Flinabe Melting Experiment - Preliminary Report

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Other Contributors:

INEL: Flibe preparation, discussions, data

SNL Contributors:

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Tina Tanaka: equipment, planning, sample prep, analysis
Ken Troncosa: equipment, sample prep
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Flibe (LiF+BeF₂) - coolant/breeder for molten salt (fission) reactors.

- LiF-BeF₂ ($T_{\text{melt}}$ of 363°C) has is viscous.
- 2LiF-BeF₂ has lower viscosity but melts at 460°C.

- ORNL and Russian data (50’s/60’s) show a useful eutectic at ~290°C (Toropov) but also some disparity in mixtures and temperatures.

- In APEX, Rognlien (LLNL) found a $T_{\text{surface}}$ limit of ~500-530°C for flowing Flibe first walls due to F (impurity) in a detached plasma.
- APEX developed a chamber design with a flowing Flinabe wall. We assumed Flinabe with a cold leg temperature of 312°C.

- INEEL has capability to produce Flinabe but work was not funded.
- Sandia recently initiated small scale tests to melt Flinabe mixtures.
Ternary Phase Diagrams - Background

**Fig. 1542.**—System LiF–NaF–BeF₂.


**Fig. XII.**—Perspective drawing of a space model of a ternary system with a simple eutectic and no ternary compound.

Modified from R. Vogel, Die heterogenen Gleichgewichte, in G. Masing, Handbuch der Metallphysik, Vol. II, Fig. 266, p. 370, 1937.

*Figures from Phase Diagrams for Ceramists by Levin, Robbins & McMurdie, ed. Reser, ACS 1964*
We are investigating three mixtures:

1. 0.33 BeF2 – 0.33 NaF – 0.33 LiF (240°C typo, 400-420°C?)
2. 0.37 BeF2 – 0.32 NaF – 0.31 LiF (315-340°C?)
3. 0.33 BeF2 – 0.43 NaF – 0.24 LiF (320<Tm<480°C?)

Composition related engineering issues:

- More BeF2 - higher viscosity, lower T_m.
- Less LiF - less breeding potential, lower Tm.
- LiF-NaF is simpler (fewer phases) than NaF-BeF2 & LiF-BeF2.
LiF–NaF

Fig. 1467.—System LiF–NaF.

LiF–BeF₂

Fig. 1469.—System LiF–BeF₂.

NaF–BeF₂

Fig. 1482.—System NaF–BeF₂.
See also Erich Thilo and Hansjürgen Schröder, Z. physik. chem., 197, 41 (1951).

Materials - Flikbe?

• Are other materials useful?
• KF has a lower $T_{\text{eutectic}}$ than NaF.

Fig. 1467.—System LiF–NaF.
Flinabe Literature

FIG. 1542.—System LiF–NaF–BeF$_2$.


FIG. 1543.—System Li$_2$BeF$_4$–Na$_2$BeF$_4$.


Note: the Toropov diagram below is “left-handed” compared with blue horizontal line on Moore diagram at the left.
Plot by Ulrickson showing positions of liquidus surfaces extracted from diagrams of Moore and Toropov. Discrepancy for lowest temperature for melting/freezing is ~290°C (Toropov) versus ~350°C (Moore) for location indicated in the Na$_2$BeF$_4$-LiBe$_2$F$_4$ system.
Flinabe Melting Experiment - Procedure

Materials: LiF (99.98%), BeF₂ (98.95%), NaF (99%)

- We granulated/mixed dehydrated salts by weight. We received buttons of Flibe from INEEL.
- Hood surfaces were cleaned and swiped for Be.
- Premixed salts and Flibe were placed in the crucible inside a chemical hood. During pouring, mixing and transport, we used gloves and a mask.
- We heated the salt mixture in a SS crucible originally made for studying the emissivities of liquid metals.
Flinabe Melting Experiment - Layout

- TC2 135°
- TC1 0°
- TC3 225° (not shown)
- melt cavity
- heater cavity
- crucible model
- manipulator arm
- probe
- heater
- insulator
- viewport
- 6° 6 way X
- viewport
- base
- ion gage
- roughing pump exhaust ducted to hood
- pumping station (turbo + roughing pump)
- camera
Flinabe Melting Experiment - Layout

• Exhaust and PRI were vented to hood.
• RGA to indicate outgassing species.
• Controlled leak to estimate pump speed.
Flinabe Melting Apparatus

Jim McDonald observes video monitor during Flinabe melt experiment.

