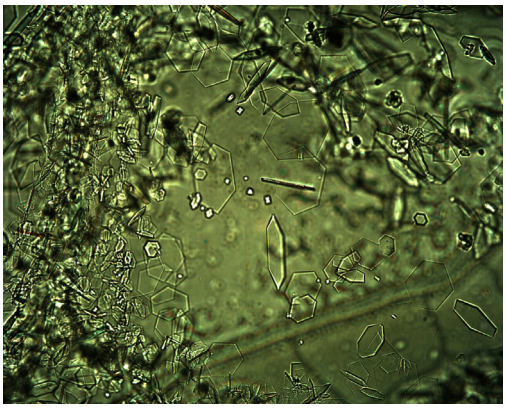
BACKGROUND

Why is nepheline formation an important consideration for nuclear waste glass reliability?

- Removes network forming atoms (Al, Si) from glass matrix
- Usually results in lowered chemical durability as measured by leach test (Product consistency test, PCT)



Hexagonal nepheline crystals in nuclear waste glass

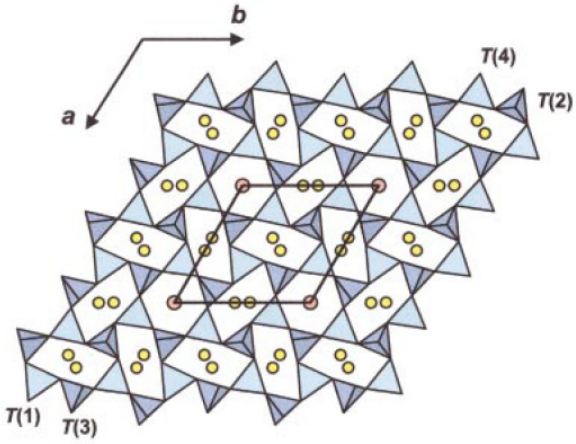
What are the factors involved in nepheline formation?

Chemical

- The right ratio of atoms must be available
- Nominally, nepheline mineral is (Na,K)$AlSiO_4$ but vacancies and other atoms such as Ca and Fe can be incorporated
- Phase diagram shows normal composition range of nepheline formation

Kinetic

- Slower cooled glass in canisters has the time to nucleate crystals and grow them, removing Al and Si from the network , reducing glass durability



Nepheline structure (Tait et al 2003) showing Si (dark tetrahedra), Al(light tetrahedra), Na (yellow) and K (red). Other atoms can substitute in this structure

How do we choose glasses that will not form nepheline?

Nepheline discriminator

- Use phase diagram to ensure enough Si (in wt%, *w*) is available relative to Al and Na such that nepheline does not form at equilibrium

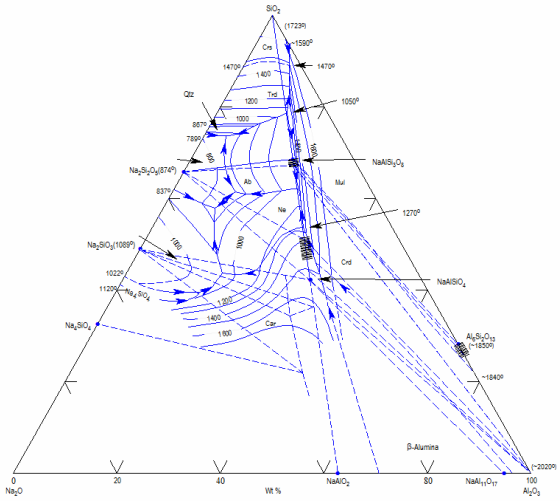
$$ND = \frac{w_{SiO_2}}{w_{SiO_2} + w_{Al_2O_3} + w_{Na_2O}} \leq 0.62$$

- Limitation: only considers Si, Al, and Na content; other atoms (e.g. B and Ca) are known to affect nepheline formation

Optical basicity

- Proposed as a supplementary criterion
- Related to chemical bonding and behavior
- Acidic (Si, B, P), basic (Na, K, Ca), and intermediate (Al)
- Calculated based on relative amounts of oxide (in mol%, *x*), number of oxygens (*q*), and tabulated relative basicity coefficients (Λ)

$$OB = \frac{\sum_i m_i q_i \Lambda_i}{\sum_i m_i q_i} \geq 0.575$$



Na_2O-Al_2O_3-SiO_2 phase diagram of Osborn and Maun 1960 in (Li et al 1997) showing nepheline (Ne), carnegeite (Car) , albite (Ab) and other phase fields

