



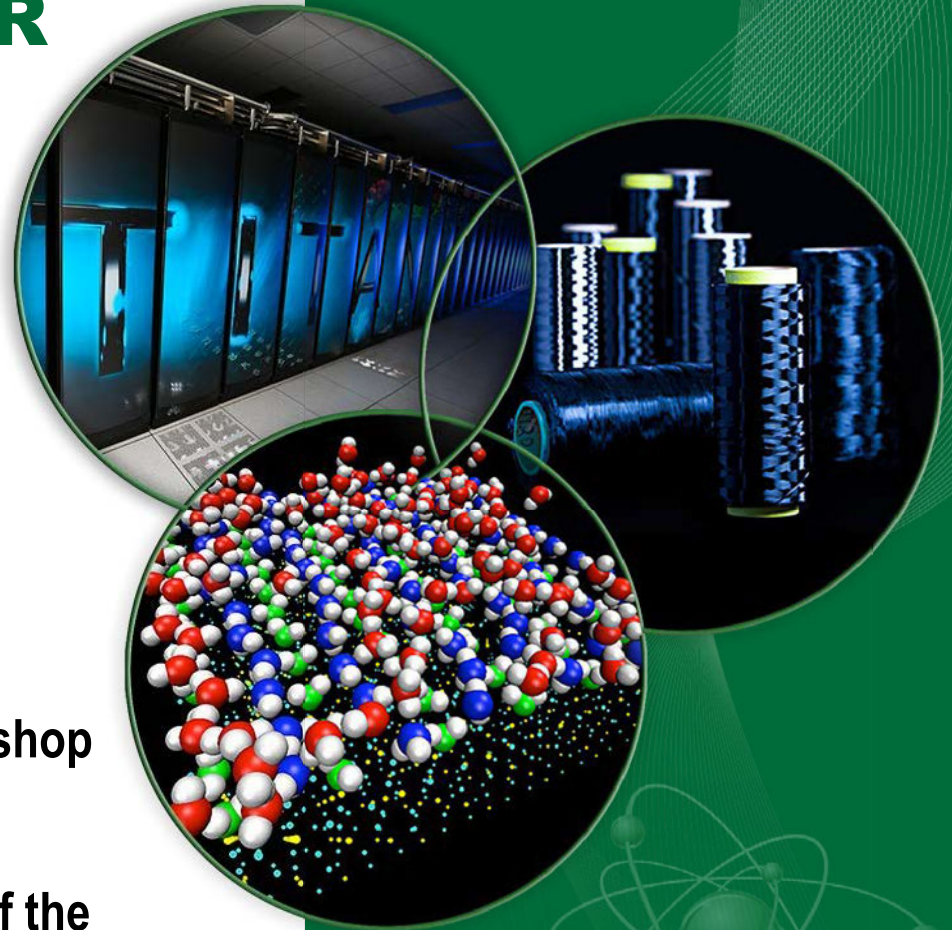
The Path Ahead - Materials Roadmap for FHR/TMSR Development

Weiju Ren, Ph.D.
Oak Ridge National Laboratory

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Molten Salt Reactor Technologies Workshop
October 15 - 16, 2015

Commemorating the 50th Anniversary of the Startup of the Molten Salt Reactor Experiment (MSRE)
Oak Ridge, Tennessee, USA



Acknowledgments

The information provided for this presentation by my ORNL colleagues is gratefully appreciated.

Tim BURCHELL

Cristian CONTESCU

Zhili FENG

David HOLCOMB

Yutai KATOH

Govindarajan MURALIDHARAN

Dane WILSON



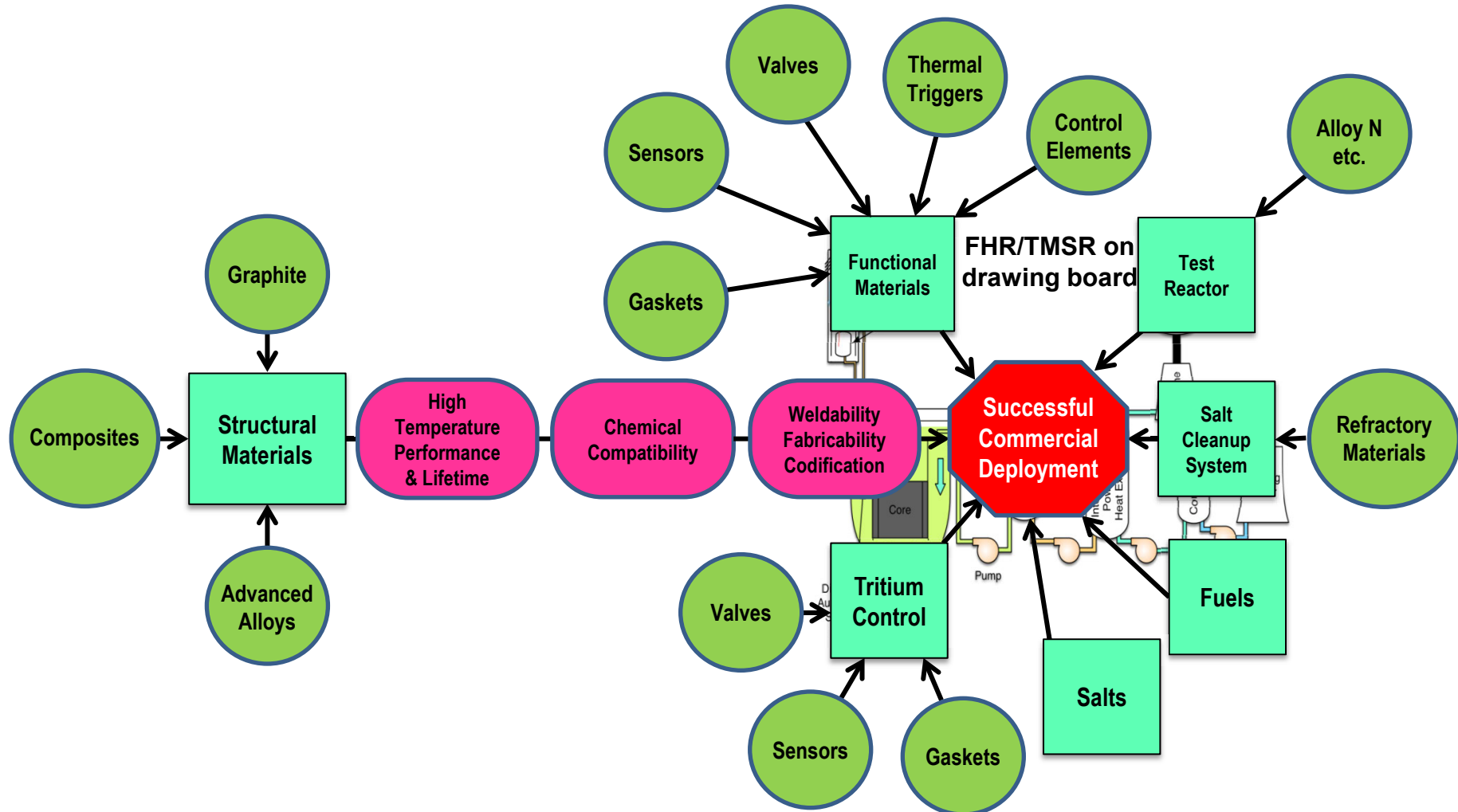
OUTLINE

- **Why a materials roadmap?**
- **Challenges, MSRE leverage, and solutions development**
- **Roadmap strategy**
- **Summary**



WHY A MATERIALS ROADMAP?

