ORNL Salt Corrosion Activities – Past to Present

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I Will Address Three Subjects In this Presentation

- History of alloy development and molten salt corrosion studies at ORNL
- Recent research results
- ORNL capabilities for future studies

Background On Aircraft Nuclear Propulsion Program

- Studies began in late 1940's with program to develop a nuclear powered airplane
- Determined that a liquid fuel offered several advantages
- In 1947 experiments were started to establish the feasibility of molten salt fuels based on:

  - High solubility for uranium
  - Among the most stable chemical compounds
  - Low vapor pressure at high temperature
  - Reasonably good heat transfer properties
  - Not damaged by radiation
  - Does not react violently with air or water
  - Inert to some common structural metals

Aircraft Reactor Experiment Was Built To Investigate Use Of Molten Fluoride Fuels

- Used fuel salt mixture of NaF, ZrF_4 and UF_4
- Used a BeO moderator
- Used Inconel 600 for containment
- INOR-8 (Hastelloy N) was being developed for salt containment
- In 1954, the ARE (test reactor) was operated successfully for 9 days
- Reactor outlet temperatures ranged up to 1580°F (860°C)
- Power ranged up to 2.5 MW (th)
- Reported no mechanical or chemical problems encountered
- Reactor was found to be stable and self-regulating
- Encouraged consideration of molten salt reactors for civilian power applications

To Confirm Design Of A Molten Salt Power Reactor, Another Experiment Was Needed

- Needed to consider the ^{235}U – ^{238}U – Pu fuel cycle and the ^{233}U – Th – ^{233}U fuel cycle
- Determined the limited moderation of neutrons by salts meant, for a thermal reactor, molten salts would not make as good a moderator as graphite
- Had to choose between single fluid (fissile and fertile materials in same salt) and two-fluid reactors (fertile material in a separate salt)

  - Single fluid simpler with lower power costs

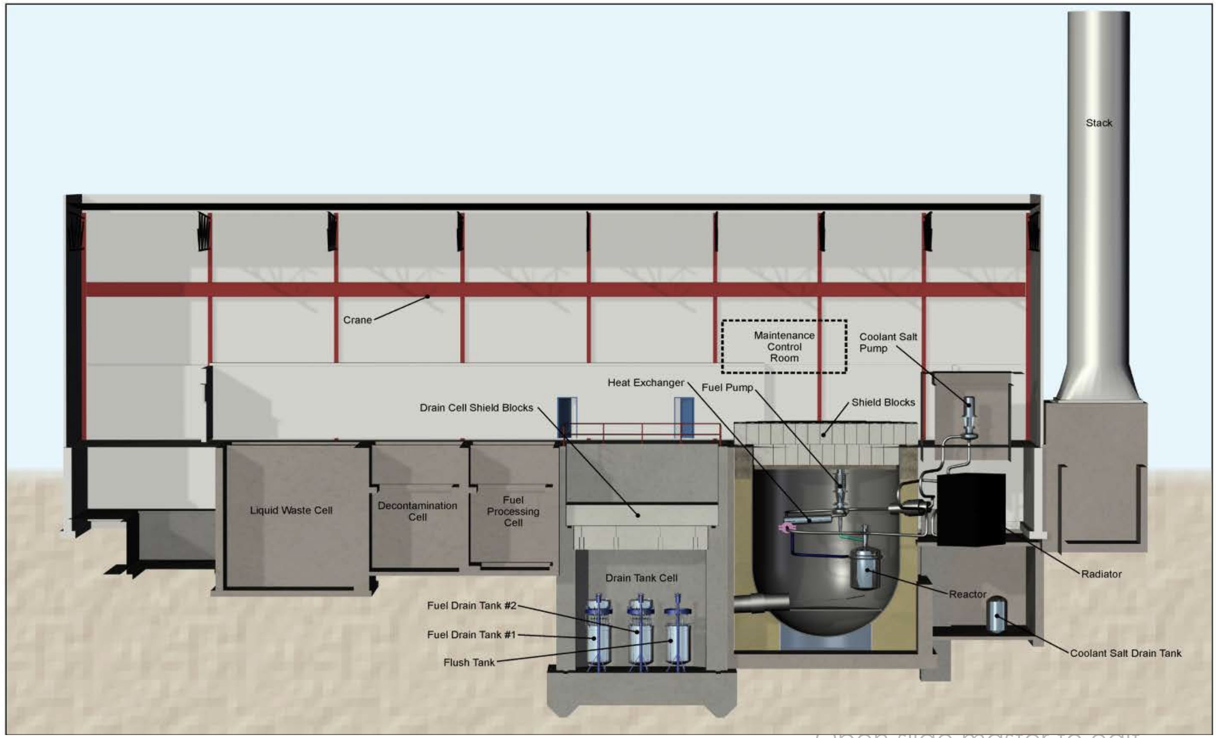
  - Two fluids expected to have better breeding ratio

Development Of An Alloy For Molten Fluoride Salt Application Required Balancing Several Issues

- A team led by Bill Manly and Hank Inouye had the task of developing a suitable alloy for containment of molten salt
- Based on free energy of formation, Ni and Mo are among the least likely to form stable fluorides
- Cr forms more stable fluorides making it a less desirable alloy component, but it is a necessary alloy component to prevent oxidation of Ni and Mo
- Oxidation studies showed a need to keep chromium content in the 5-7% range – high enough to limit alloy oxidation in air but low enough to limit availability of chromium for formation of CrF_2

