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"Developing the Next Generation of Molten Salt Reactor Systems in Russian Federation"

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Introduction

From 1976 MSR study in Russia was organized around the following issues:

- exploration of possible use and niches for MSR concepts
 - > Efficient electricity production in Th-U Converter / Breeder designs
 - Consumption of TRU's while extracting their energy
 - High temperature Fluoride Salt Cooled Reactor
 - Fusion hybrid blankets
 - Isotopes production for medicine
- reactor physics, thermal hydraulics, fuel cycles and safety
- container materials for fuel and coolant salts
- physical and chemical properties of molten salt mixtures
- heat transfer and hydraulics of fuel and coolant salts
- handling and circulation of fuel and coolant salts
- process and radiochemical tests of model installations
- radiation chemistry of fuel salt

An extensive review of MSR development in Russia through 1989 is given in the book "Molten salt nuclear energy systems - perspectives and problems" V. Novikov, V. Ignatiev, V. Fedulov, V. Cherednikov, Moscow, 1990



Introduction of MSR Technology in Nuclear Power: From FSCR to MSR

Stage 1 (FSCR): Fluoride salt as coolant + solid HTR fuel

Stage 2 (MSR-converter):

- Fluoride salt as coolant & liquid fuel
 - Graphite as moderator
 - No fuel salt processing



Boundaries and Interfaces



Stage 3 (MSR-breeder):

- Fluoride salt as coolant & liquid fuel
 - Fuel salt processing
 - Homogenious core (?)

Today different fast reactor concepts using molten salt are under consideration in Russia

- R&D studies are on-going in order to verify that fast spectrum MSR systems satisfy the goals of Gen-IV in terms of <u>technical</u> <u>feasibility, sustainability, safety and waste management</u>
- MOSART studies are done within ISTC#1606 and #3749 tasks as well as Rosatom MARS and Euratom FP6 EVOL projects
- Kurchatov Institute is a partner for EU Horizon 2020 SAMOFAR project focused on MSFR safety
- RFBR supports some experimental studies at Kurchatov Institute concerning fuel salt & material properties for MOSART
- Other groups are still interested to consider concepts with a very low technology readiness levels: the MSFR operating in U-Pu fuel cycle and MSR with direct lead cooling in primary circuit



MOSART – Transforming Reactor System

Started with TRU's Fluorides from LWR used nuclear fuel has flexible fuel cycle and can operate in different modes: •Transmuter •Self-sustainable •Breeder



System	burner /	breeder
Fluid streams	1	2
Power capacity, MWt	2400	2400
Fuel salt inlet/outlet temperature, °C	600 /720	600 /720
Fuel salt composition, mole %	72LiF 27BeF ₂ 1TRUF ₃	75LiF 16.5BeF₂ 6ThF₄ 2.5TRUF₃
Blanket salt composition, mole %	no	75LiF 5BeF ₂ 20ThF ₄





Velocity, m/s





T max fluid : 1192 K

Heat source, W/m³

0

-13

-20 -27

-33

-40 -47

-53

-60

-67

-80

-87

-93



Two Fluid Th MOSART Flowsheet

Thermal power: 2.4 GWt; Core height / diameter: 2-3.6m/2-3.4m; Radial blanket thickness: 0.2-0.6m;FP removal time: 300 efpd; TRU loading at BOL / EOL – 1.5t/3.5t; 233 U production from 150 up to 300 kg/yr;Fuel salt:73LiF-27BeF2; T_{inlet} =600C;Blanket salt: 75LiF-5BeF2-20ThF4; T_{inlet} =600C





MOSART Fuel Cycles







⁻ Feeding composition (Np+MA)/TRU=0.35

Feeding composition (Np+MA)/TRU=0.1
 Feeding composition (Np+MA)/TRU=0.45 (with U-233 recycling from blanket to fuel stream).

- Single fluid 2400MWt MOSART core containing as initial loading 2 mole% of ThF_4 and 1.2 mole % of $TRUF_3$, with the rare earth removal cycle 300 epdf after 12 years can operate without any $TRUF_3$ make up basing only on Th support as a self-sustainable system.
- At equilibrium molar fraction of fertile material in the fuel salt is near 6 mole % and it is enough to support the system with CR=1.