Successful FHR/TMSR commercial deployment must depend on overcoming multiple materials challenges.





The MSRE experience at ORNL provides a solid foundation for overcoming the materials challenges.

- Nearly 10 years of Molten Salt Reactor Experiment (MSRE) development:

- 1960: MSRE effort started; construct the reactor by 1964.
- The experiment reactor went critical in 1965.
- Operated to support various experiments until 1969.

HAPPY 50 YEARS ANNIVERSARY!



- Major structural materials were successfully developed and tested.
- Reactor components fabrication techniques, materials in/out-pile testing.
- Experiment procedures development and results documentation.

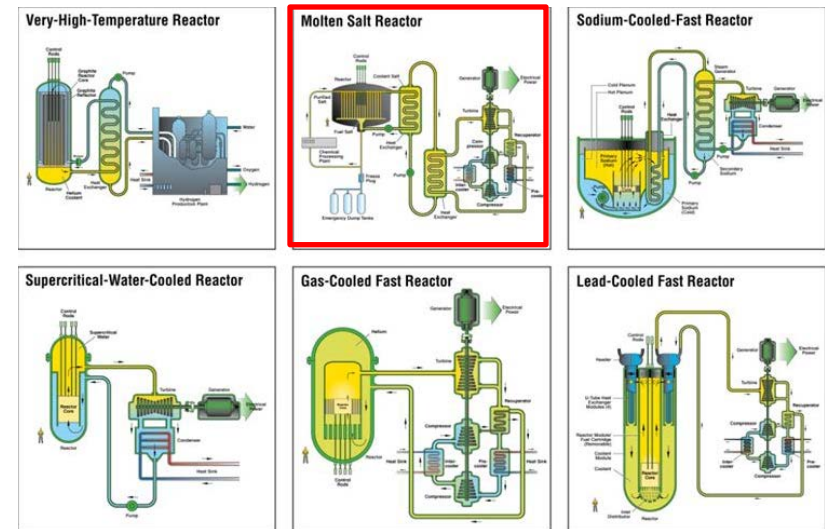
- Many MSRE participants are still available for consultation, but time is of the essence.



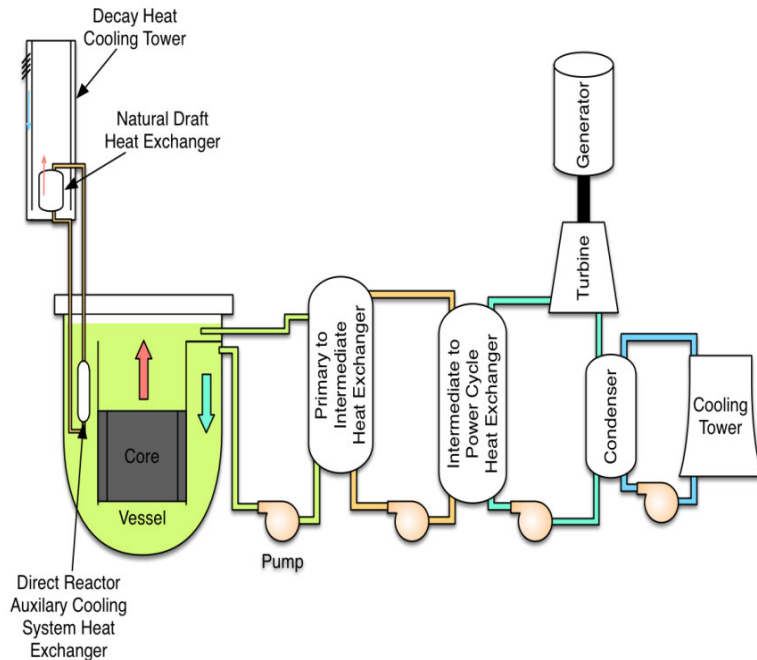


As a Gen IV reactor concept, FHR/TMSR poses many more materials challenges than MSRE. (1)

- Large commercial size components and product forms.
 - *Property stability, manufacturability, and codification*
- High temperature for energy efficiency
 - 700°C  850°C  1000°C
- Long design life for 60 years of high-temperature operation.
 - *Creep and creep-fatigue limit FHR/TMSR operation temperature.*
- Aggressive corrosion in high temperature liquid salts.
 - *Accelerated component structure deterioration impairs component integrity.*



As a Gen IV reactor concept, FHR/TMSR poses many more materials challenges than MSRE. (2)



- **New material types**
 - *SiC/SiC, C/C, CFC, sintered SiC, advanced structural and functional alloys and graphite grades*
- **New salt technologies**
 - **Chemical stability, material compatibility**
- **New nuclear safety requirements**
 - **Material strength, stability, and life prediction**

To strive for FHR/TMSR commercialization in the 2030 timeframe, multiple years of materials R&D effort are required.

It is essential to have a roadmap at the beginning of the long journey for FHR/TMSR materials R&D.

- **Holistic guidance with clear direction and goals to avoid groping forward in the dark**
 - *Planned course of action, not hodge-podge “to do” lists*
- **Systematic and consistent focus on well-defined objectives**
 - *No unnecessary redundancies, no impromptu diversions*
- **Effective coordination and leverage of stakeholder efforts**
 - *Government, industry, and academia*
 - *Domestic and international*
- **Basis for progress management**
 - *All participants on the same page via efficient communication*
 - *Optimize the use of available resources*



Roadmap development allows systematically analysis of challenges and planning for solutions.

