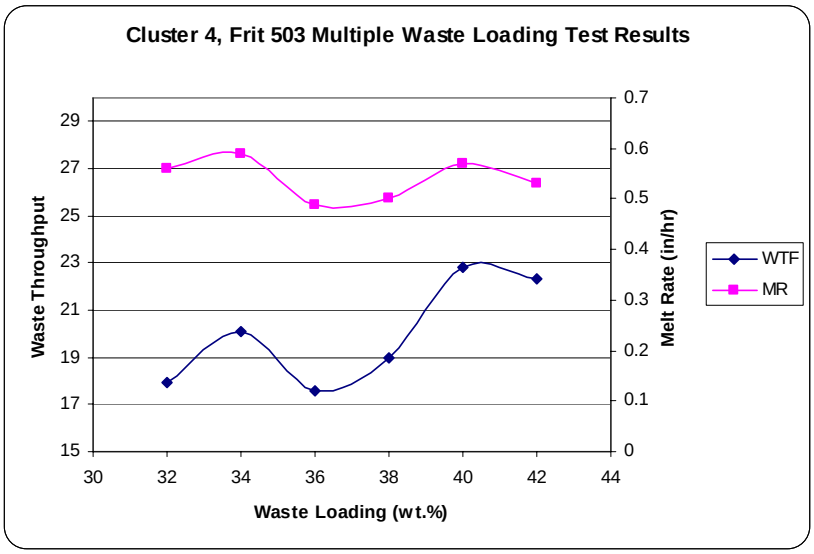


Figure 5-2: Comparison of WTF and MR with respect to WL for Cluster 4



From past melt rate testing, Cluster 2 is similar to SB4 and the melt rate for SB4 was improved with high boron frits [9]. Cluster 4 is similar to SB3 in which melt rate was improved with high alkali (sodium) frits [11]. However, past trends with these components were not consistent with the results of the initial SMR tests, as Frit SMR-5 used for Cluster 2 is a high alkali frit, and Frit 503 used for Cluster 4 is a high boron frit. A possible explanation for the observed deviation from expected trends could be attributed to feed reduction/oxidation (REDOX) state.

5.3 REDOX

Given that the melt rate results did not follow previously observed trends, it was postulated that the oxidized condition of the feed might be impacting melt rate, which later testing proved to be true. The DWPF uses a REDOX strategy and controls the melt REDOX between $0.09 \leq Fe^{2+}/\Sigma Fe \leq 0.33$. Controlling the DWPF melter at an equilibrium of $Fe^{+2}/\Sigma Fe \leq 0.33$ prevents metallic and sulfide rich species from forming nodules that can accumulate on the floor of the melter. Control of foaming, due to deoxygenation of manganic species, is achieved by converting oxidized MnO_2 or Mn_2O_3 species to MnO during melter preprocessing. At the lower redox limit of $Fe^{+2}/\Sigma Fe \sim 0.09$ about 99% of the Mn^{+4}/Mn^{+3} is converted to Mn^{+2}. Therefore, the lower REDOX limit eliminates melter foaming from deoxygenation.

Organic, nitrate, and manganese concentrations in the DWPF melter feed are the major parameters influencing melt REDOX. Organics such as formats, coal, and oxalate act as reductants, while nitrates, nitrites, and manganic (Mn^{+4} and Mn^{+3}) species act as oxidants.

5.3.1 *SRAT Adjustment*

SRAT product for Clusters 2 and 4 were vitrified with Frit 418 in a closed crucible according to procedure ITS-0052. Analyses were conducted on these products and were determined to be nearly completely oxidized, as shown in Table 5-5.

Table 5-5: Initial REDOX values for Clusters 2 and 4 SRAT products.

Sample	Cluster	REDOX
MRF-08-11	4	0.019
MRF-08-12	4	0.021
MRF-08-13	4	0.116
MRF-08-17	2	All Fe^{3+}
MRF-08-18	2	0.045
MRF-08-19	2	All Fe^{3+}

Calculations were performed to determine the amount of formic acid needed to adjust the redox to a more desirable ratio. It was determined that an additional 19.5g formic acid were needed per 1000g of Cluster 2 SRAT product, and 21.9g formic acid per 1000g Cluster 4 SRAT product to meet the 0.2 target. The REDOX adjustment was made after the initial melt rate testing had occurred; therefore, additional MRF runs were performed in order to re-assess the impact of aluminum dissolution on melt rate. Prior to utilizing the formic acid adjusted SRAT product, closed crucible testing (adjusted SRAT product with Frit 418 at 36% WL) was performed to verify that the revised acid strategy would yield a REDOX of ~ 0.2 and mitigate any confounding effects of REDOX on subsequent MRF testing. Analysis of the adjusted SRAT product (after the closed crucible test) indicate that a more suitable REDOX value of 0.2 was achieved, Table 5-6.

Table 5-6: Final REDOX values for Clusters 2 and 4 SRAT products after adjustment with formic acid.

Sample	Cluster	REDOX
SMR2-1	2	0.176
SMR2-2	2	0.191
SMR2-3	2	0.198
SMR4-1	4	0.262
SMR4-2	4	0.287
SMR4-3	4	0.267

5.4 Additional MRF Runs with the "REDOX" Adjusted SRAT Products

Based on the potential impacts of REDOX on melt rate (potentially leading to inconsistencies with historical trends), additional MRF runs were planned. A significant shift in strategy was used in this phase of testing. Although the primary focus on this second set of MRF tests was to gain insight into the impacts of Al-dissolution on melt rate, the selection of frits to be used was altered, as will be described in Section 5.4.1. This subsequent testing will be referred to as Phase 3.