Preliminary Process Hazards Analysis

System / Component	Initiating Event
Primary circuit / containment	 Failure in the main circulation pipe Failure in the primary heat exchanger Failure in the main circulation pump Unintentional control rod withdrawal Loss of blanket salt Premature criticality during filling Inflow of contaminants or unexpected isotopic ratio in the fuel salt Inadvertent release of fission gas from reactor cell and / or containment
Intermediate circuit	 Failure in the main circulation pipe Failure in the main circulation pump
Salt chemical processing	 Hydrogen reacts with fluorine in chemical processing system Excess pressure in the helium bubbler Inadequate removal of Pa or U
Drain Tank	 Improper or inadequate cooling of the drained fuel salt A partially thawed piece of the salt plug or other solid mass obstructs piping to the drain tank



MOSART Transients Analysis



The MOSART is expected not to be seriously challenged by the major, unprotected transients such as ULOF, ULOH, overcooling, or even UTOP. The system was shown to buffer reactivity insertion of up to + 1.5\$. System temperatures are expected to rise only ~300C above nominal under this severe transient conditions. The mechanical and structural integrity of the system is not expected to be impaired.



Design Aspects of MSR Safety





Severe accident with the rupture of the main fuel salt pipe and fuel discharged on the reactor box bottom

- The model based on mass transfer theory describing main radionuclides distribution between the fuel salt, metallic surfaces of the primary circuit, graphite and the gas purging system was applied for calculation releases to the containment atmosphere.
- As a criteria characterizing an isotope yield from the fuel salt is accepted the ratio of this isotope activity changed into a gas phase of a containment (A_g) to its full activity built up in a reactor by the moment of the accident (A_o)
- After accident all noble gases and metals available should move to the gas phase $(A_g / A_s = 1, where A_g / A_s the ratio of isotope activity in the gas phase of the containment after an accident to its activity concentrated in the fuel salt by the moment of the accident). However, already during the normal operation these nuclides are almost completely leave the fuel salt.$

Isotope	A _s	A_g / A_s	A_g / A_o
	/A _o		
Te129	0,25	1	0,25
Te132	0,005	1	0,005
Ru103	0,01	1	0,01
Ru106	0,001	1	0,001
Nb95	0,034	1	0,034
Zr95	0,99	0,0011	0,0011
Sr89	0,99	0,0005	0,0005
Sr90	0,98	0,0005	0,0005
La140	0,98	0,026	0,025
Ce141	0,99	0,0024	0,023
Ce144	0,96	0,0024	0,023
<i>I131</i>	0,62	0,43	0,27
<i>I133</i>	0,94	0,43	0,43
Cs137	0,7	0,016	0,011

For MSR the total release of radioactivity would be significantly lower (by I - 2 orders of magnitude compared to PWR), though for several particular nuclides such I¹³¹ and I¹³³ the differences are smaller



Frequency distribution for the probability of accidents in the MSR and the LWR on the degree of contamination risk



Consequences of Accidents

- ✓ Probability of an accident with a relatively low impact for MSR is higher than for LWR. This is due to the possibility of leakage of radioactive liquid fuel in case of accidents in the pump, piping, valves.
- ✓ The consequences of severe accidents in particular, leading to the release of radioactive products into the environment for MSR significantly less than for LWRs.

Taube M., Fast and thermal molten salt reactors with improved inherent safety // TANS, 1981, Summer meeting, pp. 490-498

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Components	Breeder	Burner
Solvent major constituents	LiF, BeF2	LiF, NaF, KF, BeF2
Fertile additives	ThF4	Fertile-free, UF4
Fissile additives	UF4, PuF3	PuFз, AmFз
Soluble fission products	CeF3, NdF3, LaF3	CeF3, NdF3, LaF3
Gaseous reaction products	T (D)	T(D)
Alloys major constituents	Ni-Mo; Ni-W	Ni-Mo; Ni-W



The data on PuF_3 solubility in molten salt fluorides appear to follow a linear relationship within the experimental accuracy of the measurements when plotted as log of molar concentration of AnF_3 vs. 1/T(K)

LiF	NaF	KF	BeF ₂	ThF₄	Т, К	A	-B●10 ⁻³
46.5	11.5	42	0	0	823-973	5.59	3.949
73	0	0	27	0	825-1000	3.927	3.099
66	0	0	34	0	800-900	3.231	3.096
15	58	0	27	0	825-925	3.639	2.750
17	58	0	25	0	800-900	3.253	2.578
78	0	0	0	22	873-973	2.58	1.73
75	0	0	5	20	873-1023	2.06	1.34
77	0	0	17	6	848-998	3.61	2.91

