Critical issues of nuclear energy systems employing molten salt fluorides

from ISTC #1606 to #3749
and
EVOL / MARS co-operation

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Introduction

Strong need for flexible and effective processes & systems is resulted, particularly, in growing interest worldwide to employ molten salts technology for:

1. Consumption of TRU's while extracting their energy (MOSART)
2. Efficient electricity production in Th-U breeder cycle (MSFR)
3. Process heat applications (AHTR)
4. Pyrochemical fuel reprocessing (ACSEPT)
5. Isotopes production for medicine (e.g. Mo 99)

- Reference configurations for MSR have been defined, allowing concentrating R&D on critical areas: verification of fuel salt properties for reference compositions and qualification of high performance container materials (Sourse: Jacques Bouchard, GIF Symposium 2009, Paris)

ISTC #1606 (2001-2007)

Main focus has been placed on experimental and theoretical evaluation of MOlten Salt Actinide Recycler & Transmuter (MOSART) system fuelled by different compositions of TRU's from LWR spent fuel without U-Th support.

WP 1: New computational tools were developed to understand MOSART system behavior and conduct parametric studies. New fast-spectrum cores and salt compositions with high enough solubility for actinide trifluorides are being examined because of new goals.

WP 2: Experimental consideration included following properties of fuel salts: phase transition behavior, trifluorides/oxides solubility for actinides and lanthanides, viscosity, thermal conductivity, density, as well as different methods of fuel salt clean up in solvents selected: electrodeposition, oxide precipitation, reductive extraction.

WP 3: Experimental verification of Ni-Mo alloys for fuel circuit in corrosion loops (T_{max} =700C), including PuF_3 and Te with redox measurement.

ISTC#1606: MOSART concept

• The single-stream 2400MWt MOSART concept proposed has a fast spectrum core (no-moderator).

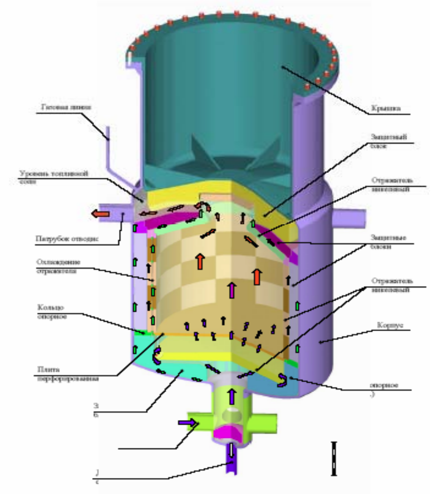
• MOSART fuelled with compositions of plutonium plus minor actinide trifluorides from LWR spent nuclear fuel—either once-through SNF or mixed-oxide SNF.

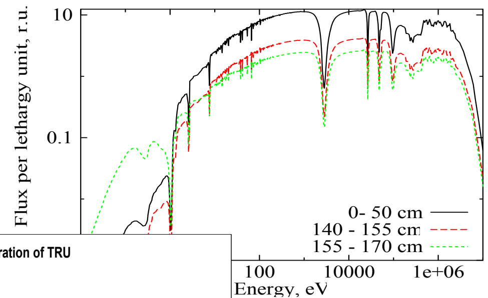
• MOSART salt contains no uranium or thorium and thus is a pure actinide burner. As a consequence, the reactor destroys the maximum quantities of actinides per unit of energy output.

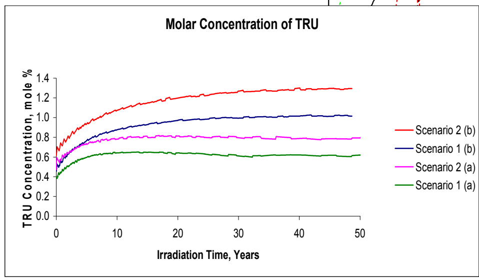
•Basis for MOSART concept is the use of Li,Be/F or Li,Na,Be/F solvents with decreased of BeF_2 (27-25 mole %) content and its high enough solubility for AnF_3 (2 to 3 mole % at 600°C).

• Optimized configuration of homogeneous core meets most important safety issues: (1) areas of reverse, stagnant or laminar flow are avoided, (2) max temperature of solid reflectors was minimized and (3) temperature coefficients of reactivity in core with 0.2 m graphite reflector in the range 900-1600K are strongly negative (– 4.125 pcm/K).

• MOSART is expected not to be seriously challenged by the major, unprotected transients such as ULOF, ULOH, overcooling, or even UTOP.







	MOSART	MSBR
Thermal capacity, MWt	2400	2250
Reactor vessel ID,m	4.43	6.77
Vessel wall thickness, cm	5.5	5.1
Vessel design pressure, N/m^2	$5.2 \cdot 10^5$	$5.2 \cdot 10^5$
Core height, m	3.6	3.96
Radial thickness of reflector, cm	20	76.2
Volume fraction of salt in core	1	0.13/0.37
Average core power density, MW/m^3	75.0	22.2
Peak core power density, MW/m^3	163	70.4
Average neutron flux, $n \cdot cm^{-2} \cdot s^{-1}$	10^{15}	$2.6 \cdot 10^{14}$
Max graphite damage flux, $n \cdot cm^{-2} \cdot s^{-1}$	$1.5 \cdot 10^{14}$(>180keV)	$3.3 \cdot 10^{14}$(>50keV
Max graphite temperature, K	1084	982
Estimated useful life of graphite, yrs	3-4	4
Total weight of graphite in reactor, t	20	304
Flow velocity of salt in core, m/s	0.5	1.3
Total fuel salt in reactor vessel, m^3	40.4	30.4
Total fuel salt in primary system, m^3	56.2	48.7
Cycle time for salt inventory, efpd	300	10 - 30

ISTC # 3749 (2009 -2012)

Project title: "Experimental study on critical issues of nuclear energy systems employing liquid salt fluorides"
Participating institutions: VNIITF (Snezhinsk), Kurchatov Institute (Moscow) and IHTE (Yekaterinburg)
Project duration: 36 months

- The main work in ISTC # 3749 is focused on fast Th-fuelled system to produce energy in a competitive way (in co-operation with FP7 Euroatom EVOL project).

WP 1: Choice of molten salt compositions for detailed studies. Special attention will be given to the following fuel solvent systems: Li,Th/F and Li,Be,Th/F.

WP 2: Measurement of key physical and chemical properties for selected salts. Special attention will be given to molten salt preparation and clean up.

WP 3: Combined materials compatibility & salt chemistry control. Special attention will be given to advanced Ni-Mo and Ni-W alloys.

WP 4: Evaluation of neutron physics, thermal hydraulics and fuel cycle properties of nuclear energy systems selected.

- **Some experimental effort will be placed on evaluation of the potential of advanced MS fluorides mixtures for pyrochemistry partitioning application (in co-operation with FP7 ACSEPT Euroatom project).**

First year of #3749 activity

- Choice of fuel salts, core configurations and FP clean up methods for detailed consideration
- Evaluation of physical-chemical properties for the salt compositions selected
- Update of computational tools to understand Th-U two fluid MSFR system behavior
- Development and manufacturing of test sections for experimental studies
- Design development and construction of corrosion loops, including section for Redox potential measurements
- Purification of fuel salt components
- Preliminary testing of the technique with molten salts and choice of the most prospective technique approach for further studies

Reference Th-U MSFR concept (CNRS)

- Sel initial: 77,5%LiF, 20%ThF_4, 2,5%$^{233}UF_4$
- Température de fonctionnement: 700 à 850 °C
- Puissance: 3 GW_{th} (1,67 $GW_{él}$)

- Inventaire initial d'^{233}U par réacteur: 5060 kg
- Inventaire initial d'^{233}U par $GW_{él}$: 3030 kg

- Volume de sel: 18 m^3
  - 1/2 dans le cœur et plénums
  - 1/2 dans les échangeurs et tuyaux

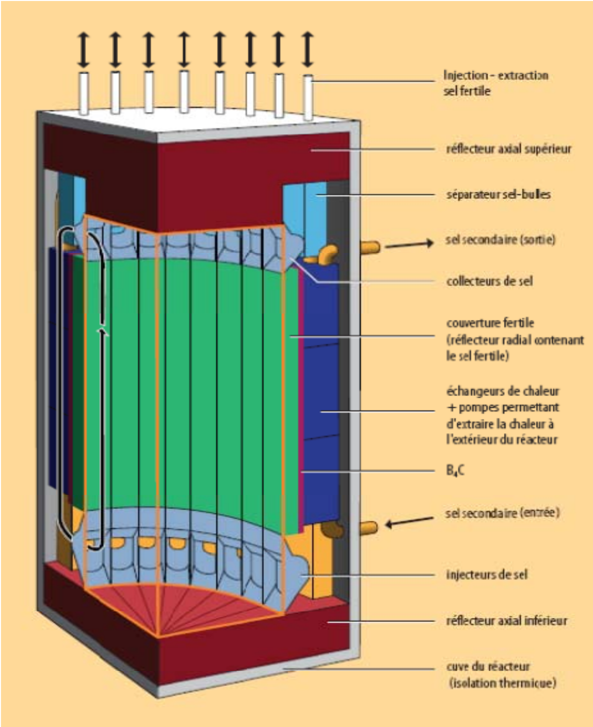
- Retraitement du cœur: 40 l/j

- Diamètre intérieur du cœur: 2,26 m
- Hauteur cœur plus plenums: 2,26 m
- Hauteur des plenums: 2 x 0,16 m

- Epaisseur de la couverture: 50 cm
- Volume de la couverture: 7,7 m^3
- Sel de la couverture: 75,5%LiF, 22,5%ThF_4
- Retraitement de la couverture: 40 l/j

- Coefficient de température: de -5,3 à - 4,8 pcm/K
  - Densité: de -3,7 à -3,3 pcm/K
  - Doppler: de -1,6 à -1,5 pcm/K

- Production d'^{233}U: 95 kg/an
- Temps de doublement: 56 ans



- Sel initial: 77,5%LiF, 16%ThF_4, 5,7%PuF_3, 0,8%$(AM)F_3$
- Température de fonctionnement: 700 à 850 °C
- Puissance: 3 GW_{th} (1,67 $GW_{él}$)

