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GLASS COMPOSITIONS FOR THE NEPHELINE PHASE III STUDY

Co-author: K. M. Fox
Co-author: T. B. Edwards

JUNE 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-08SR22470

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REVIEWS AND APPROVALS

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LIST OF ACRONYMS

ACT™	Activated Complex Theory™
DWPF	Defense Waste Processing Facility
EVs	Extreme Vertices
LWO	Liquid Waste Organization
PCCS	Product Composition Control System

1.0 EXECUTIVE SUMMARY

A series of 29 test glass compositions were selected for Phase III of the nepheline study using a combination of two approaches. The first approach was based on evaluating the glass composition region allowable by all of the Defense Waste Processing Facility (DWPF) Product Composition Control System (PCCS) models with the exception of the current nepheline discriminator. This approach was taken to determine whether there are glass compositions that, while predicted to crystallize nepheline upon slow cooling, would otherwise be acceptable for processing in the DWPF. The second approach was based on quasicrystalline theory of glass structure, which helped predict compositional regions where nepheline should form. A detailed description of this methodology is forthcoming. The selection strategy outlined here will provide an opportunity to determine experimentally whether the glasses that fail the current nepheline discriminator but pass the newly proposed nepheline discriminator are indeed free of nepheline after slow cooling. If this is the case, these data will serve as a significant step toward reducing conservatism in the current nepheline discriminator.

The 29 glass compositions selected for testing address both the PCCS model and quasicrystalline theory approaches in evaluating both a reduction in conservatism for the current nepheline discriminator and possible implementation of the newly proposed discriminator based on glass structural theory. These glasses will be fabricated and characterized in the laboratory, with the results and conclusions described in a technical report.

2.0 INTRODUCTION

Two routes – one based on the relationship of the current nepheline discriminator model to the other Defense Waste Processing Facility (DWPF) Product Composition Control System (PCCS) models[1] and the other based on theory of crystallization in mineral and glass melts – were considered in selecting glasses for this phase of the nepheline study. The current nepheline discriminator model limits access to certain compositional regions based solely on the concentrations of silica, alumina and soda in the glass. While this model has been shown to be very effective in identifying glasses that are prone to nepheline crystallization upon slow cooling for DWPF-type compositions,[2] other waste glass compositions have revealed compositional regions that, while predicted to be prone to nepheline crystallization, are in fact free of nepheline upon slow cooling and have acceptable chemical durabilities.[3]

A Phase I study confirmed that some conservatism exists in the current nepheline discriminator.[4] Several glass compositions, particularly compositions that targeted higher Al_2O_3 concentrations, were shown to be very durable while their nepheline discriminator values were well below the current nepheline discriminator limit of 0.62. Increased concentrations of B_2O_3 and CaO were shown to improve durability responses and suppress the formation of nepheline. These results provided incentive to revise the nepheline discriminator to reduce some of this conservatism and incorporate the influence of B_2O_3. The Phase I study suggested that a second phase be undertaken to provide additional data in support of this revision.[4]

Twenty five glass compositions were subsequently selected for a Phase II study on reduction of conservatism in the nepheline discriminator.[5] The glass compositions were restricted to regions that fell within the validation ranges of the DWPF PCCS models. The glasses were fabricated in the laboratory and characterized for crystallization and chemical durability after both quenching and slow cooling. Nepheline was identified in one of the quenched glasses and several of the CCC glasses. A partitioning algorithm was used to identify trends in crystallization behavior based on glass composition. Generally, for the slowly cooled glasses MnO influenced the crystallization of spinels and B_2O_3 and SiO_2 influenced the crystallization of nepheline. Durability responses varied from acceptable to unacceptable depending on the glass composition and type and extent of crystallization that occurred. It was not possible to identify any linear effects of composition on chemical durability performance for this set of study glasses. The results of the Phase II study alone were not sufficient to recommend modification of the current nepheline discriminator. It was recommended that the next series of experiments continue to focus not only on compositional regions where the PCCS models are considered applicable (i.e., the model validation ranges), but also be restricted to compositional regions where acceptable glasses are predicted to be produced but are disallowed by the current nepheline discriminator.[5]

The intent of this Phase III study is to investigate whether there are compositional regions available, particularly glasses with higher aluminum concentrations to support higher waste loadings that are acceptable by all of the PCCS models with the exception of the nepheline discriminator. That is, is there unnecessary conservatism present in the current nepheline discriminator model that disallows access to glass compositions that are both acceptable by all of the other PCCS models and in fact free of nepheline crystallization? Two approaches, outlined in the sections below, were taken to select glass compositions for this study.

