FLiBe Electrochemistry and Materials Corrosion Research at UW-Madison

Thomas Chrobak, Karl Britsch, Dr. Guoping Cao, Dr. Kumar Sridharan, Dr. Mark Anderson

Tritium Workshop, Salt Lake City, UT

10/27/2015

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison

Outline

- Introduction to $LiF\text{-}BeF_2$ (FLiBe)
  - Fluoride Salt Chemistry
  - Molten Salt Corrosion
- Electrochemistry Studies on Fluoride Salts
  - FLiBe Redox Measurements
- Static Corrosion Test
  - Experimental design and materials
- FLiBe Natural Circulation Flow Loop
  - Flow-assisted corrosion testing in FLiBe convection loop

Research Questions to be answered

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison

- Will a 0.3V difference in the **redox potential** of FLiBe salt cause a significant **increase in corrosion behavior**?
  - (-1.71V) As-purified vs. (-1.41V) Be-reduced
- Does the presence of **graphite** in the salt facilitate **corrosion**?
  - Liner vs. without liner
- What is the effect of **flow** on **corrosion?**
- Is there a significant difference in **corrosion behavior** of samples in the **cold or hot leg** of a natural circulation flow loop?
- What is the **compatibility** of new selected **materials**?

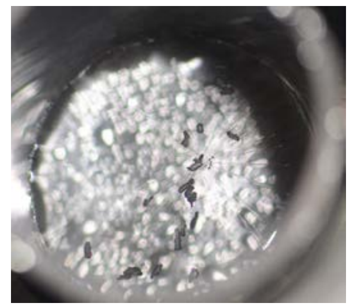
More Research Questions for Consideration

Department of Engineering Physics
College of Engineering — University of Wisconsin-Madison

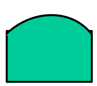
- What is the **optimum amount of Be** that should be added to FLiBe?
  - Balance between over and under-reduction → smallest quantity possible sequentially added

Stoichiometric vs. Excess ?






- Does the **over-abundance of Be metal** in the salt cause enhanced **corrosion** to **carbon-containing parts**?
  - Possible formation of a BeC passivation layer that can keep salt redox low while protecting C from further corrosion?
  - Increased wetting of glassy carbon crucible following Be reduction
    - Convex surface before reduction vs. concave surface after reduction.




Why Use FLiBe as Liquid Salt Coolant?

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison

- Higher outlet temperatures lead to:
  - More valuable process heat applications
  - Greater cycle efficiencies→ $\eta_{Carnot} = 1 - \frac{T_C}{T_H}$

	Operating Temperature [°C]	Operating Pressure [MPa]	Thermal Conductivity [W/m-K]	Volumetric Heat Capacity [kJ/m^3-K]	Viscosity [Pa-s]
Water	300	**15**	0.55	3970	8.8×10^{-5}
Helium	850	7.5	0.29	**20.9**	4.2×10^{-5}
Sodium	550	Atmospheric	**62**	1008	2.3×10^{-4}
Lead	550	Atmospheric	18.25	1499	1.67×10^{-3}
FLiBe	650	Atmospheric	1.0	**4683**	5.6×10^{-3}

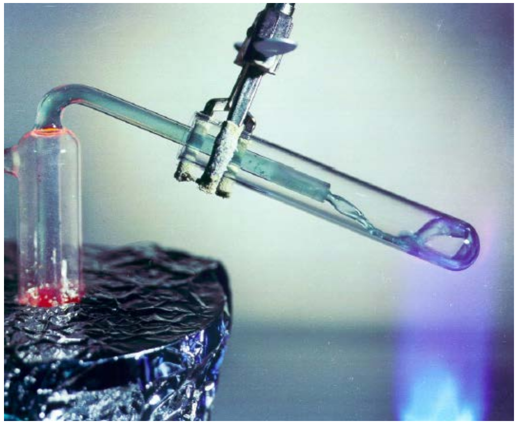
- No ideal heat transfer fluid exists
- Molten fluoride salts offers a good compromise of properties

Properties of FLiBe meet most requirements for FHR Salt

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison

- Molten Salt Primary Coolant Requirements
  1. ✓ Exhibit chemical stability at T > 800 °C
  2. ✓ Stable in an intense radiation field
  3. ✓ Consist of low thermal cross section elements
  4. ✓ Melt at useful temperature (<500 °C) without being volatile
  5. ? Compatible with high-temperature alloys and graphite

MSRE Salt. Blue tint from dissolved UF_4

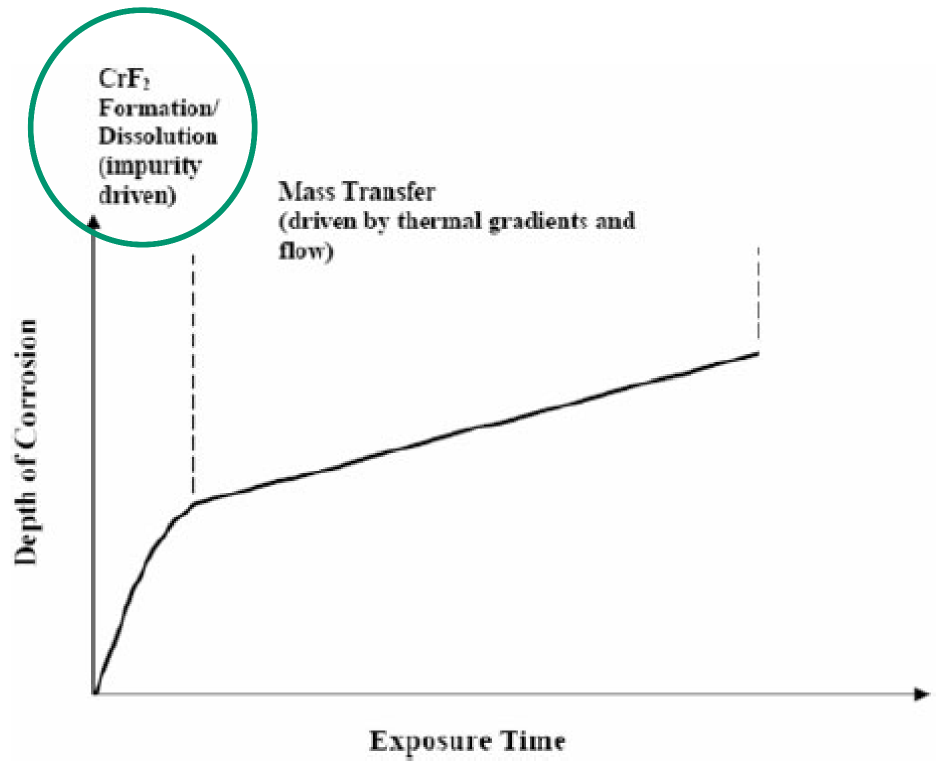


- $LiF\text{-}BeF_2$ – FLiBe as primary coolant
  - + Atmospheric pressure operation
  - + Good heat transfer properties
  - + Neutron transparent
  - + Wealth of MSRE experience
  - − Tritium production from ^{6}Li
  - − Beryllium toxicity
  - − **Corrosive without chemistry control or proper materials**

