This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

WSRC-TR-2005-00370
Revision 0

NEPHELINE FORMATION POTENTIAL IN SLUDGE BATCH 4 (SB4) AND ITS IMPACT ON DURABILITY: SELECTING GLASSES FOR A PHASE 2 STUDY

T. B. Edwards
D. K. Peeler

August 2005

Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

DISCLAIMER

Printed in the United States of America

Prepared For
U.S. Department of Energy

The Savannah River National Laboratory is operated for the U.S. Department of Energy by Westinghouse Savannah River Company.

WSRC-TR-2005- 00370
Revision 0

Key Words: *durability, process control, SB4, variability study*

Retention: *Permanent*

NEPHELINE FORMATION POTENTIAL IN SLUDGE BATCH 4 (SB4) AND ITS IMPACT ON DURABILITY: SELECTING GLASSES FOR A PHASE 2 STUDY

T. B. Edwards
D. K. Peeler

August 2005

Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

REVIEWS AND APPROVALS

AUTHORS:

Thomas B Edwards 9-20-05
T. B. Edwards, Statistical Consulting Section Date

David Peeler 9-19-05
D. K. Peeler, Immobilization Technology Section Date

TECHNICAL REVIEWER:

Connie C. Herman 9-19-05
C. C. Herman, Immobilization Technology Section Date

APPROVERS:

EW Holtzscheiter 9-26-05
E. W. Holtzscheiter, Manager, Immobilization Technology Section Date

Sharon L Marra 9/22/05
S. L. Marra, Manager, Glass Formulation & Process Development Date

EXECUTIVE SUMMARY

The likelihood for the formation of nepheline in Sludge Batch 4 (SB4) glass systems and the potential impact of nepheline on the durability of these systems is part of the frit development efforts for SB4. The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Perhaps one of the most significant effects is the type and extent (or fraction) of crystallization and the change to the residual glass composition. A strong increase in glass dissolution (or decrease in durability) has been observed in previous studies in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ (nepheline) and $LiAlSi_2O_6$, and crystalline SiO_2.

Although it is well known that the addition of Al_2O_3 to borosilicate glasses enhances the durability of the waste form (through creation of network-forming tetrahedral Na^+-$[AlO_{4/2}]^-$ pairs), the combination of high Al_2O_3 and Na_2O can lead to the formation of nepheline ($NaAlSiO_4$). Given the projected high concentration of Al_2O_3 in SB4 and the potential use of a high Na_2O based frit to improve melt rate and a high Na_2O sludge due to settling problems, the potential formation of nepheline in various SB4 systems continues to be assessed.

The most recent compositional projections from the Closure Business Unit (CBU) for SB4 may be framed around three decision areas: the sodium molarity of the sludge (at values of1M Na and 1.6M Na), the SB3 heel that will be included in the batch (expressed in inches of SB3 sludge with values of 0, 40, and 127”), and the introduction of an ARP stream into the sludge (which is represented by six options: no ARP, ARPa, ARPe, ARPk, ARPm, and ARPv). Candidate frits are being identified for these options via a paper study approach with the intent of downselecting to a set of key frits whose operating windows (i.e., waste loading intervals that meet Product Composition Control System (PCCS) Measurement Acceptability Region (MAR) criteria) are robust to and/or selectively optimal for these sludge options. The primary or key frits that appear attractive on paper (i.e., down selected via the paper study) will be transferred into SRNL’s experimental studies supporting SB4; specifically, the melt-rate studies, chemical process cell flowsheet runs and, if needed, a glass variability study.

Based upon earlier work by Li et al. (2003), glasses that satisfy the constraint:

$$\frac{SiO_2}{SiO_2 + Na_2O + Al_2O_3} > 0.62$$

where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase. As the waste loadings are increased for many SB4 glass systems, this constraint is not met (before PCCS MAR processing criteria are not met) due to the high aluminum content of the sludge and the high sodium concentrations targeted for the final glass (high sodium concentrations are anticipated as being necessary to attain attractive melt rates).

Based on the 1.6M Na, 40” and 1.6M Na, 127” sludge options, 28 glasses have been selected to complement the earlier nepheline study (Peeler et al. 2005b) by continuing the investigation into the ability of the above constraint to predict the occurrence of a nepheline primary phase for SB4 glasses and into the impact of such primary phases on the durability of the SB4 glasses. In general, glasses were selected for study to cover waste loadings (WLs) over which nepheline was the only criterion restricting access to higher WLs.

The selected glasses are to batched and fabricated using standard procedures. Visual observations and other analytical techniques are to be used, as needed, to assess the presence of crystals and specifically, a nepheline primary phase. The durability of these glasses (for both quenched and centerline canister cooled versions) is to be measured using the ASTM Product Consistency Test (PCT) Method A. The results from these efforts are to be documented in a subsequent report.

The results of this study will provide valuable input for the frit development efforts and subsequent feedback to the CBU regarding the relative viability of the various SB4 options under consideration. Specifically, if the formation of nepheline for SB4 glasses is found through this study to have an impact on durability that is overly detrimental, then candidate frits, that lessen the likelihood of the formation of nepheline over an interval of waste loadings of interest to the Defense Waste Processing Facility (DWPF), would move up the list of preferred frits. On the other hand, if the presence of nepheline has no appreciable, adverse impact on durability, then as decisions regarding the viability of the SB4 options and the down select of candidate frits are pursued, little weight will be given to minimizing the likelihood of nepheline and the decisions will be dominated by waste throughput criteria.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

ARP	Actinide Removal Process
CBU	Closure Business Unit
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
ComPro™	Composition – Properties database
MAR	Measurement Acceptability Region
MST	monosodium titanate
PCCS	Product Composition Control System
PCT	Product Consistency Test
SB	Sludge Batch
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TT&QA	Task Technical and Quality Assurance (plan)
TTR	Technical Task Request
WL	Waste Loading

1.0 INTRODUCTION

The Defense Waste Processing Facility (DWPF) is currently processing Sludge Batch 3 (SB3) as a “sludge-only” composition by combining SB3 with Frit 418, melting the slurry mix of sludge and frit, and pouring the molten glass in stainless steel canisters to create the final waste form for this high-level waste at the Savannah River Site (SRS). In preparation for the qualification and receipt of the next sludge batch, Sludge Batch 4 (SB4), development and definition of the baseline flowsheet were initiated using options from Lilliston (2005) and have progressed to using options provided by Elder (2005a and 2005b). The latter options center around three primary decision points for SB4: the sodium (Na^+) molarity for the batch (either 1M or 1.6M Na^+), the SB3 heel contribution to the batch (either a 0”, 40”, or 127” SB3 heel), and the contribution (if any) of an Actinide Removal Process (ARP) stream to the batch (either no contribution or an ARP contribution as represented by five alternatives that are discussed below). These options are being evaluated for SB4 in an effort to meet critical Closure Business Unit (CBU) objectives including those associated with the durability of the DWPF glass waste form and the efficiency and effectiveness of the DWPF operation. Critical components of DWPF’s operational efficiency and effectiveness include sludge/frit processability, melter attainment (the percentage of time DWPF’s melter is pouring), melt rate, waste loading, and canister production rates.