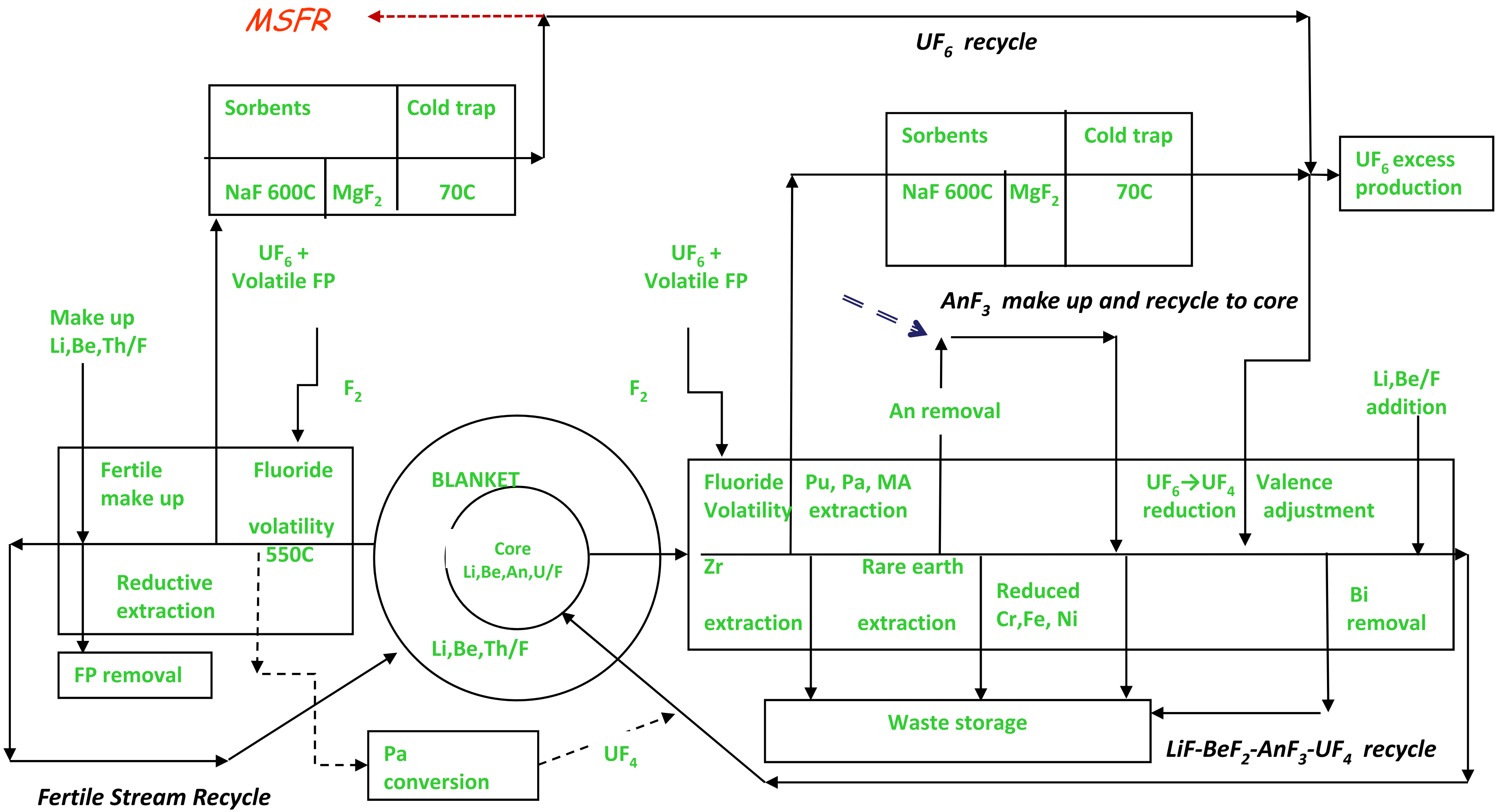
- Inventaire initial de Pu par réacteur: 11200 kg
- Inventaire initial de Pu par $GW_{él}$: 6700 kg

Difficulties: higher fuel concentration for criticality => higher operation temperature => materials compatibility

Hybrid MOSART^{+Th} Flowsheet

Thermal power – 2.4 GWt; Core height / diam.: 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; ^{3}U production from 150 up to 250 kg/yr;

Fuel salt : 73LiF-27BeF$_2$ or 17LiF-58NaF-25BeF$_2$ (in mole %); T_{inlet} = 600C
Blanket salt: 77LiF–23ThF$_4$; 67LiF-5BeF$_2$-28ThF$_4$; 75LiF-5BeF$_2$-20ThF$_4$ or 70LiF-8CaF$_2$-22ThF$_4$ (in mole%); T_{inlet}=600C



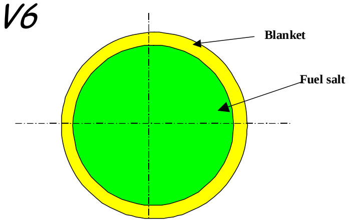
Hybrid MOSART^{+Th} Characteristics

Code: MCNP-4B with ENDF/B-V,VI

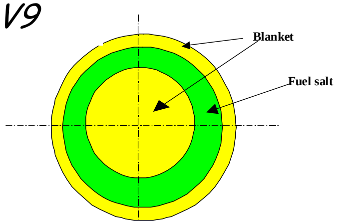
V1-V5,V7: $17LiF-58NaF-25BeF_2$

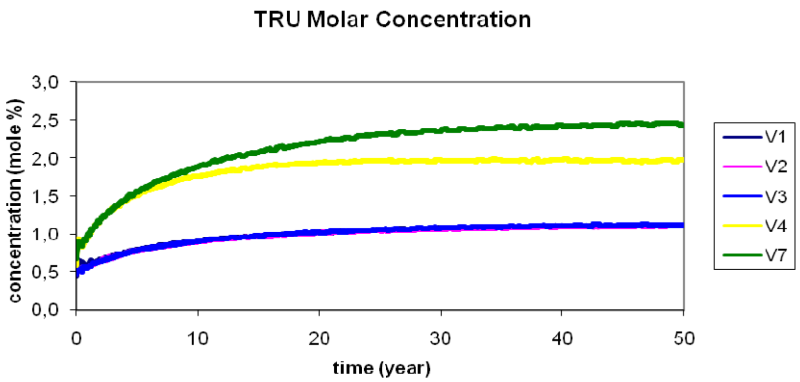
V6,V8,V9: $73LiF-27BeF_2$

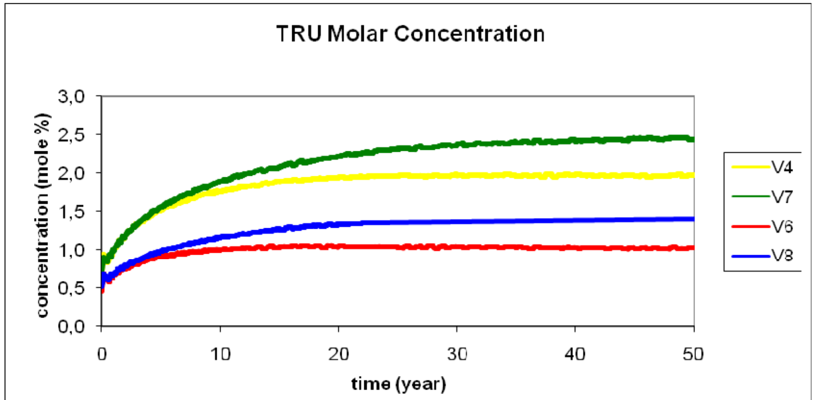
V1-V6

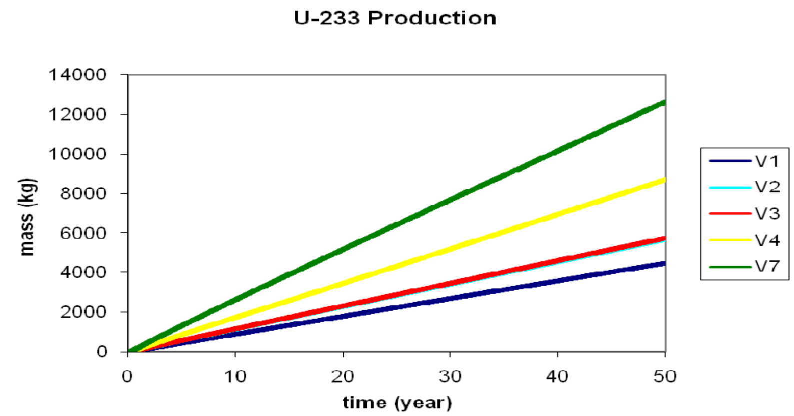


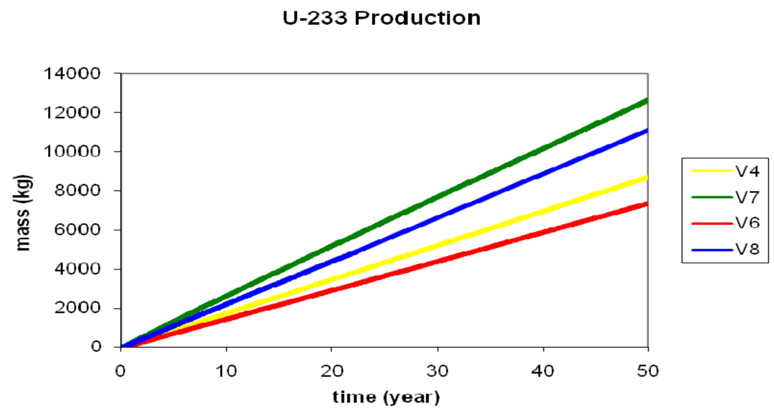
V7-V9











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 (NH_4HF_2, $T_m \approx 125\ ^0C$), 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.

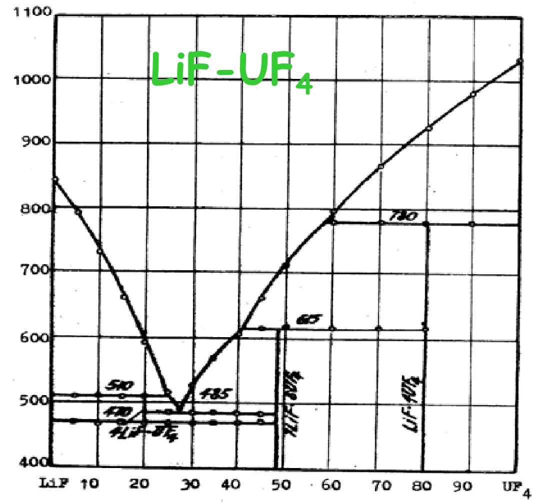
$$MeO_2 + 4NH_4HF_2 \rightarrow MeF_4 + 4NH_4F \uparrow + 2H_2O \uparrow \ (T_{max} = 350\text{-}400\ ^0C)$$

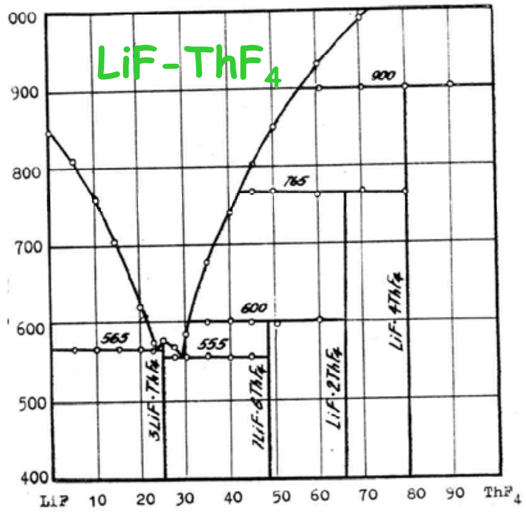
- To carry out these processes do not require expensive equipment and special safety measures. The purified anhydrous fluorides of metals was obtained, which are used for the preparation of fluoride salt melts of different composition.

