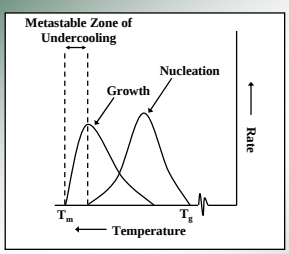
Kinetic Studies of Nepheline Formation in Advanced Silicate Glass Compositions

Amanda L. Billings, Jake W. Amoroso, David K. Peeler, Savannah River National Laboratory, Aiken, SC

Objective

Recent developments in advanced silicate glasses suggest that step function improvements in waste loadings of HLW in glass are possible. One significant advancement is the development of glasses with significantly higher Al content than would be currently allowed by nepheline precipitation constraints. Waste glass compositions are very complex and predicting the thermodynamics and kinetics of crystal precipitation as a function of composition are extremely difficult. The goal of this study is to examine nepheline precipitation as a function of kinetics in waste glasses as for varying compositions in order to refine the current nepheline constraints.

Crystallization Kinetics in Glass



Effect of temperature on the rates of nucleation and crystal growth for a glass forming melt

What controls crystallization in glass?

- Glass composition
  - Initial glass composition
  - Residual glass composition
- Cooling rate (Kinetics)
- Thermal history
  - T_M, T_g and T_L
- Insolubles
  - Noble metals
  - Other crystalline phases

Na_2O-Al_2O_3-SiO_2 Ternary

Nepheline Phase Field

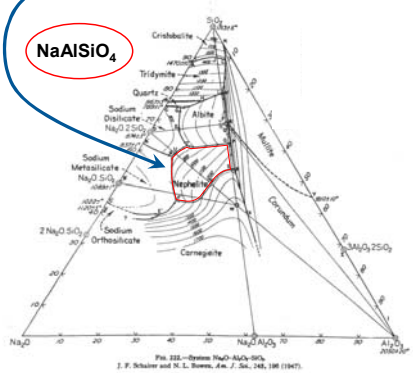
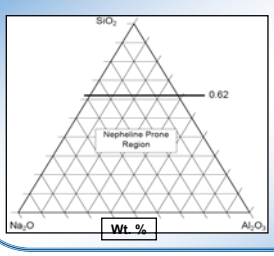


Fig. 332.—System Na_2O-Al_2O_3-SiO_2.
J. F. Schairer and N. L. Bowen, *Am. J. Sci.*, 245, 196 (1947).

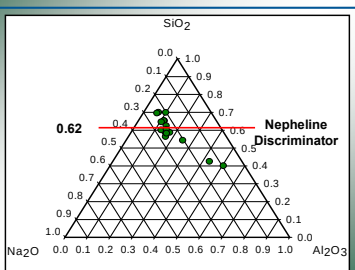
Nepheline Discriminator

$$0.62 < \frac{SiO_2}{Na_2O+Al_2O_3+SiO_2} \text{ (wt \%)}$$



- Discriminator based on the primary phase field used to reduce the tendency to form nepheline upon slow cooling
- Glasses which have a discriminator greater than 0.62 are predicted to not form nepheline
- Appears to be conservatism in the 0.62 value

Selected Glass Compositions



Impacts of Nepheline Formation in HLW Glasses

- Nepheline precipitation in high-level waste glass adversely affects the measured chemical durability and overall waste form performance
  - The precipitation of nepheline depletes the glass network of the stronger glass network formers
    - *Al_2O_3*
    - *SiO_2*
- Durability depends on:
  - Crystal type
    - *Spinel crystals → no impact*
    - *Nepheline → severe impact, depletes glass structure*
  - Crystal amount (wt %)

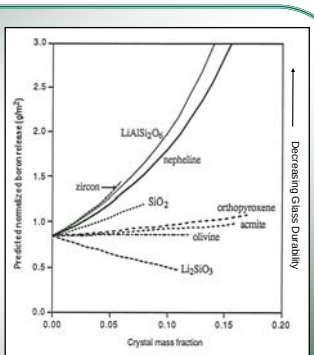


Figure from D. Kim, D. Peeler, and P. Hrma, "Effect of Crystallization on the Chemical Durability of Simulated Nuclear Waste Glasses", Ceramic Transactions, Vol 61, pp. 177 – 185.

