High Temperature Molten Salt Coolants

Key Research & Development (R&D) Challenges

Literature Review for INPRO COOL

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Outline

(1) Introduction
- Coolants
- INPRO COOL CP

(2) Molten Salt Coolants
- Applications/Types
- Thermophysical Properties
- Heat Transfer
- Corrosion and Materials
- R&D Programs

(3) Conclusions

1. Introduction

Coolants

- Functions of coolant:
  - Extract heat from reactor core
  - Transfer heat to energy conversion system (e.g. electricity generator, hydrogen production, desalination plant)
  - Assure safety by providing a degree of thermal inertia

- Coolants operating at high temperatures (600 -1000ºC)
  - Increase thermal efficiency of reactor
  - Thermochemical hydrogen production
  - Typical coolants: Gas (helium) and liquids (molten salts and liquid metals)

INPRO COOL CP

“Investigation of technological challenges related to the removal of heat by liquid metal and molten salt coolants from reactor cores operating at high temperatures [600-1000ºC]”

High Temperature Low-Pressure Coolants

- Molten Salts: *Different types*
- Liquid Metals: *Lead (Pb) and Lead-Bismuth Eutectic (Pb-Bi)**
  - High boiling points, low enough melting points, chemically stable and generally compatible with materials at high temperatures,
  - Favourable nuclear properties (especially for lead in Fast Reactor systems)*

*__IAEA TWG-FR__ *TECDOCs and data on lead coolants (FRs and ADS)*
OECD/NEA *Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies*
(2007 Edition): available on NEA website

INPRO COOL R&D Challenges

Preliminary list of issues

(for operation between 600-1000ºC & beyond):

- Thermophysical properties (at high temperatures)
- Thermal Hydraulics (heat transfer correlations/CFD codes)
- Phase change studies
- Online monitoring and control of coolant chemistry
- Materials and components (for service in intimate contact with the high temperature coolants)

2. High Temperature Molten Salt Coolants

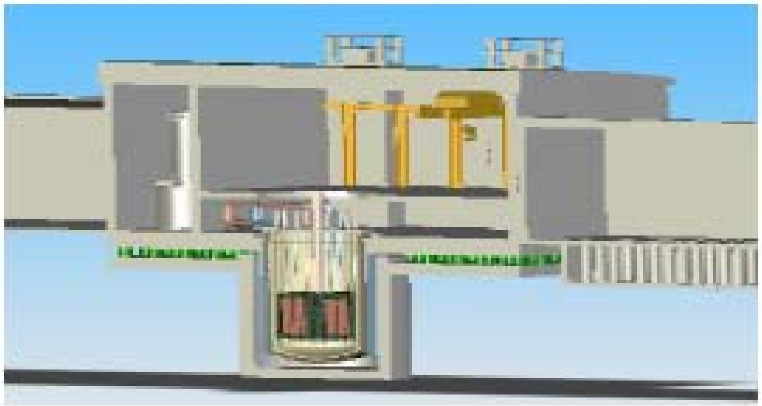
General Types of Molten Salt

- Types:
  - Fluorides (LiF)
  - Chlorides (NaCl – table salt)
  - Fluoroborates ($NaBF_4$) + others
- Mixtures:
  - e.g. LiF-BeF_2,
    LiF-NaF-KF, KCl-$MgCl_2$
- Eutectic compositions (optimum proportions)
  - e.g. LiF-BeF_2 (66-33 % mol)
- Different mixtures/compositions have different properties