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

Phase diagram

$77.5LiF\text{-}22.5ThF_4$
$70LiF\text{-}8CaF_2\text{-}22ThF_4$
$75LiF\text{-}5BeF_2\text{-}20ThF_4$
$77.5LiF\text{-}20ThF_4\text{-}2.5UF_4$
$71LiF\text{-}27BeF_2\text{-}2UF_4$
$73LiF\text{-}27BeF_2$
$73LiF\text{-}25BeF_2\text{-}2UF_4$





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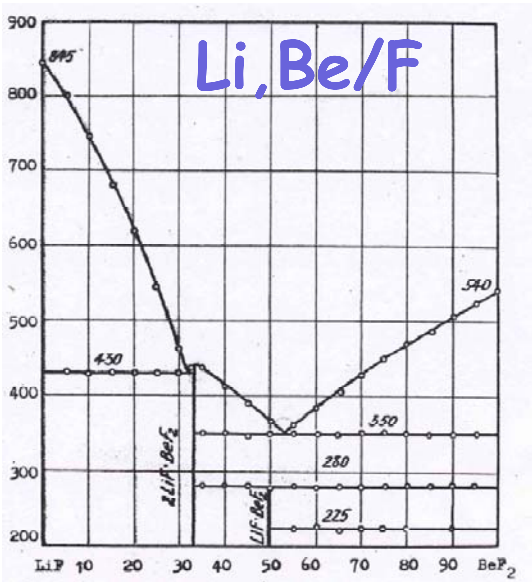
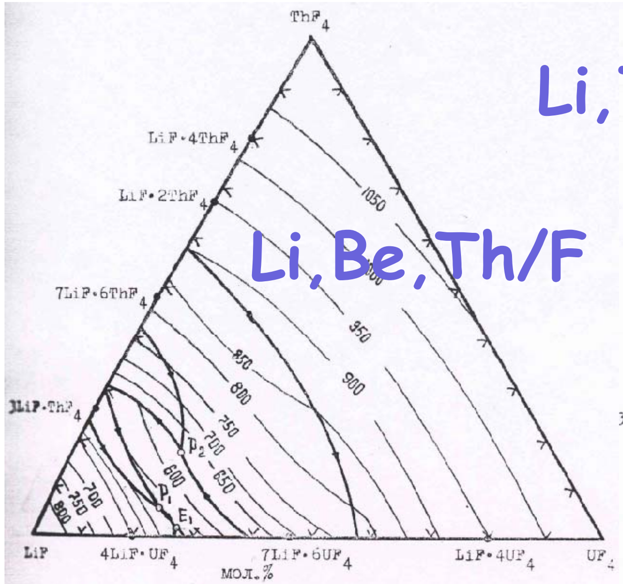
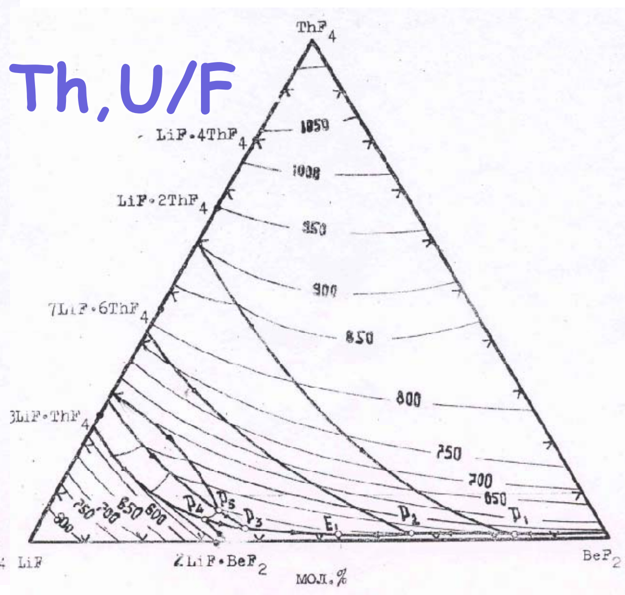






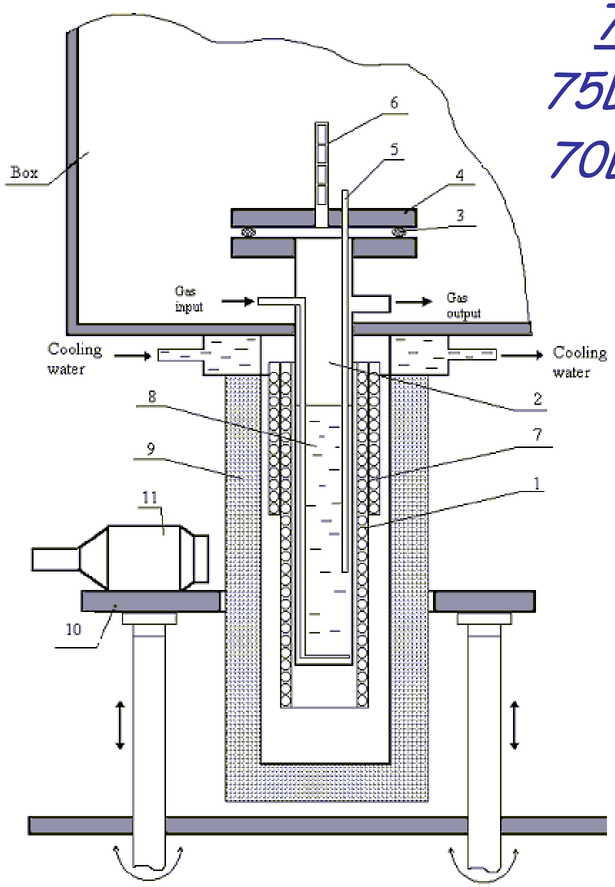
Measurement of PuF_3 solubility

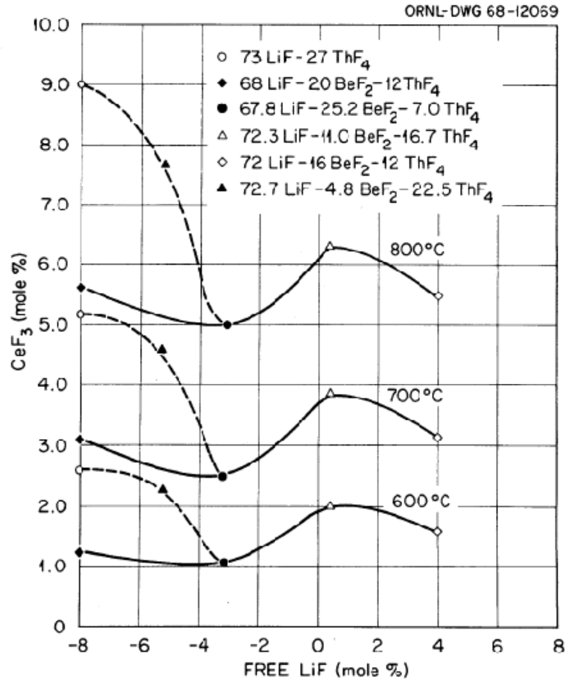
Due to the solubility limit, main concern for MSFR start up loading is expected with An dissolved as trifluorides in:

$77.5LiF-22.5ThF_4+AnF_3$

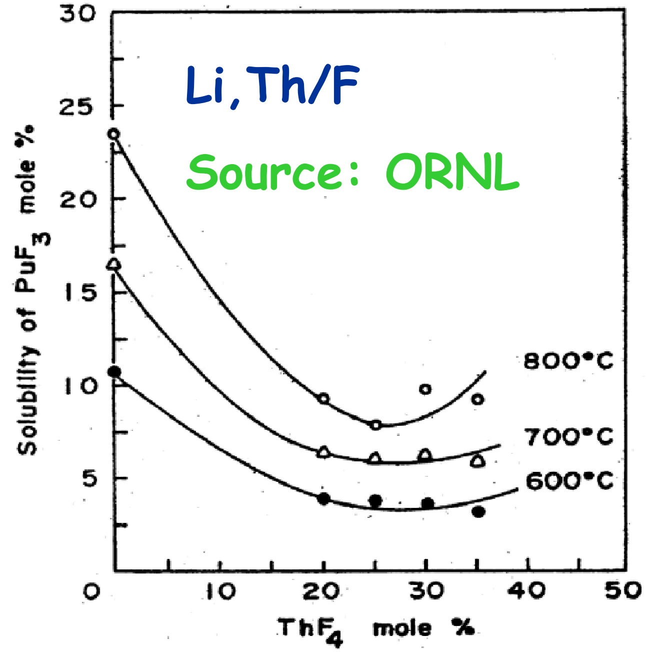
$75LiF-5BeF_2-20ThF_4+AnF_3$

$70LiF-8CaF_2-22ThF_4+AnF_3$

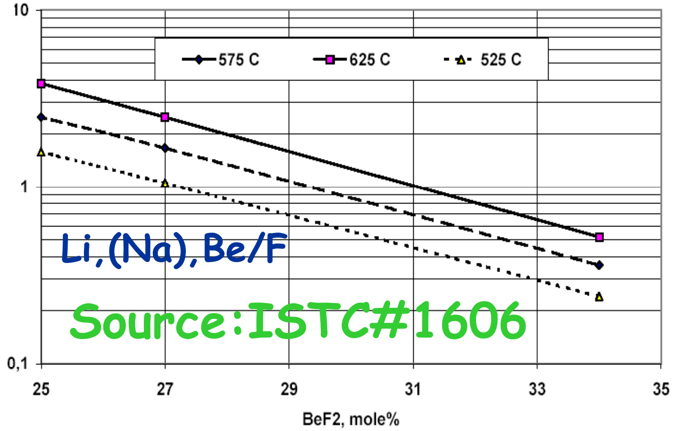




Pu irradiation intensity vs. [239]Pu concentration:
8-Na,Li,Be/F, 11-NaI(Tl) detector



SOLUBILITY OF PuF_3 IN $LiF-ThF_4$ MELTS.



Evaluation of transport properties

Density (g/cm^3)

0.78LiF-0.22ThF$_4$
$\rho = 4.7332 - 0.728 \times 10^{-3}T$
0.72LiF-0.16BeF$_2$-0.12ThF$_4$
$\rho = 3.825 - 0.650 \times 10^{-3}T$
0.75 LiF-0.05BeF$_2$-0.20ThF$_4$
$\rho = 4.554 - 0.714 \times 10^{-3}T$

Viscosity (cP)

0.78LiF-0.22ThF$_4$
$\eta = 391.8 \times exp(-T/209.7) + 2.799$
0.72LiF-0.16BeF$_2$-0.12ThF$_4$
$\eta = 583.8 \times exp(-T/194.2) + 2.332$
0.75LiF-0.05BeF$_2$-0.20ThF$_4$
$\eta = 457.6 \times exp(-T/205.1) + 2.728$

Thermal conductivity (W/m·K)

$\lambda = -0.34 + 0.5 \cdot 10\text{-}3T(K) + 32/M$

Heat capacity ($cal \cdot g^{-1} \cdot K^{-1}$)

0.78LiF-0.22ThF$_4$
Cp = 0.305
0.72LiF-0.16BeF$_2$-0.12ThF$_4$
Cp = 0.356
0.75 LiF-0.05BeF$_2$-0.20ThF$_4$
Cp = 0.312

- The analysis of input data used in calculations revealed a considerable discrepancy of experimental values of properties found for melts having same chemical composition.
- It would be reasonable to revise the experimental data on density and viscosity of LiF-BeF$_2$ melts that present the basis for evaluation of properties of molten multicomponent fuel compositions with fluorides of thorium, uranium, and plutonium.
- Also, future experimental studies should concentrate on both measurements of the thermal conductivity themselves and a more rigorous and justified selection of the input data for its evaluation.