Isotope	F	Be	Li-7	B-11	Zr	Rb	Na
Thermal Cross Section	0.009	0.010	0.033	0.05	0.18	0.37	0.53

Overall Corrosion Process

- Impurity-driven corrosion dominates initial phase
- Thermodynamically-driven leads to continuous corrosion

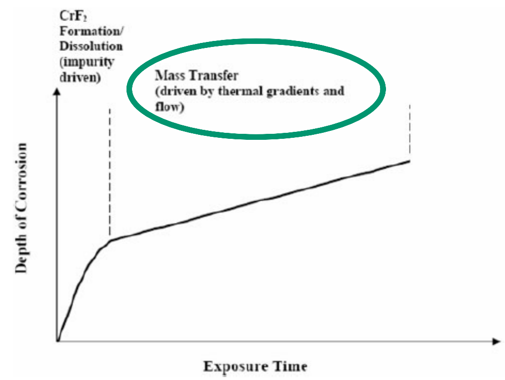


Possible Corrosion Solutions

- Minimize thermal gradients?
- Use high Ni, low Cr Alloys?
- ➢ Implement chemistry control of salt with **redox potential measurement** to maintain high salt quality

Thermodynamically Driven Corrosion

- Non-favorable reactions slowly occurring
- Assisted by a temperature gradient and mass flow

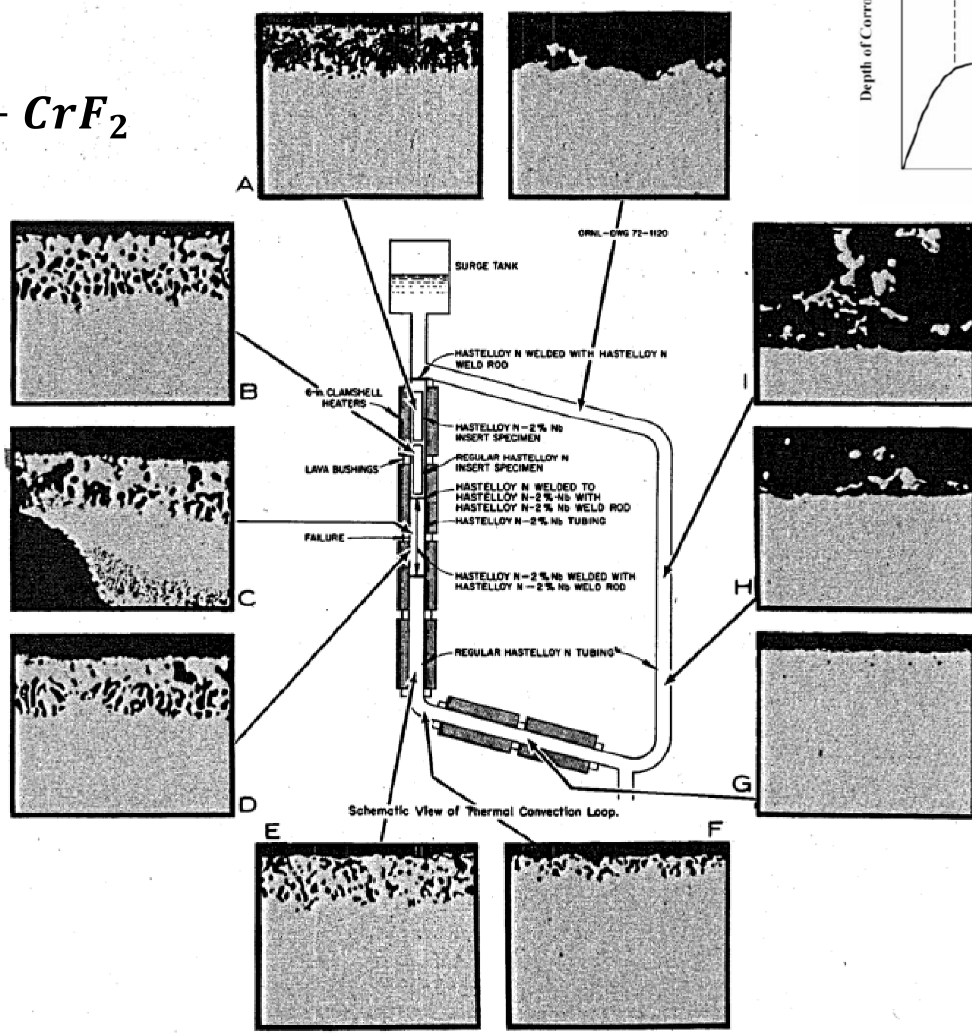


$$BeF_2 + Cr \leftrightarrow Be + CrF_2$$

$$K_{eq} = \frac{[Be][CrF_2]}{[BeF_2][Cr]}$$

K_{eq} = 8.66 x 10^{-13}

at 700 °C



K_{eq} = 2.76 x 10^{-14}

at 600 °C

Impurity Driven Corrosion

- Thermodynamically favorable reactions due to unstable impurities
- Occurs quickly in initial corrosion stages

Metal Fluoride Impurity Reactions

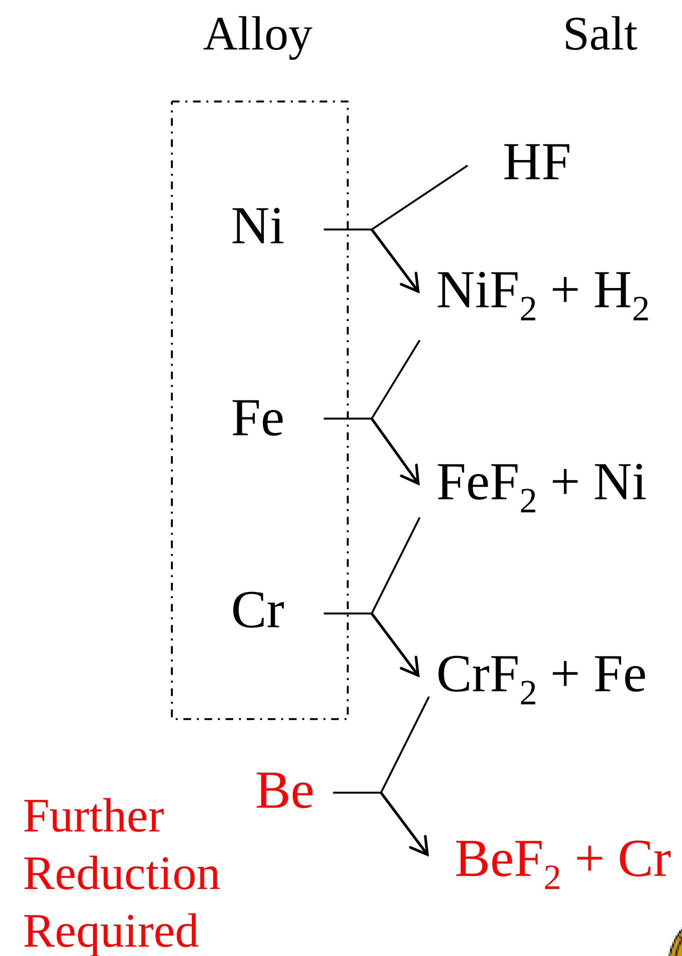
$$\boldsymbol{M_{alloy}(s) + M_{imp}F_x(d) \rightarrow M_{alloy}F_y(d) + M_{imp}(s)}$$

