U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
SOLAR ENERGY TECHNOLOGIES OFFICE

SETO CSP Program Summit 2019

Development of In-Situ Corrosion Kinetics and Salt Property Measurements

Rensselaer Polytechnic Institute (RPI)
Virginia Polytechnic Institute and State University (VT)

Li (Emily) Liu (RPI), Associate Professor; Robert Hull (RPI), Professor
Jinsuo Zhang (VT), Professor; *Kemal Ramic (RPI)*, Postdoctoral Associate

Member Groups/Roles and Technical Gaps/Challenges

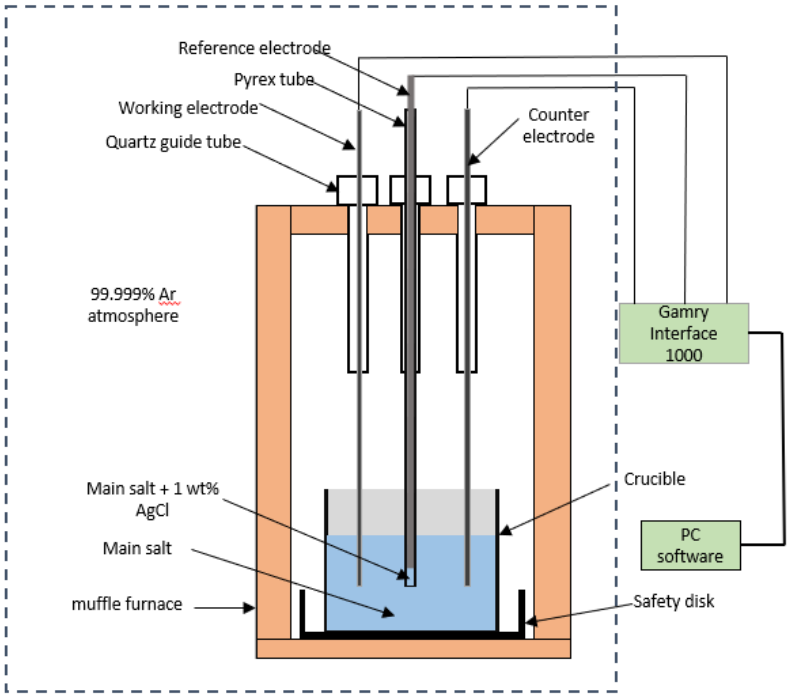
Investigators	Institution	Role
Li (Emily) Liu	Rensselaer Polytechnic Institute	Lead the project; develop and implement the *in-situ* Neutron Reflectometry (NR) and VISION spectroscopies.
Robert Hull	Rensselaer Polytechnic Institute	Develop and implement the *in-situ* Transmission Electron Microscope (TEM) and X-ray Photoelectron Spectroscopy (XPS) methodologies.
Jinsuo Zhang	Virginia Tech	Develop and implement the electrochemistry studies; lead salt property modeling efforts.

Technical Gaps and Challenges

Salt Chemistry: Develop, validate, and publish thermophysical, thermodynamic, and transport properties for the candidate salt compositions across the range of planned operating temperature using reagent-grade salts. Determine impurity effect on properties from industrial-grade salts.

Materials Selection/Compatibility: Develop the correlations between corrosion kinetics and salt structure/dynamics which will lead to potential recommendations of selections of containment material and salts.

