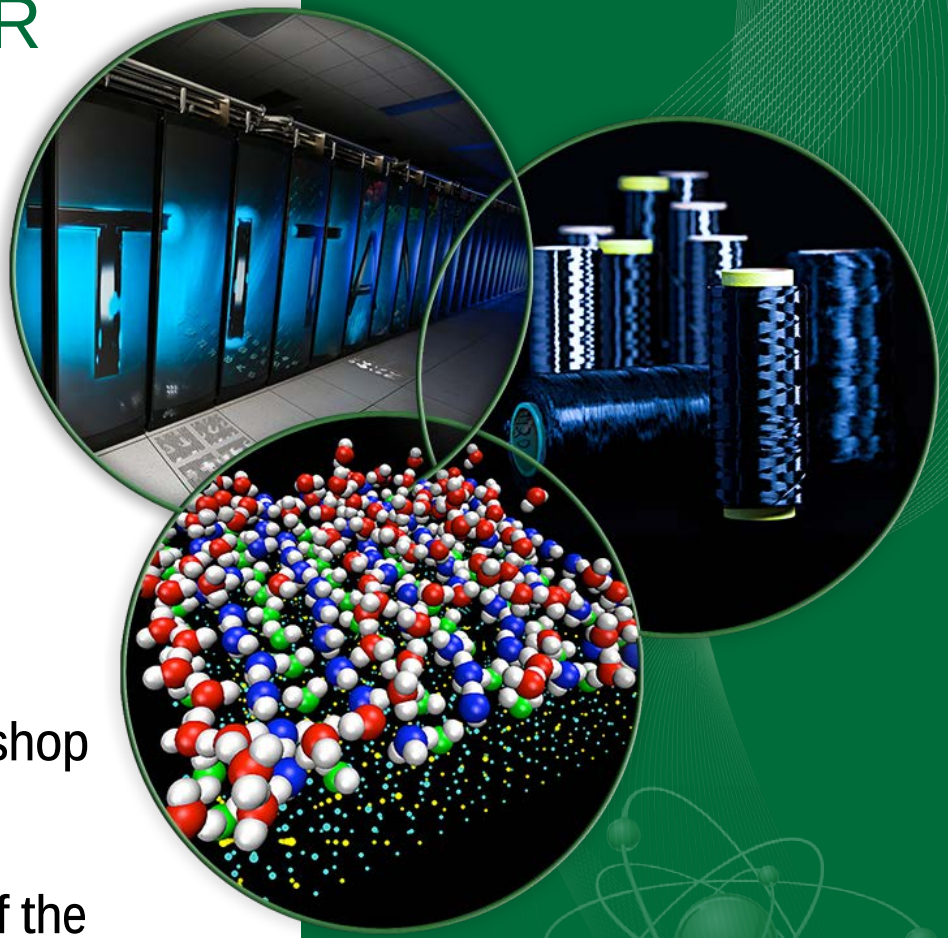
The Path Ahead - Materials Roadmap for FHR/TMSR Development



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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

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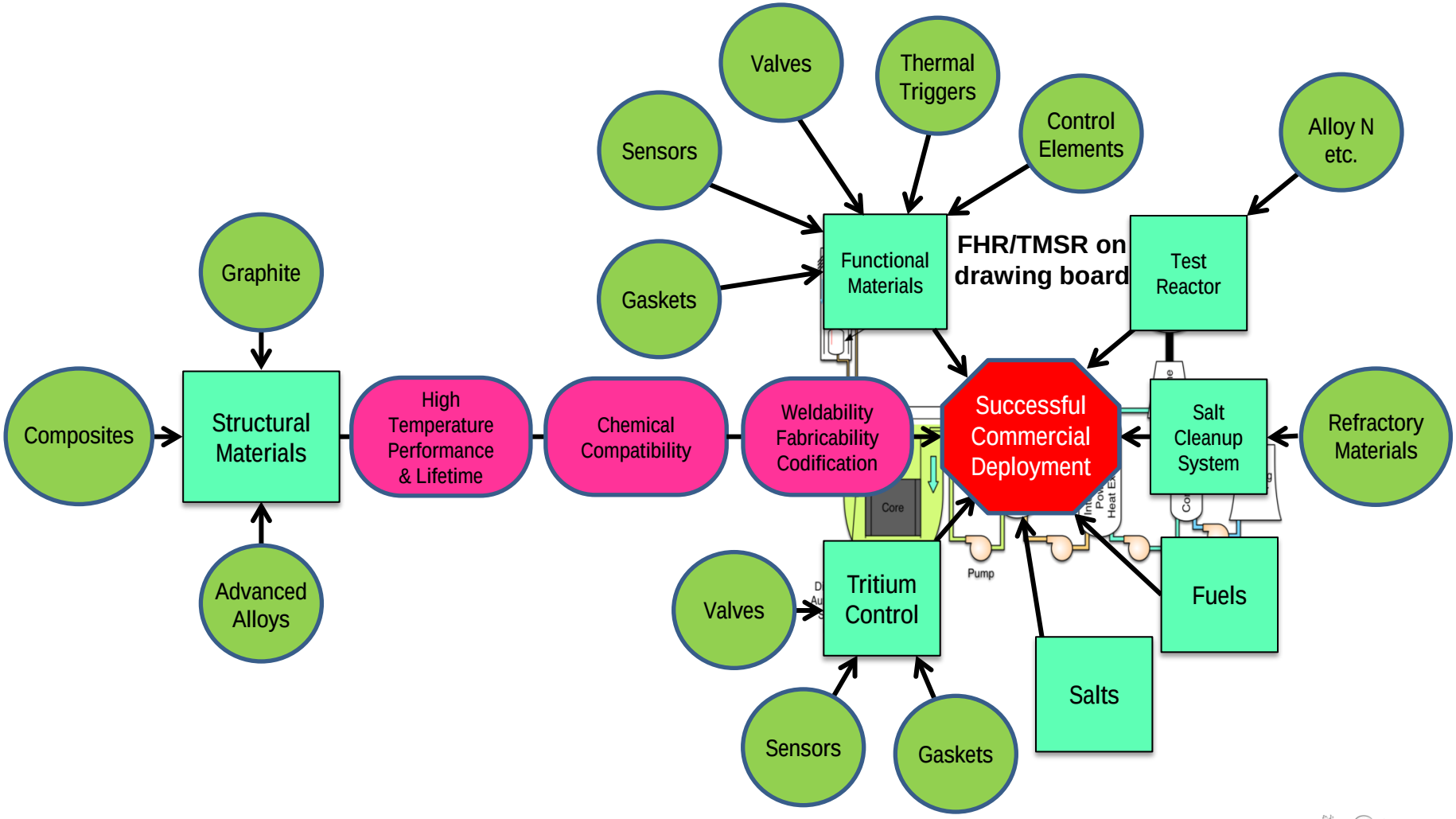
OUTLINE