This work is performed in response to a request[6] from the Liquid Waste Organization (LWO) and is controlled under a Task Technical and Quality Assurance Plan.[7]

3.0 DISCUSSION

PCCS MODEL APPROACH

A statistically driven design of experiments was used to determine the compositional region that is ruled out by the current nepheline discriminator yet otherwise acceptable by the other PCCS models. If a sub-region within this compositional space can be identified where the glasses do not form nepheline, it may be possible to revise the nepheline discriminator to incorporate this region, potentially allowing access to higher waste loadings for the DWPF.

Twelve of the major oxides in a DWPF-type glass composition were considered in developing the compositional region for study. Concentration ranges for these major oxides were chosen using the model applicability and model validation ranges for the PCCS models and recent reduction of constraints studies[8] as a guide to represent possible compositions that could be processed at the DWPF. These concentration ranges are given in Table 3-1. Note that uranium will not be used in fabricating the study glasses to simplify sample handling. The compositions will be normalized to 100 wt % without the U_3O_8 component. This will not impact the objectives of this task, although follow-on work would likely include uranium before any changes were implemented in PCCS.

Table 3-1. Concentration ranges for the major oxides and Others.

Oxide	Minimum (wt %)	Maximum (wt %)
Al_2O_3	3.25	18.00
B_2O_3	4.5	14.00
CaO	0.00	4.00
Cr_2O_3	0	0.20
Fe_2O_3	5.00	21.00
Li_2O	4.00	7.00
MgO	0.00	1.50
MnO	0.30	5.50
Na_2O	10.00	18.00
NiO	0.00	2.50
SiO_2	30.00	55.00
TiO_2	0.00	2.00
U_3O_8	0.00	9.50
Others	0.00	2.00

Note that an Others category is also included in Table 3-1. This category represents a group of minor oxides typically present in a DWPF-type glass composition. The average concentrations of the oxides included in the Others category are given in Table 3-2.

Table 3-2. Average composition of the Others category.

Oxide	Average concentration (wt %)
BaO	4.00
Ce_2O_3	18.03
CdO	14.82
CuO	6.41
La_2O_3	4.89
PbO	10.82
SO_4^{2-}	24.04
ZnO	6.73
ZrO_2	10.26

A statistical analysis software package[a] was used to identify a region within the bounds defined in Table 3-1 where the compositions fail the current nepheline discriminator but are acceptable by the other DWPF PCCS control models. The software was then used to optimally select 14 compositions from the corner points, or extreme vertices (EVs), of this sub-region. The compositions of the 14 EVs (optimally selected for a linear model of the 13 major oxides plus the Others category) are listed in Table 3-3 after removing the radioactive components and normalizing to 100 wt %. These define the compositions of the first set of glasses to be fabricated and characterized in the laboratory.

Since the EVs represent the extremes of the compositional region where the glasses are acceptable by all of the PCCS models except for the nepheline discriminator, a second strategy was used to select additional glasses within the region of interest. An approach based on a space-filling algorithm was used to identify glass compositions that fall within the extreme vertices to better map the compositional space. Approximately 400 space-filling compositions were identified. This number was chosen as a compromise between sufficient coverage of the compositional space and reasonable computing times. The compositions resulting from the space-filling approach were then evaluated against the PCCS MAR. These evaluations yielded 15 of the space-filling glasses that passed all of the model constraints except for the nepheline discriminator. These compositions define the second set of glasses to be examined experimentally, and their compositions are listed in Table 3-4 after removing the radioactive components and normalizing to 100 wt %.

[a] JMP™, Ver. 6.0.3, SAS Institute Inc., Cary, NC (2006).

Table 3-3. Target compositions of the EV glasses.