1. Electrochemical Study: Corrosion Characteristics of Corrosion Products and Salt Mixture

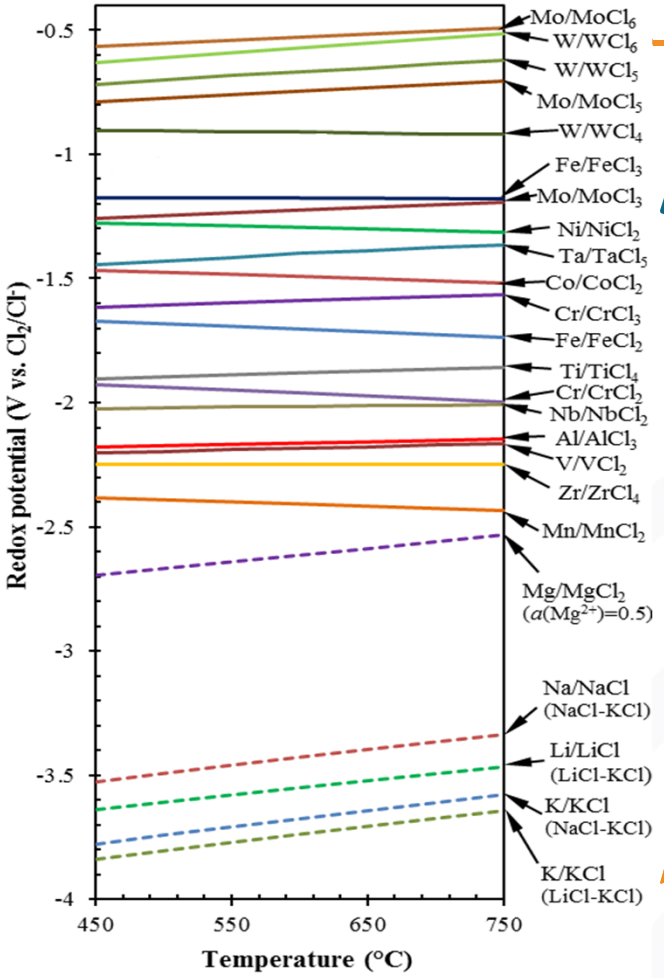


- Redox potential
- Activity Coefficient
- Initial Corrosion rate
- Diffusion coefficient
- Gibbs Formation Energy
- Identification of Stable Ions
- Phase diagram
- Vapor pressure
- Activity of each component
- Redox potential control
- Molten salt Structure
- Exchange Current density

Currently working on

Ab-initial Molecular Dynamic (AIMD) Simulations

Current Stage



Measured Ni corrosion product redox potential, formation potential, and activity coefficient at two concentrations (1wt% and 3 wt% $NiCl_2$ in $MgCl_2$ (44.7 wt%)-KCl (25.8 wt%)-NaCl (29.4 wt%) eutectic salt) for 773K-973 K.

Observations

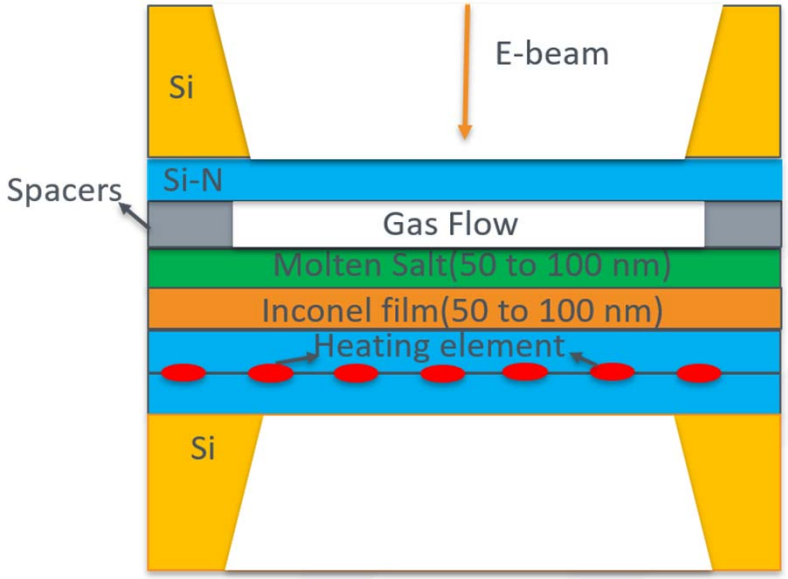
1. The redox potential of Ni^{2+}/Ni is higher at higher concentration.
2. The activity coefficient of $NiCl_2$ is higher at higher temperature and/or higher concentration.