Design Of Molten Salt Reactor Experiment Began In 1960

- A single fluid design was chosen but a fertile material was not added to the salt
- $^7LiF\text{-}BeF_2\text{-}ZrF_4\text{-}UF_4$ (65-29.1-5.0-0.9 mole%) was selected as the fuel salt
- Unclad graphite was used as the moderator
- All system metallic parts that contacted the molten salt were fabricated from INOR-8
- Maximum power of the reactor was ~8,000 kW
- Heat was recovered by a $^7LiF\text{-}BeF_2$ coolant salt and rejected to the atmosphere



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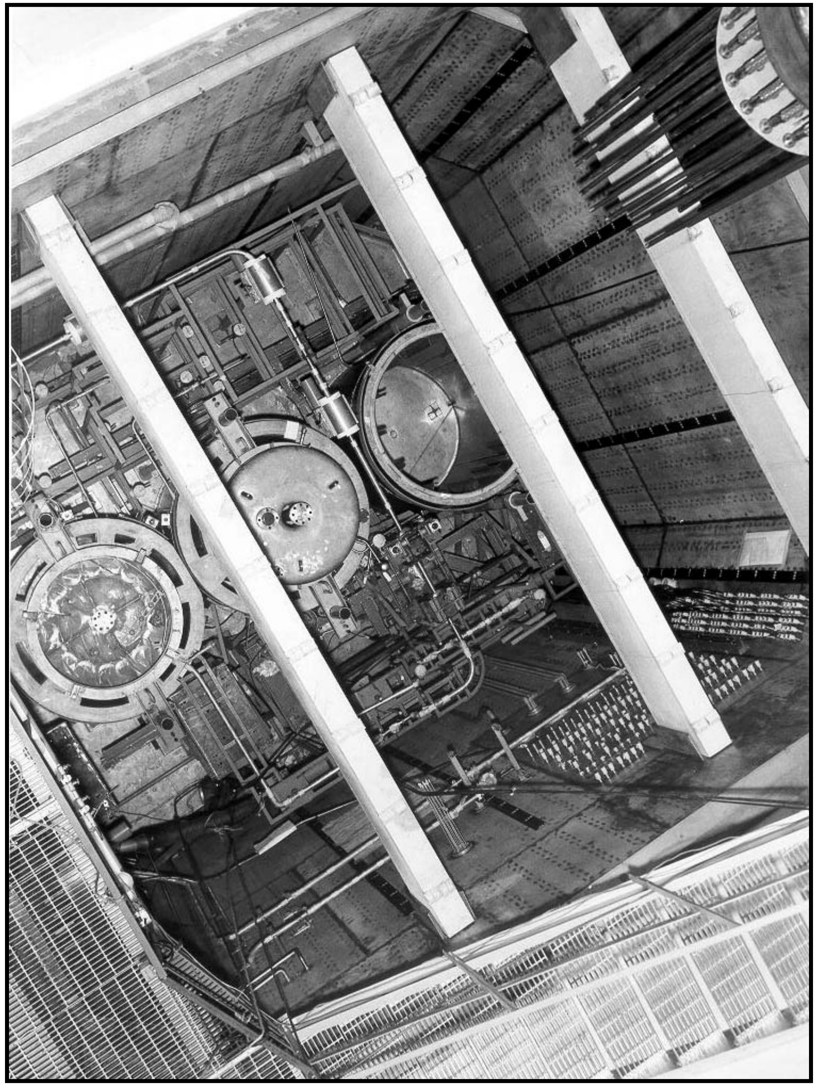
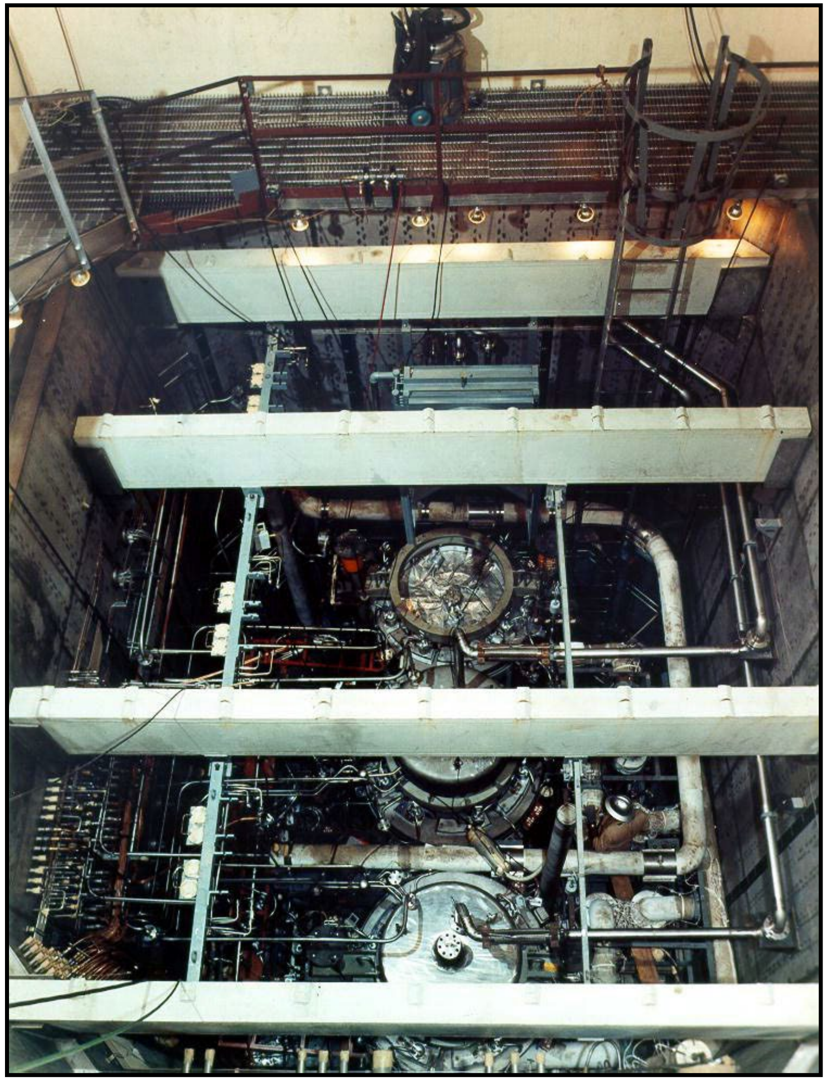
Salt Drain Tanks: (left) During Construction; (right) Near Completion





Can you find the man wearing the hard hat?

