"Historical MSR programme in Russia"

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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 power systems - perspectives and problems" V. Novikov, V. Ignatiev, V. Fedulov, V. Cherednikov, Moscow, 1990

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

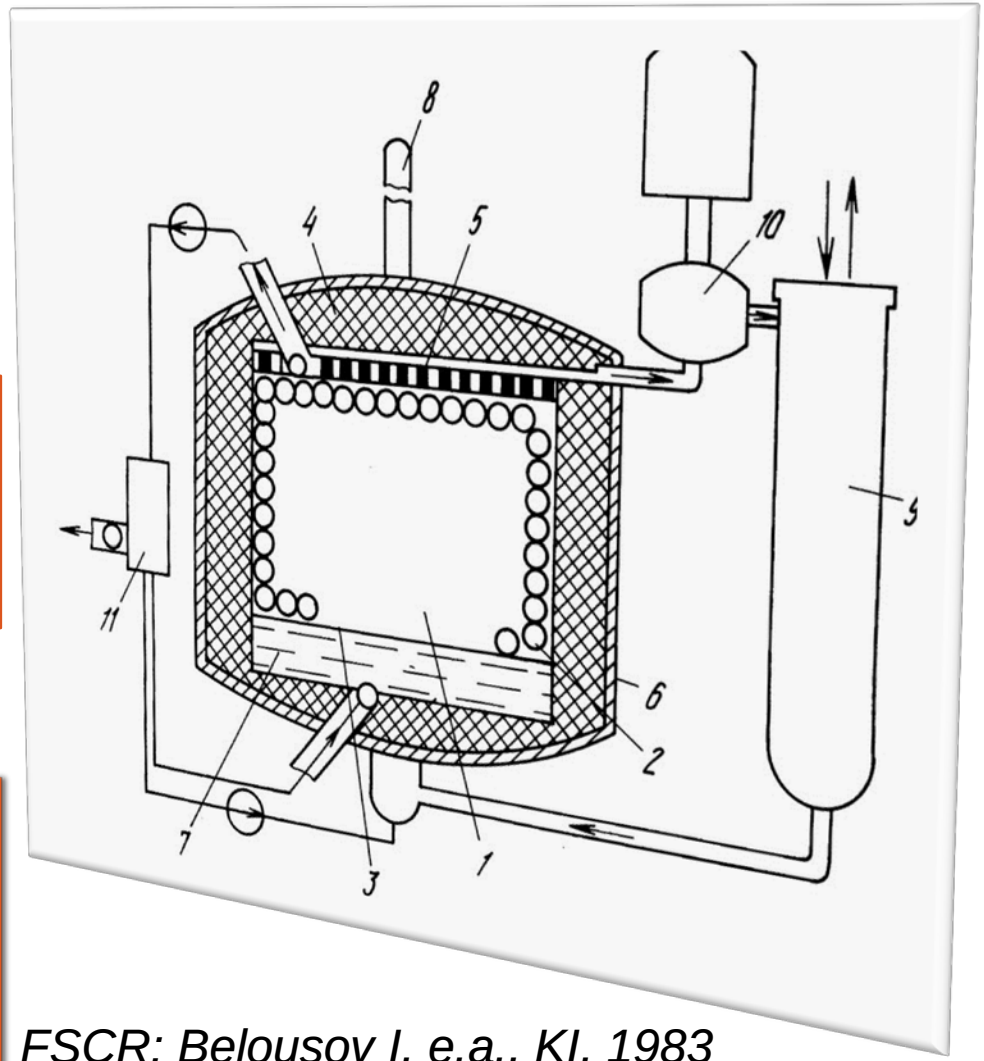
- *R&D studies are on-going in order to verify that fast spectrum MSR systems satisfy the goals of Gen-IV in terms of <u>technical feasibility, sustainability, non-proliferation, safety and waste management</u>*
- *MOSART studies are done within ISTC#1606 and #3749 tasks as well as Rosatom MARS and Euratom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

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

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

Stage 2 (MSCR):
- *Fluoride salt as coolant & liquid fuel*
- *Graphite as moderator*
- *No fuel salt processing*

Stage 3 (MOSART):
- *Fluoride salt as coolant & liquid fuel*
- *Homogeneous core*
- *Fuel salt processing*
- *All actinides recycling*



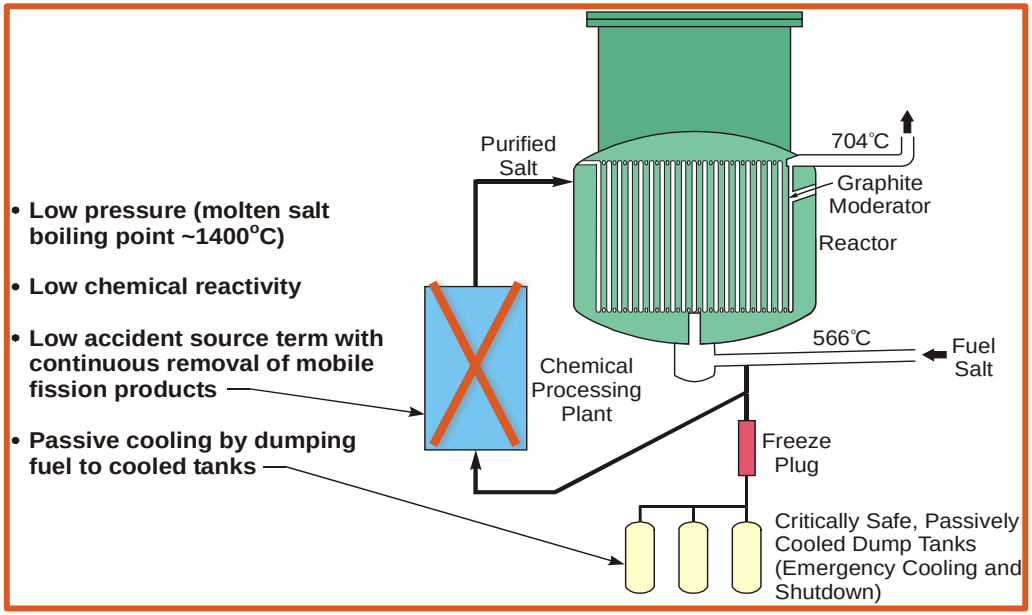
FSCR: Belousov I. e.a., KI, 1983

MSCR has a high efficiency of natural U and Th resources consumption and different safety approach that allows passive safety in large unit

Reactor	Fuel	Cycle	MWe yr / t (U_{nat}+ Th)
LWR	UO_2	open, 3yr	3.5
		closed, 3 yr	6.3
	Th-met.	open, 3 yr	3
		closed, 3 yr	12.6
MSCR	UF_4 (20%^{5}U)	open, 30 yr	11
	UF_4 (90%^{5}U)	open, 30 yr	17.2
	UF_4 (90%^{5}U)	closed, 30 yr	31.2

Q(t) – energy produced for the period *t*
G(t) – integral consumption of natural U and Th

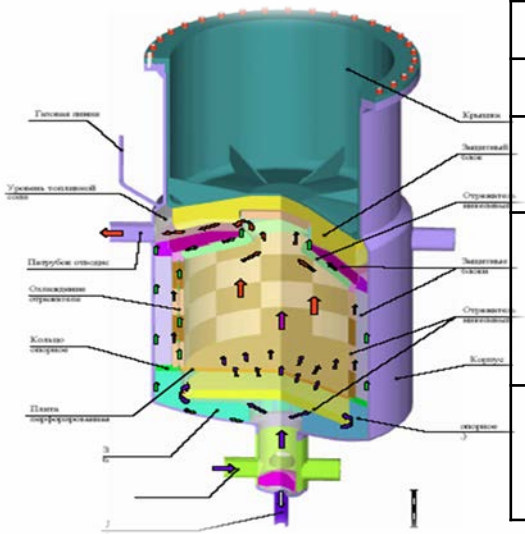
$$\alpha(t) = Q(t) / G(t)$$



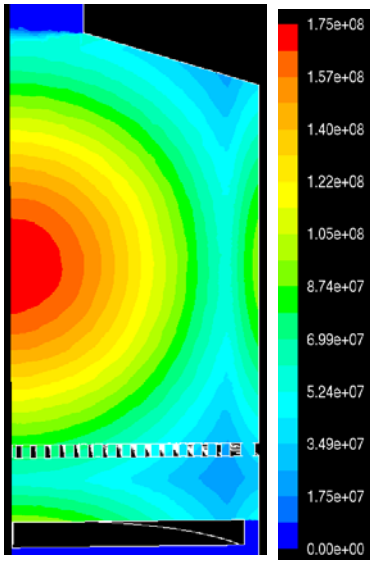
MOSART –Transforming Reactor System

Started with TRU's Fluorides from LWR used nuclear fuel has flexible fuel cycle and can operate in different modes:

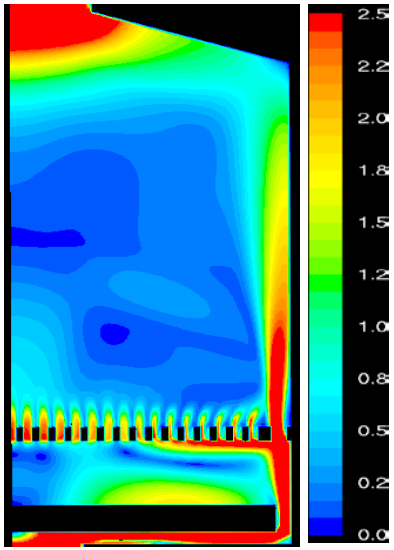
- *Transmuter*
- *Self-sustainable*
- *Breeder*



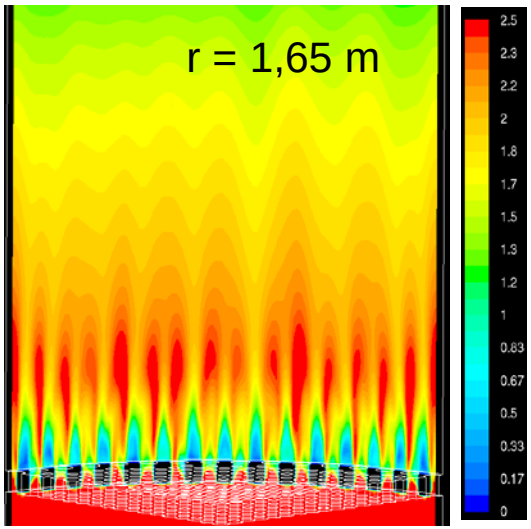
System	Burner /	Breeder
Fluid streams	1	2
Power capacity, MWt	2400	2400
Fuel salt inlet/outlet temperature, ^oC	600 /720	600 /720
Fuel salt composition, mole %	72LiF $27BeF_2$ $1TRUF_3$	75LiF $16.5BeF_2$ $6ThF_4$ $2.5TRUF_3$
Blanket salt composition, mole %	no	75LiF $5BeF_2$ $20ThF_4$