Phase diagram & Heat capacity

Differential thermal analysis (DTA)

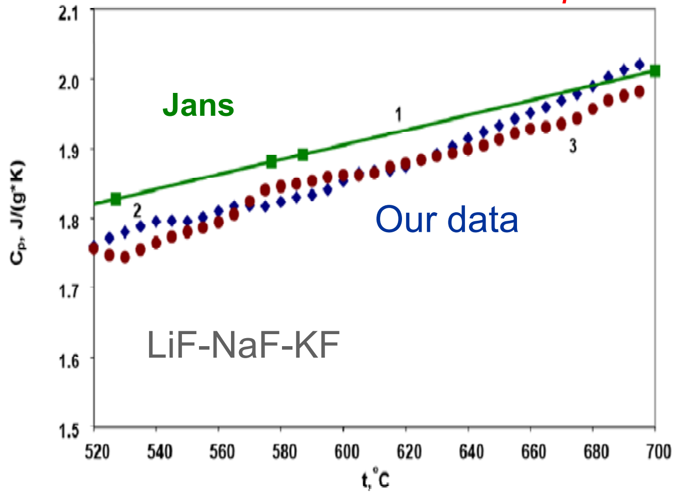
Differential scanning calorimetry (DSC)

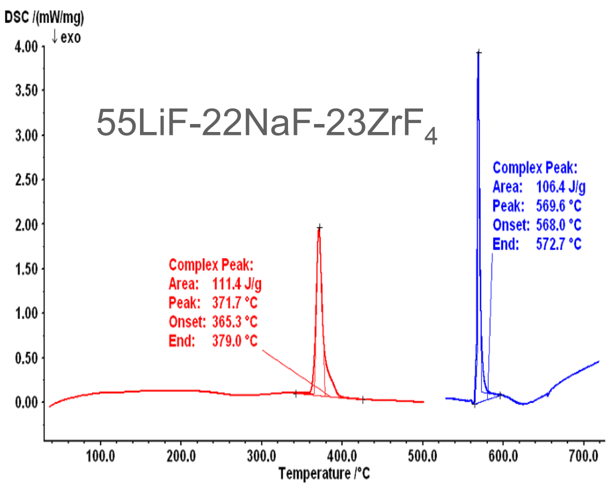
Thermograviometry (TG)

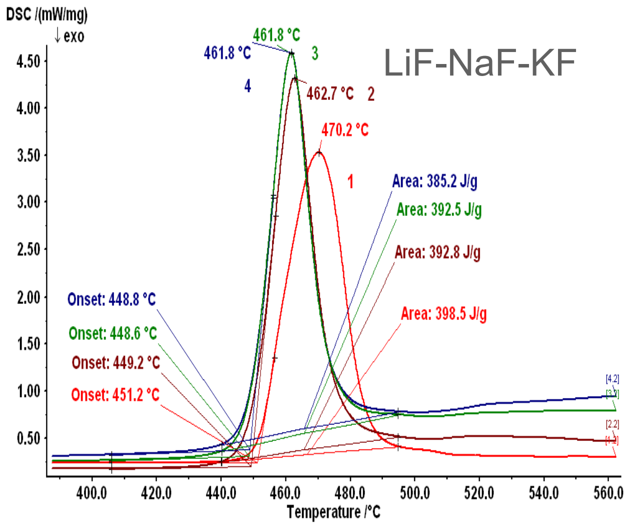
mole, %	$T_{пл}$, °C	$T_{кр}$, °C	$T_{лик}$, °C
75LiF-25BeF$_2$	460±2	460±2	604±2
73.1LiF-26.9BeF$_2$	460±2	460±2	580±2
71.2LiF-28.8BeF$_2$	460±2	460±2	540±2
81LiF-19CaF$_2$	775±2	775±2	-
70LiF-20CaF$_2$-10BaF$_2$	725±2	725±2	-
65LiF-15CaF$_2$-20BaF$_2$	723±2	723±2	-
46.5LiF-11.5NaF-42KF	449 ±1	449 ±1	-
55LiF-22NaF-23ZrF$_4$	568±1	568±1	-

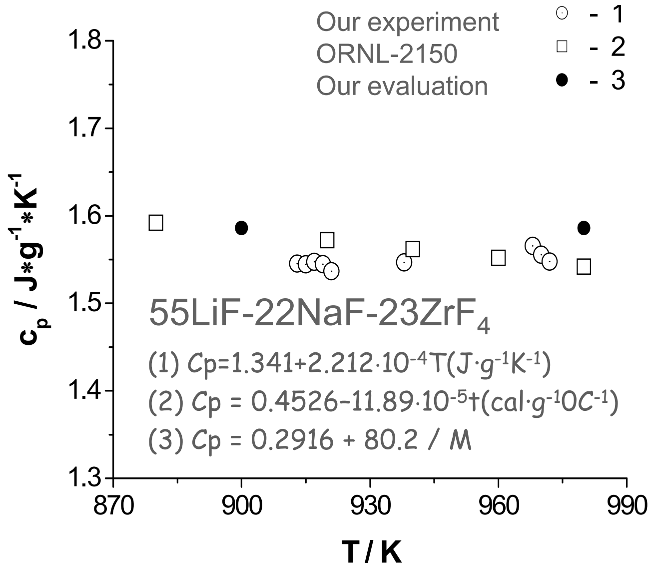
Synchronic thermoanalyzer

- 78LiF – 22ThF$_4$
- 71LiF – 29ThF$_4$

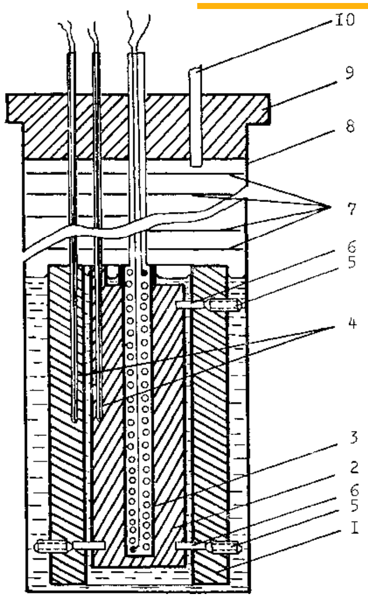




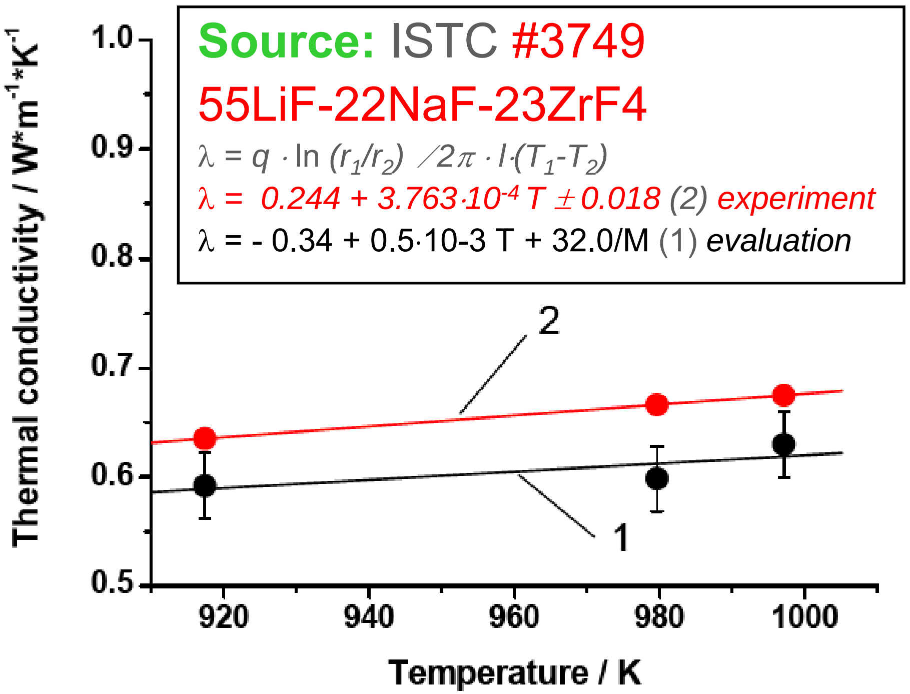


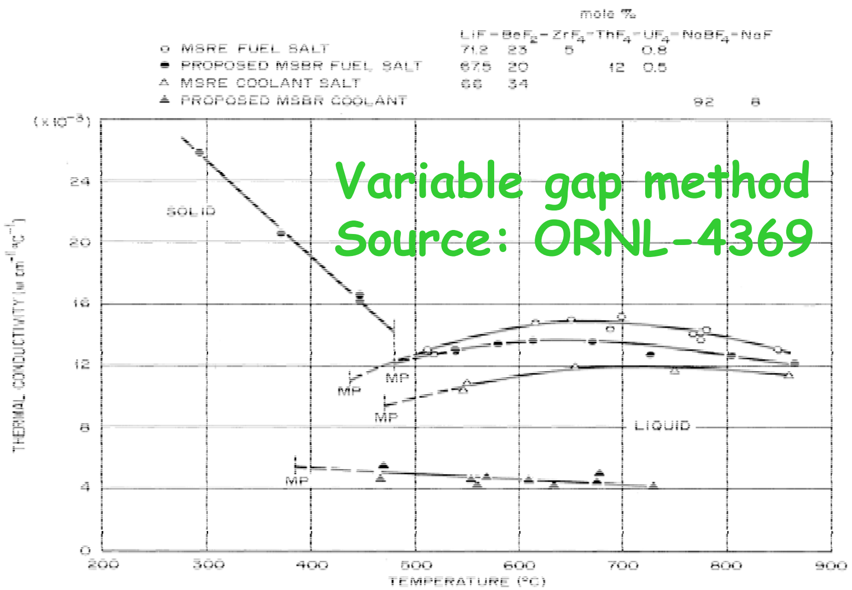


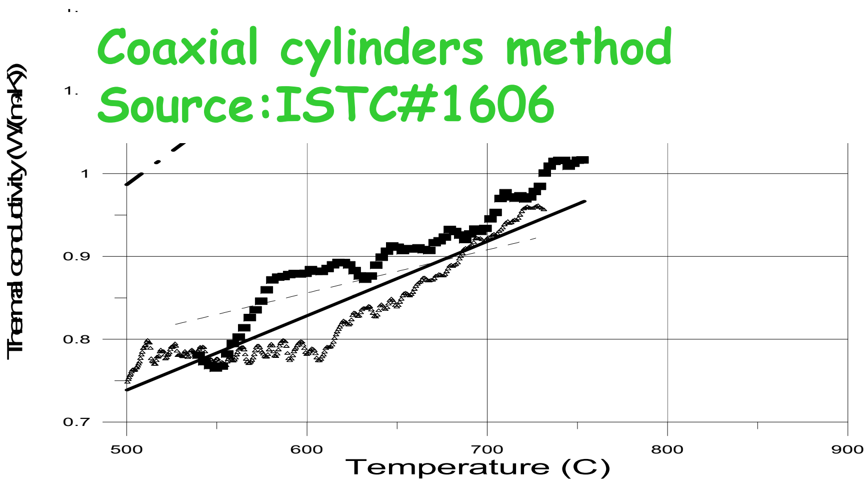
Measurement of thermal conductivity



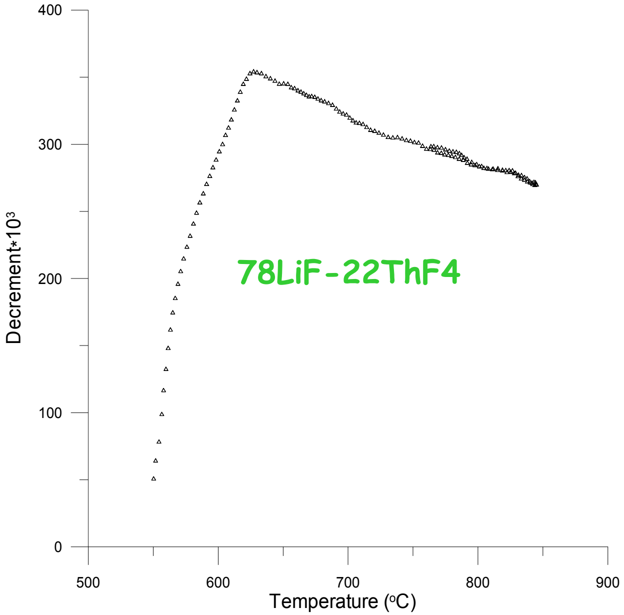
- *78LiF - 22ThF$_4$*
- *71LiF - 29ThF$_4$*