MSRE Operating History

- For the initial operation, the reactor went critical in 1965 operating with fuel salt containing $^{235}UF_4$ in LiF, BeF_2 and ZrF_4 and operating temperature of ~650°C
- No corrosive attack observed on metallic and graphite components
- In 1968 the fuel salt was treated with fluorine gas in the Fuel Processing Cell to remove the ^{235}U as UF_6 i.e. $UF_4 + F_2 \rightarrow UF_6$
- Subsequent examination showed significant corrosion likely occurred to the fuel processing vessel
- A charge of ^{233}U fluoride was then added to the LiF-BeF_2-ZrF_4 carrier salt and on October 2, 1968, the reactor went critical with the ^{233}U-containing fuel
- Eventually, a small amount of plutonium fluoride (as PuF_3) was added to the salt

MSRE Operation Completed/Terminated In December, 1969

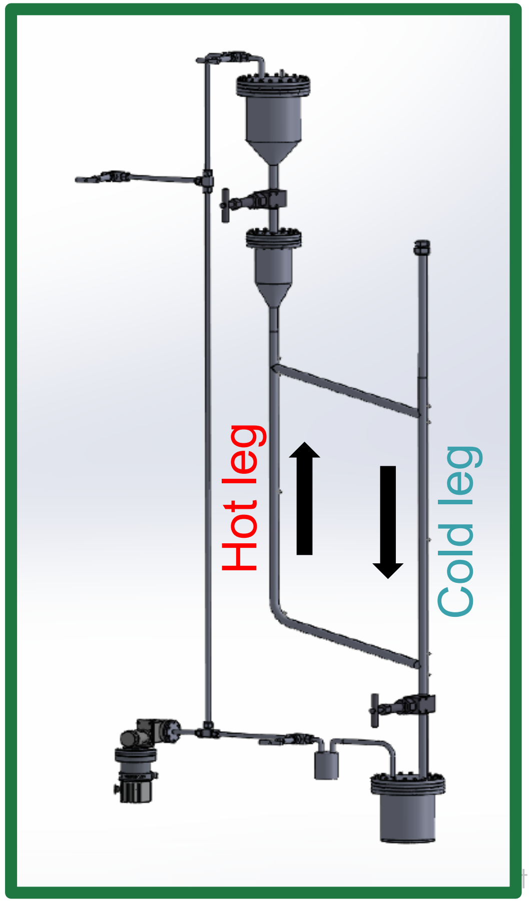
- Maintained fuel salt temperature of 1200°F (~650°C)
- This phase of operation was the first to successfully demonstrate operation with ^{233}U as the fissile component
- After completion of operation, the fuel salt was drained from the reactor into the two fuel salt drain tanks
- During the 1970-1998 period, radiolytic production of fluorine in the solidified salt contained in the drain tanks was addressed by annual annealing of the tanks with the expectation that fluorine and beryllium would recombine
- Eventually, the ^{233}U was removed from the two drain tanks but most fission products remained in the frozen salt

Several Post-Operation Issues Were Identified Which Need To Be Addressed For Future INOR-8 Applications

- Thermal/activity gradient mass transfer of the least noble alloy components, as predicted by DeVan and Evans, resulted in removal of Cr from the hottest metal surfaces with deposition of Cr on the coolest surfaces
- INOR-8 suffered radiation-induced embrittlement primarily attributed to helium produced by interaction of thermal neutrons with ^{10}B which is an impurity in the alloy
- Fission product tellurium caused shallow intergranular cracking in INOR-8 exposed to the fuel salt
- Moisture, oxides and other impurities accelerated corrosion

Post-MSRE Studies Were Directed Toward Molten Salt Breeder Reactor, And Now, Gen IV Molten Salt Reactors

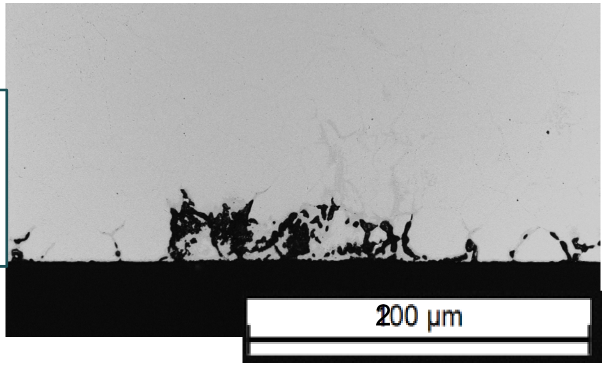
- Studies have included capsule tests with chloride and fluoride salts
- FLiBe capsule studies have included exposure of graphite and silicon carbide coupons as well as 12 metallic alloys
- Thermal convection loops have been operated with fluoride and chloride salts
- A pumped loop circulating FLiNaK operated briefly and is being prepared for restarting
- High temperature wear studies and pressurized salt intrusion studies have been conducted



Many MS Reactor Designs Call For 316H Stainless Steel To Be Used For The Primary Containment Material