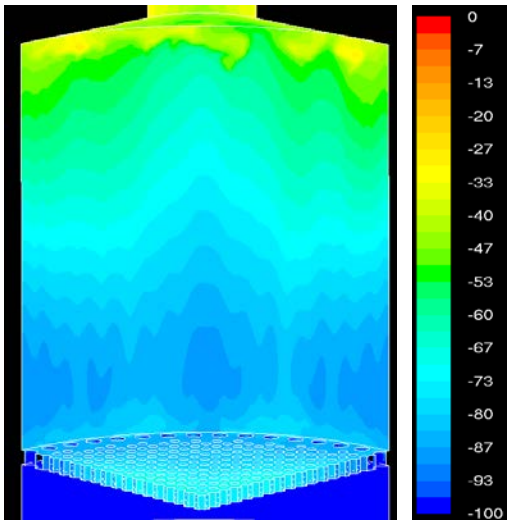
Heat source, W/m³



Velocity, m/s

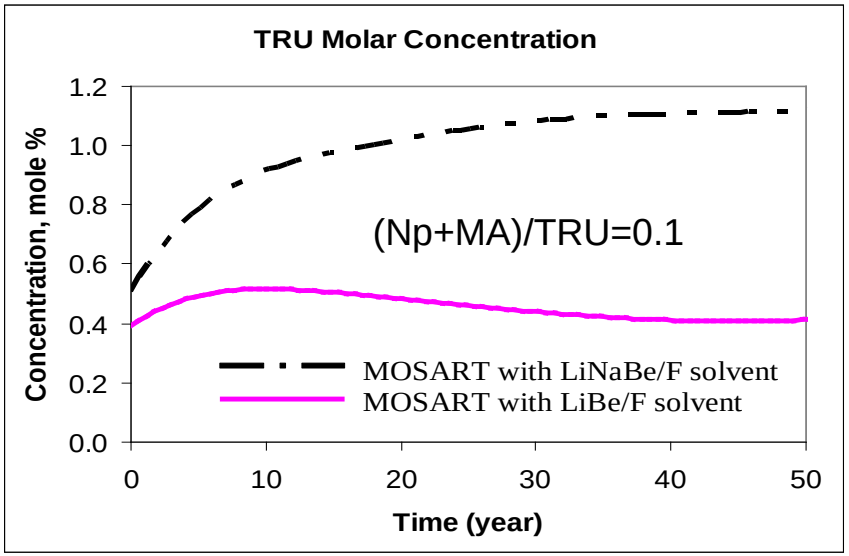


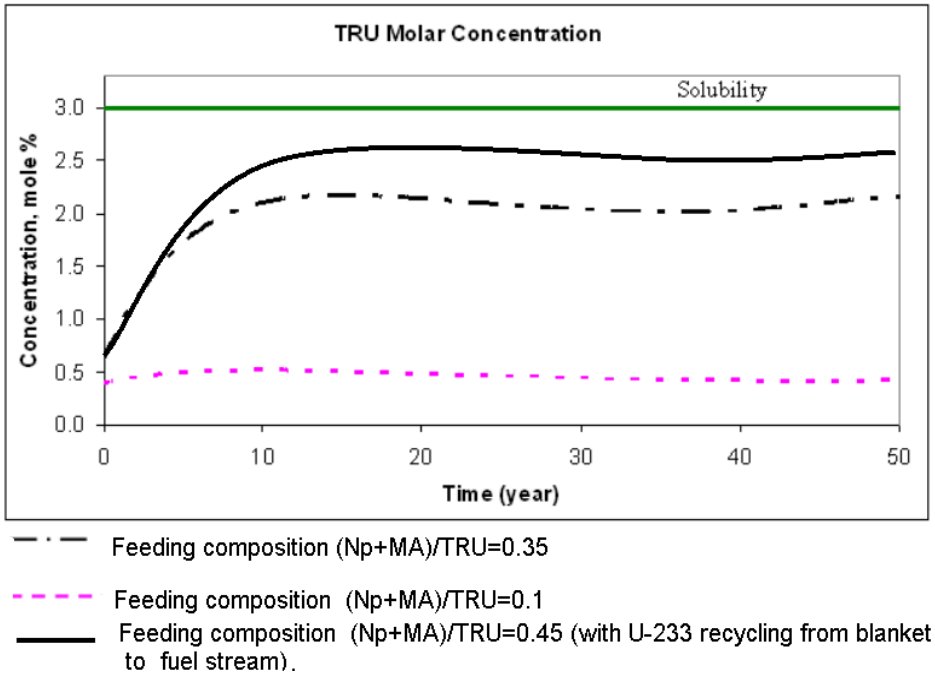
$T_{max\ wall}$: 947 K;

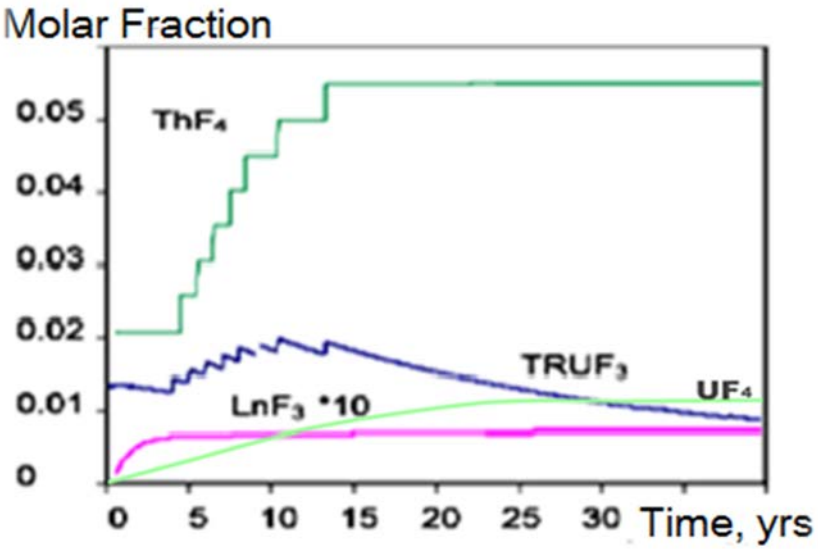


$T_{max\ fluid}$: 1192 K

MOSART Fuel Cycles

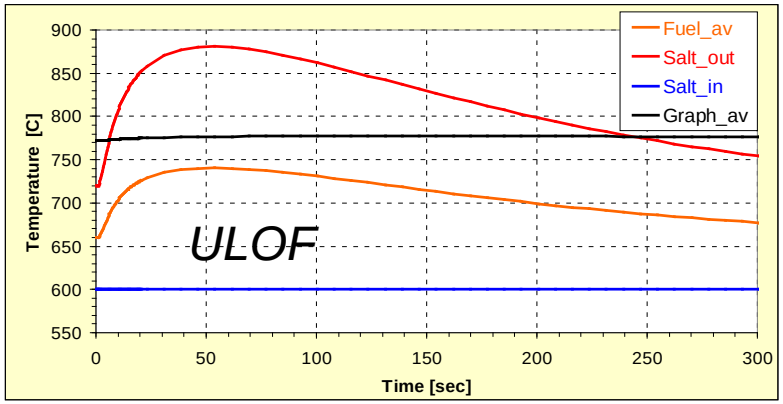


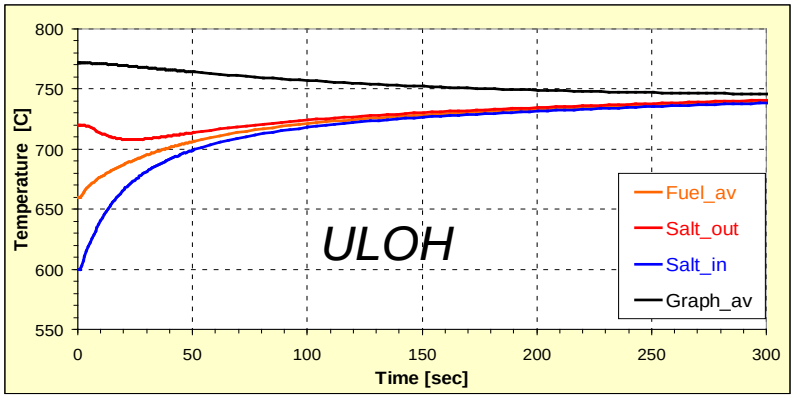


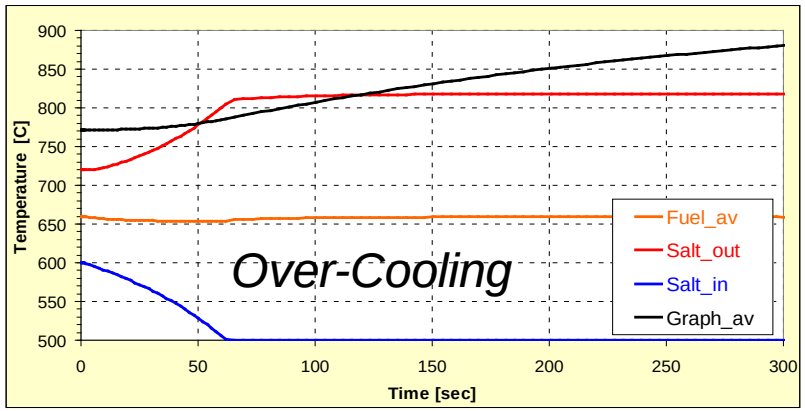


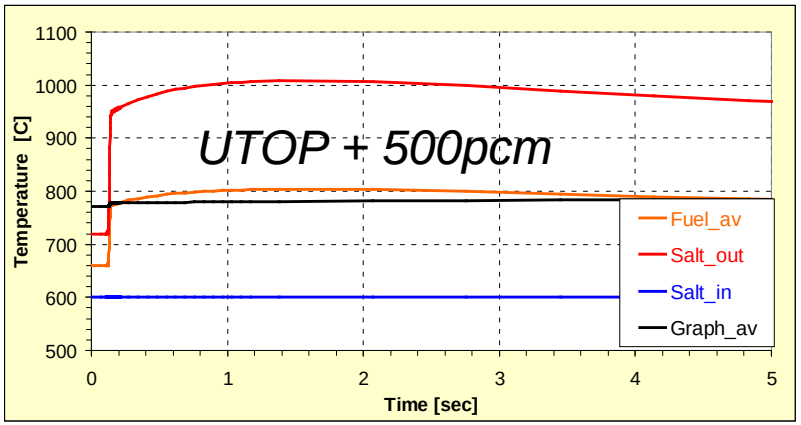
- *Single fluid 2400MWt MOSART core containing as initial loading 2 mol% of ThF_4 and 1.2 mol % of $TRUF_3$, with the rare earth removal cycle 300 epdf after 12 yrs can operate without $TRUF_3$ make up basing only on Th support as a self-sustainable system.*
- *At equilibrium molar fraction of fertile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

MOSART Transients Analysis



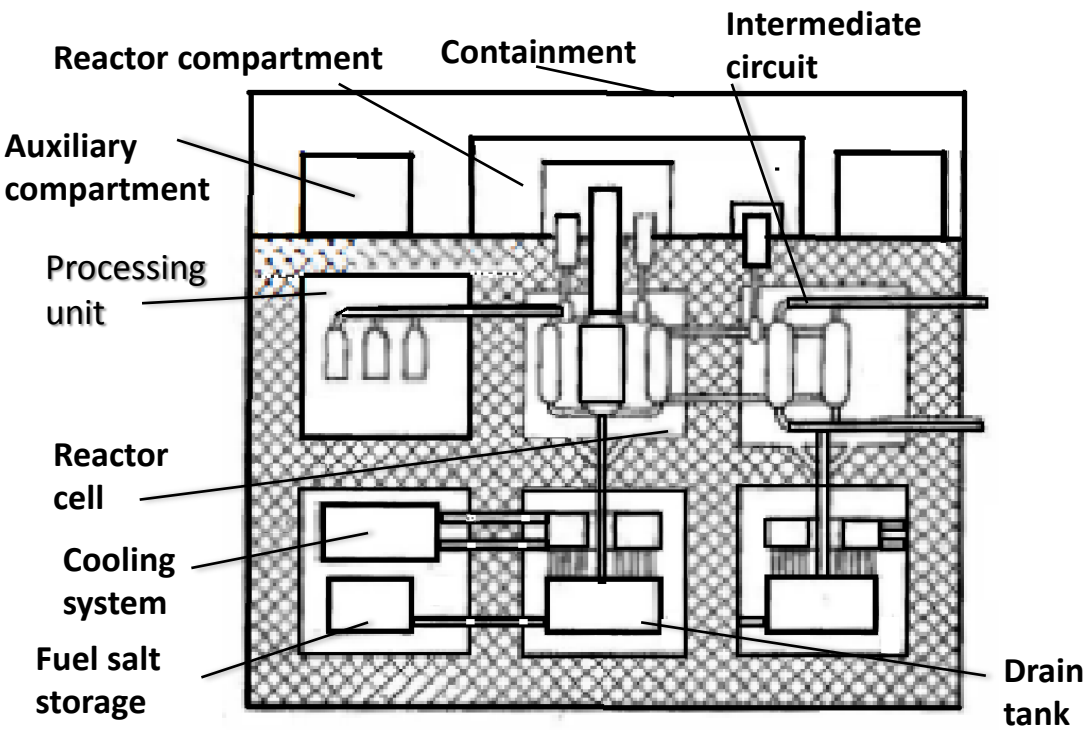


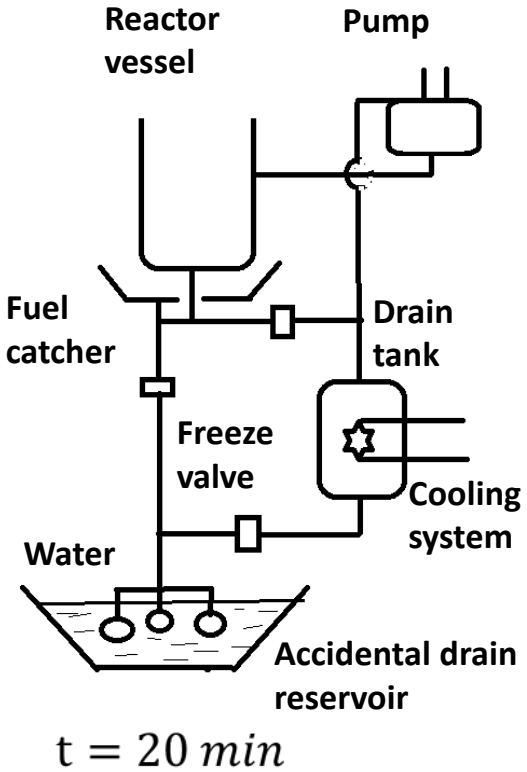




The MOSART is expected not to be seriously challenged by the major, unprotected transients such as ULOF, ULOH, overcooling, or even UTOP. The system was shown to buffer reactivity insertion of up to + 1.5$. System temperatures are expected to rise only ~300°C above nominal under this severe transient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

Two independent safety systems based on (1) control rods and (2) fuel salt transfer to subcritical drain tanks are envisaged in different MSR designs





The reactor and containment must be designed so that the fuel salt that is heated by decay heat reaches the drain tank under any credible accident conditions.