- **Start with realistically identifying technology challenges to materials development for FHR/TMSR.**
 - *All the foreseen challenges will be scrutinized for significance to the eventual commercial deployment of FHR/TMSR.*
 - *Issues and problems will be prioritized for considering the course of R&D action.*
- **Carefully evaluate and rank viability and effectiveness of all approaches proposed for possible solutions.**
 - **Opinions from multiple experts included.**
- **Define strategies and tasks for achieving the envisioned solutions.**
 - *Initial Go/No-go tasks will be formulated to rule out ineffective approaches as early as possible.*





Currently eight material topic areas have been identified for roadmap consideration.

- Metallic materials
 - Composite materials
 - Graphite materials
 - Materials irradiation
 - Salt technologies
 - Materials joining
 - Functional materials
 - New alloys development
- A team of subject matter experts must be organized to support R&D activities in the identified topic areas.
 - *Team members are being identified at ORNL and SINAP.*
 - *More experts will also be added from academia, industry, and national laboratories as needed.*



Key team members will participate in developing the roadmap during FY 2016.



CHALLENGES, MSRE LEVERAGE, AND SOLUTIONS DEVELOPMENT



Structural alloys are challenged by a combination of high temp strength and corrosion resistance.

- **Structural alloys are needed for various components, large and small, in the commercial FHR/TMSR system.**
 - *Nuclear island, conventional island, and balance of plant*
 - *Components facing major challenges include reactor vessel, coolant circulation loop piping, heat exchanger, valves, and pumps.*
- **Majority of existing engineering structural alloys cannot resist the prospective FHR/TMSR service environments.**
 - *Most high temperature alloys are developed for high strength without the desired corrosion resistance to the FHR/TMSR salt environments.*
- **Commercial deployment requires qualification of alloys for nuclear applications by recognized codes and standards.**
 - *Time-consuming data generation is required for codification.*
 - *Some FHR/TMSR design rules may not exist in codes or standards.*



Hastelloy N invented at ORNL for MSRE provides a solid baseline for development of the FHR/TMSR.

- **The alloy performed successfully during five years of service in the MSRE operation.**
 - *Salt was loaded in 1964; nuclear operations ended in December 1969.*
 - *The alloy withstood 2-1/2 years of cumulative fuel loop circulation.*
 - *Various components were fabricated and evaluated on the testing reactor scale.*
- **Commercial use of the alloy for non-nuclear applications.**
 - *Codified for ASME BPVC Section III up to 704°C.*
- **Challenges still exist for deploying the alloy in commercial FHR/TMSR use.**
 - **Nuclear applications, particularly with the desired 60-year Gen IV reactor design life for ASME BPVC Section III codification and associated developments, considerable efforts are required.**
 - **For operation above 704°C, Hastelloy N performance deteriorates.**

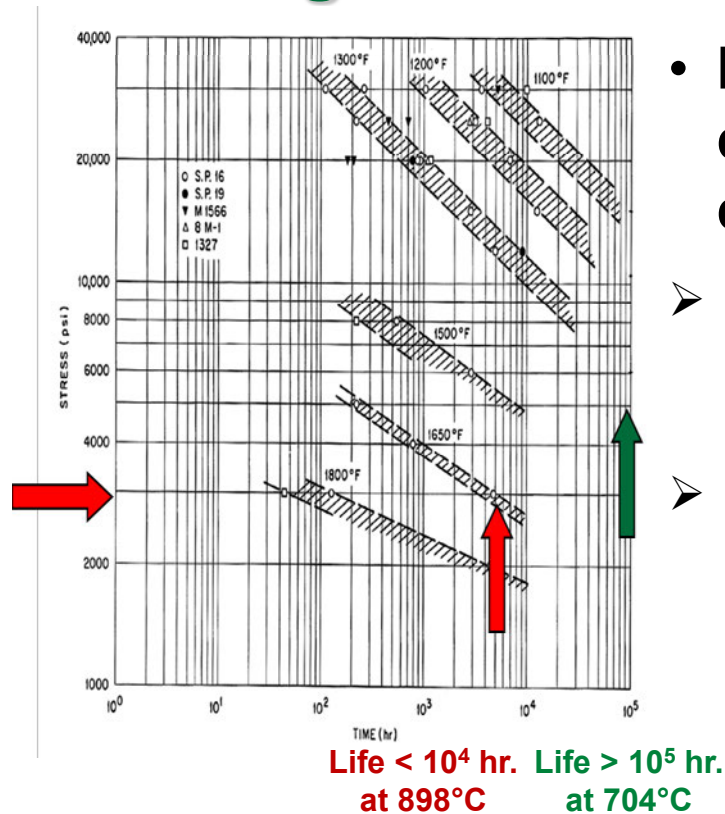


Several approaches for addressing the challenges facing structural alloys for FHR/TMSR (1)

- **International collaboration for data generation/collection for nuclear codification of Hastelloy N (UNS N10003)**
 - *Combine existing data from MSRE and U.S. industries with new data from SINAP on GH3535 (UNS N10003) and any other sources.*
 - *Initially develop a limited-term, extendable ASME Code Case to support testing reactor design and construction.*
- **Cladded high-temperature, high-strength alloy for long-term performance in liquid fluoride salts**
 - *Clad pure Ni on Incoloy 800H or other superalloys for a combination of high temperature strength and corrosion resistance.*



Several approaches for addressing the challenges facing structural alloys for FHR/TMSR (2)

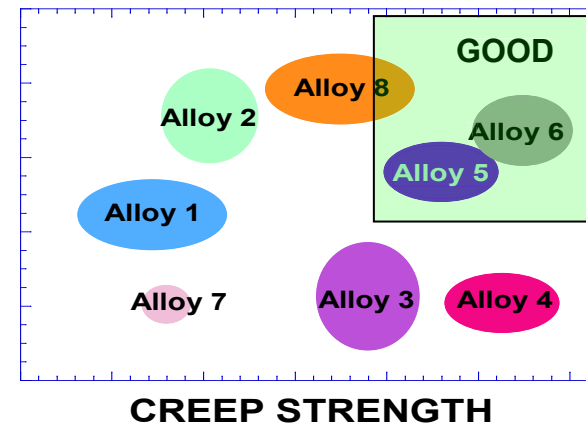


- Development of new alloys with combined high temperature and corrosion resistance for FHR/TMSR
- Existing Ni-based superalloys with good creep strength at high temperatures have poor resistance to fluoride salt.
- Chromium added for oxidation resistance is detrimental to resistance to liquid fluorides.