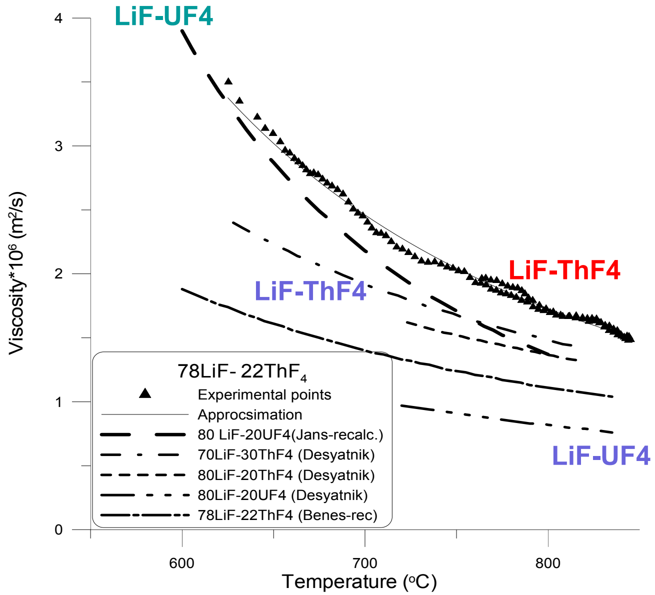


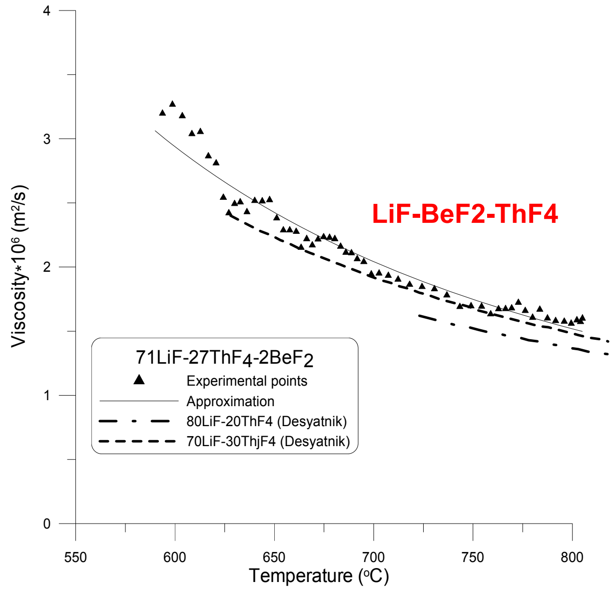


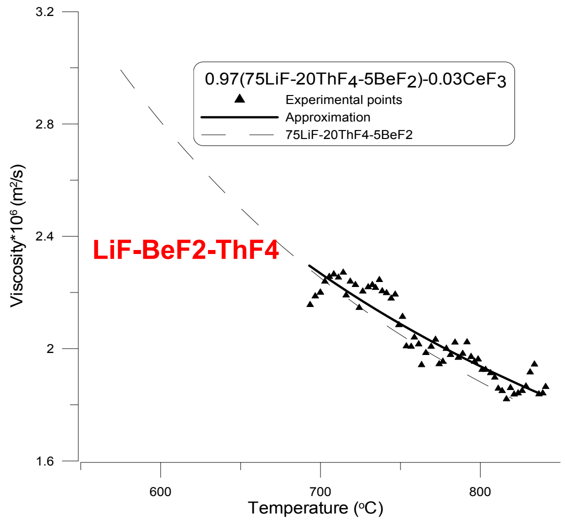


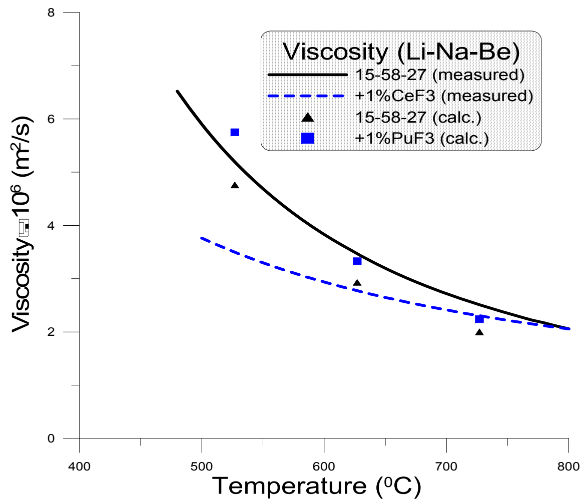
Measurement of viscosity for Li,Th(Be)/F systems





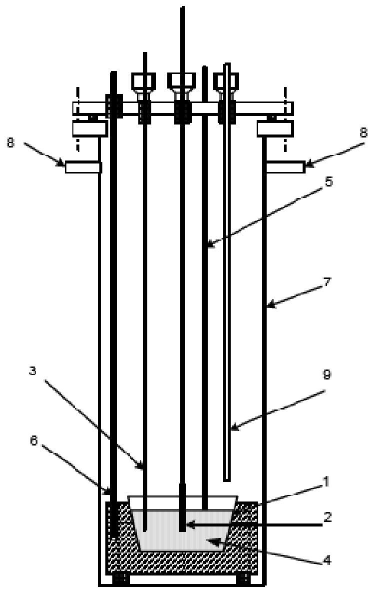




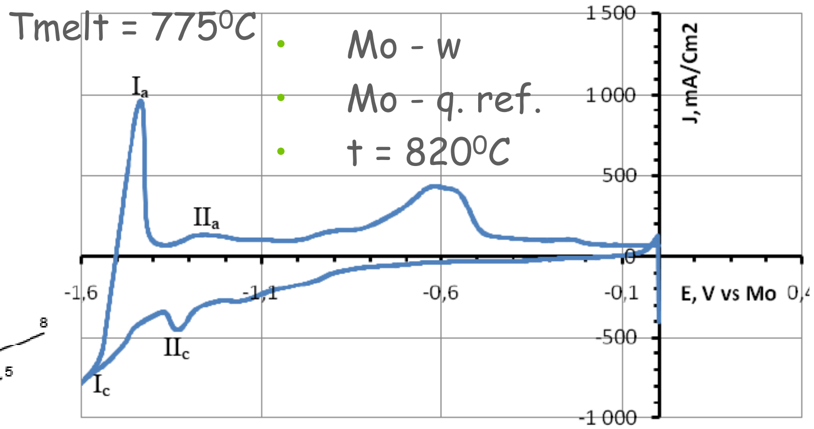


Electrochemical properties of lanthanides and actinides

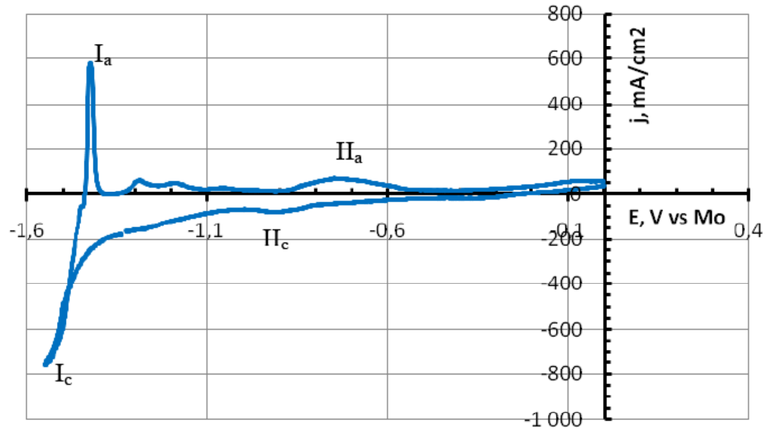
Test section



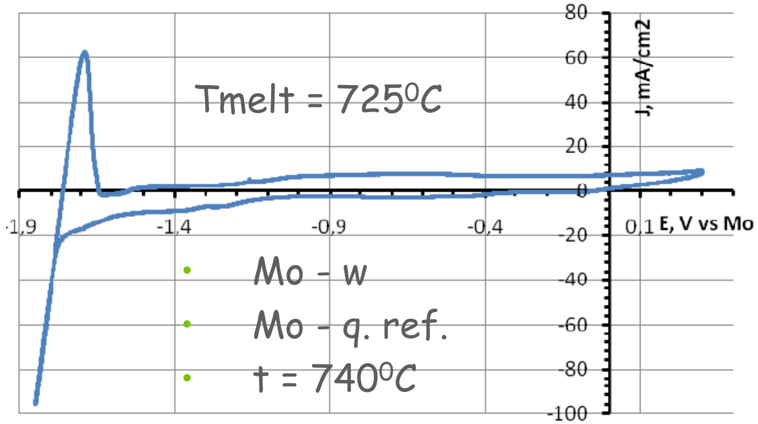
$80LiF-20CaF_2$



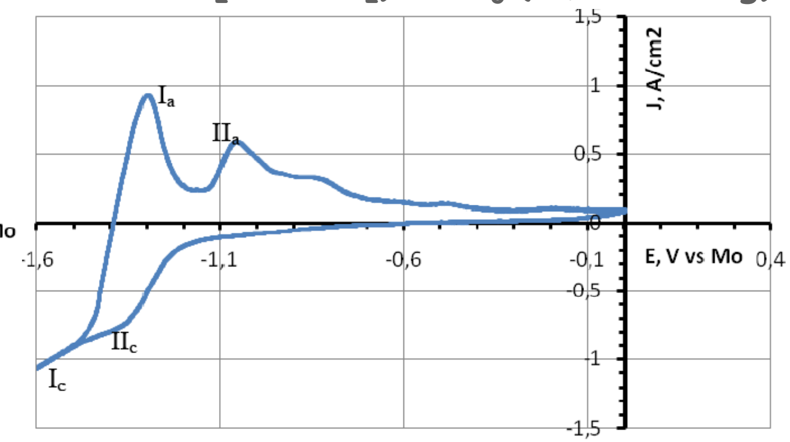
$(80LiF-20CaF_2) + NdF_3$ (0,05 mol/kg)



$65LiF-15CaF_2-20BaF_2$



$(65LiF-15CaF_2-20BaF_2)+NdF_3$ (0,05 mol/kg)



Next: $(80LiF-20CaF_2) + PuF_3$ $(65LiF-15CaF_2-20BaF_2) + PuF_3$

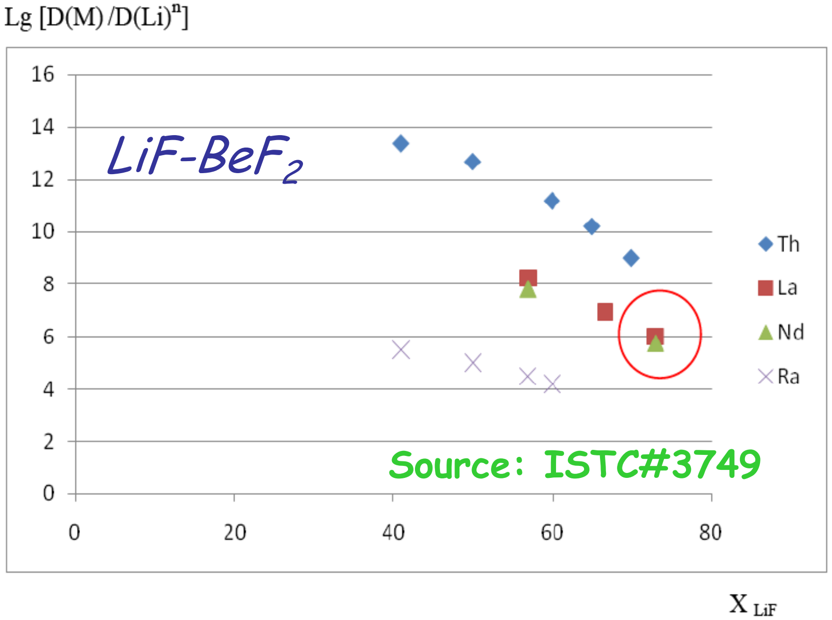
An / Ln distribution in molten salt / liquid metal system

Relative extractabilities of elements are determined by measuring equilibrium distribution coefficients in the two phase system : ***MF_n(melt) + nLi^o(Bi) ⇔ M^o(Bi) + nLiF(melt)***