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

WHY A MATERIALS ROADMAP?

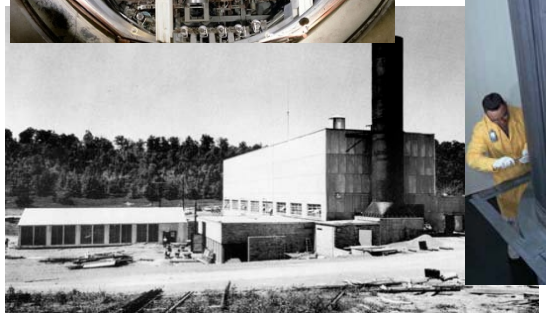
Successful FHR/TMSR commercial deployment must depend on overcoming multiple materials challenges.



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

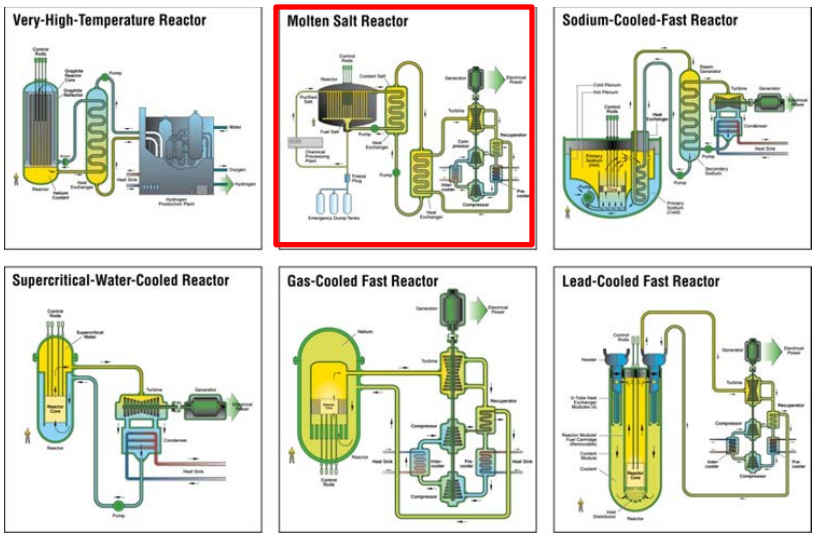
- **Nearly 10 years of Molten Salt Reactor Experiment (MSRE) development:**
  - ***1960: MSRE effort started; construct the reactor by 1964.***
  - ***The experiment reactor went critical in 1965.***
  - ***Operated to support various experiments until 1969.***
- **Major structural materials were successfully developed and tested.**
  - ***Reactor components fabrication techniques, materials out-pile testing.***
  - ***Experiment procedures development and results documentation.***
- **Many MSRE participants are still available for consultation, but time is of the essence.**

HAPPY 50 YEARS ANNIVERSARY!

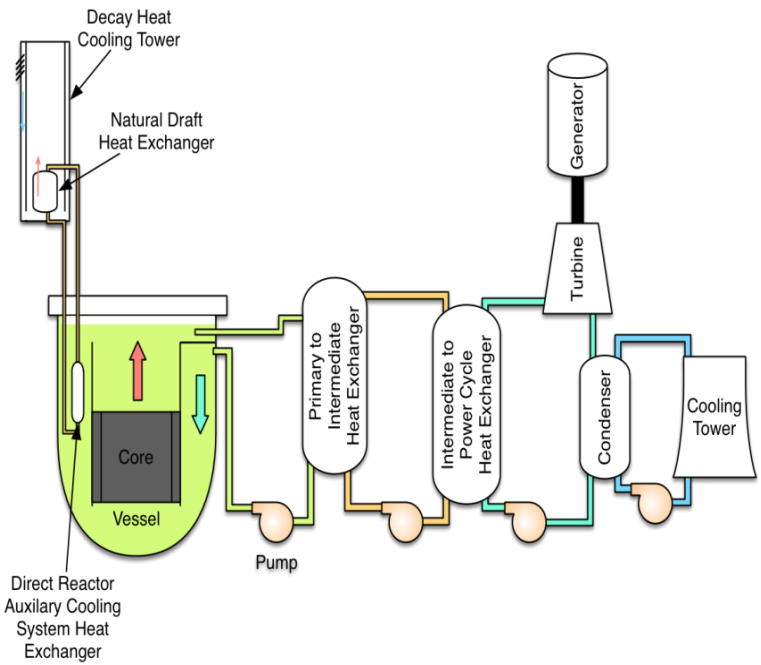


As a Gen IV reactor concept, FHR/TMSR poses many more materials challenges than MSRE. (1)