An early yet meaningful assessment of the processability of a sludge option and of the durability of the corresponding waste form for candidate frits at various waste loadings is provided by using predictions generated by property/composition models. The models employed are the same as those used by DWPF’s Product Composition Control System (PCCS) (Brown et al. 2002), and the investigation of candidate sludge/frit glass systems may be described as a paper study whose purpose is to identify a viable frit or frits for each sludge option being studied. A frit is deemed viable if its composition allows for economic fabrication and if, when it is combined with a sludge option under consideration, DWPF’s property/composition models indicate that the combination has an operating window (a waste loading interval over which the sludge/frit glass system satisfies processability and durability constraints) that allows DWPF to meet its goals for waste loading and canister production.

The Savannah River National Laboratory (SRNL) was asked via technical task requests (TTRs) (Washburn 2004a, 2004b) to provide frit development support for SB4. In response, SRNL issued task technical and quality assurance (TT&QA) plans (Peeler 2004a, 2000b). Under these plans, subsequent reports were issued that identified candidate frits and assessed their viability for the SB4 options (with and without the ARP streams) as provided by Lilliston (2005) (see Peeler and Edwards 2005a and 2005b) and by Elder (2005a and 2005b) (see Peeler and Edwards 2005c). While these assessments were strictly model-based and included no experimental work, experimental work in support of the SB4 program has been planned and is underway.

There are three areas of experimental work underway to support frit development for SB4. Experiments on melt rate, the first area, were planned as part of the support for SB4 (Peeler and Smith 2004) since the results from melt rate studies are a critical input to the final selection of a frit for SB4. Results from the frit development efforts will be used to help guide the melt rate studies as the SB4 program progresses. In addition, as the likely composition of SB4 becomes more well-defined and the list of candidate frits is correspondingly reduced, the issue of the need for an experimental, variability study for SB4 can be addressed. As part of the qualification of each sludge batch, there is a requirement to demonstrate that the durability/composition models (Jantzen et al. 1995) in DWPF’s PCCS are applicable for the glass system anticipated by the processing of that sludge. This demonstration of applicability typically takes the form of a variability study that involves the making of glasses and the testing via the Product Consistency Test (PCT) (ASTM 2002) of their durability. The predicted durability is then compared to the measured durability to assess the applicability of the durability/composition models. While this is a second area of potential experimental work, another way to assess model applicability involves identifying glasses that are representative of the glass system and that have already been made and tested (i.e., historical data). The model predictions for these glasses could then be compared to the previously recorded PCT results to demonstrate applicability of the durability/composition models. A preliminary assessment of the need for experimental work to support the SB4 variability study has been completed by Peeler and Edwards (2005d). This assessment used a systematic approach that was developed and utilized to determine whether or not historical glasses contained within the ComPro™ database (Taylor et al. 2004) lie within the projected SB4 compositional region of interest. The results from that assessment suggested that there was a risk of a lack of direct applicability of historical glass/durability data to satisfy the need for a SB4 variability study and reinforced the potential benefit of an experimental program to generate glass compositions and PCT data to complement ComPro and to help meet the intent of the SB4 variability study.

The assessment of the need for an experimental glass study to complement historical data in ComPro merges with the third area of potential experimental work for SB4's frit development effort. Given the projected high concentration of Al_2O_3 in the SB4 options under consideration and the likely targeting of a glass system (i.e., a SB4/frit combination) with high Na_2O content to improve melt rate or waste loading, there is a potential for the formation of nepheline for various SB4 glass systems. Nepheline formation or crystallization raises a concern regarding glass durability.

The effect of crystallization on glass durability is complex and depends on several interrelated factors including the change in residual glass composition, the formation of internal stress or microcracks, and the preferential attack at the glass-crystal interface. Perhaps one of the most significant effects is the type and extent (or fraction) of crystallization and the resulting change to the residual glass composition. A strong increase in glass dissolution (or decrease in durability) has been observed in previous studies (Bickford and Jantzen (1984), Cicero et al. (1993), Kim et al. (1995), Marra and Jantzen (1993), Li et al. (1997), and Riley et al. (2001)) in glasses that formed aluminum-containing crystals, such as $NaAlSiO_4$ (nepheline) and $LiAlSi_2O_6$, and crystalline SiO_2.

Li et al. (2003) indicate that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within the nepheline primary phase field. In particular, durable glasses with $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$, where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase. Using this inequality as a nepheline formation guide or "discriminator," the potential for the formation of this troubling component has been tracked as part of the frit development studies and led to the selection of 12 glasses (as Phase 1 of the nepheline study) that were batched and subjected to the PCT (Peeler et al. 2005a). The results from that study (Peeler et al. 2005b) suggested that a nepheline discriminator value of 0.62 was a useful guide to predict the formation of this primary phase for the SB4 glass systems. The results also suggested that the presence of nepheline (or other aluminum-containing crystals) in the SB4 glasses does have an impact on the durability of glasses but not to the extent that acceptability or predictability was jeopardized - all of the glasses had acceptable durabilities (as determined by comparisons against the durabilities of the Environmental Assessment (EA) glass (Jantzen et al. 1993)).

The purpose of this report is to expand on the results from Phase 1 of the nepheline study (as a result of projected compositional changes of SB4 primarily due to the removal of Tank 4) by identifying additional glasses for experimental study to further the investigation into the applicability of the nepheline discriminator and the potential for detrimental effects on SB4 glass durability due to the presence of nepheline. There is a discussion of the objectives of this task in Section 2. In Section 3, possible glass systems that are anticipated for SB4 are reviewed, and Section 4 identifies a set of SB4 glass compositions to help support the objectives of this study. The information presented in this report is summarized in Section 5.

2.0 TASK OBJECTIVES

The objective of this task is to further the investigation into the potential for the formation of nepheline as a primary crystalline phase for SB4 glass systems, the ability of the nepheline discriminator to predict this formation, and the impact of nepheline (if it does form) on the durability of the SB4 glass systems. The results of this study will provide valuable input for the frit development efforts and subsequent feedback to the CBU regarding the relative viability of the various SB4 options under consideration. Specifically, if the formation of nepheline for SB4 glasses is found through this study to have an impact on durability that is overly detrimental (i.e., challenges acceptability and/or model predictability), then candidate frits that lessen the likelihood of the formation of nepheline over intervals of waste loading of interest to DWPF would move up the list of preferred frits. On the other hand, if the presence of nepheline has no appreciable, adverse impact on durability, then as decisions regarding the viability of the SB4 options and the downselect of candidate frits are pursued, little weight will be given to minimizing the likelihood of nepheline and the decisions will be dominated by waste throughput criteria.

3.0 SB4 GLASS SYSTEMS

This section investigates the SB4 options that are currently being considered as part of the frit development effort. For completeness, the compositions of the sludge options, which originated from Elder (2005a and 2005b) and which were modified by Herman (2005) to cover the possible introduction of ARP, are presented in this section. The compositions of select candidate frits employed during the paper studies of these options are provided, and the discriminator used to predict the potential for the formation of a nepheline primary crystalline phase is discussed.