Develop Fundamental thermodynamic and kinetic data on Nickel corrosion product.

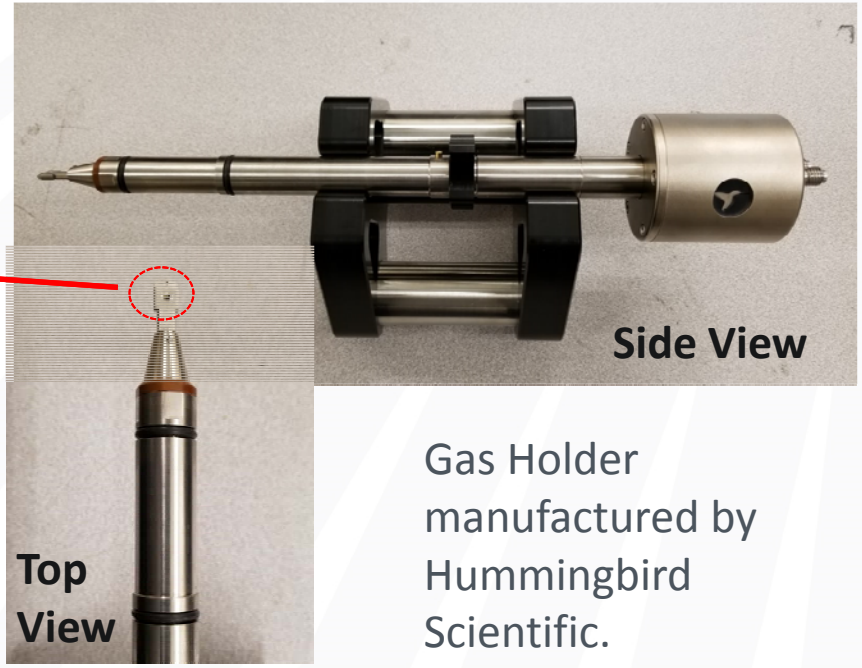
Adding all others to make a phase diagram for $MgCl_2$:KCl:NaCl ternary salt

2. In-situ TEM studies: Experimental Design – new in-situ capabilities

In-situ TEM imaging and diffraction of Inconel corrosion at controlled changes in temperature and partial pressures of varying gases (oxygen, water vapor)



Schematic of in-situ TEM sample

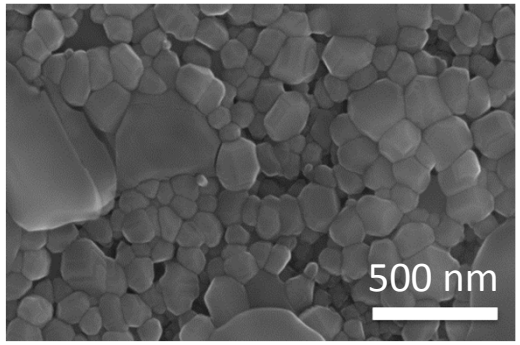


Gas Holder manufactured by Hummingbird Scientific.

Current stage: In-situ TEM studies - Sample Design and Fabrication

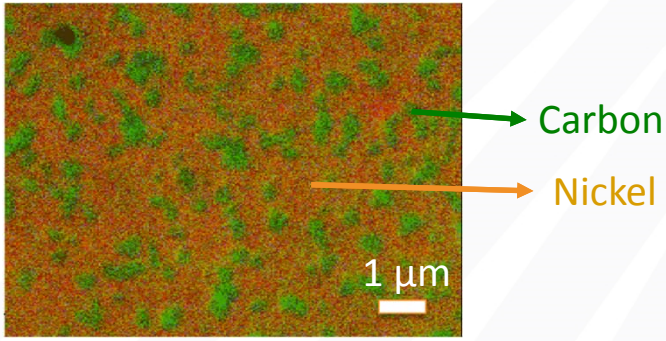
Inconel film fabrication: > 100 nm average grain sizes to differentiate inter- vs intra-granular mechanisms

Surface morphology (SEM)