Oxide	EV-350	EV-352	EV-354	EV-349	EV-356	EV-348	EV-358	EV-359	EV-357	EV-346	EV-347	EV-353	EV-355	EV-351
Al_2O_3	10.53	12.69	12.86	13.38	14.51	14.38	14.65	14.20	16.08	14.70	16.18	17.02	17.19	18.00
B_2O_3	4.51	7.22	8.82	4.62	12.11	11.23	11.51	8.66	6.64	7.43	7.07	7.86	7.87	5.30
BaO	0.00	0.08	0.08	0.00	0.09	0.08	0.00	0.00	0.09	0.08	0.00	0.00	0.06	0.08
CaO	4.00	0.00	4.00	0.19	0.00	0.01	1.46	3.04	4.42	0.99	0.00	0.92	0.00	4.00
CdO	0.00	0.30	0.30	0.00	0.32	0.31	0.00	0.00	0.33	0.30	0.00	0.00	0.21	0.30
Ce_2O_3	0.00	0.36	0.36	0.00	0.39	0.38	0.00	0.00	0.40	0.36	0.00	0.00	0.25	0.36
Cr_2O_3	0.20	0.00	0.10	0.00	0.22	0.05	0.00	0.00	0.00	0.00	0.22	0.20	0.15	0.00
CuO	0.00	0.13	0.13	0.00	0.14	0.14	0.00	0.00	0.14	0.13	0.00	0.00	0.09	0.13
Fe_2O_3	9.03	8.67	10.90	11.56	5.39	15.75	14.85	7.16	5.76	11.79	13.08	9.14	5.00	11.94
La_2O_3	0.00	0.10	0.10	0.00	0.11	0.10	0.00	0.00	0.11	0.10	0.00	0.00	0.07	0.10
Li_2O	4.00	4.00	4.00	4.96	5.41	4.23	4.22	6.37	4.71	4.36	7.20	4.10	4.88	7.00
MgO	1.50	0.00	0.00	0.00	1.62	0.12	0.32	0.90	0.00	1.51	0.00	0.00	0.00	0.00
MnO	3.50	5.50	3.45	0.31	0.32	0.69	2.66	0.69	0.33	1.99	3.98	0.64	4.38	0.30
Na_2O	17.34	15.56	13.69	18.48	15.27	11.24	11.32	14.04	13.19	13.26	11.01	13.53	18.00	11.73
NiO	1.88	0.00	0.46	0.00	0.00	0.51	0.00	2.39	2.76	0.00	0.46	0.41	2.36	0.00
PbO	0.00	0.22	0.22	0.00	0.23	0.23	0.00	0.00	0.24	0.22	0.00	0.00	0.15	0.22
SO_4^{2-}	0.00	0.48	0.48	0.00	0.52	0.51	0.00	0.00	0.53	0.48	0.00	0.00	0.34	0.48
SiO_2	41.51	42.37	39.43	46.51	42.19	37.56	36.98	42.36	43.90	41.95	40.79	45.67	38.77	37.73
TiO_2	2.00	2.00	0.28	0.00	0.80	2.12	2.03	0.18	0.00	0.00	0.00	0.52	0.00	2.00
ZnO	0.00	0.14	0.14	0.00	0.15	0.14	0.00	0.00	0.15	0.14	0.00	0.00	0.09	0.13
ZrO_2	0.00	0.21	0.21	0.00	0.22	0.22	0.00	0.00	0.23	0.21	0.00	0.00	0.14	0.20

Table 3-4. Target compositions of the SF glasses.

