Specific Support Actions

Assessment of LIquid Salts for Innovative Applications

ALISIA

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REVIEW REPORT ON LIQUID SALTS FOR VARIOUS APPLICATIONS

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Table of contents

1 Introduction

Recent studies in Europe (national programmes and Euratom 5th and 6th FWP projects) have confirmed the potential of MSR for breeding and waste minimization on both thermal and fast neutron spectrum. In parallel, viability analyses, performed mainly in the USA but also in France, have highlighted the assets of liquid salts as a vector for heat transport at high temperature for various applications.

This renewal and diversification of interests have led to shift the R&D orientations and objectives initially promoted in the MOST project [Renault,2003,2005], so as to encompass in a consistent body the different applications envisioned today for molten and liquid salts [Forsberg,2007]. This is the framework of the ALISIA project.

Cross-cutting R&D areas are being identified. A major commonality is the understanding and mastering of liquid salt technologies: behaviour of liquid salts, with or without actinides (corrosion of structural materials, salt components solubility and stability), measurement of physical properties, chemical control of salt state and composition,…

As a first step, the ALISIA objective is to review the selection criteria and to propose a reference selection of salt compositions for the different promising applications of molten and liquid salts. In the mean time, an evaluation of salt coolants for reactor applications has been published recently [Williams,2008], exploring the use of molten salts as primary coolants in a new generation of solid-fueled, thermal spectrum, high temperature reactors.

2 Potential application of liquid salts in fission systems

In a Molten Salt Reactor (MSR), the fuel is dissolved in a fluoride salt coolant. The technology was partly developed in the 1950s and 1960s. With changing goals for advanced reactors and new technologies, there is currently a renewed interest in MSRs. The new technologies include (1) Brayton power cycles (rather than steam cycles) that eliminate many of the historical challenges in building MSRs and (2) the conceptual development of several fast-spectrum MSRs that have large negative temperature and void reactivity coefficients, a unique safety characteristic not found in solid-fuel fast reactors.

Earlier MSRs were thermal-neutron-spectrum reactors. Compared with solid-fueled reactors, MSR systems have lower fissile inventories, no radiation damage constraint on attainable fuel burn-up, no spent nuclear fuel, no requirement to fabricate and handle solid fuel, and a single isotopic composition of fuel in the reactor. These and other characteristics may enable MSRs to have potentially unique capabilities and competitive economics for actinide burning and extending fuel resources.

Table 1 summarizes some essential characteristics and performances of different MSR concepts.

Table 1: List of MSR concepts, breeder and burner, both containing fertile and fertile-free fuels

Family	Concepts	F/T	Fuel cycle	Thermal power (MW)	Comments
MSR-Breeder	MSBR	T	^{233}U/Th	2 250	Reference breeder concept BR > 1.05 Feedback reactivity coefficient > 0 (slightly)
	AMSTER-B	T	^{233}U/Th	2 250	BR > 0.95
	REBUS	F	U/Pu	3 700	
	FUJI	T	^{233}U/Th	150-200 electrical	
	TMSR	T or F	^{233}U/Th	2 500	BR > 1 Feedback reactivity coefficient < 0 (T and F)
MSR-Burner	AMSTER-I	T	U-Pu-MA	2 250	
	SPHINX	F	Pu-MA	1 208	
	MOSART	F	Pu-MA	2 400	Feedback reactivity coefficient < 0

F- fast, T- thermal neutron spectrum

Apart from MSR systems, other advanced concepts are being studied, which use the liquid salt technology. In the last five years, there has been a rapid growth in interest in the use of high-temperature (700 to 1000℃) liquid fluoride salts as coolants and for other functions in nuclear power systems. This interest is a consequence of new applications for high-temperature heat and the development of new reactor concepts. The liquid salt fluorides coolants have melting points between 315 and 500ºC and are, therefore, of use only in high-temperature systems. At lower temperatures, nitrate salts have been used on a large industrial scale for 60 years as coolants in heat transport systems in the chemical industry.

Thus a large-scale experience base exists for salt-based heat-transport systems. However, because these salts decompose at ~600℃, highly stable salt s are required at higher temperatures. Chloride salts are another option, but the technology is less well developed.

Liquid salt fluorides score high with respect to other coolants (thermal-hydraulic properties, high boiling temperature, optical transparency). These liquid salts offer opportunities for compactness, chemical compatibility and high temperature applications (competitiveness ↗, safety ↗) in solid fuel designs. Two types of solid-fuel liquid-salt-cooled reactors are being investigated, the Advanced High-Temperature Reactor (AHTR) and the Liquid-Salt-cooled Fast Reactor (LSFR).

The Advanced High-Temperature Reactor (AHTR) uses clean liquid salts (fluoride salts) as a coolant and the same graphite fuels as gas-cooled reactors such as the VHTR. The better heat transport characteristics of salts compared to helium enable power levels up to 4000 MW(t) with passive safety systems. The fuel cycle characteristics are essentially identical to the VHTR. The AHTR is a longer term high-temperature reactor option with potentially superior economics because of the properties of the salt coolant. It can be built in larger sizes, it operates at lower pressure and the equipment is smaller because of the superior heat transfer capabilities of liquid salt coolants compared to helium.

The LSFR is a reactor concept with a design that is similar to the AHTR, except that the reactor core is replaced by a modified metal-clad fast reactor core and a liquid fluoride salt with minimal neutron moderation in the core. The fuel-clad materials limitations imply operating temperatures between 700 and 800℃.

For Sodium Fast Reactors (SFR), one option that is being examined is a salt-cooled intermediate loop between the sodium-cooled primary system and a steam-water or a supercritical carbon dioxide power cycle — an advanced power cycle with potentially higher efficiency and lower capital costs than the traditional steam cycles. Liquid salts offer two potential advantages: (1) smaller equipment size because of the higher volumetric heat capacity of the salts and (2) no chemical reactions between the reactor, intermediate loop, and power cycle coolants. There is experience with this type of system because the Aircraft Reactor Experiment (the first MSR) used a sodium-cooled intermediate loop.

The development of higher temperature salts as coolants would open new nuclear and non-nuclear applications. These salts are being considered for intermediate heat transport loops within all types of high-temperature reactor systems (helium and salt cooled) and for hydrogen production concepts, oil refineries, and shale oil processing facilities amongst other applications. For most of these applications, the heat would have to be moved from hundreds of meters to kilometres.

3 Definition of specific criteria for the choice of salt chemical species and compounds from the different viewpoints

The first attempt to establish a screening logic for selecting molten salt fuels and coolants was done by Grimes many years ago [Grimes,1967,1970]. Grimes first considered all the elements that could possibly be used in MSR based on thermal neutron-capture cross-sections (values < 1 barn). This list is shown in Table 2. Obviously for the secondary coolant, this requirement is not so important as cost of salt components.

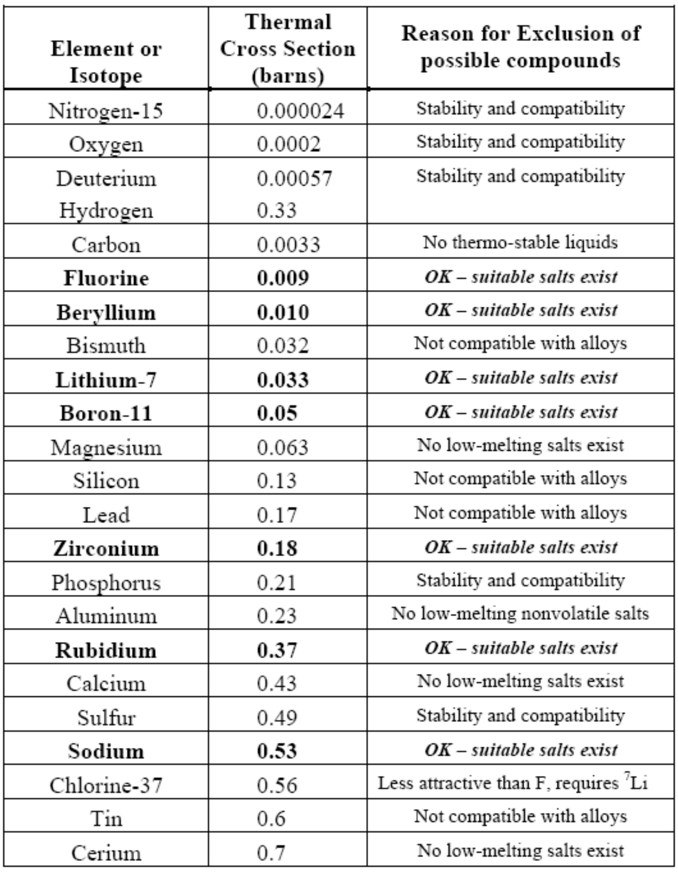
Grimes then applied a number of additional screening criteria to candidate compounds. He required that elements must form compounds that:

1. exhibit chemical stability at T > 800ºC,
2. are stable under intense radiation,
3. melt at useful temperatures (< 525ºC) and are not volatile,
4. are compatible with high-temperature alloys and graphite,
5. dissolve required quantities of fertile and fissile material.

In addition, the salt must be suitable for fuel reprocessing (full scale or limited).

The relevance of the last item is limited to MSR concepts (actinide-containing liquid fuel) and does not apply to the selection of primary or secondary coolants in other reactor systems using solid fuel elements (SFR, VHTR, AHTR).

Table 2: Grimes' list of elements for molten salt systems



Element or Isotope	**Thermal Cross Section (barns)**	**Reason for Exclusion of possible compounds**
Nitrogen-15	0.000024	Stability and compatibility
Oxygen	0.0002	Stability and compatibility
Deuterium Hydrogen	0.00057 0.33	Stability and compatibility
Carbon	0.0033	No thermo-stable liquids
Fluorine	**0.009**	***OK – suitable salts exist***
Beryllium	**0.010**	***OK – suitable salts exist***
Bismuth	0.032	Not compatible with alloys
Lithium-7	**0.033**	***OK – suitable salts exist***
Boron-11	**0.05**	***OK – suitable salts exist***
Magnesium	0.063	No low-melting salts exist
Silicon	0.13	Not compatible with alloys
Lead	0.17	Not compatible with alloys
Zirconium	**0.18**	***OK – suitable salts exist***
Phosphorus	0.21	Stability and compatibility
Aluminum	0.23	No low-melting nonvolatile salts
Rubidium	**0.37**	***OK – suitable salts exist***
Calcium	0.43	No low-melting salts exist
Sulfur	0.49	Stability and compatibility
Sodium	**0.53**	***OK – suitable salts exist***
Chlorine-37	0.56	Less attractive than F, requires ^{7}Li
Tin	0.6	Not compatible with alloys
Cerium	0.7	No low-melting salts exist

Useful salt compositions are shown in Table 3 with some factors than can be viewed as stand-alone parameters for screening candidates. Melting temperature is important in all cases. Vapour pressure should be minimized (< 1 mm Hg) to assure salt stability at high temperature. Neutron capture and moderation effect are important for graphite-moderated concepts.

Table 3: Typical salt compositions with some characteristic parameters

Salt	**Melting point (℃)**	**Vapor pressure at 900℃ (mm Hg)**	**Neutron capture relative to graphite**	**Moderating ratio**
LiF-BeF$_2$	**460**	**1.2**	**8**	**60**
NaF-BeF$_2$	**340**	**1.4**	**28**	**15**
LiF-NaF-BeF$_2$	**315**	**1.7**	**20**	**22**
LiF-ZrF$_4$	**509**	**77**	**9**	**29**
NaF-ZrF$_4$	**500**	**5**	**24**	**10**
KF-ZrF$_4$	**390**		**67**	**3**
Rb-ZrF$_4$	**410**	**1.3**	**14**	**13**
LiF-NaF-ZrF$_4$	**436**	**~5**	**20**	**13**
LiF-NaF-KF	**454**	**~0.7**	**90**	**2**
LiF-NaF-RbF	**435**	**~0.8**	**20**	**8**

Three basic salt systems have been extensively studied because they exhibit usefully low melting points and also have the potential for neutronic viability and materials compatibility with alloys: (1) alkali (Li, Na, K, Rb) fluoride salts, (2) ZrF_4- containing salts, and (3) BeF_2-containing salts. Another group (4) represents alkali fluoroborate salts usually used in MSR concepts as secondary coolant. The principal advantages of these coolants are low cost and low viscosity. The actual freezing point is somewhat higher than desired, but penalties associated with this freezing point are not great.

The renewed vision of potential applications requires re-opening the investigation of liquid salts beyond the typical salt systems studied in the past.

Figure 1 attempts at showing the whole set of criteria to be considered.

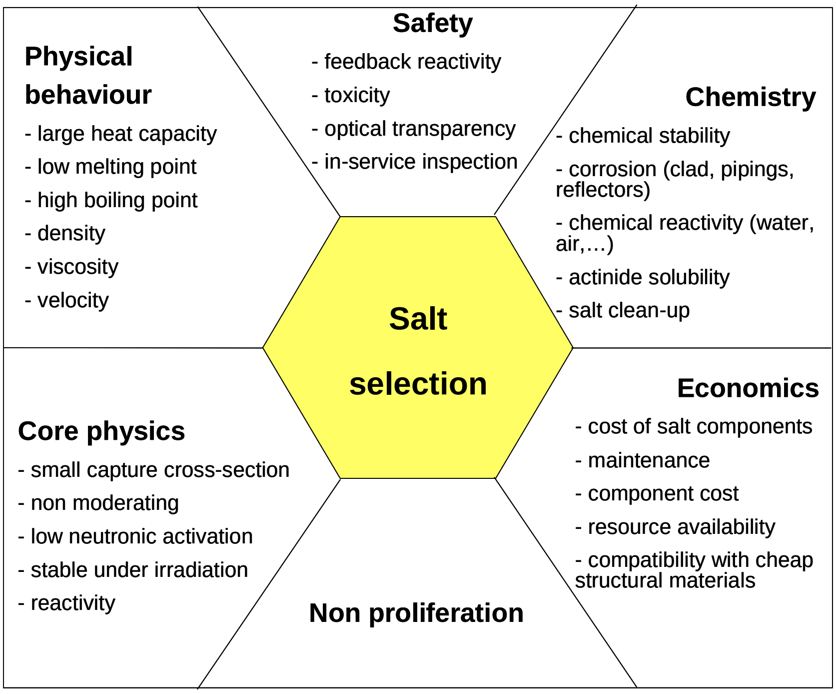


Figure 1: Rationale for salt selection

The relevance of salt selection results from a compromise, the best choice being dependant of the application that is considered.

Tables 4 and 5 show candidate salts for the different applications.

Table 4: MSR breeder and burner concepts

Family	F/T	Fuel	Fuel cycle	Concepts	Salt type	Selection criteria
MSR-Breeder	T (epithermal)	liquid fuel	^{233}U/Th	primary coolant	$LiF-BeF_2-(HN)F_4$	melting temperature, low neutron absorption
				secondary coolant	$NaBF_4-NaF$ (*MSBR*)	chemical compatibility with water, low cost
MSR-Breeder	F (non-moderated)	liquid fuel	^{233}U/Th	primary coolant	$LiF-(HN)F_4$	low melting temperature, low neutron absorption and moderation
				secondary coolant		
MSR-Burner	F	liquid fuel	Pu-MA	primary coolant	$NaF-LiF-BeF_2-(HN)F_3$	actinide (Pu, MA) solubility
				secondary coolant	$NaBF_4-NaF$	low cost, tritium trapping
MSR-Burner	F	liquid fuel	MA	primary coolant	$LiF-NaF-KF-(HN)F_3$	MA solubility > 10 mole%
				secondary coolant	$NaBF_4-NaF$	low cost, tritium trapping

Table 5: Liquid salt cooled concepts

Family	F/T	Fuel	Fuel cycle	Concepts	Salt type	Selection criteria
AHTR	T	solid fuel	U/Pu	primary coolant	BeF_2 salts, NaF salts	melting temperature, low cost
VHTR	T	solid fuel		intermediate coolant (H2)	$LiCl-KCl-MgCl_2$, $KF-KBF_4$, FLiNaK	heat transfer efficiency, low cost
SFR	F	solid fuel	U/Pu	primary coolant	$NaF-KF-ZrF_4$	low melting temperature, low neutron absorption and moderation
				secondary coolant	nitrates, chlorides?, hydroxides?	low melting temperature, chemical compatibility with water

Table 6 shows the most probable salt compositions that fulfil the criteria according to previous studies.

Table 6: Probable salt compositions for different applications

Reactor type	Neutron spectrum	Application	Reference	Alternatives
MSR-Breeder	Thermal	Fuel	^{7}LiF-BeF2-ThF4	
		Coolant	NaF-$NaBF_4$	LiF-BeF_2
	Fast	Fuel	LiF-ThF_4	LiF-CaF_2-ThF_4 $NaCl$-UCl_3-$PuCl_3$
		Coolant	NaF-$NaBF_4$	
MSR-Burner	Fast	Fuel	NaF-LiF-BeF_2-AnF_3	NaF-LiF-KF-AnF_3 NaF-LiF-RbF-AnF_3
AHTR	Thermal	Coolant	^{7}LiF-BeF_2	
VHTR	Thermal	Heat transfer	LiF-NaF-KF	$LiCl$-KCl-$MgCl_2$
LSFR	Fast	Coolant	$NaCl$-KCl-$MgCl_2$	NaF-KF-ZrF_4
SFR	Fast	Heat transfer	$NaNO_3$-KNO_3	

An' represents the actinides Pu, Am and Cm

3.1 Chemical behaviour

3.1.1 Introduction

The boundary box within which the molten salt components can be chosen is clearly defined by the type of application: reactor fuel, coolant or heat transfer fluid. The chemistry of the molten salt is an important parameter for the choice of the salt composition, complementary to neutronic, reactor physics and economic considerations. In this context, "chemistry" should be considered in the broadest sense of the word, meaning that it ranges from physico-chemical properties of the salt to redox behaviour of specific salt components.

The most important "chemistry" criteria for any salt are the following:

- Melting temperature: The liquid range of the salt must fit with the foreseen application and include a sufficiently wide margin toward freezing (solidification). In addition, the vapour pressure of the salt must be low in the relevant temperature range.
- Solubility for actinides (for fuel only): The fuel salt must be able to contain the required amount of fissile heavy nuclides, again with a sufficient margin, in this case to avoid precipitation of the fissile elements.
- Physico-chemical properties: Since the prime goal of the salt in any application is the transport of heat, its thermohydraulic behaviour is crucial. The flow of the salt is determined by the viscosity and the density, whereas the heat transfer is determined by the heat capacity and the thermal conductivity.
- Chemical reactivity: A chemical stability with respect to other fluid media (e.g. fuel salt-coolant mixing, water, sodium) will be required, depending on the environment in which the salt is employed.
- Tritium control: The necessity of trapping some portion of the tritium in the secondary coolant should influence the selection process.

Table 1.1 summarises the importance of these criteria for the various applications considered in this report. It is clear that melting temperature and physico-chemical properties are relevant to all of them, whereas solubility and chemical reactivity should be considered for specific applications only.

Table 1.1: Design significant criteria for various reactor applications

Reactor type	Neutron spectrum	Application	Melting temperature	Actinide solubility	Physico-Chemical properties	Chemical Reactivity	Tritium trapping
MSR-Breeder	Thermal	Fuel	●	●	●		
		Coolant	●		●	●^{1}	●
	Fast	Fuel	●	●	●		
		Coolant	●		●	●^{1}	●
MSR-Burner	Fast	Fuel	●	●	●		
		Coolant	●		●	●^{1}	●
AHTR	Thermal	Coolant	●		●		●
VHTR	Thermal	Heat transfer	●		●		●
LSFR	Fast	Coolant	●		●	●^{1}	
SFR	Fast	Heat transfer	●		●	●^{2}	

^{1}with water; ^{2}with sodium

Considering these criteria and taking into account the neutronic considerations for reactor fuels, the following chemical families can be discriminated:

- Fluorides of metals with low neutron capture cross sections that can be used in reactor cores, where a moderation effect is not wanted for fast neutron cores. This principally includes most of the alkali metals (^{7}Li, Na and Rb) as well some alkaline-earth metals (Be, Ca). The system ^{7}LiF-BeF$_2$ is the reference for this family, eventually extended to ^{7}LiF-NaF-BeF$_2$. Although zirconium also has a low neutron capture cross section in the thermal part of neutron spectrum, its volatility is relatively high and it can only be considered as salt component in exceptional cases. In non-moderated cores, also KF can be considered as major constituent in the fuel solvent system.

- Fluorides for application outside reactor cores, such as LiF-NaF-KF (FLiNaK), NaF-$NaBF_4$ and KF-KBF_4, for which no neutronic considerations apply.
- Chlorides of metals with low neutron capture cross sections that can be used in fast reactor cores. For this application, LiCl, NaCl and $MgCl_2$ and their mixtures can be considered.
- Nitrates can be an alternative to chlorides and fluorides for heat transfer applications at low temperatures. The system $NaNO_3$-KNO_3 is the probable choice.

In the following sections, the most probable salt compositions that fulfil the criteria will be discussed (cf. Tables 4, 5 and 6).

Thermodynamic approach

The binary phase diagrams are assessed based on the experimental data, mostly on the solidus, liquidus and phase transition data points. The excess energy of the solutions (in most of the systems only the liquid solution) is optimized in order to obtain the best possible agreement between phase diagrams and measurements. It is of great importance to model the higher order systems. These are extrapolated on a basis of the binary data according to the Kohler symmetric or Toop asymmetric formalism. Thus obtained higher order phase diagrams (ternary, pseudoternary etc.) are compared to the experimental data (if these are known) and if necessary adjusted by introducing the ternary excess energy parameters.

3.1.2 MSR-Breeder concept (epithermal)

3.1.2.1 Fuel salt: LiF-BeF_2-$(HN)F_4$ (HN = Th, U)

Melting temperature

Assuming that the primary coolant contains constant amounts of ThF_4 = 12.0 mol% and UF_4 = 0.3 mol% (values from the MSBR concept), the lowest melting temperature of the LiF-BeF_2-ThF_4-UF_4 system according to the thermodynamic model (assessed by Van der Meer [Van der Meer,2006]) is T = 784 K (511℃). The overall composition that corresponds to this point is LiF-BeF_2-ThF_4-UF_4 (67.3-20.4-12.0-0.3). The experimental melting temperature found for this composition is T=773 K (500℃), and thus very good agreement between the model and the experiments is achieved. Since the designed inlet temperature of the MSBR is T=839 K, a sufficient safety margin is kept here.

The pseudo-binary phase diagram of the LiF-BeF_2 system with constant amounts of ThF_4 (12 mol%) and UF_4 (0.3 mol%) is shown in Figure 1.1. This diagram should be compared to the binary LiF-BeF_2 phase diagram shown in Figure 1.8. The complex phase relations in the sub-liquidus field are due to the existence of numerous binary phases of the LiF with ThF_4 and UF_4. Since Figure 1.1 only serves to demonstrate the liquidus, the phase fields have not been identified.

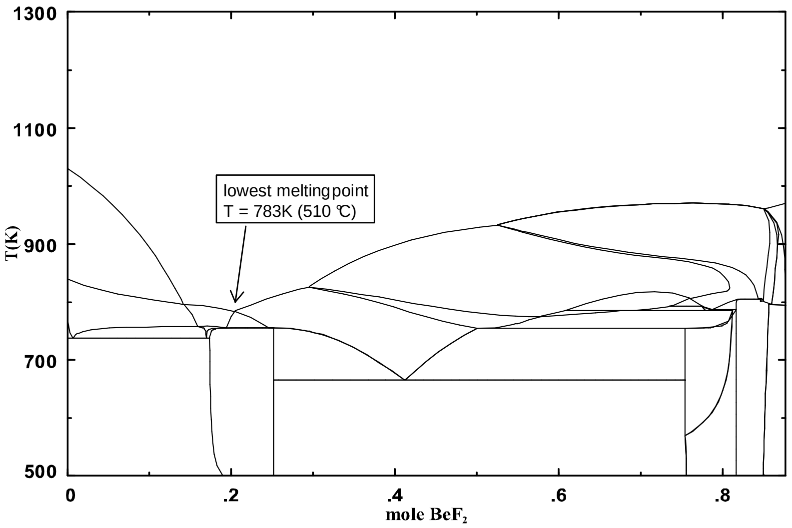


Figure 1.1: Pseudo-binary phase diagram of the LiF-BeF_2 system with constant amounts of ThF_4 (12 mol%) and UF_4 (0.3 mol%)

According to this phase diagram, it is also possible to reduce the amount of BeF_2 to 18.3 mol%, where the melting temperature still falls within a 50 K safety margin, T=789 K at LiF-BeF_2-ThF_4-UF_4 (69.4-18.3-12.0-0.3).