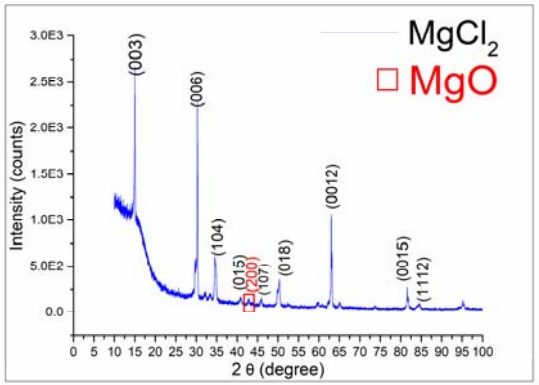
Average grain size ~125nm

Compositional Map [Ni+C+Si] (AES)



No detection of substrate Si

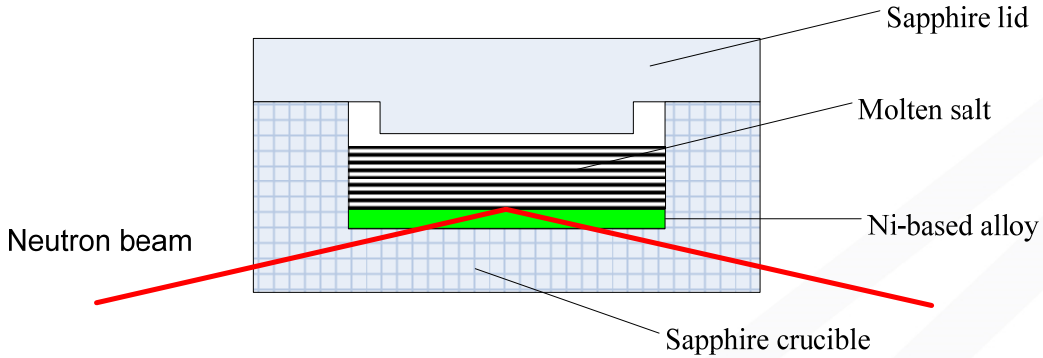
$MgCl_2$ powder 800 C in N_2 for 1.5 hours and cooled to RT



Salt (44.7 $MgCl_2$+25.8 KCl+29.4 NaCl mol%) film fabrication challenges

- Producing stoichiometric salt films - different vapor pressure
  May need separate deposition sources for solid film dep. (melt in TEM)
- Decomposition of $MgCl_2.xH_2O$ on heating - ($MgCl_2.xH_2O \rightarrow MgO+HCl$)
  Minimize air exposure and quantify MgO production

3. Neutron Reflectometry study of metal/interface/salts



Reflectivity and dynamic structure factor of neutrons from metal, salts, and interface

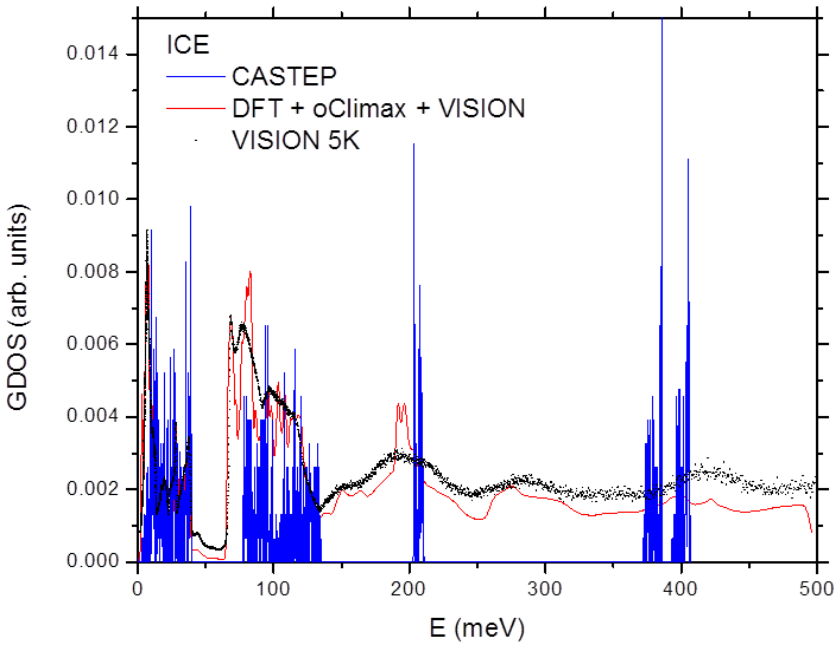
in-situ density, roughness, composition, structure, etc.