Current research approach

- Compile existing data for glasses with reported nepheline vol% crystallization and/or PCT response
- Calculate ND and OB for these and test utility of OB criterion
- Examine regions where data is sparse and make new glasses, testing nepheline crystallization and PCT
- Compare ND vs. OB graphs to others based on Al-Na-Si ternary

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Optical basicity as an indicator for nepheline formation in high-level waste glasses

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Procedure

- Made ~70 new glasses, many based on HLW-E-ANa-05 (Matlack et al 2007) and EM09-Li20m-B (McCloy et al 2010), most of which are in Quadrant IV, the region of immediate interest.
- Quantitative XRD on these glasses as well as some SRNL (SB5NEPH, NE3, NP2 series) and VSL (HWI-E-Al, HLW-E-Al series) (~125 total)
- Different data visualization tools (Excel, Sigmaplot, OriginPro) used to investigate data (954 datapoints in crystallization dataset)

Interim results

- OB criterion does predict behavior of glasses where CaO and B_2O_3 are added. The ND vs. OB quadrant system does appear to parse the data in a meaningful way.
- HLW-E-Al-05 glasses precipitate nepheline while EM09-Li20m-B glasses precipitate lithium aluminosilicates (i.e. eucryptite or spodumene).
- OB criterion does not consistently predict the crystallization behavior of glasses in Quadrant IV with the base compositions HLW-E-ANa-05 and EM09-Li20m-B families
- Some other factor must also be involved, so ternaries were also investigated to provide additional insight

Base glass compositions

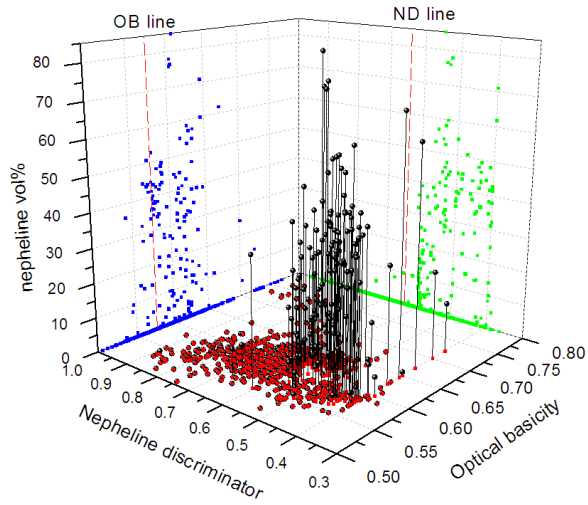
Weight %

Wt% oxides	Em09-Li20m-B	HLW-E-ANa-05
Al_2O_3	27.47	23.61
B_2O_3	9.42	14.41
BaO	0.00	0.03
Bi_2O_3	1.34	1.28
CaO	1.23	0.80
CdO	0.00	0.01
Cr_2O_3	0.60	0.79
F	0.76	0.25
Fe_2O_3	6.76	3.11
K_2O	0.16	0.73
Li_2O	9.14	3.58
MgO	0.13	0.24
Na_2O	4.10	14.06
NiO	0.45	0.11
P_2O_5	1.21	2.24
PbO	0.47	0.10
SO_3	0.00	0.24
SiO_2	36.29	33.89
TiO_2	0.00	0.19
ZnO	0.00	0.20
ZrO_2	0.45	0.14
Total	99.98	100.1
ND	0.474	0.535

