## Acid/Base Behavior and Buffering Capacity in Molten Fluoride Salts

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**future** lanl.gov/projects/future

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![](_page_1_Picture_9.jpeg)

![](_page_1_Picture_10.jpeg)

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![](_page_1_Picture_12.jpeg)

**U.S. Department of Energy** 

![](_page_1_Picture_14.jpeg)

![](_page_1_Picture_15.jpeg)

# Solvoacidity is a measure of a melt's degree of dissociation.

![](_page_2_Figure_1.jpeg)

# Acidity, redox, and salt structure are related.

![](_page_3_Figure_1.jpeg)

# The current understanding: melts of higher basicity favor oxidation.

• Since the oxidized form is (charge) stabilized by the electron pair offered by the base [5]

![](_page_4_Figure_2.jpeg)

# The corrosivity of basic melts was demonstrated in the MSRE.

#### TABLE 2.2.5. EQUILIBRIUM CONCENTRATIONS OF CHROMIUM FLUORIDES WITH ALKALI FLUORIDE AND ZrF<sub>4</sub>-BEARING FUEL MIXTURES

	Chromium Concentration (ppm)	
	In NaF•KF•LiF•UF <sub>4</sub>	In No F-Zr F <sub>4</sub> -UF <sub>4</sub>
Experimental results for melt treated with pure chromium, (Cr) = 1.0*	more fluorobasic	more fluoroacidic
At 600°C	1100	2400
At 800°C	2600	2550
Results calculated for equilibration of melt with Inconel, (Cr) = 0.16*		
At 600°C	7 10	1320
At 800°C	1660	1400
*Concentration of chromium in mole fraction.		
	ΔT thermodynamic driver of Inconel	
	for corrosion is ~12x higher for	
)RNL 2106, pg 98	fluoroba	sic melt Berkele

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[6]

#### AIMD study modeled melts of various pFs and how they solvate Cr.

- 2KF-NaF
- 2LiF-BeF<sub>2</sub>
- 3LiF-AIF<sub>3</sub>
- With & without Cr<sup>0</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>

![](_page_6_Figure_5.jpeg)

(2LiF-BeF2 with Cr<sup>2+</sup>)

[2] Winner, Nicholas, et al. "Ab-initio simulation studies of chromium solvation in molten fluoride salts." J Molec Lig (2021)

# The mechanism of Cr solvation is affected by pF.

![](_page_7_Figure_1.jpeg)

![](_page_7_Picture_2.jpeg)

## pF depends on characterization of acidic or basic behavior.

![](_page_8_Figure_1.jpeg)

High brF and/or capacity for undercoordination (multiple CNs) → acid/base buffering capacity

Ability to produce dsF in response to consumption of dsF by solvation of Cr cation

![](_page_8_Picture_4.jpeg)

# **Experimental studies to probe how diffusivity changes with pF:**

 Measurement of diffusivity of Cr<sup>2+</sup>, Cr<sup>3+</sup> electrochemically and changes with oxidation state, temperature, prev studies

Cr<sup>3+</sup> expected to diffuse more slowly (forms stronger associates).

Possible stronger influence of pF on D(Cr<sup>3+</sup>) since it is more likely solvated by dsF.

![](_page_9_Figure_4.jpeg)

**Fig. 8.** Self-diffusion coefficients of solute Cr ions in flibe and flinak at 973 K. Error bars represent one sigma standard error of the mean.

![](_page_9_Picture_6.jpeg)

Molten 2KF-NaF in the furnace with electrodes
Berkeley

[7] Nam, H. O., et al. "First-principles molecular dynamics modeling of the molten fluoride salt with Cr solute." *JNucMat* (2014)

### In summary,

- Chromium in various oxidation states can incorporate into the polymer network of acidic molten salts.
  - Higher activity of F<sup>-</sup> is not necessary to stabilize corrosion products.
- Acid-base buffering capacity:
  - is a melt's ability to produce dsF in response to consumption of dsF by a (chromium) cation.
  - is determined by brF and ucC.
  - describes the likelihood of pF to change, which is relevant to corrosivity.

![](_page_10_Picture_7.jpeg)

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## **Questions?**

![](_page_11_Picture_8.jpeg)