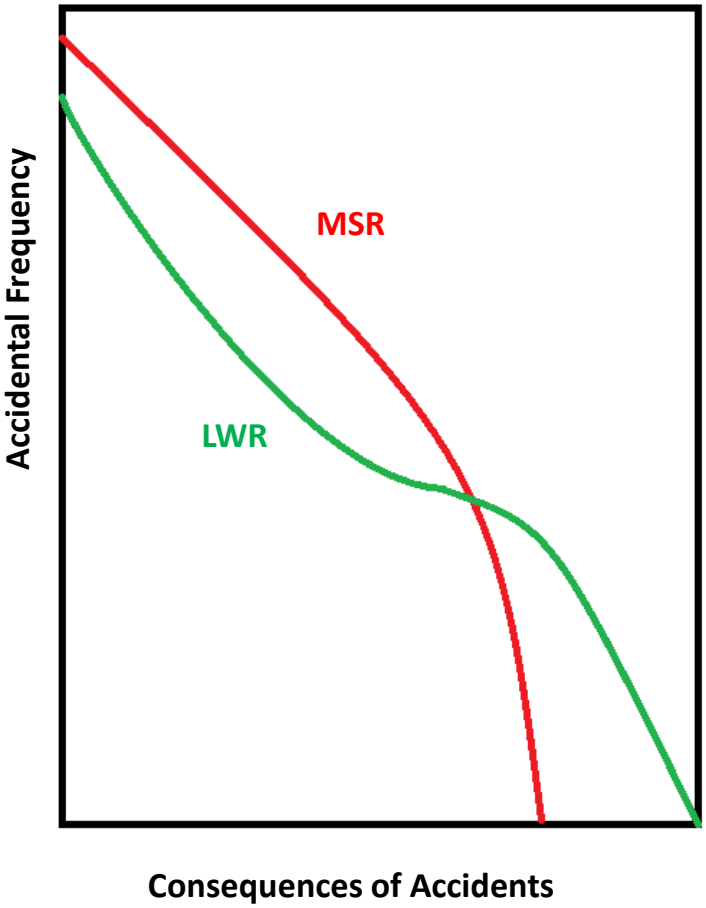
Severe accident with the rupture of the main fuel salt pipe and fuel discharged on the reactor box bottom

- *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_0)*
- *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_o	A_g /A_s	A_g /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
I131	0,62	0,43	0,27
I133	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 I^{131} and I^{133} the differences are smaller*

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



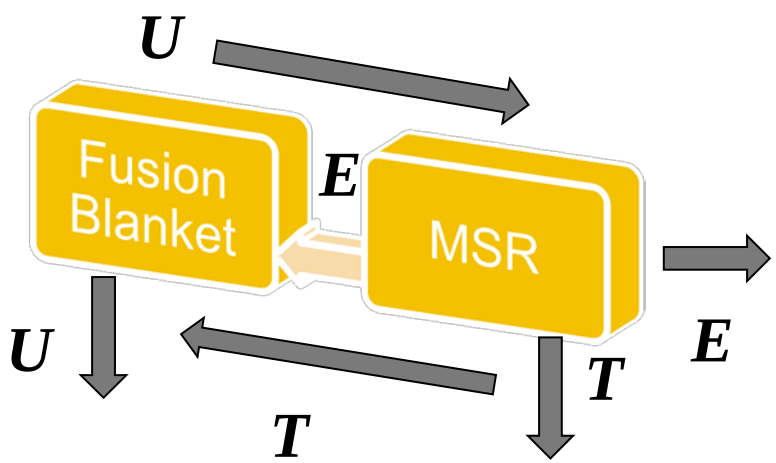
- ✓ *Probability of an accident with a relatively low impact for MSR is higher than for LWR. This is due to the possibility of leakage of radioactive liquid fuel in case of accidents in the pump, piping, valves.*
- ✓ *The consequences of severe accidents in particular, leading to the release of radioactive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

Fusion MSB with Suppressed Fission

- *Reliable, safe, low waste and effective source for ^{233}U production*
- *Molten salt mixture containing ThF_4 is circulating in a such fusion blanket*
- *Simple blanket salt processing, mainly is focused on the on-line removal of ^{233}U*

50	20	15	0.5	0.5	cm
Graphite	Na(Li),Be,Th/F -100%	Be-88%; Nb-2%; Na(Li),Be,Th/F -10%	Molten salt	First wall, Nb	Plasma



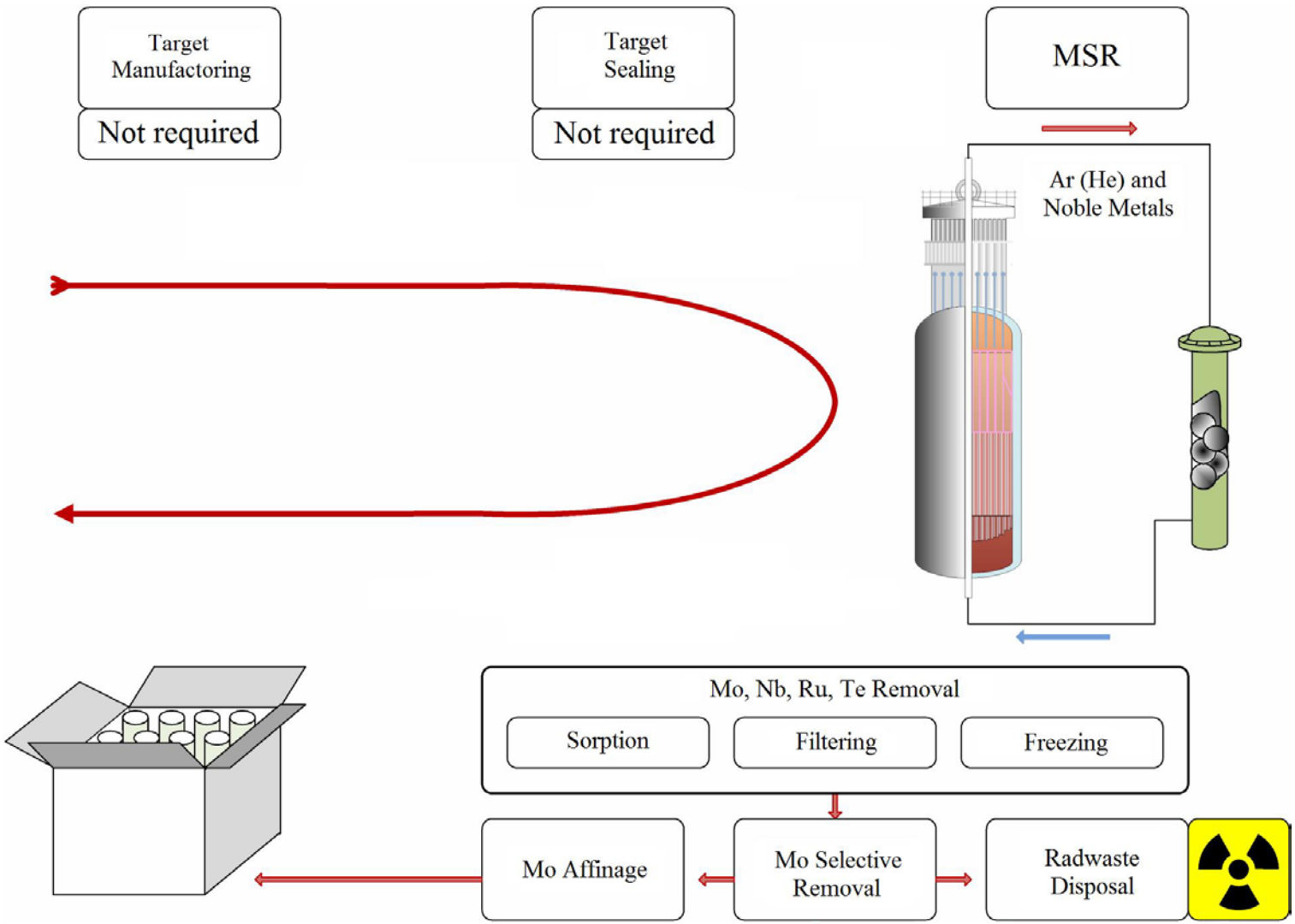
Source: Novikov V., e.a., KI, 1990

Activity Material	Ci/W	Ci/cm³
Niobium	1.0 -2.5	200-500
Fuel salt	0.4	1.8

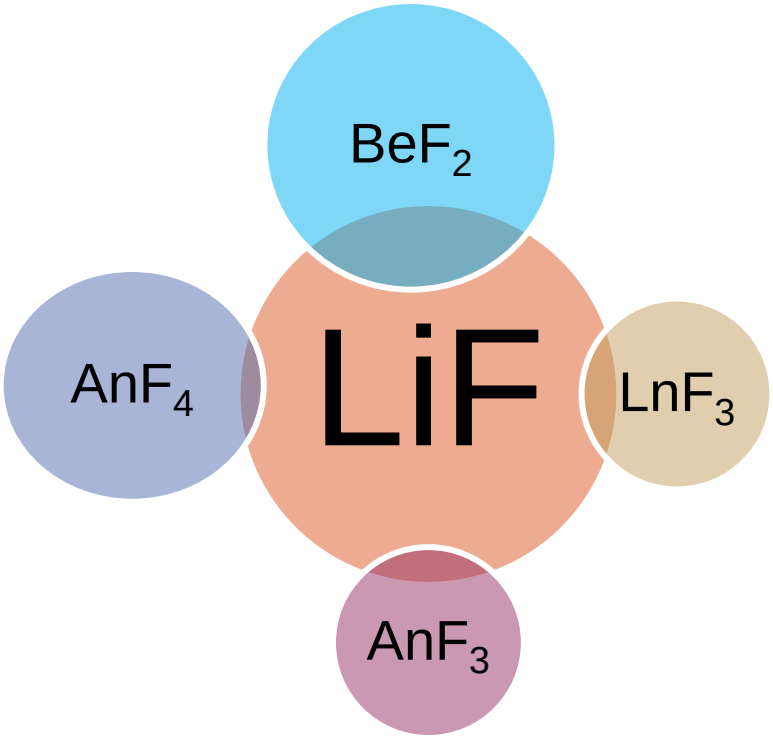
U, Pa removal time -10 days; q=1MW/m²

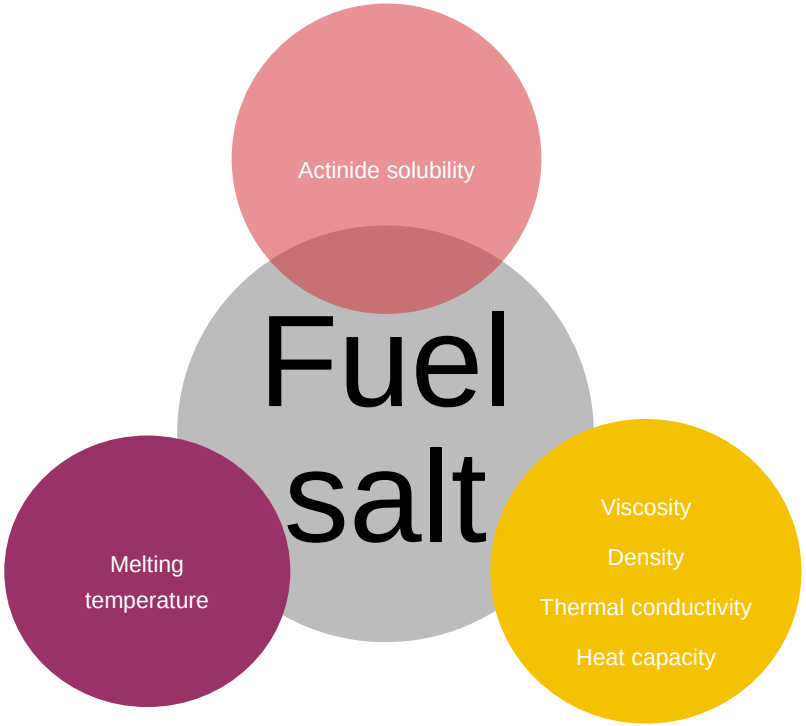
Salt, mole%	k_U	k_T	Fissions Number on Th
^7LiF -71 BeF_2 - 2 ThF_4-27	1.6	0.035	0.0085
NaF -71 BeF_2 - 2 ThF_4-27	1.5	0	0.011

^{99}Mo Production in 1MWt MSR



In most cases the base-line fuel / coolant salt is lithium-beryllium fluoride salt as it has best properties