The distribution coefficient for M is defined by : ***$D = X_M / X_{MFn}$***

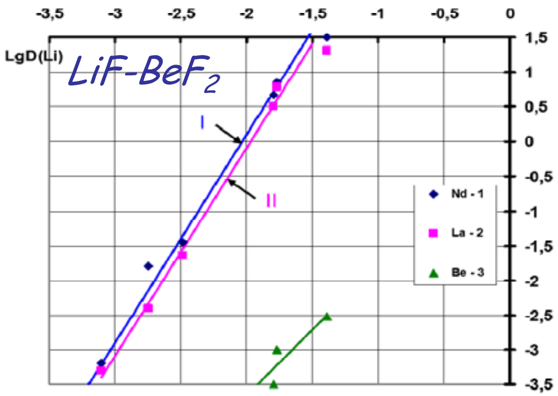
The ratio of distribution coefficients (***$\Theta = D_1 / D_2$***) features the separation of the two components between phases

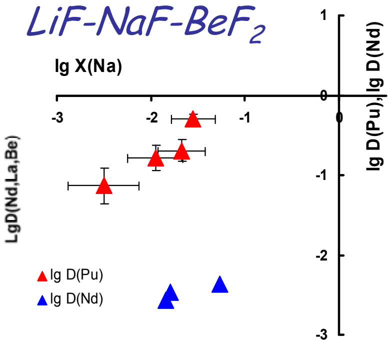
The separation factors for different elements with the same valence - *n* (e.g. actinides and lanthanides) could be given by: *$ln\Theta = -\{\Delta G^o{}_f(Ln, T) - \Delta G^o{}_f(An, T)\}/(RT)$*



	Separation factor relative to plutonium, T=873 K		
	$LiF-BeF_2$/Bi	$LiF-BeF_2-ThF_4$/Bi	$15LiF-58NaF-27BeF_2$/Bi
Pu	1	1	1
Am	-	1.5	-
Cm	6	8	-
Nd	3000	1500	100
La	25000	2300	> 300

$73LiF-27BeF_2$
$77.5LiF-22.5ThF_4$
$75LiF-5BeF_2-20ThF_4$





Source:ISTC#1606

Metallic materials

Early ORNL materials studies led to the development of a nickel-base alloy Hastelloy N, for use with fluoride salts. Later improvements: (1) "radiation hardening" due to accumulation of helium at grain boundaries, (2) resistance to selective chromium corrosion, (3) resistance to Te intergranular cracking.

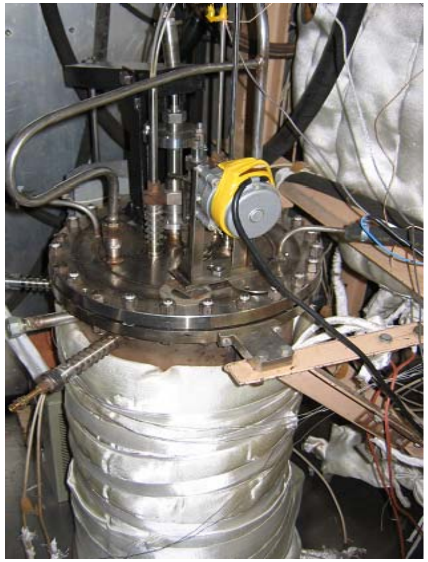
Concept	Tmax, C	Melt	Alloy	Problems & Required tests
MSRE	654	Li,Be,Zr,U/F	Hastelloy N	Irradiation embrittlement
MSBR	704	Li,Be,Th,U/F	2%Ti Hastelloy NM	Te intergranular attack
MSBR	*635*	*NaF-NaBF4*	*2%Ti Hastelloy NM*	Generalized corrosion
MOSART	720	Li,Be,Na,An/F	1% Al HN80MTY	Tests: Properties / Irradiation/
MSFR	850	Li,Th,U/F	Ni-W-Cr alloy	Thermal / Forced convection

Element	Hasteloy N US	Hasteloy NM US	HN80M-VI Russia	HN80MTY Russia	MONICR Czech Rep	Ni-W-Cr alloy France
Ni	base	base	82	82	base	68.8
Cr	7,52	7,3	7,61	6,81	6,85	5.7
Mo	16,28	13,6	12,2	13,2	15,8	0.07
Ti	0,26	0,5–2,0	0,001	0,93	0,026	0.13
Fe	3,97	< 0,1	0,28	0,15	2,27	0.05
Mn	0,52	0,14	0,22	0,013	0,037	0.086
Nb	-	-	1,48	0,01	< 0,01	-
Si	0,5	< 0,01	0,040	0,040	0,13	0.065
Al	0,26	-	0,038	1,12	0,02	0.08
W	0,06	-	0,21	0,072	0,16	25.2

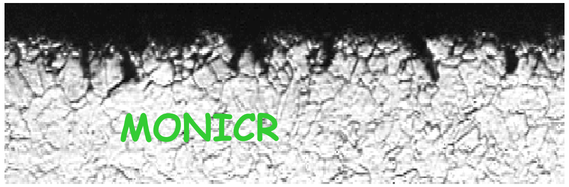
Resistance of Ni-Mo alloys to Te corrosion in Li,Na,Be/F

(Cr_3Te_4 as a Te source) depend on: (1) melt redox potential, (2) thermal- mechanical loads, (3) exposure time

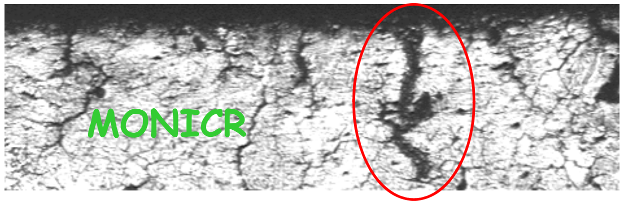
HN80MTY alloy is most resistant to tellurium IGC of Ni-Mo alloys under study. The intensity of its cracking under stress is K=680pc/cm×μm (20 times lower as that of MONICR alloy). According our evaluation its corrosion and mechanical properties completely meet MOSART requirements



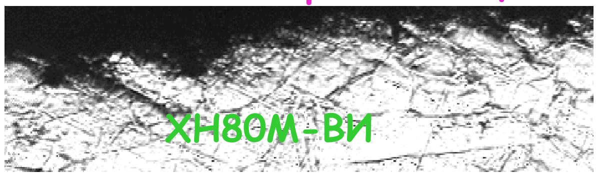
Without load | With load 80 MPa



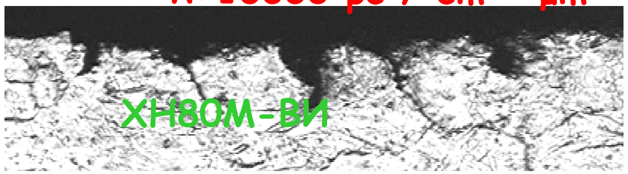
K=3590 pc / cm × μm



K>10000 pc / cm × μm

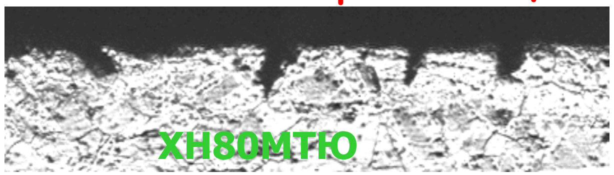


K=690 pc / cm × μm



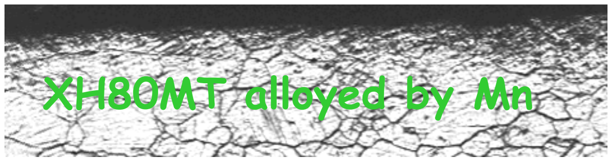
K= 1560 pc / cm × μm

K=380 pc / cm × μm

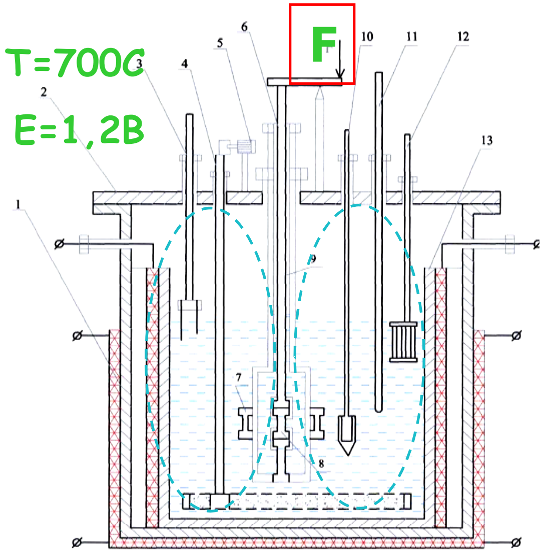


K=680 pc / cm × μm

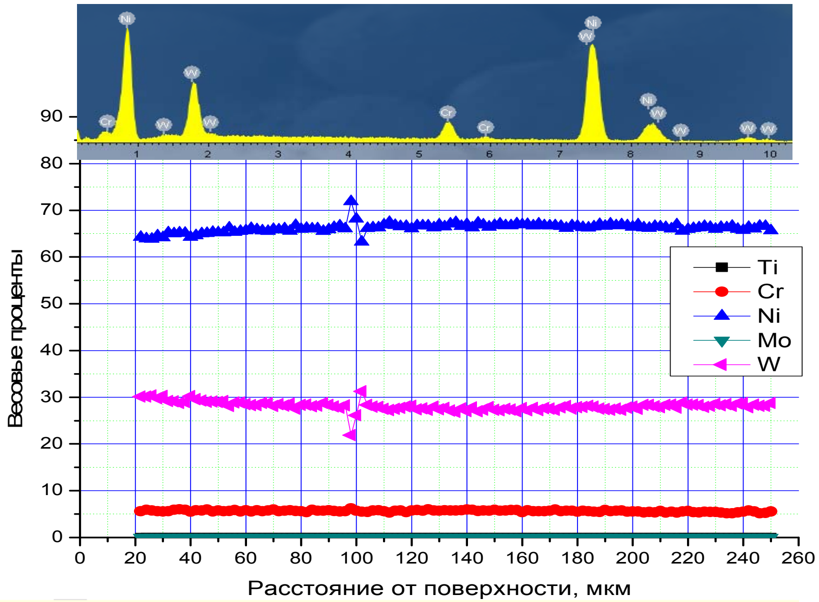
Addition of Mn gives significant increase in the alloy resistance to tellurium IGC.