Moisture Impurity Reactions

$$\boldsymbol{\frac{x}{2}H_2O + M_{salt}F_x \rightarrow M_{salt}O_{\frac{x}{2}} + xHF}$$

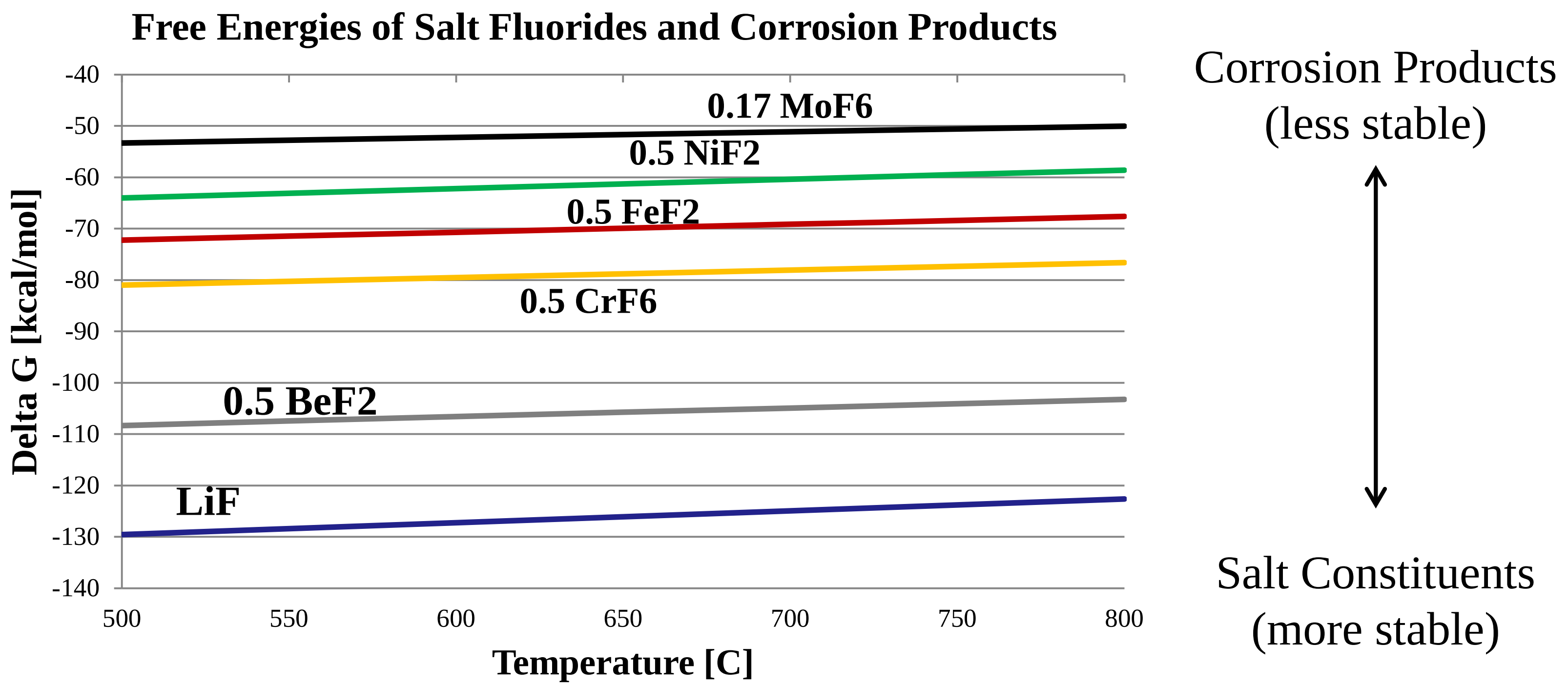
$$\boldsymbol{xH_2O + M_{salt}F_x \rightarrow M_{salt}(OH)_x + xHF}$$