3.1 The Current Set of SB4 Options

Tables 3-1 and 3-2 provide the normalized sludge composition (as mass fraction calcine oxides) for each of the options provided by Elder (2005a and 2005b) and subsequently modified by Herman (2005) to include preliminary ARP compositions. The ARP stream to be transferred to DWPF will contain monosodium titanate (MST), entrained sludge, and various soluble sodium compounds as the result of filter cleaning and stream composition adjustment for transfer. Given both are still being defined; some uncertainty exists with regards to the composition and volume of the stream that will be transferred to DWPF. Herman (2005) reviewed the various material balances for several different processing scenarios provided by Subosits (2004). Based on that review, scenarios were selected to bound the range of possible components (with potential impacts on the glass formulation) that could be transferred to DWPF. The assumption is that if glass formulation efforts can accommodate the bounding components, then concentrations of the ARP components within the bounds should also be acceptable. Five ARP options were selected for assessment: Appendices A, E, K, M, and V, which are denoted as ARPa, ARPe, ARPk, ARPm, and ARPv, respectively. To determine the impact of the ARP stream on the DWPF SRAT product or glass composition, the five projected ARP stream compositions were each blended with the SB4 options as provided by Elder (2005a and 2005b).

Table 3-1. Composition of SB4 Options as Mass Fractions – Part 1

Type	Al_2O_3	BaO	CaO	Ce_2O_3	Cr_2O_3	CuO	Fe_2O_3	K_2O	La_2O_3	MgO
SB4-1M-0"	0.3648	0.0016	0.0179	0.0020	0.0028	0.0008	0.1965	0.0231	0.0008	0.0038
SB4-1M-0"-ARPa	0.3591	0.0016	0.0177	0.0020	0.0028	0.0008	0.1951	0.0227	0.0008	0.0037
SB4-1M-0"-ARPe	0.3462	0.0015	0.0176	0.0020	0.0027	0.0008	0.1945	0.0217	0.0008	0.0036
SB4-1M-0"-ARPk	0.3370	0.0015	0.0171	0.0020	0.0026	0.0007	0.1897	0.0211	0.0008	0.0035
SB4-1M-0"-ARPm	0.3512	0.0016	0.0179	0.0020	0.0027	0.0008	0.1988	0.0220	0.0008	0.0037
SB4-1M-0"-ARPv	0.3439	0.0015	0.0173	0.0020	0.0027	0.0007	0.1914	0.0216	0.0008	0.0036
SB4-1M-40"	0.3120	0.0015	0.0201	0.0020	0.0027	0.0008	0.2233	0.0179	0.0008	0.0111
SB4-1M-40"-ARPa	0.3073	0.0015	0.0199	0.0020	0.0026	0.0008	0.2214	0.0176	0.0008	0.0109
SB4-1M-40"-ARPe	0.2968	0.0015	0.0197	0.0020	0.0026	0.0008	0.2195	0.0169	0.0008	0.0105
SB4-1M-40"-ARPk	0.2891	0.0014	0.0192	0.0020	0.0025	0.0007	0.2140	0.0164	0.0008	0.0102
SB4-1M-40"-ARPm	0.3012	0.0015	0.0201	0.0021	0.0026	0.0008	0.2242	0.0171	0.0009	0.0106
SB4-1M-40"-ARPv	0.2947	0.0014	0.0194	0.0020	0.0026	0.0007	0.2163	0.0168	0.0008	0.0104
SB4-1M-127"	0.2792	0.0014	0.0205	0.0020	0.0025	0.0008	0.2289	0.0151	0.0009	0.0140
SB4-1M-127"-ARPa	0.2751	0.0014	0.0203	0.0020	0.0025	0.0008	0.2269	0.0149	0.0009	0.0137
SB4-1M-127"-ARPe	0.2661	0.0014	0.0201	0.0020	0.0024	0.0008	0.2248	0.0142	0.0009	0.0132
SB4-1M-127"-ARPk	0.2593	0.0014	0.0196	0.0020	0.0024	0.0007	0.2191	0.0139	0.0008	0.0128
SB4-1M-127"-ARPm	0.2702	0.0015	0.0205	0.0021	0.0025	0.0008	0.2295	0.0145	0.0009	0.0134
SB4-1M-127"-ARPv	0.2642	0.0014	0.0198	0.0020	0.0024	0.0008	0.2215	0.0142	0.0008	0.0131
SB4-1.6M-0"	0.3333	0.0014	0.0163	0.0018	0.0025	0.0007	0.1796	0.0211	0.0007	0.0034
SB4-1.6M-0"-ARPa	0.3282	0.0014	0.0162	0.0018	0.0025	0.0007	0.1785	0.0207	0.0007	0.0034
SB4-1.6M-0"-ARPe	0.3168	0.0014	0.0161	0.0018	0.0025	0.0007	0.1787	0.0198	0.0007	0.0033
SB4-1.6M-0"-ARPk	0.3085	0.0014	0.0157	0.0018	0.0024	0.0007	0.1743	0.0193	0.0007	0.0032
SB4-1.6M-0"-ARPm	0.3215	0.0014	0.0165	0.0019	0.0025	0.0007	0.1827	0.0201	0.0008	0.0034
SB4-1.6M-0"-ARPv	0.3146	0.0014	0.0159	0.0018	0.0024	0.0007	0.1756	0.0197	0.0007	0.0033
SB4-1.6M-40"	0.2985	0.0014	0.0192	0.0019	0.0025	0.0007	0.2136	0.0171	0.0008	0.0106
SB4-1.6M-40"-ARPa	0.2940	0.0014	0.0190	0.0019	0.0025	0.0007	0.2119	0.0168	0.0008	0.0105
SB4-1.6M-40"-ARPe	0.2842	0.0014	0.0188	0.0020	0.0024	0.0007	0.2105	0.0161	0.0008	0.0100
SB4-1.6M-40"-ARPk	0.2768	0.0014	0.0184	0.0019	0.0024	0.0007	0.2052	0.0157	0.0008	0.0098
SB4-1.6M-40"-ARPm	0.2884	0.0015	0.0192	0.0020	0.0025	0.0008	0.2150	0.0163	0.0008	0.0102
SB4-1.6M-40"-ARPv	0.2822	0.0014	0.0186	0.0019	0.0024	0.0007	0.2073	0.0160	0.0008	0.0100
SB4-1.6M-127"	0.2618	0.0014	0.0199	0.0019	0.0023	0.0007	0.2217	0.0140	0.0008	0.0141
SB4-1.6M-127"-ARPa	0.2580	0.0013	0.0197	0.0019	0.0023	0.0007	0.2199	0.0137	0.0008	0.0138
SB4-1.6M-127"-ARPe	0.2499	0.0013	0.0195	0.0019	0.0023	0.0007	0.2181	0.0132	0.0008	0.0132
SB4-1.6M-127"-ARPk	0.2435	0.0013	0.0190	0.0018	0.0022	0.0007	0.2126	0.0128	0.0008	0.0129
SB4-1.6M-127"-ARPm	0.2537	0.0014	0.0199	0.0019	0.0023	0.0007	0.2227	0.0133	0.0008	0.0134
SB4-1.6M-127"-ARPv	0.2480	0.0013	0.0192	0.0019	0.0022	0.0007	0.2149	0.0131	0.0008	0.0132

