Nepheline Crystallization from Aluminosilicate Melts

- Naturally occurring nepheline: $Na_3K[Al_2Si_2O_{16}]$. Carnegieite ($Na[AlSiO_4]$) is its higher T variation
- Crystallization of nepheline is prone to occur during the slow cooling (CCC) of certain Al/Na-rich silicate melts
- Formation of nepheline can be deleterious to glass product quality (increased leach rate)
- Consequently, nepheleine formation can limit waste loadings and increase glass volumes
- In view of the large volume of high-Al HLW, there is a significant driver for the development of improved methods for nepheline control

Formulation Considerations Include:

- Crystallization
- Durability
- Processability
- Melt Rate
- Materials Corrosion

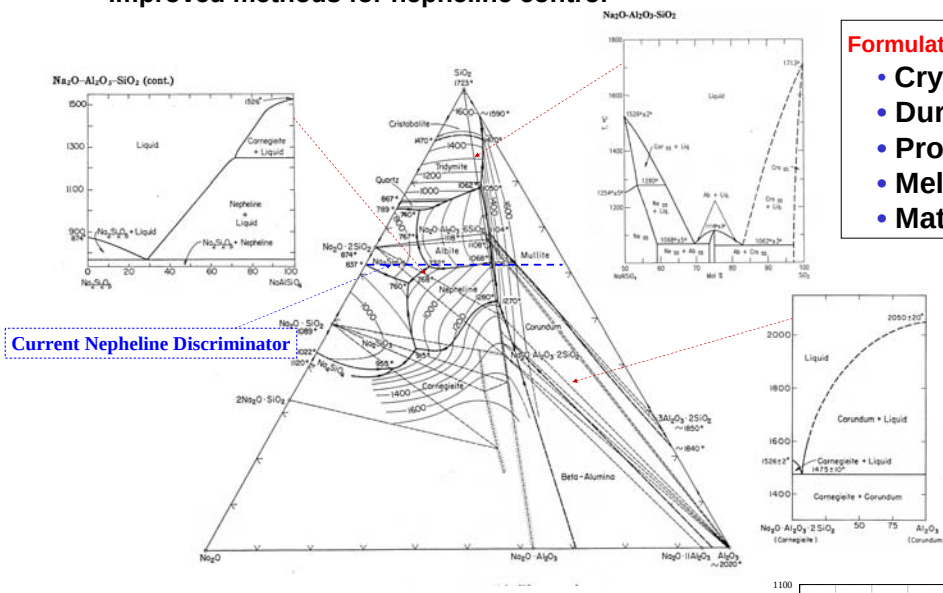

Figure 1. Phase Diagrams of Na_2O-Al_2O_3-SiO_2 [1]

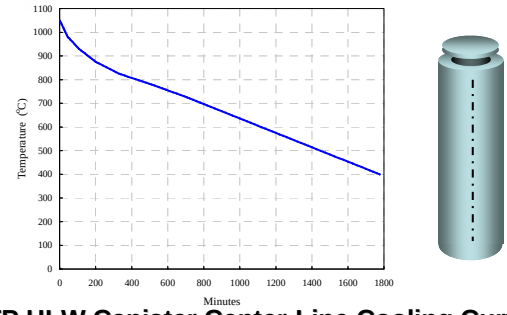

Figure 2. WTP HLW Canister Center-Line Cooling Curve (CCC)

Al-limited and Al/Na-limited Hanford HLW

Waste Component	Al Limited Waste	Al and Na Limited Waste
Al_2O_3	49.21%	43.30%
B_2O_3	0.39%	0.74%
CaO	2.21%	1.47%
Fe_2O_3	12.11%	5.71%
Li_2O	0.35%	0.15%
MgO	0.24%	0.44%
Na_2O	7.35%	25.79%
SiO_2	10.05%	6.22%
TiO_2	0.02%	0.35%
ZnO	0.17%	0.36%
ZrO_2	0.81%	0.25%
SO_3	0.41%	0.44%
Bi_2O_3	2.35%	2.35%
ThO_2	0.37%	0.04%
Cr_2O_3	1.07%	1.44%
K_2O	0.29%	1.34%
U_3O_8	7.25%	4.58%
BaO	0.11%	0.06%
CdO	0.05%	0.02%
NiO	0.82%	0.20%
PbO	0.84%	0.18%
P_2O_5	2.16%	4.10%
F-	1.37%	0.46%
Total	100.00%	100.00%

Reference [2]