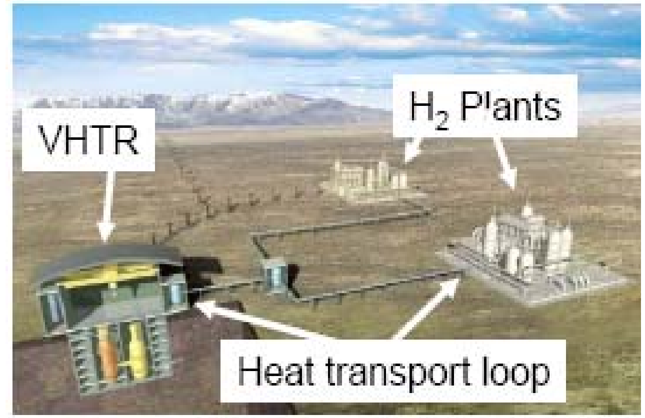
Pictures of the Salt

***Picture sources: Top: Anderson et al. [UW, NHI Semiannual Program Review, Idaho 2007]**
Bottom: Renault & Forsberg [ALISIA Final Meeting 2008]*

Nuclear Applications of High Temperature Molten Salts



Advanced High Temperature Reactor AHTR

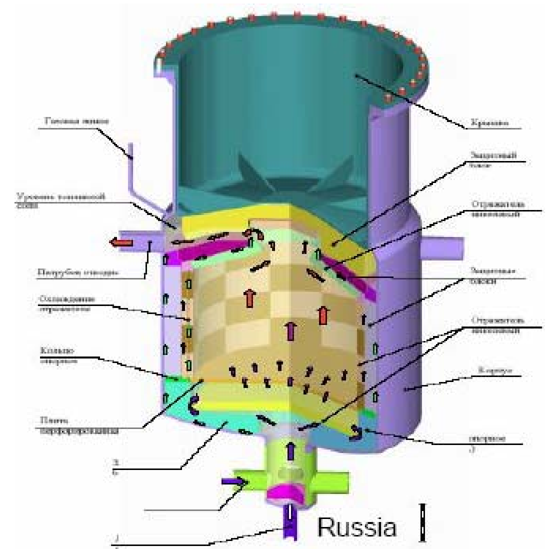


Heat Transfer Loop* (e.g. Hydrogen Production)

Molten Salt Reactors MSRs

MSRE

MOSART



Picture sources: Renault & Forsberg [ALISIA Final Meeting 2008] & *Anderson et al. [UW, NHI Semiannual Program Review, Idaho 2007]

(+Fusion Reactors)

Nuclear Applications and Choice of Salt

Reactor type	Neutron spectrum	Application	Reference	Alternatives
MSR-Breeder	Thermal	Fuel	$_{7}LiF\text{-}BeF_2\text{-}ThF_4$	
		Coolant	$NaF\text{-}NaBF_4$	$LiF\text{-}BeF_2$
	Fast	Fuel	$LiF\text{-}ThF_4$	$LiF\text{-}CaF_2\text{-}ThF_4$ $NaCl\text{-}UCl_3\text{-}PuCl_3$
		Coolant	$NaF\text{-}NaBF_4$	
MSR-Burner	Fast	Fuel	$NaF\text{-}LiF\text{-}BeF_2\text{-}AnF_3$	$NaF\text{-}LiF\text{-}KF\text{-}AnF_3$ $NaF\text{-}LiF\text{-}RbF\text{-}AnF_3$
AHTR	Thermal	Coolant	$_{7}LiF\text{-}BeF_2$	
VHTR	Thermal	Heat transfer	LiF-NaF-KF	$LiCl\text{-}KCl\text{-}MgCl_2$
FR	Fast	Coolant	$KCl\text{-}NaCl\text{-}MgCl_2$	$NaF\text{-}KF\text{-}ZrF_4$
SFR	Fast	Heat transfer	$NaNO_3\text{-}KNO_3$	

An' represents the actinides Pu, Am and Cm

Picture source*: *Ignatiev [ALISIA Final Meeting 2008]