Table 3-2. Composition of SB4 Options as Mass Fractions – Part 2

Type	MnO	Na_2O	NiO	PbO	SO_4	SiO_2	ThO_2	TiO_2	U_3O_8	ZnO	ZrO_2
SB4-1M-0"	0.0451	0.1897	0.0427	0.0023	0.0073	0.0278	0.0005	0.0002	0.0662	0.0011	0.0031
SB4-1M-0"-ARPa	0.0452	0.1936	0.0421	0.0023	0.0077	0.0274	0.0005	0.0052	0.0656	0.0011	0.0031
SB4-1M-0"-ARPe	0.0462	0.2024	0.0411	0.0023	0.0088	0.0266	0.0005	0.0118	0.0648	0.0011	0.0031
SB4-1M-0"-ARPk	0.0452	0.2093	0.0400	0.0022	0.0093	0.0259	0.0004	0.0244	0.0631	0.0010	0.0030
SB4-1M-0"-ARPm	0.0475	0.2001	0.0418	0.0023	0.0086	0.0271	0.0005	0.0001	0.0661	0.0011	0.0031
SB4-1M-0"-ARPv	0.0452	0.2044	0.0407	0.0022	0.0088	0.0264	0.0005	0.0184	0.0639	0.0011	0.0030
SB4-1M-40"	0.0501	0.2038	0.0364	0.0021	0.0080	0.0286	0.0005	0.0002	0.0741	0.0011	0.0029
SB4-1M-40"-ARPa	0.0501	0.2075	0.0359	0.0021	0.0084	0.0282	0.0005	0.0052	0.0733	0.0011	0.0029
SB4-1M-40"-ARPe	0.0509	0.2156	0.0352	0.0020	0.0095	0.0274	0.0004	0.0118	0.0721	0.0011	0.0029
SB4-1M-40"-ARPk	0.0497	0.2221	0.0343	0.0020	0.0099	0.0266	0.0004	0.0244	0.0703	0.0011	0.0028
SB4-1M-40"-ARPm	0.0522	0.2134	0.0359	0.0021	0.0093	0.0278	0.0004	0.0002	0.0735	0.0012	0.0029
SB4-1M-40"-ARPv	0.0498	0.2175	0.0348	0.0020	0.0095	0.0271	0.0004	0.0184	0.0712	0.0011	0.0028
SB4-1M-127"	0.0505	0.2328	0.0325	0.0019	0.0094	0.0279	0.0004	0.0002	0.0752	0.0011	0.0027
SB4-1M-127"-ARPa	0.0504	0.2359	0.0322	0.0019	0.0098	0.0275	0.0004	0.0053	0.0744	0.0011	0.0027
SB4-1M-127"-ARPe	0.0513	0.2427	0.0316	0.0019	0.0108	0.0266	0.0004	0.0118	0.0731	0.0011	0.0027
SB4-1M-127"-ARPk	0.0501	0.2484	0.0308	0.0018	0.0112	0.0259	0.0004	0.0244	0.0713	0.0011	0.0027
SB4-1M-127"-ARPm	0.0526	0.2409	0.0322	0.0019	0.0106	0.0271	0.0004	0.0002	0.0746	0.0012	0.0028
SB4-1M-127"-ARPv	0.0502	0.2445	0.0312	0.0018	0.0108	0.0264	0.0004	0.0185	0.0722	0.0011	0.0027
SB4-1.6M-0"	0.0413	0.2561	0.0390	0.0021	0.0101	0.0254	0.0004	0.0001	0.0605	0.0010	0.0028
SB4-1.6M-0"-ARPa	0.0414	0.2588	0.0385	0.0021	0.0104	0.0251	0.0004	0.0052	0.0600	0.0010	0.0028
SB4-1.6M-0"-ARPe	0.0426	0.2645	0.0377	0.0021	0.0115	0.0244	0.0004	0.0118	0.0594	0.0010	0.0028
SB4-1.6M-0"-ARPk	0.0417	0.2696	0.0367	0.0020	0.0118	0.0237	0.0004	0.0244	0.0579	0.0010	0.0028
SB4-1.6M-0"-ARPm	0.0438	0.2630	0.0384	0.0021	0.0113	0.0248	0.0004	0.0001	0.0607	0.0010	0.0029
SB4-1.6M-0"-ARPv	0.0416	0.2662	0.0373	0.0020	0.0114	0.0242	0.0004	0.0184	0.0586	0.0010	0.0028
SB4-1.6M-40"	0.0480	0.2357	0.0348	0.0020	0.0103	0.0274	0.0004	0.0002	0.0709	0.0011	0.0027
SB4-1.6M-40"-ARPa	0.0480	0.2388	0.0344	0.0019	0.0106	0.0270	0.0004	0.0053	0.0702	0.0011	0.0027
SB4-1.6M-40"-ARPe	0.0489	0.2454	0.0338	0.0019	0.0116	0.0262	0.0004	0.0118	0.0691	0.0011	0.0027
SB4-1.6M-40"-ARPk	0.0478	0.2511	0.0329	0.0019	0.0120	0.0255	0.0004	0.0244	0.0674	0.0010	0.0027
SB4-1.6M-40"-ARPm	0.0502	0.2437	0.0344	0.0020	0.0115	0.0266	0.0004	0.0002	0.0705	0.0011	0.0028
SB4-1.6M-40"-ARPv	0.0478	0.2472	0.0334	0.0019	0.0116	0.0259	0.0004	0.0185	0.0682	0.0011	0.0027
SB4-1.6M-127"	0.0487	0.2660	0.0306	0.0018	0.0107	0.0268	0.0004	0.0002	0.0727	0.0011	0.0026
SB4-1.6M-127"-ARPa	0.0487	0.2685	0.0302	0.0018	0.0110	0.0264	0.0004	0.0053	0.0720	0.0011	0.0025
SB4-1.6M-127"-ARPe	0.0496	0.2738	0.0298	0.0018	0.0120	0.0256	0.0004	0.0118	0.0708	0.0011	0.0026
SB4-1.6M-127"-ARPk	0.0485	0.2786	0.0290	0.0017	0.0124	0.0249	0.0003	0.0244	0.0690	0.0010	0.0025
SB4-1.6M-127"-ARPm	0.0509	0.2723	0.0304	0.0018	0.0118	0.0261	0.0004	0.0002	0.0722	0.0011	0.0026
SB4-1.6M-127"-ARPv	0.0485	0.2754	0.0294	0.0017	0.0120	0.0254	0.0004	0.0185	0.0699	0.0010	0.0025

3.2 Candidate Frits

A subset of the candidate frits considered during the frit development efforts (Peeler and Edwards 2005c) is provided in Table 3-3. A closer review of the frits listed in Table 3-3 indicates fixed concentrations of B_2O_3 and Li_2O at 8 wt% with only the Na_2O and SiO_2 concentrations varying. In general, the progression of frit compositions from Frit 418 (the most refractory frit listed) to Frit 320 is a 1% increase in Na_2O concentration with the difference being accounted for by an equivalent decrease in SiO_2 content. This system is referred to as a "sliding Na_2O scale" concept which has been developed to accommodate potential Na_2O concentration differences in the sludge as a result of varying blending and/or washing strategies being considered. A more detailed discussion of the "scaled" approach and of the complete set of candidate frits considered is provided in Peeler and Edwards (2005c).