Solubility of ThF_4 in the LiF-BeF_2 melts

The solubility of ThF_4 in the LiF-BeF_2 matrix has been calculated for T=839 K (inlet of MSBR) keeping a constant ratio of LiF/BeF_2 = 0.766/0.233. This ratio corresponds to the one that has been found in the fuel composition described in the previous paragraph (LiF-BeF_2-ThF_4-UF_4 (67.3-20.4-12.0-0.3)). Figure 1.2 shows the ternary phase diagram of the LiF-BeF_2-ThF_4 system at T=839 K. The red line (the bold one in black/white printout) represents the LiF/BeF_2 ratio at 0.766/0.233 within the whole field of the diagram. It is obvious that the solubility of the ThF_4 in the LiF-BeF_2 matrix is between 4.7 mol% and 18.2 mol%. The borders of the solubility are represented by the ''A'' and ''B'' signs respectively.

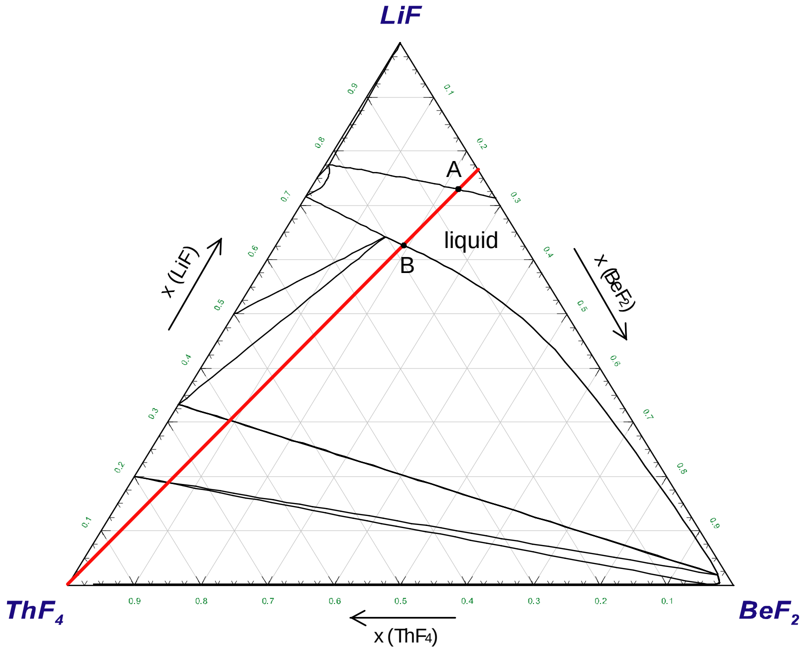


Figure 1.2: LiF-BeF_2-ThF_4 phase diagram plotted at T=839 K

Density and viscosity

The density and viscosity of the LiF-BeF_2-ThF_4 system of several compositions have been measured by Cantor [Cantor,1971] and the results are summarized in the MOST report [Konings,2005] and in the paper by Van der Meer *et al* [Van der Meer,2007].

The viscosity of the quaternary LiF-BeF_2-ThF_4-UF_4 (71-16-12-1) composition has been reported in [Powers,1963] for a temperature range 873 K–1073 K, giving:

$$\mu = 0.062\, exp(4636/(T/K)) \qquad \text{(mPa.s)}$$

Thermal conductivity

Araki and Kato [Araki,1987] measured the thermal diffusivity of liquid LiF-BeF_2-ThF_4 (64-18-18) from which they derived the thermal conductivity, using their heat capacity data and an estimated density. The results indicate an almost constant value in the temperature range 850 K to 1000 K: $0.95\ Wm^{-1}K^{-1}$ to $0.98\ Wm^{-1}K^{-1}$

Vapour pressure

Based on the thermodynamic assessment by Van der Meer et al [Van der Meer,2006] the vapour pressure of the eutectic composition (LiF-BeF_2-ThF_4-UF_4 (67.3-20.4-12.0-0.3)) has been calculated for a temperature range T=839–1039 K, giving:

$$log_{10}\ p = 11.465 - 11076/(T/K) \qquad \text{(Pa)}$$

3.1.2.2 Secondary coolant: $NaBF_4$-NaF

This eutectics can be used for all MSR concepts under consideration, not only thermal MSR breeder. Alternative for secondary circuit is ternary Li,Na,Be/F mixture with melting temperature 315°C.

Melting behaviour

The equilibrium diagram of the NaF-$NaBF_4$ system has been studied by Selivanov and Stender [Selivanov,1958] and Barton *et al* [Barton,1970]. Both studies indicate that it is a simple eutectic system, but the eutectic temperatures and compositions differ considerably. In view of their more careful sample preparation, the results of Barton *et al* are preferred. They found x{eut} = (92 ±1) mol% $NaBF_4$ with T{eut}=(657 ±1) K.

Density

The density of NaF-$NaBF_4$ (92-8) was measured by Cantor [Cantor,1971] from 673 K to 864 K. The results can be represented by the equation:

$$\rho = 2446.3 - 0.711(T/K) \qquad (\text{kg.m}^{-3})$$

Viscosity

The viscosity of NaF-$NaBF_4$ (92-8) was measured by Cantor [Cantor,1971] from 682 K to 810 K. The results can be represented by the equation:

$$\mu = 0.0877\, exp(2240/(T/K)) \qquad (\text{mPa.s})$$

Thermal conductivity

Cantor [Cantor,1968] reported preliminary measurements of the thermal conductivity of pure liquid $NaBF_4$ by Cooke, giving $\lambda = 0.51\ Wm^{-1}K^{-1}$.

Vapor pressure

Based on the experimental results by Cantor et al [Cantor,1967] who measured the vapour pressure of BF_3 above the NaF-$NaBF_4$ melt, the vapour pressure of the NaF-$NaBF_4$ (92-8) composition has been determined, giving:

$$log_{10}\, p = 11.638 - 6550.6/(T/K) \qquad (\text{Pa})$$

3.1.3 MSR-Breeder concept (non moderated)

3.1.3.1 Fuel salt: LiF-$(HN)F_4$ (HN = Th, U)

Melting temperature and solubility

The calculated LiF-UF_4-ThF_4 phase diagram in Figure 1.3 shows the liquid field at T=789 K.

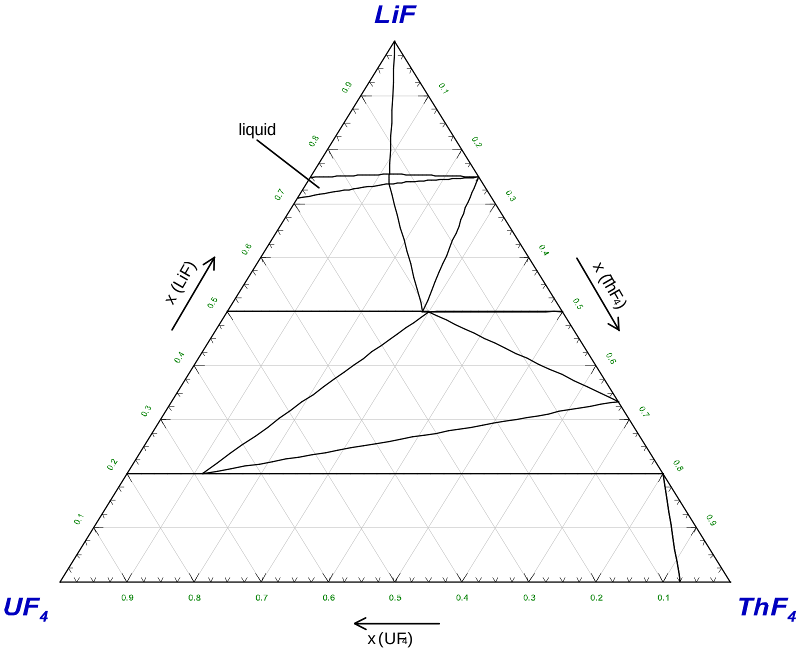


Figure 1.3: LiF-ThF_4-UF_4 ternary phase diagram for T=789 K

This temperature is 50 K lower than the inlet of the reactor according to the MSBR concept (Tinlet=839 K). It shows that the maximum solubility of the ThF_4 is 12 mol%, which would be sufficient, however this solubility is only possible when around 14 mol% of UF_4 are present. In order to keep the concentration of UF_4 at 1 mol% (estimate of the UF_4 concentration, based on previous studies) while keeping the ThF_4 solubility at 12 mol%, the temperature must be increased to T=1020 K. This would mean to have an inlet temperature of the reactor at T=1070 K and that is rather high. Another option is to increase the content of the ThF_4, while keeping the UF_4 concentration at 1 mol%, up to 21.5 mol%. The melting temperature of such a composition (LiF-ThF_4-UF_4 (77.5-21.5-1)) is T=837 K (meaning 887 K as an inlet to the reactor core) and that can be acceptable for a MSR fuel.

Viscosity and density for LiF-ThF_4 system

The density of LiF-ThF_4 mixtures were measured by Porter and Meaker [Porter,1966] and Hill *et al* [Hill,1967]. The data are in good agreement. The results clearly indicate a linear dependence of the molar volume with composition, confirming ideal behaviour as outlined in the MOST report [Konings,2005]. The same ideal behaviour has been found in case of the LiF-UF_4 system.

The viscosity of LiF-ThF_4 mixtures was measured by Chervinskij et al [Chervinskij,1982] from 0 to 100 mol% of ThF_4. The results show a strong positive deviation from ideal behaviour around the eutectic composition.

Vapour pressure

Based on the thermodynamic assessment by Van der Meer et al [Van der Meer,2006] the vapour pressure of the eutectic composition (LiF-ThF_4-UF_4 (77.5-21.5-1.0)) has been calculated for a temperature range T=839–1039 K, giving:

$$log_{10}\ p = 11.465 - 11076/(T/K) \qquad \text{(Pa)}$$

3.1.3.2 Fuel salt: NaCl-UCl_3-$PuCl_3$

NaCl-UCl_3-$PuCl_3$ is another system considered as a fast breeder fuel. It is based on the REBUS-3700 concept [Mourogov,2006] where the fuel composition is NaCl-UCl_3-$PuCl_3$ (55-38-7). The calculated melting temperature of such a composition has been found at T=873 K [Benes,2008], exactly 50 K below the proposed inlet temperature of the REBUS-3700 concept. Thus it is acceptable as a fuel choice.

The vapour pressure of the eutectic composition has been calculated at p=2.25 Pa for T=1003 K, which is the designed outlet temperature of the REBUS-3700 concept.

3.1.4 MSR-Burner concept (fast spectrum)

3.1.4.1 Fuel salt: LiF-NaF-BeF_2-$(HN)F_3$, (HN)=Pu, MA

The fuel in the MOSART concept [Zherebtsov, 2008] can be based on the ternary LiF-NaF-BeF_2 matrix or as alternative on LiF-BeF_2, with BeF_2 content in the system of about 27 mol%. The start-up and feed material scenarios include plutonium and minor actinides from PWR enriched uranium or mixed-oxide spent nuclear fuel. Depending upon the feed material, the salt at equilibrium contains 1.05 to 1.3 mol% of actinide and lanthanide trifluorides. The proposed inlet core temperature of such reactor is 873 K, thus the melting temperature of the fuel should be at highest 823 K in order to keep the 50 K safety margin.

Melting behaviour

The LiF-NaF-BeF_2-PuF_3 phase diagram has not been measured.

Based on the present thermodynamic assessment, the preliminary pseudoternary phase diagram with constant concentration of PuF_3 of 1.3 mol% has been calculated (to be published) and is shown in Figure 1.4 as a projection of liquid surface. Calculated lowest melting temperature is at T=837 K and LiF-NaF-BeF_2-PuF_3 (37.9-45.2-15.6-1.3), thus 14 K higher than the criterion temperature of 823 K.

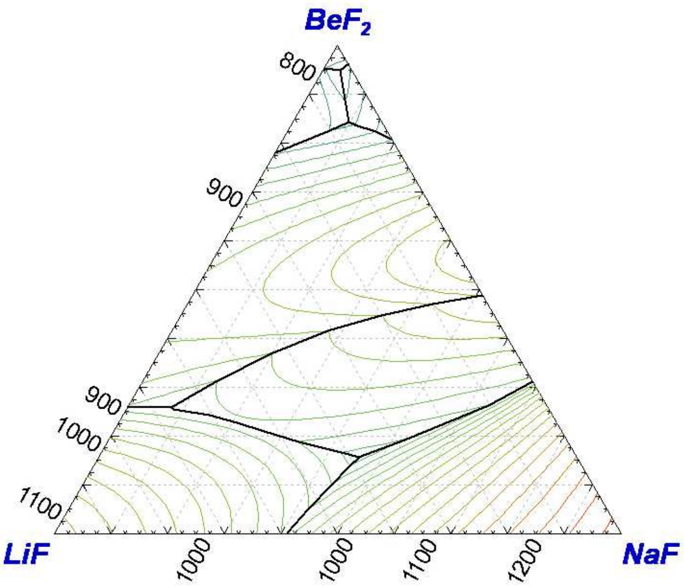


Figure 1.4: Calculated liquid surface of the preliminary phase diagram of the LiF-NaF-BeF_2 system with X(PuF_3) = 1.3 mol%. Isotherms are labelled in K with interval of 25 K

Solubility of PuF_3

Solubility of PuF_3 in the ternary melt of LiF-NaF-BeF_2 (17.5-56.5-26) and LiF-NaF-BeF_2 (60.1-2.1-37.8) has been measured by Barton *et al* [Barton,1959], and Ignatiev *et al* [Ignatiev,2007] measured the PuF_3 solubility in the melts of LiF-NaF-BeF_2 (15-58-27) and LiF-NaF-BeF_2 (17-58-25). Their data are shown in Figure 1.5 and compared with the calculated results obtained from the present thermodynamic assessment. Based on the experimental results and the calculated ones, it has been found that the solubility of PuF_3 in the matrix of LiF-NaF-BeF_2 mixture is very low and therefore the melting behaviour of the fuel is highly affected by even small addition of the PuF_3 compound. For comparison, the lowest eutectic point in the ''pure'' LiF-NaF-BeF_2 system measured by Moore *et al* (unpublished work cited by Braunstein et al [Braunstein,1975]) is at T=588 K, whereas the lowest melting point found in the pseudoternary phase diagram containing 1.3 mol% of PuF_3 (shown in Figure 1.4) is at T=837 K.

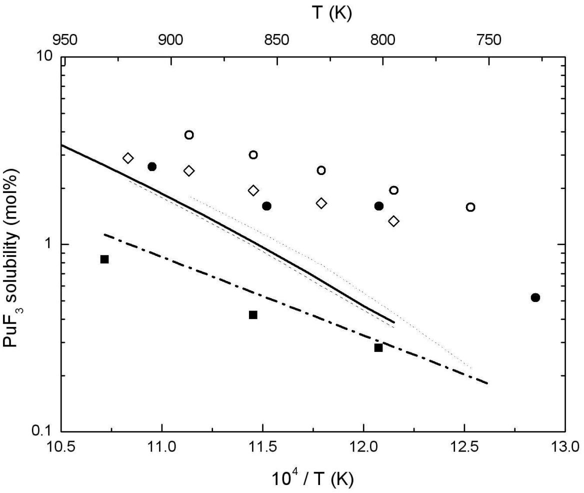


Figure 1.5: Measured and calculated data of the PuF_3 solubility in the matrix of:

A. LiF-NaF-BeF_2 (60.1-2.1-37.8): ■ experimental data by Barton [Barton,1959], dash-dot line - calculated data according to preliminary phase diagram (present study);

B. LiF-NaF-BeF_2 (17.5-56.5-26): ● experimental data by Barton [Barton,1959], solid line - calculated data according to preliminary phase diagram (present study);

C. LiF-NaF-BeF_2 (15-58-27): ◊ experimental data by Ignatiev *et al* [Ignatiev,2007];

D. LiF-NaF-BeF_2 (17-58-25): ○ experimental data by Ignatiev *et al* [Ignatiev,2007].

Density and viscosity

There are no data on viscosity and density of the LiF-NaF-BeF_2-PuF_3 system, but these can be estimated based on the results from the LiF-NaF-BeF_2 system, see MOST report [Konings,2005]. Although it has been found that the melting behaviour is highly influenced by the presence of PuF_3, it is not expected that the addition of PuF_3 would influence the viscosity significantly since the most viscous compound in this quaternary is BeF_2. It has been observed that the densities of the fluoride systems have ideal behaviour (or very close to ideal), thus it is not expected that the presence of PuF_3 would change this trend.

Vapour pressure

According to present thermodynamic data, vapour pressure of the pseudo-ternary eutectic composition (LiF-NaF-BeF_2-PuF_3 (37.9-45.2-15.6-1.3)) has been calculated for the temperature range T=840–1200 K.

$$log_{10}\, p = -2.6497 + 0.00243(T/K) - 5223413(T^2/K) \qquad \text{(Pa)}$$

3.1.4.2 Fuel salt: LiF-NaF-(KF)-(RbF)-(HN)F_3, (HN)=Pu, MA

The fuel salt for of the MOSART concept [Zherebtsov,2008] (Actinide Burner concept) is based on a LiF-NaF-BeF_2 matrix in which the actinides are dissolved in form of trifluorides. This matrix provides adequate solubility for the TRU trifluorides from PWR spent fuel. The study tried to see the thermodynamic behaviour of the fuel, where the BeF_2 compound is avoided and replaced by either KF or RbF. The specific salt candidates were chosen, in part, because of their suitable freezing points and higher solubility for actinides trifluorides compared to LiF-NaF-BeF_2 matrix.

Melting behaviour

The criterion for the melting temperature of the fuel has been defined as T=823 K as a 50 K safety margin of the proposed inlet temperature (T=873 K) based on [Zherebtsov,2008]. In Figures 1.6 and 1.7, the calculated LiF-NaF-KF and LiF-NaF-RbF pseudoternary phase diagrams [Benes,2008a] are plotted as a liquidus projection and the lowest melting points correspond to the eutectic temperatures shown with arrows. Both phase diagrams are plotted with a constant amount of PuF_3 at 1.3 mol%. This value is the total concentration of actinides (in form of trifluorides) in the proposed fuel based on the MOSART concept. Note that this assumption does not take into account neutronic aspects of LiF-NaF-BeF_2 replacement on LiF-NaF-KF or LiF-NaF-RbF in MOSART homogeneous core without moderator (see details in sections 3.3 and 3.5).

In case of LiF-NaF-KF-(PuF_3=1.3 mol%), the lowest melting temperature was calculated at T=723 K and LiF-NaF-KF-PuF_3 (43.3-14-41.4-1.3) and, in case of LiF-NaF-RbF-(PuF_3=1.3 mol%), it is T=706 K and LiF-NaF-RbF-PuF_3 (39.5-14-45.2-1.3). Thus both systems fulfil the melting criteria for a molten salt reactor based on the MOSART concept.

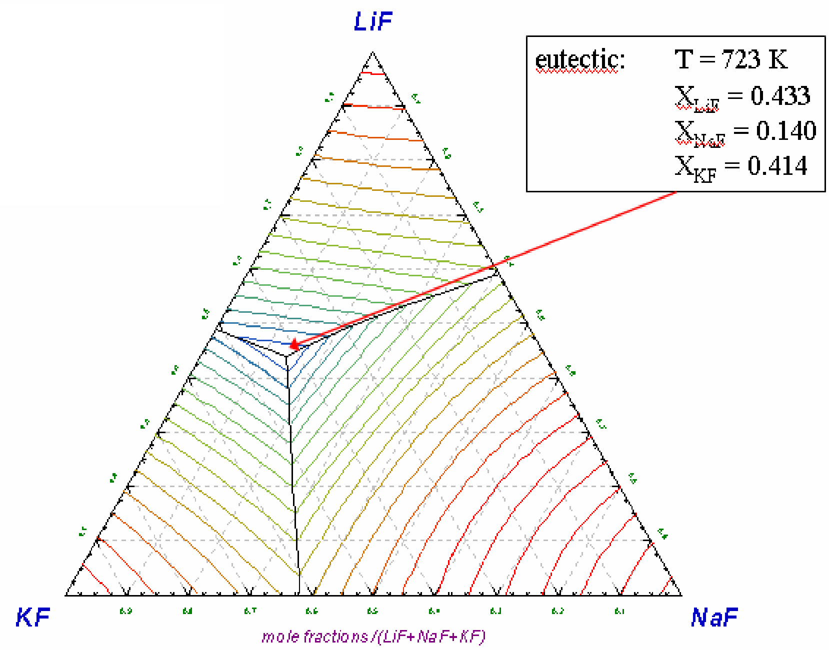


Figure 1.6: Liquidus projection of the LiF-NaF-KF pseudoternary phase diagram with constant amount of PuF_3 = 1.3 mol%

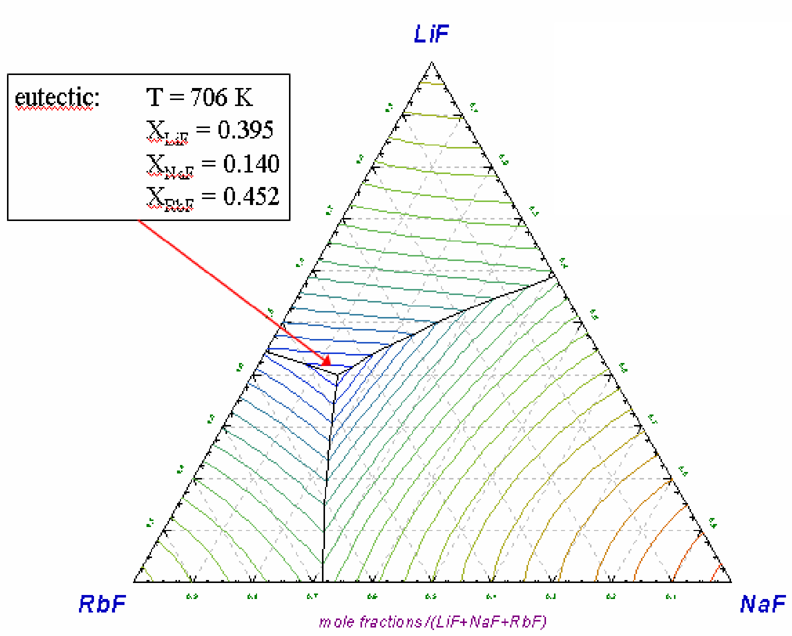


Figure 1.7: Liquidus projection of the LiF-NaF-RbF pseudoternary phase diagram with constant amount of PuF_3 = 1.3 mol%.

Solubility of PuF_3 in the alkali metal fluoride matrix

The calculated maximal solubility of PuF_3 in the matrix of LiF-NaF-KF (43.9-14.2-41.9) (corresponding ratio of the LiF-NaF-KF matrix components at the eutectic point found in Figure 1.6) at Tinlet=873 K has been found at $c(PuF_3)$=19.3 mol%.

The calculated maximal solubility of PuF_3 in the matrix of LiF-NaF-RbF (40.0-14.2-45.8) (corresponding ratio of the LiF-NaF-RbF matrix components at the eutectic point found in Figure 1.7) at Tinlet=873 K has been found at $c(PuF_3)$=22.8 mol%.

Density and viscosity

Nor density, nor viscosity of the LiF-NaF-KF-PuF_3 and LiF-NaF-RbF-PuF_3 systems have been experimentally determined. However, in case of the LiF-NaF-KF-PuF_3 system, these properties can be estimated based on the results performed on the FLiNaK system (LiF-NaF-KF) discussed in section 3.1.6.1.

Vapour pressure

The calculated vapour pressure of the LiF-NaF-KF-PuF_3 (43.3-14-41.4-1.3) composition valid for a temperature range T=823–1023 K is given below:

$$log_{10}\ p = 11.036 - 11065/(T/K) \qquad \text{(Pa)}$$

The calculated vapour pressure of the LiF-NaF-RbF-PuF_3 (39.5-14-45.2-1.3) composition valid for a temperature range T=823–1023 K is given below:

$$log_{10}\ p = 10.699 - 10073/(T/K) \qquad \text{(Pa)}$$

3.1.5 AHTR-(thermal spectrum)

Since the AHTR is a reactor concept based on a thermal spectrum, the primary coolant that flows through the reactor core must have very low thermal neutron capture cross section. Therefore, only the compounds like ^{7}LiF, BeF_2 or ZrF_4 can be part of the coolant. Since the ZrF_4 compound has very high vapour pressure at high temperatures, it is excluded from the coolant choice and only $(Li,Be)F_x$ binary solution is considered as a candidate.

3.1.5.1 Primary coolant: LiF-BeF_2

Melting behaviour

Several studies of the LiF-BeF_2 equilibrium diagram have been reported [Roy,1953,1954,1950], [Novoselova,1952], [Jones,1962], but the early results are often affected by oxygen impurities in the salts. Thoma *et al* [Thoma,1968] and subsequently Romberger *et al* [Romberger,1972] established definitely the phase relations in this system. The system shows two mixed compounds: Li_2BeF_4 which melts congruently and $LiBeF_3$ which decomposes to Li_2BeF_4 and BeF_2. In addition, two eutectic points were found at T=730 K and X(BeF_2)=0.33 and T=643 K and X(BeF_2)=0.52, see Figure 1.8.