Oxide	SF-179	SF-284	SF-145	SF-328	SF-172	SF-193	SF-295	SF-286	SF-136	SF-129	SF-106	SF-84	SF-272	SF-307	SF-58
Al_2O_3	10.71	11.68	11.58	11.93	12.30	13.21	13.63	14.36	14.15	14.68	17.13	17.96	18.31	17.75	18.01
B_2O_3	6.35	9.84	5.43	5.53	9.12	6.30	5.28	7.86	11.82	7.37	7.32	5.89	5.11	10.31	10.38
BaO	0.05	0.07	0.08	0.05	0.01	0.02	0.07	0.00	0.05	0.05	0.06	0.01	0.06	0.06	0.00
CaO	0.06	4.18	3.79	3.69	3.86	0.30	3.36	1.15	3.97	4.07	3.42	1.37	2.32	0.02	3.04
CdO	0.17	0.25	0.29	0.18	0.03	0.06	0.25	0.01	0.17	0.19	0.22	0.02	0.22	0.24	0.00
Ce_2O_3	0.21	0.30	0.35	0.22	0.04	0.07	0.31	0.01	0.20	0.23	0.26	0.03	0.26	0.29	0.01
Cr_2O_3	0.20	0.16	0.13	0.08	0.12	0.13	0.05	0.14	0.12	0.01	0.13	0.21	0.01	0.11	0.06
CuO	0.07	0.11	0.13	0.08	0.01	0.02	0.11	0.01	0.07	0.08	0.09	0.01	0.09	0.10	0.00
Fe_2O_3	6.91	7.07	10.34	5.47	7.64	5.17	5.60	10.15	5.45	5.96	5.57	7.88	6.84	5.69	8.19
La_2O_3	0.06	0.08	0.10	0.06	0.01	0.02	0.08	0.00	0.05	0.06	0.07	0.01	0.07	0.08	0.00
Li_2O	4.99	4.64	4.38	5.92	5.19	5.69	7.31	4.58	5.18	5.14	7.09	5.11	5.55	4.81	4.29
MgO	0.53	0.20	0.37	1.34	0.85	0.18	0.94	0.06	0.29	1.19	0.83	0.32	1.37	0.52	0.76
MnO	1.42	4.74	1.50	0.44	0.93	1.48	5.59	3.51	3.73	0.47	3.26	3.79	2.12	2.05	4.69
Na_2O	17.71	13.35	15.25	15.34	14.01	17.76	13.05	13.51	11.09	16.78	12.20	16.98	14.65	13.79	14.48
NiO	2.33	0.67	1.51	2.21	0.58	0.00	0.79	0.92	0.03	1.59	0.49	1.05	1.30	1.21	0.53
PbO	0.12	0.18	0.21	0.13	0.02	0.04	0.18	0.01	0.12	0.14	0.16	0.02	0.16	0.18	0.00
SO_4^{2-}	0.27	0.40	0.47	0.29	0.05	0.09	0.41	0.02	0.27	0.31	0.35	0.04	0.35	0.39	0.01
SiO_2	47.50	39.97	42.01	46.09	44.35	48.47	41.17	42.06	42.64	40.99	39.68	38.63	39.98	42.09	35.10
TiO_2	0.14	1.83	1.75	0.75	0.84	0.94	1.50	1.62	0.40	0.46	1.41	0.64	0.96	0.05	0.44
ZnO	0.08	0.11	0.13	0.08	0.01	0.03	0.11	0.01	0.08	0.09	0.10	0.01	0.10	0.11	0.00
ZrO_2	0.12	0.17	0.20	0.13	0.02	0.04	0.17	0.01	0.12	0.13	0.15	0.02	0.15	0.17	0.00

GLASS CRYSTALLIZATION THEORY APPROACH

In parallel with development of the PCCS model approach (Section 0), an effort to develop an alternative nepheline discriminator has been undertaken based on quasicrystalline theory of glass structure. This effort will be documented in detail in a forthcoming report.[2] Briefly, Activated Complex Theory (ACT™) was used to relate simple ratios of the cation components of a series of glasses (a database of 136 DWPF-type compositions where crystallization data after slow cooling were available) to the quasicrystalline phases calculated using NORMCALC™.[3] In evaluating various combinations of the cation ratios, it was hypothesized that the tendency of a particular glass composition to crystallize nepheline upon slow cooling may be related to the inequality:

$$\frac{\mathrm{Si + B + P}}{\mathrm{Si + B + P + Na + K + Al + Fe}} > 0.50$$

where the atomic symbols indicate molar percentages of that cation. Glass compositions where this ratio is less than 0.50 are predicted to be prone to nepheline crystallization.

This theory was applied to both sets of glass compositions selected using the PCCS models as described earlier. A comparison of the nepheline discriminator values of the selected glasses using both the current nepheline discriminator and the newly proposed nepheline discriminator is provided in Figure 1. The current nepheline discriminator is represented by the blue, horizontal line (>=0.62) and the newly proposed nepheline discriminator is represented by the red, vertical line (>0.50). Four of the selected glasses fall above the current nepheline discriminator on this plot. However, when measurement uncertainty is applied in the PCCS MAR assessment, these compositions fail the current nepheline discriminator.

The selected glasses fall on either side of the newly proposed nepheline discriminator (vertical line in Figure 1). The selection strategy outlined here will provide an opportunity to determine experimentally whether the glasses that fail the current nepheline discriminator but pass the newly proposed nepheline discriminator are indeed free of nepheline after slow cooling. If this is the case, these data will serve as a significant step toward reducing conservatism in predicting nepheline crystallization.

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[2] Technical report currently in draft by Carol Jantzen at SRNL.
[3] Jantzen and Pareizs, *Journal of Nuclear Materials,* accepted for publication.