 $log SPuF_3$, мол% = A + B/T,K



An and Ln Trifluoride Solubility





Temperature, K	72,5LiF-7ThF ₄ -	-20,5UF ₄	78LiF-7ThF ₄ -15UF ₄		
1	PuF ₃	CeF ₃	PuF ₃	CeF ₃	
873	0,35±0,02	1,5±0,1	1,45±0,7	2,6±0,1	
923	4,5±0,2	2,5±0,1	5,6±0,3	3,6±0,2	
973	8,4±0,4	3,7±0,2	9,5±0,5	4,8±0,3	
1023	9,4±0,5	3,9±0,2	10,5±0,6	5,0±0,3	

Near the liquidus temperature for $78LiF-7ThF_4-15UF_4$ and $72,5LiF-7ThF_4-20,5UF_4$ salts, the CeF₃ significantly displace PuF₃



Viscosity Measurements







U and Pa Removal from Fuel Salt by Fluoride Bubbling

The rate of $UF_4 + F_2 \leftrightarrow UF_6$ reaction at 500—600°C is very high



- <u>In static conditions</u> at temperature of 750°C and fluorine pressure of 50 kPa the normalized rate of PaF_5 removal from the Li,Be/F salt surface into the fluorinator's "cold" zone with the wall temperature of 400°C was $\Delta m/m/\tau \approx 5 \cdot 10^{-2} \text{ hr}^{-1}$. In this case the ²³³Pa recovery from the salt reached 98%.
- Using fluorine bubbling, the process of U and Pa removal can be intensified by an order of value as compared to static fluorination method.



Electrochemical Properties

CV's of PuF_3 (0.05 mole %) in LiF-NaF for various potential scan rates. WE - Mo, RE – Mo. T=1023K



CV's of PuF_3 (0.1 mole %) in LiF-NaF-BeF₂ for various potential scan rates. WE - Mo, RE - Mo. T=853K

• Equilibrium potentials of the Pu³⁺/Pu, Zr²⁺/Zr, Be²⁺/Be, Na⁺/Na couples in 15LiF-58NaF-27BeF₂ and 60LiF-40NaF (in mole %) melts were determined

- It was shown, that plutonium is deposited on molybdenum cathode earlier than beryllium and sodium. Difference of plutonium and beryllium deposition potentials is equal ~ 0.15 V, plutonium and sodium deposition potentials – ~ 0.30 V.
- Diffusion coefficients of zirconium and plutonium ions in 15LiF-58NaF-27BeF₂ and 60LiF-40NaF melts were estimated





Reductive Extraction with Liquid Bi-Li

Reductive extraction of actinides from molten salt into liquid bismuth with their subsequent re-extraction into purified salt flow is the most acceptable technological method of actinide recycling. In order to determine particular parameters of this stage, it will be necessary to conduct additional experimental studies with selected salt composition on enlarged facilities



Pu distribution coefficient in 15LiF-58NaF-27BeF₂/Bi is much less than in LiF-BeF₂/Bi system

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Selection of Materials for Components

Ni-based alloy Circuits, Heat exchangers 600 / 720 ° C Creep, Creepfatigue, Thermal fatigue, Aging, Welds...

> Ni-based alloy Intermediate circuit -455 / 620° C Aging, Welds, Compatibility NaF-NaBF₄, Oxidation, Wastage...



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Ni-based alloy / SS Vessel - 600 ° C Negligible creep C, Ni Reflector600-750 ° C Negligible creep SiC Distribution plate-

Distribution plate-600°C, High irradiation

- <u>Max temperature</u> of the fuel salt in the primary circuit made of special Nialloy is mainly limited by Te IGC depending on salt Redox potential
- <u>Min temperature</u> of fuel salt is determining not only its melting point, but also the solubility for AnF_3 in the solvent for this temperature



Because the products of oxidation of metals by fluoride melts are quite soluble in corroding media, passivation is precluded, and the corrosion rate depends on other factors, including: <u>Oxidants, Thermal gradients, Salt flow rate, Galvanic coupling</u>

Molten salt

Gas

Creep, Creep-

fatique, Aging,

Welds...

fatigue, Thermal

Redox, Heat

up, Velocity ...



MSRE Experience

• Hastelloy N was susceptible to damage from He formation in a fast neutron flux. Later it was found that modified alloys that had fine carbide precipitates within grains would hold He and restrain this migration to the grain boundaries

• The reasoning in 1970's was that the 2% titanium addition would impart good resistance to irradiation embrittlement and that the 0 to 2% niobium addition would impart good resistance to intergranular tellurium embrittlement.