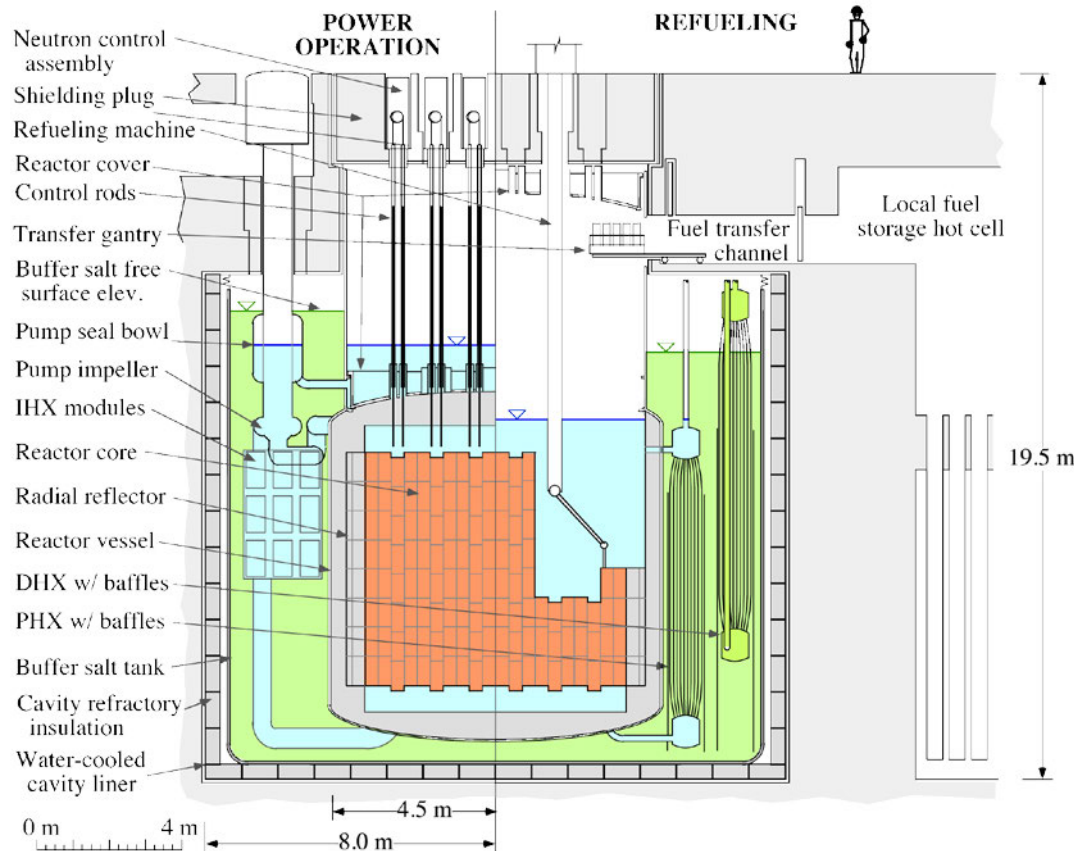
- Reinvestigating feasibility of 316 stainless steel

➤ *University of Wisconsin*

RESISTANCE TO LIQUID SALT



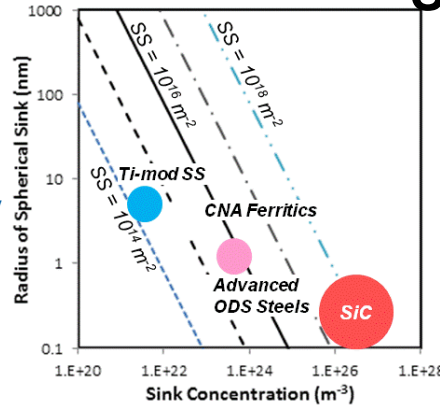
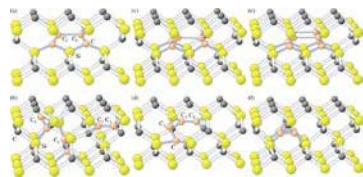
Advancement in composite technology provides material options not available in the MSRE era.



- **Core barrel and other internals**
 - *C/C for 850 ~ 1000°C*
 - *SiC/SiC for 1000°C*
- **Control rods and internal drives**
 - *C/C for 700 ~ 1000°C*
- **PHX and DRACS**
 - *C/C, SiC/SiC, and Monolithic SiC for 1000°C*

Investigation of composite use in FHR/TMSR can leverage studies on the material for other areas.

SiC self-stabilizes during irradiation: radiation-induced radiation insensitivity



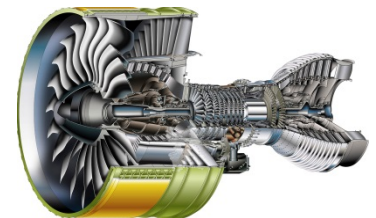
SiC/SiC for Gen IV reactor concepts

Reactor Concept	Application	Operating Condition	Project / Design Examples	Possible Deployment
Fusion	• Blanket structures • Various functions	• He, Pb-Li • 400-900°C • >50 dpa	• ARIES • EU-PPCS • DREAM	• Long-term
HTGR VHTR	• Reaction control systems • Core support	• He • 600-1100°C • Up to ~40 dpa	• NGNP • PBMR • GT-HTR300C	• Near-term
LWR	• Channel box • Grid spacer • Fuel cladding	• Water • 300-500°C • ~10 dpa	• PWR (WHC) • BWR (EPRI)	• Mid-term? (ATF)
FHR AHTR	• Core structures • RCS	• Liquid salt • ~700°C • >10 dpa	• AHTR • DOE IRP • SMR's	• Long-term
SFR	• Core structures • Fuel cladding/support	• Liquid sodium • 500-700°C • >100 dpa	• CEA	• Long-term
GFR	• Core structures • Fuel cladding/support	• He • 700-1200°C • >100 dpa	• CEA • GA EM ²	• Long-term

ASME Code qualification for high temperature reactors in progress



Increased applications for SiC/SiC in aircraft engines



R&D needs for composites are being defined for development of the materials roadmap.

Category	Near Term R&D Needs
Technology Development Roadmap	<ul style="list-style-type: none"> Develop updated Composite Technology Development Roadmap Define technological readiness levels for key elements
Design & Qualification	<ul style="list-style-type: none"> Develop ASME design code and necessary standards Define specific requirements and start developing supplemental C&S document
Radiation Effects	<ul style="list-style-type: none"> Confirm integrity retention for entire life envelope (SiC/SiC) Determine life envelope (C/C)
Environmental Effects	<ul style="list-style-type: none"> Examine compatibility Examine synergistic effects of radiation
Manufacture and Integration	<ul style="list-style-type: none"> Develop integration technology for large components Start addressing radiation and environmental effects on integrated elements

Category	Long Term R&D Needs
Technology Development Roadmap	<ul style="list-style-type: none"> Refine Technology Development Roadmap
Design & Qualification	<ul style="list-style-type: none"> Develop supplemental C&S document to meet specific needs
Manufacture and Integration	<ul style="list-style-type: none"> Advance manufacture technologies Establish integration technology Address radiation and environmental effects on integration elements
NDE and ISI	<ul style="list-style-type: none"> Establish NDE and in-service inspection
Radiation and Environmental Effects	<ul style="list-style-type: none"> Determine performances of advanced material options Develop predictive capability for material evolutions Establish chemical compatibility in integrated environment



Graphite plays important structural and functional roles, and its challenges must be fully addressed.