Tom Lutz sets heater control on PC and monitors TC data.
Results - Flinabe Mix #2

• We observed melting and freezing. 
  data: 2 videos, 4 TCs, P, RGA spectra

• The “freezing plateau” for Flinabe mix #2 suggests a composition close to a eutectic mixture.
Results - Flinabe Mix #3

$T_{pool}$ decreased as freezing progressed.

Example: change in temperature & composition on freezing path.

a. liquid cools
b. initial solids form; composition adjusts along liquidus surface
c. path proceeds along valley of liquidus surface.

Observations:
- “Cloudiness” at ~350°C shows onset of solidification.
- High $dT/dt$ at 350-318°C implies a steeper liquidus and then low $dT/dt$ (valley?) at 318-296°C if solids have same heat of fusion.
More on Flinabe #3

Freezing path is consistent with ternary phase diagram.

- 350°C isotherm
- Example composition with primary and secondary legs in solidification paths
Other Observations

We found HF, F & H₂O as the melt outgassed.
We expect the following:
• adsorbed H₂O, esp. in granulated salts
• F & HF from the purification process
• F & HF from water reactions with salts.

• With outgassing complete (>350-400°C), the fluid became clear and the meniscus shape changed.

• At ~360°C, mix #3 was watery and clear but became grease-like at ~320°C
Flinabe Melting - Thermal Model

3D thermal model (PATRAN/ABAQUS)
- half of crucible and melt pool
- Radiation from top, upper inside, outside, bottom and (for cooling) from surface above heater.

heating timelines
- At Z=2.03 heat penetrates up from bottom.
- At Z=3.13 heat penetrates in from sides.
Flinabe Freezing Thermal Model

Timelines during freezing:

- At $Z=3.13$ (top), plot shows cooling with contracting isothermal region from before 5887 to 7586s as pool freezes outside to inside.

- At $Z=2.03$ (bottom), solidification is more rapid near bottom of crucible. Isothermal region occurs only for one timeline.

*Time bracket did not catch solidification before 5887 timeline.*
Flinabe “TC” Histories - Thermal Model

Initial results with two values of $H_{\text{melt}}$ and $k$

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<th>$H_{\text{melt}}$</th>
<th>$k$</th>
<th>time</th>
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<tr>
<td>486</td>
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<td>1250</td>
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<td>2200</td>
</tr>
<tr>
<td>1000</td>
<td>0.200</td>
<td>1950</td>
</tr>
</tbody>
</table>

• Result (plateau time) is consistent with 486 J/g value of $H_{\text{melt}}$ reported for Flibe but not conclusive.

• “Plateau time” for mix #2 was ~800-1200s.
Flinabe Melting Experiment - Closing Remarks

A Flinabe mixture with a low melting temperature is confirmed.

- Mixture #2 has a clear “freezing plateau” at ~305°C.
- Mixture #3 shows progressive solidification from ~360° to 296°C.
- In outgassing, we see evolution of significant HF along with water.
- The volume change on melting/freezing is ~25% for these salts.
- The miniscus shape changes when water has finally been purged.

- We will measure Mix #3, repeat Mix #1 and try a mixture with KF.
- We have expertise at Sandia in salts and salt chemistry and can investigate this ternary phase system with summer students.
- These salts were developed for fission reactors. Maybe there are also other mixtures of interest (e.g., potassium salts?).