Table 3-3. Composition of Candidate Frits
(as mass fractions)

Frit ID	B_2O_3	Li_2O	Na_2O	SiO_2
320	0.08	0.08	0.12	0.72
417	0.08	0.08	0.11	0.73
425	0.08	0.08	0.10	0.74
426	0.08	0.08	0.09	0.75
418	0.08	0.08	0.08	0.76

3.3 Potential for Nepheline Formation

The glass systems defined by the sludge compositions of Table 3-1 in combination with the frits of Table 3-2 were investigated for their projected operating windows over waste loadings of 25% to 60% using the models and constraints of PCCS (Peeler and Edwards 2005c), and these glass systems are the focus of this study. As the investigation was conducted, the operating windows were also evaluated against the nepheline constraint provided by Li et al. (2003). The results from that study indicated that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary fall within the nepheline primary phase field. In particular, glasses that satisfy the constraint

$$\frac{\mathrm{SiO_2}}{\mathrm{SiO_2} + \mathrm{Na_2O} + \mathrm{Al_2O_3}} > 0.62 \tag{1}$$

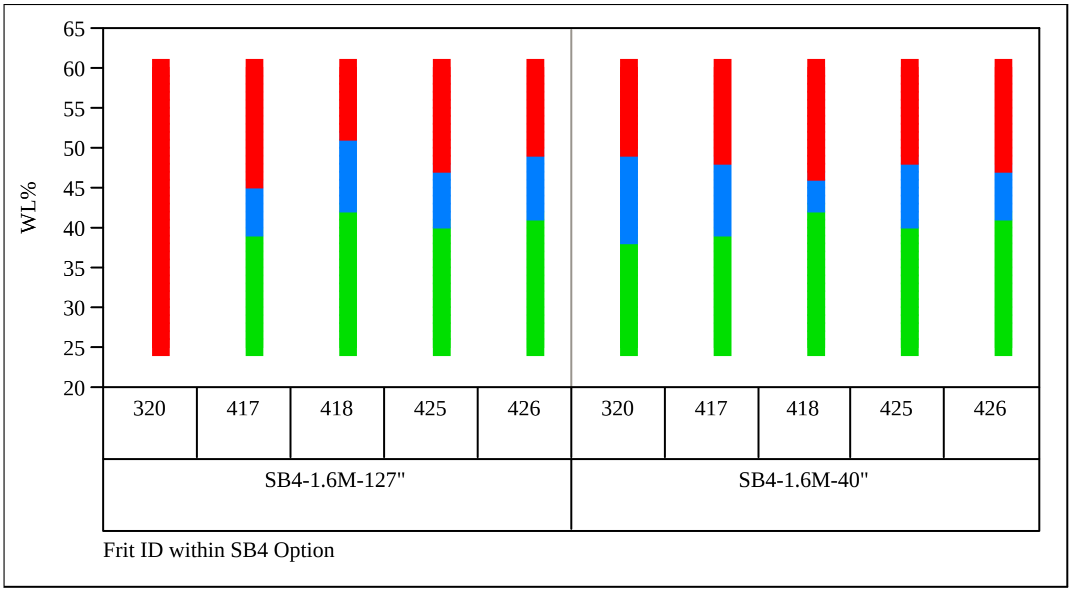
where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase. The impact of the application of this guide or discriminator on the operating windows of the SB4 glass systems defined by the sludge options of Tables 3-1 and 3-2 and the candidate frits of Table 3-3 is discussed by Peeler and Edwards (2005c). In that study, as in this one, the discriminator was used as defined by (1) (i.e., 0.62 was used as the critical value as established by Li et al. (2003) and recommended by Peeler et al. (2005b) for SB4).

4.0 SELECTING THE NEPHELINE STUDY GLASSES

The number of glass systems investigated by Peeler and Edwards (2005c) following the approach outlined above (but with a more extensive set of candidate frits) was on the order of 828, with each of these glass systems involving only one of the nominal sludge compositions from Tables 3-1 and 3-2 and an individual candidate frit. As part of the frit development effort, the Nominal Stage assessment, as this approach is described, was followed by a Variation Stage assessment that introduced variation in each of the sludge options carried forward to this stage of the frit development effort. The results of this assessment are also provided in Peeler and Edwards (2005c), but they will not be discussed here. That is because in selecting glasses for this phase of the nepheline study, the decision was made to select the glasses from the compositions generated as part of the Nominal Stage assessment. While compositions from the Variation Stage may have been more bounding of the SB4 glass systems relative to the compositions from the Nominal Stage, compositions from the Nominal Stage provide the opportunity for direct feedback on the sludge options and the candidate frits which could be important if problems or troubling issues arise from this phase of the nepheline study.

To increase the potential for valuable feedback, only two SB4 options were considered: 1.6M Na^+ with a 40” SB3 Heel and No ARP and 1.6M Na^+ with a 127” SB3 Heel and No ARP – both “sludge-only” based flowsheets. Based upon the current thinking, these two options are seen as providing the better (i.e., more likely) representations of SB4 (at least during the early stages of SB4 processing). Each of these options was combined with frits 320, 417, 418, 425, and 426 from Table 3-3 at WLs from 25 through 60% (in WL increments of 1%) to provide the initial set of glass compositions from which the nepheline glasses were selected. Figure 4-1 provides a look at the operating windows for these SB4 glass systems. For this plot the interpretation of the colors is as follows**: red indicates WLs that are restricted by PCCS**, **blue indicates WLs that are “restricted” only by the concern for the potential for the formation of a nepheline primary phase field using a 0.62 value**, and **green indicates WLs that are acceptable by PCCS.**

Figure 4-1 Operating Windows for Select SB4 Glass Systems



As seen in this plot, the SB4-1.6M-127" option with Frit 320 fails the PCCS MAR over the entire WL interval primarily driven by predictions of durability. PCCS MAR results hide the fact that the nepheline constraint is also challenged over a portion of the 25 to 60% WL interval for this glass system (see Peeler and Edwards 2005c for a more complete discussion). For this system, two glasses were selected that challenged the nepheline constraint while failing only the durability MAR of PCCS. Thus these glasses provide an opportunity to investigate for conservatism in the durability model for this SB4 system while giving additional insight into the possible impacts of nepheline within a Frit 320-based SB4 glass (especially since Frit 320 is a candidate for use with other SB4 options).[1] For the other glass systems, the plot indicates that the operating window for each system would be expanded if the nepheline constraint were challenged. This provides the basis for selecting glasses for Phase 2 of the nepheline study - glasses are to be selected that are prone to nepheline formation so that they may be experimentally assessed for the occurrence of nepheline and for its impact (or lack thereof) on durability for glasses heat treated to bound possible thermal impacts).

For each glass system (except the SB4-1.6M-127" option with Frit 320), glasses were selected for study to cover the WLs in the blue shaded areas of Figure 4-1. More specifically, the minimum WL defining the lower interface between the green and blue regions was selected as well as the upper WL defining the boundary between the blue and red regions. When warranted (i.e., the upper and lower WLs defining the nepheline formation region were far enough apart), a third WL was selected as an intermediate WL point. For example, consider the Frit 320 – 1.6M, 40" sludge case. The WL interval over which nepheline is challenged was 39 – 49% WL. Three glasses were selected to represent this system based on WLs of 39, 44, and 49% WL. The two specific systems in which only two WLs were selected include the Frit 418 – 1.6M, 40" case and the Frit 320 – 1.6M, 127" case. For the Frit 418 – 1.6M, 40" sludge case, the WL interval over which nepheline was challenged was 43 – 46% WL. Therefore selecting a third, intermediate WL was not seen to be of much value. For the SB4-1.6M-127" option with Frit 320, WLs of 39% and 42% were selected. Again, a third intermediate WL would be of little value in this system.

The glass compositions generated by this process are given in Tables 4-1 and 4-2. Unique identifiers for these glasses are provided in the first row of each table, and the value of the nepheline discriminator for each glass is also included in these tables.