Three General Categories of Application

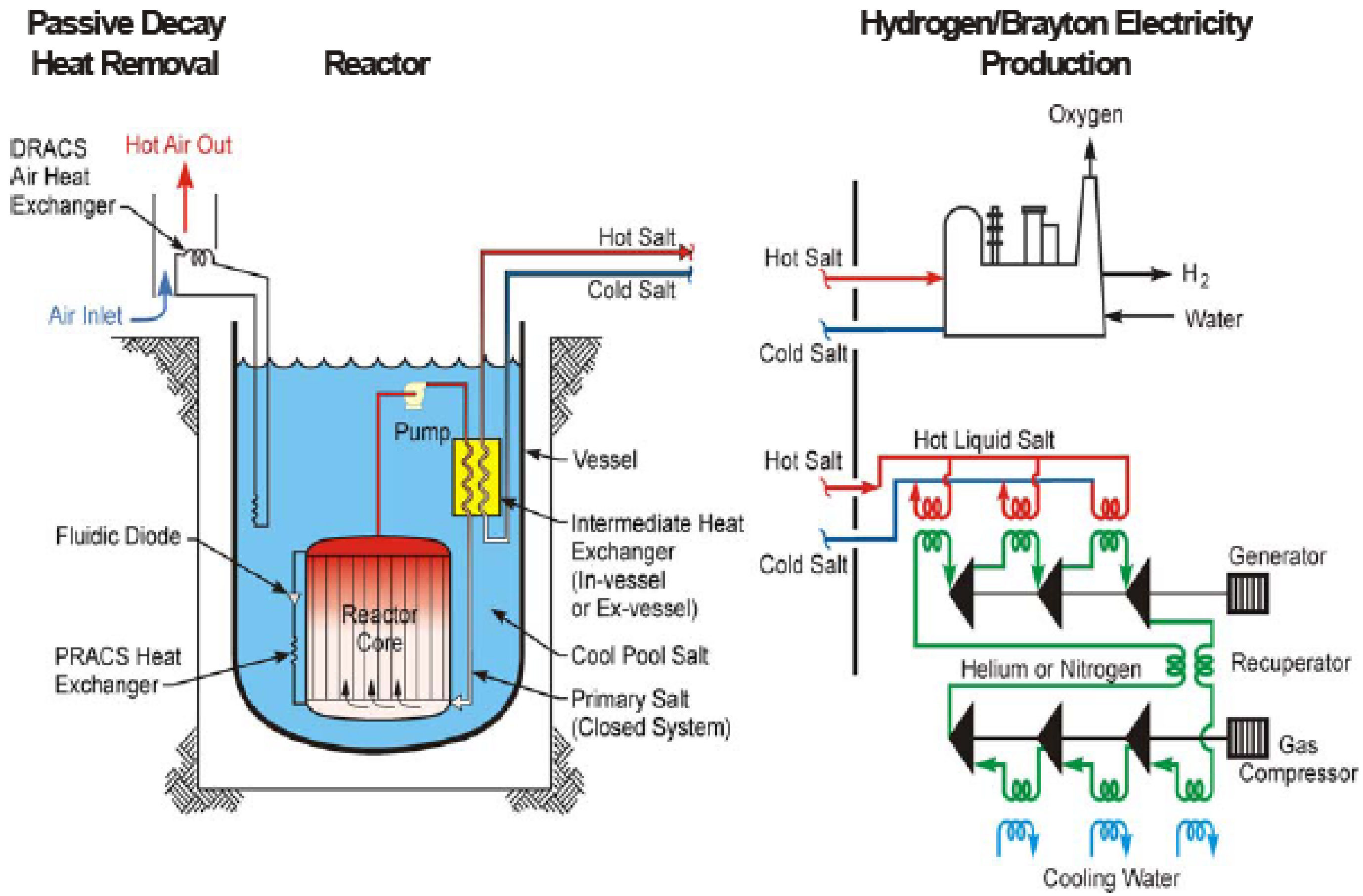
a) Primary Loop Coolants (AHTR)

b) Heat Transfer Loop Coolants (NGNP/NHI / Secondary Loop AHTR)

c) Fuel-Salt (MSR)