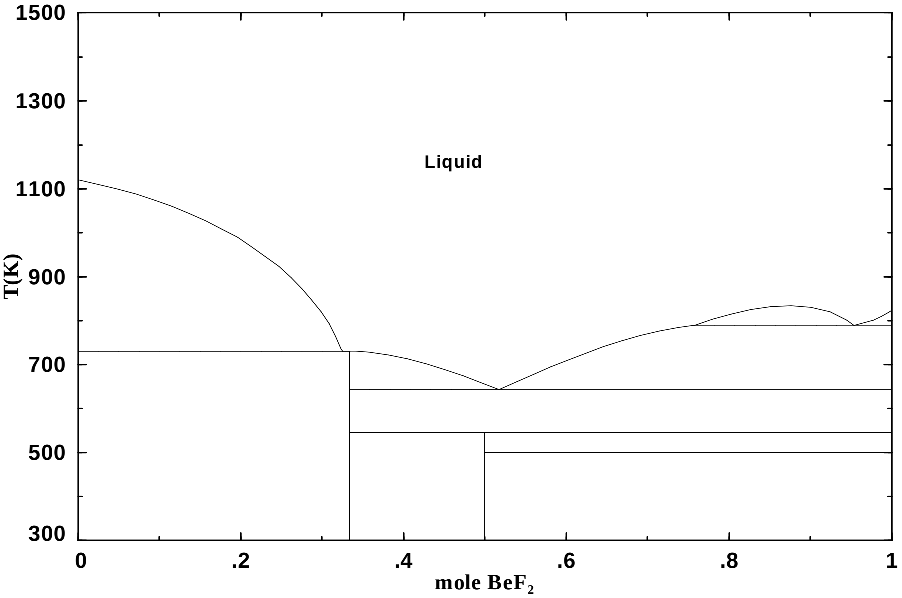


Figure 1.8: LiF-BeF_2 binary phase diagram

Vallet and Brainstein [Vallet,1977] suggested that a miscibility gap may occur at the BeF_2-rich side of the diagram, based on model calculations. Van der Meer *et al* [Van der Meer,2006] arrived at the same conclusion based on phase diagram optimisation.

Heat Capacity, density, viscosity and thermal conductivity

The results from the heat capacity, density and viscosity measurements are summarized in the MOST report [Konings,2005].

Vapour pressure

Based on the thermodynamic assessment from [Van der Meer,2006], the vapour pressure of the LiF-BeF_2 (67-33) eutectic composition has been calculated for a temperature range between 823 K and 1023 K giving:

$$log_{10}\, p = 11.830 - 11048 / (T / K) \qquad \text{(Pa)}$$

3.1.6 VHTR-(thermal spectrum)

3.1.6.1 Intermediate coolant: LiF-NaF-KF (FLiNaK)

Melting behaviour

The calculated phase diagram of the LiF-NaF-KF system published in [Benes,2007] is shown in Figure 1.9 as a projection of the liquidus surface. The lowest melting point corresponds to T=726 K at LiF-NaF-KF (45.3-13.2-41.5). It is nearly identical to what was found experimentally by Bergman and Dergunov [Bergman,1941].

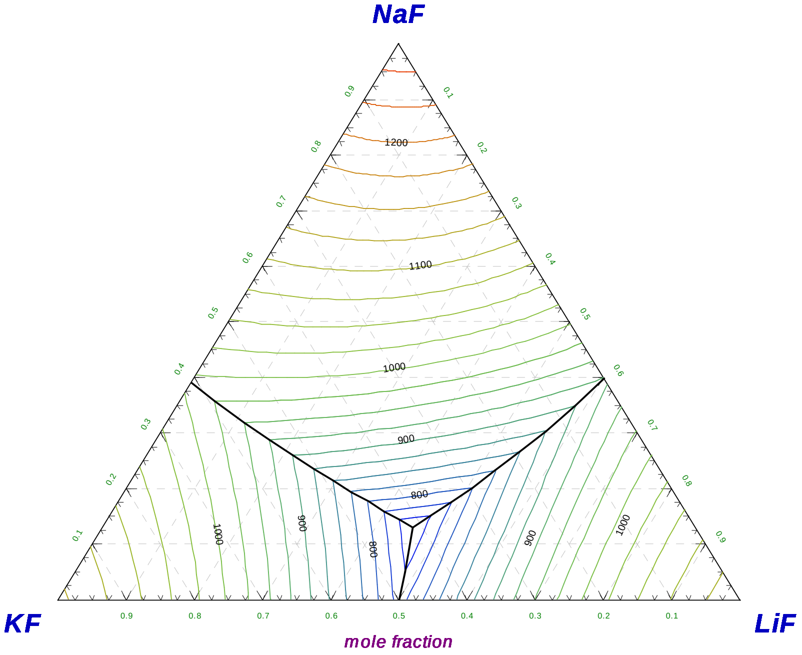


Figure 1.9: Liquidus projection of the LiF-NaF-KF system

Density

The density of the eutectic melt of the LiF-NaF-KF system has been measured by Chrenkova *et al* [Chrenkova,2003] for the temperature range 940-1170 K. The obtained density equation as a function of temperature is given below:

$$\rho = 2.4089 - 6.240.10^{-4}\, t(°C) \qquad (\mathrm{g.cm^{-3}})$$

Viscosity

The viscosity of the eutectic melt of the LiF-NaF-KF system has been measured by Chrenkova *et al* [Chrenkova,2003] for the temperature range 773-973 K. The obtained viscosity equation as a function of temperature is given below:

$$log_{10}\, \mu = -1.6044 - 1944\,/\,(T\,/\,K) \qquad (\mathrm{mPa.s})$$

The exact composition of the LiF-NaF-KF melt measured in [Chrenkova,2003] was LiF-NaF-KF (46.5-11.5-42), thus very close to the eutectic point found from the thermodynamic assessment in the present study.

Vapour pressure

According to the present thermodynamic assessment [Benes,2007], the vapour pressure of the LiF-NaF-KF (45.3-13.2-41.5) composition has been calculated for the temperature range between 823–1023 K. The result is given in equation below:

$$log_{10}\, p = 11.042 - 11063\,/\,(T\,/\,K) \qquad (\mathrm{Pa})$$

3.1.6.2 Intermediate coolant: LiCl-KCl-$MgCl_2$

Melting behaviour

The LiCl-KCl-$MgCl_2$ phase diagram has been calculated by Chartrand *et al* [Chartrand,2001] and is shown in Figure 1.10 as a projection of the liquidus surface. It indicates the lowest eutectic at T=602 K and LiCl-KCl-$MgCl_2$ (42.8-46.6-10.6). It thus melts more than 100 K lower than the FLiNaK system (T=726 K) on one hand, but on the other hand the vapour pressure at T=1000℃ is according to the calculations 1400 Pa, much higher than that of FLiNaK that has vapour pressure 190 Pa at T=1000℃.

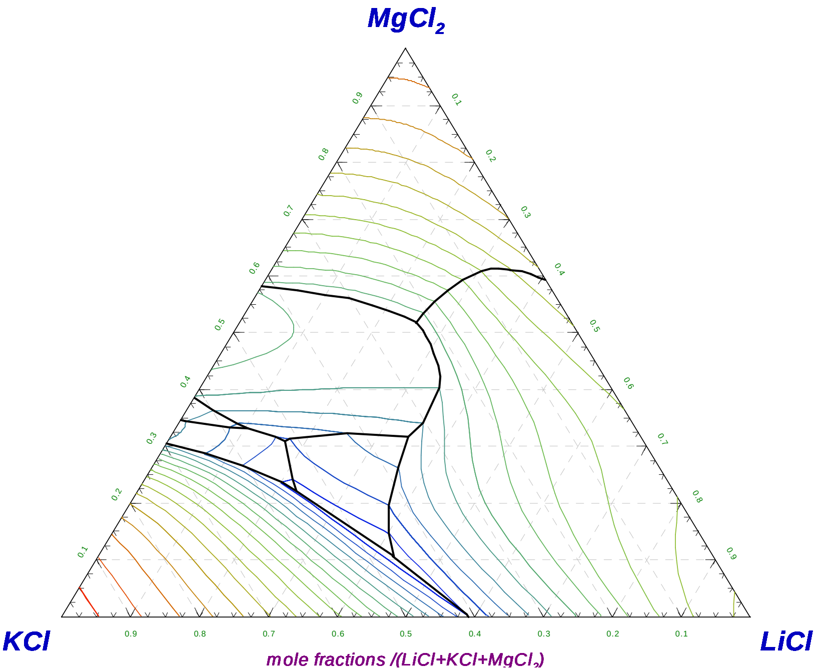


Figure 1.10: Liquidus projection of the LiCl-KCl-$MgCl_2$ system

3.1.7 LSFR-(fast spectrum)

3.1.7.1 Primary coolant: NaCl-KCl-$MgCl_2$

The group of Pr Todreas from MIT proposed the NaCl-KCl-$MgCl_2$ system to be a good candidate for a fast reactor primary coolant. It has been thermodynamically assessed by Chartrand *et al* [Chartrand,2001], indicating the lowest eutectic at T=625 K and NaCl-KCl-$MgCl_2$ (25-40-35). The liquidus projection of the NaCl-KCl-$MgCl_2$ system is shown in Figure 1.11.

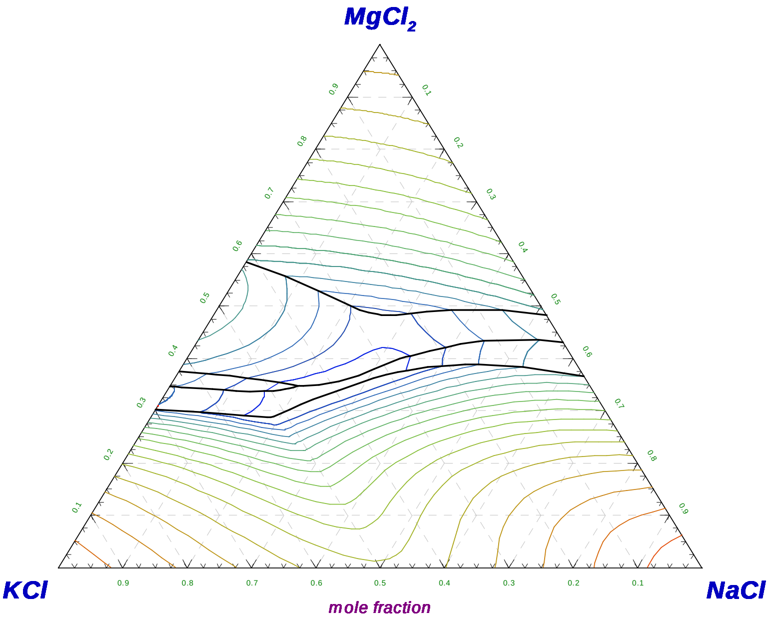


Figure 1.11: Liquidus projection of the NaCl-KCl-$MgCl_2$ system

The vapour pressure of the NaCl-KCl-$MgCl_2$ (25-40-35) composition for T=1000℃ has been calculated to p=522 Pa.

3.2 Material compatibility

3.2.1 Metallic materials

A critical technical distinction between the MSR and other liquid salt applications should be noted. The corrosion rates of systems containing clean liquid fluoride salts with the proper materials of construction are very low; it is the impurities that are primarily responsible for corrosion. Appropriate alloys of construction have been found for MSRs. However, the peak temperatures may be limited to less than 750℃ because the same alloys have low strength at higher temperatures. This constraint does not exist for clean liquid salt systems.

The success of a Molten Salt Reactor (MSR) is strongly dependent on the readiness of structural material with long service lifetime at the intended high temperature of use [Allen,2008]. This includes creep resistance and compatibility with the molten media used as the primary and possibly as secondary coolant. Corrosion is the most unique and critical materials requirement, since many alloying elements commonly used in high-temperature structural alloys exhibit some degree of solubility in molten fluoride salts. The reliance on a protective oxide layer is not practical because oxides are chemically unstable in molten fluoride salt environments. Resistance against high-temperature air oxidation is a further criterion on materials, since the outer surface of the molten salt containment will likely interface with air.

USA (especially ORNL), Europe and former Soviet Union have accumulated significant knowledge in the operation of molten fluoride salt test loops using many coolants (NaF-ZrF_4, LiF-NaF-KF, LiF-BeF_2 etc.) w/o UF_4 and ThF_4. Implementation of two major experimental programs in USA ([Mac Pherson,1985], [Forsberg,2005]), the Aircraft Reactor Experiment (ARE), that used UF_4-ZrF_4-NaF fuel and moderated by BeO, and the Molten Salt Reactor Experiment (MSRE), fuelled with ^{7}LiF, UF_4, ThF_4 and BeF_2, also provides a valuable feedback.

The composition of candidate metallic structural materials with Ni-base is in Table 2.1. Only few of them are alloys with ASME code certification for high temperature application.

Table 2.1: Alloy composition (in wt%) of MSR candidate structure materials [Ingersoll,2004]

Alloy	Cr	Mo	W	Ta	Al	Ti	Fe	C	Co	Ni	Nb	Zr
Hastelloy- X	20.5	8	0.2				17	0.05	0.5	bal.		
Hastelloy-N	6.31	16.1	0.06		0.01	4.03	0.03	0.03	0.15	72.2		
M22	5.7	2	11	3	6.3			0.13		bal.		0.6
HP- modified	24						bal.	0.37		34	1.2	
Nickel-200										99		
Incoloy-800H	19				0.15	0.15	bal.	0.05		30		
Haynes 230	22	2	14				3		5	57		
Nb-1Zr											98.9	1.1
Haynes 214	16				4.5		3	0.05		75		0.1
Inconel 617	24	10			0.8	0.6	3	0.15	15			
Haynes 242	8	25			0.5		2	0.03	2.5	65		
Hastelloy B-3	1-3	27-32	3		0.5	0.2	1-3	0.01	3	bal.	0.2	

Early studies at ORNL on candidate metallic materials showed Ni-based alloys and austenitic stainless steels to be generally promising candidates for molten salt environment ([Manly,1960] and [Williams,2006B]). These tests were performed in a temperature gradient system with various fluoride media and different temperatures (maximum temperature and temperature gradient). Table 2.2 reports the corrosion depth of specimens depending on the maximum temperature in the loop and the time of exposure. Chromium, which is added to most alloys for high-temperature oxidation resistance, is quite soluble in molten fluoride salts [Kroger,1972]. Metallurgical examination of the surveillance specimens showed the corrosion to be associated to outward diffusion of Cr through the alloy. It was concluded that the **chromium content shall be maintained as low as reasonably possible** to keep appropriate air oxidation properties. Corrosion rate is marked by initial rapid attack associated with dissolution of Cr and is largely driven by the impurities in the salt [Williams,2006B]. This is followed by a period of slower linear corrosion rate behaviour, which is controlled by a mass transfer mechanism dictated by thermal gradients and flow conditions. **Minor impurities in the salt can enhance corrosion by several orders of magnitude** and must be kept to a minimum. Dissolution can be mitigated by a chemical control of the redox in salts for example by small additions of elements such as Be. Corrosion increased dramatically as the temperature was increased and is coupled to plate-out in the relatively cooler regions of the system, particularly in situations where high flow is involved. Tests performed at 815℃ especially showed Ni-based alloys to be superior to Fe-based alloys. This led to the development of a tailored Ni-based alloy, called INOR-8 or Hastelloy-N, with a composition of Ni-16%Mo-7%Cr-5%Fe-0.05%C, which has successfully functioned in molten fluoride salt at maximum 650℃ for 26000 h.

Table 2.2: Summary of corrosion results of metallic materials in some molten salts [Williams,2006A,2006B]

Loop	Alloy	Salt	Time of exposure [h]	Temp [℃]	Corrosion depth [µm]
116	316SS	FLiNaK + NaK	500	815	4
119	316SS	FLiNaK + NaK	500	815	2
347	Inconel	50NaF-50ZrF4	3000	815	11
518	Inconel	NaF-ZrF4	3000	815	11
346	Inconel	50NaF-50ZrF4	2000	815	9
519	Inconel	NaF-ZrF4	2000	815	12.5
78	Inconel	FLiNaK	1000	815	13
	Inconel	NaF-ZrF4	1000	815	3
278	Inconel	NaF-ZrF4	1000	815	5
399	Inconel	NaF-ZrF4	1000	815	10
	Inconel	60NaF-40ZrF4	1000	815	5
	Inconel	50NaF-50Be2	1000	815	8
	Inconel	70NaF-30BeF2	1000	815	6
	Inconel	24LiF-53NaF-23BeF2	1000	815	5
	Inconel	36LiF-49NaF-15BeF2	1000	815	3
	Inconel	74LiF-26ThF4	1000	815	6
517	Inconel	NaF-ZrF4	822	815	5.5
337	Inconel	NaF-ZrF4	575	815	8
214	Inconel	FLiNaK + NaK	500	815	3
230	Inconel	36NaF-18KF-46ZrF4	500	815	10
348	Inconel	50NaF-50ZrF4	500	815	5.5
	Inconel	FLiNaK	500	815	7
934	Inconel	60NaF-40ZrF4	500	815	5
935	Inconel	60NaF-40ZrF4	500	815	5
	Inconel	NaF-BeF2	500	815	10
	Inconel	LiF-NaF-BeF2	500	815	5
246	Inconel	52NaF-48ZrF4	500	815	8
262	Inconel	57NaF-43BeF2	500	815	9
277	Inconel	50NaF-50ZrF4	500	815	5
276	Inconel	NaF-ZrF4	500	815	8
277	Inconel	NaF-ZrF4	500	815	4
336	Inconel	NaF-ZrF4	500	815	6
341	Inconel	NaF-ZrF4	500	815	5.5
342	Inconel	NaF-ZrF4	500	815	6
516	Inconel	NaF-ZrF4	500	815	6
338	Inconel	NaF-ZrF4	500	815	6
411	Inconel	NaF-ZrF4	250	815	4.5
410	Inconel	NaF-ZrF4	100	815	4
400	Inconel	NaF-ZrF4	50	815	3
1181	Inconel	71LiF-29ThF4	8760	732	6.5
1239	Inconel	71LiF-16BeF2-13ThF4	8760	732	7.5
9377-6	Inconel	71LiF-16BeF2-13ThF4	13155	704	13
1188	Inconel	35LiF-27NaF-38BeF2	8760	677	9
1210	Inconel	71LiF-29ThF4	8760	677	5
1235	Inconel	71LiF-16BeF2-13ThF4	7789	677	4
1214	Inconel	FLiNaK	4673	677	13
1169	Inconel	71LiF-29ThF4	1000	677	1
1177	Inconel	71LiF-29ThF4	1000	677	1.5
1173	Inconel	58NaF-35BeF2-7ThF4	1000	677	4
1176	Inconel	58LiF-35BeF2-7ThF4	1000	677	1
1234	Inconel	71LiF-16BeF2-13ThF4	1000	677	1
9344-2	Inconel	FLiNaK	8760	649	8
9344-2	Inconel	FLiNaK	8735	649	8
1172	Inconel	35LiF-27NaF-38BeF2	1000	607	2
1175	Inconel	FLiNaK	1000	607	1
MSRE	INOR-8	67LiF-33BeF2	26000	649	0
9354-3	INOR-8	35LiF-27NaF-38BeF2	19942	649	0
1194	INOR-8	FLiNaK	1000	607	0
1195	INOR-8	35LiF-27NaF-28BeF2	1000	607	0
LDRD	INOR-8	FLiNaK	3048	815	0.1
1209	INOR-8	71LiF-29ThF4	8760	732	0
1216	INOR-8	58LiF-35BeF2-7ThF4	8760	732	1
1240	INOR-8	71LiF-16BeF2-13ThF4	8760	732	0
MSRP7	INOR-8	71LiF-16BeF2-13ThF4	20000	704	1
MSRP8	INOR-8	58LiF-35BeF2-7ThF4	9633	704	0
15A	INOR-8	73LiF-2BeF2-25ThF4	39476	677	0.05
1208	INOR-8	FLiNaK	8760	677	1
1190	INOR-8	58NaF-35BeF2-7ThF4	8760	677	1
1233	INOR-8	71LiF-16BeF2-13ThF4	8760	677	0
1213	INOR-8	71LiF-29ThF4	3114	677	0
15	INOR-8	73LiF-2BeF2-25ThF4	2003	677	0
1165	INOR-8	FLiNaK	1340	677	0
1164	INOR-8	58NaF-35BeF2-7ThF4	1000	677	0
1221	INOR-8	71LiF-29ThF4	1000	677	0
1228	INOR-8	71LiF-16BeF2-13ThF4	1000	677	0
MSRE	INOR-8	67LiF-33BeF2	26000	649	0
9354-3	INOR-8	35LiF-27NaF-38BeF2	19942	649	0
1194	INOR-8	FLiNaK	1000	607	0
1195	INOR-8	35LiF-27NaF-28BeF2	1000	607	0

However, during MSRE operation, Hastelloy-N appeared to be sensitive to in-service embrittlement due to two processes. On the one hand, the interaction with the fission product tellurium causes an intergranular attack and, on the other hand, irradiation by delayed neutrons produces helium. Additions of small amounts of Nb and Ti were shown to improve the strength of Hastelloy.

Recent Russian studies [Azhazha,2005] have shown further possibilities for compositional modifications of Hastelloy-N for improving its resistance to embrittlement in high-temperature molten fluoride salt environment. About 70 Ni-base different casts were tested in the KI (Russian Federation) with alloying elements such as W, Nb, V, Al and Cu. The chemical composition of tested material samples is in Table 2.3 [Zherebtsov,2008]. Some results of corrosion tests of Ni-base alloys in molten Li,Na,Be/F salts with PuF_3 and Te additions are reported in Table 2.4 [Ignatiev, 2008]. It was concluded that addition of alloying elements can provide resistance against tellurium embrittlement (see last coloumn of Table 2.4) together with keeping the good corrosion properties of the alloy. Reliability and efficiency of diaphragm-free device with dynamic reference electrode was also confirmed in the thermal convection corrosion loop operated more than 1200 hrs with fluoride melts containing beryllium difluoride mixture (mol%) at a maximum temperature of about 700°C [Afonichkin, 2008].

Corrosion proved to be highly sensitive to impurity contents in the salts, to temperature and to the alloy chemical composition. Chemical composition of the salt, temperature gradient, hydrodynamics are also likely to play a role. Corrosion must be mitigated by using the appropriate combination of materials and salt chemistry. This implies to select corrosion-resistant high temperature alloys and to chemically control the redox in salts.

Table 2.3: Chemical composition of material samples tested in KI (Russia) [Zherebtsov,2008]

Element	HN80M-VI	HN80MTY	MONICR**	Hastelloy-N (Cabot-Carpor)*	Alloy No 29	Alloy No 30	Alloy No 31	Alloy No 32
Ni	base	base	base	base	base	base	base	base
Cr	7.61	6.81	6.85	7.52	7.1	7.1	7.15	7.1
Mo	12.2	13.2	15.8	16,28	11.8	12.2	12.0	12.1
Ti	0.001	0.93	0.026	0.26	0.56	0.56	0.6	0.57
Fe	0.28	0.15	2.27	3,97	–	–	–	–
Mn	0.22	0.13	0.037	0,52	–	–	0.25	–
Nb	1.48	0.01	< 0.01	–	1.0	1.0	1.0	1.0
Si	0.040	0.040	0.13	0,5	–	–	–	
Al	0.038	1.12	0.02	0,26	–	–	–	
W	0.21	0.072	0.16	0,06	–	–	–	
Cu	0.12	0.020	0.016	0,02	–	–	–	
Co	0.003	0.003	0.03	0,07	–	–	–	
Re	–	–	–	–	–	1.08	–	
Zr	–	–	0.075	–	–	–	–	
Y	–	–	–	< 0.01	–	–	–	0.001
B	0.008	0.003	<0.003	0,004	–	–	–	
S	0.002	0.001	0.003	0,007	–	–	–	
P	0.002	0.002	0.003	0,05	–	–	–	
C	0.02	0.025	0,014		0.007	0.021	0.016	0.04

* Alloy of American fabrication

– Not analyzed, but no intentional addition made of this element

** Alloy of Czech fabrication

Table 2.4: Corrosion loop results of metallic materials in molten Li,Na,Be/F salts with PuF_3 and Te additions at salt redox potential 1.2-1.3 [V. Ignatiev, 2008]

Specimens	Exposure time [hr]	Temperature [℃]	* m [mg/cm^2]	**V_k [µm/yr]	***K (at 700℃) [pc×µm/cm]
MONICR	200	640 to 655	-(0.81 to 0.82)	-	
	1200	620 to 640	-(1.11 to 2.00)	9 to 17	
	1200	650 to 700	-(2.15 to 2.28)	18 to 19	> 10000
HN80MTY	200	640 to 655	-(0.22 to 0.23)	-	
	1200	615 to 645	-(0.23 to 0.24)	2…3	
	1200	650 to 700	-(0.38 to 0.59)	3 to 5	880
HN80M-VI	200	620 to 655	-(0.17 to 0.21)	-	
	1200	645 to 650	-(0.23 to 0.49)	2 to 4	
	1200	650 to 700	-(0.32 to 0.59)	3 to 5	1760

* m – mass losses of alloy specimens during exposure time

**V_k – calculated corrosion rate per year, related to the exposure time in the melt

***K - parameter “K” which is equal to the product of cracks number on 1 cm length of longitudinal section of specimens subjected to tensile strain, multiplied by an average cracks depth in m

From the material point of view, the need is for further assessment of existing materials and the selection of new materials for which less data exist. Nickel being the most resistant element to dissolution in salts, Ni-based alloys such as Hastelloys are the most promising candidates for application up to 750℃. Selection of appropriate alloying elements should provide for the resistance to embrittlement by Te-attack and He production. These optimized Ni-base alloys shall be resistant to irradiation damages and be licensed for nuclear power plant applications in accordance with international standards and codes (for example ASME code). Candidate materials with ASME code certification are in Table 2.5. From the standpoint of creep strength, there are a number of commercial Ni-based alloys that could be used between 750 and 850℃. However, extensive long-term corrosion evaluation of these alloys in molten fluoride salts is required and the possibility to use coatings may be investigated. Temperature greater than 850℃ would require the use of new solutions s uch as refractory alloys or graphite.