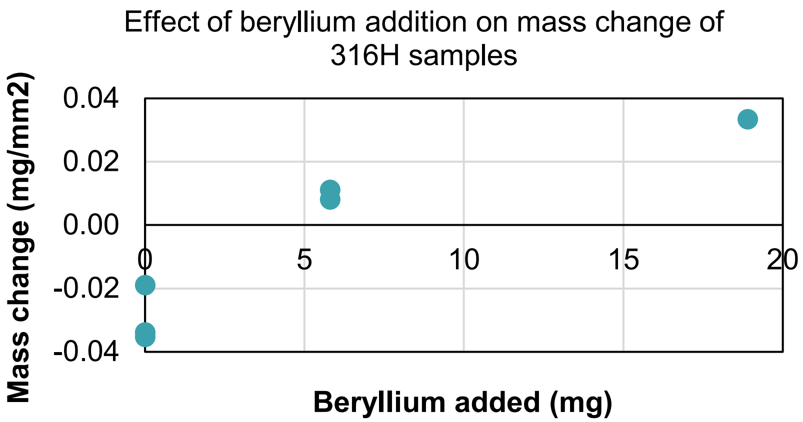
- This addresses the need for a material that is a qualified pressure vessel material
- Because of the higher chromium content of 316H (nominally 16-18 wt%) corrosion by molten salt is a concern
- Many capsule and loop corrosion studies have been conducted
- Addition of a reactive metal, like beryllium or lithium, is proposed as a means to react with fluoride salt impurities and reduce the corrosivity
- Magnesium additions have been proposed for chloride salts

316H SS exposed 1000 h in static FLIBe at 750°C

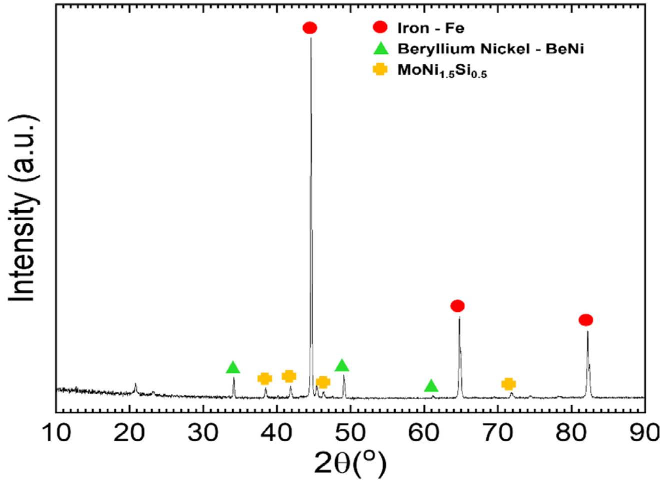


Recent Studies Investigated Effect On 316H Stainless Steel Of Be Addition To FLiBe

- Added 5.8 or 18.9 mg of Be to about 34 g of FLiBe in Mo capsule containing 316H coupon (0.017-0.053 wt%)
- Capsules exposed 1000 h at 750°C
- All coupons exposed in salt with Be additions had weight gains while coupons exposed in FLiBe without Be additions had weight losses
- XRD of sample surface showed presence of NiBe intermetallic compound



XRD of 316H coupon after FLiBe+Be exposure identified the NiBe intermetallic



Figures from Keiser et al. Journal of Nuclear Materials 565 (2022) p153698

Examination Of Coupon Exposed To Salt With 5.8 mg Be Addition Showed Formation Of Intermetallic Compounds

Spot No.	Be	Cr	Mn	Fe	Ni	Mo
1	55.0	0.95	0.12	4.63	39.3	0.01
2	54.2	1.60	0.17	6.35	37.6	0.04
3	52.7	2.72	0.29	9.63	34.5	0.10
4	11.7	22.6	2.24	48.0	6.29	8.92
5	22.5	18.2	1.34	35.4	6.32	16.1
6	1.68	18.2	2.22	73.8	1.91	0.73
7	0.20	30.3	2.90	60.6	1.93	3.69
8	1.81	35.1	2.83	59.7	1.74	3.57