5.4.1 *Phase 3 Frit Composition Selection*

To support Phase 1, the frit selection was primarily driven from the ability of the frit to provide relatively large operating windows for both Cluster 2 and Cluster 4 as well as being MAR acceptable. As discussed in previous sections, although conceptually effective, the MRF results suggested melt rate trends that were inconsistent with historical trends observed in both SRNL testing as well as in DWPF operations. The frit selection for Phase 1 was also rather limited from a compositional perspective and did not provide the opportunity to assess specific compositional impacts. For Phase 3, the selection of frit compositions was based strictly on providing the opportunity to gain insight into the specific compositional effects of interest without regard to projected operating windows. That is, design a set of frits that would challenge previous melt rate trends by spanning a relatively large composition region and ignore the requirement of being MAR acceptable or providing reasonable operating windows.

Frit compositions for Phase 3 are listed in Table 5-7. A primary driver for this selection process was to minimize the number of frit components changing and to establish a basis from which direct comparisons could be made. For example, all of the Phase 3 frits have a fixed Li_2O content. The first three frits shown in Table 3-7 also have a fixed B_2O_3 content with the Na_2O contents ranging from 12% (in Frit 320) to 3% (in Frit 422) – SiO_2 making up the difference. This series of frits should provide the opportunity to assess the impact of higher Na_2O contents on melt rate for both with and without Al-dissolution. The later two frits (Frit 510 and 1888) fix both the Na_2O and Li_2O concentrations but vary in B_2O_3 content. These frits, along with Frit 422 will provide insight into the impact of higher B_2O_3 contents on melt rate for both flowsheets.

Table 5-7: Frit Composition for Additional MRF Runs

Frit	B_2O_3	Na_2O	Li_2O	SiO_2
320	8	12	8	72
418	8	8	8	76
422	8	3	8	81
510	14	8	8	70
1888	18	8	8	72

5.4.2 *MRF Results*

Melt rate tests were performed as detailed in the melt rate run plan [12]. SRAT product, adjusted for REDOX, from Cluster 2 and Cluster 4 were used at a waste loading target of 36%. The melt rate results are presented in Table 5-8 and Table 5-9.

Table 5-8: Cluster 2 Melt Rate Data for Phase 3 Frits

Cluster	Frit	WL	LMR (in/hr)	WTF
2	320	36	0.61	22.0
2	418	36	0.48	17.3
2	510	36	0.67	24.1
2	1888	36	0.62	22.3

Table 5-9: Cluster 4 Melt Rate Data for Phase 3 Frits

Cluster	Frit	WL	LMR (in/hr)	WTF
4	320	36	0.71	25.6
4	418	36	0.63	22.7
4	510	36	0.81	29.2
4	1888	36	0.79	28.4

The data presented in Figure 5-3 support trends seen in the past, with the exception of Cluster 4 (with Al-dissolution). Previous results indicated that the melt rate driver for low Al_2O_3 SB3 (i.e. Cluster 4) was mainly sodium concentration, with boron having little effect [8]. However, examination of the data in

Figure 5-4 would lead one to draw the conclusion that boron provides a greater contribution to melt rate than was previously expected. Frits 418, 1888, and 520 all had the same sodium concentration at 8 wt. %. As lithium is held constant throughout all frits tested in this batch, boron concentration appears to be either the limiting or enabling constraint. When the sum of boron and sodium concentrations are considered as the driving force for melt rate in these scenarios, the expected trend can be seen, as in Figure 5-3.

Caution must be taken, however, with the interpretation of these data, as these frits were selected without consideration to MAR acceptability and is devoid of any impacts that may be caused due to rheology constraints.

When considering MAR acceptability, only Frits 418, 320, and 418 pass MAR criteria for Cluster 2, while 422 and 418 pass for Cluster 4 (Figure 5-5). MAR results for these frits can be found in Appendix, Table A6 and are graphically represented in Figure 3-7. The results obtained from Figure 5-5 supports the trends seen for previous sludge batches. SB3 was analogous to Cluster 4. SB3 was processed using Frit 418, just as the highest MR for a MAR acceptable frit was with Frit 418. SB4 was similar to Cluster 2. SB4 is being processed with Frit 510. For Cluster 2, Frit 510 had the highest MR of the frits that were tested. Based on the MAR acceptable frits, there does appear to be a slight advantage in melt rate with the "without Al-dissolution" flowsheet using Frit 510 as compared to the Frit 418 based "with Al-dissolution flowsheet". However, the reader is cautioned on two fronts: (1) the difference in melt rate data between these two systems may be within the uncertainty of the MRF (i.e., although a higher melt rate was measured for the Frit 510 based system, the two systems may not be of practical difference) and (2) the possible impacts of feed rheology are not accounted for in either system which could acerbate a difference if accounted for.

Figure 5-3: Graphical Representation of Cluster 4 Melt Rate Data for All Phase 3 Frits (MAR independent)