Table 2.5: Candidate materials with ASME code certification for high temperature applications [Ingersoll,2004]

	Candidate materials	Metallurgical stability	Irradiation resistance	Fabricability	Alloy maturity	Codified
Coated	9Cr-1MoV	Fair	Good	Good	High	Sect. III,VIII
	304	Good	Good	Good	High	Sect. III,VIII
	316	Good	Good	Good	High	Sect. III,VIII
	347	Good	Good	Good	High	Sect. III,VIII
	Alloy 800H or HT	Good	Good	Good	High	Sect. I,III, VIII
Monolithic	Hastelloy N	Good	Good	Good	High	Sect. III,VIII
	Haynes 242	Good	Adequate	Good	Low	Sect. VIII
	Alloy 800H or HT	Good	Good	Good	High	Sect. III,VIII

First priority R&D needs in corrosion for metallic materials of primary and secondary circuit are to focus on the pre-selected salts for the different concepts (cf. Table 6). For fuel salts, interest is on ^{7}LiF-(NaF)-ThF_4 and ^{7}LiF-(NaF)-BeF_2-ThF_4. For coolant salts, ^{7}LiF-BeF_2 is the main candidate for in-core use and NaF-$NaBF_4$ as well as ternary LiF-NaF-BeF_2 mixture with melting temperature 315℃ for secondary coolant for systems producing tritium. Finally, $NaNO_3$-KNO_3(-$NaNO_2$) is cited for heat transfer applications. For these systems, redox control must be experimentally demonstrated and the operating temperature range for acceptable resistance to dissolution has to be established.

Table 2.6: Candidate structural materials for high temperature applications [Williams,2006A]

	Candidate materials	Salt corrosion resistance	Air corrosion resistance	Long-term strength at 1000℃	Highest usage temperature (℃)	Potential AHTR (MSR) component usage*
Monolithic	Hastelloy N	Excellent	Good	Very good	730	
	Haynes 242	Very good	Good	Very good	540	
	Alloy 800H or HT	Poor-fair	Good	Very good	980	
Coated	Inconel 617	Needs evaluation	Good	Very good	1000	PM,P,V,HX
	VDM 602CA	Needs evaluation	Good	Good	1000	P,V,HX
	Alloy 800H	Needs evaluation	Poor	Good	1000	P,HX
	Haynes 230	Needs evaluation	Marginal	Good	900	P,HX
	Hastelloy X or XR	Needs evaluation	Poor	Good	900	P,HX
	HP modified	Needs evaluation	Good	Excellent	1100	V
Monolithic	Haynes 214	Very good	Good	Good	1000	V,HX,CHX
	MA 956	Very good	Good	Good	?	HX,CHX
	MA 754	Very good	Good	Good	?	HX,CHX
	Cast Ni superalloys	Very good	Good	Good	?	PM

*PM-pump, P-piping, V-valves, HX-heat exchanger, CHX-compact HX

3.2.2 Graphite

MSRs may use graphite as a moderator and reflector. The MSRE program used graphite in the core as a neutron moderator, with no observable deleterious reactions after long-term direct contact with molten salt.

There are two technical challenges: the need for stability of the material against radiation-induced distortion and low permeability to salt and gas ingress.

Radiation damage that changes the geometry necessitates replacement of the graphite moderator — an expensive maintenance task. For conventional graphite irradiated up to fluences > 2. 10^{22} neutrons/cm^2 (E > 50 keV), volume changes lead to formation of cracks sufficiently large for salt intrusion. To address this, fine grained nuclear grade graphites must be used for in-core applications and cross-cutting can be found with the development of graphites for gas cooled reactors.

In MSR, cracks and crevices in the graphite can allow the xenon gas to remain in the reactor core where it is a strong neutron absorber and where it will significantly reduce the breeding ratio of the reactor. Low porosity levels are thus desirable in order to prevent salt ingress. The approach taken in the MSBR program was to seal the graphite surface with pyrocarbon to exclude xenon. No work has been done in several decades to lower the permeability of graphite for MSR service.

If these technologies do not meet future MSR requirements, new methods for sealing graphite need to be developed. Appropriate tests under irradiation must be conducted to demonstrate the sealing of graphite surfaces.

The R&D needs for graphite as moderator and/or reflector are thus mainly directed toward qualification of radiation-stable grades, sealing technology to reduce gas ingress and fabrication issues.

3.2.3 *Materials for fuel processing units*

Preliminary considerations on problems and required tests for materials of fuel processing components and systems are formulated in brief in Table 2.7.

Table 2.7: Fuel processing materials development

Concept	Process	Material	Problems and required tests
MSRE	U-fluorination (UF6, HF)	1) Ni-base alloys 2) Mo, graphite,Ta, braze alloys	1) Frozen salt layer 2) Chemical compatibility tests, capsule & thermal convection, fabrication joining techniques
MSBR	Reductive extraction:		
TMSR	MS / Bi-Li-Th		
MOSART	MS / Bi-Li		

3.2.4 *Materials for large scale components*

Material-molten salt compatibility and structure integrity depend as a rule on the component scale.

In the framework of the MSRE, primary circuit components (reactor structure, salt pump, pipelines, salt-air heat exchanger etc.) and consequently their material compatibility with the fuel salt were tested in the scale corresponding to the thermal power rate of 8 MW.

No tests were performed on salt-water/steam and salt gas (CO_2, N_2...) heat exchangers neither at small nor at large scale.

3.3 Neutronic aspects

3.3.1 Introduction

This section is focused on important key-points relating to MSR operation (salt composition and temperature distribution) and safety from the point of view of neutronics (especially the concern on temperature feedback coefficients). Since the termination of the 5th FWP MOST project, more concern has been given to fast spectrum concepts, therefore new tools and data (neutronics, thermalhydraulics, nuclear data) are needed together with analysis and optimization of cores for the new concepts.

This section gives the status of reactor physics for the different concepts. For each reactor (thermal thorium breeder, fast thorium breeder, fast uranium breeder, fast TRU burner, Liquid Salt cooled Fast Reactor – LSFR –, Liquid Salt Cooled HTR – AHTR –), it is shown what has been demonstrated, what is still to be addressed.

The feasibility studies of the different reactors aim at assessing the two following objectives:

- Safety,
- Fuel cycle efficiency (breeding for the breeder concepts and burning for the burners…).

This evaluation can be made in two steps for each of these criteria:

1. The first step is the preliminary calculation of the kinetic coefficients (feedback coefficients, delayed neutron fraction…) for safety, and the calculation of fuel isotopic evolution (coupled with the simplified reprocessing if needed) for fuel cycle efficiency. A first optimisation of the concepts can be done at this level to determine a preliminary design.

2. The second step consists in the evaluation with more precise (and complex) tools of the preliminary design: 2D-3D computer codes, coupled neutronics/thermal-hydraulics tools for static and transients conditions. At this stage, experiments can also be needed for the reduction of uncertainties: differential of integral nuclear data measurements, thermal-hydraulics experiments…

This section begins with general physics grounds and the main conclusions are given for each concept. All these conclusions are summed up in a general Table (Table 3.3).

3.3.2 Preliminary physics considerations

The different kinds of reactors using molten salt as a fuel or as a simple coolant use a very wide range of neutron spectra, from very moderated to fast spectrum.

3.3.2.1 Breeding in thermal spectrum

Breeding in thermal spectrum: MSBR / epithermal TMSR / low power epithermal TMSR.

- Why a thermal breeder? Low fissile inventory compared to fast spectrum (good for safety and deployment speed)
- How? Necessity of thorium and associated fissile isotope ^{233}U to reach this objective (see Table 3.1 with the values of η, the number of neutrons produced by each neutron absorbed by the fissile isotope). To allow breeding, the η value has to be enough higher than 2 (which is the case for ^{239}Pu and ^{241}Pu for fast neutrons but not for thermal neutrons). Concerning ^{233}U, breeding is possible in both thermal and fast spectrum (it allows lower breeding gain than Pu in fast spectrum).

Table 3.1: η values of the main fissile isotopes for fast/thermal neutrons

	^{233}U	^{235}U	^{239}Pu	^{241}Pu
Fast	**2.31**	1.93	**2.49**	**2.72**
Thermal	**2.28**	2.07	2.11	2.15

- Necessity of graphite to moderate neutrons (very low capture, good slowing down cross section). Other moderating materials exist (BeO, B_4C…) but the best known is carbon C which has a good compatibility with molten salts. The associated problem (see section 3.2) is its weak resistance under irradiation (especially under fast neutron flux) requiring to change graphite every 4 years in the MSBR or 2 years in the epithermal TMSR. This motivates the study of very low power reactors with the objective of 40 years graphite life with the concept called very low power epithermal TMSR.

- Why on-line reprocessing? Like in other reactors, the fission products (FP) capture a lot of neutrons, especially in thermal spectrum. They have to be discarded. Furthermore, when breeding is looked for, the speed of FP elimination has to be increased. The Molten Salt Reactor allows the on-line reprocessing of the fuel and is particularly well fitted to thorium breeding which has a tight neutron economy.

In Figure 3.1 (left part), one can notice the predominance of ^{149}Sm over all other fission products, followed by ^{147}Pm, ^{147}Nd, ^{151}Sm, ^{145}Nd and ^{152}Sm. By considering these fission products by element (Figure 3.1, right part), Samarium is the most disturbing poison. The following ones (like Neodymium or Promethium) belong to the same chemical family, the lanthanides (red part of the Figures). Among other contributing fission products, Zirconium represents more than 50% of the captures produced by elements other than lanthanides.

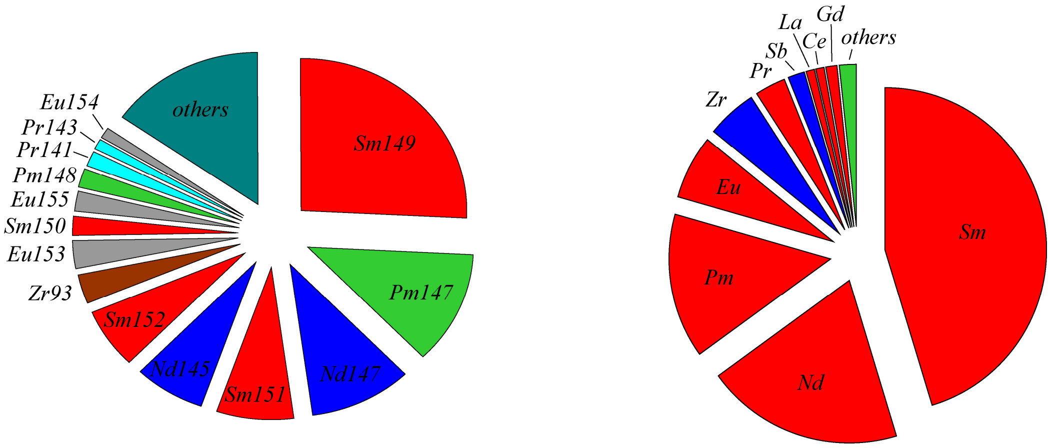


Figure 3.1: Distribution of the capture rate in the fission products by isotope (left) and by chemical element (right) in the core after helium bubbling only for a thermal breeder

On the other side, FPs have very low capture in fast spectrum. Therefore, a lower reprocessing rate is needed for fast neutron concepts (see Table 3.2).

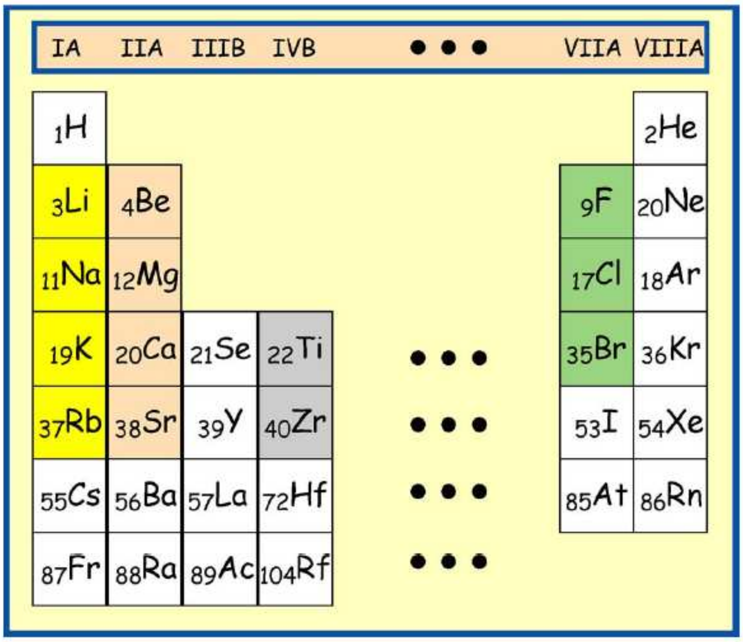


Figure 3.2: Choice of the salt constituent (solvent)

The following elements have been considered for the constitution of the salt: F, Cl and Br as the primary salt component, and Li, Na, K, Rb, Be, Mg, Ca, Sr, Ti, Zr as secondary components (Figure 3.2).

The choice between the different carriers is very quickly made because the need for breeding implies low capture cross section in thermal spectrum, which is the case just only for fluorine (see the fluorine, chlorine and bromine capture cross-sections, Figure 3.3). That is why **only fluorides are considered when breeding is required in thermal spectrum.**

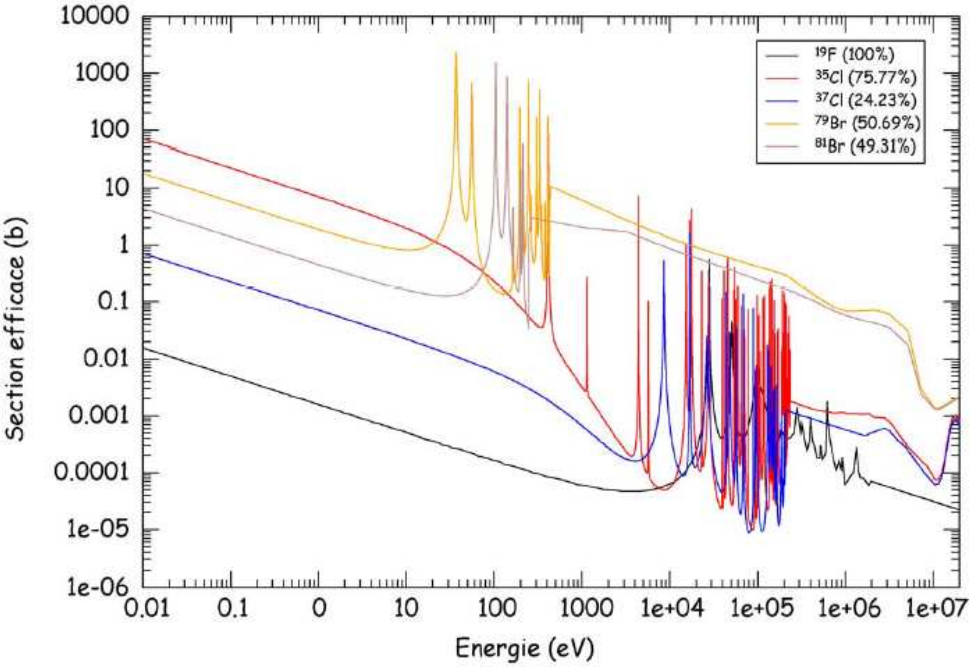


Figure 3.3: Comparative capture cross-sections for F, Cl and Br

Chlorine can be considered for fast spectrum because capture cross sections are small.

For the other constituents of the salt, the capture cross-section is given in Table 3.2 for typical thermal spectrum, fast (/intermediate) spectrum with fluoride salt, and fast spectrum with chloride salt.

Table 3.2: Comparative capture cross-sections for fluoride and chloride salts in thermal and fast spectrum

(n,γ)	Thermal - Fluoride	Fast - Fluoride	Fast - Chloride
$_{3}$Li	.00073	.000087	
$_{4}$Be (n,α) (n,2n)	.00038 (.0046) (.0121)	.0001 (.0044) (.0116)	
$_{9}$F	.00072	.00076	
$_{11}$Na		.00386	.0011
$_{12}$Mg		.00108	.00155
$_{17}$Cl	.0081	.003	.0036
$_{19}$K	.098	.094	.0295
$_{20}$Ca	.0168	.0055	.0037
$_{22}$Ti	.0042	.0013	.00126
$_{35}$Br	2.35	.92	.337
$_{37}$Rb	.17	.084	.0215
$_{38}$Sr	.0248	.018	.0129
$_{40}$Zr	.39	.17	.0464

3.3.2.2 Breeding in fast spectrum

Two main options are considered:

1. Breeding in ^{238}U-Pu cycle (see values of η, Table 3.1): REBUS, LSFR
2. Breeding in Th-^{233}U cycle: non moderated TMSR

1. How fast is fast enough for breeding in ^{238}U-Pu cycle?

For ^{238}U-Pu breeding, a fast spectrum is necessary because the neutron excess value per Pu fission is rapidly increasing with the neutron energy (Figure 3.4). If the spectrum is not hard enough, breeding is no more possible.

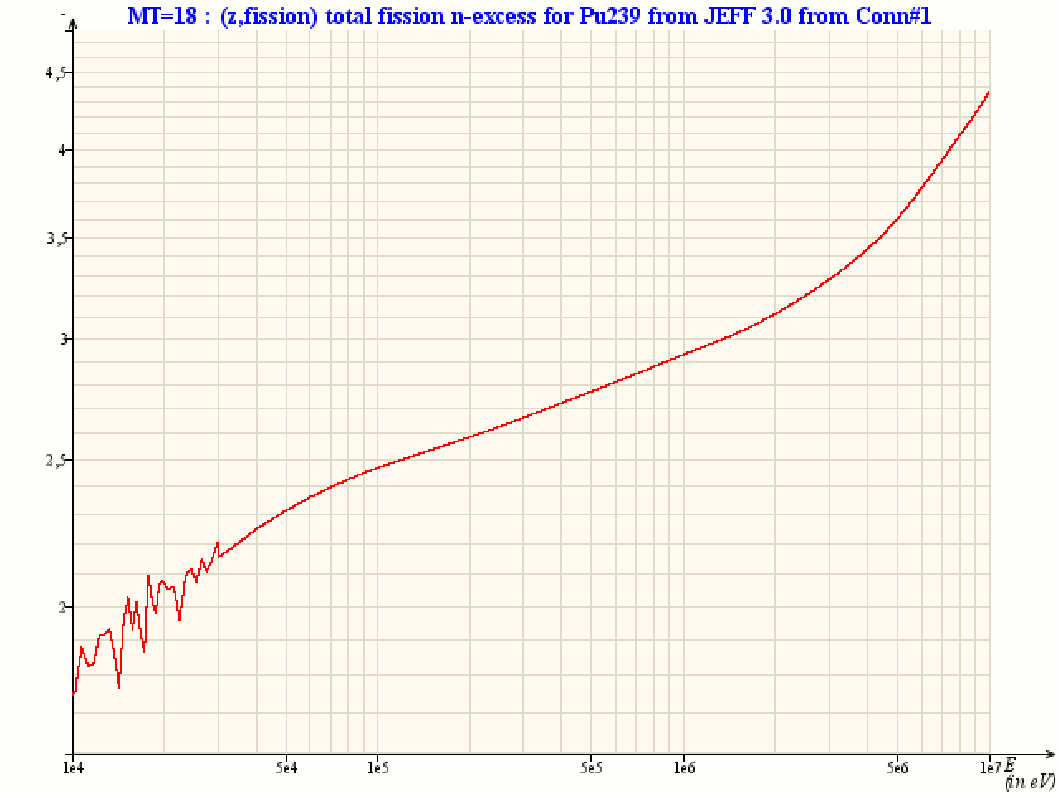


Figure 3.4: Neutron excess per fission for Pu (fast neutron range)

Choice of the primary salt constituent (solvent)

Figure 3.5 shows that fluorine (F) has a higher scattering cross-section than chlorine (Cl) in the fast range (10^4 to 10^6 eV) with high scattering resonance. Furthermore, F (A=19) is twice lighter than Cl (A=35 to 37), so that its slowing down power per collision is higher. That is why chlorine (Cl) is better than fluorine (F) as far as breeding in ^{238}U-Pu cycle is concerned.

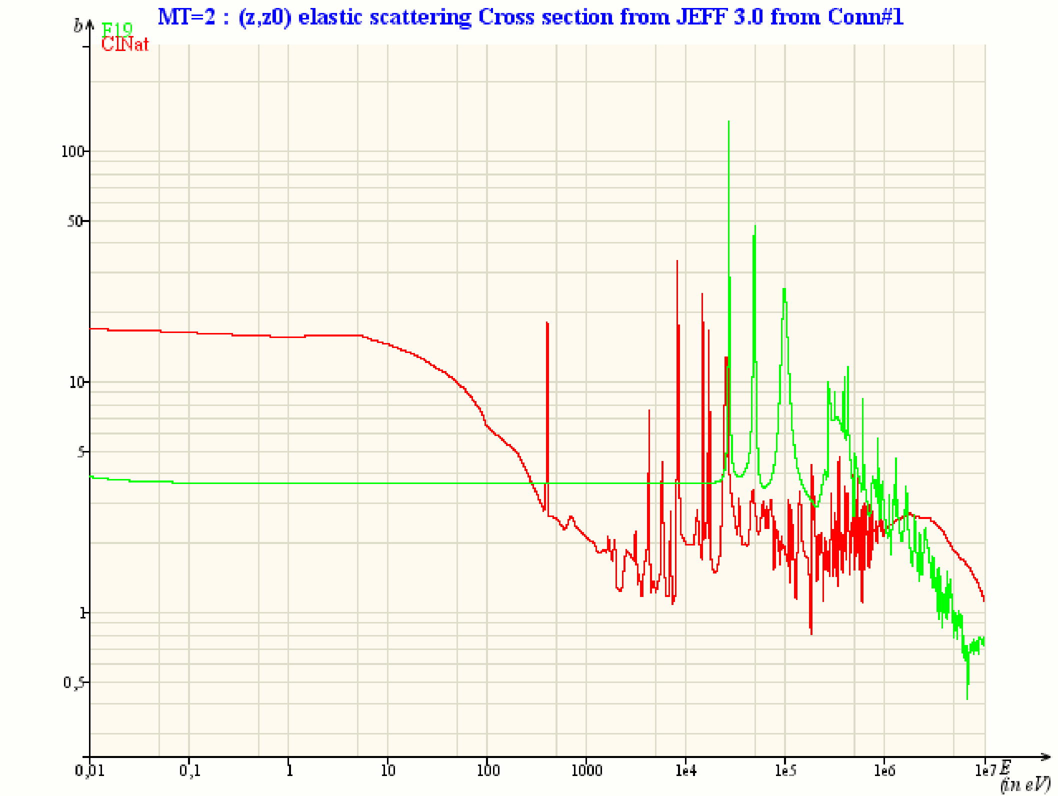


Figure 3.5: Comparative F and Cl scattering cross-sections (fast neutron range)

Figure 3.6 shows the spectra for non-moderated fluoride and chloride salts The spectrum of non moderated fluoride salt is rather fast, but less than for chloride salts which is thus better for breeding with ^{238}U-Pu fuel.