(focus for INPRO COOL is on coolant applications, but overlapping fuel-salt technologies should be considered)

Molten salt cooled AHTR Layout



Picture Source: Forbserg et al. [8026 Proc. ICAPP 2008]

Thermophysical Properties
a) Primary Coolant Loop (AHTR)

Fluorides	
Class	**Composition (% mol)**
Alkali Flourides	**LiF-KF (50-50)** **LiF-RbF (44-56)** **LiF-NaF-KF (47-12-42)** **LiF-NaF-RbF (42-6-52)**
ZrF_4 Salts	**LiF-ZrF_4 (51-49)** **NaF-ZrF_4 (59.5-40.5)** **RbF-ZrF_4 (58-42)** **KF-ZrF_4 (58-42)** **LiF-NaF-ZrF_4 (26-37-37)**
BeF_2 Salts	**LiF-BeF_2 (67-33)** **NaF-BeF_2 (57-43)** **LiF-NaF-BeF_2 (31-31-38)**

*Data review**

- Melting Points and Phase diagrams
- Density: empirical T dep. equations
- Vapour Pressure: measured values (900ºC)

  Dependence on salt composition, vapour species studies
- Viscosity: measured (700-800ºC), T dependence referred

  More measured data, T dependence
- Heat capacity: some approximate measurements (700ºC) & predictive method

  More accurate measurements, T dependence
- Thermal conductivity: limited/scattered measurements & predictive method (700ºC)

  More consistent / accurate data needed

Candidate compositions and summarised data reviews sourced from: [ORNL Report TM-2006/12] (D.Williams, 2006)