Current Status

- Design and initial company shopping are finished.
- In progress: Ordering substitutes, building, and finalizing first test date

4. Vibrational Spectroscopy – VISION: Density of States

- We can match density of states measured from VISION experiments and calculated from density functional theory (DFT)



Current Status:

- Experiments on March 15: measurement at 5K for clear solid state and >643K (370°C) for liquid state
- Build DFT models and oClimax methods for both commercial and VWR salts: Characterize and fine trace phase diagram and structural information

K. Ramić, et al., *Annals of Nuclear Energy*, 120, pp. 778-787 (2018).

K. Ramić, thesis title: "From Experiments to DFT Simulations: Comprehensive Overview of Thermal Scattering for Neutron Moderator Materials."

SUMMARY

1) Developing 4 in-situ methodologies.

2) To Study Salt Chemistry & Materials Selection/Compatibility.

Questions & Answers

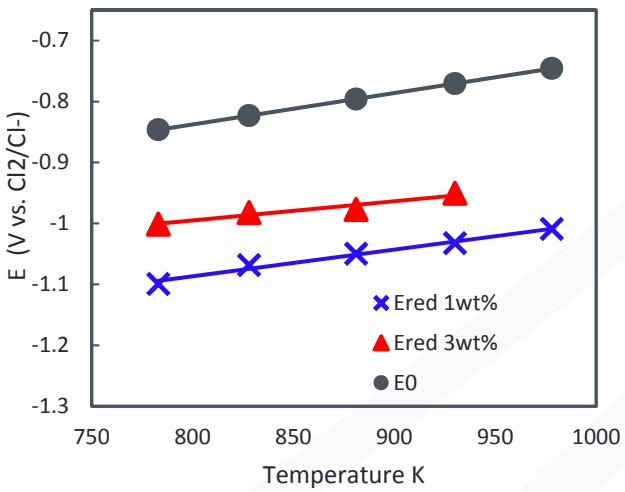
Students involved

- **Graduate Students**: Jie Hou, Jinghua Feng, Prachi Pragnya, Venkata Siva Varun Sarbada (RPI), and Mingyang Zhang (VT)
- **Undergraduate students**: Ryan Bedell (RPI)

Backup slides

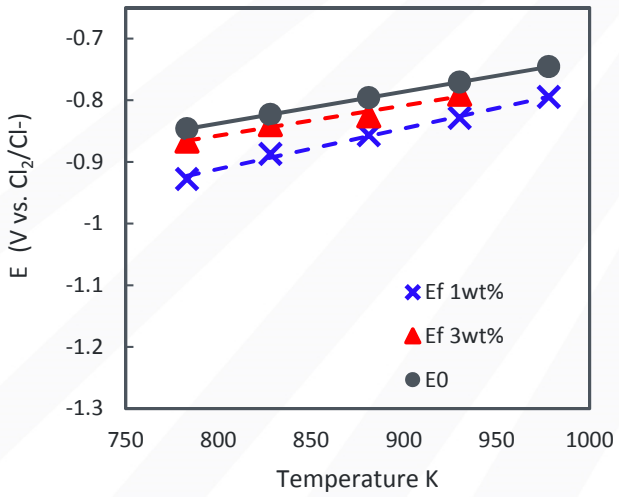
Current Stage

- Completed the major components of experimental setup and be ready to test the salts and containing materials.
- In progress: Fundamental thermodynamic and kinetic data on Nickel corrosion product is processing.