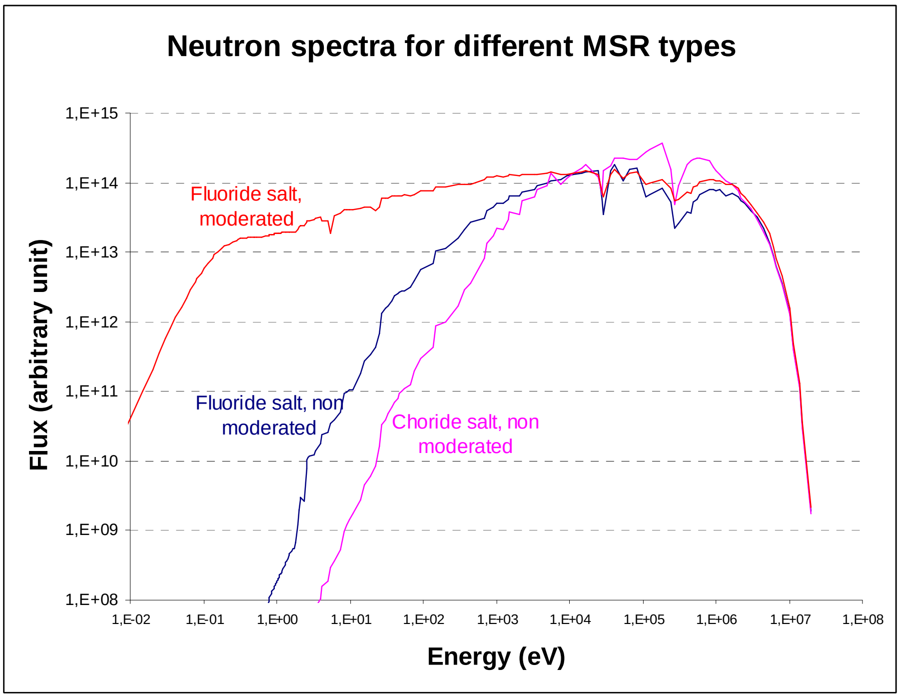


Figure 3.6: MSR neutron spectrum with chloride salt (non moderated) and fluoride salt (moderated or not)

2. Th-^{233}U breeding in non moderated spectrum

An intermediate/fast spectrum is enough for breeding in Th/U cycle because ^{233}U neutron excess per fission is rather independent from the spectrum (Figure 3.7) compared to Pu.

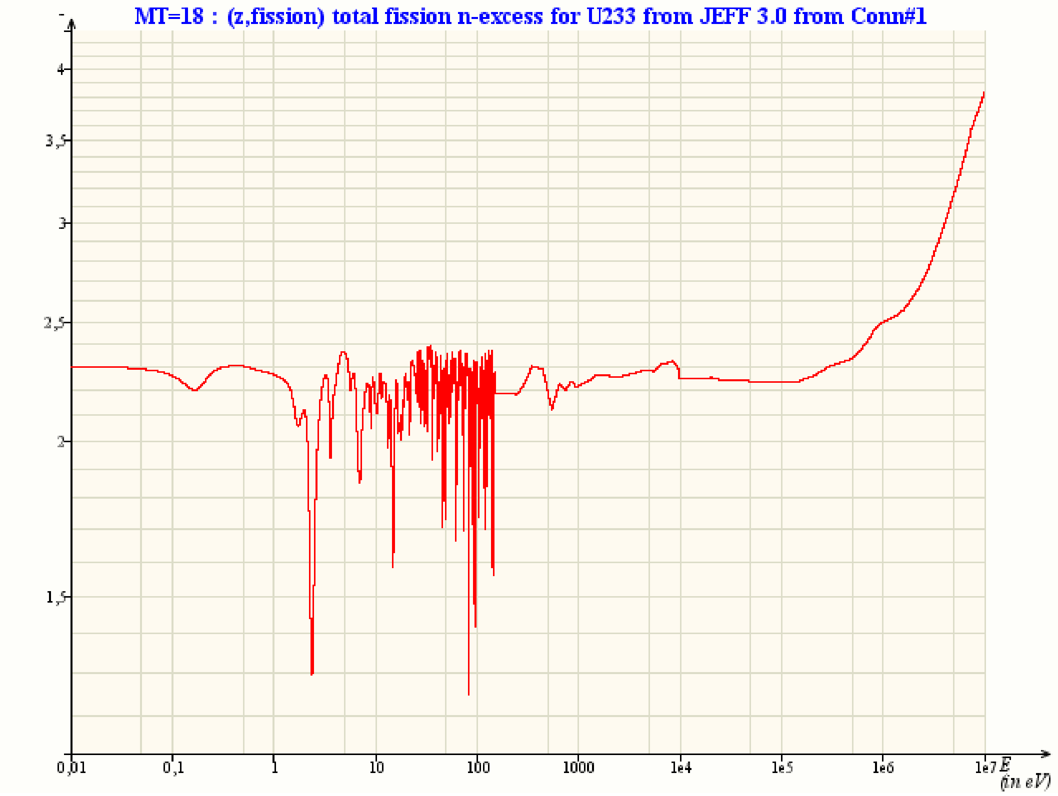


Figure 3.7: Neutron excess per fission for ^{233}U

Thermalisation by fluorine (F) does not impair the breeding of ^{233}U, therefore a fluoride salt can be used for this application.

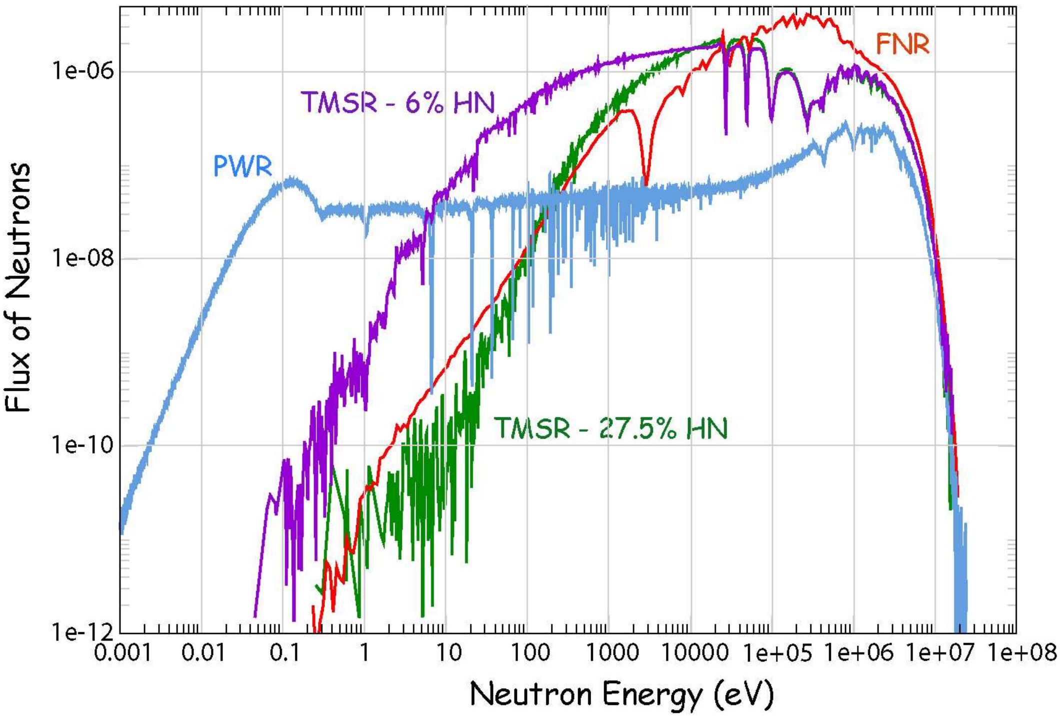


Figure 3.8: MSR neutron spectrum with fluoride salt (effect of HN fraction in the salt)

Choice of secondary salt constituents: for Th-^{233}U breeding, where spectrum hardness is not required, any addition of Li, Be, Na, Mg, K, Ca, Ti, Rb, Sr, Zr can be considered.

3.3.2.3 Non moderated burner

Non moderated MSR is efficient for actinide burning because fast spectrum is favourable for TRU burning in general. This is due to the probability of fission per neutron absorbed which is much higher in fast spectrum than in thermal spectrum, especially for isotopes non fissionable by thermal neutrons (^{244}Cm, ^{242}Pu, ^{240}Pu, ^{241}Am…) (Figure 3.9).

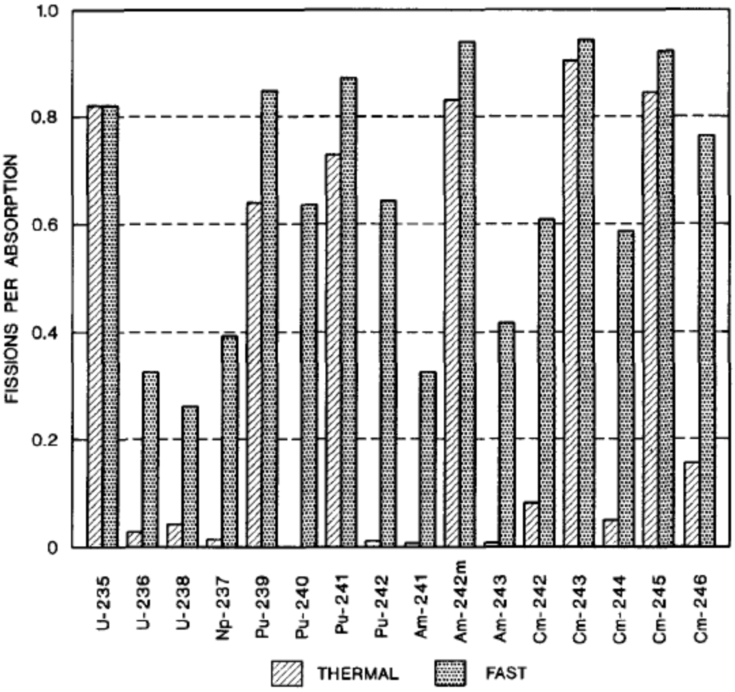


Figure 3.9: Probability of fission per neutron absorbed of some heavy nuclei (Thermal/Fast)

The burner MSR has no fertile elements (Th or ^{238}U). The main constraint for this type of reactor is to remain below the solubility limit of TRU in the salt.

3.3.2.4 Negative temperature coefficients for non moderated MSR

One specific safety feature of non moderated MSR, as compared to standard fast spectrum reactors, is the very negative salt dilatation coefficient (~ - 5 pcm/℃).

This is why:

1. Non-moderated MSR breeders are the only breeder with a negative coolant dilatation (or void) effect (unlike solid-fuelled Fast Breeder Reactors).

2. Non-moderated MSR burners allow fuel without fertile isotope (with a very bad Doppler effect) thanks to the highly negative salt dilatation coefficient.

3.3.3 Main conclusions on the different concepts

The main neutronic characteristics for the different concepts are listed in Table 3.3. One can see that the different goals pursued by the different types of reactors (burning, breeding) and different choices (liquid/solid fuel) lead to very distinctive choices for salt composition.

Thermal Breeders (MSBR, moderated TMSR, low power moderated TMSR)

The weak point of graphite-moderated TMSR (like MSBR) is the graphite lifetime (less than two years for TMSR, 4 years for MSBR). The safety parameters are good, the fissile inventory is low (3 t ^{233}U/GWe)., but an alternative to graphite has to be found ($^{11}B_4C$, BeO…). If graphite is recycled, 49 kg (per GWe) has to be reprocessed each day.

A strong reduction of the flux has been considered to increase the graphite lifetime (up to 40 years, which is approximately the reactor lifetime). This variant is called *TMSR epithermal with low power*. To reach this objective, a really low reactor power has to be chosen, 150 MWe. This leads to a reduction of graphite mass to be recycled (7 kg/day/GWe). The very low unit power leads to very high fissile inventory (15 t ^{233}U/GWe) and certainly to poor economical performances.

Non-moderated Thorium breeder MSR (non moderated TMSR)

The reference salt is 82.5%LiF-17.5%HNF$_4$ in molar proportion. There is no neutronic penalty to add a third component to the salt e.g. NaF, BeF$_2$ or CaF$_2$ (or even small quantities of Mg, K, Ti, Rb, Sr, Zr) to improve the chemistry (for reprocessing and compatibility with structural materials). The safety coefficients are excellent (salt temperature coefficient -7 pcm/℃). The initial fissile inventory is higher than for thermal breeder (4.7 t ^{233}U/GWe). The possibility to start these reactors directly with Pu has to be analysed from the chemistry point of view because it has been shown possible with respect to neutronics. The very good potential of this option makes it the reference breeder solution to investigate in future projects.

Non moderated Uranium breeder MSR (REBUS)

A preliminary evaluation of a non-moderated MSR, with a classical U$_{depleted}$/Pu cycle has been done. This concept, called REBUS-3700, uses a chloride salt (38UCl$_3$-7TRUCl$_3$-55NaCl) because a preliminary study showed that breeding is hard to reach with a fluoride salt (because of the too high neutron moderation by fluorine). This preliminary design has very good safety coefficients (-6 pcm/℃) and an initial fissile (Pu) mass comparable to other Fast Breeder Reactors (11.7 t Pu/GWe). The fuel reprocessing is adjusted to be as slow as possible while keeping the breeder capability (47 kg HN/day/GWe).

The following step of evaluation for the fast uranium breeder would be to check again if breeding is really impossible with a fluoride salt, because chloride salts have been less investigated than fluoride salts for use as reactor fuels.

Non moderated TRU burner (MOSART)

For MOSART, the analysis highlighted fuel salt mixtures based on ternary Li,Na,Be/F and binary Li,Be/F solvent systems with decreased content of beryllium difluoride (25-27 mol%), having satisfactory melting temperatures (T_{melt} (Li,Na,Be/F) ≈ 480°C and T_{melt} (Li,Be/F) ≈ 530°C), required solubility of actinide trifluorides (> 2 mol%), adequate thermo-physical properties, as well as suitable costs. Considered compositions have very high radiation resistance and relatively low corrosivity to graphite and Ni-Mo alloys. Actinides and soluble fission products can be easily removed from molten LiF-BeF$_2$–based mixtures. Optimum spectrum for MOSART is intermediate spectrum of homogeneous MSR without graphite moderator. Due to intensive production of ^{245}Cm in spectrum typical of such a core, it can operate without additional neutron sources. The equilibrium inventory of TRU is 6.3 t/GWe, which remains under the solubility limit. The safety is excellent, with a very negative salt temperature coefficient (-4 pcm/℃). The reactor is fed with TRU coming from PWR spent fuel.

The very good potential of this option makes it the reference burner solution to investigate in the future. Particularly, an interesting point would be to study its ability to burn TRU (MA and excess Pu generated by breeding) coming from solid fuel Fast Breeder Reactors or even only minor actinides from solid fuel reactors. Obviously, the latest scenario will require new fuel solvent systems with higher solubility for MA (e.g. LiF-NaF-KF) compared to Li,Na,Be/F or Li,Be/F MOSART fuel salt matrix.

Liquid salt cooled fast reactor (solid fuel LSFR)

Only fluoride salts have been studied as the primary coolant for a solid fuel FBR. Among them, NaF-KF-ZrF_4 remains the least unfavorable (with respect to capture and neutron moderation). The Pu enrichment is approximately 17% and internal breeding gain –5%. The weakest point of these concepts is the high positive value of the coolant void coefficient (+ 8500 pcm, at least 4 times the typical SFR value). The reason for that is the high moderation caused by fluoride salts.

The only way to avoid this unacceptable void effect would be to use chloride salt as coolant because of chlorine (Cl) lower neutron moderation compared to fluorine (F). But the study has not been done yet.

Liquid Salt cooled Pebble Bed reactor (LSPBR)

A preliminary choice has been made among the different salts: $^7LiF-BeF_2$ (66-34), $NaF-BeF_2$ (57-43), ^7LiF-NaF-KF (46.5-11.5-42), $NaF-ZrF_4$ (50-50), $NaF-ZrF_4$-KF (10-48-42), $^7LiF-NaF-ZrF_4$ (42-29-29), NaF-$Na^{11}BF_4$ (8-92).

The only one to give satisfying temperature effects is $^7LiF-BeF_2$ (66-34). The reason is the negative coolant density effect: -2 pcm/℃ (while all other coolants present a high positive coolant temperature effect ~ +30 pcm/℃).

3.3.4 Preliminary conclusions

Different options have been investigated. The most attractive concepts are two non-moderated concepts, one breeder (non moderated TMSR) and one burner (MOSART).

These two concepts will be further investigated in the future. They have a number of common properties:

- Very similar thermal-hydraulics;
- Similar questions on criticality issues because of the high fissile inventory (like in other fast spectrum reactors) in liquid form;
- Similar behaviour in accidental transients (both have a –5 pcm/℃ salt coefficient and the same recirculation of delayed neutron precursors);
- Similar coupling with the reprocessing unit.

The safety issues are similar for both concepts. But fuel cycle questions are specific to each concept (breeding/burning).

Table 3.3: Neutronic characteristics of the reactor concepts considered in the ALISIA project

Reactor type		**MSR**						**Solid fuel, liquid salt cooled**	
Main function		**Breeder**				**Pu+MA Burner**		**Breeder**	**High t°**
Fuel cycle		**Thorium**			**Uranium**	**Inert support**	**Thorium support**	**Uranium**	**Uranium**
Spectrum		**(epi)thermal**		**fast**	**fast**	**fast**	**fast**	**fast**	**thermal**
Name		**TMSR epithermal & low power**	**TMSR epitherma (moderated)**	**TMSR non moderated**	**REBUS – 3700 (non moderated)**	**MOSART (non moderated)**	**TMSR (Pu+MA started)**	**LSFR**	**LSPBR**
Unit power (MWe)		**150**	**1000**	**1000**	**1540**	**1000**	**1000**	**1000**	**1000**
Salt (reference)		78LiF-22HNF$_4$	78LiF-22HNF$_4$	82,5LiF-17,5HNF$_4$	38UCl$_3$-7TRUCl$_3$-55NaCl	58NaF-15LiF-27BeF$_2$	82,5LiF-17,5HNF$_4$	NaF-KF-ZrF	66^{7}LiF-34BeF$_2$
Fuel cycle	Burnup (at eq)		0.7 at%	2.4 at%	4.8 at%	11.6 at%	2.4 at%	10 at%	10 at% ?
	Reprocessing time(efpd)	500 efpd	150 efpd	418 efpd	1500 efpd	300 efpd	418 efpd	~1500 efpd	no reproc.
	Heavy nuclei reprocessed kg/day (at eq.)	194	334	100	47	21	100		X
	Fertile feed (kg/TWhe)	100 kg Th	100 kg Th	100 kg Th	100 kg U_{dep}	0	100 kg Th	100 kg U_{dep}	
	Fissile feed (kg/TWhe)	0	0	0	0	100 kg Pu+MA	0	0	
	Initial HN mass (kg/GWe)	625 000	50 160	41 800	74 600	2 746	41 800		
	Initial TRU mass (kg/GWe)	0	0	0	11 700	2 746	11 000		
	Initial U233 mass(kg/GWe)	14 525	1 920	4 650	0	0	0		
	Equilibrium HN mass (kg/GWe)	625 000	50 160	41 800	74 600	6 280	41 800		
	Equilibrium TRU mass (kg/GWe)	low	18.5	650	11 700	6 280	650		
	Equilibrium U233 mass (kg/Gwe)	9 960	1 920	7 500	0	0	7 500		
Graphite	Lifetime (years)	40	1.75	ZrC reflector	Metal reflector	4	ZrC reflector		
	wastes (kg/day)	7	49.3	low	X	13.7	X		NC
Safety parameters (at eq.)	≅-total, pcm/K	-0.5	-2.37	-7	-6	-3.7	-5		-8.5
	≅-coolant, pcm/K	-2.0	-2.89	-7	-6	-3.7	-5		-1.
	≅-fuel, pcm/K								-7.5
	≅-moderator, pcm/K	1.4	+0.52	X	X	X	X		
	≅-reflector, pcm/K	NC	NC	NC	NC	-0,05	NC		
	≅-eff, pcm (with moving fuel correction)	190	190	190	250	200	190		
Comments								Coolant void effect: + 8500 pcm	12 gU/pebble, 10% enr

NC = Not Computed

3.4 *Processing, reprocessing*

3.4.1 *Introduction*

The development of fuel salt clean-up technology (MSR fuel reprocessing) represents a very specific area of pyrochemical separation methods in radiochemical technology. The problem is determined by the direct connection of the reprocessing technology to the primary fuel circuit of the MSR. The main reason for the fuel salt clean-up is to provide a composition of the fuel salt in primary circuit within the required limits, which enables to keep the reactor in operation for a long run. The task of the fuel reprocessing is then removal of fission products, which are appreciable neutron poisons, extraction of newly constituted fissile material or its precursor and finally refueling of the reactor by some fresh fissile and/or fertile material.

Fuel salt clean-up is a part of MSR fuel cycle technologies. The technological processes used for fuel salt clean-up are generally based on the pyrochemical separation methods and techniques using molten salts. The use of individual separation processes could be dependent on the type of fuel composition in MSRs, which could consist of uranium and thorium fluorides, fluorides of transuranium elements or their mixtures. As MSRs can be used as actinide burners or thorium breeders, each of this type has some individual requirements for its spent fuel reprocessing.

The processing of fresh transuranium fuel for MSR working as actinide burner covers the “classical” reprocessing technologies either based on hydrometallurgical PUREX process and subsequent advanced hydrometallurgical separation methods with final conversion into fluorides, or some advanced pyrochemical technologies like fluoride volatility process [Uhlir, 2003]. These technologies are not based on the use of molten salts and therefore they are not in the scope of the ALISIA project. However some advanced pyrochemical separation methods devoted to the reprocessing of future solid fuel types of current LWRs or future fast reactors or ADS are also based on electrochemical or liquid metal extraction processes from molten salts – chloride or fluoride systems. Therefore, some partial link between these processes and the technology of MSR fuel salt clean-up evidently exists. For all that, two main differences here exist:

- Whereas the reprocessing in the frame of solid fuel technology is focused to the separation of individual actinides with a maximum purity, the MSR fuel salt clean-up is focused to the removal of fission products (with exception of U-233) and the individual element separation is not necessary.
- Whereas the choice of carrier molten salt in the frame of solid fuel technology is generally free, the choice of carrier salt in MSR technology is significantly determined by the connection to the MSR physics.

3.4.2 *Main results in the area of fuel salt clean-up achieved during the MSRE and MSBR programs in ORNL*

The MSR fuel cycle chemistry was studied intensively during MSRE operation and MSBR design development. The MSRE liquid fuels were processed. However, the MSR spent fuel reprocessing was never fully realized either in a pilot scale. For all that, considerable effort was carried out in radiochemical laboratory research to develop separation processes for uranium, protactinium, plutonium, minor actinides and rare earth elements from the carrier molten salt. Also the basic flow-sheeting work was done during the MSBR program to design the main principles of MSBR spent fuel on-line reprocessing [Rosenthal,1971].

The MSRE project was focused predominantly to verify the MSR system itself and the area of MSR fuel cycle represented only a secondary role. In spite of this, the fuel processing technology was coming up in the focus of interest of the researchers, who were more and more interested in the preparation of the following MSBR project.

There were at minimum two important problems from the fuel cycle area which were solved during the MSRE program. The first was the cleaning of xenon, krypton and noble metals from the circulating fuel, the other was the substitution of uranium-235 by uranium-233 in the fuel (primary) circuit.

Separation of xenon and krypton from the fuel salt of MSRE – A gas extraction technology
Among the fission products, noble gases (mainly xenon-135) were some of the most neutron poisoning elements in the circulating fuel salt. Therefore the removal of noble gases from the circulating fuel had to be provided when the reactor was in operation. Noble gases have very low solubility in the fuel salt (LiF–BeF_2–UF_4), which makes possible to strip them from the salt and reduce the poisoning effect of Xe-135.

The removal was provided by sparging the salt with helium, which was then passed through charcoal traps in an off-gas clean-up system [Rosenthal,1971]. The contact for noble gases (xenon and krypton) removal was produced by spraying of salt through the cover gas (helium) and into the pool of salt in the fuel pump bowl. At the end of the MSRE program, helium was temporarily replaced by argon, which has a very much lower solubility in the fuel salt. Experiments at lower power showed substantial differences in the amounts of gas in the core with argon and with helium. When the reactor was operated at the power with argon cover gas, the xenon poisoning at high void fractions was about the same as it was with helium, but the xenon poisoning was higher with argon when only small amounts of gas circulated with the salt.

Separation of noble metals from the fuel salt of MSRE

In addition to noble gases, some other fission product elements tended to leave the MSRE fuel salt. It referred to the group of noble metals like niobium, molybdenum, ruthenium, antimony and tellurium, which did not form stable fluorides in normal environment in the MSRE. The bulk of the fission product elements (lanthanides) form stable and soluble fluorides and remained with the fuel salt. Noble metals were partially fallen in the noble gases striping system and they accompanied then xenon and krypton in the purge stream.