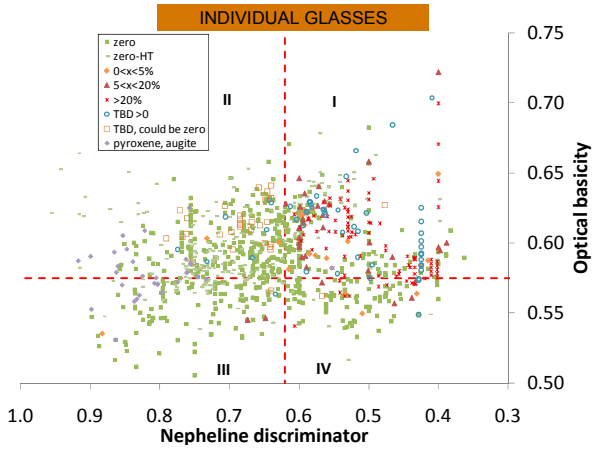
Mol %

Mol% oxides	Em09-Li20m-B	HLW-E-ANa-05
Al_2O_3	17.75	16.039
B_2O_3	8.92	14.30
BaO	0.00	0.01
Bi_2O_3	0.19	0.19
CaO	1.45	0.99
CdO	0.00	0.01
Cr_2O_3	0.26	0.36
F	2.65	0.91
Fe_2O_3	2.79	1.35
K_2O	0.11	0.54
Li_2O	20.16	8.30
MgO	0.22	0.41
Na_2O	4.36	15.70
NiO	0.40	0.10
P_2O_5	0.56	1.09
PbO	0.14	0.03
SO_3	0.00	0.21
SiO_2	39.80	39.04
TiO_2	0.00	0.17
ZnO	0.00	0.17
ZrO_2	0.24	0.08
Total	100.0	100.0
OB	0.571	0.577