$$\boldsymbol{M_{alloy}(s) + xHF \rightarrow M_{alloy}F_x(d) + H_2}$$



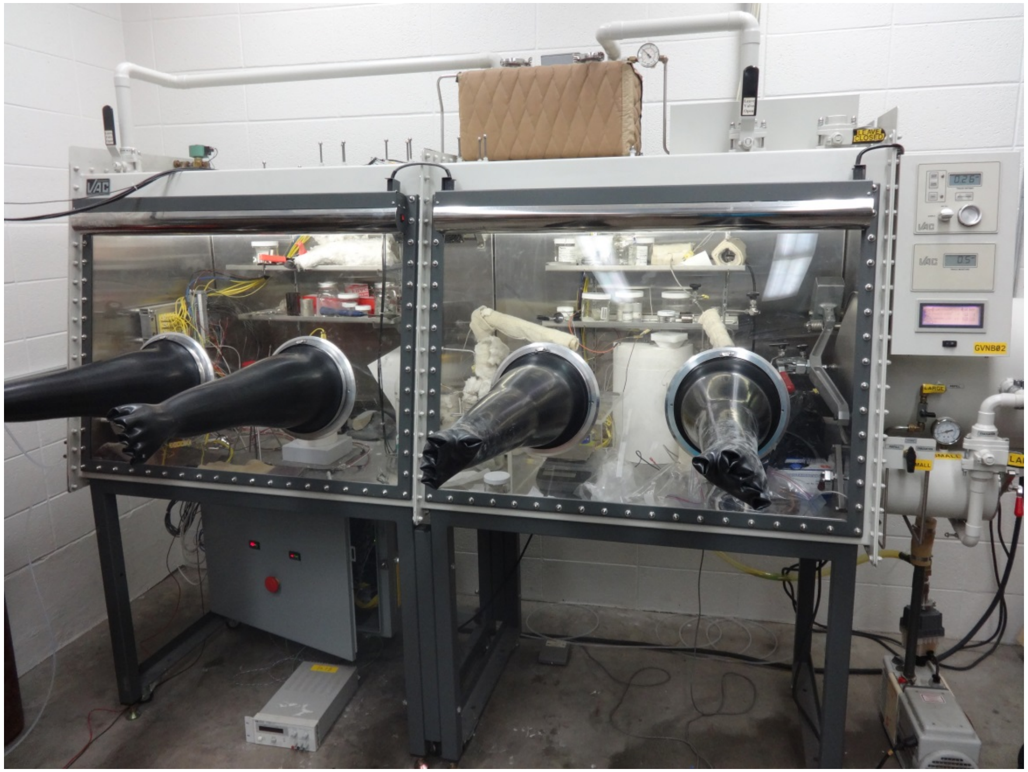
Fluoride Salt Corrosion Mechanisms

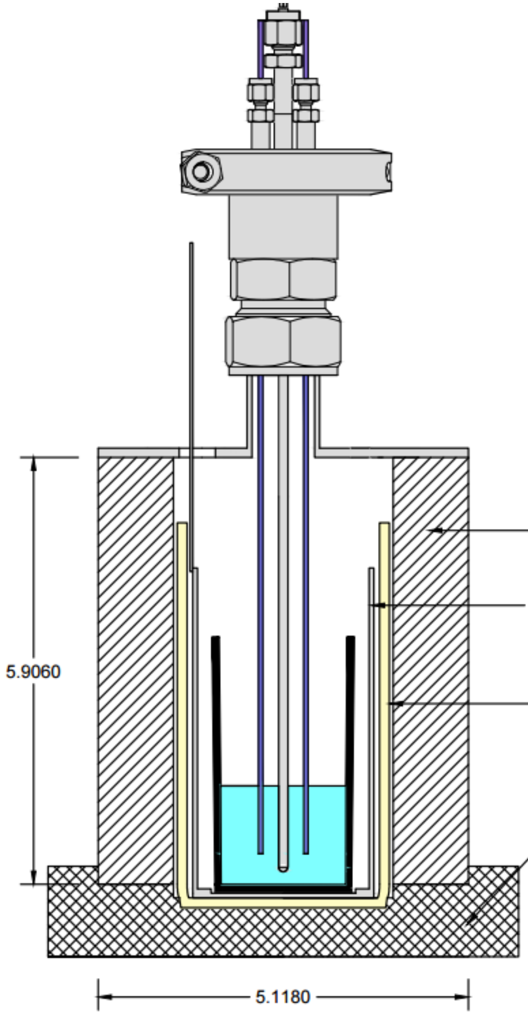
DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison



- Salt constituents are more stable than metal fluorides
- Almost no corrosion expected from pure FLiBe
- How can we ensure purity of FLiBe? → Redox potential

Experimental facilities for electrochemical testing of FLiBe





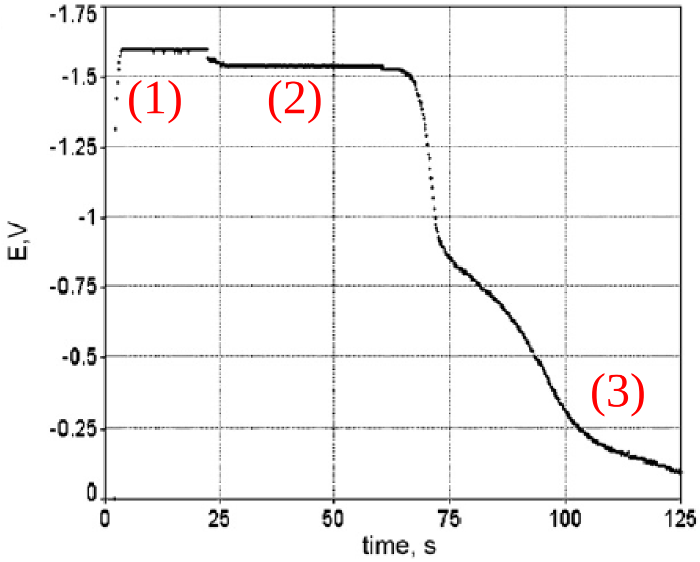
- HP 3616A Power Supply
- Ar glovebox. O_2 and Moisture <1 ppm
- Radiant heater, PID used to maintain 500±0.5°C

Dynamic reference probe design for compact redox potential testing of FLiBe

- O-Ring
- BN Spacer
- Glassy Carbon Anode
- Mo Cathode
- Mo Indicator
- Mo TC well
- K-Type TC

Dynamic Reference Electrode Measurements

- Combination of Dynamic and Static Techniques



(Afonichkin, 2009)

First Phase

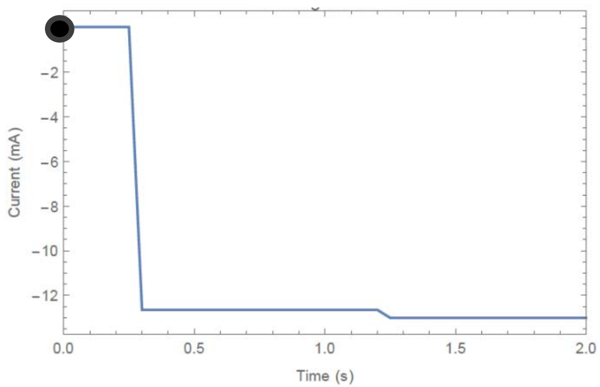
- Beryllium is plated from the salt onto an electrode (1)

Second Phase

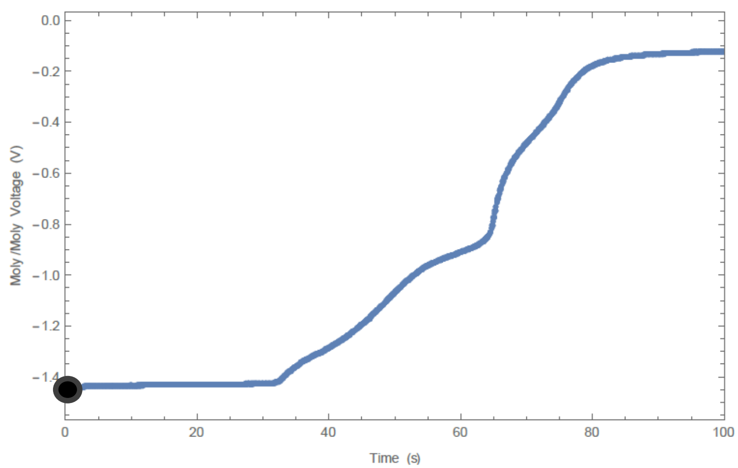
- Voltage is cut, beryllium allowed to redissolve back into the salt
- Be|BeF_2 reference voltage is formed from dissolution reaction (2)
- As plated products deplete, voltage relaxes back to zero (3)