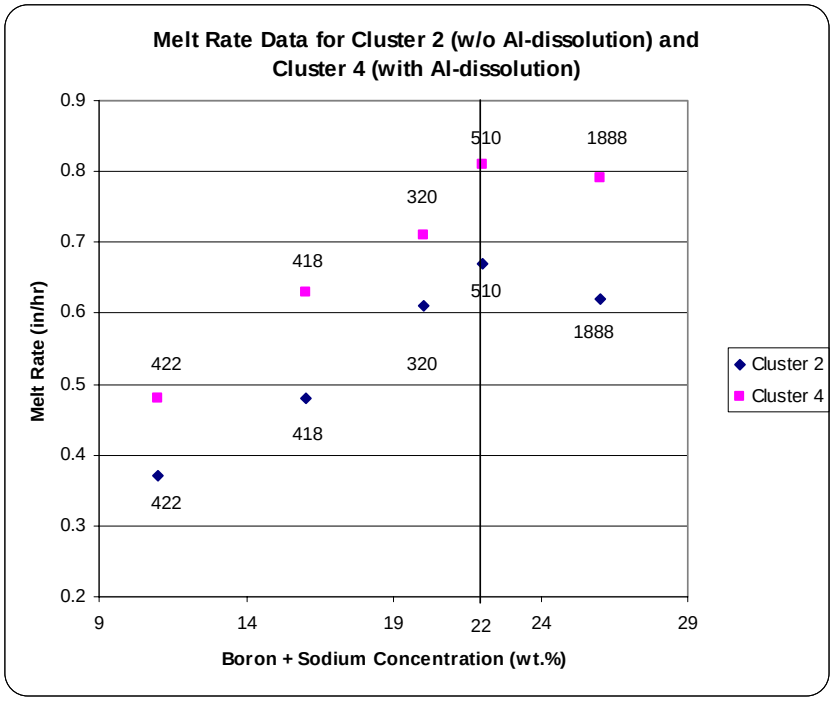


Figure 5-4: Melt Rate for Clusters 2 and 4 with Respect to Sodium Concentration

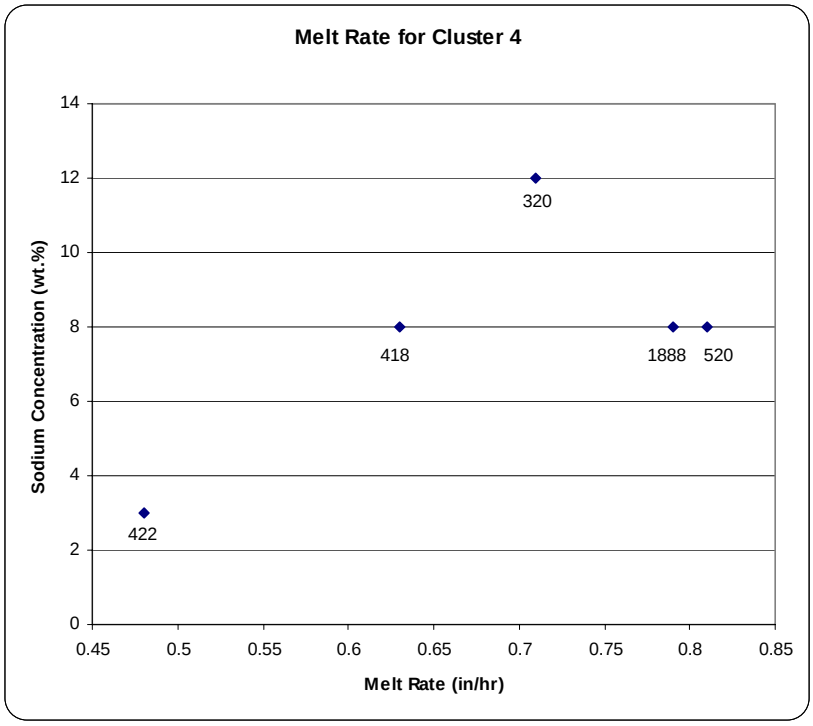
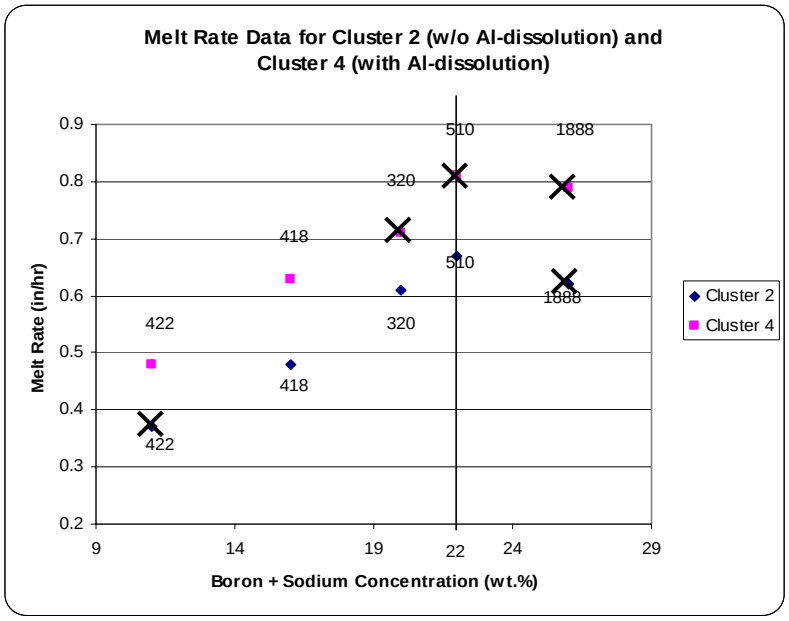


Figure 5-5: MAR acceptability enforced for Phase 3 frits



6.0 Conclusion

The objective of this study was to provide assessments of some of the downstream impacts of decisions regarding the implementation of Al-dissolution to support sludge mass reduction and processing, with respect to melt rate. Based on future sludge batch compositional projections, assessments have been made with respect to the ability to maintain comparable projected operating windows for sludges with and without Al-dissolution. Twelve sludge batches were identified based on implementation of high temperature Al-dissolution, while fourteen sludge batches represent the without Al-dissolution flowsheet. The assessments utilized two primary metrics to evaluate differences between the two flowsheet options: (1) the projected operating window size, defined as the waste loading interval over which glasses are classified as acceptable using current process control models, and (2) the number of frits that provide relatively large operating windows, which provides insight into the potential to adjust melt rate for a specific sludge batch.

In general, paper study assessments indicated that most of the future sludge batches, both with and without Al-dissolution, had multiple frits that were available that yielded relatively large operating windows. Using the 17-point waste loading window width as a guide for "reasonable operating window size", there generally appeared to be more flexibility in frit selection for the without Al-dissolution flowsheets. This larger frit compositional platform could allow frit development efforts to make more significant adjustments to melt rate, which ultimately could lead to a shorter mission life.

Based on the general observations of the paper study assessments there is essentially no clear distinction between the two flowsheets based on the projected operating windows to drive an Al-dissolution decision. Comparable operating windows for both flowsheets can be achieved through the frit development and selection process. However, these conclusions did not address

one of the key issues: melt rate. Does aluminum dissolution have any effect, be it positive or negative, on melt rate?