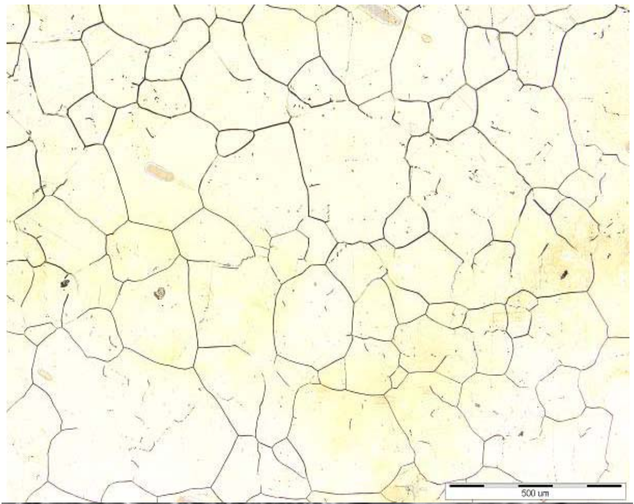


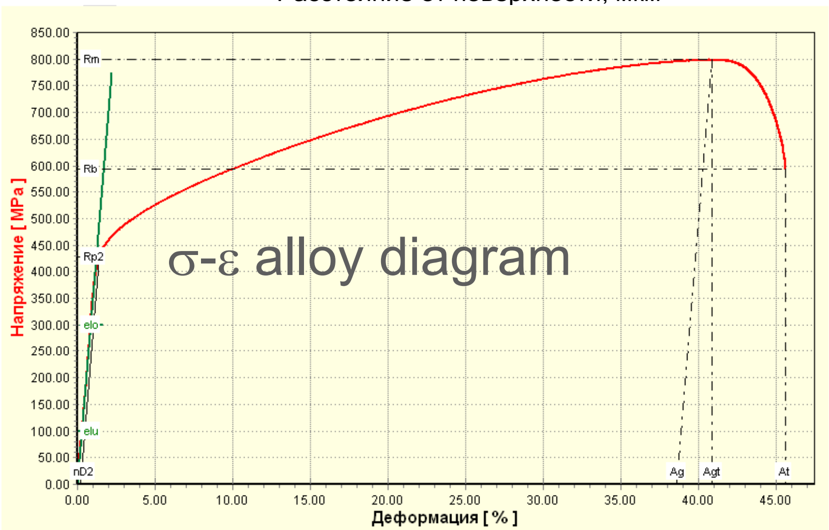
K= 0 pc / cm × μm

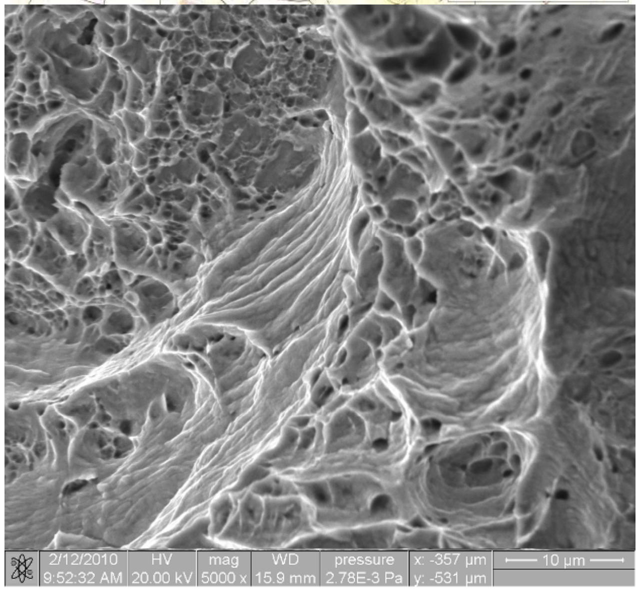


Examination of 65Ni-28W-7Cr alloy properties before exposure in melt



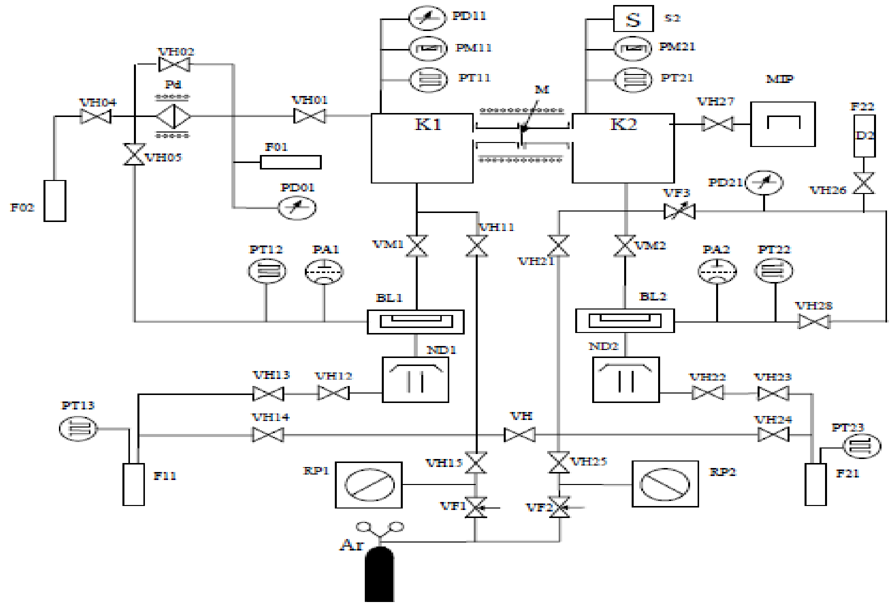


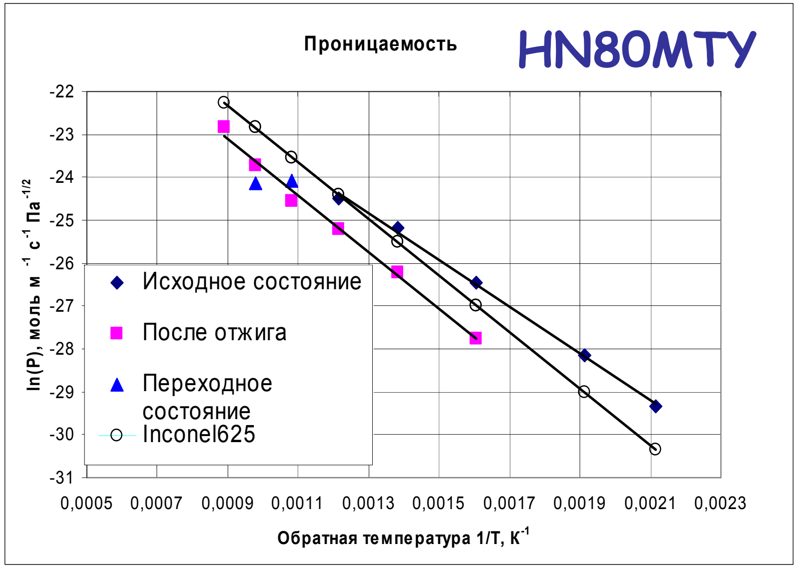


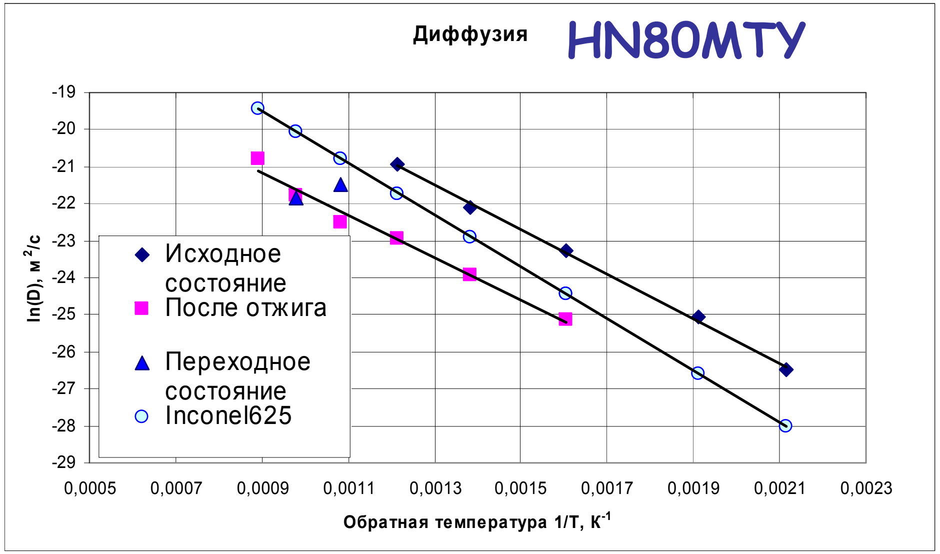


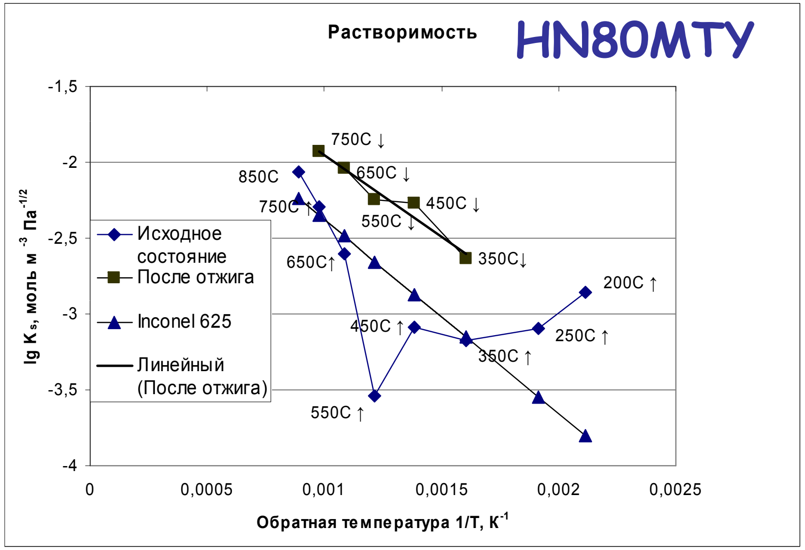
65Ni-28W-7Cr alloy sample along with viscous has traces of fragile destruction.

Hydrogen permeation studies in Ni-base alloys

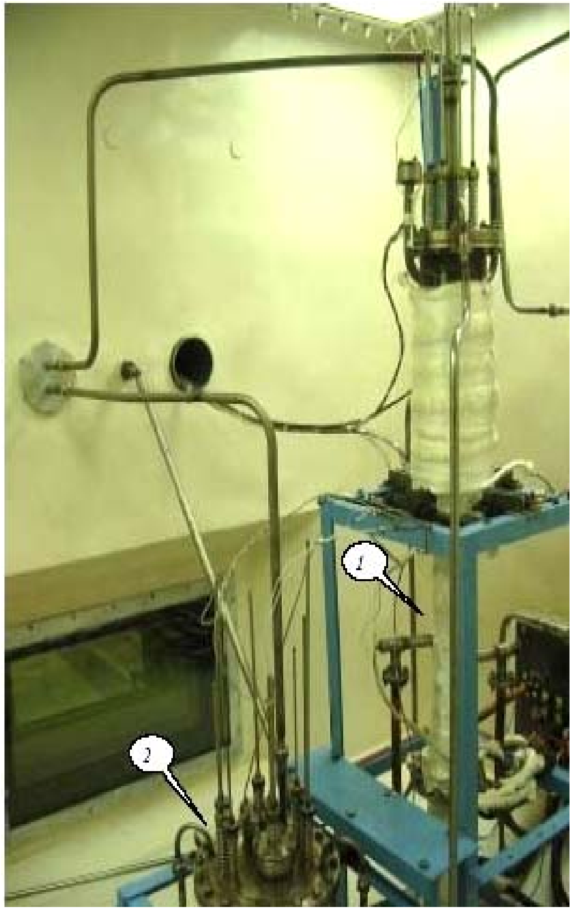








UF_4 containing corrosion loops



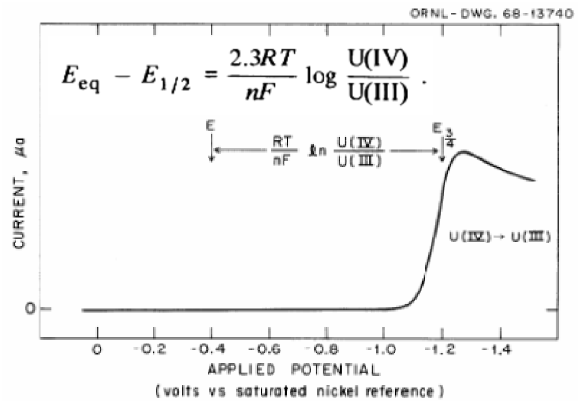
77.5LiF-20ThF$_4$-2.5UF$_4$+Te:

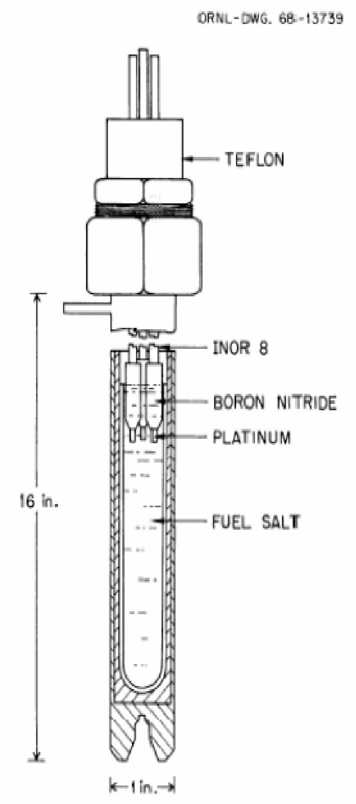
U4+/U3+=100-300

U4+/U3+=10-30

75LiF-20ThF$_4$ +5BeF$_2$+xUF$_4$+Te:

U4+/U3+=10-30



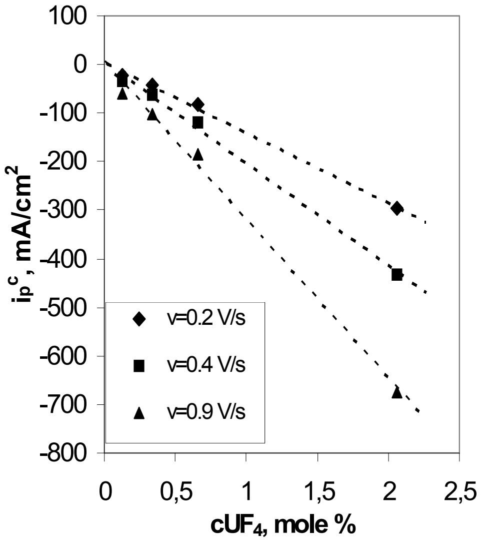


A simple voltammetric method was developed at ORNL for the determination of U(IV)/U(III) ratio. The method involves the measurement of the potential difference between the equilibrium potential of the melt, measured by an inert platinum electrode immersed in melt and voltammetric equivalent of the standard potential for the U(IV)/U(III) couple $E_{1/2}$.