- **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.***

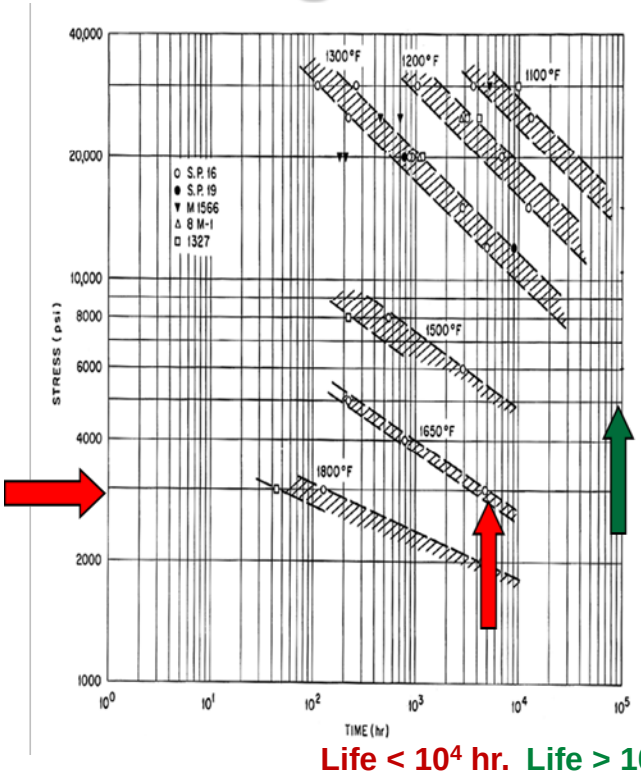
Hastelloy N invented at ORNL for MSRE provides a solid baseline for development of the FHR/TMSR.

- **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 IIIV up to 704°C.***
- **Challenges still exist for deploying the alloy in commercial FHR/TMSR use.**
  - **Nuclear applications require considerable efforts, particularly with the desired 60-year Gen IV reactor design life, for ASME BPVC Section III codification and associated developments.**
  - **For operation above 704°C, Hastelloy N performance deteriorates.**

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

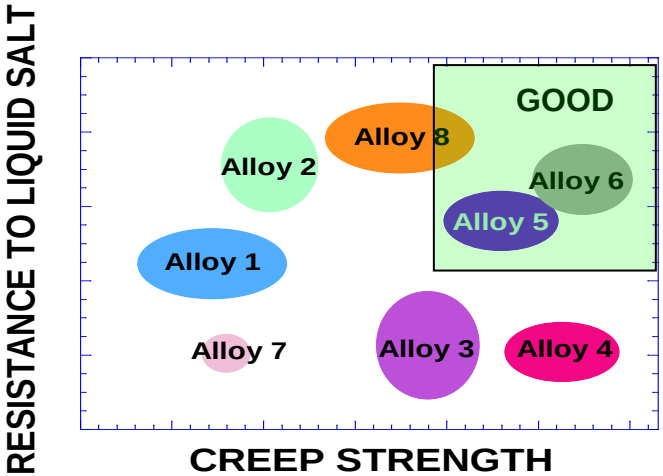
- **International collaboration for data generation/collection for nuclear codification of Hastelloy N**
  - ***Combine existing data from MSRE and U.S. industries with new data from SINAP on GH3535 (UNS N10003) and any other sources.***
  - ***Initially develop a limited-term, extendable ASME Code Case 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)