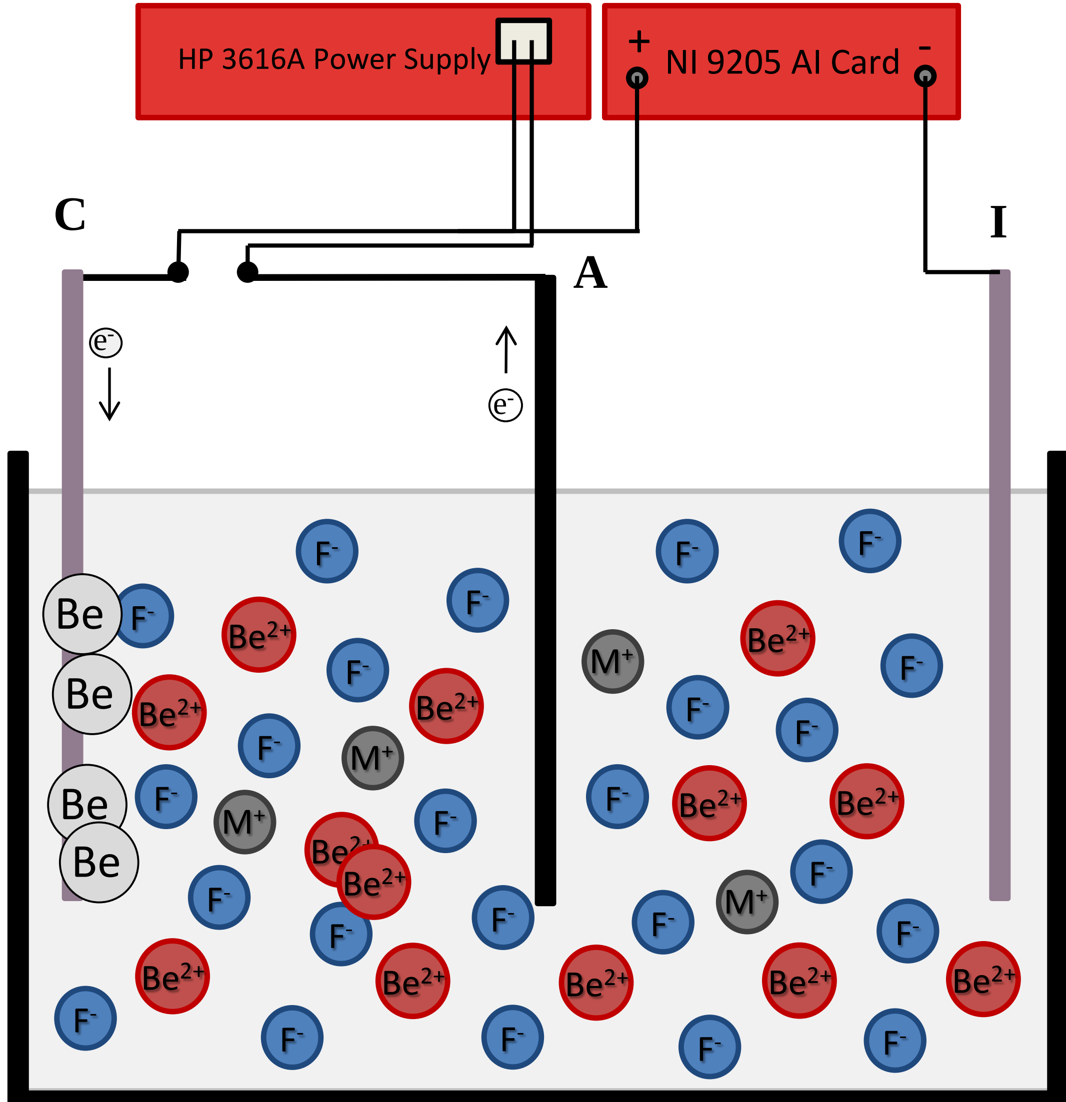
Redox Probe Measurement Process

Phase I: Plating



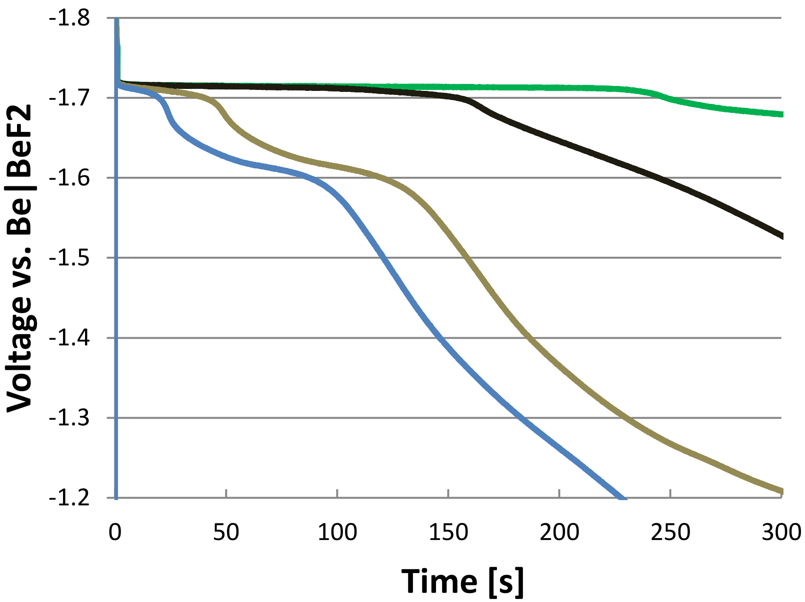
Phase II: Voltage Measurement

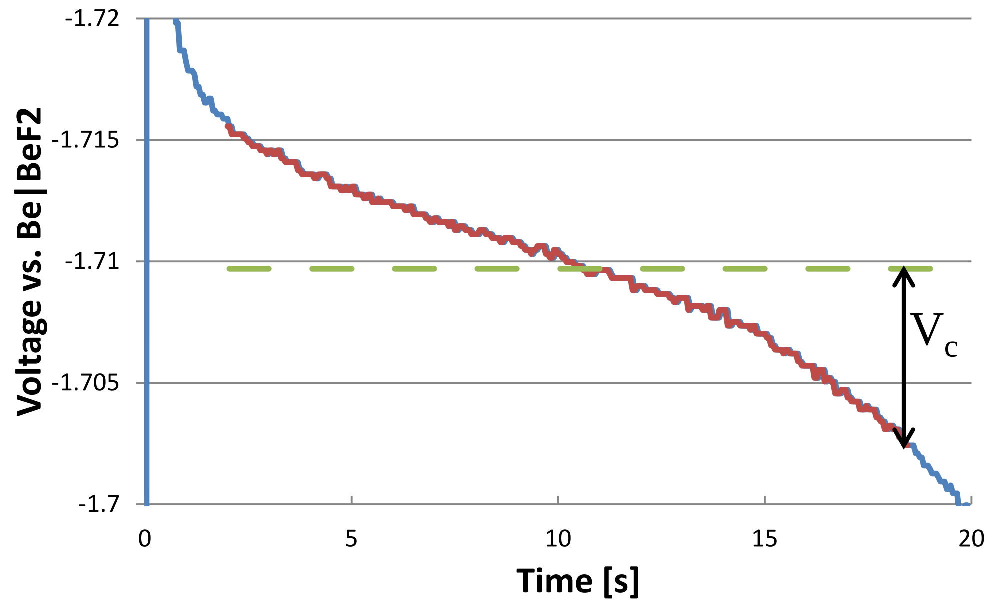




Plateau voltage of Be dissolution indicates redox potential of FLiBe

DEPARTMENT OF
Engineering Physics
College of Engineering University of Wisconsin-Madison





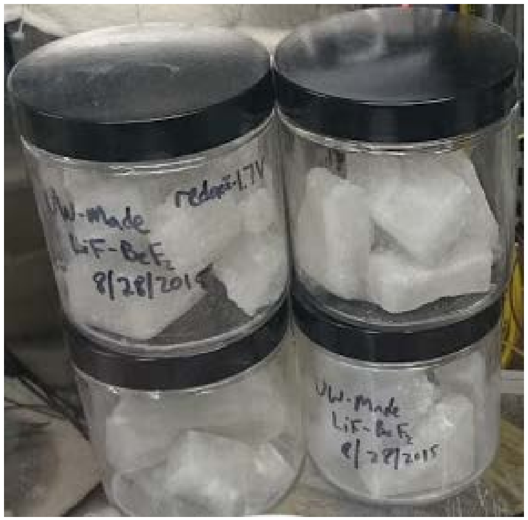
Procedure:
- Start after plating time + 1 second
- (current point – moving average) < V_c?
  - If true, move on to next point, update average