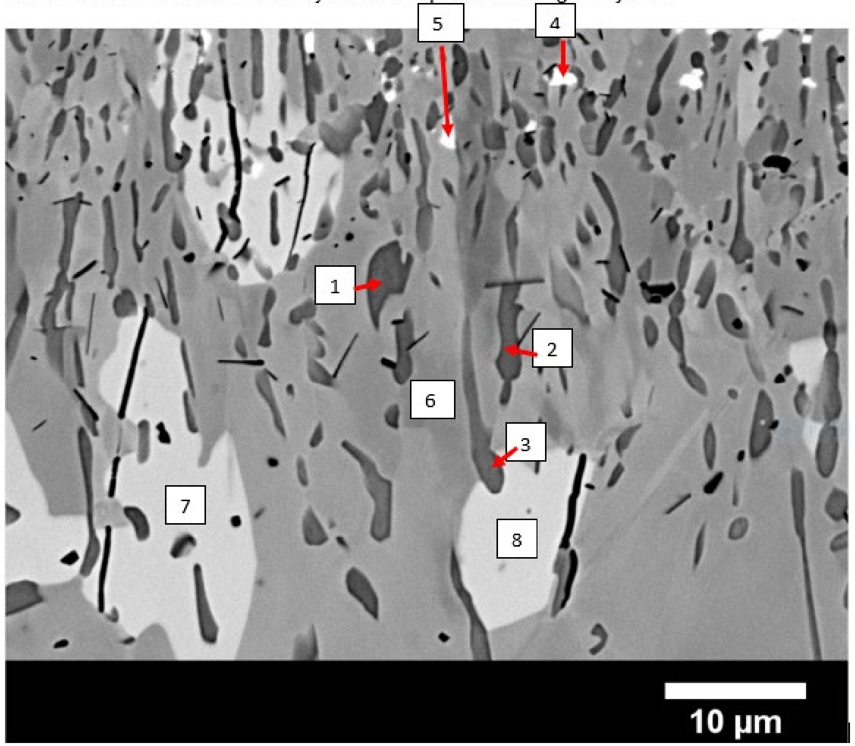


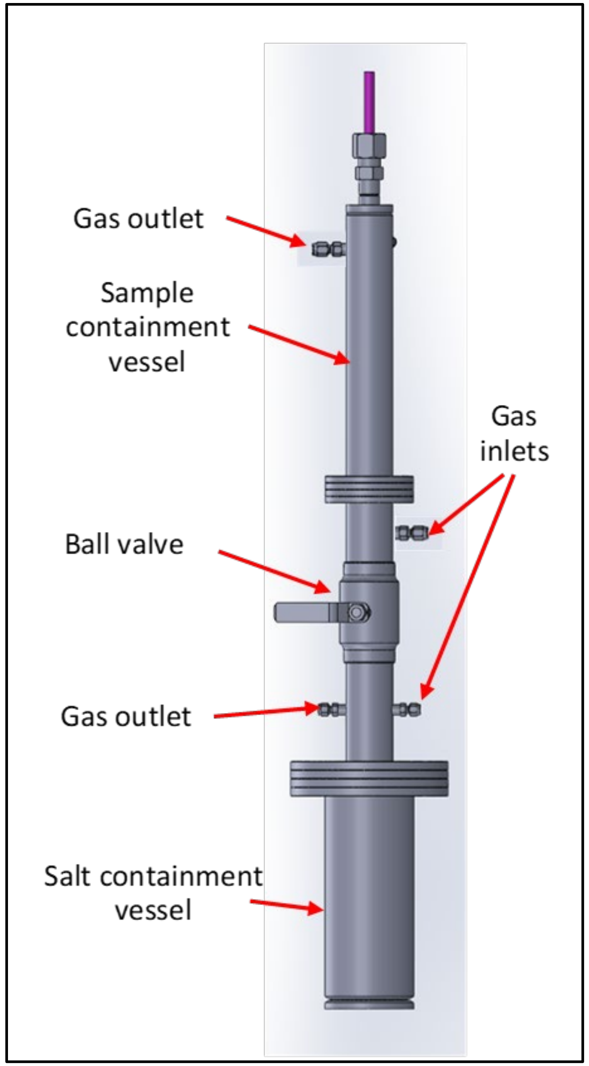
Figure and Table from Keiser et al. Journal of Nuclear Materials 565 (2022) p153698

- Tensile test of single sample exposed to FLiBe with added Be showed detrimental effect on mechanical properties (ductility loss)
- Further tests are needed to determine acceptable level for addition of reductants to molten salt

ORNL Has Conducted Many Capsule And Thermal Convection Loop Tests With Fluoride And Chloride Salts

- For the MSBR project, many loops operated with the MSBR fuel salt – $LiF\text{-}BeF_2\text{-}ThF_4\text{-}UF_4$
- In the last few years, loops have operated with FLiNaK, FLiBe and a chloride salt
- ORNL currently has five enclosures for operation of loop tests
- All loops have chains of samples in the hot and cold legs
- Most loops have facilities for electrochemical measurement of the oxidation potential
- Dozens of capsule tests have been conducted with various fluoride and chloride salts

Studying Molten Salt Intrusion Of Graphite



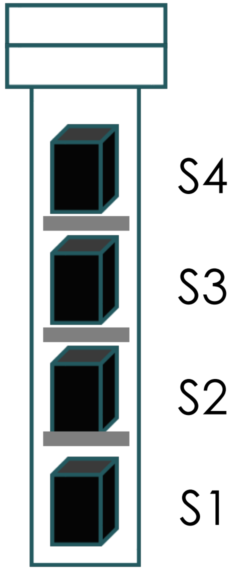
- Designed and built high pressure salt intrusion testing system
- System is designed for operation at temperatures up to 750°C and pressures up to 10 bar
- It includes an all-graphite holder that can accommodate up to six samples – no metal contacts the salt
- System permits holding samples under vacuum prior to immersion in molten salt as well as cooling under gas pressure after removal from salt

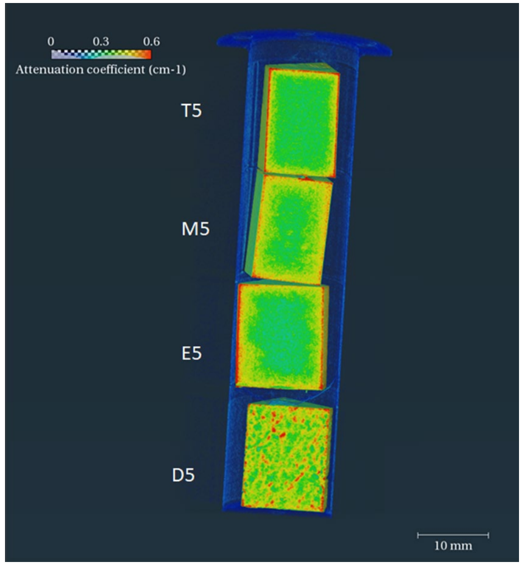
Many Grades Of Graphite Are Being Evaluated In Our Tests