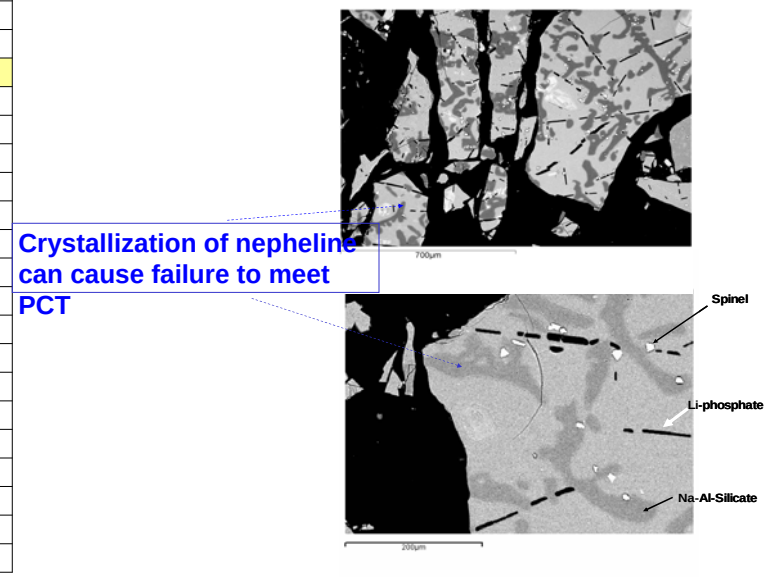

Figure 3. Crystallization *during canister cooling* is principal waste loading limiting factor

Print

Close

Nepheline Formation in Al-rich HLW Glass and Potential Formulation Constraints

Hao Gan and Ian L. Pegg

Vitreous State Laboratory, The Catholic University of America, Washington, D.C.

Prediction of Nepheline Crystallization: Nepheline Discriminator

Current Nepheline Discriminator, *D* ([3]):

$$D = \frac{SiO_2}{(SiO_2 + Al_2O_3 + Na_2O)} > 0.62$$

- Applicability appears limited to high-Si region (lower waste loading)
- Ignores the influence of non-nepheline glass components (e.g., B_2O_3) and Al coordination
- Many exceptions (especially, low SiO_2 glasses)

Consequences for Waste Loading

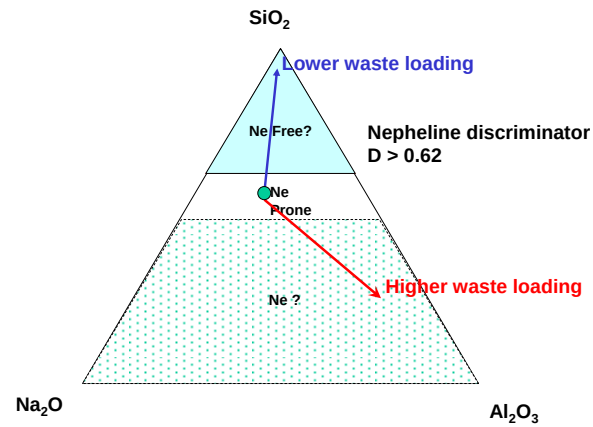

Figure 4. Schematic diagram of Na_2O-Al_2O_3-SiO_2 and glass formulation region

High-Al Glass Formulation: Silica Content

- Traditional HLW glasses have maintained relatively high silica contents of > ~40 - 55 wt%: US (DWPF, WVDP, HWVP CVS), France, UK, Germany/Belgium, Japan
- VSL pioneered low-silica waste glasses for low-level and mixed waste vitrification in the early 1990s: Weldon Spring (1992), Fernald (1993), TWRS HLW glasses (1997) and later to WTP glasses
- Unnecessarily high silica levels have several disadvantages: Silica takes up "space" and therefore restricts waste loadings. For high Al wastes, high silica tends to promote nepheline formation

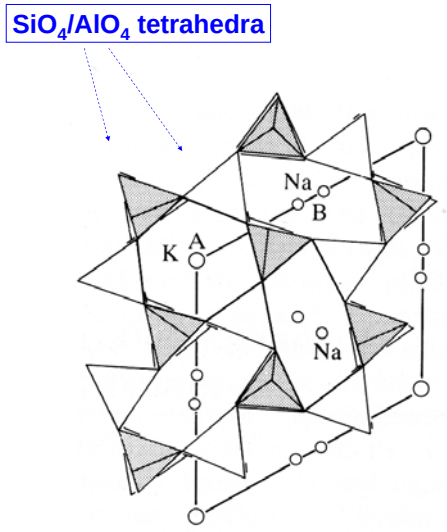

Figure 5. Crystal structure of nepheline viewed along z; A, hexagonal site; B, oval site [4]

Sub-Lattice Model of Nepheline Crystallization from High-Al Melts

Development of An Improved Nepheline Discrimator, Neph-D, for High-Al, Low-Si HLW Glass