---

[1] It should be noted that the durability limits being used in this assessment are those proposed by Edwards et al. (2003) but which have not been implemented in DWPF. Although these new limits reduce some of the conservatism of the current DWPF models, identifying additional conservatisms relative to specific glass systems of interest to DWPF provides incentive for the continued investigation into alternatives for assessing the durability of DWPF wasteforms.

Table 4-1. Compositions of Selected Glasses for the SB4-1.6M-127" Option

(as wt%'s)

#	NEPH2-13	NEPH2-14	NEPH2-15	NEPH2-16	NEPH2-17	NEPH2-18	NEPH2-19	NEPH2-20	NEPH2-21	NEPH2-22	NEPH2-23	NEPH2-24	NEPH2-25	NEPH2-26
Frit ID	320	320	417	417	417	425	425	425	426	426	426	418	418	418
%WL	39	42	40	43	45	41	44	47	42	46	49	43	47	51
nepheline	0.617	0.596	0.618	0.596	0.581	0.619	0.597	0.573	0.620	0.589	0.565	0.620	0.588	0.556
Al_2O_3	10.210	10.995	10.472	11.257	11.781	10.734	11.519	12.304	10.995	12.043	12.828	11.257	12.304	13.352
B_2O_3	4.880	4.640	4.800	4.560	4.400	4.720	4.480	4.240	4.640	4.320	4.080	4.560	4.240	3.920
BaO	0.053	0.057	0.054	0.058	0.061	0.055	0.059	0.064	0.057	0.062	0.066	0.058	0.064	0.069
CaO	0.776	0.836	0.796	0.856	0.896	0.816	0.876	0.936	0.836	0.916	0.976	0.856	0.936	1.015
Ce_2O_3	0.073	0.078	0.075	0.080	0.084	0.076	0.082	0.088	0.078	0.086	0.091	0.080	0.088	0.095
Cr_2O_3	0.091	0.098	0.093	0.100	0.105	0.095	0.102	0.109	0.098	0.107	0.114	0.100	0.109	0.119
CuO	0.028	0.031	0.029	0.031	0.033	0.030	0.032	0.034	0.031	0.033	0.036	0.031	0.034	0.037
Fe_2O_3	8.648	9.313	8.870	9.535	9.979	9.092	9.757	10.422	9.313	10.200	10.866	9.535	10.422	11.309
K2O	0.545	0.587	0.559	0.601	0.629	0.573	0.615	0.657	0.587	0.643	0.685	0.601	0.657	0.713
La_2O_3	0.031	0.034	0.032	0.035	0.036	0.033	0.035	0.038	0.034	0.037	0.039	0.035	0.038	0.041
Li_2O	4.880	4.640	4.800	4.560	4.400	4.720	4.480	4.240	4.640	4.320	4.080	4.560	4.240	3.920
MgO	0.548	0.590	0.562	0.604	0.633	0.576	0.618	0.661	0.590	0.647	0.689	0.604	0.661	0.717
MnO	1.901	2.047	1.949	2.095	2.193	1.998	2.144	2.290	2.047	2.242	2.388	2.095	2.290	2.485
Na_2O	17.695	18.133	17.241	17.709	18.021	16.807	17.305	17.804	16.393	17.098	17.626	15.999	16.744	17.488
NiO	1.192	1.284	1.223	1.314	1.375	1.253	1.345	1.437	1.284	1.406	1.498	1.314	1.437	1.559
PbO	0.069	0.074	0.071	0.076	0.080	0.072	0.078	0.083	0.074	0.081	0.087	0.076	0.083	0.090
SO_4	0.417	0.449	0.428	0.460	0.481	0.439	0.471	0.503	0.449	0.492	0.524	0.460	0.503	0.546
SiO_2	44.964	42.884	44.871	42.761	41.355	44.758	42.618	40.478	44.624	41.731	39.562	44.471	41.538	38.605
ThO_2	0.015	0.016	0.015	0.016	0.017	0.016	0.017	0.018	0.016	0.017	0.019	0.016	0.018	0.019
TiO_2	0.007	0.008	0.008	0.008	0.008	0.008	0.008	0.009	0.008	0.009	0.009	0.008	0.009	0.010
U_3O_8	2.836	3.054	2.908	3.126	3.272	2.981	3.199	3.417	3.054	3.345	3.563	3.126	3.417	3.708
ZnO	0.042	0.045	0.043	0.046	0.048	0.044	0.047	0.050	0.045	0.049	0.052	0.046	0.050	0.055
ZrO_2	0.100	0.107	0.102	0.110	0.115	0.105	0.112	0.120	0.107	0.117	0.125	0.110	0.120	0.130

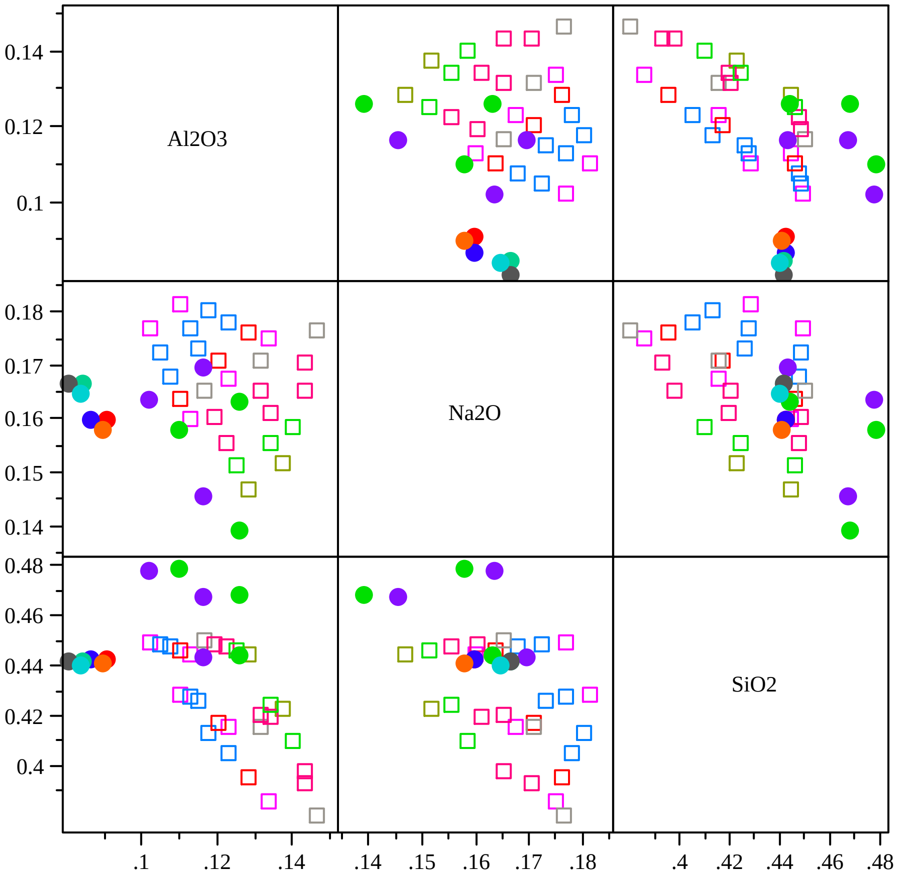
Table 4-2. Compositions of Selected Glasses for the SB4-1.6M-40” Option

(as wt%’s)