Thermophysical Properties
b) Heat Transfer Coolant Loop

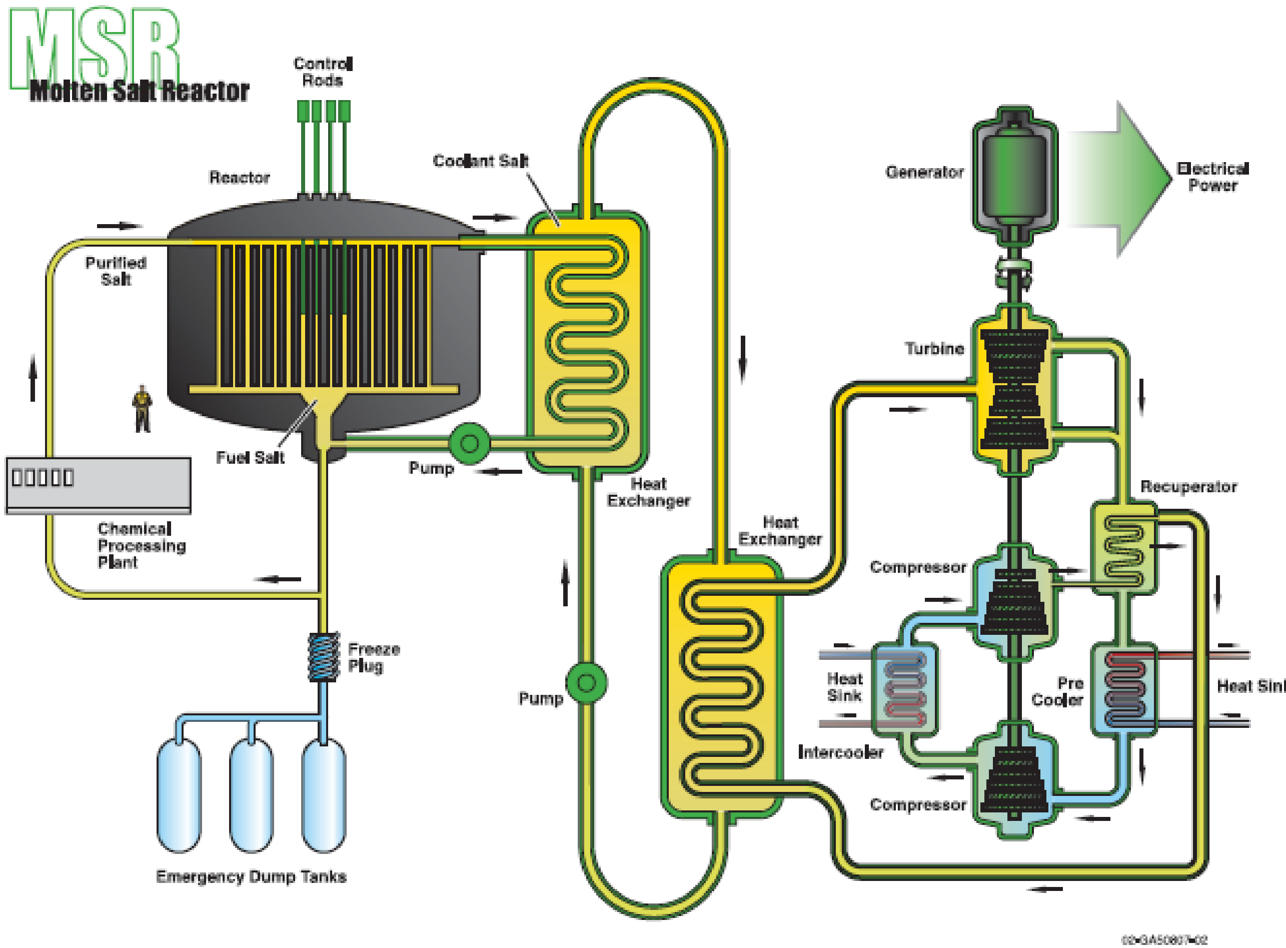
CHLORIDES, FLUOROBORATES & FLUORIDES	
Class	**Composition (% mol)**
Chlorides	**LiCl-KCl (59.5-40.5)** **LiCl-RbCl (58-42)** **$NaCl-MgCl_2$ (68-32)** **$KCl-MgCl_2$ (68-32)**
Fluoroborates	**$NaF-NaBF_4$ (8-92)** **$KF-KBF_4$ (25-75)** **$RbF-RbBF_4$ (31-69))**
Fluorides (see previous)	**LiF-NaF-KF (47-12-42)** **$NaF-ZrF_4$ (59.5-40.5)** **$KF-ZrF_4$ (58-42)** **$LiF-NaF-ZrF_4$ (26-37-37)**

Candidate compositions and summarised data reviews from: [ORNL Report TM-2006/69] (D.Williams)

*Data review**

- Melting Points and Phase diagrams
- Density: empirical T dep. equations
- Vapour pressure: some estimated/ measured data is given (900ºC), some T dep. equations given
  More measured data (esp. Cl's), vapour species and effects for BF's
- Viscosity: some experimental (T dep.) equations (to 900ºC)& predictive method
  More measured data
- Heat capacity: predictive method & some measured (~700ºC); similarities
  More measured data, T dep.
- Thermal conductivity: scattered measured, predictive method
  More accurate measurements, T dependence

Molten Salt Reactor (MSR) Gen IV



Picture Source: http://www.ne.doe.gov/genIV/documents/gen_iv_roadmap.pdf

Thermophysical Properties
c) Primary Fuel-Salt Loop (MSR)

Fuel-Fluorides	
Class	**Composition (% mol)**
$LiF-BeF_2-AnF_n$ (MSR-Breeder)	**$LiF-BeF_2-ThF_4-UF_4$** $LiF-BeF_2-ThF_4$ $LiF-BeF_2-UF_4$
$LiF-NaF-BeF_2-AnF_n$	**$LiF-NaF-BeF_2-PuF_3$** $LiF-BeF_2-PuF_3$ $NaF-BeF_2-ThF_4$ $NaF-BeF_2-UF_4$ $NaF-BeF_2-PuF_3$ $LiF-NaF-UF_4$ $NaF-ZrF_4-UF_4$
$NaF-ZrF_4-AnF_n$	**$NaF-ZrF_4-UF_4$**