To address this question, candidate frit compositions were selected to assess melt rate as a function of waste loading for the glass systems representing average "with" and "without" Al dissolution flowsheets (based on a cluster analysis). These frits were chosen to provide the best opportunity to show the optimal operating windows for all future sludge batches and to ensure experimental assessments of melt rate for both with and without Al-dissolution were represented under the best possible conditions.

This frit selection process was driven by reviewing compositional trends that have been seen historically to influence melt rate as well as identifying systems with relatively large operating windows. More specifically, increasing the Na_2O content (typically used for PUREX or high Fe_2O_3 sludges – e.g., SB3) and increasing the boron and/or sodium content (typically used for HM or high Al_2O_3 sludges – e.g., SB4) are strategies that were pursued. With respect to the identification of sludge batches, average compositions representing with and without Al-dissolution, Clusters 2 and 4, were developed using a statistical grouping routine. Ultimately, five frits were identified for each cluster that utilized the historical trends in composition that have influenced melt rate in DWPF operations. For each cluster, melt rate assessments were performed as a function of waste loading for the five frits selected.

From the data obtained in the initial melt rate experiments, the maximum WTF for the without Al-dissolution Cluster 2 / SMR-5 feed was 25.6. The maximum WTF for the Al-dissolution Cluster 4 / Frit 503 feed was 22.8. Therefore, for this set of MRF tests, without Al-dissolution Cluster 2 feed had a WTF that was about 12% higher than Cluster 4. This data was deemed to be suspect due to the REDOX conditions of the feed. After feed adjustment, additional tests were performed in which Frit 510 proved to have the best melt rate of the selected frits for both clusters. The linear melt rate for Cluster 4 (with Al-dissolution) was slightly better than for Cluster 2 (w/o Al-dissolution) at 0.81 to 0.67 in/hr, respectively. This is the case until MAR constraints are applied. When considering MAR acceptability, only Frits 418, 320, and 510 pass MAR criteria for Cluster 2, while 422 and 418 pass for Cluster 4. Evaluating the MRF data for only the MAR acceptable frits, there appears to be a slight advantage of the Frit 510 based system without Al-dissolution relative to the Frit 418 based system with Al-dissolution. The melt rate data are in general agreement with historical trends observed at SRNL and during processing of SB3 and SB4 in DWPF. However, the reader is cautioned on two fronts: (1) the difference in melt rate data between these two systems may be within the uncertainty of the MRF (i.e., although a higher melt rate was measured for the Frit 510 based system, the two systems may not be of practical difference) and (2) the possible impacts of feed rheology are not accounted for in either system which could acerbate a difference.

7.0 Recommendation / Path Forward

It should be noted that the MRF utilizes dried Sludge Receipt and Adjustment Tank (SRAT) product (targeting the nominal cluster compositions) coupled with a frit at a targeted waste loading. The MRF does not have the ability to assess liquid feeds and, thus, rheology impacts. Instead, the MRF is a "static" test bed in which a mass of dried melter feed (SRAT product plus frit) is placed in an "isothermal" furnace for a period of time to assess melt rate. These conditions, although historically effective in terms of identifying candidate frits for specific sludge batches and mapping out melt rate versus waste loading trends, do not allow for assessments of the potential impact of feed rheology on melt rate. That is, if the rheological properties of the slurried melter feed resulted in the mounding of the feed in the melter (i.e., the

melter feed was thick and did not flow across the cold cap), melt rate and/or melter operations (i.e., surges) could be negatively impacted. Given the results of recent rheological measurements on SB4 and SB5, the possibility of this phenomenon exists. Slurry-fed Melt Rate Furnace testing using Clusters 2 and 4 could be performed in order to make a more informed decision on the impact of aluminum dissolution on DWPF throughput. This decision would need to be based on the ability of the simulant development program to produce a simulant mimicking the rheology of the radioactive sludge. If not, the SMRF testing would not capture this possible impact.

Although the Phase 3 testing did provide some degree of clarity regarding the compositional trends and their impact on melt rate, the tests were performed at only one waste loading (36%). These data provide no insight into the waste throughput curves for the Frit 418 – Cluster 4 system or the Frit 510 – Cluster 2 system. That information is needed to provide additional insight into the mission life question. Without such data, one can only speculate on the waste loading that provide maximum throughput for each system.

Given the current schedule has DWPF processing SB5 through their facility in mid-November 2008, insight into the over arching questions of melt rate, waste throughput, and mission life be best served or obtained directly from the facility. It is recommended that processing of SB5 through the facility be monitored closely and that data be used as input into the decision making process on whether to implement Al-dissolution for future sludge batches.

8.0 References

1. J.M.B. Pareizs, C.J.; Click, D.R.; Hansen, E.K.; Lambert, D.P.; Stone, M.E., *Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells using Post Aluminum Dissolution Tank 51 Sludge Slurry*, WSRC-STI-2008-00086, Savannah River National Laboratory, Aiken, SC (2008)

2. C.C. Herman, *Evaluation of LTAD Downstream Impacts - Status of SRNL 3L Tank 51 Sample Testing*, SRNL-PSE-2007-00283, Washington Savannah River Company, Aiken, SC (2007)

3. J.R. Harbour, T.B. Edwards, E.K. Hansen, and V.J. Williams, *Impact of Increased Aluminate Concentrations on Properties of Saltstone Mixes*, WSRC-STI-2007-00506, Washington Savannah River Company, Aiken, SC (2007)

4. K.M. Fox and D.K. Peeler, *Demonstration of Very High Aluminum Retention in Simulated HLW Glass*, SRNL-PSE-2007-00231, Savannah River National Laboratory, Aiken, SC (2007)

5. J.D. Newell, Edwards, T.E., Peeler, D.K., *Initial MAR Assessments to Access the Impact of Al-dissolution on DWPF Operating Windows*, WSRC-STI-2007-00688, Washington Savannah River Company, Aiken, SC (2007)