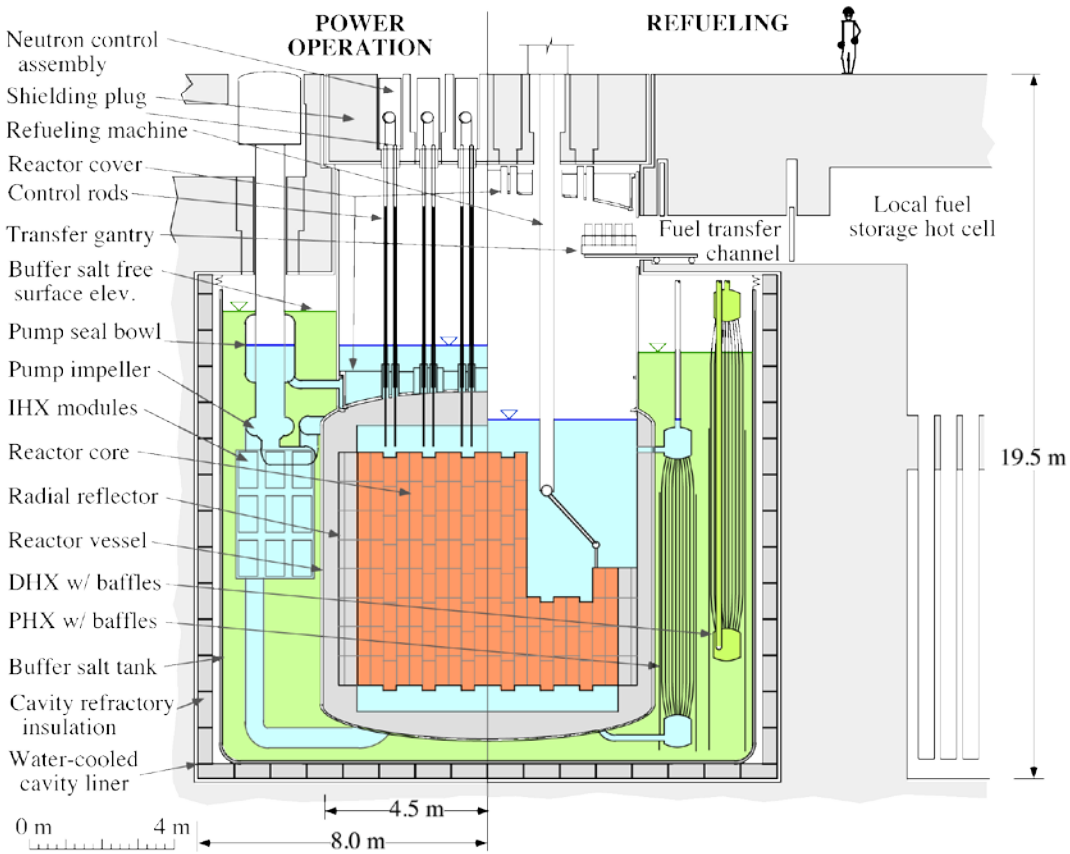
Life < 10^4 hr. at 898°C Life > 10^5 hr. at 704°C

- **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***

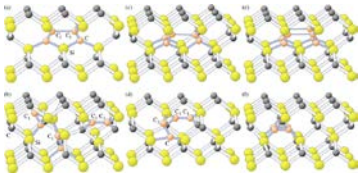
Advancement in composite technology provides material options not available in the MSRE era.

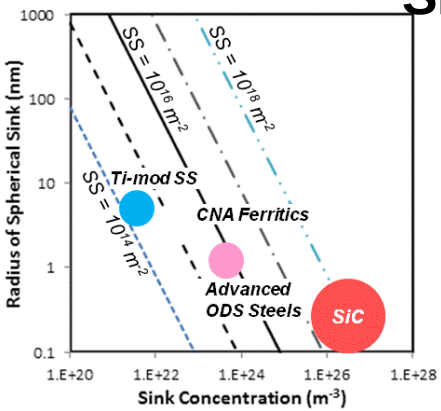


- **Core barrel and other internals**
  - ***C/C for 850 ~ 1000°C***
  - ***SiC/SiC for 1000°C***
- **Control rods and internal drives**
  - ***C/C for 700 ~ 1000°C***
- **PHX and DRACS**
  - ***C/C, SiC/SiC, and Monolithic SiC for 1000°C***

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 EM²	• Long-term

ASME Code qualification for high temperature reactors in progress

Article HHB-2000
CERAMIC COMPOSITE MATERI
(Draft 3–July 2013)

HHB-2100 GENERAL REQUIREMENTS

HHB-2110 CERAMIC COMPOSITE MATERIALS FOR COR

HHB-2111 Permitted Material Specifications

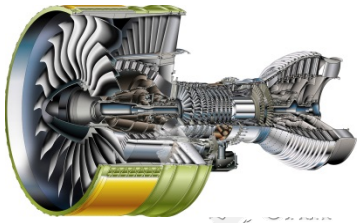
HHB-2112 Special Requirements Conflicting With Permitted Specifications

ARTICLE HHB-3000
DESIGN

HHB-3100 GENERAL DESIGN

Rules for the design of Ceramic Composite Core Components and Graph-

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	• Develop updated Composite Technology Development Roadmap • Define technological readiness levels for key elements
Design & Qualification	• Develop ASME design code and necessary standards • Define specific requirements and start developing supplemental C&S document
Radiation Effects	• Confirm integrity retention for entire life envelope (SiC/SiC) • Determine life envelope (C/C)
Environmental Effects	• Examine compatibility • Examine synergistic effects of radiation
Manufacture and Integration	• Develop integration technology for large components • Start addressing radiation and environmental effects on integrated elements

Category	Long Term R&D Needs
Technology Development Roadmap	• Refine Technology Development Roadmap
Design & Qualification	• Develop supplemental C&S document to meet specific needs
Manufacture and Integration	• Advance manufacture technologies • Establish integration technology • Address radiation and environmental effects on integration elements
NDE and ISI	• Establish NDE and in-service inspection
Radiation and Environmental Effects	• 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.***

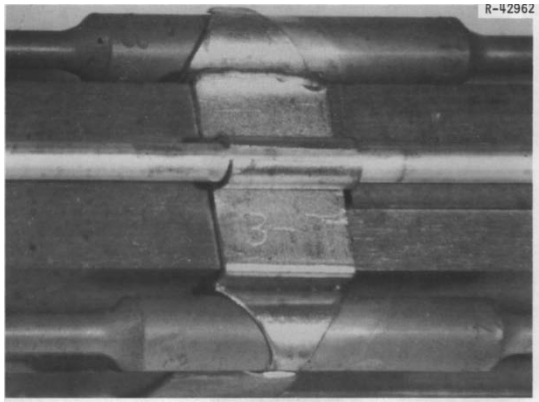


Fig. 1. Graphite and Hastelloy N Surveillance Assembly Removed from the Core of the MSRE After 72,400 Mwhr of Operation. Exposed to flowing salt for 15,300 hr at 650°C.