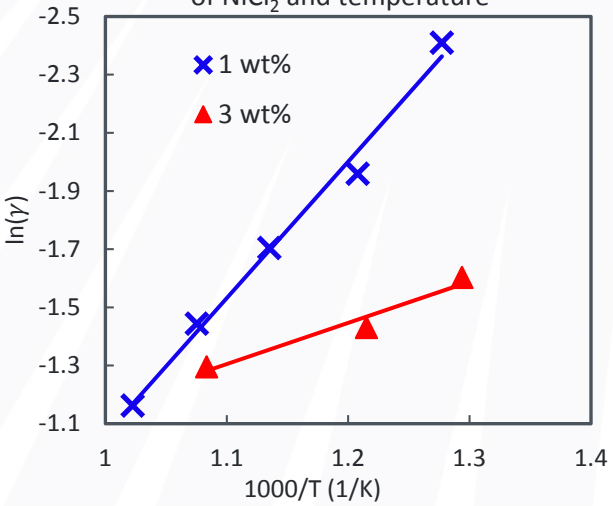
E_{Red}: redox potential of Ni^{2+}/Ni,

$$E_{Red} = [E^0_{MCl_m} + \frac{RT}{mF} ln(\gamma_{MCl_m} X_{MCl_m})]$$

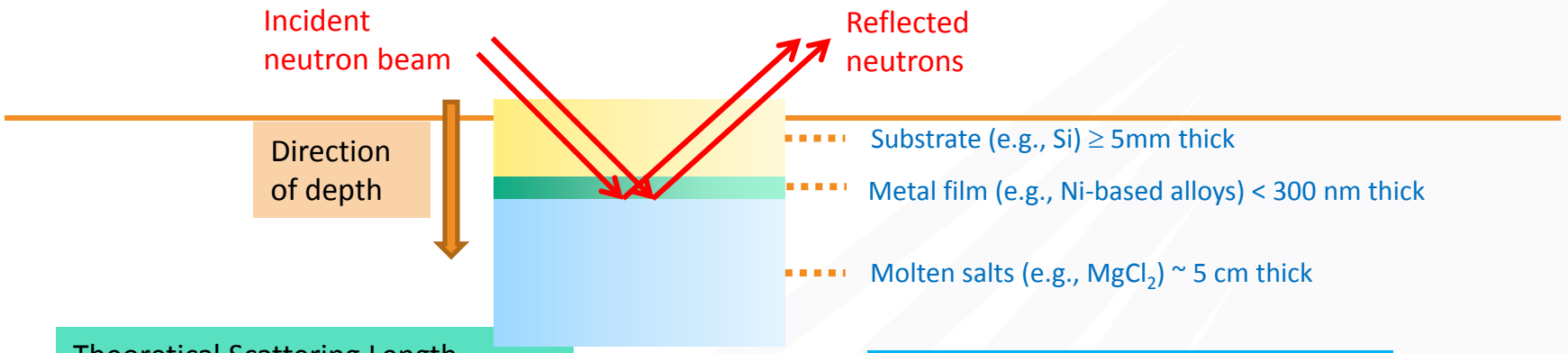


E_f: formation potential,

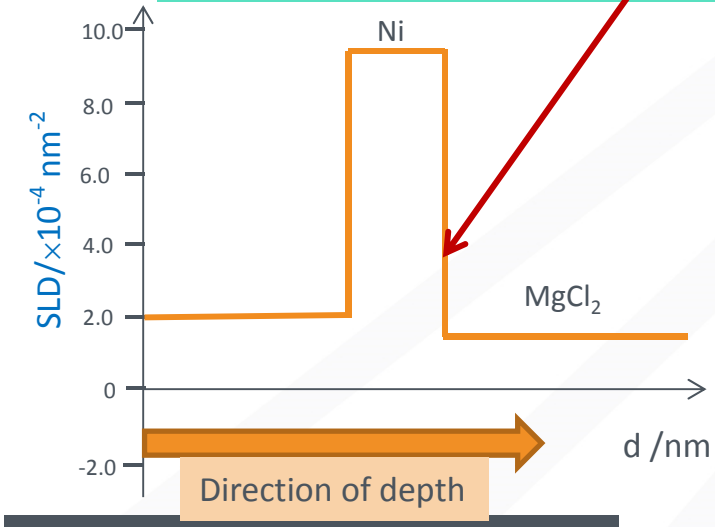
$$E_f = [E^0_{MCl_m} + \frac{RT}{mF} ln\gamma_{MCl_m}]$$