6. D.K. Peeler, M.E. Smith, M.E. Stone, T.B. Edwards, and J.D. Newell, *Frit Development for High Al_2O_3 Based Sludge: Task Technical and Quality Assurance Plan*, Washington Savannah River Company, Aiken, SC (2007)

7. M.E. Smith, T.M. Jones, and D.H. Miller, *Sludge Batch 4 Baseline Melt Rate Furnace and Slurry-Fed Melt Rate Furnace Tests with Frits 418 and 510*, WSRC-STI-2007-00450, Washington Savannah River Company, Aiken, SC (2007)

8. M.E. Smith, Miller, D.H., Jones, T.M., *Slurry-fed Melt Rate Furnace Test for the SB3/Frit 320 Feed System*, WSRC-TR-2004-00459, Washington Savannah River Company, Aiken, SC (2004)

9. M.E. Smith, Jones, T.M., Miller, D.H., *Sludge Batch 4 Baseline Melt Rate Furnace and Slurry-Fed Melt Rate Furnace Tests with Frits 418 and 510*, WSRC-STI-2007-00450, Washington Savannah River Company, Aiken, SC (2007)

10. D.H. Miller, *Melt Rate Furnace Plane - Waste Loading for Aluminum Dissolution Frit*, SRNL-PSE-2008-00071, Washington Savannah River Company, Aiken, SC (2008)

11. M.E. Smith, Jones, T.M., Miller, D.H., *Slurry-Fed Melt Rate Furnace Tests for the SB3/Frit 320 Feed System*, WSRC-TR-2004-00459, Washington Savannah River Company, Aiken, SC (2004)

12. D.H. Miller, *Melt Rate Furnace Tests for Sludge Mass Reduction Frit Selection*, SRNL-PSE-2008-00151, Washington Savannah River Company, Aiken, SC (2008)

Appendix A

Table A1. Projected Compositions With High Temperature Al-Dissolution: SB6 – SB17
(source: SBP_R-2_6_19_07_WAD)

Oxide	SB6	SB7	SB8	SB9	SB10	SB11	SB12	SB13	SB14	SB15	SB16	SB17
Al_2O_3	22.827	18.228	13.449	12.577	11.945	13.564	17.461	16.577	15.648	13.044	13.663	13.810
BaO	0.257	0.240	0.250	0.244	0.246	0.227	0.232	0.261	0.273	0.277	0.262	0.251
CaO	1.909	2.896	2.959	3.391	3.659	3.510	3.652	3.405	3.243	2.905	2.950	2.935
Ce_2O_3	0.197	0.816	0.580	0.809	0.957	0.748	0.531	0.337	0.269	0.273	0.507	0.608
Cr_2O_3	0.312	0.255	0.311	0.297	0.291	0.365	0.374	0.401	0.407	0.382	0.330	0.301
CuO	0.097	0.077	0.095	0.085	0.082	0.080	0.123	0.132	0.135	0.130	0.112	0.101
Fe_2O_3	25.744	37.353	33.829	38.049	40.684	41.223	36.186	31.258	29.653	29.492	33.970	35.534
K_2O	0.166	0.157	0.197	0.193	0.192	0.198	0.284	0.289	0.286	0.260	0.225	0.205
La_2O_3	0.074	0.261	0.209	0.273	0.314	0.257	0.217	0.164	0.145	0.141	0.198	0.221
MgO	0.618	0.560	0.459	0.522	0.569	0.578	0.453	0.406	0.381	0.345	0.389	0.404
MnO	8.788	6.887	10.664	8.243	6.693	3.812	4.259	3.153	2.681	2.934	2.391	2.094
Na_2O	19.910	20.314	20.620	21.289	21.410	21.712	21.879	21.452	21.177	21.216	21.017	20.624
NiO	4.510	1.974	2.118	1.089	0.650	0.447	0.337	1.218	1.614	1.828	1.494	1.309
PbO	0.087	0.338	0.247	0.332	0.389	0.295	0.251	0.170	0.143	0.148	0.236	0.274
SO_4	1.878	0.607	0.510	0.288	0.158	0.108	0.090	0.151	0.176	0.231	0.198	0.183
SiO_2	2.315	1.793	4.008	4.181	4.108	7.255	6.774	7.017	6.758	5.219	3.804	3.126
ThO_2	1.208	0.642	3.117	3.077	3.086	1.253	0.538	0.201	0.089	0.031	0.012	0.005
TiO_2	1.116	2.717	2.783	2.810	2.817	2.876	2.885	2.829	2.798	2.696	2.499	3.891
U_3O_8	7.460	3.250	2.910	1.537	1.013	0.630	2.571	9.726	13.293	17.656	14.993	13.400
ZnO	0.143	0.081	0.117	0.084	0.068	0.243	0.238	0.215	0.210	0.206	0.162	0.140
ZrO_2	0.384	0.557	0.568	0.627	0.668	0.618	0.666	0.639	0.622	0.585	0.589	0.583

Table A2. Projected Compositions Without High Temperature Al-Dissolution: SB6 – SB19
(source: SBP_R-1_7_12_06_NAD)