		Class	Density [g/cm³]	Country of origin	Irradiation data	Forming process	Availability
AGC-Campaign	**H-451**	Medium	1.71	SGL USA	Low dose	Extruded	
	NBG-17	Medium-fine	1.86	SGL (Germany/ France)	Low dose	Vibro-molded	
	NBG-18	Medium	1.87	SGL (Germany/ France)	Low dose	Vibro-molded	
	PCEA	Medium-fine	1.79	GrafTech (USA)	Low dose	Extruded	
	IG-110	Fine < 100	1.76	Toyo (Japan)	Low dose	Iso-molded	
	IG-430 (dropped)	Fine < 100	1.80	Toyo (Japan)	Low dose	Iso-molded	
	2114 (added)	Superfine < 50		Mersen (France-USA)	Low dose		
MSRE	**CGB**	Medium	1.86	Union Carbide (USA)		Extruded	
OTHER fine grain graphites	**POCO-ZXF-5Q**	Microfine < 2	1.78	USA	Low dose	Iso-pressing	
	POCO-AXF-50	Ultrafine < 10	1.78	USA	Low dose	Iso-pressing	
	POCO-TM	Ultrafine < 10	1.82	USA	Few data	Iso-pressing	
	G347A	Ultrafine < 10	1.85	Tokai (Japan)	High dose	Iso-pressing	
	IGS743NH	Superfine < 50	1.80	Nippon (Japan)	Low dose	Iso-molded	
	ETU-10	Superfine < 50	1.74	Ibiden (Japan)			

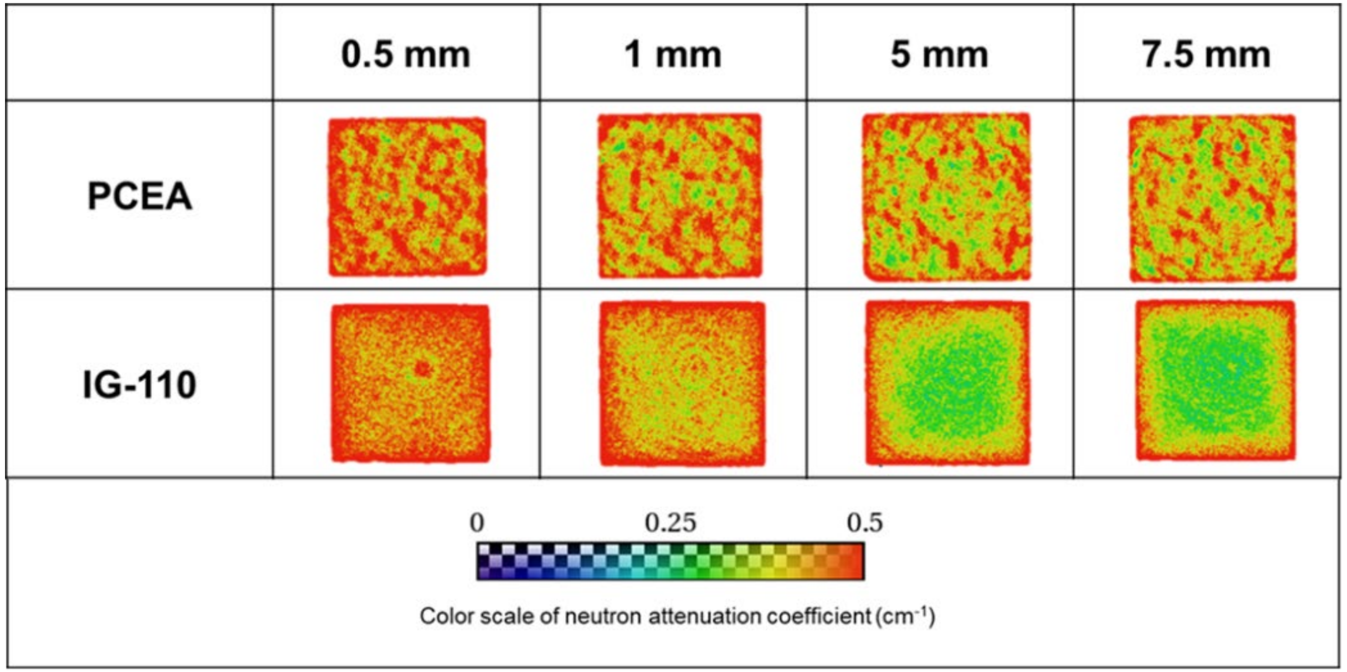
Tests have included capsule exposures in FLiBe and intrusion tests in FLiNaK

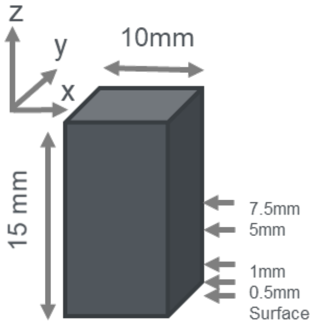
Neutron Imaging Used To Characterize Salt Intrusion