• Hastelloy N was deteriorating in its properties as a result of intergranular attack caused by Te. Later work showed that this Te attack could be controlled by keeping the fuel on the reducing side. This is done by adjustment of the chemistry so that: about 2%UF₃ as opposed to 98%UF₄



In temperature range 500-800°C about 70 differently alloyed specimens of HN80MT were tested. Among alloying elements there were W, Nb, Re, V, AI and Cu

Element	Hasteloy N US	Hasteloy NM US 1972	Hasteloy NM US 1976	HN80M-VI Russia	HN80MTY Russia	MONICR Czech Rep	E-721 France
Ni	base	base	base	base	base	base	base
Cr	7,52	7,3	7,3	7,61	6,81	6,85	8
Мо	16,28	13,6	13,6	12,2	13,2	15,8	0.7
Ti	0,26	0,5—2,0	—	0,001	0,93	0,026	0.3
Fe	3,97	0,1	0,1	0,28	0,15	2,27	0.63
Mn	0,52	0,14	0,14	0,22	0,013	0,037	0.26
Nb	-	-	1 - 2	1,48	0,01	< 0,01	-
Si	0,5	< 0,01	< 0,01	0,040	0,040	0,13	0.25
AI	0,26	-	-	0,038	1,12	0,02	0.05
W	0,06	-	-	0,21	0,072	0,16	10

• Experiments results in polythermal loops with redox potential measurement demonstrated that operations with Li,Be/F salt, also fuelled by UF₄ or PuF₃, are feasible using carefully purified molten salts and loop internals.

- Russian HN80MTY alloy with 1% added aluminum is the most resistant with fuel Na,Li,Be,Pu/F; Li,Be,U/F; Li,Th,U/F and Li,Be,Th,U/F salt mixtures up to temperature 750°C with [U(IV)]/[U(III)] ≤ 100. Corrosion rate was <5µm/yr. No intergranular corrosion of alloy is observed.
- Alloys modified by Ti, Al and V have shown the best post irradiation properties.

Te Corrosion in Li,Be,Th,U/F salt



Test	[UF ₃ +UF _{4]}] mole %	[U(IV)]/ [U(III)]	T °C	Impurity	content i	in the fuel %	l salt after	test, wt.
				Ni	Cr	Fe	Cu	Te
1	0.64	0.7	735	0.0034	0.0018	0.054	0.002	0.015
2	2.1	4	735	0.0041	0.0019	0.006	0.0012	0.0032
3	2.1	20	735	0.009	0.0055	0.003	0.001	0.015
4	2.0	500	735	0.26	0.024	0.051	0.019	0.013
5	2.0	100	750	0.22	0.031	0.065	0.055	0.034

•The experimental facility was developed to study compatibility of Ni-based alloys under various mechanical loads to the materials specimens with fuel salts containing Cr_3Te_4 with redox potential measurement

•LiF-BeF₂-ThF₄-UF₄: 5 tests of 250 hrs each at fuel salt temperature till to 750°C and [U(IV)]/[U(III)] ratio from 0.7 to 500

•LiF-BeF₂-UF₄: 3 tests of 250 hrs each at fuel salt temperature till to 800°C and [U(IV)]/[U(III)] ratio from 30 to 90

N-alloys Compatibility With Fuel Salts Strongly Depends on Redox Potential



Li,Be,U/F U(IV)/(UIII)

30 without loading at 760°C

60

90

without

760°C

without

800°C

loading at

Hastelloy N, enlargement ×160

No



 $K = 3500 pc \times \mu m/cm$; $I = 69 \mu m$



 $K = 4490 pc \times \mu m/cm$; $I = 148 \mu m$



Decrease of RedOx potential by metallic Be





N-alloys Compatibility With Fuel Salts Strongly Depends on Redox Potential

U(IV)/(UIII)	EM-721, enlargement ×160	HN80MTY, enlargement × 160
30 without loading at 760°C	No	No
60 without loading at 760°C	$K = 3380 pc \times \mu m/cm$; $I = 117 \mu m$	No
90 without loading at 800°C	K = 5830pc ×μm/cm ; I = 286μm	K = 530pc ×μm/cm ; I = 26μm



N-alloys Compatibility With Fuel Salts Strongly Depends on Redox Potential

Li,Be,Th,U/F	HN80MT-VI	HN80MTY
[U(IV)]/[U(III)]	К =3360pc×µm/cm; I =166µm	K=1660pc×µm/cm; I=68µm
500 without loading at 735°C		
[U(IV)]/[U(III)]	К =8300pc×µm/cm; I =180µm	K = 1850pc×µm/cm ; I=80µm
Loading 25MPa 750°C		
[U(IV)]/[U(III)]	no	no
100 Loading 25MPa 750°C		
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• MSR concepts offer alternative options for new fuel breeding and long lived waste incineration with the added value of liquid fuel (intrinsic safety features, fuel cycle flexibility, simplified fuel processing, in-service inspection, no fuel transportation and refabrication required).