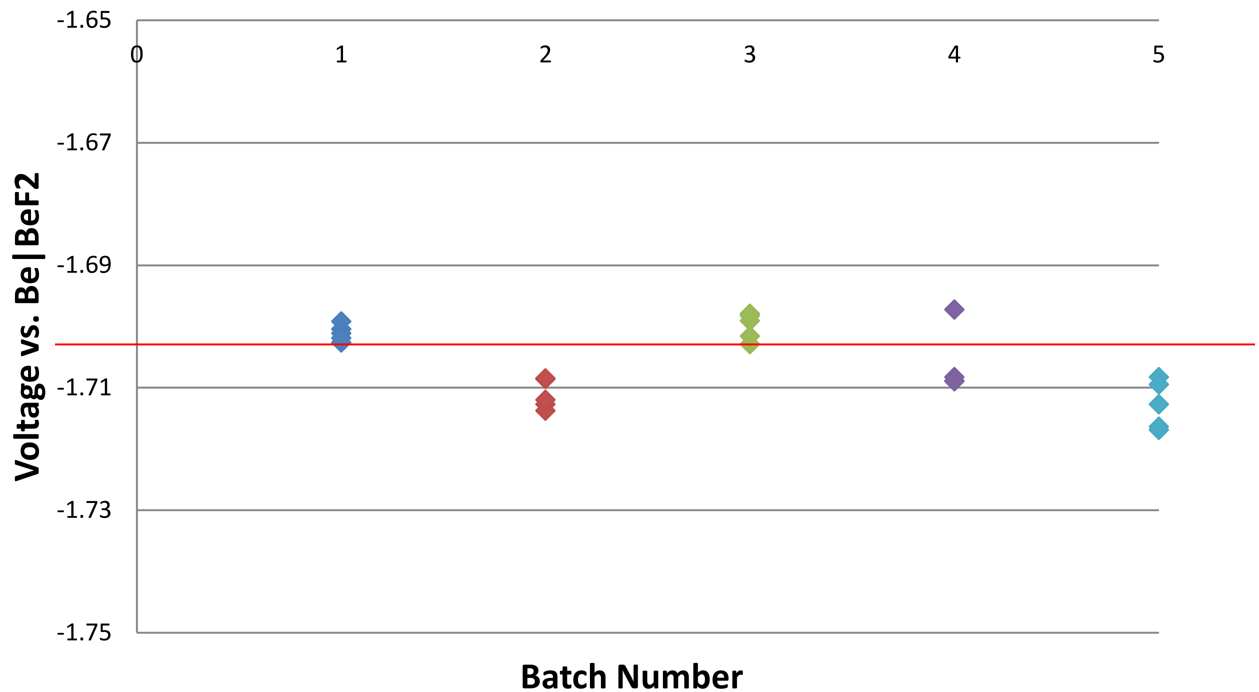
Blue: Original data
Red: Plateau data points
Green: Average of red points
-Used as Redox Voltage

- Points collected and averaged until end point exceeds a set cutoff voltage, V_c.

Redox potential testing of purified, unreduced UW-made FLiBe

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison

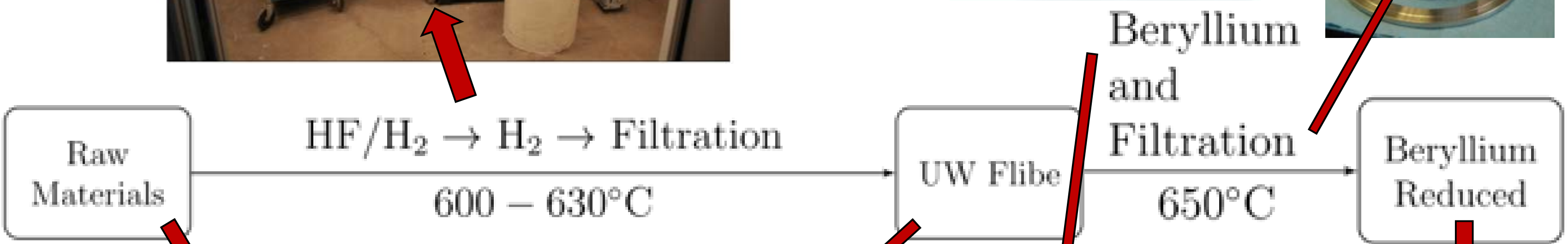


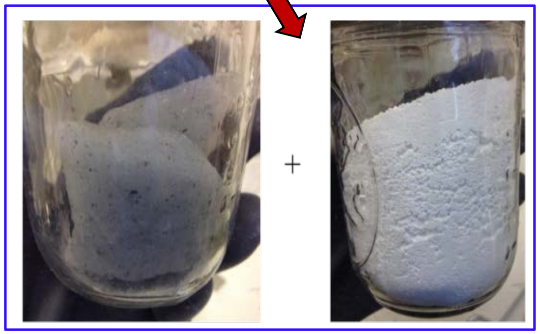


- 24 Measurements total, average of -1.708V with standard deviation of 6.2 mV
- Average standard deviation within each batch of 3.11 mV
- All batches will be mixed together prior to crucible loading

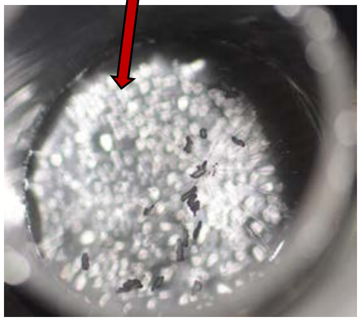
Production, purification and reduction of UW-made FLiBe