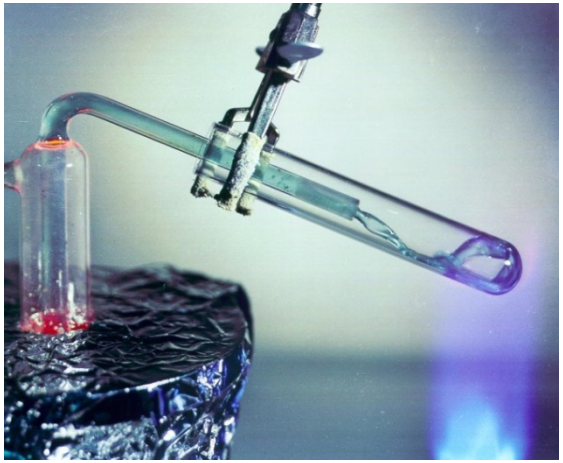
- **Irradiation behavior of selected graphite**
  - ***Based on historical data, damage mechanism is understood.***
  - ***Grade-specific data for irradiation effects are needed.***
- **Tritium retention in graphite**
  - ***Adsorption and diffusion of tritium in graphite has been studied in connection 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 for recognized codes and standards**

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

- **Heat exchangers: salt to working fluid for power generation (WFPG), salt to salt**
  - ***Materials with fluoride salt corrosion resistance, WFPG corrosion resistance, and high tensile strength and creep resistance at temperature***
  - ***Materials with fluoride salt corrosion resistance, plus moderate tensile strength and creep resistance at 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)

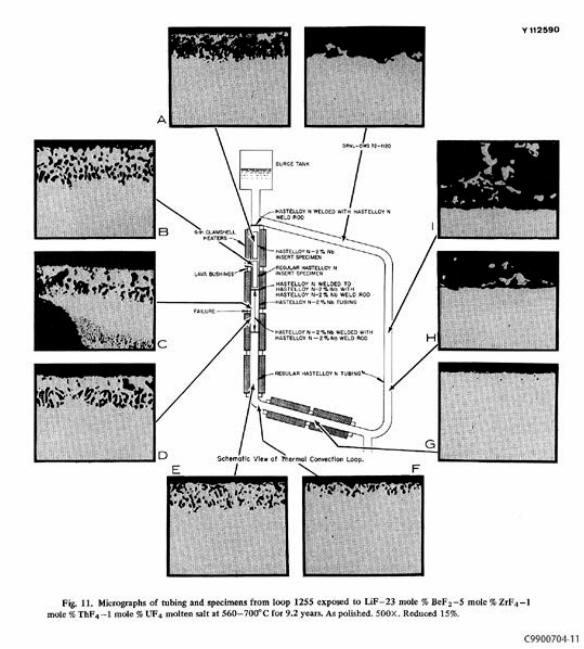
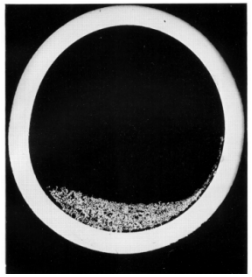


Fig. 11. Micrographs of tubing and specimens from loop 1255 exposed to LiF–23 mole % BeF_2–5 mole % ZrF_4–1 mole % ThF_4–1 mole % UF_4 molten salt at 560–700°C for 9.2 years. As polished. 500×. Reduced 15%.



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***

Cast & fired

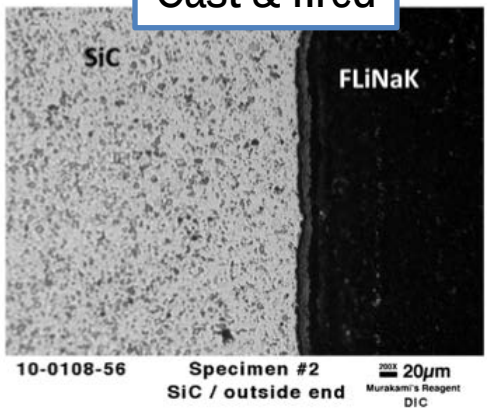
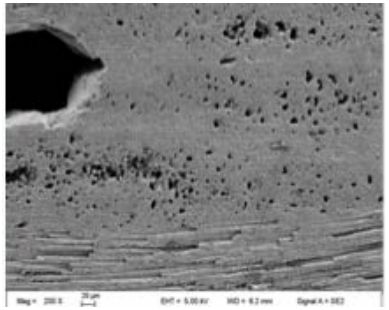
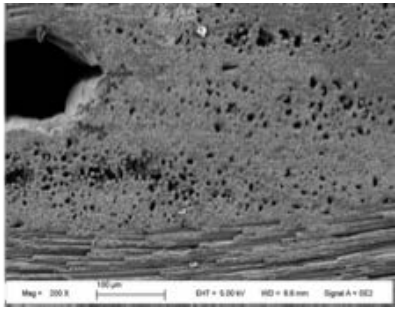
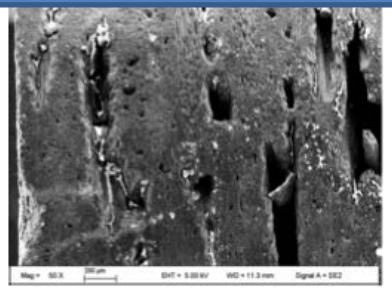


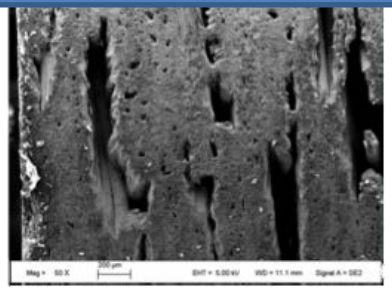
Fig. 6. SiC specimen after 90 day exposure to 700 °C FLiNaK salt.