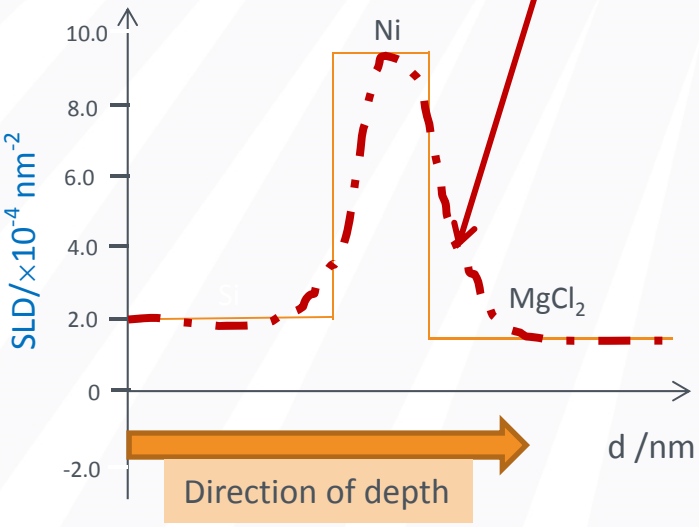
Theoretical correlation between T & γ is $ln\gamma = A\frac{1}{T} + B$



Theoretical Scattering Length Density (SLD) without corrosion

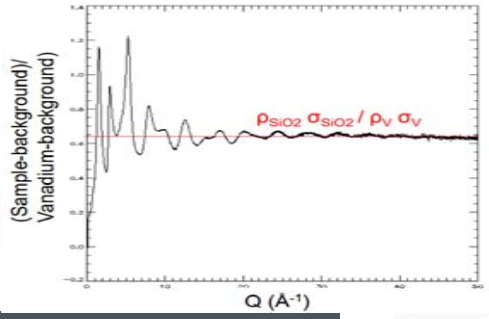


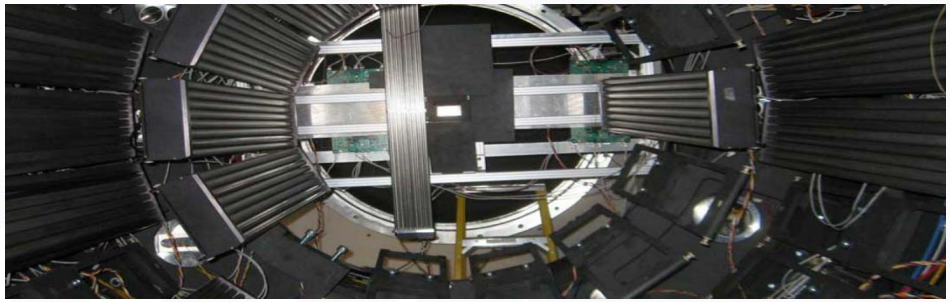
SLD when atomic level interaction or density change occurs



Neutron Spectroscopy - NOMAD

- NOMAD is a diffractometer designed for studies of a large variety of samples ranging from liquids, solutions, glasses, polymers and nanostructured materials to longrange ordered crystals.
- NOMAD gives an access to high-resolution pair distribution functions (PDF), small-contrast isotope substitution experiments, small sample sizes, parametric studies and in-situ diffraction.