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison





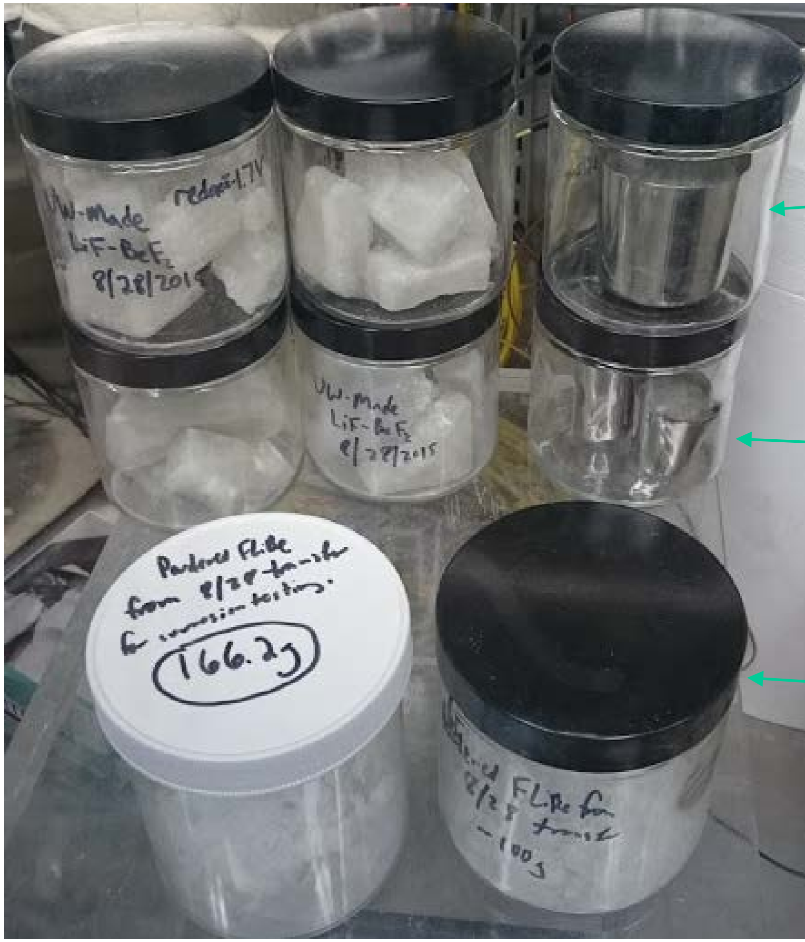
As-received BeF_2 As-received LiF



Video of FLiBe being poured from vessel into tray in glovebox

Glovebox inventory of FLiBe for all future experiments

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison



Four nickel crucibles are fully filled and stored in jars.

Approximately 250 g of granulated salt was separated for one crucible in corrosion test.

Total of 2.2 kg of UW-made FLiBe currently stored in glass jars in Ar glovebox.

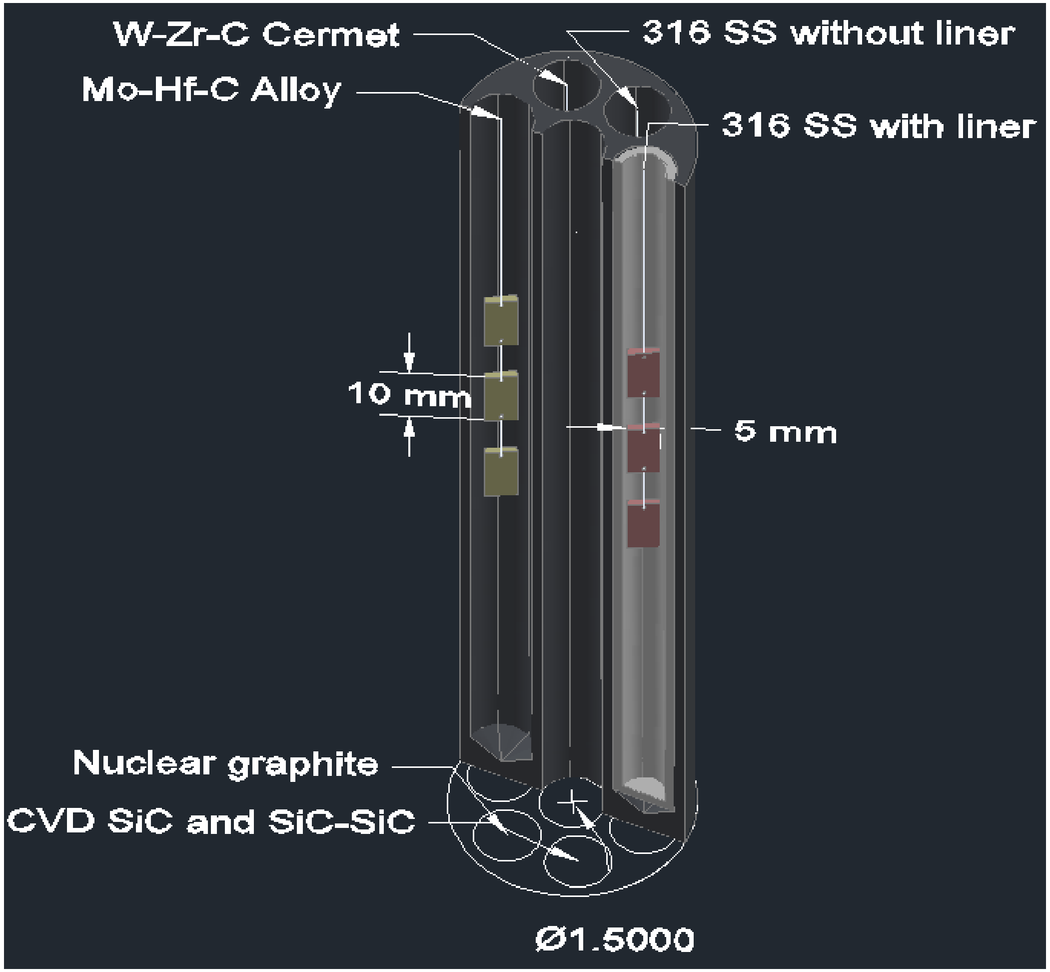
Next static corrosion experiment will test multiple variables

- Metrics to test against corrosion:
  - **Redox potential effect**
    - HF/H_2 Purified salt (redox potential = -1.71V)
    - Beryllium Reduced salt (redox potential = -1.41V)
  - **Effect of carbon from IG-110 graphite crucible**
    - Corrosion test with or without liner for 316 SS
  - **New materials testing in FLiBe**
    - GA SiC-SiC
    - Mo-Hf-C alloy
    - Zr/C-W Cermet

Experimental Design of Static Corrosion Experiment in FLiBe

DEPARTMENT OF Engineering Physics
College of Engineering University of Wisconsin-Madison

Crucible 1: -1.7V UW FLiBe	Crucible 2: -1.4V UW FLiBe
Hole 1: SiC → 3x SiC-SiC samples, 1x bulk SiC sample	
Hole 2: Nuclear Graphite → 3x matrix graphite samples, 1x IG-110 sample	
Hole 3: No liner. Mo-Hf-C → 3x Mo-Hf-C alloy samples with Mo wire suspension*	
Hole 4: No liner. W-Zr-C → 3x W-Zr-C Cermet samples with W wire suspension*	
Hole 5: No liner. 316 SS → 3x 316 samples with SS wire suspension*	
Hole 6: With 316 SS liner. 316 SS → 3x 316 samples with SS wire suspension*	