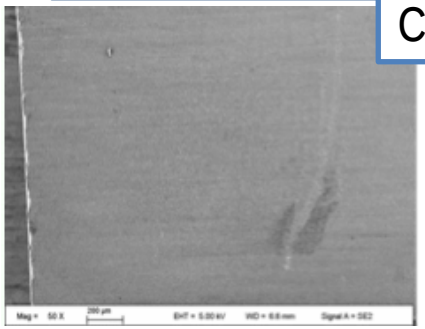
CVI SiC composites exhibit small weight loss

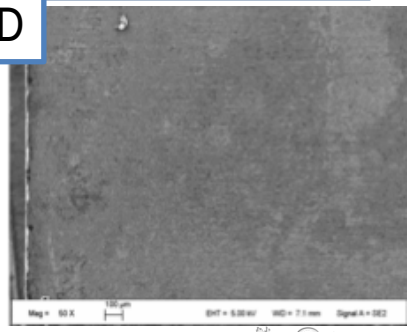




High purity SiC exhibits little corrosion

CVD





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

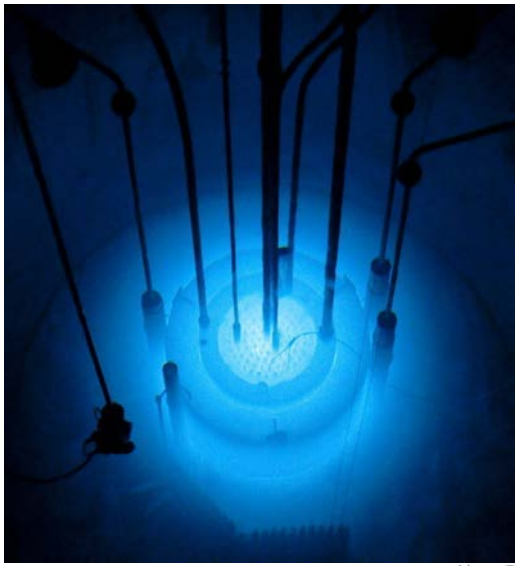
- **Fluoride salt cleanup technology**
  - ***Establish optimal gas ratios and flow rates, treatment duration, and filtration for cleaning salt***
  - ***Establish techniques to monitor treatment progress and endpoint***
  - ***Develop on-line techniques for monitoring salt chemistry***
- **Fluoride 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 x 10^{19} neutrons/cm^2 and 1.3 x 10^{20} neutrons/cm^2***
  - ***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.***

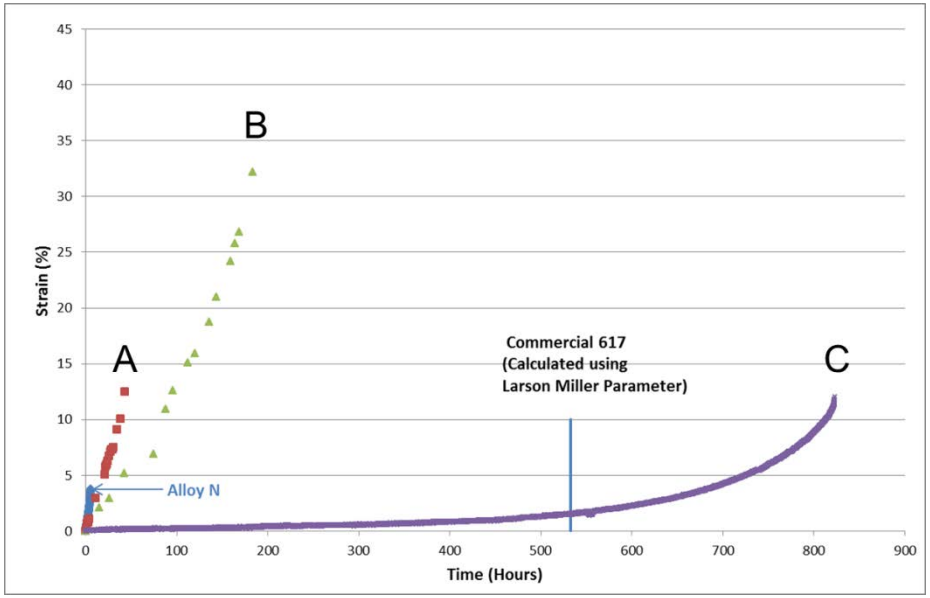
For commercial deployment of FHR/TMSR, studies on irradiation effects must be planned.