Oxide	SB6	SB7	SB8	SB9	SB10	SB11	SB12	SB13	SB14	SB15	SB16	SB17	SB18	SB19
Al_2O_3	25.734	25.242	25.619	25.779	25.825	26.600	22.827	20.047	19.139	22.583	26.589	30.316	32.653	34.308
BaO	0.230	0.206	0.196	0.192	0.191	0.160	0.190	0.219	0.273	0.245	0.200	0.183	0.180	0.183
CaO	1.741	2.432	2.732	2.829	2.860	2.448	2.314	2.380	2.340	2.736	2.891	2.862	2.809	2.837
Ce_2O_3	0.120	0.529	0.723	0.787	0.807	0.677	0.540	0.325	0.208	0.245	0.640	0.407	0.258	0.196
Cr_2O_3	0.285	0.244	0.224	0.216	0.214	0.238	0.241	0.296	0.358	0.344	0.250	0.271	0.303	0.323
CuO	0.071	0.066	0.063	0.062	0.062	0.051	0.071	0.093	0.100	0.135	0.089	0.117	0.095	0.085
Fe_2O_3	21.811	28.667	31.980	33.063	33.416	34.253	29.807	25.694	24.350	28.550	33.562	29.271	21.828	18.705
K_2O	0.238	0.192	0.167	0.159	0.156	0.130	0.151	0.189	0.187	0.271	0.196	0.258	0.226	0.213
La_2O_3	0.085	0.192	0.242	0.258	0.263	0.221	0.188	0.138	0.106	0.135	0.227	0.176	0.126	0.105
MgO	0.863	0.584	0.496	0.468	0.460	0.430	0.355	0.322	0.347	0.273	0.383	0.280	0.337	0.375
MnO	8.788	7.873	6.429	5.904	5.739	4.148	3.001	1.876	1.214	3.292	2.387	4.102	2.549	1.786
Na_2O	20.909	20.128	20.057	20.061	20.050	19.545	19.119	19.305	21.887	21.092	20.891	20.754	26.436	27.853
NiO	3.942	1.900	0.970	0.664	0.569	0.360	0.810	1.244	2.697	1.665	0.560	0.172	0.260	0.319
PbO	0.055	0.220	0.298	0.324	0.332	0.276	0.234	0.151	0.087	0.159	0.288	0.226	0.119	0.070
SO_4	0.722	0.311	0.214	0.186	0.177	0.184	0.184	0.164	0.161	0.206	0.227	0.236	0.191	0.168
SiO_2	3.569	3.075	2.710	2.584	2.544	3.729	2.748	4.112	5.192	4.064	2.980	3.514	6.631	8.271
ThO_2	1.659	1.713	1.625	1.592	1.580	1.836	1.586	0.769	0.248	0.076	0.023	0.007	0.002	0.001
TiO_2	2.517	3.043	3.198	3.245	3.259	3.353	3.263	3.256	3.209	3.314	3.194	2.145	2.729	3.096
U_3O_8	6.218	2.853	1.491	1.051	0.915	0.714	11.770	18.797	17.278	9.821	3.756	3.960	1.651	0.542
ZnO	0.108	0.076	0.060	0.054	0.053	0.201	0.148	0.151	0.143	0.231	0.118	0.193	0.125	0.092
ZrO_2	0.335	0.455	0.506	0.522	0.528	0.447	0.453	0.470	0.477	0.562	0.549	0.551	0.493	0.473

Table A3: Acid Equation Inputs and Results

Sludge Analyses for Acid Calculations	**SMR-2**	**SMR-4**	
Fresh Sludge Mass without trim chemicals	16,500.0	16,700.0	g slurry
Fresh Sludge Weight % Total Solids	22.85	22.55	wt%
Fresh Sludge Weight % Calcined Solids	17.00	17.40	wt%
Fresh Sludge Weight % Insoluble Solids	16.20	15.95	wt%
Fresh Sludge Density	1.210	1.210	kg / L slurry
Fresh Sludge Nitrite	16,700	14,000	mg/kg slurry
Fresh Sludge Nitrate	9,870	9,205	mg/kg slurry
Fresh Sludge Oxalate	879	2845	mg/kg slurry
Fresh Sludge Formate	0	0	mg/kg slurry
Fresh Sludge Coal/Carbon source	0.000	0.000	wt% dry basis
Fresh Sludge Manganese (% of Calcined Solids)	2.690	3.445	wt % calcined basis
Fresh Sludge Slurry TIC (treated as Carbonate)	923	872	mg/kg slurry
Fresh Sludge Hydroxide (Base Equivalents) pH = 7	0.661	0.836	Equiv Moles Base/L slurry
Fresh Sludge Mercury (% of Total Solids in untrimmed sludge)	0.0000	0.0000	wt% dry basis
Fresh Sludge Supernate manganese	0	0	mg/L supernate
Fresh Sludge Supernate density	1.04	1.04	kg / L supernate
SRAT Processing Assumptions	**SMR-2**	**SMR-4**	
Conversion of Nitrite to Nitrate in SRAT Cycle	25.00	25.00	gmol NO_3^-/100 gmol NO_2^-
Destruction of Nitrite in SRAT and SME cycle	100.00	100.00	% of starting nitrite destroyed
Destruction of Formic acid charged in SRAT	10.00	10.00	% formate converted to CO_2 etc.
Destruction of oxalate charged	50.00	50.00	% of total oxalate destroyed
Percent Acid in Excess Stoichiometric Ratio	130.00	130.00	%
SRAT Product Target Solids	25.00	25.00	%
Nitric Acid Molarity	10.534	10.534	Molar
Formic Acid Molarity	23.600	23.600	Molar
DWPF Nitric Acid addition Rate	2.0	2.0	gallons per minute
DWPF Formic Acid addition Rate	2.0	2.0	gallons per minute
REDOX Target	0.200	0.200	Fe^{+2} / ΣFe
REDOX Equation (7 for Mn^{+7}, otherwise assumes Mn^{+4})	7	7	Enter 7 for new redox equation
Trimmed Sludge Target Ag metal content	0.00000	0.00000	total wt% dry basis after trim
Trimmed Sludge Target wt% Hg dry basis	0.00000	0.00000	total wt% dry basis after trim
Trimmed Sludge Target Pd metal content	0.00000	0.00000	total wt% dry basis after trim
Trimmed Sludge Target Rh metal content	0.00000	0.00000	total wt% dry basis after trim
Trimmed Sludge Target Ru metal content	0.00000	0.00000	total wt% dry basis after trim
Trimmed Sludge Target Wt% Coal/carbon source dry basis	0.00	0.00	total wt% dry basis after trim
Trimmed Sludge Target oxalate after trim (wt % not mg/kg)	0.385	1.262	total wt% dry basis after trim
Water to dilute fresh sludge and/or rinse trim chemicals	500.000	500.000	g
Total Water added to flush the Nitric and Formic Acid Lines	50.0	50.0	g
Sample Mass of Trimmed sludge (SRAT Receipt sample, if any)	0.0	0.0	g
Mass of SRAT cycle samples	0.000	0.000	g
Wt% Active Agent In Antifoam Solution	10	10	%
Basis Antifoam Addition for SRAT (generally 100 mg antifoam/kg slurry)	100.00	100.00	mg/kg slurry
Number of basis antifoam additions added during SRAT cycle	7.00	7.00	