Extraction of uranium from the fuel salt of MSRE – Fused salt volatilization

The volatilization technique based on bubbling of fluorine gas into fused fluoride salt containing elements forming volatile fluorides was studied in ORNL mainly during the MSRE program in 1960s and 1970s. The main objective of the program was the development and verification of a possibility to remove uranium (in the form of volatile UF_6) from the molten fluoride salt carrier (based on LiF-BeF_2 or LiF-BeF_2-ZrF_4 mixtures). The processes were quite successfully verified with complete separation of uranium from the salt in 1968. The carrier molten fluoride salt, in which uranium was dissolved, was LiF–BeF_2 eutectics. Uranium was recovered from the carrier salt as uranium hexafluoride by sparging the salt with fluorine gas [ORNL,1966]. Special equipment for continual fluorination of the salt was designed and realized. The crucial part of the equipment was the continuous fluorination reactor with frozen wall for corrosion protection. The carrier molten salt containing dissolved UF_4 flowed into the top of the fluorination reactor and was contacted by a counter current stream of fluorine gas, which stripped out the uranium in the form of volatile UF_6. Similar technology was under development in ORNL during ensuing MSBR program in the beginning of 1970s aimed mainly to design an on-line reprocessing scheme for MSRs working under ^{232}Th–^{233}U fuel cycle.

Extraction of protactinium and rare earth elements (lanthanides)

The MSBR Program, which was formally underway in 1970–1976, was *de facto* opened during the MSRE period. Some experimental R&D work, concerning the MSBR fuel processing, was under development in Chemical Division of ORNL. The main result of the work was a preliminary design of MSBR fuel cycle based on continuous (on-line) MSBR fuel processing, which crucial purposes were the separation of protactinium (for subsequent ^{233}U retrieval) and removal of fission products represented by rare earth elements (lanthanides) from the circulating fuel [ORNL,1974].

The main principles of the radiochemical technology were based on selective molten salt/liquid metal reductive extraction into liquid bismuth in multi-stage counter-current extraction system.

Extraction to the liquid bismuth was proposed due to its suitable properties. Bismuth has a low melting point (271°C), negligible vapour pressure in the temperature of interest (500–700°C) and good solubility of lithium, thorium, protactinium, uranium and lanthanides. Bismuth is also essentially immiscible with molten halides. Reductive extraction between metal in molten salt and liquid metal phases can be expressed by following general reaction:

$$MX_n + nLi\,(Bi) \leftrightarrow M\,(Bi) + nLiX$$

in which a metal halide MX_n in the salt reacts with lithium from the bismuth phase to produce M in the bismuth phase and the respective lithium halide in the salt phase. There are three possible ways, how to influence selectivity of the method:

- Technique utilizing dependency of distribution coefficients on used carrier molten salt and on concentration of reducing agent added in the form of alloy with molten metal (Bi),
- Technique utilizing selective reducing agents (this technique can be hardly used in MSR fuel reprocessing due to strict requirement on the chemical composition of carrier molten salt.),
- Non-selective technique using direct addition of high concentration of reducing agent into the liquid metal.

Protactinium removal from the MSR salt was intensively studied in the frame of MSBR project. Protactinium ^{233}Pa results in the reactor core from ^{232}Th by nuclear reactions. The half-live of radioactive decay of ^{233}Pa is about 27 days and its only daughter is ^{233}U. However, the arising protactinium, which is also a mighty neutron poison, has to be immediately removed from the fuel salt circulating in the reactor to preempt undesirable nuclear reaction. Suitable technology for protactinium removal from the fluoride molten salt carrier was selective fluoride molten-salt/liquid metal reductive extraction. The simplified scheme of protactinium isolation process according to the ORNL proposal [Rosenthal,1971] is shown in Figure 4.1. A similar technology was proposed for the rare earth elements removal. A great number of experiments were done at ORNL and a number of distribution data for individual elements was obtained as for fluoride as for chloride molten salt systems.

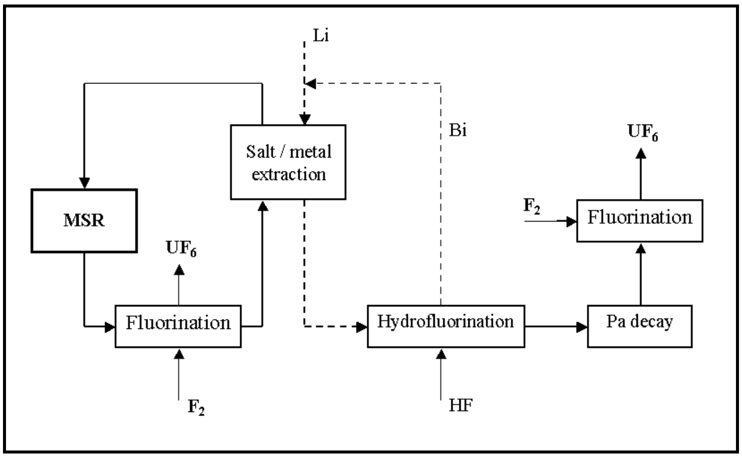


Figure 4.1: Simplified scheme of protactinium isolation from MSR fuel

The distribution data obtained for rare earth elements included in MSR spent fuel between bismuth and carrier fuel salt (LiF–BeF_2) showed that a multistage extraction process for step by step separation of lanthanides from thorium is impossible in fluoride system, because the separation factors are close to unity. Therefore, another separation system, between molten LiCl and liquid bismuth was chosen for separation of individual elements, but the common non-selective extraction of all metals dissolved in carrier fluoride salt remained to be as the first stage.

Based on this intensive chemical technological research program, the basic conceptual flow-sheet of MSBR fuel processing technology was proposed and designed (Figure 4.2).

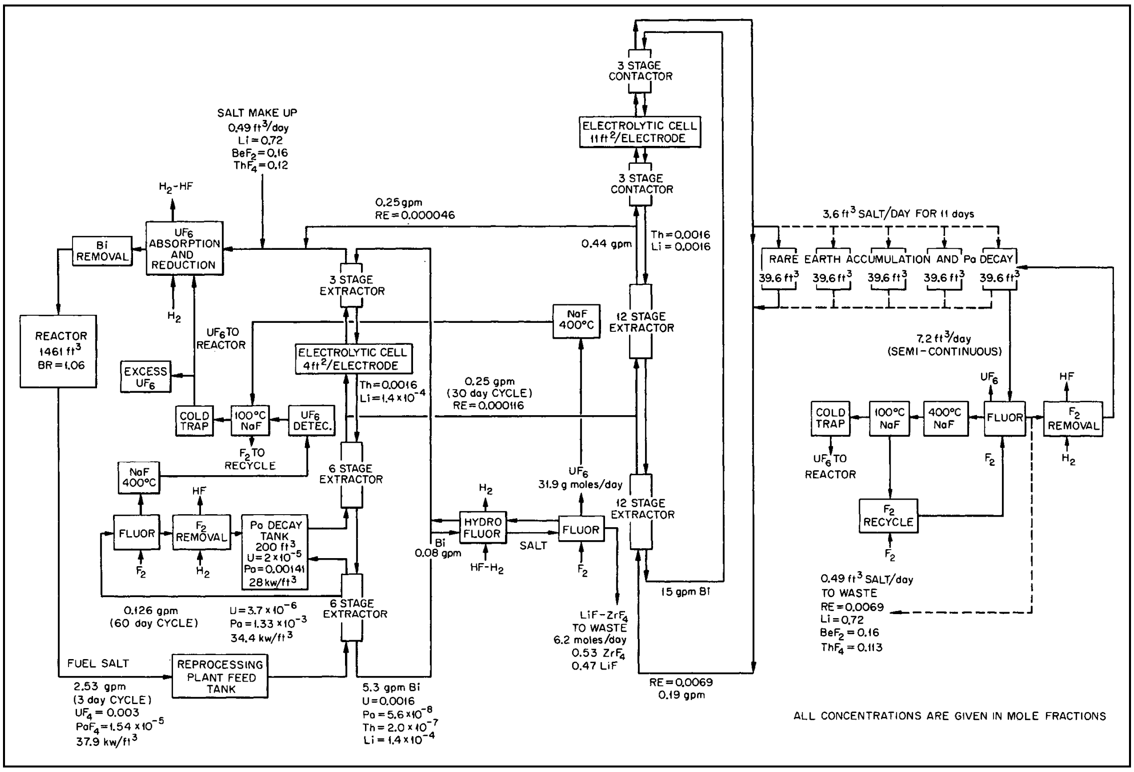


Figure 4.2: Conceptual flow-sheet for MSBR on-line fuel processing [Rosenthal,1971]

The proposal is still a respected reference flow-sheet for current research and development in the area of MSR including the MSR Gen IV systems [GIF,2002]. Alternative MSBR conceptual arrangements with non-diversion features were also proposed at ORNL. They include, in particular, MSBR with rare earth fission product removal by (1) exchange with CeF_3 and (2) by vacuum distillation.

3.4.3 Current designs of MSR reprocessing technologies (Euratom FWP projects)

There were three European projects during the FWP5 and FWP6, which interfered the nuclear chemical technology of molten salts. The **FWP5 project PYROREP** was devoted to the basic development of pyrochemical partitioning techniques using molten chlorides and fluorides. Even though the project was not primarily focused to the MSR technology, the utilizability of molten salt separation techniques for MSR fuel cycle was discussed here and in addition the project also covered the MSR fuel cycle flow-sheeting area [Boussier,2003]. The **FWP5 project MOST** [Renault,2005] which was directly focused to the reevaluation of MSR reactor technology had a special work-package addressing the MSR fuel cycle technology [Uhlir,2003]. The main aim of the work-package was directed to the description of original ORNL technology and to the subsequent analysis of original and newly proposed fuel cycle flow-sheets as for MSR actinide burners as for MSR thorium breeders. Here the assessment of flow-sheets came out also from the experience obtained during the experimental work done by individual participants.

In the **FWP6**, there was the **EUROPART integrated project** devoted to the experimental R&D in the partitioning area [Madic,2006]. In addition to the hydrometallurgical topics, the project also had a pyrometallurgical part covering separation methods from molten salt media. As chloride as fluoride systems were investigated and as molten salt liquid metal extraction as electrochemical separation were studied. R&D of electrochemical separation techniques devoted to the MSR technology was appreciable part of the project. The EUROPART project was rounded off in June 2007.

In ALISIA, three institutions participating in the ALISIA project have been involved in the theoretical and experimental activities devoted directly to the development of reprocessing studies of MSR fuel salt (CNRS, RRC-KI, NRI). All three studies come from the original activities of ORNL, but the flow-sheet designs correspond to individual MSR concepts proposed by individual institutions.

TMSR concept

The reprocessing scheme proposed by CNRS for the TMSR concept is given in Figure 4.3.

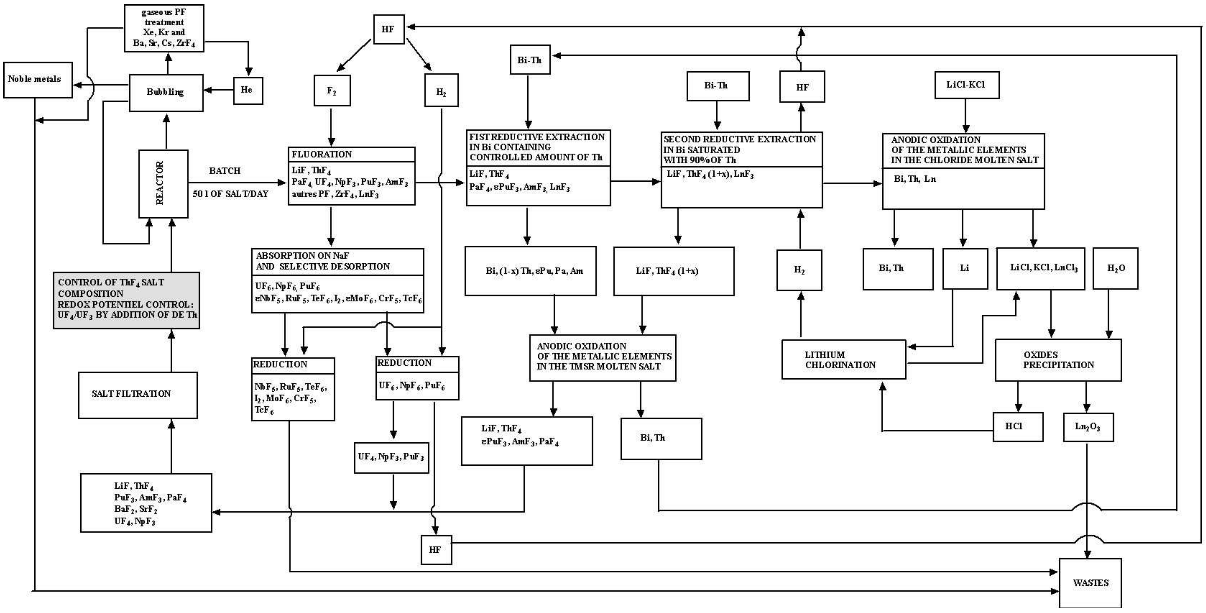


Figure 4.3: Reprocessing scheme for TMSR concept (CNRS research program)

The TMSR fuel salt is constituted of LiF-ThF_4 (and eventually NaF or CaF_2). The different steps can be described as:

- Helium bubbling for extraction of Kr, Xe and of a large part of ZrF_4. Ba, Sr and Cs daughter nuclides of Xe and Kr. Depending on the bubbling efficiency, they will be removed during this step. Moreover, the bubbling contributes to the extraction of the noble metals (under particles form in the molten salt) by a process close to the flotation one.

- Fluorination process for extraction of U, Np, Pu, Te, Nb, Ru, I_2, Mo, Cr, Tc under gaseous states. UF_6, PuF_6 and NpF_6 are, after reduction, re-introduced in the fuel salt.
- A first reductive extraction step in liquid Bi whose redox potential is controlled by a given quantity of metallic thorium (pool 1). The objective of this step is to remove all actinides present in the fuel salt and to leave the lanthanides in the salt.
- A second reductive extraction step in a second pool of liquid Bi saturated with 90% of thorium (pool 2). Due to the very low redox potential obtained at the Bi interface in these conditions, the reduction of almost all lanthanides is expected.
- Anodic oxidation of actinides. The fuel salt after removing of actinides and lanthanides is contacted with the pool 1 for anodic oxidation of actinides. The reactions involved in this step are given in Table 4.1.
- Anodic oxidation of lanthanides in a chloride medium. The anodic oxidation of lanthanides is performed by contacting the pool 2 with the chloride medium LiCl-KCl.
- Oxide precipitation of lanthanides. This precipitation is realized by a H_2O/HCl gaseous mixture bubbling in the chloride molten salt. The oxides so precipitated are sent to a waste storage. HCl gas is used for chlorination of metallic Li obtained at the cathode during the anodic oxidation of lanthanides. The reaction between Li and HCl produces H_2 gas which is used to balance the excess of ThF_4 in the cleaned fuel salt.

Table 4.1: Chemical reaction involved in the reductive extraction steps

Actinide extraction	
Reductive extraction by Th	$4/3AcF_3 + Th(Bi) = ThF_4 + 4/3Ac(Bi)$
Anodic oxidation of Ac(Bi) Anode Cathode	 $Ac(Bi) + 3F^- = AcF_3 + 3e$ $ThF_4 + 4e = Th + 4F^-$
Balance	$4/3AcF_3 + Th(Bi) + 4/3\ Ac(Bi) + 4F^- + ThF_4 + 4e =$ $ThF_4 + 4/3Ac(Bi) + 4/3\ AcF_3 + 4e + Th + 4F^-$
Lanthanides extraction	
Reductive extraction by Th	$4/3LnF_3 + Th(Bi) = ThF_4 + 4/3Ln(Bi)$
Anodic oxidation of Ln(Bi) in chloride media Anode Cathode	 $Ln(Bi) + 3Cl^- = LnCl_3 + 3e$ $LiCl + e = Li + Cl^-$
Lanthanide oxide precipitation	$2LnCl_3 + 3H_2O = Ln_2O_3 + 6HCl$
Lithium chlorination	$Li + HCl = LiCl + 1/2H_2$
Reduction of ThF_4 with H_2	$ThF_4 + 2H_2 = Th(Bi) + 4HF$
Balance	$4/3LnF_3 + Th(Bi) + 4/3Ln(Bi) + 4Cl^- + 4LiCl + 4e$ $+ 4/3LnCl_3 + 2H_2O + 4Li + 4HCl + ThF_4 + 2H_2 =$ $ThF_4 + 4/3Ln(Bi) + 4/3LnCl_3 + 4e + 4Li + 4Cl^- +$ $2/3Ln_2O_3 + 4HCl + 4LiCl + 2H_2 + Th(Bi) + 4HF$ $4/3LnF_3 + 2H_2O = 2/3\ Ln_2O_3 + 4HF$

The French research experimental program has been defined based on this reprocessing scheme to determine the efficiency of the extraction steps.

MOSART concept

One of the task set under the ISTC#1606 project activities was to prepare fuel salt clean-up scheme for Li,Na,Be/F MOSART concept [Zherebtsov, 2008]. Methods and cycle times for fission products removal and TRU recycling are given in Table 4.2. As expected, removal of lanthanides from Li,Na,Be/F salt solvent is the most complicated task in the fuel salt clean-up. The results of experimental ISTC#1606 studies with selected Li,Na,Be/F salt solvent showed that, for removing of lanthanides, fluorine-oxygen exchange and electrodeposition on solid inert electrodes are not effective due to active participation of main solvent constituents (fluorides of beryllium and sodium) in corresponding processes. Experiments on reductive extraction of lanthanides in molten Li,Na,Be/F - liquid bismuth system also demonstrated that it is not possible to remove lanthanides from molten salt effectively, as far as in the extraction process significant amount of sodium moves to bismuth from salt solvent.

As far as methods studied within the project appeared to be not effective for Li,Na,Be/F MOSART fuel salt clean-up, the other alternatives of lanthanides removal by distillation and co-crystallization were considered.

Studies on plutonium distribution in molten Li,Na,Be/F-liquid bismuth system demonstrated the possibilities of reductive extraction for recycling actinides in MOSART fuel salt clean-up unit. However, the experimental data obtained have shown that the required degree of actinides extraction (99.9%) can be achieved only in multistage process using sodium, dissolved in bismuth, as reducer. Sodium concentration in bismuth should be rather high (tens of atomic percents).

Table 4.2: Methods and cycle times for fission products removal and TRU recycling

Component	Removal time	Removal operation
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 hr	Plating out on surfaces+ To off gas system
Zr	1-5 yr	Reductive extraction Distillation and cocrystallization
Ni, Fe, Cr		
Np, Pu, Am, Cm		
Y, La, Ce, Pr, Nd, Pm, Gd, Tb, Dy, Ho, Er, Sm, Eu		
Sr, Ba, Rb, Cs	>30 yr	
Li, Be, Na		Salt discard

Basing on experimental results received within the project and analysis of prior ORNL data, it was proposed a possible scheme of Li,Na,Be/F MOSART fuel salt clean-up (Figure 4.4). As can see, at the initial stage, “noble” metals and zirconium are extracted into liquid metal (cadmium, zinc, bismuth). Then, actinides are extracted into liquid bismuth. At the final stage of the process, all actinides and admitted amount of fission products are re-extracted into purified salt in order to return actinides into the fuel circuit without any delay.

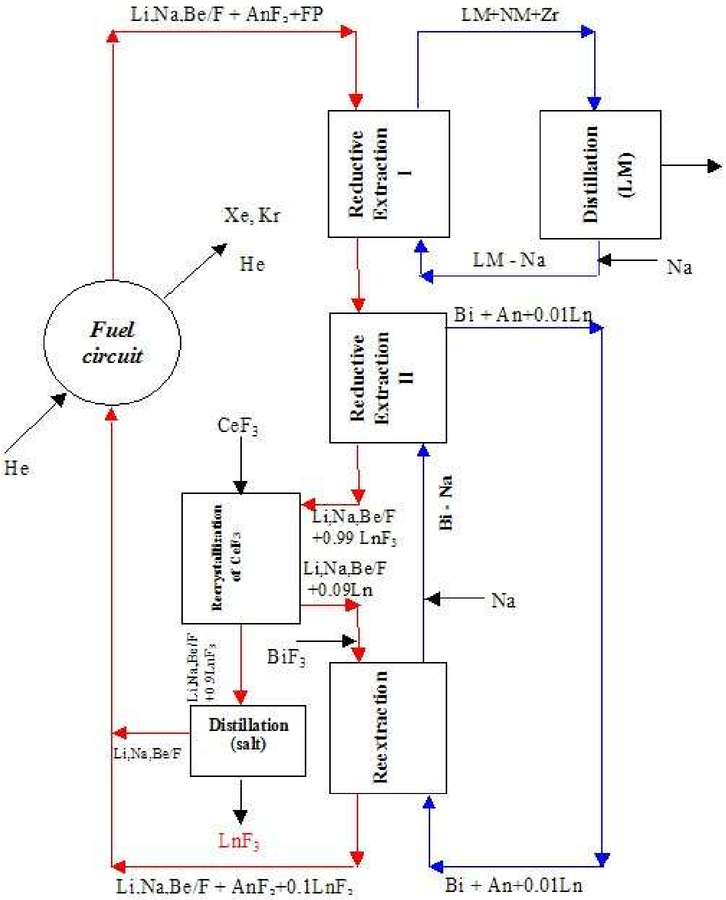


Figure 4.4: Conceptual scheme of Li,Na,Be/F MOSART fuel salt clean up

At intermediate stage between extraction and re-extraction of actinides, salt solvent is purified from lanthanides. To manage it, the salt is heated up to 800-850°C, then the salt is saturated by cerium trifluoride. After salt cooling down to 500°C, the main part of lanthanides accumulated in the salt co-crystallized together with cerium trifluoride and precipitates. About 10% of initial amount of lanthanides (mainly cerium) remains in dissolved state in salt.

Then, purified salt goes for actinides re-extraction for subsequent recycling together with actinides to fuel circuit. Precipitate of lanthanides with salt residues is directed to distillation facility for vacuum evaporation of salt constituents. Lanthanides (may be with some amount of salt constituents, mainly sodium fluoride), after salt distillation, are directed to the waste stream.

The conceptual scheme of Li,Na,Be/F fuel salt clean-up looks more complex than possible scheme of Li,Be/F MOSART fuel salt processing (for example system based on 73%LiF–27%BeF_2 (in mol%) solvent).

The fuel salt clean-up scheme of Li,Be/F MOSART could be based on reductive extraction in liquid bismuth:

(1) In molten Li,Be/F-liquid Bi system, An/Ln distribution coefficients are higher than that for molten Li,Na,Be/F-liquid Bi system by factor 10-100, and

(2) Lanthanides could be removed from LiF-BeF_2 based fuel salt by reductive extraction in liquid bismuth without any problem.

SPHINX concept

A certain R&D work performed within the SPHINX project has been devoted to the MSR flow-sheeting, mainly to the flow-sheet design for MSR An-burner, partially also to flow-sheet design of MSR Th-breeder. The present conceptual flow-sheets proposed by NRI Řež plc for MSR also take into account the original ORNL flow-sheet. But new technological operations are proposed to avoid some bottlenecks of original ORNL technology.

The on-line reprocessing technology originally proposed for MSBR fuel was based on the combination of three separation processes: (1) gas extraction (originally called He-bubbling method) appointed for removal of xenon, krypton and some noble metals, (2) fused salt volatilization proposed for extraction of uranium and (3) molten salt/liquid metal reductive extraction proposed for extraction of protactinium and removal of rare earth elements (lanthanides).

However, the use of fused salt volatilization process and molten salt/liquid metal reductive extraction process in the long run of MSR could be problematic because both processes can negatively affect the composition of the fuel salt circuit. The typical fuel salt composition of MSR Th-breeder reactor could be based on ^{7}LiF – BeF_2 eutectic in which about 12 mol% of ThF_4 and 0.3 mol% of UF_4 is dissolved. The redox potential conditions in primary circuit should be kept in slightly reductive range to protect the reactor structural materials – nickel alloys. Moreover, the fission reaction in the reactor core is an oxidizing process. Therefore, the mission of the on-line reprocessing technology is not only to reprocess the fuel, but also to compensate the reactor chemistry and to keep the redox potential in desired range. Therefore, the combination of extremely oxidative technology based on fused salt fluoride volatilization process and subsequent molten salt/liquid metal reduction requires permanent feeding of relatively large amount of reducing agent – lithium (in case of MSR, it is enriched ^{7}Li) into the fuel circuit system. These constant additions of ^{7}Li may be problematic in a long run of reactor.