Glasses selected for kinetic testing based upon:

- Distribution of nepheline discriminator values
  - Glasses with observed nepheline formation after slow cooling
  - Glasses with no nepheline observed upon slow cooling which were predicted to form nepheline
- Varying ratios of major chemical components
  - Al, Si, B, Na, Li and Fe
- Potential impact to glass durability

We Put Science To Work™
SRNL is managed and operated for the U.S. Department of Energy by Savannah River Nuclear Solutions, LLC

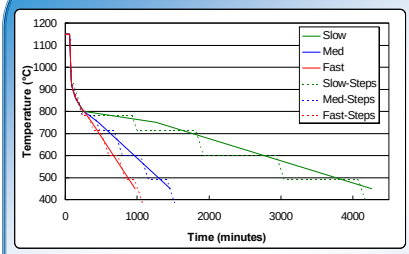
Print

Close

Kinetic Studies of Nepheline Formation in Advanced Silicate Glass Compositions

Amanda L. Billings, Jake W. Amoroso, David K. Peeler, Savannah River National Laboratory, Aiken, SC

Kinetic Impacts Using Cooling Profiles



Method:

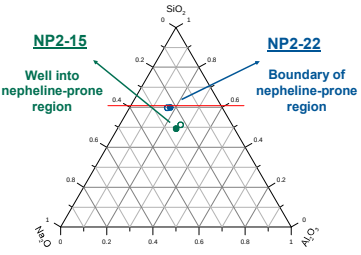
Samples of each glass composition are subjected to 6 different slow cooling profiles

- Held at TM for 1 hour before cooling
- Medium-Step is the same as the current DWPF Centerline Canister Cooling (CCC) profile
- Subjected to step-wise and smooth cooling profiles based on non-rad melter demonstration CCC data
- Samples analysis using SEM and quantitative XRD

Basis:

- Historic T-T-T diagrams → nepheline is not observed until below ~800°C
- Current CCC curve in use → large regions of constant rate during cooling

Selected Results and Observations



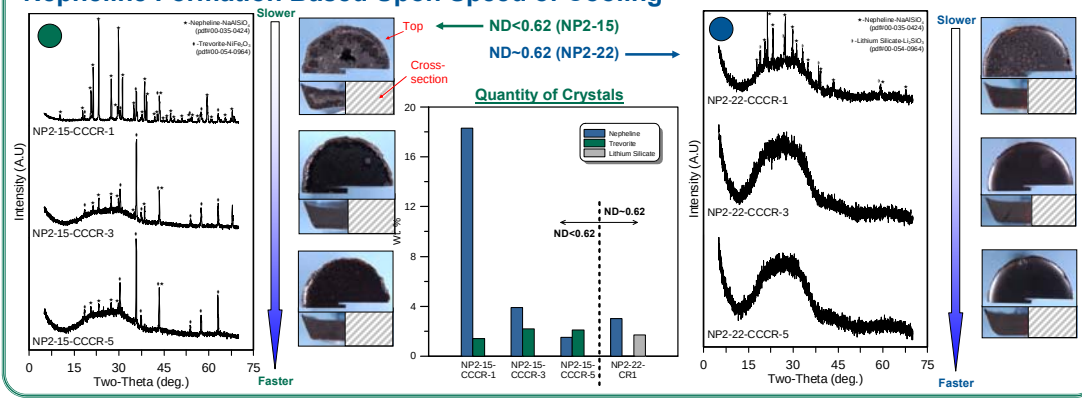
ND<0.62 (NP2-15)

Amount of nepheline increases with slower cooling
Similar amount of trevorite observed in all samples

ND~0.62 (NP2-22)

Nepheline only present in slowest cooled glass

Nepheline Formation Based Upon Speed of Cooling



Effects of Sampling on XRD Results

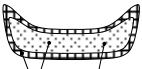
- Cross-section of heat-treated samples reveals an inhomogeneous sample
  - Surface crystallization
    - *Crucible walls and top surface*

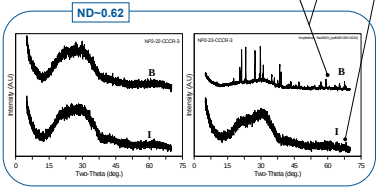
Cross-section of heat-treated sample

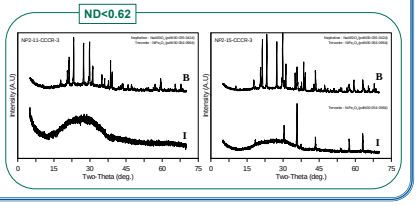
- Bulk glasses are cross-sectioned and a slice of the center is removed and analyzed separate from a section containing both surface and interior material

I = interior section

B = bulk section





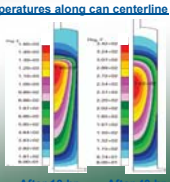


- Nepheline was not detected for glasses with a ND~0.62 or a ND<0.62 for interior sections but detected in the bulk section
- Surface crystallization of nepheline appears to dominate the crystal peaks observed in XRD patterns

Future Work

- Continue to explore the kinetics of nepheline (and other crystalline phase) formation in waste glasses on various compositions using the established cooling profiles and isothermal heat treatments
- Use computer modeling methods to predict projected cooling rates during actual waste processing
- Combine kinetic and compositional effects to explore and use glass compositions that traditionally lie in the nepheline-prone region to achieve higher waste loadings and future waste predictions

Simulated temperatures along can centerline during cooling



We Put Science To Work™

SRNL is managed and operated for the U.S. Department of Energy by Savannah River Nuclear Solutions, LLC

Print

Close