Useful Salt Compositions

Alkali fluorides

LiF
743°C, *20 mole %*

NaF
727°C, *24 mole %*

LiF-KF
(50-50) 492°C

LiF-RbF
(44-56) 470°C

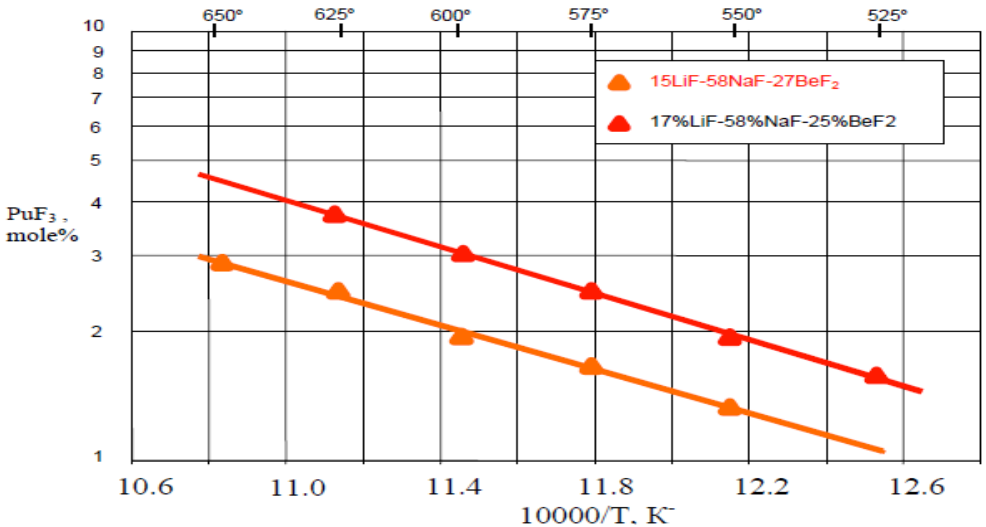
LiF-NaF-KF
(46.5-11.5-42) 454°C

ThF_4-based

LiF-ThF_4
(71-29) 555°C
3.69 mole %

LiF-BeF_2-ThF_4
(71-16-13) 499°C
1.41 mole %

LiF-BeF_2-ThF_4
(64-20-16) 460°C
1.21 mole %



T,°C	Indvidual solubility, mole%		Joint solubility, mole %	
	PuF_3	UF_4	PuF_3	UF_4
550	6,1±0,6	15,3±0,8	1,16±0,14	1,75±0,26
600	11,1±1,1	24,6±1,2	2,9±0,3	3,5±0,5
650	21,3±2,1	34,8±1,7	13,2±1,6	11,0±1,6
700	32,8±3,3	44,7±2,2	19,1±2,3	17,3±2,6
750	No data	No data	21,0±2,5	19,0±2,8
800	No data	No data	22,5±2,7	20,0±3,0

ZrF_4-based

NaF-ZrF_4
(59.5-40.5) 500°C
1.8 mole *%*

LiF-NaF-ZrF_4
(42-29-29) 460°C

LiF-NaF-ZrF_4
(26-37-37) 436°C

KF-ZrF4
(58-42) 390°C
NaF-KF-ZrF_4
(10-48-42)
385°C

BeF_2-based

LiF-NaF-BeF_2
(15-58-27) 479°C
1.94 mole %

LiF-BeF_2
(66-34) 458°C
0.47 mole %

NaF-BeF_2
(57-43) 340°C
0.26 mole%

LiF-NaF-BeF_2
(31-31-38) 315°C
0.43 mole %

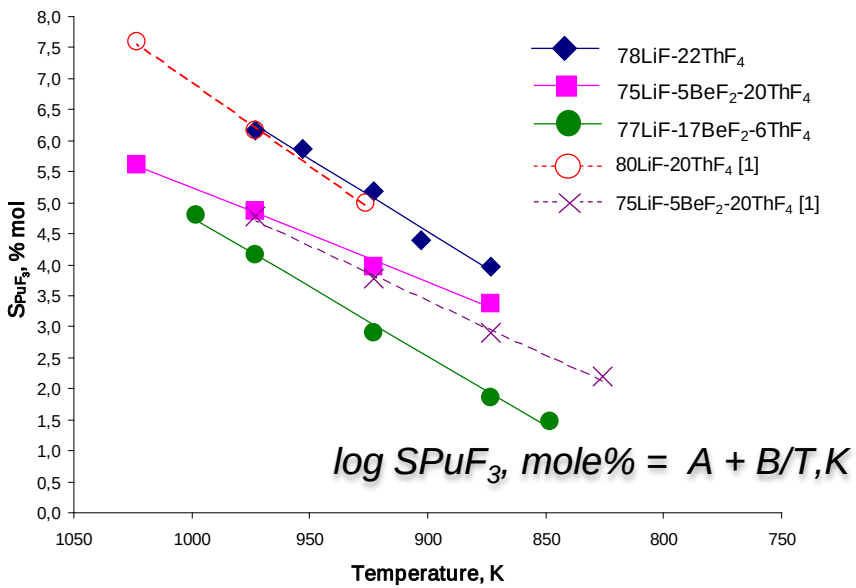
Fluoroborate

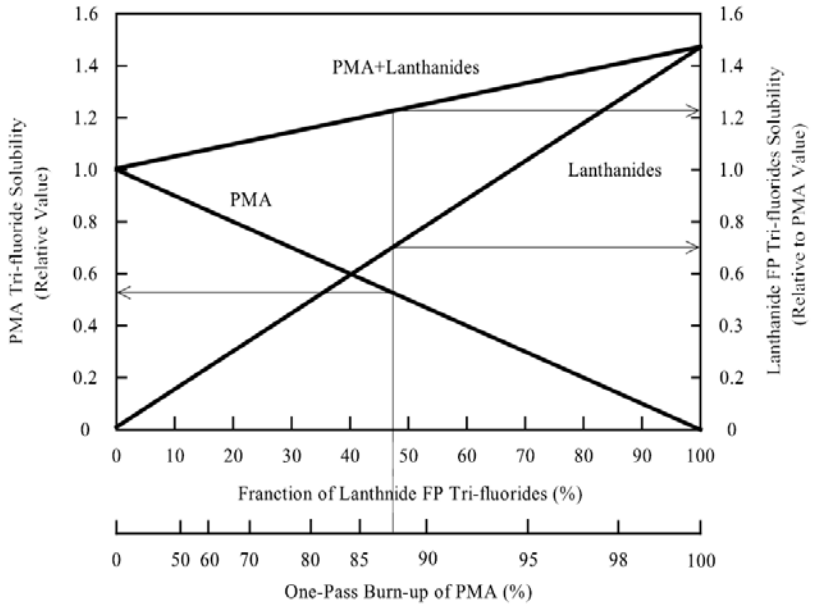
KF-KBF4
(25-75) 460°C

RbF-$RbBF_4$
(31-69) 442°C

NaF-$NaBF_4$
(8-92) 384°C

The data on An (Ln) trifluoride 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). If more than one such trifluoride is present, they crystallize as a solid solution of all the trifluorides on cooling of a saturated melt. If so, the total (Ln plus An) trifluorides in the reactor might possibly exceed their combined solubility.

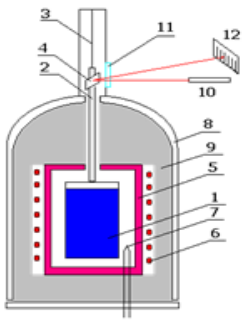


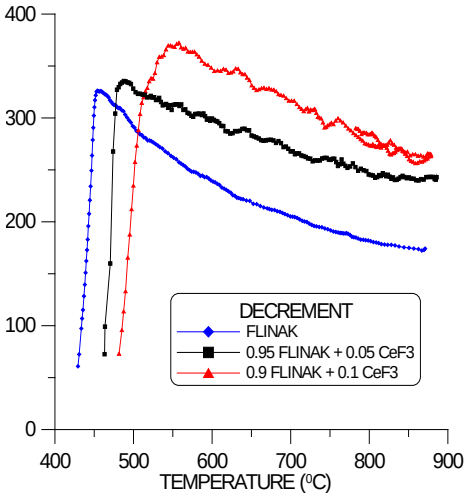


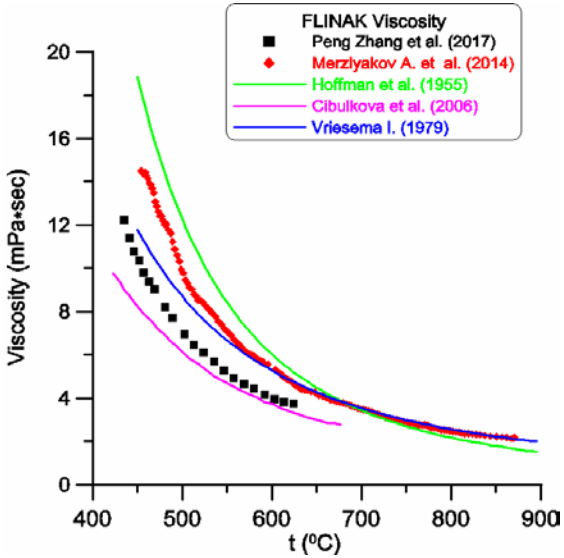
Temperature, K	72,5LiF-7ThF$_4$-20,5UF$_4$		78LiF-7ThF$_4$-15UF$_4$	
	PuF$_3$	CeF$_3$	PuF$_3$	CeF$_3$
873	0,35±0,02	1,5±0,1	1,45±0,7	2,6±0,1
923	4,5±0,2	2,5±0,1	5,6±0,3	3,6±0,2
973	8,4±0,4	3,7±0,2	9,5±0,5	4,8±0,3
1023	9,4±0,5	3,9±0,2	10,5±0,6	5,0±0,3

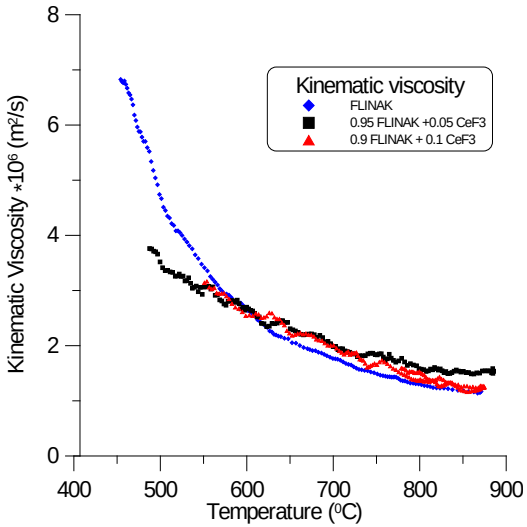
Note: Near the liquids temperature for molten 78LiF-7ThF$_4$-15UF$_4$ and 72.5LiF-7ThF$_4$-20.5UF$_4$ salts the CeF$_3$ significantly displace PuF$_3$