Surface





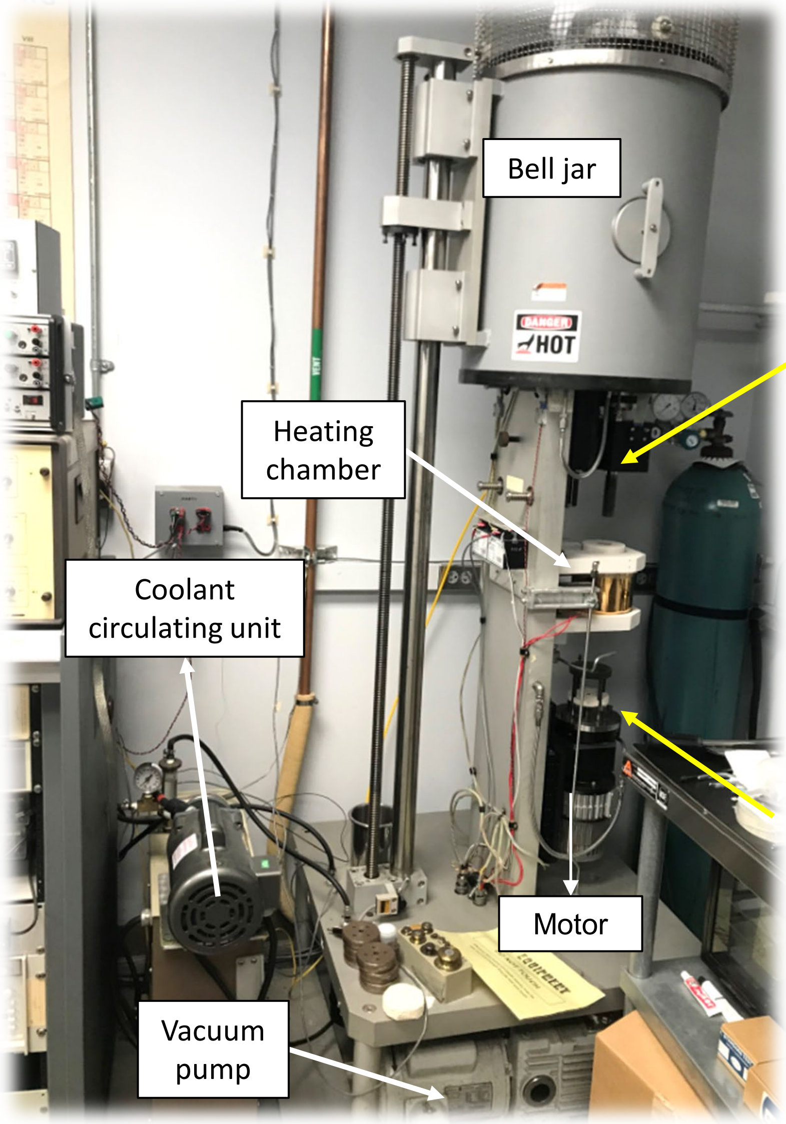
- Neutron imaging shows some grades of graphite allow salt penetration deep into the sample

We’ve Expanded Our Capabilities For Handling FLiBe

Installed and commissioned a 3-glove glovebox for welding and handling of Be-containing static capsules

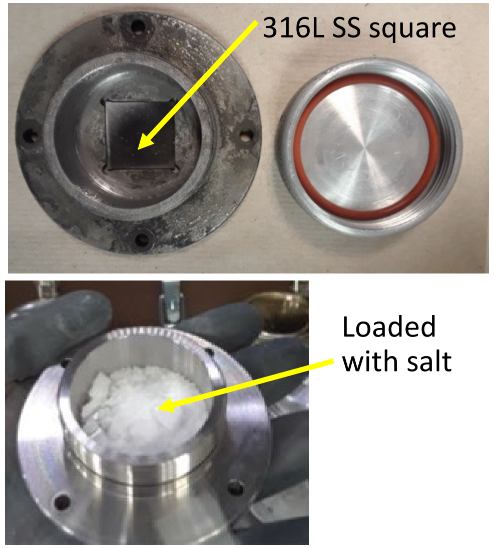
Designed and built a second salt-intrusion system, located inside a new 4-glove glovebox

Wear Testing Conducted In Chloride And Fluoride Salts



Pin holder

Sample holder

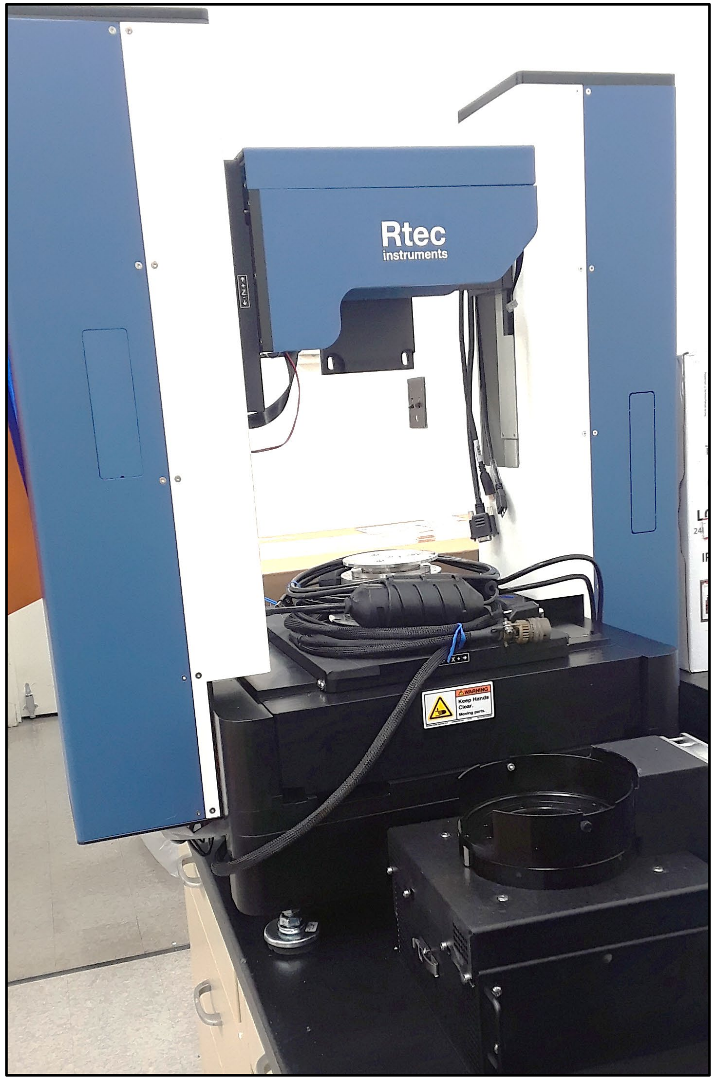


Experimental*:

- Graphite or metallic pin sliding against 316L SS surface
- Salt: LiF-NaF-KF or NaCl-KCl-$MgCl_2$
- Temperature: up to 1000 ºC
- Gas environment: Ar
- Normal load: up to 100 N
- Rotating speed: up to 1000 rpm

*Chloride salt studies were funded by CSP project

Glovebox And Tribometer Have Been Purchased Which Will Permit Wear Studies With Molten FLiBe



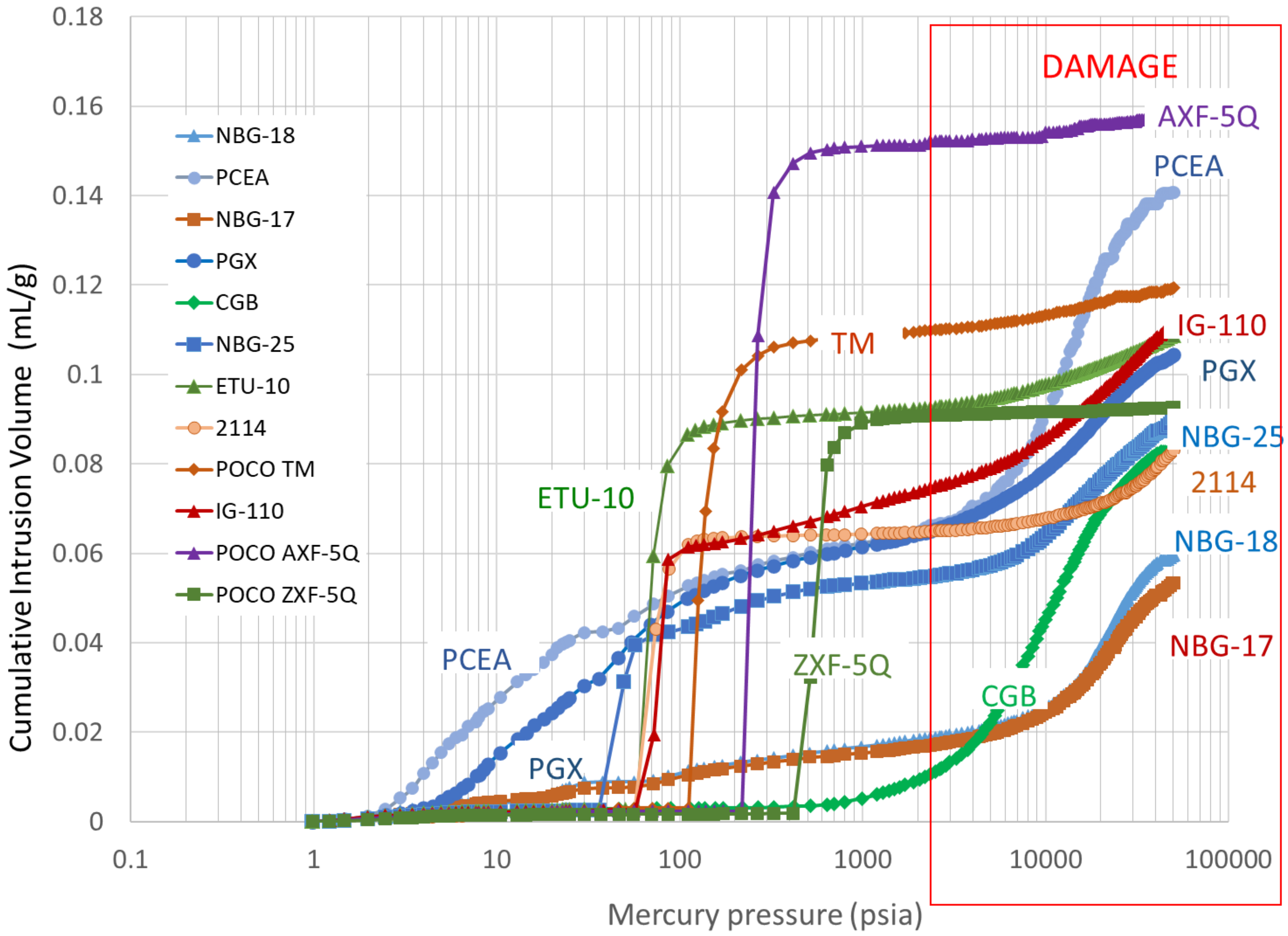
Summary

- ORNL has a 70+ year history in molten salt projects beginning with the ARE and development of INOR-8
- ORNL's Molten Salt Reactor Experiment is the only molten salt reactor ever operated
- With the renewed interest in molten salt reactors (and CSP) in recent years, ORNL has conducted molten salt corrosion tests using capsules and loops with fluoride and chloride salts
- ORNL has built and/or remodeled facilities for conducting pressurized salt intrusion and salt lubricated wear tests
- ORNL is completing construction of facilities for conducting pressurized salt intrusion and salt lubricated wear tests in FLiBe

CREDITS

- Funding provided by ART and NEUP with Georgia Tech
- Research conducted by Ercan Cakmak, Nidia Gallego, Xin He, Jim Keiser, Michael Lance, Tracie Lowe, Jisue Moon, Jun Qu, Dino Sulejmanovic, Adam Willoughby

Mercury Intrusion Showed A Wide Range Of Porosity Distributions For A Variety Of Graphite Grades



- Fine grade graphites showed a sharp uptake after a given threshold pressure
- Medium and large grain graphites showed a continuing uptake over the whole pressure range

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