Results of Acid Calculation			
	SMR-2	**SMR-4**	
Acid Addition Amount	**1.61**	**1.85**	**g/mol per liter**
Ratio of Formic Acid to total Acid	**0.891**	**0.867**	**mol formic/mol acid**

Table A4: ICP Data for Frits 422 and 1888

SRNL Process Science Analytical Laboratory
Customer: David Newell
Date: 8/7/08
Samples: Frit 422, Frit 1888
Lab ID: 08-1563-1564
Units: elemental and oxide wt%
Sample Preparation: LiBO2 and Na2O2 Preps
Comments: Samples run in duplicate

Sample ID	Lab ID	B	Li	Na	Si	
Frit 422 (A)	08-1563	2.49	3.67	2.06	38.3	
Frit 422 (B)	08-1563	2.49	3.70	2.02	38.0	
Frit 1888 (A)	08-1564	5.52	3.71	5.62	31.0	
Frit 1888 (B)	08-1564	5.50	3.72	5.61	30.8	
		B2O3	Li2O	Na2O	SiO2	Total
Frit 422 (A)	08-1563	8.02	7.89	2.8	82.0	100.7
Frit 422 (B)	08-1563	8.02	7.96	2.7	81.3	100.0
Frit 1888 (A)	08-1564	17.8	7.98	7.59	66.3	99.7
Frit 1888 (B)	08-1564	17.7	8.00	7.57	65.9	99.2

Table A5: ICP Data for SMR-X Frits

SRNL Process Science Analytical Laboratory
Customer: David Newell
Date: 4/9/08
Samples: SMR 1-8
Lab ID: 08-0795-0802
Units: elemental and oxide wt%
Sample Preparation: LiBO2 and Na2O2 Preps
Comments: Samples run in duplicate

Sample ID	Lab ID	Al	B	Ca	Li	Na	Si	
SMR-1 (A)	08-0795	0.160	2.62	0.015	3.93	8.04	33.5	
SMR-1 (B)	08-0795	0.152	2.63	0.015	3.98	7.98	33.5	
SMR-2 (A)	08-0796	0.337	3.49	0.034	3.94	6.58	32.9	
SMR-2 (B)	08-0796	0.332	3.61	0.031	3.95	6.49	32.5	
SMR-3 (A)	08-0797	0.182	4.62	0.020	3.97	5.06	32.3	
SMR-3 (B)	08-0797	0.180	4.59	0.019	3.96	5.21	32.9	
SMR-4 (A)	08-0798	0.479	4.95	0.039	3.88	3.72	33.2	
SMR-4 (B)	08-0798	0.482	5.03	0.030	3.90	3.79	33.2	
SMR-5 (A)	08-0799	0.158	3.03	0.013	3.79	6.21	35.0	
SMR-5 (B)	08-0799	0.155	2.91	0.013	3.89	6.03	35.3	
SMR-6 (A)	08-0800	1.20	3.20	0.094	3.79	5.07	34.6	
SMR-6 (B)	08-0800	1.18	3.13	0.092	3.77	5.13	34.5	
SMR-7 (A)	08-0801	0.320	3.59	0.023	3.86	4.46	34.0	
SMR-7 (B)	08-0801	0.355	3.58	0.025	3.86	4.68	34.1	
SMR-8 (A)	08-0802	0.295	3.69	0.025	3.75	4.57	35.2	
SMR-8 (B)	08-0802	0.313	3.69	0.028	3.75	4.66	35.8	
		Al2O3	B2O3	CaO	Li2O	Na2O	SiO2	Total
SMR-1 (A)	08-0795	0.302	8.44	0.021	8.45	10.9	71.7	99.5
SMR-1 (B)	08-0795	0.287	8.47	0.021	8.56	10.8	71.7	99.5
SMR-2 (A)	08-0796	0.637	11.2	0.048	8.47	8.88	70.4	99.0
SMR-2 (B)	08-0796	0.627	11.6	0.043	8.49	8.76	69.6	98.5
SMR-3 (A)	08-0797	0.344	14.9	0.028	8.54	6.83	69.1	99.4
SMR-3 (B)	08-0797	0.340	14.8	0.027	8.51	7.03	70.4	101
SMR-4 (A)	08-0798	0.905	15.9	0.055	8.34	5.02	71.0	100
SMR-4 (B)	08-0798	0.911	16.2	0.042	8.39	5.12	71.0	101
SMR-5 (A)	08-0799	0.299	9.76	0.018	8.15	8.38	74.9	101
SMR-5 (B)	08-0799	0.293	9.37	0.018	8.36	8.14	75.5	101
SMR-6 (A)	08-0800	2.27	10.3	0.132	8.15	6.84	74.0	99.5
SMR-6 (B)	08-0800	2.23	10.1	0.129	8.11	6.93	73.8	99.1
SMR-7 (A)	08-0801	0.605	11.6	0.032	8.30	6.02	72.8	98.7
SMR-7 (B)	08-0801	0.671	11.5	0.035	8.30	6.32	73.0	99.2
SMR-8 (A)	08-0802	0.558	11.9	0.035	8.06	6.17	75.3	101
SMR-8 (B)	08-0802	0.592	11.9	0.039	8.06	6.29	76.6	103