• Significant progress has been made on the resolution (or cancellation) of critical viability issues (material compatibility, salt physical & chemical properties, reprocessing feasibility, intrinsic safety).

• Experimental infrastructures (analytical and integral salt loops with real fuel salts) are required to proceed further in the mastering of MSR technologies (e.g. tritium control) and components (long shuft pump, heat exchanger, etc.) testing.

• The innovative and commercially unproven nature of MSRs, as with many other advanced reactor concepts, presents significant challenges and risks in terms of financing, licensing, construction, operation and maintenance.

Preparative Chemistry and Salt Purification

Most suppliers of halide salts do not provide materials that can be used directly

The major impurities that must be removed to prevent severe corrosion of the container metal are moisture/oxide contaminants

Once removed, these salts must be kept from atmospheric contamination by handling and storage in sealed containers

During the US MSR program, a considerable effort was devoted to salt purification by HF/H_2 sparging of the molten salt. In addition to removing moisture/oxide impurities, the purification also removes other halide contaminants, such as chloride and sulfur.

In our purifications the gaseous agent (HF) was in some cases replaced by solid ammonium hydrofluoride (NH₄HF₂, Tm ≈ 125 °C), which is safer and more convenient in use for the removal of impurity oxide compounds from metal fluorides and for the conversion of U and Th oxides to fluorides.

 $MeO_2 + 4NH_4HF_2 \rightarrow MeF_4 + 4NH_4F \uparrow + 2H_2O \uparrow (T_{max} = 350-400 \ ^{o}C)$

 To carry out these processes do not require expensive equipment and special safety measures. The purified anhydrous fluorides of metals was obtained, which are used for the preparation of fluoride salt melts of different composition.

Production of anhydrous constituents->Melting -> Filtration -> Zone recrystallization -> met.Th or Zr or Be treatment



Hydrogen Isotopes Behavior

Main strategies for mitigation include: advanced materials for the piping and heat exchangers, inert gas sparging, additional coolant lines and metal hydride addition or chemical removal

Material	Temperature /	Equations	
	Pressure	Activation energy in kJ/mole	
HN80MTY	4731123K	Diffusion D=1,1·10 ⁻⁷ exp(-47,7/R·T) , [m ² /s]	
Mo-13,2% _{mass}	0.1…90 кРа	Permeability $P=3,5\cdot10^{-8}exp(-55,0/R\cdot T)$, [mole/m × s × Pa ^{1/2}]	
		Solubility Ks=0.41·exp(-8,85/R·T) [mole/ $m^3 \times Pa^{1/2}$]	
HN80MTY oxidation film	Same	Permeability $P=3,8\cdot10^{-8}exp(-48,8/R\cdot T)$, [mole/m ×s ×Pa ^{1/2}]	
EM721	Same	Diffusion $D=4,5\cdot10^{-7}exp(-45,7/R\cdot T)$, $[m^2/s]$	
W-25,2% _{mass}		Permeability $P=3,7\cdot10^{-8}exp(-55,4/R\cdot T), [mole/m \times s \times Pa^{1/2}]$	
		Solubility Ks=0.13·exp(-9,6/R·T) [mole/ $m^3 \times Pa^{1/2}$]	
77LiF-6ThF ₄ -17BeF ₂	973-1073K	Diffusion $D=7,7\cdot10^{11}exp(-393,5/R\cdot T)$, $[m^2/s]$	
Tm =560°C (833K)	4-70 кРа	Permeability $P=1,5\cdot10^{-15}exp(-38,8/R\cdot T)$, [mole/m × s × $Pa^{1/2}$]	
		Solubility Ks=2,0 exp(-390, 1/R·T) [mole/ $m^3 \times Pa^{1/2}$]	

- Additional development of permeation-resistant coatings, including W-Si
- Ultrasonic degassing to facilitate removal of tritium, reducing required total bubble volume for gas sparging
- Refinement of geometric configuration of the intermediate heat exchangers, minimizing tritium flux
- Discovery of reusable solvents for direct tritium removal from molten salt
- The chemistry of sodium fluoroborate and the trapping process by which tritium is retained by the salt