- Mixing of major glass components in their disparate sub-lattices of distinctive structure
- Mixing of tetrahedral Si(IV), Al(IV), and B are considered within one sub-lattice (molar basis with Na and K as charge-balancing cations)
- Mixing of Si(IV), Al(IV) and probably B are approximately random involving little heat of mixing [5]

$$Neph - D = \frac{Si(IV)Al(IV)}{(Si(IV) + Al(IV) + B)^2}$$

High Al HLW Glass Formulation and Prediction of Nepheline Crystallization During CCC

Glass Composition Ranges

Oxides	Mean (wt%)	Minimum (wt%)	Maximum (wt%)
Al_2O_3	11.65	1.93	33.09
B_2O_3	9.42	0.00	22.45
CaO	2.56	0.00	18.20
Fe_2O_3	7.15	0.19	14.02
K_2O	0.61	0.00	6.00
Li_2O	3.36	0.00	8.00
MgO	1.11	0.00	2.99
Na_2O	15.00	4.80	22.04
SiO_2	41.74	25.44	50.10
ZrO_2	1.61	0.00	9.54

Data Sources:

105 VSL glasses

40 SRNL glasses

26 PNNL glasses

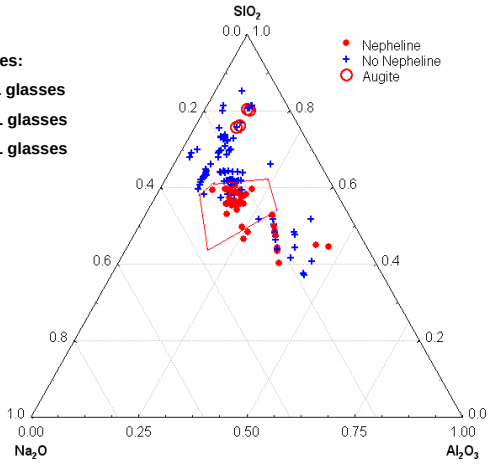

Figure 6. Crystallization on CCC for Various HLW Glasses

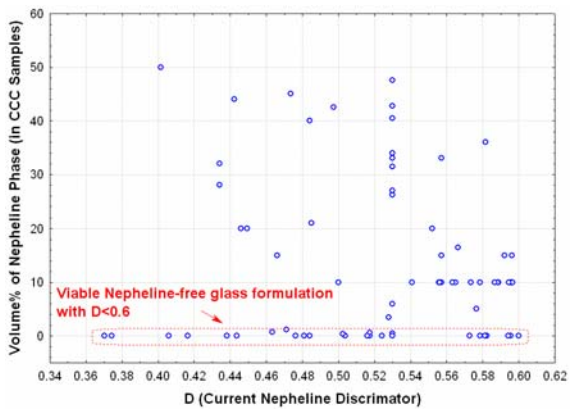

Figure 7. Crystallization of nepheline vs. Current Discriminator for samples with D<=0.6

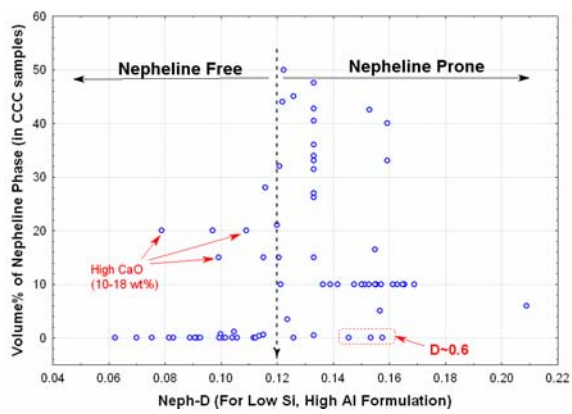

Figure 8. Crystallization of nepheline vs. the proposed discriminator *Neph-D* for low-Si, high-Al glasses (D<=0.6

Summary

- Nepheline formation during CCC and its impact on PCT can limit waste loadings for high-Al HLW glass
- Formation of nepheline depends strongly on glass composition. The current nepheline discriminator (*D*) is conservative and rejects otherwise acceptable high waste loading formulations, especially those with low SiO_2
- A complementary nepheline discriminator *Neph-D* is proposed for high-Al_2O_3 and low-SiO_2 formulations. Based on the data set analyzed, *Neph-D* appears to work effectively for glasses with D<0.62 and low CaO
- Results suggest a less conservative tiered approach that employs both discriminators:
  - Accept IF D>=0.62 OR Neph-D <=0.12 AND CaO is low (< ~5 wt%)
- Additional work is in progress to further test and refine this approach

References

[1] Phase Diagrams for Ceramists; [2] VSL Final Report (VSL-07R1010-1); [3] Li, et. al. (1997), Mat. Res. Soc. Proc., Vol. 465; [4] Deer, Howie and Zussman (1992), Rock-Forming Minerals; [5] A. Navrotsky (1986), Thermodynamics of Silicate Melts and Glasses in Mineralogical Association of

Print Close