*Data review**

- Experimental: ORNL reports
- Theoretical models and predictive methods (e.g. using pure compounds, ideal mixtures), for different fuel multi-systems

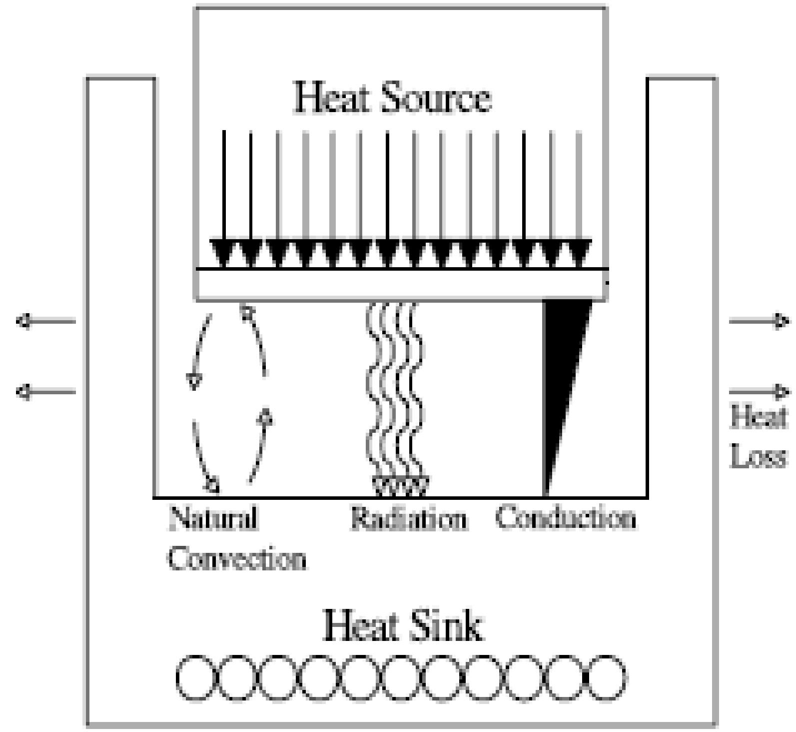
More data and updated databases needed, for different fuel-salt compositions.

Sources: ****Experimental: [TM-2316] (S. Cantor, 1968)***
****Predictive methods: (Konings et al. 2009) and (Ignatiev et al. 2009) [J. Fluor. Chem., vol. 130]***

Heat Transfer

- Convection regimes:
  Forced/Free
  Laminar/Transitional/Turbulent

- Heat transfer coefficients and "correlations" are used to model the physical behaviour



Picture Source: Ambrosek et al., 2009 [Nuc. Tech. 165 p166]