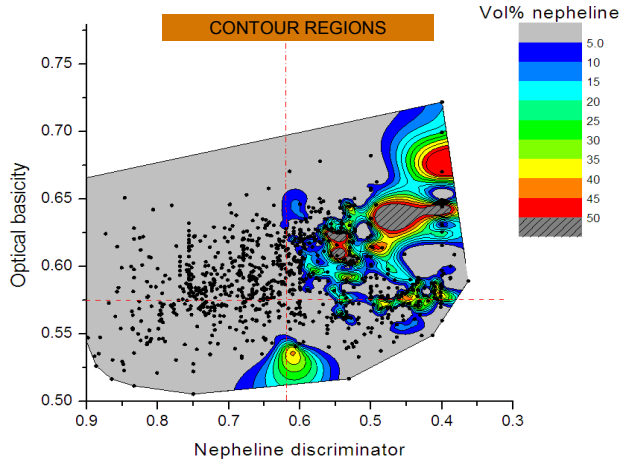
3-D SCATTERPLOT



INDIVIDUAL GLASSES

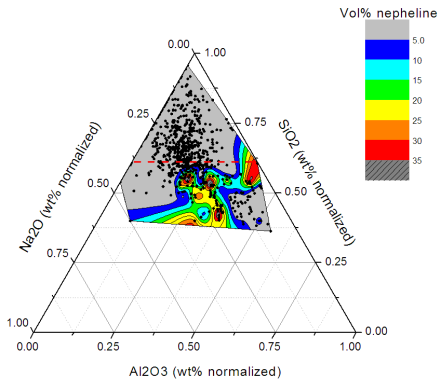


CONTOUR REGIONS

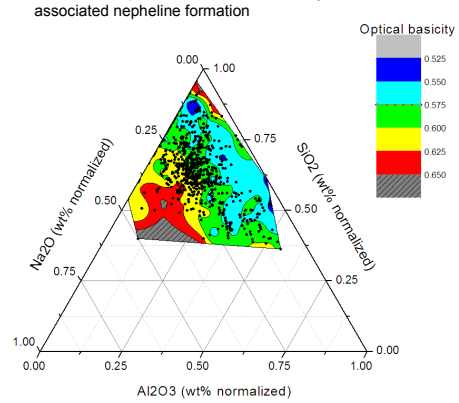


SUMMARY

Al-Na-Si TERNARY PHASE DIAGRAMS

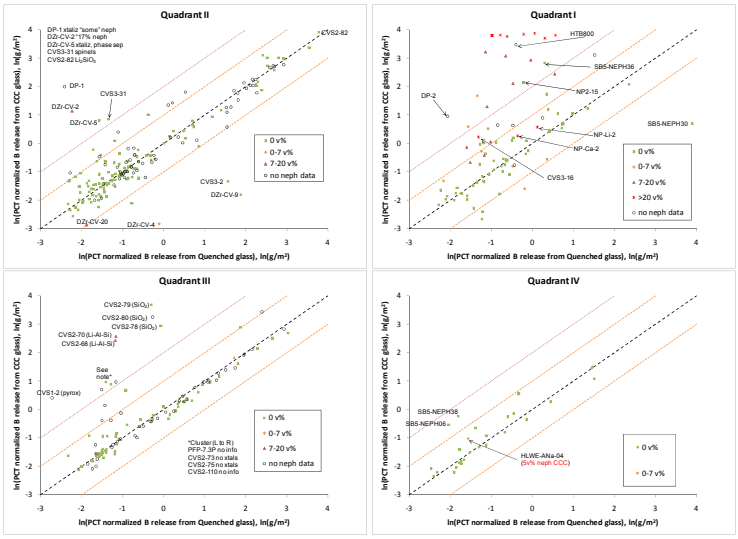


Traditional nepheline discriminator ternary and associated nepheline formation



Variation of optical basicity with composition. Note regions of high basicity in high SiO_2 region due to high basicity components other than Na_2O

CHEMICAL DURABILITY (PCT) BY QUADRANT



Discussion

Large data sets used for analysis

- ~1000 data points in nepheline volume fraction study
- ~400 data points in PCT study

Quadrant system

- In Quadrant I there is a risk of crystallization and poor PCT
- Optical basicity seems to explain effects of additions of CaO and B_2O_3 seen in (Fox et al 2007). CaO substituted for Na_2O on an equimolar basis reduces the susceptibility to nepheline crystallization whereas CaO in addition to Na_2O raises the susceptibility. Higher OB leads to nepheline formation. B_2O_3, on the other hand, is very acidic, so additions lead to less likelihood of nepheline formation.

Composition effects on durability

- PCT(Q vs CCC) and relationship to crystallization pioneered by (Kim et al 1995). Parsing the data by quadrant shows again that glasses in Quadrant I are the most problematic for nepheline crystallization and poor durability.
- Additional glasses from this study (HLW-E-ANa-05 glasses and EM09-Li20m-B glasses) are currently being tested to see if PCT is more predictable with crystallization in Quadrant IV than in Quadrant I

Conclusions

- Inclusion of optical basicity criterion allowed refinement of the composition region of excessive nepheline crystallization and resulting poor chemical durability (Quadrant I)
- Some glasses in Quadrant IV still have excessive crystallization, and the specific nature of these compositions is currently under investigation
- Considering the concept of basicity has allowed an additional means of parsing large datasets to investigate regions for possible high waste-loading, high-Al_2O_3 glasses

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References

1.Tait, K.T., E. Sokolova, and F.C. Hawthorne, "The Crystal Chemistry of Nepheline," *The Canadian Mineralogist, 41, 61-70 (2003).*

2.Li, H., J.D. Vienna, P. Hrma, D.E. Smith, and M.J. Schweiger, "Nepheline precipitation in high-level waste glasses: compositional effects and impact on the waste form acceptability," *Proc. Materials Research Society* 465, 261-268 (1997).

3.Duffy, J.A. and M.D. Ingram, "An interpretation of glass chemistry in terms of the optical basicity concept," *Journal of Non-Crystalline Solids*, 21(3), 373-410 (1976).

4McCloy, J. and J.D. Vienna, "Glass Composition Constraint Recommendations for Use in Life-Cycle Mission Modeling," PNNL-19372, Pacific Northwest National Laboratory, Richland, WA (May 2010).

5Matlack, K.S., H. Gan, W. Gong, I.L. Pegg, C.C. Chapman, and I. Joseph, "High Level Waste Vitrification System Improvements," VSL-07R1010-1, Vitreous State Laboratory, the Catholic University of America, Washington, D.C. (April 16, 2007).

6McCloy, J.S., C. Rodriguez, C. Windisch, C. Leslie, M.J. Schweiger, B.J. Riley, and J.D. Vienna, "Alkali/ Alkaline-Earth Content Effects of Properties of High-Alumina Nuclear Waste Glasses," In *Ceramic Transactions*, Vol. 222, 63-76 (2010).

7Kim, D.S., D.K. Peeler, and P. Hrma, "Effect of Crystallization on the Chemical Durability of Simulated Nuclear Waste Glasses," In *Ceramic Transactions*, Vol. 61, 177-185 (1995).

8Fox, 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," WSRC-STI-2007-00659, Savannah River National Laboratory, Aiken, South Carolina

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