- **Graphite corrosion caused by the salt**
 - *Surface structural damage and reduction of properties*
 - *Penetration of salt in pores, cracking*
 - *In-pore salt-graphite interactions*
- **Irradiation behavior of selected graphite**
 - *Dimensional and property changes*
 - *Creep effects on properties*
- **Tritium retention in graphite**
 - *Excessive tritium inventory*
 - *Safety and decommissioning issues*





Investigation of graphite can draw upon previous experience and historical accomplishments.

- **Graphite corrosion caused by the salt**

- *Unprotected graphite does corrode in fluoride salts at 500 ~ 600°C.*
- *Protection layers (pyrolytic and/or glassy carbon) provide better corrosion resistance.*

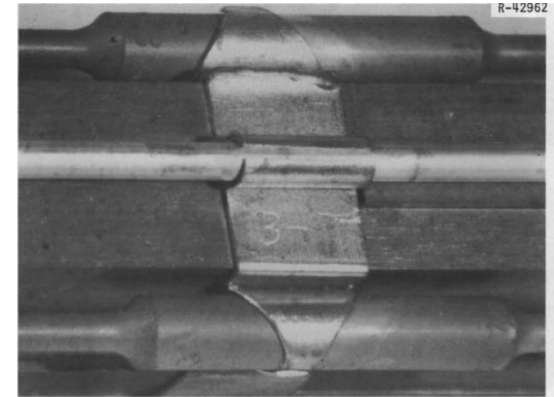


Fig. 1. Graphite and Hastelloy N Surveillance Assembly Removed from the Core of the MSRE After 72,400 Mwhr of Operation. Exposed to flowing salt for 15,300 hr at 650°C.

- **Irradiation behavior of selected graphite**

- *Damage mechanism is understood based on historical data.*
- *Grade-specific data for irradiation effects are needed.*

- **Tritium retention in graphite**

- *Adsorption and diffusion of tritium in graphite has been studied in connection with fusion reactors.*
- *Tritium decorates high energy sites in graphite and defective lattice sites in irradiated graphite.*

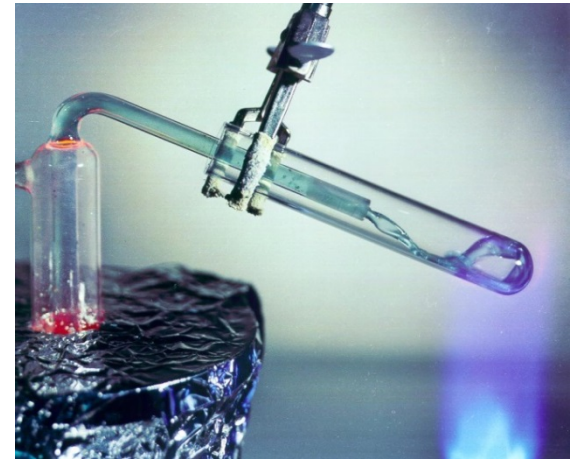


Approaches and possible resolutions are being formulated for development of the roadmap.

- **Define graphite types (small pores) and coating**
 - *Will matrix graphite be used (TRISO fuel)?*
 - *Adherent, impermeable, stable on graphite?*
- **Study of (coated) graphite/molten fluoride salt interactions**
- **Determine irradiation behavior of selected graphite**
 - *Stability of coating under irradiation conditions*
- **Investigate tritium retention and surface interactions on coated graphite**
- **Study irradiation damage effects on dimensions, properties, tritium retention, and corrosion resistance**
- **Qualify graphite for FHR/TMSR for recognized codes and standards**

Fluoride salts pose considerable challenges to materials not present in other reactor concepts. (1)

- Heat exchangers: salt to salt, salt to working fluid for power generation (WFPG)
 - *Materials with fluoride salt corrosion resistance, and tensile strength and creep resistance at high temperature*
 - *Materials with fluoride salt corrosion resistance, WFPG corrosion resistance, and tensile strength and creep resistance at high temperature*
- Materials for controlling/directing tritium
 - *Compatible with fluoride salt at temperature (with or without redox control)*
 - *Permeable to tritium with rapid kinetics*
 - *Suitable for tritium stripping structures*
- Nuclear grade graphite
 - *Very low porosity and not wetted by the fluoride salt (with or without redox control)*



Fluoride salts pose considerable challenges to materials not present in other reactor concepts. (2)

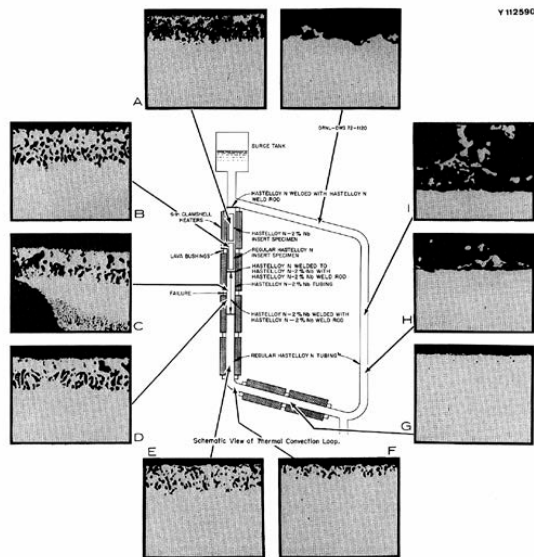
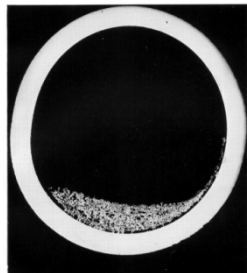


Fig. 11. Micrographs of tubing and specimens from loop 1255 exposed to LiF-23 mole % BeF₂-5 mole % ZrF₄-1 mole % ThF₄-1 mole % UF₆ molten salt at 560-700°C for 9.2 years. As polished. 500x. Reduced 15%.