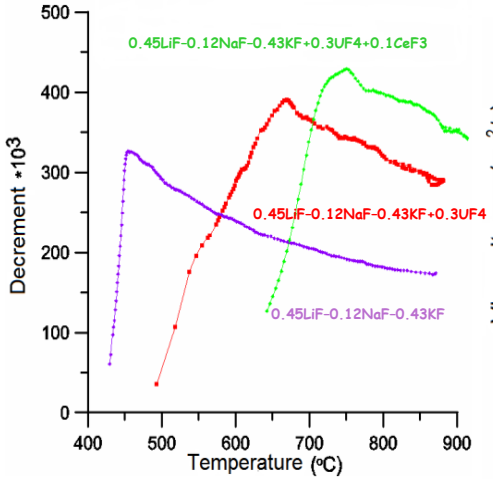
Viscosity Measurements

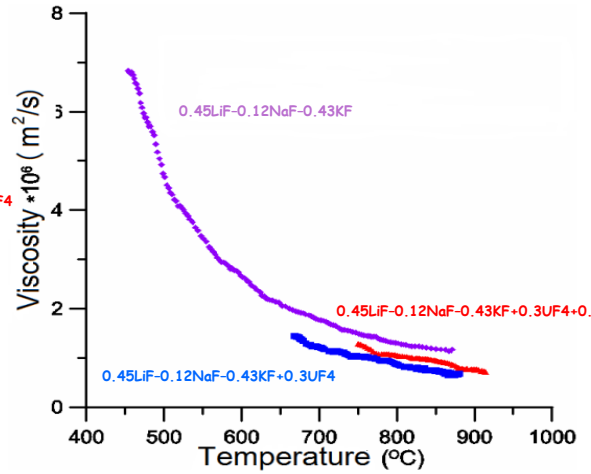


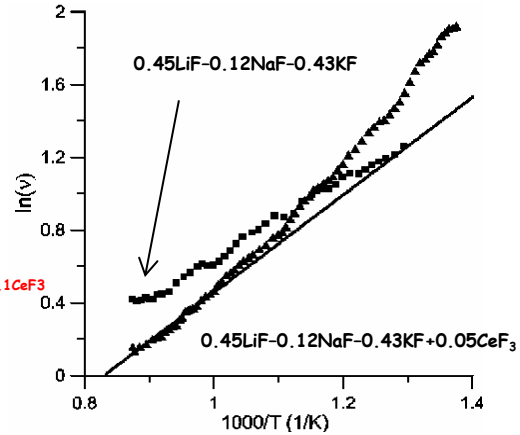




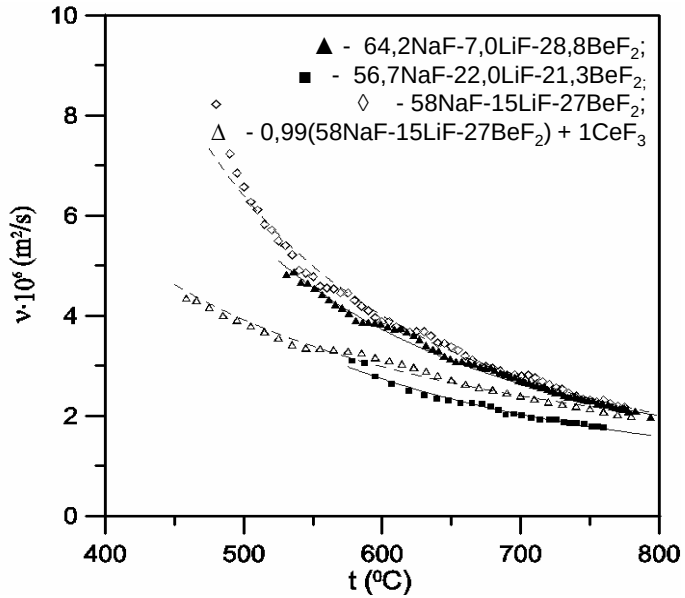


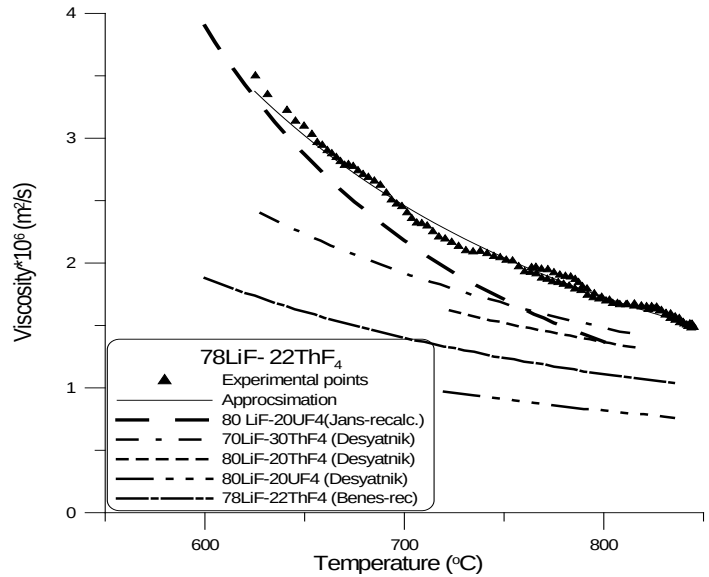


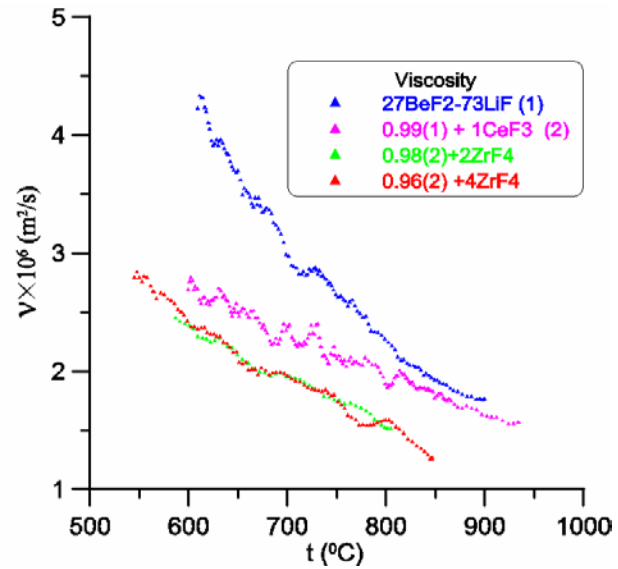


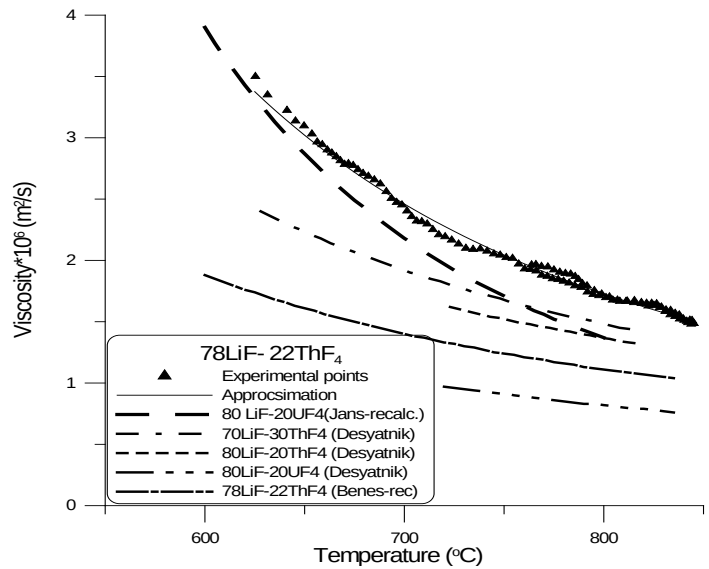


Viscosity Measurements

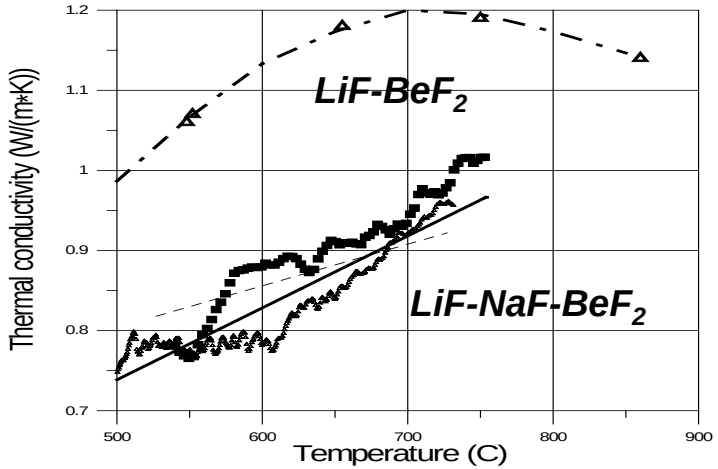








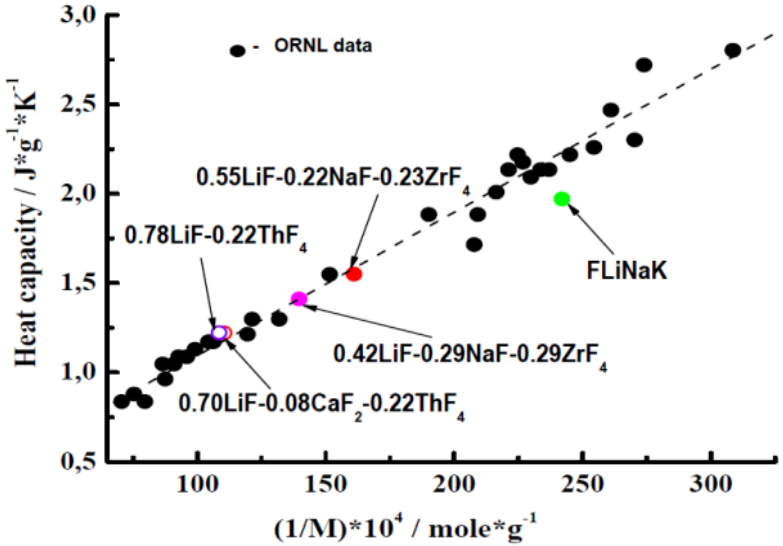
Fuel Salt Transport Properties

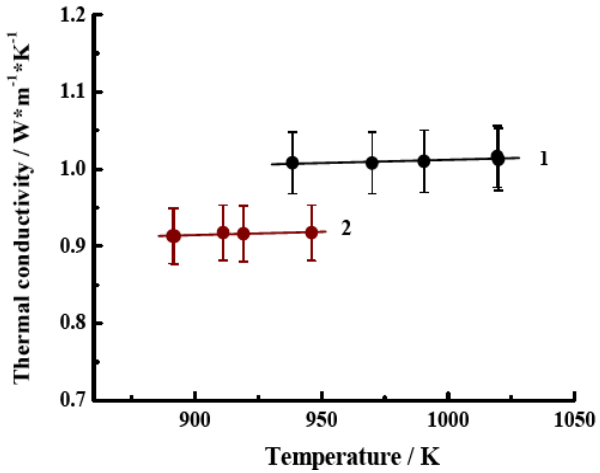


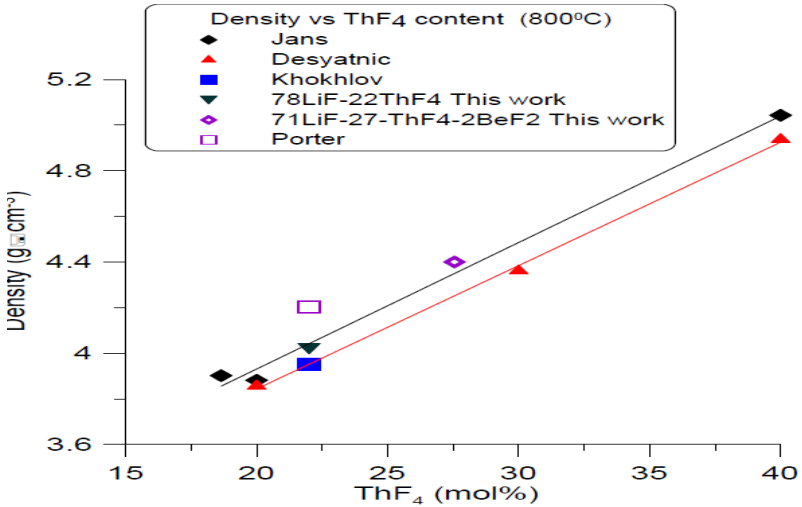
$\lambda = -0.34 + 0.5\cdot10^{-3}T(K)+32/M$

$\lambda = 0.928 + 8.397\cdot10^{-5}T \pm 0.054$ $(0.78LiF - 0.22ThF_4)$ и

$\lambda = 0.842 + 8.062\cdot10^{-5}T \pm 0.038$ $(0.70LiF-0.08CaF_2-0.22ThF_4)$.



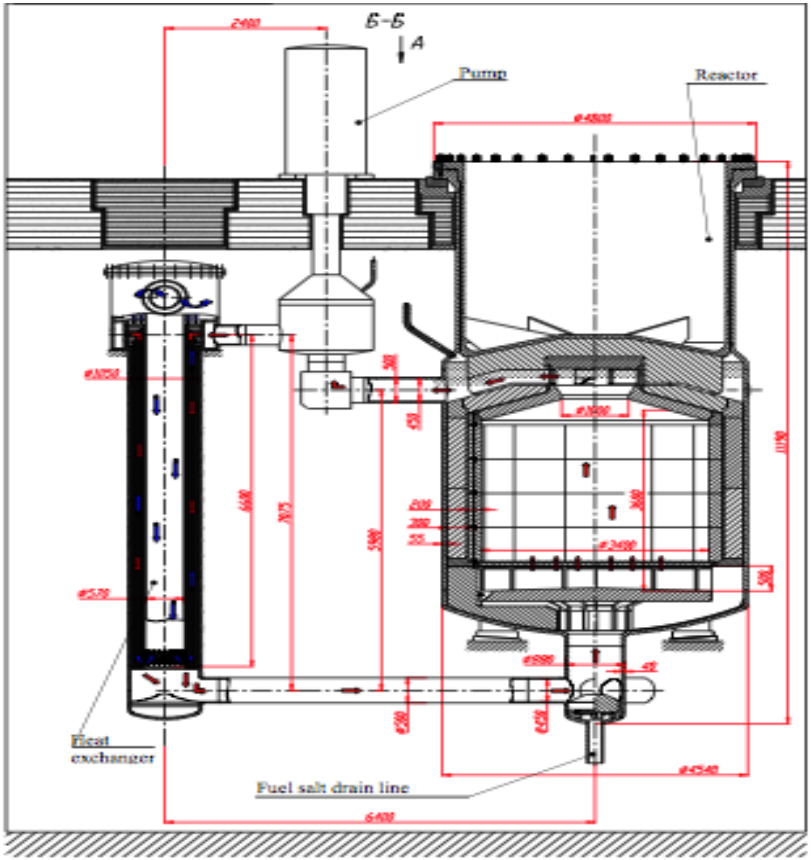




Selection of Materials for Components

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

Ni-based alloy
Intermediate circuit - *455 / 620 ° C* Aging, Welds, Compatibility $NaF-NaBF_4$, Oxidation, Wastage…



Ni-based alloy / SS
Vessel - *600 ° C*
Negligible creep

C, Ni
Reflector*600-750 ° C*
Negligible creep

SiC
Distribution plate- *600 ° C*,
High irradiation

- *<u>Max temperature</u> of the fuel salt in the primary circuit made of special Ni-alloy 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*

In temperature range 500-800^{0}C about 70 differently alloyed specimens of HN80MT were tested. Among alloying elements there were W, Nb, Re, V, Al and Cu

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

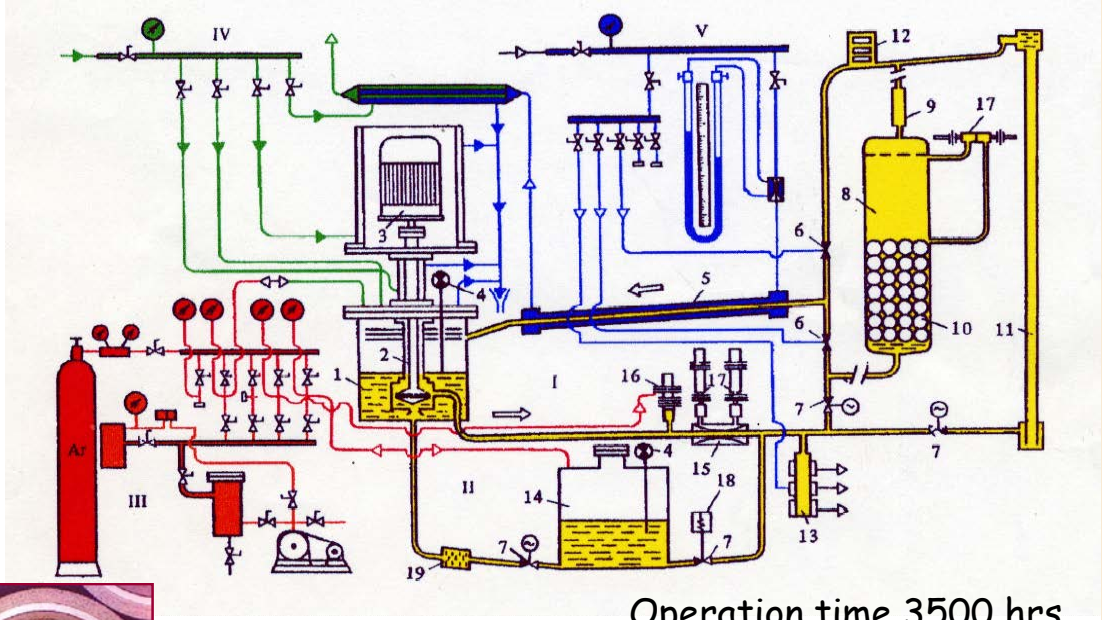
- *Experiments results in polythermal loops with redox potential control demonstrated that operations with Li,Be/F salt, also fuelled by UF_4 or PuF_3, are feasible using carefully purified molten salts and loop internals.*
- *Russian HN80MTY alloy with 1% added aluminum is the most resistant with fuel 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.*