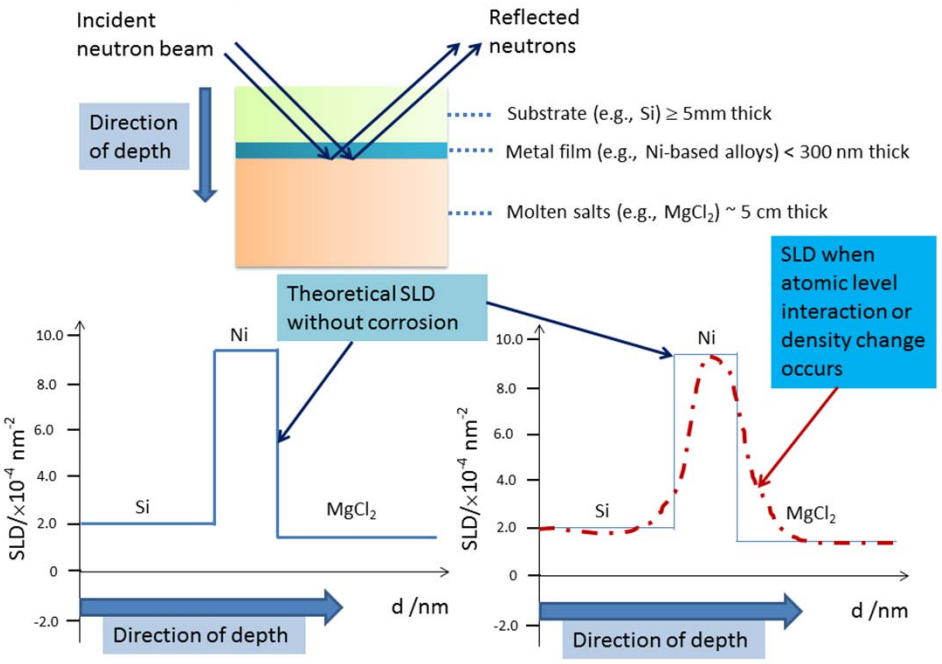




- Submit a proposal to measure salts for temperatures up to 800 C
- Simulate the salts using Molecular Dynamics to calculate the PDF, and improve the MD simulation until the PDF matches the experimental, hence obtain the structure of the salt in liquid phase

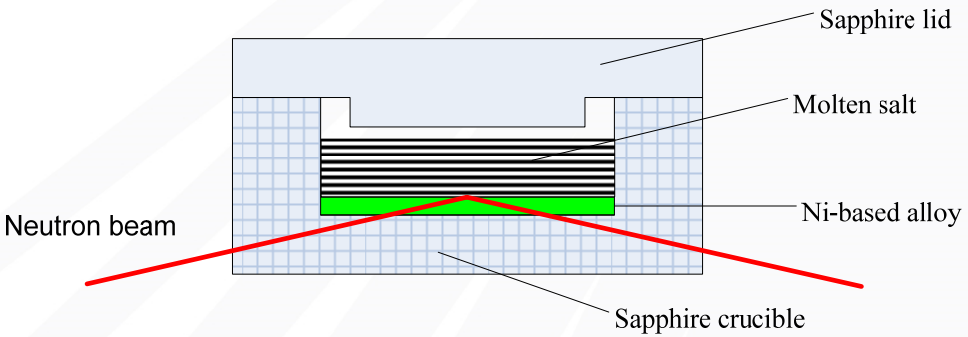
Neutron Reflectometry (NR)

- NG-7 Horizontal NR at NIST
- Neutron reflectivity spectra
  - $\log R$ vs q, R - reflection, q - momentum transfer
  - At different temperatures, times, impurities
- Reflectivity spectra + Scattering length density (SLD) → SLD depth profile
  - $SLD = N \cdot b$, N – number density, b – scattering length
  - Reflectivity sensitive to SLD
  - $SLD \propto N$



Neutron Reflectometry

- Salt container – sapphire
  - Can withstand high temperature
  - Low neutron cross section of Al, O
  - Single crystalline, avoid coherent scattering from container



- Neutron transmit through bottom of crucible
  - Relatively small neutron attenuation through Al_2O_3
  - Salt can be ensured to attach the coating