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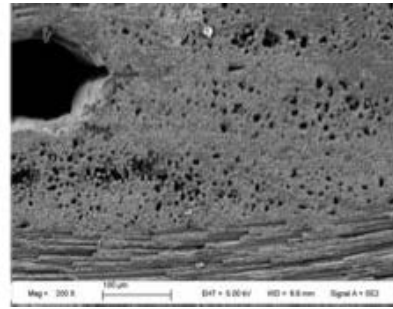
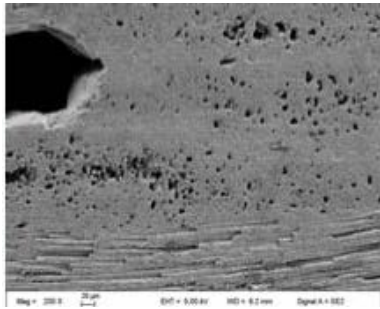


Cr deposits in loop cold leg

- **Loop of coolant**
 - *Attack and void formation in hotter area*
 - *Deposition in cooler regions*
- **Pumps and valves**
 - *Materials with fluoride salt corrosion resistance and creep resistance at temperature, and cavitation resistance*
 - *Materials compatible with fluoride salts at temperature for seals*
- **Reactor vessel**
 - *Materials with fluoride salt corrosion resistance, and moderate tensile strength and creep resistance at temperature*

Fluoride salts pose considerable challenges to materials not present in other reactor concepts. (3)

- Silicon carbide compatibility with fluoride salts largely depends on purity and stoichiometry
 - Free silicon readily forms SiF_4
 - Binder phase oxides readily dissolve in fluoride



CVI SiC composites exhibit small weight loss

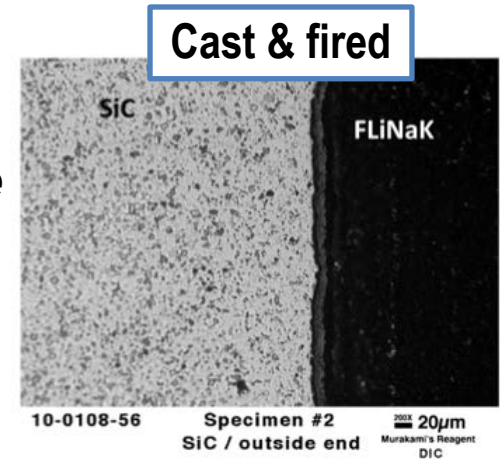
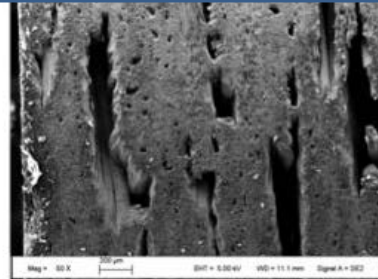
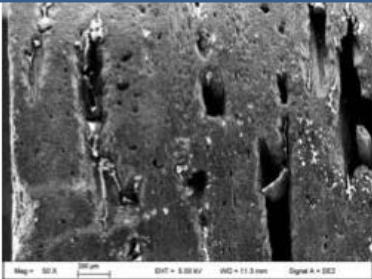
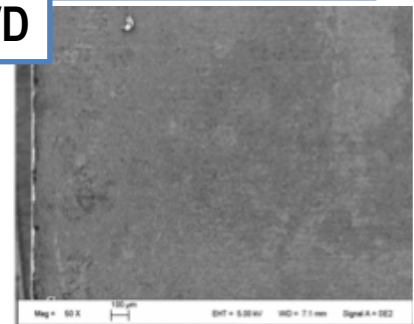
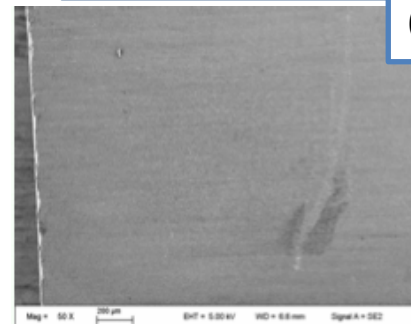


Fig. 6. SiC specimen after 90 day exposure to 700 °C FLiNaK salt.

High purity SiC exhibits little corrosion





Several other salt technologies must also be developed for commercial FHR/TMSR deployment.

- **Fluoride salt cleanup technology**
 - *Establish optimal gas ratios and flow rates, treatment duration, and filtration for cleaning salt*
 - *Establish techniques to monitor treatment progress and endpoint*
 - *Develop on-line techniques for monitoring salt chemistry*
- **Fluoride salt chemical analysis**
 - *Establish techniques to digest salts*
 - *Develop spectroscopic techniques for analysis of salt impurities*
- **Redox control of fluoride salts**
 - *Identify and demonstrate redox control buffers*
 - *Develop electrochemical techniques to assist in redox control*
- **On-line salt flow rate monitoring**
 - *Develop high temperature flow meter*

Material properties deterioration from radiation effects were reported from the MSRE operation.

- **Hastelloy N deteriorated from thermal fluence in MSRE.**
 - *1.3×10^{19} neutrons/cm² and 1.3×10^{20} neutrons/cm²*
 - *Creep rupture strain was reduced 10 ~ 20 times, from 20 ~ 40% to 1.5 ~ 2.2*
 - *Extensive carbide precipitation on grain boundaries*
- **Fission product Tellurium caused shallow intergranular cracking in Hastelloy N.**
- **Attempts were made to minimize deterioration from irradiation.**
 - *Addition of 1-2%Nb alleviated irradiation embrittlement and intergranular cracking.*
 - *Addition of 2%Ti, or 1-4%Nb, or 1%Ti+1%Nb improved post-irradiation creep properties.*
 - *Addition of Zr and Ti helped maintain the properties in coarse grain size.*



For commercial deployment of FHR/TMSR, more studies on irradiation effects must be planned.