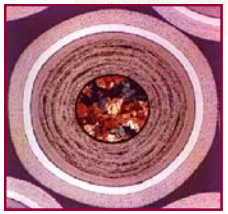
Russian Molten Salt Test Loops

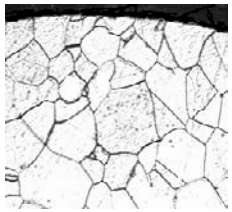
Loop	Melt, % mole	Volume, l	Alloy	$T_{макс}$,°C	ΔT, °C	Operation, hrs
SOLARIS	46,5LiF - 11,5NaF - 42KF	90	12kH18N10T	620	20	3500
KI C1	$92NaBF_4$- 8NaF	6	kHN80MT	630	100	1000
KI F1	72LiF- $16BeF_2$- $12ThF_4$+ UF_4	6	kHN80MTY	750	70	1000
KI M1	66LiF- $34BeF_2$ + UF_4	19	12kH18N10T	630	100	500
KURS-2	66LiF - $34BeF_2$ +UF_4	19	12kH18N10T	750	250	750
ISTC#1606	LiF- NaF- BeF_2+PuF_3	8	Ni - based	700	100	1600
ISTC#1606	LiF- NaF- BeF_2+ Cr_3Te_4	12	Ni -based	650	10	500
ISTC#3749	LiF- ThF_4- (BeF_2)+UF_4	8	Ni -based	750	100	1500
MARS	LiF-ThF_4- (BeF_2)+UF_4 + Cr_3Te_4	12	Ni -based	800	40	1500

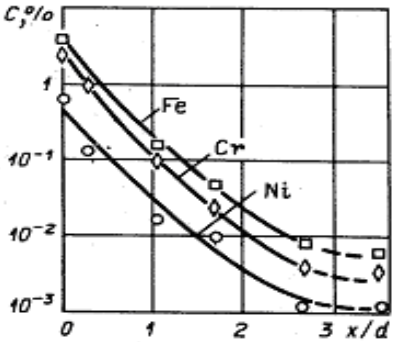
- *A number of high-temperature MS test loops with forced and natural circulation was created and successfully tested.*
- *In laboratory and in reactor tests lasting from 500 till 3500 hrs at temperatures 500-800°C working capacity of loops components and system is shown.*
- *Modes of start-up and shut down installations are fulfilled and also ways for impurities removal and redox- potential measurement are improved.*
- *Questions of interaction with constructional materials, radiation resistance, heat and mass transfer in molten salt fluorides are studied.*

LiF-NaF-KF Forced Convection Loop

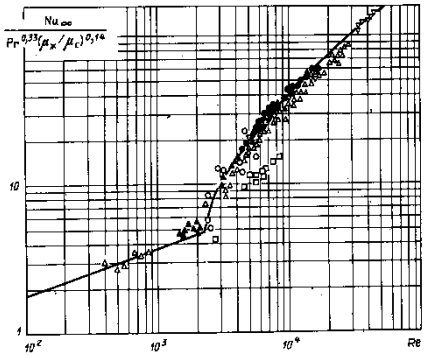


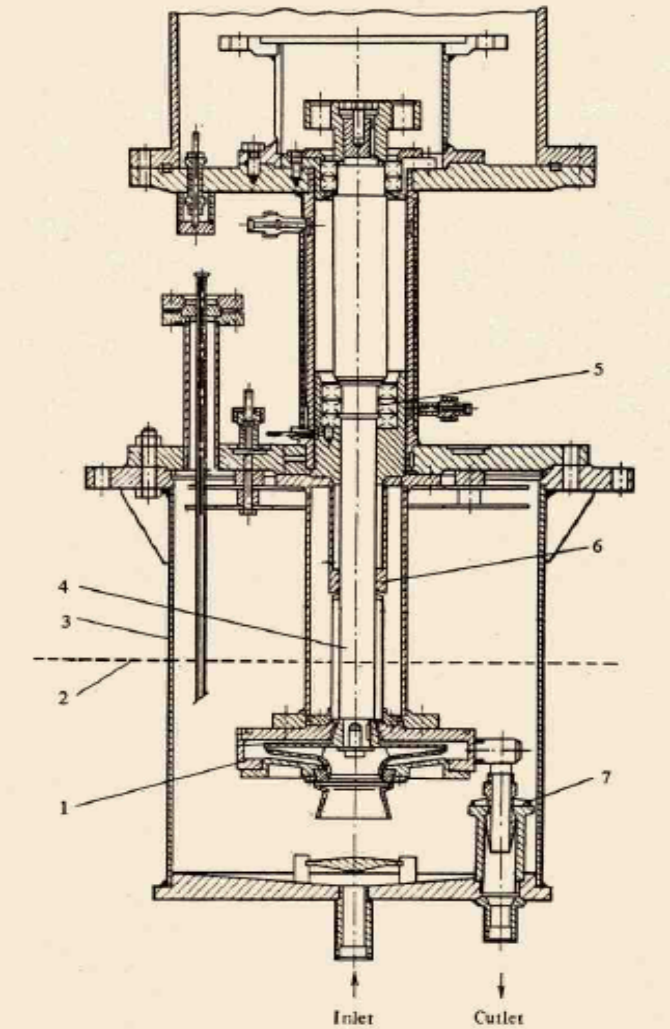






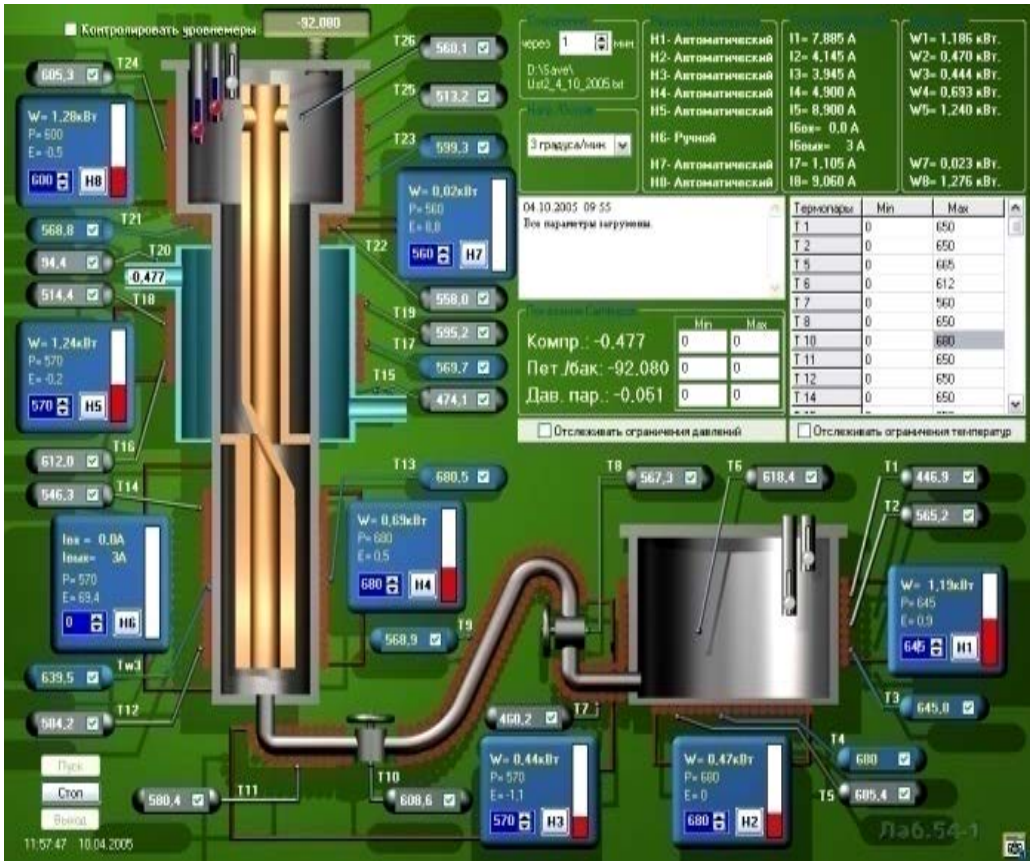
Operation time 3500 hrs

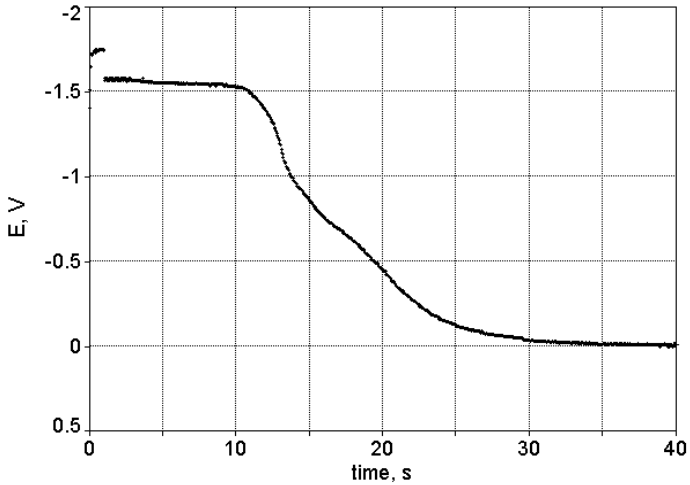


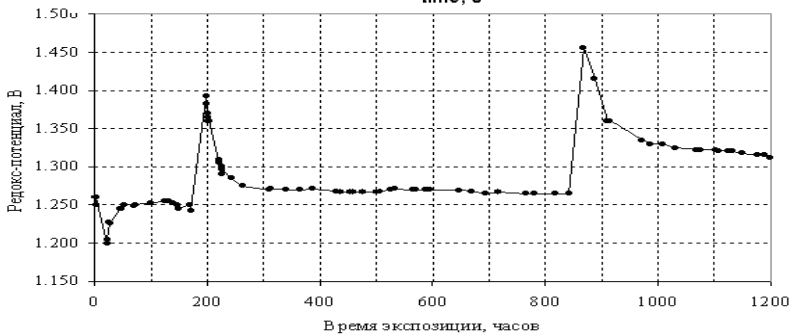


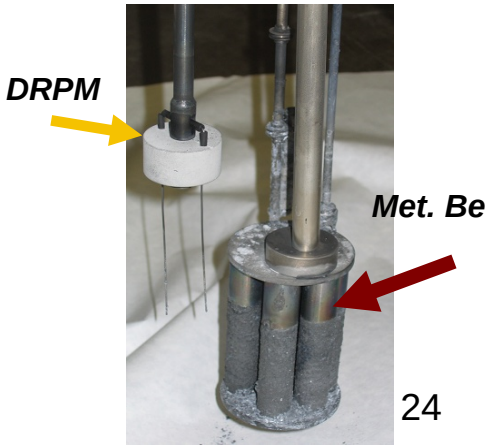
At NRC–KI we know how to make reliable short-shaft centrifugal pumps for molten salt test loops, having built and operated with capacities to 2000 rpm.

Li,Be,Na,Pu/F Thermal Convection Loop



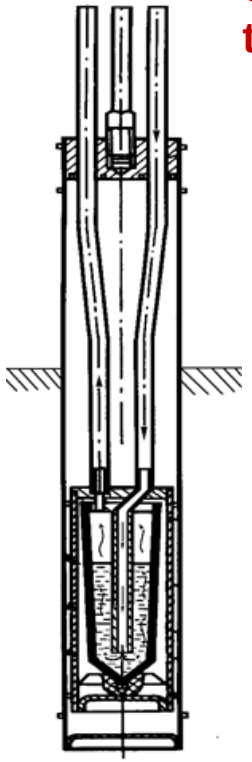






It was developed three electrode design for <u>measurement of redox potential</u> with non-stationary dynamic beryllium reference electrode (DRPM). It is highly sensitive to variation of redox potential in molten BeF_2 - containing mixtures and ensures good reproducibility of measured values.

ORNL tests strongly suggested that the F_2 generation had at the high temperature not occurred (gas was generating mainly via reaction $^6Li(n,\alpha)T$), but had occurred by radiolysis of the mixture in the solid state. F_2 evolution at 35°C corresponded to about 0,02 molecules per 100 eV absorbed, could be completely stopped by heating to 100°C or above, and could be reduced by chilling to -70°C. The F_2 evolution resumed, usually after a few hours, when temperature was returned to 35 to 50°C.