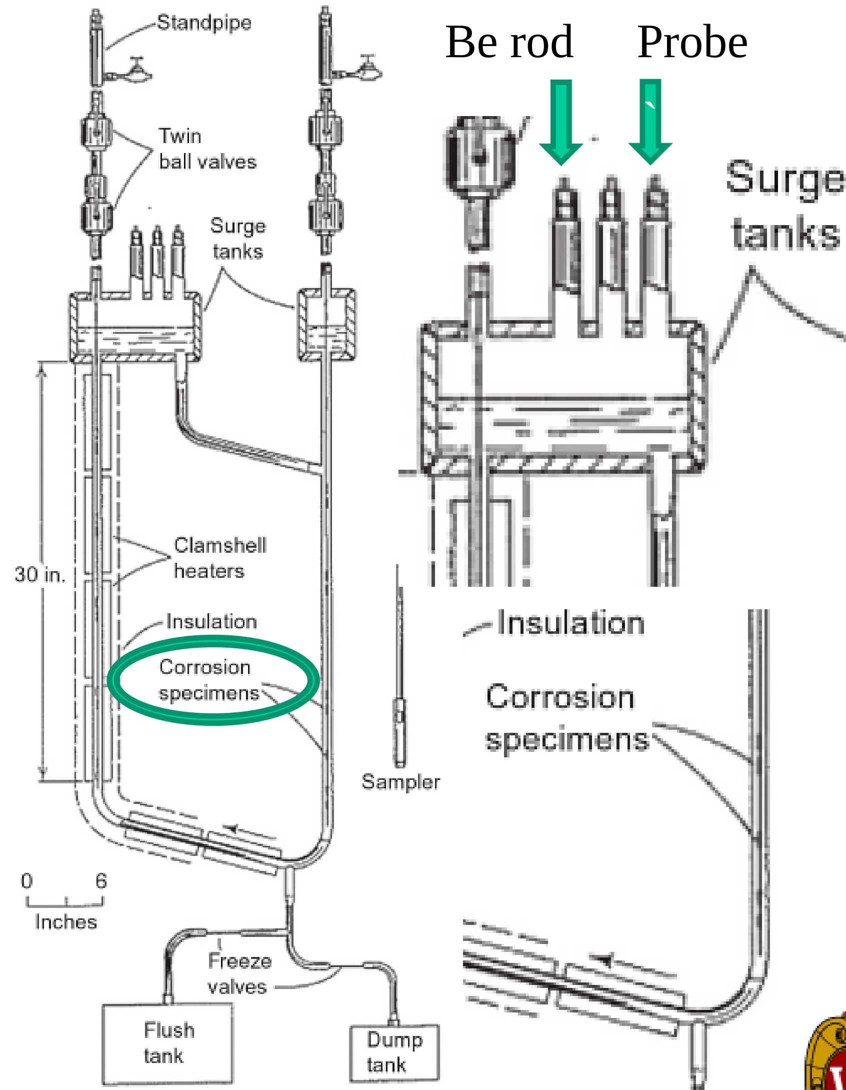
*Avoid dissimilar materials in contact in FLiBe wherever possible

Immediate Future Work

- Flow-assisted corrosion in natural circulation FLiBe loop
  - Corrosion samples in hot and cold legs of loop
  - Thermo-physical properties of FLiBe can be measured
  - Surge tank on top of loop for in-situ salt measurements and chemical control

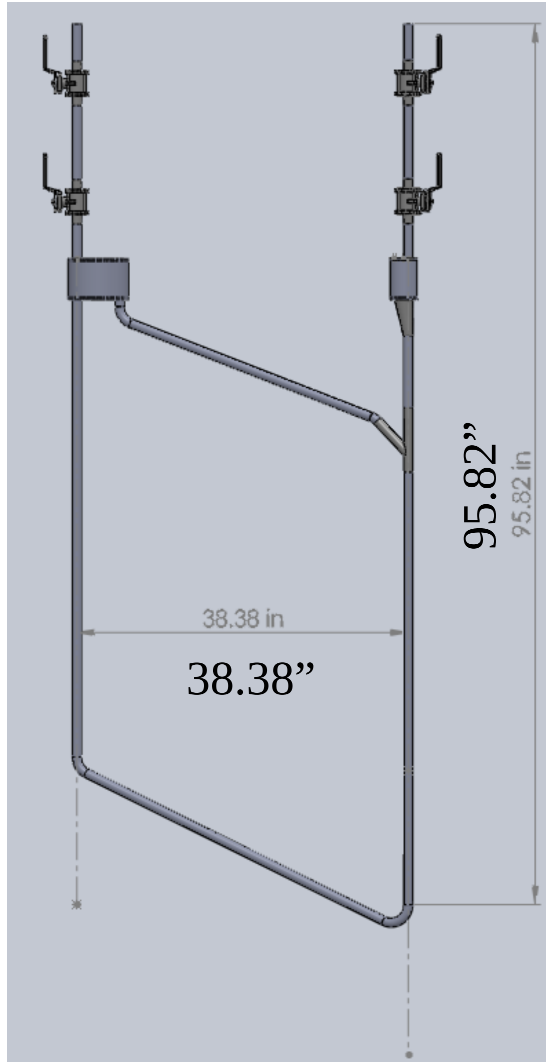
FLiBe Natural Convection Loop 1/2

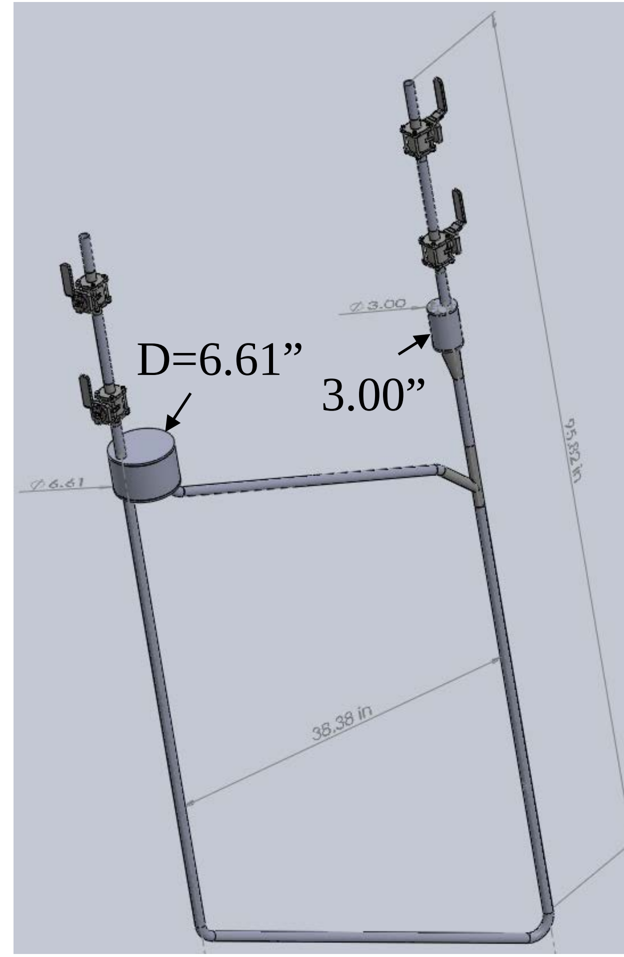
- FLiBe natural convection loop to be built
  - Incorporate Be-addition, redox measurement, and corrosion tests.
  - Use ports in surge tank for:
    1. Sacrificial Be rod with bellow
    2. 3-electrode redox probe
    3. Port-hole
    4. Anything else?



FLiBe Natural Convection Loop 2/2

- 1” OD Stainless Steel tubing
  - Composition matching important
- Two double ball valves to support in-loop corrosion tests.





Thank you for your attention!

Questions?

DEPARTMENT OF
Engineering Physics
College of Engineering University of Wisconsin-Madison