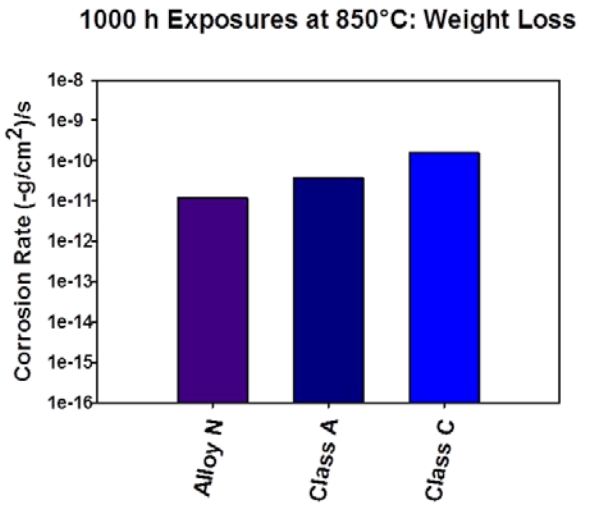
- **Irradiation investigation of Hastelloy N / GH3535 (UNS N10003)**
  - ***Provide additional data to understand and quantify irradiation effects***
  - ***Establish protocol for future new materials irradiation investigation***
- **Irradiation investigation of graphite materials**
- **Irradiation investigation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



New alloy development 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***



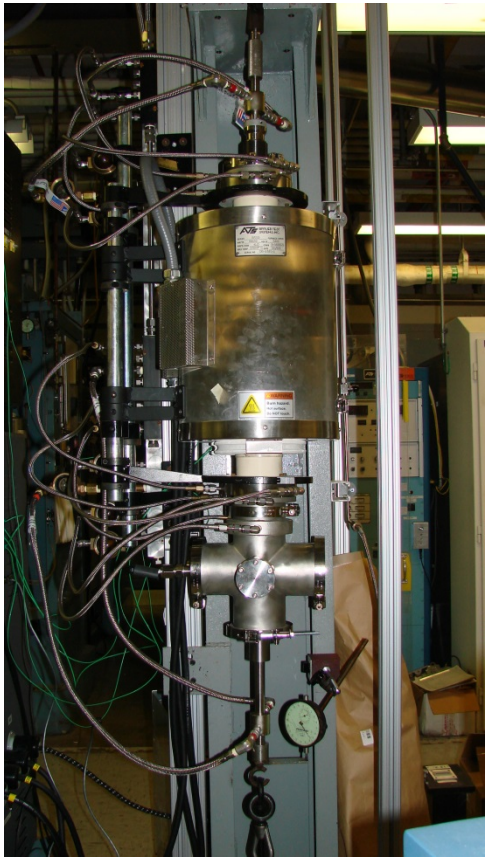


Alloy N: Commercial heat (Vacuum processed)

Alloy A and C: Lab-processed in inert atmosphere

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.**

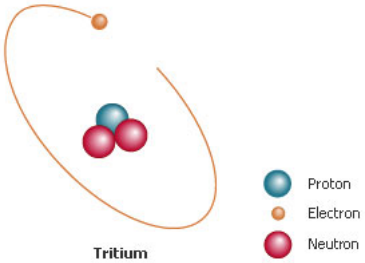


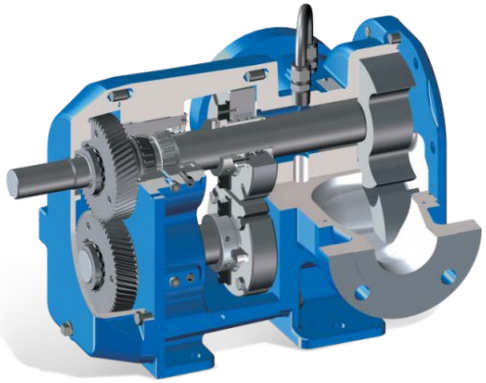
Materials joining is usually the weakest link in structural integrity of high temperature systems.