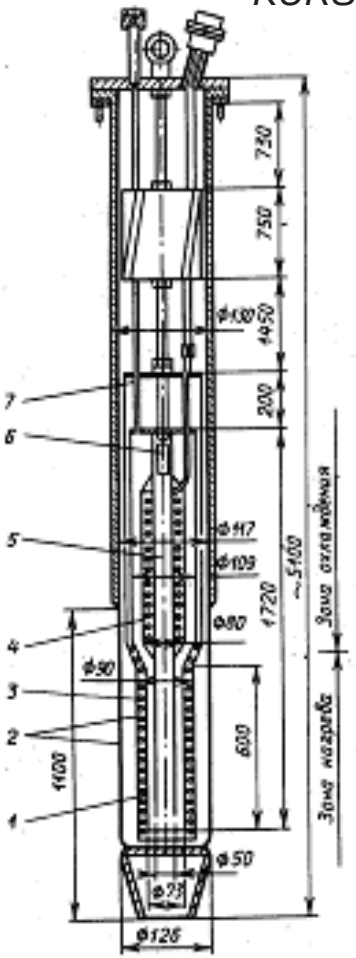
KI in reactor tests	Liquid phase		Solid phase	
Fuel salt, mole %	T,°C	$G(F_2)$,10^{-5} mol/100eV	T,°C	$G(F_2)$,10^{-2} mol/100eV
$66LiF\text{-}33BeF_2\text{-}1UF_4$	615	7	50	1
$69LiF\text{-}31BeF_2$	680	2		0.2
$71.7LiF\text{-}16BeF_2\text{-}12ThF_4\text{-}0.3UF_4$	740	3	25	0.6
$65.6^7LiF\text{-}34.39BeF_2\text{-}0.3UF_4$	740	0.2	25	-
$73.6iF\text{-}25.9.2ThF_4\text{-}0.5UF_4$	1200	2	-	2.5
$74NaF\text{-}25.9ThF_4\text{-}0.9UF_4$	1150	0.15	50	2

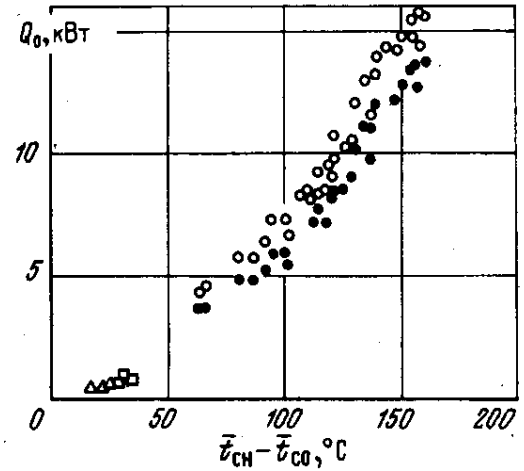
These and subsequent experiences, including operation of the 8MWe MSRE at US ORNL, strongly indicate that radiolysis of the molten fuel at reasonable power densities is not a problem. It seems unlikely, though it is possible, that MSR fuels will evolve F_2 on cooling. If they do, arrangements must be made for their storage at elevated temperature until a fraction of the decay energy is dissipated

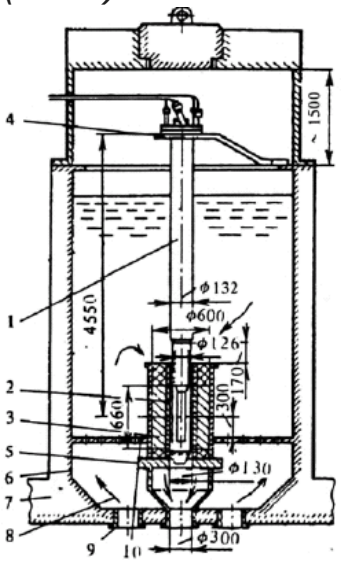
In Reactor Li,Be,U/F Natural Convection Loop

KURS-2 exposure time~ 750 hrs

T_{max}=750 °C; Φ = 0,76•10^{14} neutron/(см^2•s)

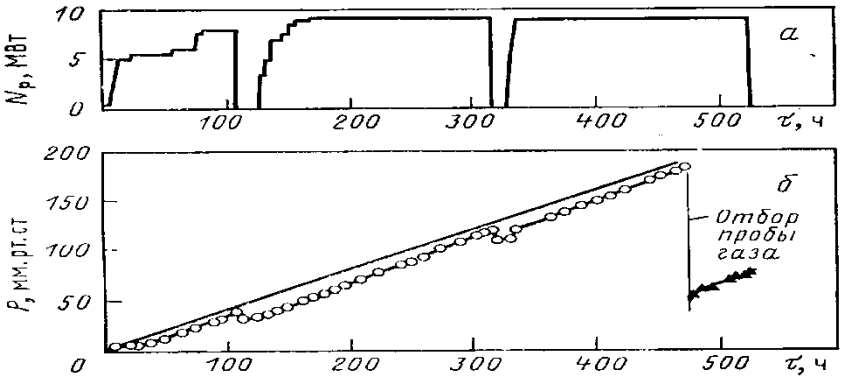






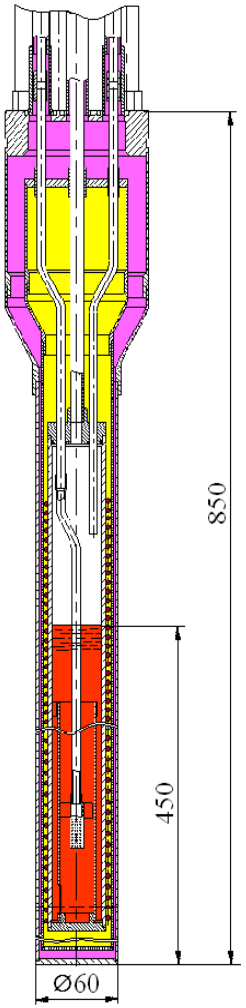
Helium was generating through reaction

$6LiF + {}^1n \rightarrow He + 1/2T_2 + 1/2F_2$



Measured F evaluation by radiolysis corresponded to 3·10 $^{-6}$ молmolecule per 100 eV absorbed

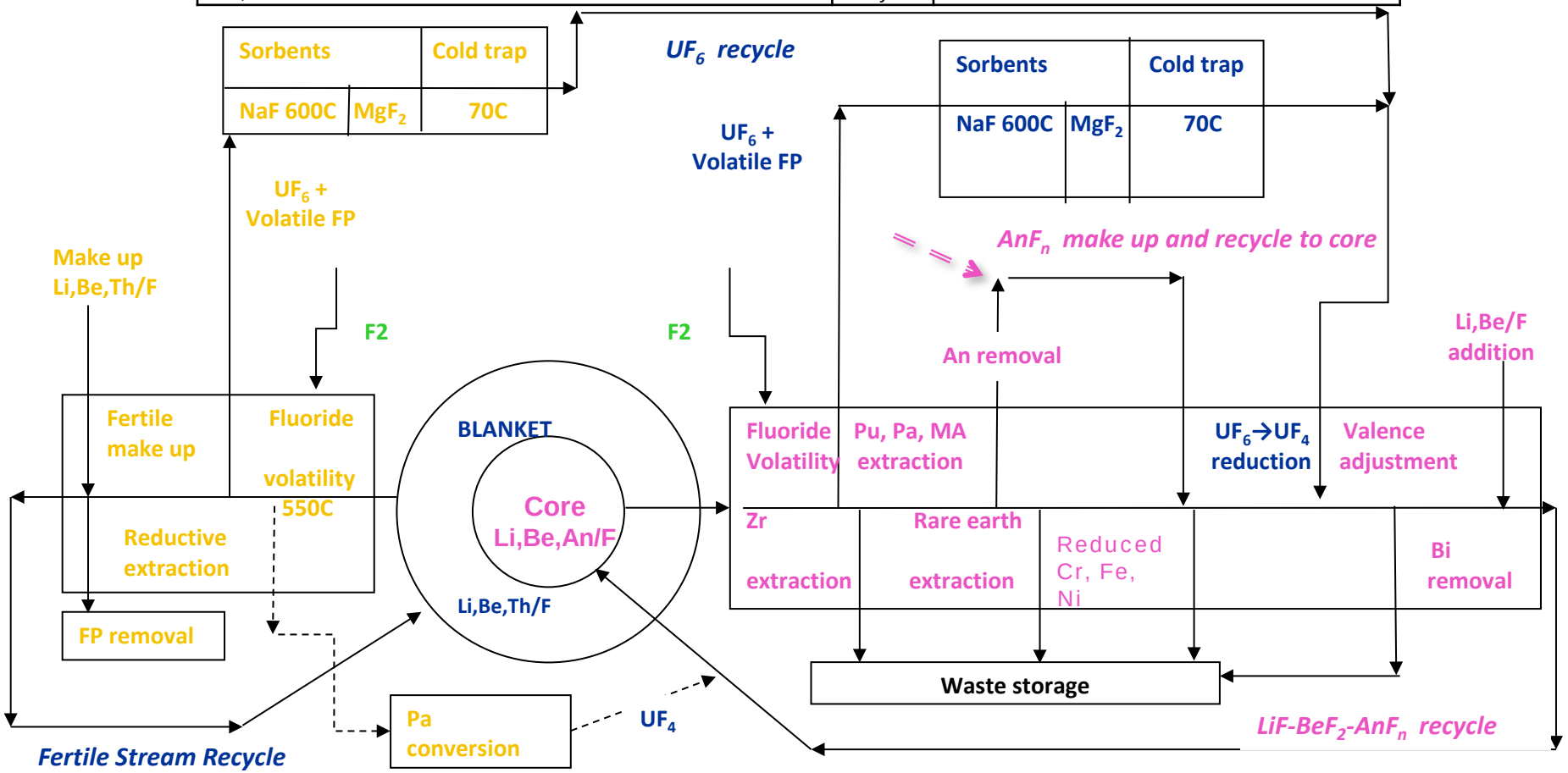
In reactor Li,Be,U/F Facility for Mo production



IR-8 test reactor power	*8 MWt*
Container material	*SS 316*
Diameter (in the reflector)	*60 mm*
Height	*10.1 m*
Fuel salt, mole%	*66LiF-34BeF$_2$-UF$_4$*
^{235}U Enrichment	*90 %*
Temperatures	*600-700 ^{0}C*
Salt volume	*410 cm^3*
Purge gas	*He with Kr u Xe admixture*
Gas flow rate	*1 cm^3/s*
Pressure upon the salt surface	*0,08 MPa (abs)*

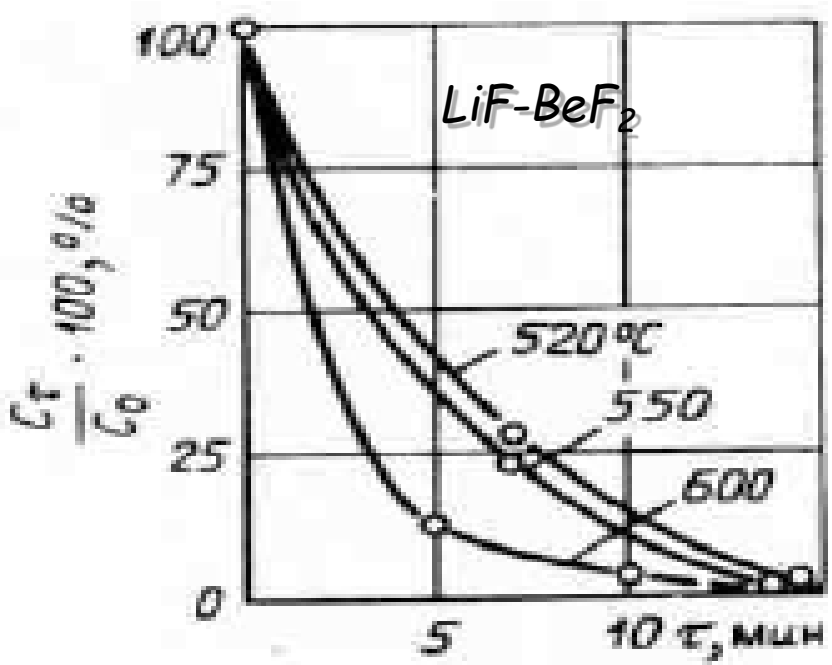
Two Fluid Th MOSART Flowsheet

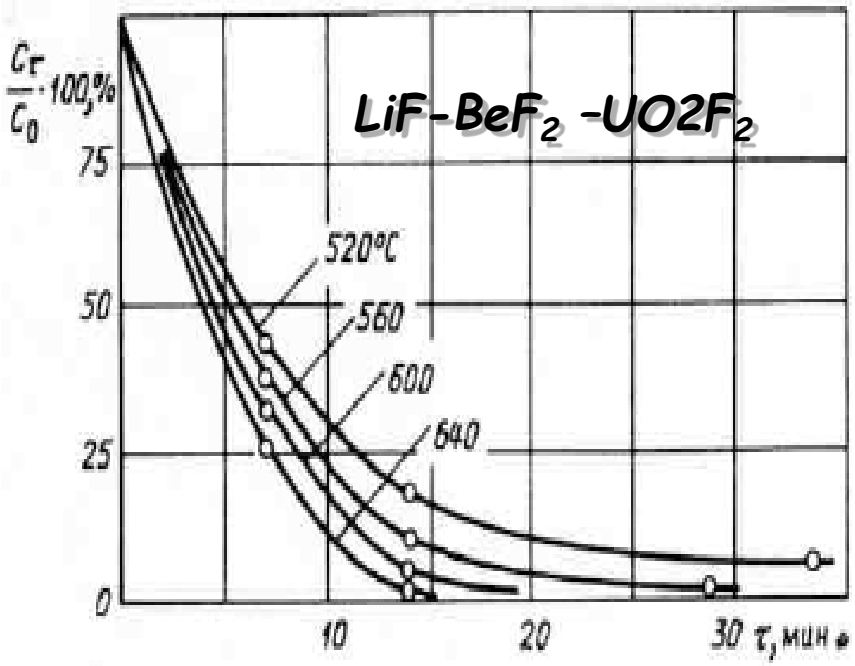
Element	Time	Method
Kr, Xe	50 s	Sparging with He
Zn, Ga, Ge, As, Se, Nb, Mo, Ru, Rh, Pd, Ag, Tc, Cd, In, Sn, Sb, Te	2-4 hrs	Plating on surfaces, to off-gas system, filtering
^{233}U,^{234}U,^{235}U,^{236}U,^{237}U	10 d	Fluorination
Zr, ^{233}Pa	1-3 yrs	Reductive extraction in liquid Bi
Ni, Fe, Cr	1-3 yrs	
Pu, Am, Cm, Np	1-3 yrs	
Y, La, Ce, Pr, Nd, Pm, Gd, Tb, Dy, Ho, Er	1-3 yrs	
Sm, Eu	1-3 yrs	