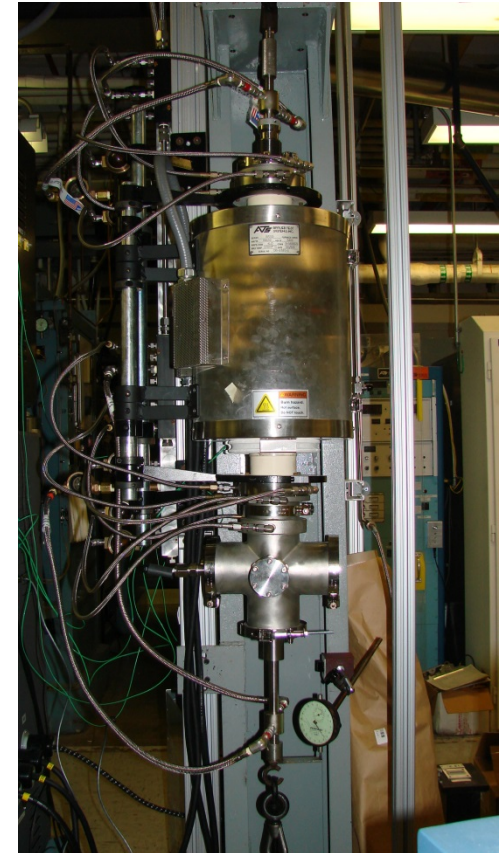
- Irradiation investigation of Hastelloy N / GH3535 (UNS N10003)
 - *Provide additional data to understand and quantify irradiation effects*
 - *Establish protocol for future new materials irradiation investigation*
- Irradiation investigation of graphite materials
- Irradiation investigation of composite materials
 - *Overlap tasks with those under the graphite materials topic*





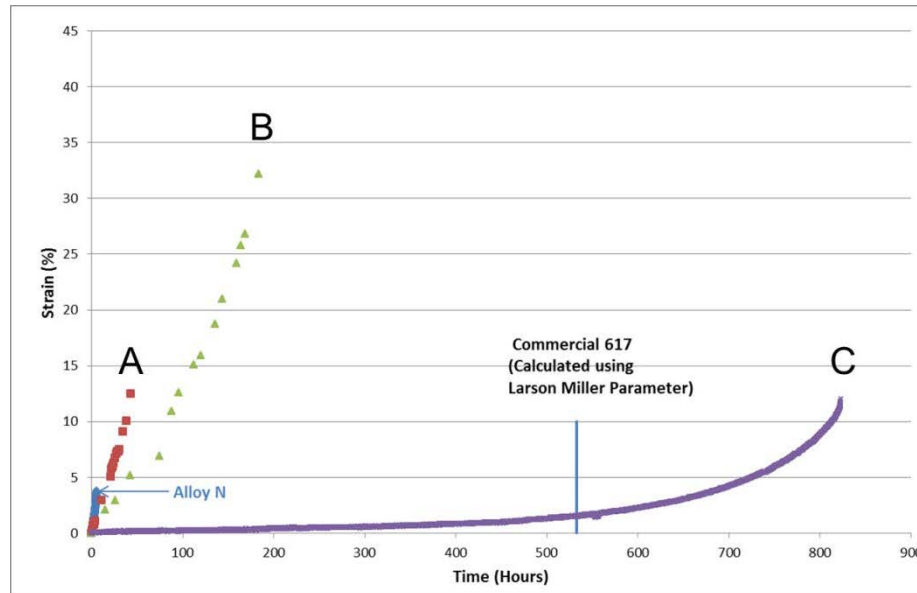
New alloy development is a very challenging topic area that cannot be ignored for FHR/TMSR.

- To operate above 704°C for thermal efficiency, new alloys are needed.
- Specific systems for testing alloys in fluoride salts at high temperature must be further developed.
- Tests of large heats, long-term creep properties, and salt resistance must be conducted.
- Loop and component fabrication and testing are required.
- Qualification by recognized codes and standards for nuclear applications must be completed.

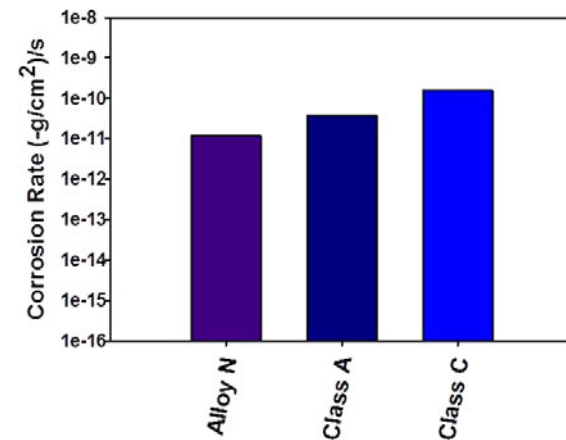


New alloy development can leverage preliminary accomplishments in some ORNL LDRD projects.

- Creep resistance of new alloys at 850°C and 12 ksi in inert atmosphere is significantly better than that of Hastelloy N.
 - *Potential to improve lifetimes by > 10X in components for low stresses*
 - *Key enabling materials for components at high stresses*



1000 h Exposures at 850°C: Weight Loss



Alloy N: Commercial heat (Vacuum processed)

Alloy A and C: Lab-processed in inert atmosphere



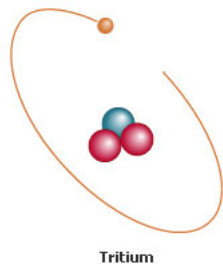
Weld is usually the weakest link in structural integrity of high temperature systems.

- **Weld joint performance assessment methodology**
 - *Weld microstructure effects on long-term performance of Hastelloy N, especially in critical joints such as pipe to plate, multi-pass and intersection cross welds vulnerable to premature failure.*
- **Weldability of new alloys developed for FHR/TSMR**
 - *Filler metals and welding procedures must also be developed.*
- **In-situ synchrotron, neutron, and simulation investigation of weldment design and fabrication**
 - *Understand formation and evolution of weld microstructure and weld residual stresses governing long term performance and structure integrity of welded components.*



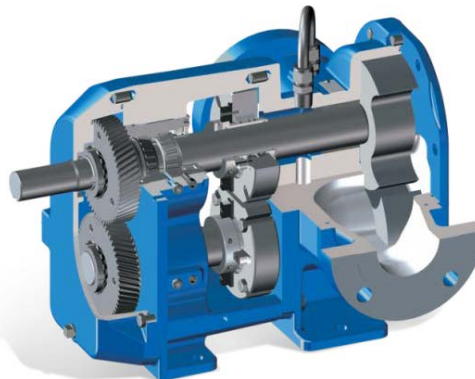
Functional materials also play an important role in FHR/TMSR operation and safety.