For linear sweep voltammetry at a stationary electrode, the polarographic half-wave potential $E_{1/2}$ corresponds to the potential on voltammogram at which the current is equal to 85.2% of the peak current.

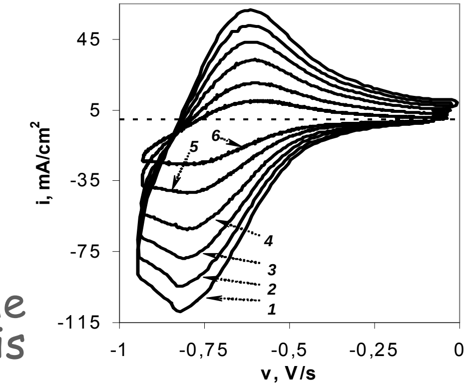
Electroanalytical Method for the Redox Potential Evaluation

- A necessary condition for the use of this method is reversibility of the process of cathode reduction of the ions U (IV) to U(III).
- To determine the applicability of this method for control of redox potential in molten 77LiF-23ThF$_4$ (mole%) with additions of UF$_4$ the kinetics of electroreduction of U (IV) on platinum, molybdenum and tungsten electrodes was studied.

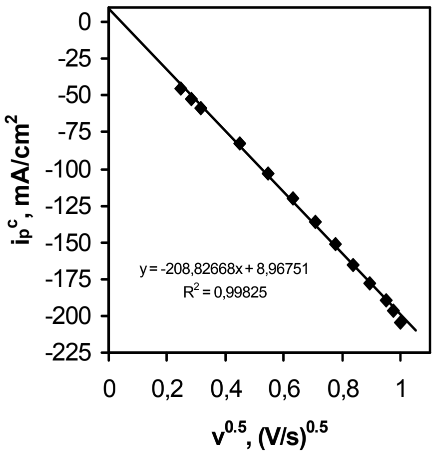


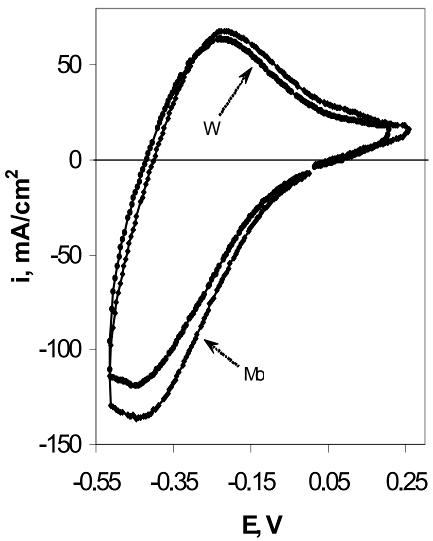
- Curves presented, are analyzed using standard criteria of reversibility and linear dependence

(i_p^c vs. $v^{1/2}$) – linear dependence ;
(i_p^c vs. [UF$_4$]) – linear dependence ;
(E_p^c vs. v) – no dependence.



- Conclude that one-electron process of the charge transfer is reversible and is limited by the ions diffusion rate.
- Therefore, the [U(IV)]/[U(III)] ratio in these salt mixtures can be controlled by the voltammetric method. There are no major limitations on its use at the potential sweep rate of up to 1 V/s.
- Platinum, tungsten or molybdenum can be used as the material of the reference and working electrodes. If the electrodes are made of different materials, it should be noted that the thermal emf affects the results of potentiometric and voltammetric measurements.





Rosatom/Euroatom co-operation: MARS project

Subgroup: Fuels and fuel cycles
Subgroup leader: Mikhail Kormilitsyn (kormilitsyn@niiar.ru)

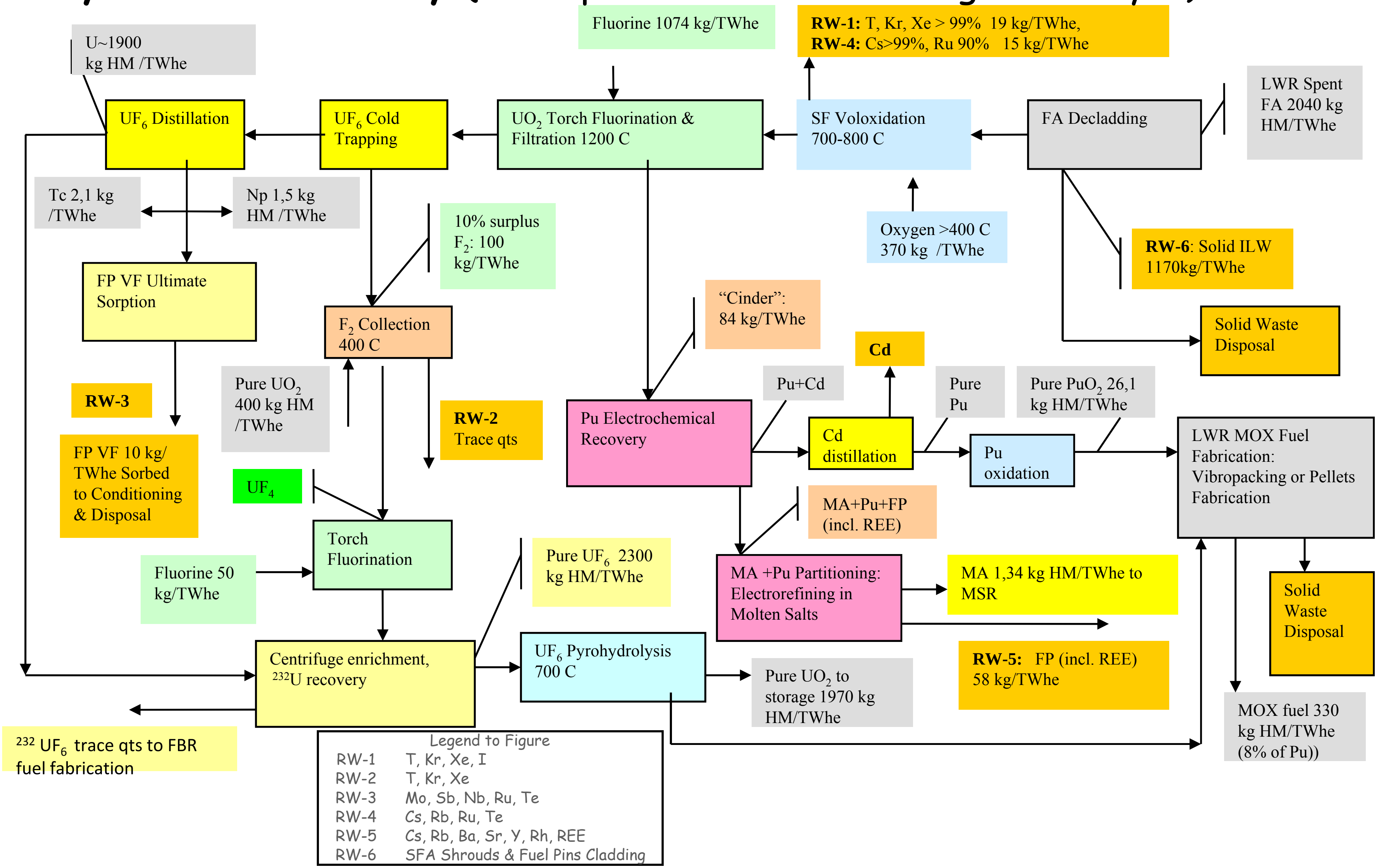
Project title: Experimental and calculated study on fundamental issues of nuclear energy systems using molten fluoride salts.
Short reference: MARS (Minor Actinides Recycling in Salts)

Leading institution: RIAR (Dimitrovgrad)
Participating institutions: RRC-Kurchatov Institute, VNIITF (Snezhinsk), IHTE (Yekaterinburg), VNIIKhT (Moscow)
Project manager: Victor Ignatiev (ignatiev@vver.kiae.ru)

Project duration: 36 months (2010-2012)

Project funding: 35 million rubles

Reprocessing of SNF from LWR by Fluoride Volatility & Pyroelectrochemistry (Burnup: 50 GWd/t ; Cooling time: 3 yrs)



Expected MARS developments

- **Project objective** is to get answers on the key questions, which require experimental studies, in order to evaluate the feasibility of nuclear energy systems providing effective minor actinides (MA) consumption.

- **Main project task** is to test and select molten salts and metallic structural materials, which will operate successfully under the conditions of promising nuclear energy systems for effective MA consumption. Main emphasis will be focused on the study of the key properties for molten salt mixtures including as main constituents LiF, NaF, CaF2, BeF2, KF etc. as well as structural Ni- based materials compatibility with molten salt mixtures selected.

Expected MARS developments

- **Determination of fundumental physical and chemical properties of selected salt compositions.** Choice of fuel salt mixture for MA burner system and measurement of the trifluorides fluorides solubility in the solvent system selected; investigation of the rare earths fluorides effect on the actinides trifluoridesfluorides solubility; determination of physical properties of selected melts: density, viscosity, thermal conductivity and heat capacity; study on the effect of trifluoride and tetrafluoride additives on physical and chemical properties of the selected salt systems; determination of electrochemical properties of basic and trace constituents of the system; development of the procedure for determination of melt redox potential; search of methods of rare earth removal from selected salt system and their experimental development.

Expected MARS developments

- **Materials compatibility and melt chemical control.** Experimental study of corrosion and mechanical characteristics of container metals before and after testing in the molten salt environment selected at a temperatures up to 700-750°C. Main requirements to the investigations are as follows: (1) maintenance of required salt purity, (2) effective control of salt redox potential to minimize corrosion activity of the system, (3) identification of main corrosion mechanisms in the systems with a temperature gradient, (4) study of influence of fuel salt composition and tellurium on the corrosion processes.

Expected MARS developments

- **Assessment of molten salt characteristics and optimization of MA burner system configuration on the basis of experimental data obtained.** Based on the selected fuel salt compositions and structural materials, perform neutronic calculations of the molten salt MA burner efficiency in various fuel cycle scenarios, as well as system thermal hydraulics, radiation damages, fission products clean up, etc.