Glass ID #	NEPH2-27	NEPH2-28	NEPH2-29	NEPH2-30	NEPH2-31	NEPH2-32	NEPH2-33	NEPH2-34	NEPH2-35	NEPH2-36	NEPH2-37	NEPH2-38	NEPH2-39	NEPH2-40
Frit ID	320	320	320	417	417	417	425	425	425	426	426	426	418	418
%WL	39	44	49	40	44	48	41	45	48	42	45	47	43	46
nepheline	0.615	0.579	0.541	0.616	0.587	0.556	0.617	0.587	0.563	0.618	0.594	0.579	0.618	0.594
Al_2O_3	11.641	13.133	14.626	11.939	13.133	14.327	12.238	13.432	14.327	12.536	13.432	14.029	12.835	13.730
B_2O_3	4.880	4.480	4.080	4.800	4.480	4.160	4.720	4.400	4.160	4.640	4.400	4.240	4.560	4.320
BaO	0.056	0.063	0.071	0.058	0.063	0.069	0.059	0.065	0.069	0.060	0.065	0.068	0.062	0.066
CaO	0.749	0.845	0.941	0.769	0.845	0.922	0.788	0.865	0.922	0.807	0.865	0.903	0.826	0.884
Ce_2O_3	0.075	0.085	0.095	0.077	0.085	0.093	0.079	0.087	0.093	0.081	0.087	0.091	0.083	0.089
Cr_2O_3	0.098	0.110	0.123	0.100	0.110	0.120	0.103	0.113	0.120	0.105	0.113	0.118	0.108	0.115
CuO	0.029	0.033	0.037	0.030	0.033	0.036	0.031	0.034	0.036	0.031	0.034	0.035	0.032	0.034
Fe_2O_3	8.330	9.398	10.466	8.544	9.398	10.252	8.757	9.612	10.252	8.971	9.612	10.039	9.184	9.825
K2O	0.669	0.755	0.840	0.686	0.755	0.823	0.703	0.772	0.823	0.720	0.772	0.806	0.737	0.789
La_2O_3	0.032	0.036	0.040	0.033	0.036	0.039	0.033	0.037	0.039	0.034	0.037	0.038	0.035	0.037
Li_2O	4.880	4.480	4.080	4.800	4.480	4.160	4.720	4.400	4.160	4.640	4.400	4.240	4.560	4.320
MgO	0.415	0.468	0.522	0.426	0.468	0.511	0.436	0.479	0.511	0.447	0.479	0.500	0.458	0.490
MnO	1.872	2.112	2.352	1.920	2.112	2.304	1.968	2.160	2.304	2.016	2.160	2.256	2.064	2.208
Na_2O	16.514	17.093	17.671	16.030	16.533	17.036	15.565	16.108	16.516	15.121	15.558	15.850	14.697	15.164
NiO	1.358	1.532	1.706	1.393	1.532	1.672	1.428	1.567	1.672	1.463	1.567	1.637	1.498	1.602
PbO	0.076	0.086	0.096	0.078	0.086	0.094	0.080	0.088	0.094	0.082	0.088	0.092	0.084	0.090
SO_4	0.402	0.453	0.505	0.412	0.453	0.495	0.423	0.464	0.495	0.433	0.464	0.484	0.443	0.474
SiO_2	44.987	41.524	38.061	44.894	42.084	39.273	44.782	41.931	39.793	44.649	42.481	41.036	44.497	42.299
ThO_2	0.016	0.018	0.020	0.017	0.018	0.020	0.017	0.019	0.020	0.017	0.019	0.020	0.018	0.019
TiO_2	0.007	0.008	0.009	0.007	0.008	0.009	0.008	0.008	0.009	0.008	0.008	0.009	0.008	0.009
U_3O_8	2.765	3.120	3.474	2.836	3.120	3.403	2.907	3.190	3.403	2.978	3.190	3.332	3.049	3.261
ZnO	0.042	0.048	0.053	0.043	0.048	0.052	0.044	0.049	0.052	0.045	0.049	0.051	0.046	0.050
ZrO_2	0.107	0.120	0.134	0.109	0.120	0.131	0.112	0.123	0.131	0.115	0.123	0.128	0.117	0.126

As discussed in the Introduction section, an earlier nepheline study was conducted by Peeler et al. (2005a and 2005b). Twelve glasses were selected for that study (now designated as Phase 1). Figure 4-2 provides a scatterplot matrix showing the relationships among the concentrations of the three oxides involved in the nepheline constraint for both sets of glasses: the 12 earlier Phase 1 glasses (closed circles) and the 28 Phase 2 glasses (open squares) defined by Tables 4-1 and 4-2. As seen by this plot, the 28 glasses selected in this study expand the glass composition regions covered by the earlier nepheline study. Specifically, the compositions selected for Phase 2 of nepheline testing have higher concentrations of both Al_2O_3 and Na_2O and lower concentrations of SiO_2 as compared to the compositions selected for the Phase 1 testing. Thus, the Phase 2 glasses complement the Phase 1 glasses by extending the compositional region of the investigation. In fact, all of the Phase 2 glasses are "prone" to nepheline formation, while only two of the twelve Phase 1 glasses fell into this category.

Figure 4-2 A Scatter Plot Matrix of the Glass Compositions in Phases 1 and 2 of the Nepheline Study



The glasses in Tables 4-1 and 4-2 are to be batched and fabricated using standard procedures. Visual observations and other analytical techniques are to be used, as needed, to assess the presence of crystals and, specifically, a nepheline primary phase. The durability of these glasses (for both quenched and centerline canister cooled versions) is to be measured using the ASTM PCT Method A. The results from these efforts are to be documented in a subsequent report.

5.0 SUMMARY

SRNL's frit development effort for SB4 is being driven by the CBU options for this sludge, which based on the most recent projections may be framed around three decision areas: the sodium molarity of the sludge (at values of1M Na^+ and 1.6M Na^+), the SB3 heel that will be included in the batch (expressed in inches of SB3 sludge with values of 0, 40, and 127"), and the introduction of an ARP stream into the sludge (which is represented by six options: no ARP, ARPa, ARPe, ARPk, ARPm, and ARPv). Candidate frits are being identified for these options via a paper study approach developed by Peeler and Edwards (2005c) with the intent of downselecting to a set of key frits whose operating windows (i.e., WL intervals that meet PCCS MAR criteria) are robust to and/or selectively optimal for these sludge options. The primary or key frits that appear attractive on paper (i.e., downselected via the paper study) will then be transferred into SRNL's experimental studies supporting SB4; specifically, the melt-rate studies, chemical process cell flowsheet runs and, if needed, a glass variability study.

For SB4, there is one additional issue that is being tracked during the paper study assessments and that is the potential for the formation of a nepheline primary crystalline phase in SB4 glasses. Based upon earlier work by Li et al. (2003), glasses that satisfy the constraint:

$$\frac{SiO_2}{SiO_2 + Na_2O + Al_2O_3} > 0.62$$

where the oxides are expressed as mass fractions in the glass, do not precipitate nepheline as their primary phase. For many SB4 glass systems, as waste loadings are increased this constraint is not met (before PCCS MAR processing criteria are not met) due to the high aluminum content of the sludge and the high sodium concentrations targeted for the final glass (high sodium concentrations are anticipated as being necessary to attain attractive melt-rates).