The problem could be avoided by introducing electrochemical separation processes for on-line reprocessing technology. Here the principle of proposed on-line reprocessing is based on a combination of non-selective molten salt/liquid metal reductive extraction and selective electro-separation processes. As the fused salt volatilization process is not used in the frame of this reprocessing technology, the consumption of reducing agent can be significantly minimized. Based on current results obtained by experimental electrochemical studies, the possible conceptual flow-sheet of on-line reprocessing technology has been proposed.

These results allow designing a preliminary flow-sheet of MSR (An-burner) on-line reprocessing technology, in which the main separation method is electrochemical. The flow-sheet diagram is shown in Figure 4.5.

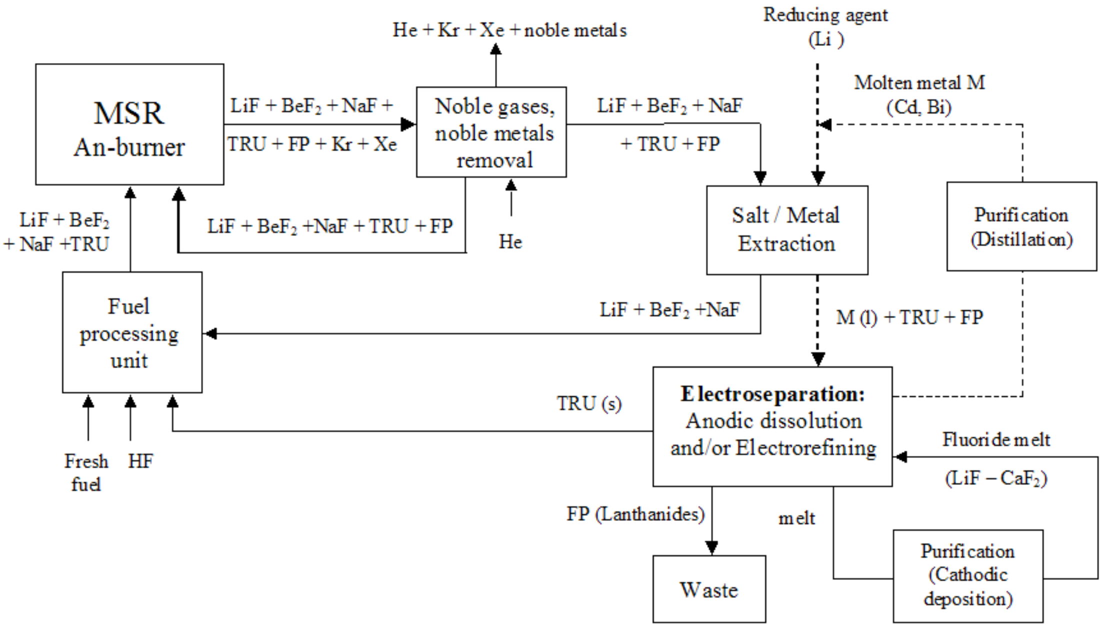


Figure 4.5. Conceptual flow-sheet of MSR-SPHINX (An-burner) fuel salt clean up

3.4.4 Selection of MSR carrier molten salt from the viewpoint of fuel salt processing

The development of on-line reprocessing (fuel salt clean-up) technology represents a very specific problem affecting even the MSR design, reactor core chemistry and the choice of structural materials. Particularly, the link to reactor core chemistry is close because the chemical reactions rates and their character in the reactor have to be compensated by the reprocessing technology. A typical example is that nuclear fission in the molten salt fuel medium is an oxidizing process, nevertheless the redox potential in the reactor must be kept in slightly reductive range to protect the reactor core and primary circuit structural materials (nickel alloys and graphite). Therefore a very special attention should be paid to the selection of carrier molten salt, which must exhibit several basic properties (e.g. good thermal conductivity, appropriate melting point, low vapour pressure, radiation stability, sufficient solubility of actinides and last but not least the reprocessability by adequate separation techniques). Based on these requirements, the ^{7}LiF–BeF$_2$ eutectics still remains the basic carrier salt candidate among several others, but the new studies enlarged the candidate carriers for some new ones.

A basic list of the molten salt carriers discussed in the reprocessing technology is following:

- ^{7}LiF–BeF$_2$ eutectics (FLiBe) – The salt is still a reference, originally proposed for MSBR. It has acceptable melting point, good solubility for uranium and thorium fluorides. However the thermodynamical stability of BeF$_2$ seems to be insufficient for electrochemical separation processes and also the solubility of transuranium fluorides is limited. On the other side, LiF-BeF$_2$ is practically immiscible with some liquid metals like bismuth and therefore it can be excellently used in molten salt/liquid metal reductive extraction process. In this process, a thermodynamical stability of the salt was testified. The molten salt/liquid metal reductive extraction technology was significantly verified in laboratory conditions during the MSRE and MSBR programs in 1960s and 70s.
- ^{7}LiF–BeF$_2$ with addition of NaF – The salt should show an increase in solubility of tranuranium elements, therefore it is often proposed for MSR actinide burners.
- ^{7}LiF–ThF$_4$ – The salt is proposed for TMSR. The reprocessability of the salt has to be verified. The advantage of the ^{7}LiF–ThF$_4$ mixture should be in elimination of problems with low BeF$_2$ thermochemical stability, the drawback could be in the significantly higher melting point.
- Fluoride salts containing ZrF$_4$, RbF and other fluorides – Reprocessability of these salts by suitable pyrochemical technologies seems to be either not known (RbF) or problematic (ZrF$_4$), the proposals usually come from the wish to eliminate beryllium-containing salts due to toxicity of beryllium or to eliminate the need of use of expensive ^{7}Li isotope in LiF or to increase solubility of AnF$_3$ in the solvent system.

- Use of LiF-NaF-KF, LiF-NaF, LiF-CaF_2 and chloride systems – These salts could be satisfactorily used for the individual electrochemical separation processes within the reprocessing technology if actinides and fission products are completely extracted from the fuel salt carrier and subsequently dissolved in molten salts mentioned above.

3.4.5 Preliminary conclusions

Successful solution of the MSR fuel salt clean-up development is one of crucial steps before industrial deployment of MSR systems. As the MSR reprocessing technology must meet special demands (like radiation resistance, compactness, exclusion of moderating agents, compatibility with the carrier molten salt type and with the structural materials of MSR primary circuit, acceptable process reaction rate and process workability by remote handling), the pyrochemical separation processes, including the molten salt separation techniques, seem to be the only technologies which can be generally applied. The selection of molten salts used for these technologies will require still broad and intensive research and development activities and careful verification experiments. Also, the waste management will have to be solved in connection to the MSR fuel reprocessing development.

3.5 Design, safety and economic aspects

Important aspects of the rationale for salt selection with respect to design and safety, and according to applications, are discussed in section 3.5. Other aspects (economics, non proliferation) also are briefly addressed in this section.

3.5.1 General considerations

Specific criteria for salt selection from the point of view of design are mainly driven by considerations of liquid salt chemistry, material compatibility, reactor physics (neutronics, thermal-hydraulics), fuel reprocessing (if relevant). These aspects are analyzed in the previous sections (sections 3.1 to 3.4).

In addition to the integration of these specific criteria into overall designs, criteria from the point of view of safety, economic performance and proliferation resistance must be analyzed and deepened.

The relevance of salt selection results from a compromise, the best compromise being dependant of the envisioned application.

The salt compositions considered more probable for the different applications are listed in Table 6 (cf. section 3). The rationale for the pre-selection of such compositions is discussed in the following sub-sections with regard to global design and safety considerations.

3.5.2 Design considerations

Section 3.5.2 was essentially derived from [Williams,2006] and [Williams,2006a].

Requirements are basically common to the different applications. When possible and suitable, a deeper screening is achieved according to applications.

Table 5.1 shows that useful salts seem to exhibit relatively similar fluid transport properties (density, heat capacity, viscosity, thermal conductivity).

Table 5.1: Summary of properties of candidate liquid salts

Salt	Melting point (℃)	Heat transfer properties at 700℃			
		ρ density (g/cm^3)	ρCp heat capacity (cal/cm^3.℃)	viscosity (cP)	thermal conductivity (W/m.K)
LiF-BeF$_2$	**460**	**1.94**	**1.12**	**5.6**	**1.0**
NaF-BeF$_2$	**340**	**2.01**	**1.05**	**7**	**0.87**
LiF-NaF-BeF$_2$	**315**	**2.00**	**0.98**	**7**	**0.97**
LiF-ZrF$_4$	**509**	**3.09**	**0.90**	**> 5.1**	**0.48**
NaF-ZrF$_4$	**500**	**3.14**	**0.88**	**5.1**	**0.49**
KF-ZrF$_4$	**390**	**2.80**	**0.70**	**< 5.1**	**0.45**
Rb-ZrF$_4$	**410**	**3.22**	**0.64**	**5.1**	**0.39**
LiF-NaF-ZrF$_4$	**436**	**2.79**	**0.98**	**6.9**	**0.53**
LiF-NaF-KF	**454**	**2.02**	**0.91**	**2.9**	**0.92**
LiF-NaF-RbF	**435**	**2.69**	**0.63**	**2.6**	**0.62**

In section 3.5.2.2, overall Figures Of Merit (FOM) are proposed to assess coolant performances (including liquid salts) regarding heat transfer and thermal-hydraulics.

3.5.2.1 Melting temperature and reactor operation

Fluid-fuel systems (MSR)

Without question, **the melting (or freezing) point is the single most important physical property for a candidate coolant**. The requirement for a low freezing temperature depends, to some degree, on the system design, and especially on the power-generation machinery. Because salt coolants possess high heat capacity, the temperature drop in the primary loop is typically small — between 50 and 100ºC. For the design and operation of salt-fueled reactors, such as the Aircraft Reactor Experiment (ARE), the Molten Salt Reactor Experiment (MSRE), and the Molten Salt Breeder Reactor (MSBR), a requirement was established that the primary-salt freeze temperature should provide a significant temperature margin (> 100ºC) to freezing throughout the plant. Thus, fuel-containing salts, which also served as the primary coolant for fluid-fueled designs, were required to have freezing points below 525ºC to be considered useful [Grimes,1967]. The 525ºC limit was also dictated by the need for the primary coolant to exchange heat in a practical manner with the secondary coolant. The previous generation of secondary coolant salts were expected to operate in a steam generator, so a secondary-salt freezing point less than 400ºC was required [Sanders,1971].

A reference value for core inlet temperature in SFR is 395℃ (SuperPhénix, EFR), thus requiring a melting temperature less than 300℃ for a liquid salt to be used as intermediate coolant. This condition on melting temperature is very restrictive: nitrate salts ($NaNO_3$-KNO_3, $NaNO_3$-KNO_3-$LiNO_3$), halogenous compounds with chloride (RbCl-CuCl, KCl-CuCl, CsCl-CuCl), some hydroxides (NaOH-KOH).

An extensive database of phase diagrams exists for salt systems of all types [Mc Murdie,1964], [Thoma,1975]. Phase diagrams are reviewed in the present report for the salt compositions considered as the most probable (cf. section 3.1). There is very little need to pursue estimation techniques. Because no single-component salt freezes at a sufficiently low temperature, multi-component mixtures of salts are required. Nearly all of the binary phase diagrams of interest have been measured, and many of the ternary systems have also been investigated. In general, the primary lowering of the freezing point (as much as 500ºC) occurs with the addition of the first salt to a pure component. Additional lowering of the freezing point can be achieved by adding a third component, but these freezing-point depressions are of a lower order (~50ºC). Additional components are typically important for reasons other than lowering of the freezing point (e.g., cost, neutronics, or some other physical property).

Certain compositions have been excluded for reasons that may not be readily apparent. For example, in the phase diagram of BeF_2 systems, there exist very low freezing-temperature compositions in the BeF_2-rich region, and it would be natural to include these in a list of low-freezing candidates. However, experience has demonstrated that these BeF_2- rich systems are not good candidates because they are very viscous due to the associative behaviour of BeF_2 in these mixtures. Some systems are normally excluded from consideration as primary coolants. Potassium-containing salts are usually excluded from consideration as a primary coolant because of the relatively large parasitic capture cross-section of potassium. However, potassium-containing salts are commonly used in non-nuclear applications and serve as a useful frame of reference (e.g., FLiNaK). In all cases, there are rubidium analogs to the potassium systems that have freezing points close to that of corresponding potassium systems. Rubidium has a parasitic thermal neutron-capture cross section much lower than potassium; however, it also possesses epithermal resonance absorption bands.

The alkali fluorides possess simple ternary low-melting eutectic compositions; therefore, phase diagrams do not need to be examined. These ternary systems possess only modest melting point depressions (~40ºC) compared to the binary eutectics. The ternary eutectic compositions are favoured in preference to the binary eutectics because they substitute inexpensive NaF for expensive ^{7}LiF and neutron-absorbing KF. The ternary eutectic in the Li-NaF-BeF_2 system possesses a 25ºC melting-point depression compared to the NaF-BeF_2 eutectic, but this mixture does not seem useful as a coolant because it does not offer a significant advantage over the NaF-BeF_2 eutectic, and yet it requires the addition of an expensive component, ^{7}LiF.

The ternary systems containing ZrF_4 offer more promising possibilities. The ternary eutectic in the LiF-NaF-ZrF_4 system possesses a large phase field with melting points below 500ºC, and distinct eutectic compositions at a Na:Zr ratio of 1. These ternary eutectics (42-29-29 and 26-37-37 mol %) are the most promising candidate coolants because (a) they maintain ZrF_4 < 40 mol % (necessary for low vapour pressure) and (b) they provide a significant melting point depression (40–64ºC) compared to the NaF-ZrF_4 binary system. The eutectic composition of 30-24-46 is not favoured because it offers little melting point advantage and yet still imposes high ZrF_4 vapour pressures and significant ^{7}Li content.

The NaF-RbF-ZrF_4 ternary system also possesses some attractive compositions with low melting points. The advantage of replacing RbF with NaF is that NaF is relatively inexpensive, it has a lower effective neutron cross-section than RbF, and compositions with lower ZrF_4 content (and thus lower vapour pressure) can be considered. Very lowest melting point regions (T < 400ºC) are not significantly different than the RbF-ZrF_4 eutectic compositions. The eutectic regions in the neighbourhood of Na:Rb = 1.44 have a number of interesting properties. Quite a few eutectic mixtures exist with melting points in the neighbourhood of 420–430ºC. The liquidus temperatures along the line Na:Rb =1.44 indicate a minimum melting point region in the neighbourhood of ZrF_4 = 39–43 mol %. A composition of 33-23.5-43.5 melting at 420ºC was selected as a candidate coolant because it is likely to have the best neutronic behaviour among these particular compositions.

It should be noted that all of the systems containing lithium will require highly enriched ^{7}Li (see section 3.5.3.1). In the family of alkali-fluoride salts, all of the mixtures with acceptable freezing points contain lithium. The BeF_2 and ZrF_4 families of salts possess low-freezing points that do not contain lithium. Numerous compositions contain no lithium and are relatively low-cost, low-freezing point mixtures that are likely to exhibit suitable physical properties. Salts containing enriched lithium will certainly have better neutronic performance than their analogs containing Na, Rb, or K, but at a significant extra expense associated with isotopic enrichment. If isotopically enriched materials are to be considered, then the boron-containing fluoroborate mixtures could be added to this list. The option of enriching boron for this particular application has never been proposed before, and there is no apparent basis for estimating the cost of enriching boron to the extreme levels required for this application (as was done for lithium). In addition to the issue of isotopic enrichment, an assessment of the BF_3 volatility in all of the fluoroborate salts will need to be considered.

The choice made for MSBR (LiF-BeF_2 salt for the primary coolant, NaF-$NaBF_4$ for the secondary coolant) certainly remains the most appropriate for TMSR (T and NM) concepts, as well as acceptable for the MOSART system.

Solid-fuel systems (AHTR, LSFR)

The situation for the AHTR is different from that of thermal and non-moderated fluid-fuel systems, but some useful analogies can be drawn. We do not know exactly what the power-generation machinery or heat-transfer loop will require of a secondary coolant, thus we cannot predict exactly what the freezing point requirements will be for the primary coolant. However, assuming that a high temperature reactor of the type envisioned by the AHTR will use gas turbines of some type for the highest-temperature portion of the power-generation machinery, this will not require freezing points as low as those required by steam systems.

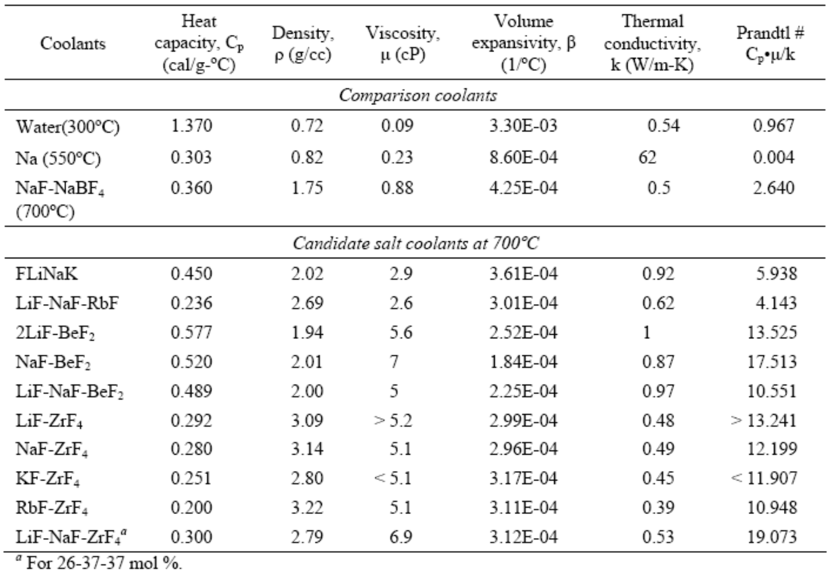
Therefore, while the requirement for a low freezing point is not as fundamental a constraint for the AHTR system as for previous systems, it will still be highly desirable for the purposes of having cheaper materials and simpler systems everywhere in the plant. The requirements for the freezing point for AHTR coolant will probably exist somewhere between the limits established previously for the MSBR fuel salt (525ºC) and secondary salt (400ºC). Because molten salts are a new technology for the nuclear industry, it is highly desirable to use a system with as low a freezing point as possible in order to simplify the materials, components, and system requirements. Salts that freeze below 400ºC should be given priority, all other factors being equal.

For the LSFR primary salt, the combination of a low melting temperature with neutronic considerations (minimisation of neutron capture and moderation) leads to the selection of NaCl-KCl-$MgCl_2$ and NaF-KF-ZrF_4. The salts exhibiting a melting temperature larger than 500℃ have been discarded. However, it will be necessary to increase the core inlet temperature with respect to SFR.

3.5.2.2 Heat transfer efficiency, figures of merit

It is useful to compare the heat-transfer performance of candidate liquid salts to other coolants with which significant experience is available, or would like to consider for related applications (secondary heat transfer fluids). With the exception of water, the temperature of 700ºC was selected for comparison because this permits properties to be evaluated more readily. A temperature of 300ºC was selected for water, because this is a typical coolant temperature used in the primary circuit of existing nuclear power plants.

Table 5.2: Properties of comparison coolants and candidate coolants at 700℃



Coolants	Heat capacity, C_p (cal/g-°C)	Density, ρ (g/cc)	Viscosity, μ (cP)	Volume expansivity, β (1/°C)	Thermal conductivity, k (W/m-K)	Prandtl # $C_p \cdot \mu/k$
Comparison coolants						
Water(300°C)	1.370	0.72	0.09	3.30E-03	0.54	0.967
Na (550°C)	0.303	0.82	0.23	8.60E-04	62	0.004
NaF-$NaBF_4$ (700°C)	0.360	1.75	0.88	4.25E-04	0.5	2.640
Candidate salt coolants at 700°C						
FLiNaK	0.450	2.02	2.9	3.61E-04	0.92	5.938
LiF-NaF-RbF	0.236	2.69	2.6	3.01E-04	0.62	4.143
2LiF-BeF_2	0.577	1.94	5.6	2.52E-04	1	13.525
NaF-BeF_2	0.520	2.01	7	1.84E-04	0.87	17.513
LiF-NaF-BeF_2	0.489	2.00	5	2.25E-04	0.97	10.551
LiF-ZrF_4	0.292	3.09	> 5.2	2.99E-04	0.48	> 13.241
NaF-ZrF_4	0.280	3.14	5.1	2.96E-04	0.49	12.199
KF-ZrF_4	0.251	2.80	< 5.1	3.17E-04	0.45	< 11.907
RbF-ZrF_4	0.200	3.22	5.1	3.11E-04	0.39	10.948
LiF-NaF-ZrF_4[a]	0.300	2.79	6.9	3.12E-04	0.53	19.073

[a] For 26-37-37 mol %.

Table 5.2 lists the properties of the coolants to be used in the heat-transfer comparisons, as well as the properties of some candidate AHTR salts.

Generalized heat-transfer metrics are a useful tool for grouping coolant performance in the absence of more detailed system designs. General figures of merit (FOM) have been provided [Bonilla,1958], based on minimal pumping power for a given coolant temperature rise as the objective function **for forced convection** (turbulent flow):

$$FOM = \mu^{0.2}\rho^{-2}c_P^{-2.8}$$

For natural convection cooling, the following groups have been proposed [Bonilla,1958] for passive cooling:

$$FOM = \left(\mu^{0.2}\beta^{-1}\rho^{-2}c_P^{-1.8}\right)^{0.36} \qquad \text{(turbulent flow)}$$

$$FOM = \left(\mu\beta^{-1}\rho^{-2}c_P\right)^{0.5} \qquad \text{(laminar flow)}$$

Where β is the volume expansivity, $\beta = \frac{1}{\rho}\frac{d\rho}{dT}$

During evaluation of secondary coolants for the MSBR, another expression of FOM was proposed [Sanders,1971], related to the area required for the primary heat exchanger:

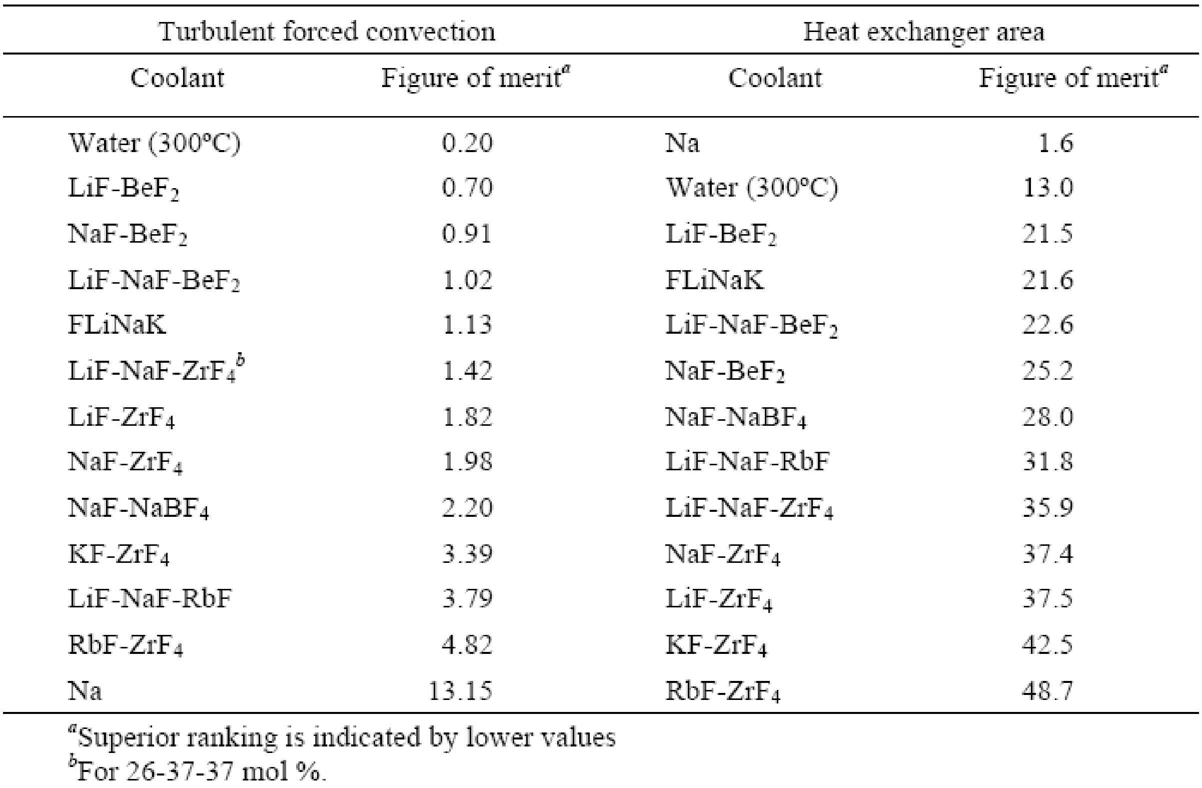
$$FOM = \mu^{0.2}c_P^{-0.6}k^{-0.6}\rho^{-0.3}$$

It was recommended that this FOM be used only for comparison within a coolant group type (salts, metals, or other).