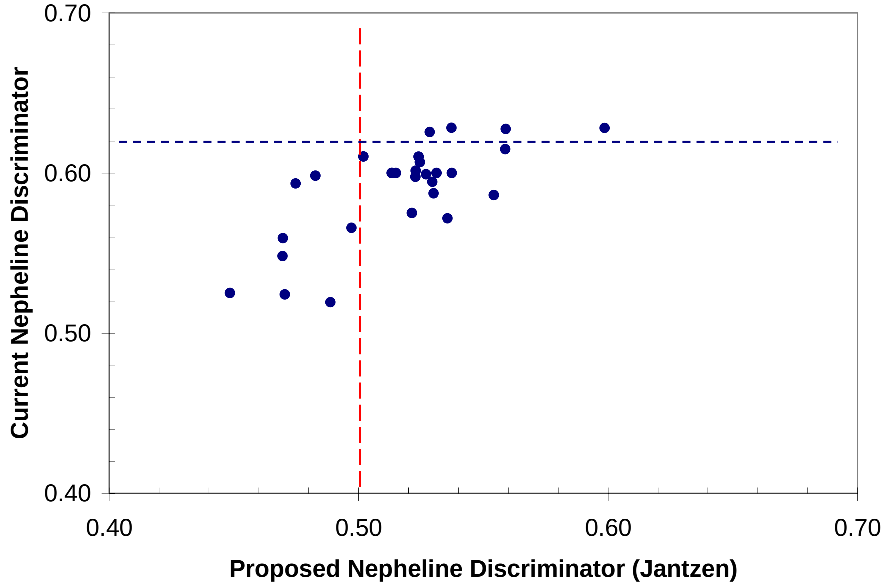

Figure 1. Plot of the nepheline discriminator values for the selected glasses using the current and newly proposed inequalities.

4.0 SUMMARY

A series of 29 test glass compositions were selected for Phase III of the nepheline study using a combination of two approaches. The first approach was based on evaluating the glass composition region allowable by all of the DWPF PCCS models with the exception of the current nepheline discriminator. This approach was taken to determine whether there are glass compositions that, while predicted to crystallize nepheline upon slow cooling, would otherwise be acceptable for processing in the DWPF. The second approach was based on quasicrystalline theory of glass structure. A detailed description of this methodology is forthcoming, but in brief, ACT™ was used to relate simple ratios of the cation components of a series of glasses to the quasicrystalline phases calculated using NORMCALC™. The 29 glass compositions selected for testing address both of these approaches in evaluating both a reduction in conservatism for the current nepheline discriminator and possible implementation of the newly proposed discriminator based on glass structural theory. These glasses will be fabricated and characterized in the laboratory, with the results and conclusions described in a technical report.

5.0 REFERENCES

1. Edwards, T. B., K. G. Brown and R. L. Postles, "SME Acceptability Determination for DWPF Process Control," *U.S. Department of Energy Report WSRC-TR-95-00364, Revision 5*, Washington Savannah River Company, Aiken, SC (2006).

2. Edwards, T. B., D. K. Peeler and K. M. Fox, "The Nepheline Discriminator: Justification and DWPF PCCS Implementation Details," *U.S. Department of Energy Report WSRC-STI-2006-00014, Revision 0,* Washington Savannah River Company, Aiken, SC (2006).

3. Fox, K. M. and D. K. Peeler, "Demonstration of Very High Aluminum Retention in Simulated HLW Glass," *U.S. Department of Energy Report SRNL-PSE-2007-00231,* Washington Savannah River Company, Aiken, SC (2007).

4. Fox, K. M., J. D. Newell, T. B. Edwards, D. R. Best, I. A. Reamer and R. J. Workman, "Refinement of the Nepheline Discriminator: Results of a Phase I Study," *U.S. Department of Energy Report WSRC-STI-2007-00659, Revision 0,* Washington Savannah River Company, Aiken, SC (2008).

5. Fox, K. M. and T. B. Edwards, "Refinement of the Nepheline Discriminator: Results of a Phase II Study," *U.S. Department of Energy Report SRNS-STI-2008-00099, Rev. 0,* Savannah River National Laboratory, Aiken, SC (2008).

6. Fellinger, T. L., "Technical Task Request: Nepheline Phase III Experimental Work," *U.S. Department of Energy Report HLW-DWPF-TTR-2009-0011, Revision 0,* Washington Savannah River Company, Aiken, SC (2009).

7. Fox, K. M., "Task Technical and Quality Assurance Plan: Nepheline Phase III Experimental Work," *U.S. Department of Energy Report SRNL-RP-2009-00508, Revision 0,* Savannah River National Laboratory, Aiken, SC (2009).

8. Raszewski, F. C., T. B. Edwards and D. K. Peeler, "Enhanced DOE High-Level Waste Melter Throughput Studies: SRNL Glass Selection Strategy," *U.S. Department of Energy Report WSRC-STI-2007-00652, Revision 0,* Washington Savannah River Company, Aiken, SC (2008).

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