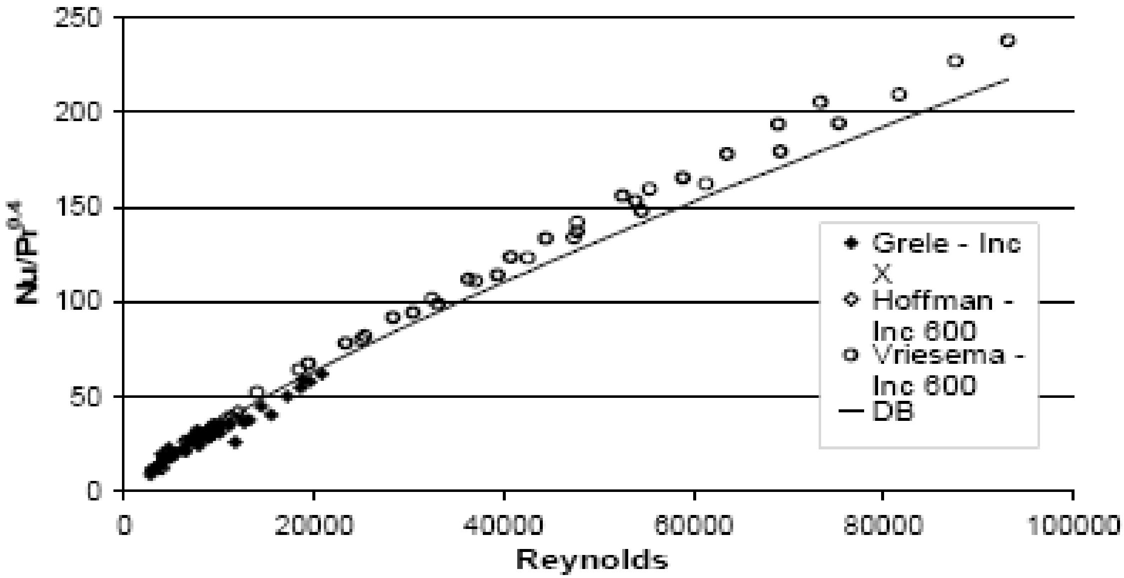
Heat Transfer: Experimental Studies

- Various (limited) results in the literature show:

  Fluorides exhibit normal fluid behaviour

- Example:

  *University of Wisconsin study on LiF-NaF-KF**



Dittus Boelter correlation validated, within ±15% of data

$Nu = 0.023Re^{0.8}Pr^{0.4}$

FLUENT code used

Sources: Anderson et al. [UW Presentation, NHI Semiannual Program Review, Idaho 2007] & Ambrosek et al., 2009 [Nuc. Tech. 165, p166]

Further Thermal Hydraulics R&D

Key Requirements

- Different geometries

- Validation at higher T, using simulant fluids or MS
- Development and benchmarking of CFD codes
- Plus other considerations*:
  - Buoyancy (free convection) (for MS at high T)
  - Thermal radiation (for MS at high T)

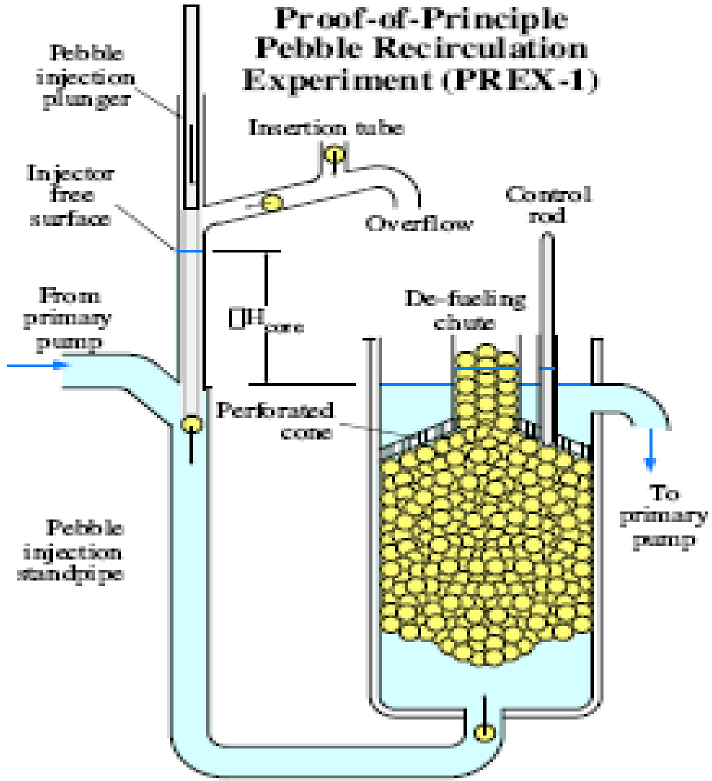


Fig. 4. Schematic representation of the PREX experiment.