- **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**

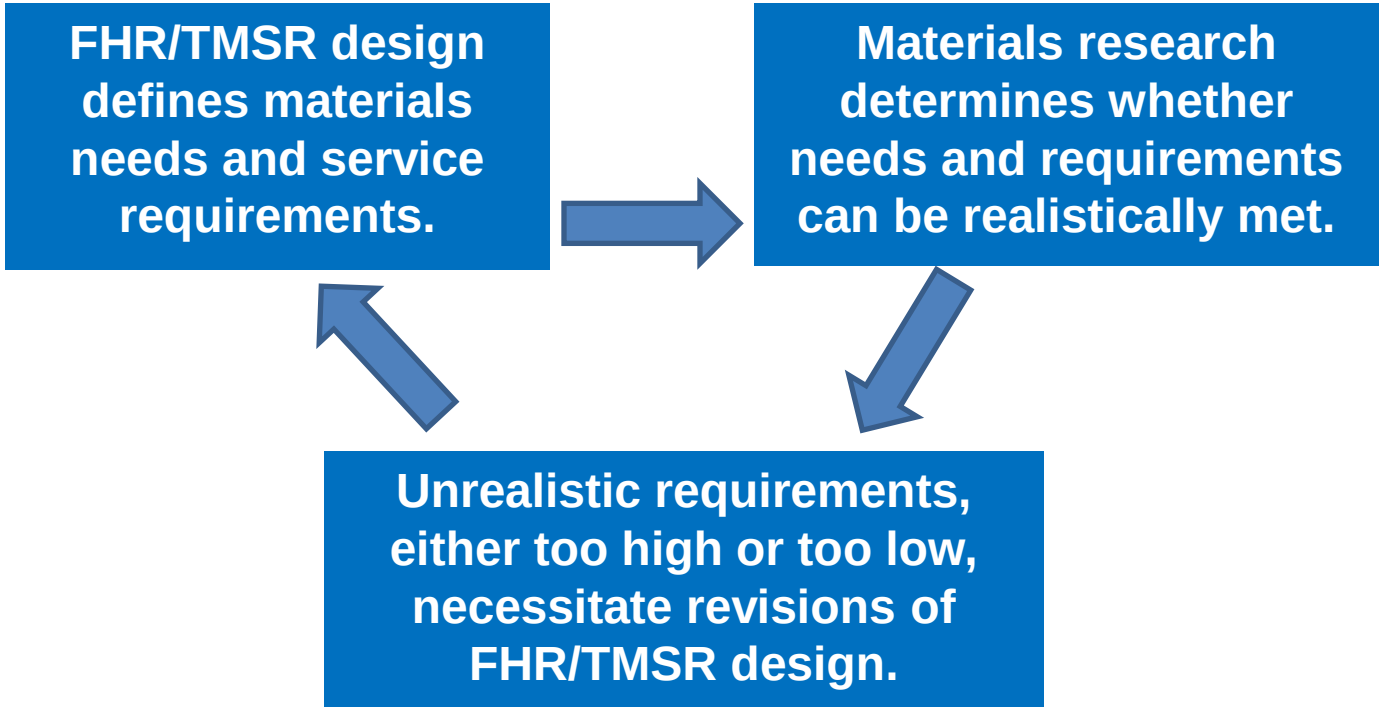




ROADMAP STRATEGY

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.**



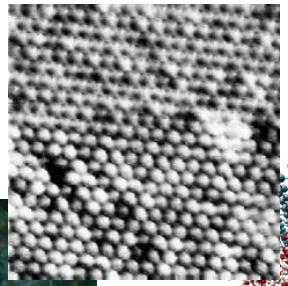
- **The iterative process may not immediately lead to a final decision, but eventually both sides should reach an optimal balance.**

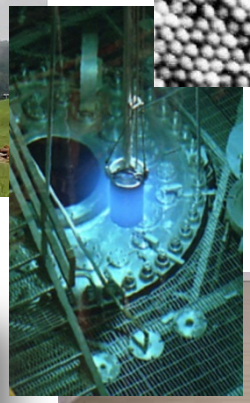
The development will include several key steps to ensure the roadmap is defensible and practical.

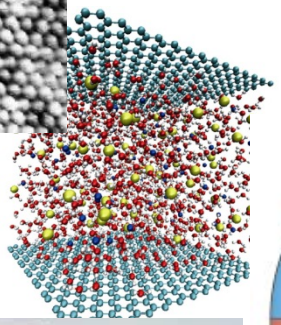
- **Development approach**
  - ***Review TMSR/FHR conceptual design to provide a good understanding of materials needs and requirements.***
  - ***Identify potential materials problems and issues.***
  - ***Propose approaches and possible solutions to define R&D tasks.***
  - ***Identify subject matter experts to write specific technical topics.***
- **Roadmap structure**
  - ***The body of the document will focus on component-oriented materials challenges, possible solutions, proposed approaches, and goals.***
  - ***Topic-area-specific appendices will define tasks and objectives that are adjustable within the constraints of the roadmap structure.***
- **Revisions and management**
  - ***The roadmap is document that allows periodic reviews and fine tuning in updated versions to address emerging issues and problems.***

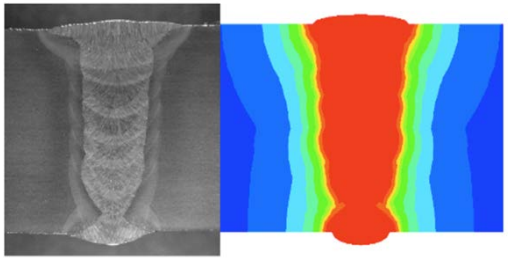
The materials roadmap will draw heavily upon MSRE experience and leverage modern technologies.

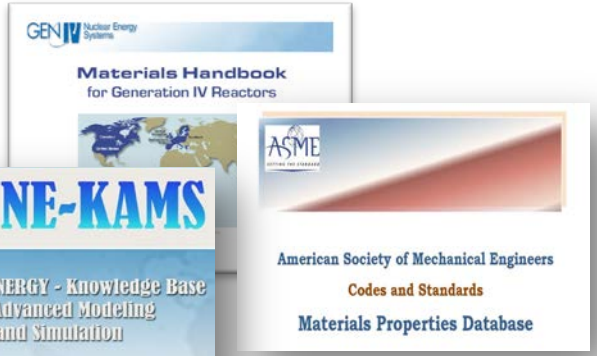
- **The wealth of MSRE reports and data will be fully explored.**
  - ***Historical documents and data collection are already underway.***
- **All applicable modern technologies will be considered.**

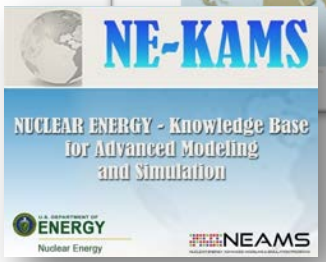


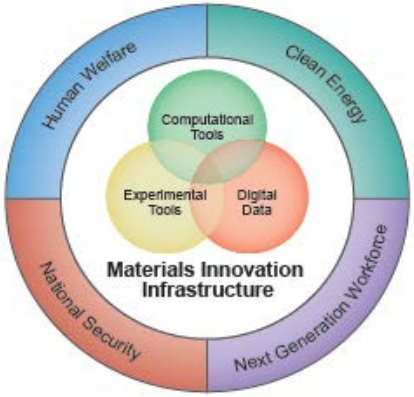












Integrated Computational Materials Engineering

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.**

ANY QUESTIONS?

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