Based on the 1.6M Na^+, 40" and 1.6M Na^+, 127" sludge options, 28 glasses have been selected to complement the earlier work of Peeler et al. (2005a and 2005b) by continuing the investigation into the ability of the above constraint to predict the occurrence of a nepheline primary phase for SB4 glasses and into the impact of such primary phases on the durability of the SB4 glasses. In general, glasses were selected for study to cover WLs over which nepheline was the only criterion restricting access to higher WLs.

The glasses in Tables 4-1 and 4-2 are to batched and fabricated using standard procedures. Visual observations and other analytical techniques are to be used, as needed, to assess the presence of crystals with specific interest in the nepheline primary phase. The durability of these glasses (for both quenched and centerline canister cooled versions) is to be measured using the ASTM PCT Method A. The results from these efforts are to be documented in a subsequent report.

The results of this study will provide valuable input for the frit development efforts and subsequent feedback to the CBU regarding the relative viability of the various SB4 options under consideration. Specifically, if the formation of nepheline for SB4 glasses is found through this study to have an impact on durability that is overly detrimental, then candidate frits that lessen the likelihood of the formation of nepheline over an interval of waste loadings of interest to DWPF would move up the list of preferred frits. On the other hand, if the presence of nepheline has no appreciable, adverse impact on durability, then as decisions regarding the viability of the SB4 options and the downselect of candidate frits are pursued, little weight will be given to minimizing the likelihood of nepheline and the decisions will be dominated by waste throughput criteria.

6.0 REFERENCES

ASTM. 2002. **Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)**, ASTM C-1285-2002.

Brown, KG, RL Postles, and TB Edwards. 2002. **SME Acceptability Determination for DWPF Process Control**, WSRC-TR-95-00364, Revision 4, Westinghouse Savannah River Company, Aiken, South Carolina.

Cicero, C.A., S.L. Marra, and M.K. Andrews. 1993. *Phase Stability Determinations of DWPF Waste Glasses (U)*, WSRC-TR-93-227, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Edwards, TB, DK Peeler, and SL Marra. 2003. **Revisiting the Prediction Limits for Acceptable Durability**, WSRC-TR-2003-00510, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Elder, HH. 2005a. **Estimate of Sludge Batch 4 Calcine Composition**, CBU-PIT-2005-00134, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Elder, HH. 2005b. **Estimate of Sludge Batch 4 Calcine Composition Additional Cases**, CBU-PIT-2005-00176, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Herman, CC. 2005. **Sludge Batch 4 Composition Projections without Tank 4 and with ARP**, SRNL-ITS-2005-00198, Westinghouse Savannah River Company, Aiken, South Carolina.

Bickford, DF and CM Jantzen. 1984. “Devitrification of SRL Defense Waste Glass”, *Sci. Basis for Nuclear Waste Management*, VII, G.L. McVay (ed). Elsevier Publ., New York, 557-565.

Jantzen, CM, NE Bibler, DC Beam, CL Crawford, and MA Pickett. 1993. **Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material**, WSRC-TR-92-346, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Jantzen, CM, JB Picket, KG Brown, TB Edwards, and DC Beam. 1995. **Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using a Thermodynamic Hydration Energy Reaction Model (THERMO)**, WSRC-TR-93-672, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Kim, DS, DK Peeler, and P Hrma. 1995. “Effect of Crystallization on the Chemical Durability of Simulated Nuclear Waste Glasses”, *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries*, Ceramic Transaction, Volume 61, pp. 177 – 185.

Li, H, JD Vienna, P Hrma, DE Smith, and MJ Schwieger. 1997. “Nepheline Precipitation in High-Level Waste Glasses – Compositional Effects and Impact on the Waste Form Acceptability”, *Mat. Res. Soc. Proc.* 465, 261- 268.

Li, H, P Hrma, JD Vienna, M Qian, Y Su, and DE Smith. 2003. "Effects of Al_2O_3, B_2O_3, Na_2O, and SiO_2 on Nepheline Formation in Borosilicate Glasses: Chemical and Physical Correlations," Journal of Non-Crystalline Solids, 331 (2003) 202 – 216.

Lilliston, GR. 2005. **Development of Elemental Sludge Compositions for Variations of Sludge Batch 4 (SB4)**, CBU-PIT-2004-00011, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Marra SL and CM Jantzen. 1993. **Characterization of Projected DWPF Glass Heat Treated to Simulate Canister Centerline Cooling**, WSRC-TR-92-142, Revision 1, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK. 2004a. **Task Technical & QA Plan: Sludge Batch and MCU Frit Optimization**, WSRC-RP-2004-00746, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK. 2004b. **Task Technical & QA Plan: Sludge Batch 4 and MCU Glass Variability Studies with Simulants**, WSRC-RP-2004-00747, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and TB Edwards. 2005a. **Frit Development Efforts for Sludge Batch 4: Model-Based Assessments**, WSRC-TR-2005-00103, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and TB Edwards. 2005b. **The Impact of the Actinide Removal Process (ARP) on the Sludge Batch 4 Projected Operating Windows**, WSRC-TR-2005-00123, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and TB Edwards. 2005c. **Frit Development Effort for SB4: Nominal and Variation Stage Assessments,** WSRC-TR-2005-00372, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and TB Edwards. 2005d. **A Preliminary Assessment of the Need for a Sludge Batch 4 Variability Study**, WSRC-TR-2005-00122, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK and ME Smith. 2004. **Investigation to Increase the Overall Waste Throughput in the DWPF Melter**, WSRC-RP-2004-00713, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK, TB Edwards, and TH Lorier. 2005a. **Nepheline Formation Potential in Sludge Batch (SB4) Glasses**,WSRC-TR-2005-00153, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Peeler, DK, TB Edwards, IA Reamer, and RJ Workman. 2005b. **Nepheline Formation Study for Sludge Batch 4 (SB4): Phase 1 Experimental Results**,WSRC-TR-2005-00371, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Riley, BJ, JA Rosario, and P Hrma. 2001. **Impact of HLW Glass Crystallinity on the PCT Response**, PNNL-13491, Pacific Northwest National Laboratory, Richland, Washington.

Subosits, SG. 2004. **Actinide Removal Process Material Balance Calculation with Low Curie Salt Feed**, X-CLS-S-00113, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Taylor, AS, TB Edwards, JC George, TK Snyder, and DK Peeler. 2004. **The SRNL Composition – Properties (ComPro™) Database**, WSRC-RP-2004-00704, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Washburn, FA. 2004a. **Technical Task Request: Sludge Batch 4 and MCU Frit Optimization**, HLW/DWPF/TTR-2004-0025, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Washburn, FA. 2004b. **Technical Task Request: Sludge Batch 4 and MCU Glass Variability Studies with Simulants**, HLW/DWPF/TTR-2004-0027, Revision 0, Westinghouse Savannah River Company, Aiken, South Carolina.

Distribution:

J.E. Marra, SRNL
E.W. Holtzscheiter, SRNL
D.A. Crowley, 999-W
S.L. Marra, 999-W
T.B. Calloway, 999-W
N.E. Bibler, SRNL
C.M. Jantzen, SRNL
J.R. Harbour, 773-42A
G.G. Wicks, SRNL
D.K. Peeler, 999-W
T.B. Edwards, 773-42A
C.C. Herman, 773-42A
A.S. Choi, 999-W
M.E. Smith, 773-42A
M.E. Stone, 999-W
D.H. Miller, 999-W
T.M. Jones, 999-W