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

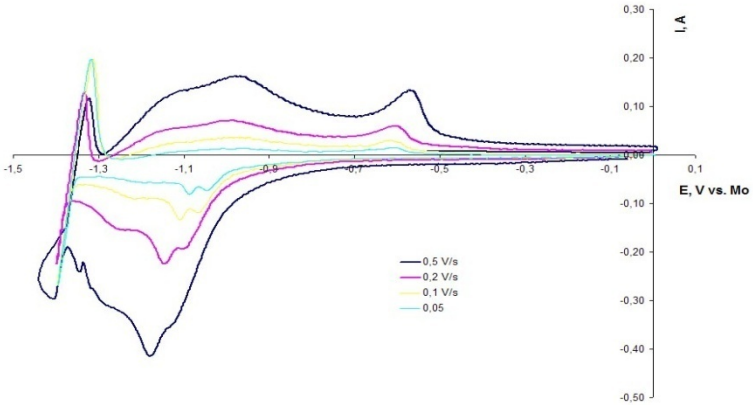


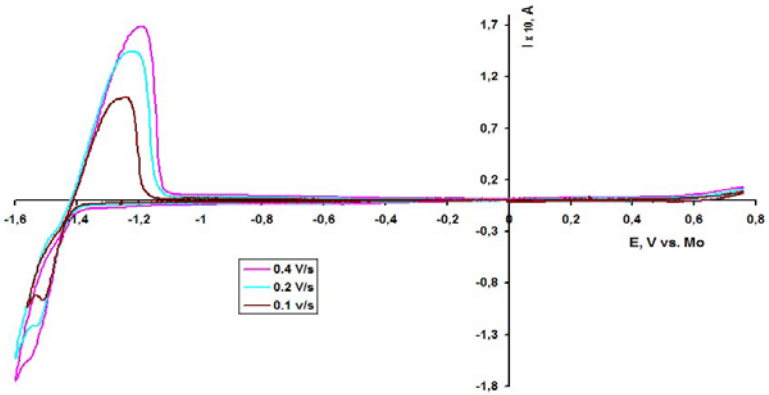


- *<u>In static conditions</u> at temperature of 750°C and fluorine pressure of 50 kPa the normalized rate of PaF_5 removal from the Li,Be/F salt surface into the fluorinator's "cold" zone with the wall temperature of 400°C was $\Delta m/m/\tau \approx 5 \cdot 10^{-2}\ hr^{-1}$. In this case the ^{233}Pa 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

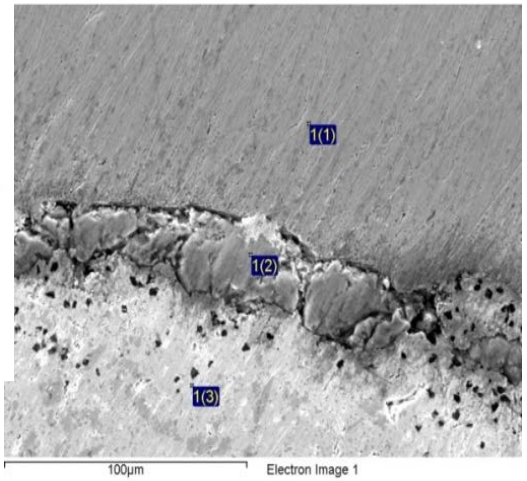
CV's of PuF_3 (0.05 mole %) in LiF-NaF for various potential scan rates. WE - Mo, RE – Mo. T=1023K

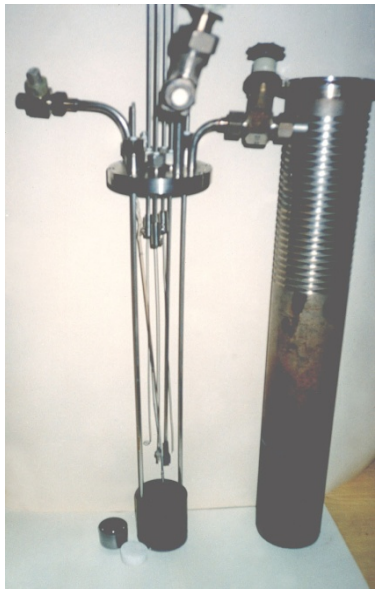




CV's of PuF_3 (0.1 mole %) in LiF-NaF-BeF_2 for various potential scan rates. WE - Mo, RE – Mo. T=853K

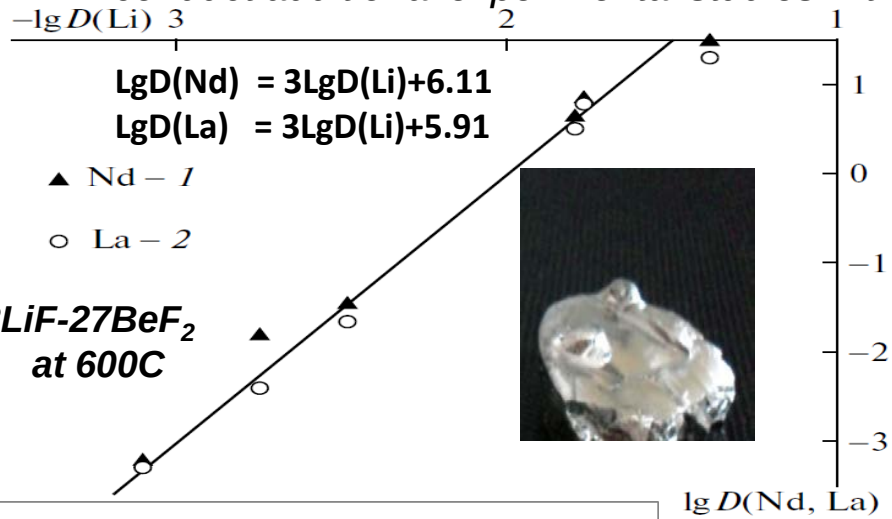
- *Equilibrium potentials of the Pu^{3+}/Pu, Zr^{2+}/Zr, Be^{2+}/Be, Na^{+}/Na couples in 15LiF-58NaF-27BeF_2 and 60LiF-40NaF (in mole %) melts were determined*
- *It was shown, that plutonium is deposited on molybdenum cathode earlier than beryllium and sodium. Difference of plutonium and beryllium 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-27BeF_2 and 60LiF-40NaF melts were estimated*

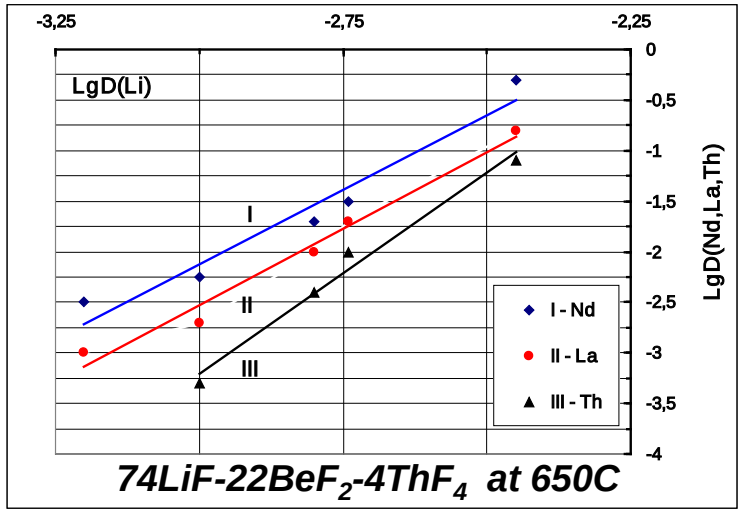


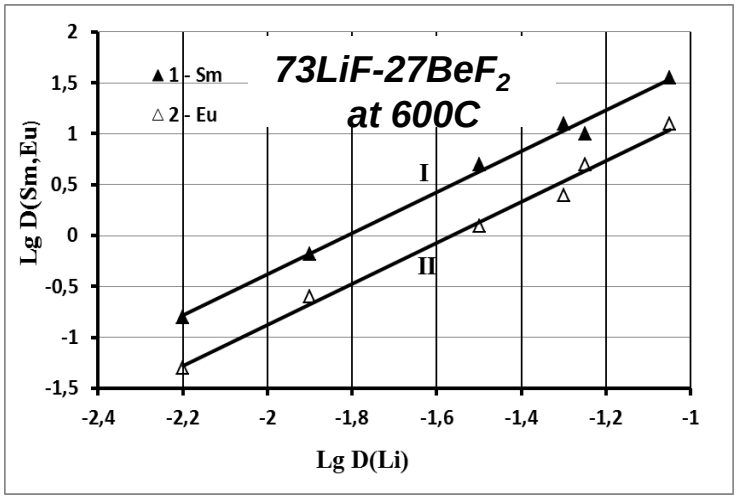


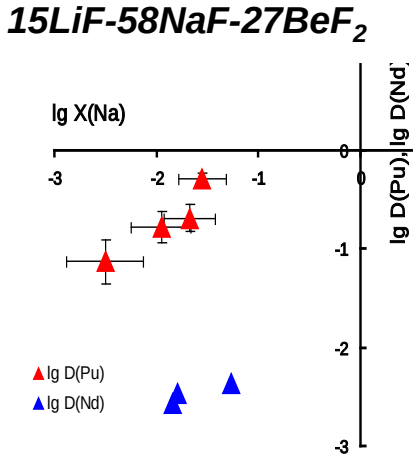
Reductive Extraction with Liquid Bi-Li

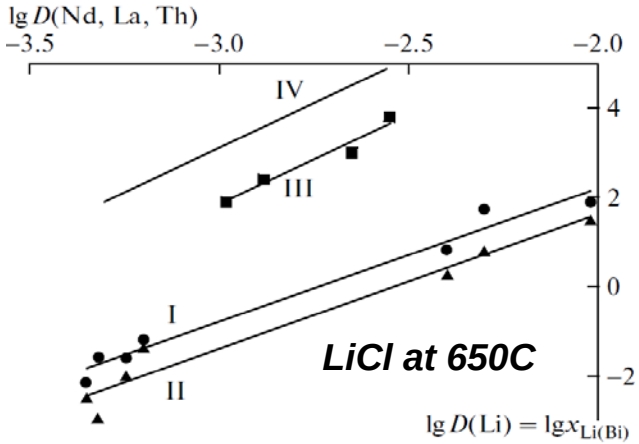
Reductive extraction of actinides from molten salt into liquid bismuth with their subsequent re-extraction into purified salt flow is the most acceptable technological method of actinide recycling. In order to determine particular parameters of this stage, it will be necessary to conduct additional experimental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











Pu distribution coefficient in 15LiF-58NaF-27BeF$_2$/Bi is much less than in LiF-BeF$_2$/Bi system

Summary

- *The molten salts have many desirable properties for mentioned above applications, and it seems likely that – given sufficient development time and money - a successful burner or breeder system could be developed*
- *Introduction of MSR technology to nuclear power might include 3 stages: FSCR, MSCR and MOSART*
- *It is obvious from the discussion above that use of molten fluorides as coolant and fuel for a reactor system of new fuel production or incinerator type operating in critical or fusion driven modes faces a large number of formidable problems. Several of these have been solved, and some seem to be well on the way to solution. But it is also clear that some still remain to be solved*
- *It may even be uncertain whether such a system would serve a useful purpose if its successful development were assured. It is certain that effort to date has thrown light on e. g. much elegant high temperature non-aqueous chemistry and has shown how molten salts can operate under hard and strong conditions*
- *Finally, it open perspectives significantly different to the present reactor and fuel cycle technology*