PREX (PB-AHTR)

Sources: Bardet, Peterson 2008 [Nuc. Tech. Vol 163 p. 344]
"TNT loop" Fusion studies

Picture Source: Peterson et al. UC Berkeley [Global 2007, Boise, Idaho, September 9-13, 2007]

Chemical Corrosion and Compatibility

- A major issue is compatibility of molten salts with reactor materials:
  - Fluorides dissolve passive oxide layers
  - Moisture and oxide impurities in fluorides cause corrosion (oxidation) of the metal alloy
- Measures to reduce this:
  - Purification
  - Development of systems to control coolant chemistry
  - Development of advanced, high temperature materials – compatible with molten salts

Chemistry Control Methods

- Main idea: maintain a “reducing” (low oxidation potential) environment in the salt - i.e. REDOX control

Redox Control and Monitoring Methods*	**Reactor Concept (Program or Institute) [refs]***
Control redox by use of metallic beryllium (Be) immersed in the salt, as an active redox agent	MOSART (ISTC#1606) Fusion coolant tests (JUPITER-II)
Control of oxide formation by use of high purity He cover gas	MSRE (ORNL)
Use of U(III)/U(IV) (i.e. UF_3/UF_4) ratio to control optimum oxidation state (redox potential) in fuel-salt	MSRE (ORNL)

***Sources (refs ordered as in table):**
Ignatiev et al. 2008 [Nuc. Tech. Vol. 164 p130]
Petti et al. 2006 [Fus. Eng. Des. Vol. 81 p1439] (fusion coolants)
Wong et al. 2004 [Presentation, ITER TBM Project Meeting UCLA
Williams et al. 2006 [ORNL-TM-2006/12]*

Materials Development

- Materials need to be high temperature (similar requirements to VHTR materials), plus corrosion resistant to molten salts (for those in coolant-contact)

Alloy Name*	**Alloy Composition (brief)**	**Resistance to salt corrosion**	**Temperatures**
Hastelloy-N	Ni base, 17% Mo, 7% Cr, 5% Fe	Very good	Use up to 750ºC
Hastelloy-X	Ni base, ~9% Mo, ~20%Fe, ~20% Cr	Needs evaluation	Use up to 900ºC
MONICR	73% Ni, 18% Mo, 7% Cr, ~2% Fe	Very good	Use up to 750 ºC
HN80M-VI	Ni base, ~8% Cr, ~12% Cr	Very good	High Temperatures

- Also, Graphite + C-C composites resistant to liquid salts

Sources (for details of each alloy in table, refs same order):
Williams et al. 2006 [ORNL-TM-2006/12]
Ingersoll et al. 2004 [ORNL/TM-2004/104]
Hosnedl 2008 [Presentation, INPRO COOL 1st meeting]
Ignatiev et al. 2008 [Nuc. Tech. Vol. 164 p130]

3. Conclusions

Conclusions

- **Molten salts and liquid metals are low pressure, high temperature coolants.**
- **Different candidate coolant salt mixtures, for different applications.**
- **Thermophysical properties data exists (most measured data from ORNL), but updated and more T dep. studies are needed.**
- **Heat transfer correlation validation at higher Ts, and more tailored thermal hydraulic assessments are needed, for each MS system design.**
- **Chemistry control methods have been demonstrated. Developed materials and alloys also need to be tested in molten salt corrosion loops, at higher Ts.**

International Programs and Literature Resources for Molten Salts

- **USA**
  - **ORNL: Past ARE, MSRE, MSBR reports**
  - **ORNL, INL, UCB, UW.. For new designs**
- **Europe**
  - **Euratom: MOST (5^{th} FP), ALISIA (6^{th}), ACSEPT (7^{th})**
  - **France (CNRS, CEA), Czech Republic (SKODA), Germany (ITU)**
- **Russia**
  - **ISTC#1606 completed & ISTC#3749 planned**
- **Others countries:**
  - **Japan, India**

For more details see internship report

Thank you!