Table A6: MAR acceptability of Phase 3 frits

% WL	Frit	Sludge Type	MAR Status
25	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv Homg
26	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
27	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
28	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
29	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
30	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
31	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
32	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
33	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
34	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
35	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
36	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
37	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
38	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	highv
39	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	
40	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	
41	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	
42	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
43	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
44	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
45	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
46	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
47	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
48	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
49	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
50	B-8;Li-8;Na-3;Si-81	Cluster 2 avg	TL
25	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	Homg
26	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
27	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
28	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
29	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
30	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
31	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
32	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
33	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
34	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
35	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
36	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
37	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
38	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
39	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
40	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
41	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
42	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
43	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
44	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	

45	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
46	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	
47	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	Neph
48	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	TL Neph
49	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	TL Neph
50	B-8;Li-8;Na-8;Si-76	Cluster 2 avg	TL Neph
25	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	Homg
26	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
27	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
28	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
29	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
30	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
31	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
32	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
33	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
34	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
35	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
36	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
37	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
38	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
39	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
40	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	
41	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv
42	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv
43	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
44	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
45	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
46	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
47	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
48	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
49	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
50	B-8;Li-8;Na-12;Si-72	Cluster 2 avg	lowv Neph
25	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	Homg
26	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
27	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
28	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
29	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
30	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
31	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
32	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
33	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
34	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
35	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
36	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
37	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
38	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
39	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	
40	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	

41	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	lowv
42	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	lowv
43	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	lowv
44	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	lowv
45	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	lowv Neph
46	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	lowv Neph
47	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	TL lowv Neph
48	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	TL lowv Neph
49	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	TL lowv Neph
50	B-14;Li-8;Na-8;Si-70	Cluster 2 avg	TL lowv Neph
25	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	Homg
26	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	
27	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	
28	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	
29	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	
30	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
31	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
32	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
33	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
34	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
35	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
36	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
37	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
38	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
39	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
40	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
41	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
42	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv
43	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv Neph
44	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv Neph
45	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv Neph
46	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	lowv Neph
47	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	TL lowv Neph
48	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	TL lowv Neph
49	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	TL lowv Neph
50	B-18;Li-8;Na-8;Si-66	Cluster 2 avg	TL lowv Neph
25	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	highv Homg hFrit
26	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	highv Homg
27	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	highv Homg
28	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	highv
29	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	highv
30	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	highv
31	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
32	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
33	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
34	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
35	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
36	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	

37	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
38	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
39	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
40	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
41	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
42	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	
43	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
44	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
45	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
46	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
47	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
48	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
49	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
50	B-8;Li-8;Na-3;Si-81	Cluster 4 avg	TL
25	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	Homg hFrit
26	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	Homg
27	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	Homg
28	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
29	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
30	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
31	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
32	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
33	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
34	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
35	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
36	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
37	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
38	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
39	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
40	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
41	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
42	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	
43	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	lowv
44	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	lowv
45	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	lowv
46	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	lowv
47	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	lowv
48	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	lowv
49	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	TL lowv
50	B-8;Li-8;Na-8;Si-76	Cluster 4 avg	TL lowv
25	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	Homg R2O hFrit
26	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	Homg R2O
27	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	Homg R2O
28	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	R2O
29	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	
30	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	
31	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	
32	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	

33	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
34	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
35	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
36	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
37	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
38	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
39	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
40	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
41	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
42	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
43	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
44	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
45	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
46	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
47	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv
48	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv Neph
49	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv Neph
50	B-8;Li-8;Na-12;Si-72	Cluster 4 avg	lowv Neph
25	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	Homg hFrit
26	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	Homg
27	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	Homg
28	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	
29	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	
30	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	
31	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	
32	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	
33	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
34	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
35	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
36	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
37	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
38	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
39	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
40	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
41	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
42	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
43	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
44	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
45	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
46	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
47	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	lowv
48	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	TL lowv
49	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	TL lowv
50	B-14;Li-8;Na-8;Si-70	Cluster 4 avg	TL lowv
25	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv Homg
26	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv Homg
27	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv Homg
28	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv

29	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
30	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
31	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
32	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
33	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
34	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
35	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
36	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
37	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
38	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
39	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
40	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
41	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
42	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
43	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
44	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
45	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
46	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
47	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	lowv
48	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	TL lowv
49	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	TL lowv Neph
50	B-18;Li-8;Na-8;Si-66	Cluster 4 avg	TL lowv Neph

This page intentionally left blank.

Distribution:

C.J. Bannochie, 773-42A
A.B. Barnes, 999-W
D.R. Best, 786-5A
J.M. Bricker, 704-27S
D.A. Crowley, 999-W
B.A. Davis, 704-27S
T.B. Edwards, 999-W
T.L. Fellinger, 704-26S
S.D. Fink, 773-A
K.M. Fox, 999-W
C.W. Gardner, 773-A
B.J. Giddings, 786-5A
J.M. Gillam, 766-H
J.C. Griffin, 773-A
B.A. Hamm, 766-H
C.C. Herman, 999-W
P. J. Hill, 766-H
J.F. Iaukea, 704-30S
D.P. Lambert, 999-W
D.D. Larsen, 776-H
M.T. Keefer, 766-H
J.E. Marra, 773-A
D.J. McCabe, 773-42A
R.T. McNew, 704-27S
D.H. Miller, 999-W
T.A. Nance, 773-42A
J.E. Occhipinti, 704-S
D.K. Peeler, 999-W
B.R. Pickenheim, 999-W
J.A. Pike, 773-42A
T.M. Punch, 766-H
F.C. Raszewski, 999-w
J.W. Ray, 704-S
H.B. Shah, 766-H
M.E. Smith, 704-30S
M.E. Stone, 999-W
P.C. Suggs, 704-S
W.R. Wilmarth, 773-42A
A.L. Youchak, 999-W