- Melt point trigger alloy development
 - *Selection, design, and demonstration of melt point trigger alloys*
- Non-galling valve parts
- Pump shaft bearings & seals
- Tritium control elements



Tritium

- Proton
- Electron
- Neutron



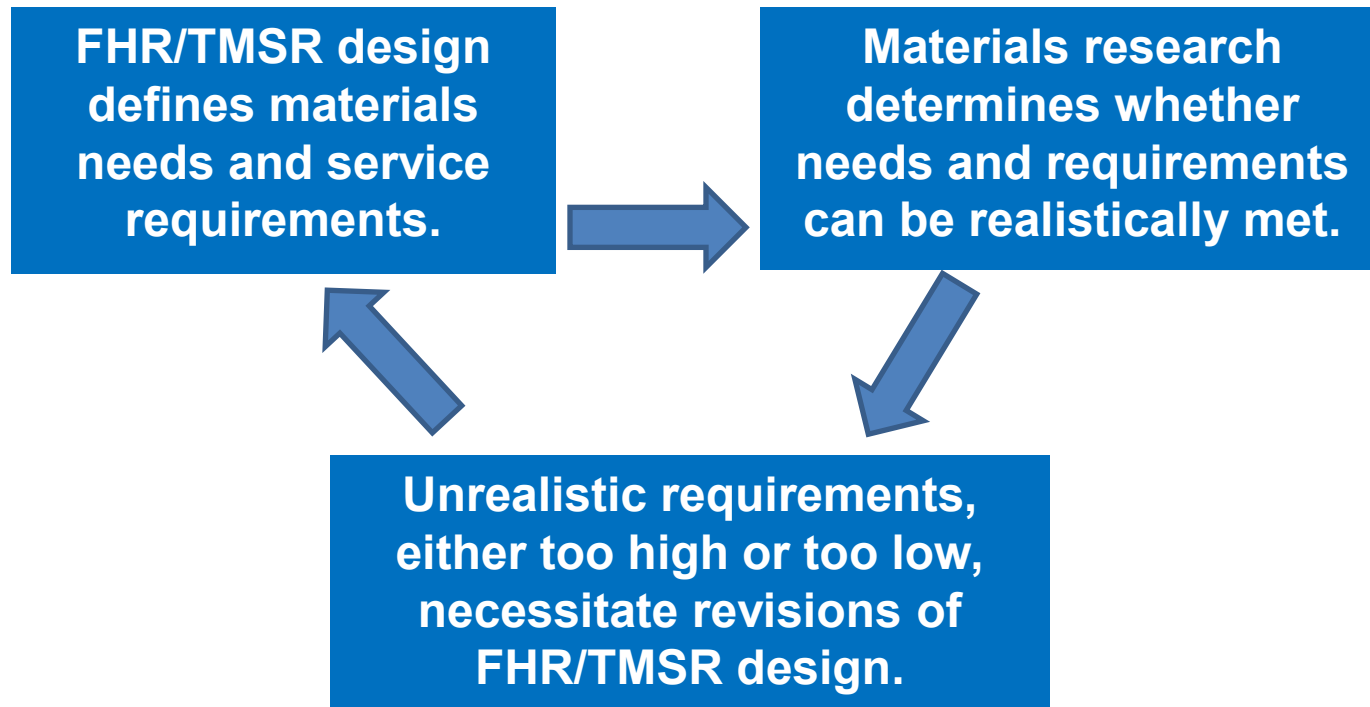


ROADMAP STRATEGY



The materials roadmap will be developed to facilitate and optimize the evolution of FHR/TMSR design.

- Iteration between FHR/TMSR design and material capacity research will drive realistic, feasible, and timely development.



- The iterative process may not immediately lead to a final decision, but eventually both sides should reach an optimal balance.



The development will include several key steps to ensure the roadmap is defensible and practical.

- **Development approach**

- *Review FHR/TMSR conceptual design to provide a good understanding of materials needs and requirements.*
- *Identify potential materials problems and issues.*
- *Propose approaches and possible solutions to define R&D tasks.*
- *Identify subject matter experts to write specific technical topics.*

- **Roadmap structure**

- *The body of the roadmap will focus on component-oriented materials challenges, possible solutions, proposed approaches, and goals.*
- *Topic-area-specific appendices will establish tasks and objectives that are adjustable within the constraints defined by the roadmap body.*

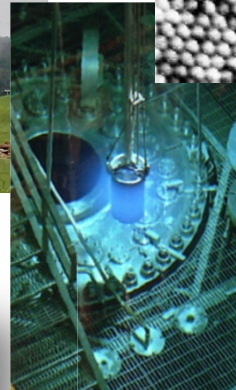
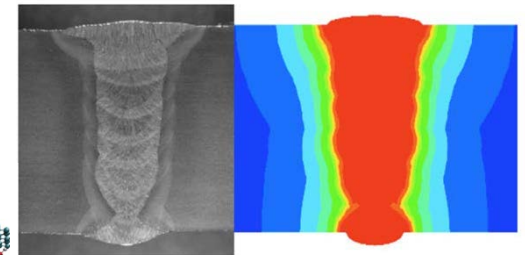
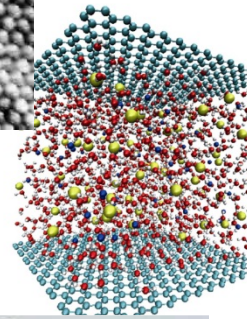
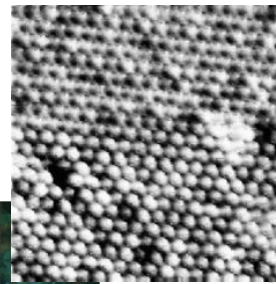
- **Revisions and management**

- *The roadmap is document that allows periodic reviews and fine tuning in updated versions to address emerging issues and problems.*

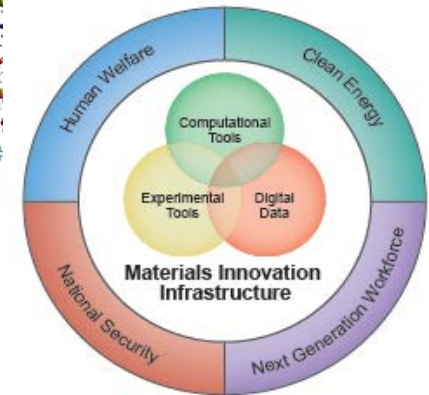


The materials roadmap will draw heavily upon MSRE experience and leverage modern technologies.

- The wealth of MSRE reports and data will be fully explored.
 - *Historical documents and data collection are already underway.*
- All applicable modern technologies will be considered.



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**Integrated Computational
Materials Engineering**



Summary

- **Almost 10 years of MSRE activities 50 years ago generated a wealth of experience, expertise, and information that will be fully explored for today's FHR/TMSR development.**
- **As a Gen IV reactor concept, FHR/TMSR poses many more materials challenges than MSRE that must be overcome with clearly defined goals, well-planned courses of action, and effectively coordinated domestic and international efforts.**
- **ORNL is ready to lead the development of a materials roadmap and provide guidance to the path ahead for a successful FHR/TMSR endeavor.**



THANK YOU FOR YOUR ATTENTION.

Contact: Weiju Ren, renw@ornl.gov, 865/576-6402