All of these FOMs are “golf-scores” — i.e., lower numbers correlate with better performance.

Tables 5.3 and 5.4 summarize the various FOMs for the comparison of candidate coolants.

Table 5.3: Turbulent convection and heat exchanger area figures of merit



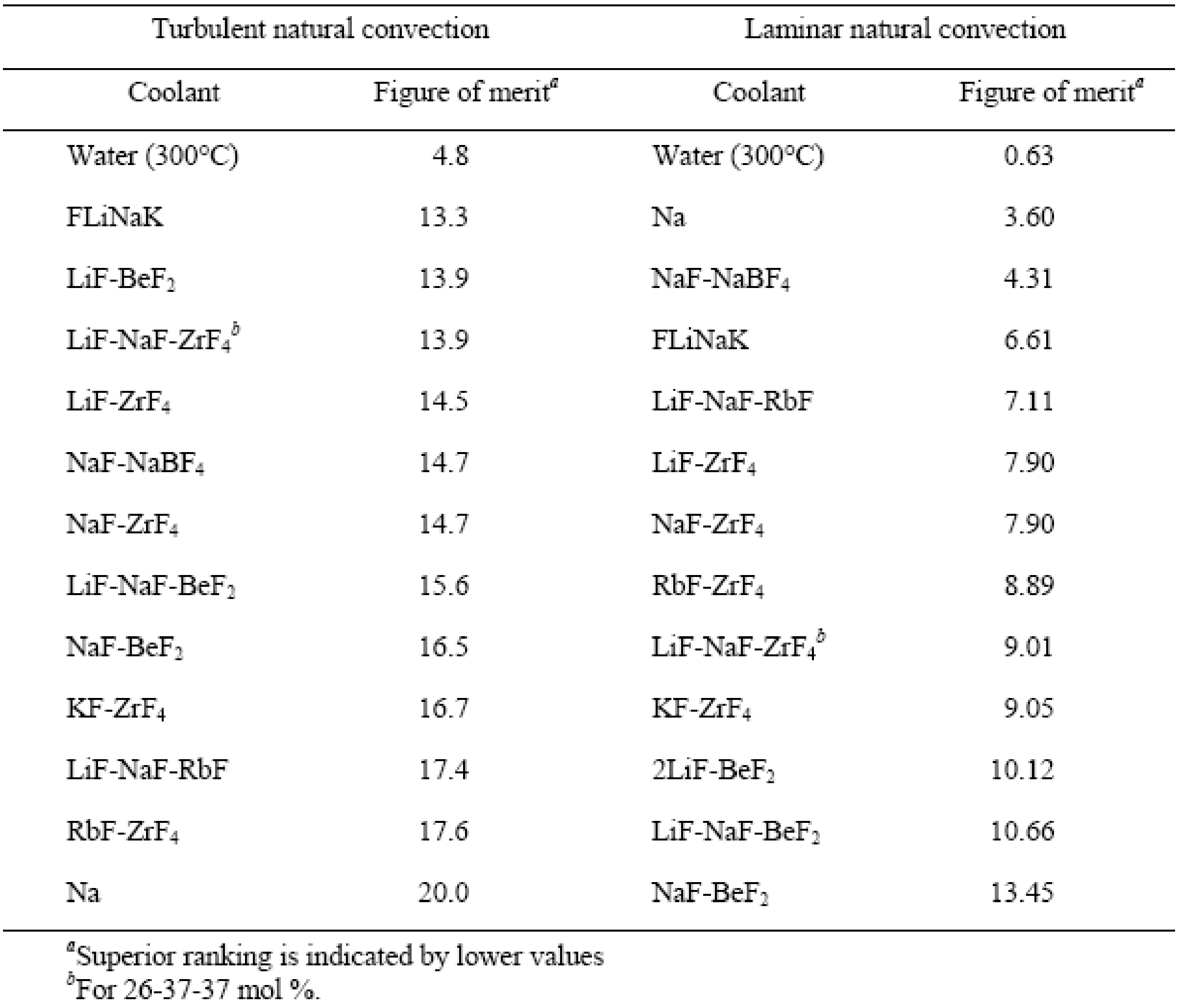
Turbulent forced convection		Heat exchanger area	
Coolant	Figure of merit[a]	Coolant	Figure of merit[a]
Water (300°C)	0.20	Na	1.6
LiF-BeF$_2$	0.70	Water (300°C)	13.0
NaF-BeF$_2$	0.91	LiF-BeF$_2$	21.5
LiF-NaF-BeF$_2$	1.02	FLiNaK	21.6
FLiNaK	1.13	LiF-NaF-BeF$_2$	22.6
LiF-NaF-ZrF$_4$[b]	1.42	NaF-BeF$_2$	25.2
LiF-ZrF$_4$	1.82	NaF-NaBF$_4$	28.0
NaF-ZrF$_4$	1.98	LiF-NaF-RbF	31.8
NaF-NaBF$_4$	2.20	LiF-NaF-ZrF$_4$	35.9
KF-ZrF$_4$	3.39	NaF-ZrF$_4$	37.4
LiF-NaF-RbF	3.79	LiF-ZrF$_4$	37.5
RbF-ZrF$_4$	4.82	KF-ZrF$_4$	42.5
Na	13.15	RbF-ZrF$_4$	48.7

[a] Superior ranking is indicated by lower values

[b] For 26-37-37 mol %.

In general, it can be concluded that the lighter molten salts (those not containing large quantities of higher-atomic-number elements, e.g., rubidium and zirconium) have somewhat better heat transfer performance than the heavy salts. The one exception is the laminar regime of natural convection. In most passive cooling situations, the turbulent natural convection component is of primary importance.

Table 5.4: Natural convection figures of merit



Turbulent natural convection		Laminar natural convection	
Coolant	Figure of merit[a]	Coolant	Figure of merit[a]
Water (300°C)	4.8	Water (300°C)	0.63
FLiNaK	13.3	Na	3.60
LiF-BeF_2	13.9	NaF-$NaBF_4$	4.31
LiF-NaF-ZrF_4[b]	13.9	FLiNaK	6.61
LiF-ZrF_4	14.5	LiF-NaF-RbF	7.11
NaF-$NaBF_4$	14.7	LiF-ZrF_4	7.90
NaF-ZrF_4	14.7	NaF-ZrF_4	7.90
LiF-NaF-BeF_2	15.6	RbF-ZrF_4	8.89
NaF-BeF_2	16.5	LiF-NaF-ZrF_4[b]	9.01
KF-ZrF_4	16.7	KF-ZrF_4	9.05
LiF-NaF-RbF	17.4	2LiF-BeF_2	10.12
RbF-ZrF_4	17.6	LiF-NaF-BeF_2	10.66
Na	20.0	NaF-BeF_2	13.45

[a] Superior ranking is indicated by lower values

[b] For 26-37-37 mol %.

3.5.3 *Safety considerations*

Safety aspects have been rather poorly addressed in recent MSR projects, like those conducted in the frame of FWP5 and FWP6. MSRs have often been presented by their designers as nuclear reactors with a high degree of safety. However, since the prematurely termination of the MSBR program in 1975, safety rules for nuclear reactors have changed and the analysis performed in the 70's is unlikely to have the adequate or comprehensive level that would be required for the licensing of MSR today. In this section, some general safety considerations for MSR concepts are recalled [Ignatiev,2000]. Then, some aspects more specific to the choice of multi-component liquid salts are addressed: boiling temperature, vapour pressure [Williams,2006], chemical reactivity of salts with other coolants [Ignatiev,2000].

3.5.3.1 Safety related issues and liquid/molten salts

A molten salt reactor can be operated with acceptable effect on the environment and safety of the public provided that the radioactive liquids and gases that circulate throughout much of the plant are managed carefully. Because the MSR processing plant is coupled directly to the reactor, there is no need for shipment of short-cooled fuel. Fission products extracted from the fuel salt are stored as solids or concentrated noble gases for shipment after long decay.

Production of tritium should be considered as a major issue for reactors where the salt composition includes LiF. It is necessary to use ^{7}Li because ^{6}Li has by order higher cross section for creation of tritium. Tritium that is produced in the fuel salt (from LiF component) in substantial quantities presents special containment problems. Much of the tritium is expected to diffuse through the walls of the tubes of the primary heat exchangers into the salt in the secondary system. Tritium can be extracted from the secondary salt and stored, but unless very special measures are taken, some tritium can be expected to diffuse into the steam system and be discharged from the plant. This steam blowdown would be the only significantly radioactive effluent from the plant during normal operation. When the primary systems of an MSR are opened for maintenance, the copious amounts of fission products distributed throughout the systems require that stringent precautions be taken to prevent undesirable releases into the atmosphere. By use of evaporators and demineralizers to process wastes and the liquids that are used for decontaminating and washing radioactive equipment during maintenance, the radioactivity discharged in these liquids can be kept to insignificant amounts.

With regard to safety from severe accidents, the use of fluid fuel places some special requirements on the design and operation of an MSR. At the same time, it eases or eliminates some requirements that are important in solid fuel reactors (e.g. mitigation of severe accidents with core meltdown). Although it is clear *a priori* that different measures must be taken to ensure safety, whether these measures are more or less complex and expensive in an MSR than in other reactor systems can be determined only by a comprehensive analysis that begins with the most basic considerations.

3.5.3.2 Fuel salt homogeneity and safety

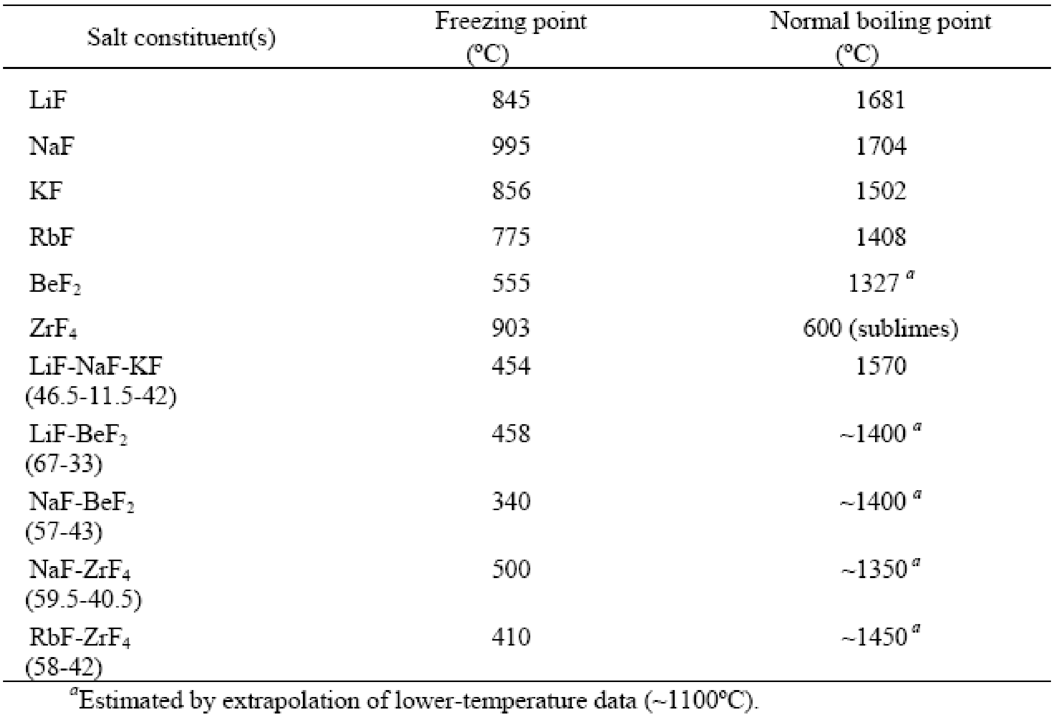
A unique consideration in fluid fuel reactors is the possibility of inhomogeneity of the fissile material in the circulating fuel. Specifically of concern is gradual segregation of fissile material outside the core, followed by rapid introduction with the incoming stream. The MSR fuel salt, is quite stable over a range of conditions much wider than the anticipated deviations. Segregation of uranium could conceivably be produced by introduction of reducing agents or oxygen into the salt, but adequate protection against this should be provided in the MSR (e.g. gettering action of the ZrF_4 for H_2O major impurity). The principal components of MSR fuel mixtures do not form intermediate compounds with PuF_3. It is anticipated therefore that in concentrations at which PuF_3 would be used, it would not be deposited preferentially from the bulk salt during the inadvertent freezing, nor at locations such as in freeze valves.

3.5.3.3 Boiling temperature, vapor pressure and vapour species

Most fluoride salts exhibit very low vapour pressures. Only compounds with higher oxidation state cations (such as BF_3, UF_6, and MoF_6) exhibit high vapour pressures. A few of the elements useful for coolants (BeF_2, ZrF_4) exhibit appreciable vapour pressures (> 1 mm Hg) at 800ºC. Table 5.5 catalogs the normal boiling and freezing points of single-component salts and of a few key multicomponent mixtures [Janz,1967].

As is evident in Table 5.5, mixtures of these pure components will always exhibit lower vapour pressures (higher boiling points) than the most volatile constituent. Therefore, these salts do not exert significant vapour pressures (> 1 bar) except at very extreme temperatures. The MSRE operated with a cover pressure of 5 psig of helium, and the MSBR was designed for a cover pressure of 40 psig.

Table 5.5 : Freezing point and boiling point of salt constituents



Salt constituent(s)	Freezing point (°C)	Normal boiling point (°C)
LiF	845	1681
NaF	995	1704
KF	856	1502
RbF	775	1408
BeF_2	555	1327 [a]
ZrF_4	903	600 (sublimes)
LiF-NaF-KF (46.5-11.5-42)	454	1570
LiF-BeF_2 (67-33)	458	~1400 [a]
NaF-BeF_2 (57-43)	340	~1400 [a]
NaF-ZrF_4 (59.5-40.5)	500	~1350 [a]
RbF-ZrF_4 (58-42)	410	~1450 [a]

[a] Estimated by extrapolation of lower-temperature data (~1100°C).

However, other factors are important. Even in a low-pressure system, the magnitude and nature of vapour produced from the salt need to be evaluated. Experience with the ARE and the MSRE shows that very low salt vapour pressures (< 1 mm Hg) simplify the off-gas system design and that certain vapour species can present problems.

In any high-temperature salt system, a purged cover gas will be necessary. The transport of significant amounts of salt vapour in this cover gas system can cause problems. In the operation of the ARE, it was found that the vapour over the ARE salt (53%NaF-41% ZrF_4 -6%UF_4) was nearly pure ZrF_4. Because ZrF_4 sublimes rather than boils, ZrF_4 “snow” was found in the exhaust piping. The ZrF_4 was not returned to the salt reservoir by condensing as a liquid and draining back to the salt reservoir. Elaborate “snow traps” were designed to mitigate this problem, but it appears that a wise choice of salt composition can eliminate it completely.

The experience with the MSRE was quite different. The MSRE salts (65%LiF-29%BeF_2-5% ZrF_4-1% UF_4) exhibited very low vapour pressure, more than 100 times lower than the ARE salt. The vapour over the MSRE salt was also of a different character. This vapour contained both LiF and BeF_2 in a proportion that melted at a low temperature, such that the condensate would drain back to the reservoir as a liquid.

Vapour pressure is the physical property that is most sensitive to salt composition. Studies have been conducted to understand the effect of composition on the vapour pressure and vapour species of the thermodynamically non-ideal systems containing ZrF_4 and BeF_2 [Sense,1957,1958]. The results of these studies are useful for understanding and selecting the optimum coolant salt composition and are briefly reviewed in the following paragraphs.

The effect of salt composition on vapor pressure can be explained with the Lewis acid-base theory [Williams,2001]. The native volatility of compounds containing the “acidic” constituent (Zr^{4+}, Be^{2+}) can be suppressed by donation of fluoride anions from the “basic” alkali fluoride constituent. The product of this donation is a low-volatility coordination-complex that is an integral part of the molten salt solution. Not all the alkali fluorides are equal in their ability to donate fluoride anions for coordination compounds. The affinity of alkali cations for their own fluoride anion decreases with increasing atomic number; thus, the heavier alkali elements will more readily donate their fluoride anions. Therefore, heavier alkali fluorides are more effective in reducing the native volatility of the compounds containing the acidic species (Zr^{4+}, Be^{2+}).

The effect of salt composition on vapour pressure is readily apparent in the BeF_2 and ZrF_4 systems, with suppression of volatility as the ratio of alkali fluoride content increases so that it satisfies the coordination-bonding demands of the polyvalent cation. The heavier alkali fluorides are more effective in suppressing the native volatility of the compound containing the polyvalent element (e.g., beryllium or zirconium).

The decrease of vapour pressure due to coordination bonding is also accompanied by a change in vapour composition. For a system rich in alkali fluoride, the vapour consists primarily of the alkali fluoride. For salt compositions that exist at the optimum ratio that just satisfies the coordination demands of the system, the vapour species is an association complex of the alkali fluoride and the polyvalent cation. For systems deficient in alkali fluoride, the volatile species is the parent compound containing the polyvalent cation.

From a practical standpoint, one should favour salt compositions with very low vapour pressures (< 1 mm Hg at 900ºC) that generate vapour species that readily melt after condensing. This corresponds to salt compositions with a ZrF_4 mole fraction in the range of ~20–45%, and with a mole fraction of BeF_2 less than ~35–45%, depending on the alkali cations present and the temperature under consideration.

3.5.3.4 Coolant salt interactions in MSR

A review of MSR coolant salt interactions and associated safety issues is presented in [Ignatiev,2000].

The eutectics of 66LiF-34BeF_2 and 92$NaBF_4$-8NaF (in mol%) were chosen as the secondary salt respectively in the MSRE and MSBR plant designs. Second, 92$NaBF_4$-8NaF was chosen because it has reasonably good coolant properties, it is relatively inexpensive, and its melting point (385℃) is low compared to that of other suitable fluoride mixtures. From the safety standpoint, it is important that mixing of fuel and coolant salt, spillage of coolant salt into the containment cells, and leakage of steam into coolant salt should not give rise to situations that would endanger the health and safety of the public or of the operators of the plant.

The only credible event that would produce mixing of fuel and coolant salts is a leak in a primary heat exchanger. No chemical reactions that would generate excessive heat or precipitate constituents of either salt would be expected to occur on mixing. Fuel salt and sodium fluoroborate are immiscible, however, so two salt phases would be present in both systems. Although the salts are immiscible, exchange occurs between the phases with lithium and beryllium fluorides entering the lighter fluoroborate phase and sodium fluoride and boron trifluoride moving into the fuel salt phase. Uranium and thorium fluorides remain in the heavy phase.

In the primary system, the exchange of constituents between salts would have no significant effect on the melting point of the fuel salt. The melting point of the coolant salt dispersed in the fuel would increase somewhat, some BF_3 would be released, and the BF_3 overpressure in the primary system would be expected to rise to about 5 atm. In the secondary system, the interaction between the fuel and coolant salts would tend to raise the liquidus temperature of the fuel containing salt but would not significantly affect the coolant salt. Since much of the secondary system normally operates at a temperature below the liquidus of the fuel salt, the fuel salt that leaked into the secondary system would initially be dispersed as frozen particles throughout much of one circuit. Whether the particles remained as solids would depend on measures taken to heat or cool the secondary circuit after the coolant salt had been drained.

None of the conditions associated with mixing of fuel and coolant salts in the primary or secondary systems appear to be capable of producing a break in either system. The secondary circuits must be heavily shielded against the radioactivity present in the coolant salt during normal operation. This shielding can be made adequate to protect against the fission products that would be introduced by the fuel salt. Repairing or replacing the faulty heat exchanger, reclaiming the fuel salt, and disposing of the contaminated coolant salt promise to be unpleasant operations. The chemical toxicity of the boron trifluoride precludes its indiscriminate release from the plant, but the presence of sodium fluoroborate does not otherwise affect the safety of those operations.

Water and steam react with sodium fluoroborate to produce primarily hydrogen fluoride and sodium hydroxyfluoroborate. The reactions are not destructively exothermic, but the hydrogen fluoride is corrosive to the metals of the reactor secondary system and the tubes that separate the fuel salt from the coolant salt. Although the corrosion rates are not catastrophic under any foreseeable circumstance, the leakage rate of water from the steam system into the secondary system and the hydrogen fluoride concentration in the secondary salt must be kept low in order to maintain a low corrosion rate of piping and equipment. In the event of a rupture of one or more tubes in a steam generator or superheater, the rapid pressurization of the secondary system and the possibility of transmitting that pressure to the primary system is the major concern. Isolation valves must be provided to stop the flow of feedwater and steam to the faulty steam generating equipment and pressure relief devices must be provided on the secondary system to keep the pressure below the system design pressure. The steam and salt that are discharged through these devices must be contained. The affected secondary system must be purged of hydrogen fluoride and moisture and the contaminated salt must be purified or replaced while repairs are made on the steam generator before operation of the plant can be resumed.

The use of a chemically reactive coolant in the secondary system of the MSR introduces some problems in designing the plant for upset conditions. The interactions of the coolant with the materials, with fluids in contiguous reactor systems, and with the cell atmospheres, however, do not appear to be so vigorous or the reaction products so aggressive as to create major safety concerns.

3.5.3.5 Chemical reactivity of liquid salts with other coolants in other systems (SFR)

The major motivation for the utilization of liquid salts in the secondary circuit of a SFR is the cancellation of the risk of direct interaction between sodium and water-steam. Liquid salts should exhibit a sufficient thermal stability in the range of SFR operating conditions (200-600℃) and avoid the problems of chemical compatibility with other fluids (primary sodium, tertiary CO_2, He-N_2, H_2O) potentially to interact in normal or accidental conditions. If any, the potential reactivity should be easily controlled.

The evaluation of the chemical compatibility of liquid salts with sodium, water, CO_2 and air should be based on the analysis of redox properties. Indeed, sodium is a very reductive species which can react with liquid salt only if the salt is or includes efficient oxidizing agents. But liquid salts usually are poorly reactive from the viewpoint of oxidation-reduction. They offer large domains of electroactivity generally limited by the oxidation of the halogenous component into the gaseous form. For example, chlorides are oxidized into chlorine (gaseous Cl_2) and fluorides into fluorine F_2. The boundary of the reduction domain is determined by the reduction of cation, for example Na^+ into Na or Li^+ into Li. This boundary indicates whether a chemical reaction between the liquid salt and sodium is thermodynamically possible or not. Existing databases give the possibility to perform all required calculations. A classical mode of representation is the Pourbaix diagram (or potential-acidity diagram) displaying the stability boundaries of the liquid salt together with the stability domain of impurities like H_2O, O_2 ou CO_2.

The analysis of phase diagrams available in the literature evidences three families of salts: nitrate (binary $NaNO_3$-KNO_3, ternary $NaNO_3$-KNO_3-$LiNO_3$), halogenous (chlorides RbCl-CuCl, KCl-CuCl, CsCl-CuCl and iodide LiI-KI), alkaline hydroxides (NaOH-KOH). In each family, it is possible to find salt systems with melting temperature lesser than 250℃. The compatibility of such salts with sodium, water, CO_2 and air must be analyzed and checked.

3.5.3.6 Compatibility of salts with structure materials

See section 3.2

3.5.4 Economics considerations

As regards economics, the following criteria must be considered:

- The market price of the liquid salt vector should be minimized (typically with reference to sodium),
- The natural availability of salt components should be sufficient (abundance, recovery effort, geographical distribution) to allow the deployment of nuclear systems under concern,
- The cost induced on the use or development of structure materials compatible with the salts (high temperature operation, corrosion resistance).

Indirect implications are the investment and maintenance cost of specific components operated with liquid salts (materials, pumps, heat exchangers, steam generators,…).

3.5.4.1 MSR capital cost evaluation

Capital cost estimates of the reference MSBR station have been compiled in during the MOST project [Matal,2003] where they are compared to those for a PWR.

According to [Matal,2003], the capitalization costs for the two reactor types are not greatly different. In a broad sense, this can be explained by the fact that about one-third of the total cost is for reactor equipment, the remainder being for the heat-power system, general facilities, and indirect costs, which are expenses somewhat similar for all thermal power plants. Variation in reactor equipment costs are not of sufficient magnitude to cause striking differences in the overall capital requirement because there are rough similarities in cost of vessels, shielding etc., and many of the differences that do exist are offsetting. However, it should be assumed that the unit power is of the same order of magnitude.

Insofar as possible, the MSBR and PWR cost estimates were put on the same basis. In both estimates, the cost of the fuel-processing plant is included in the fuel cost rather than in the plant capital cost. Both estimates are based on the January 1970 value of the dollar, and include indirect costs of about 35%. Private ownership of the plants is assumed, and interest (at 8%) during a five-year construction period is included. Neither estimate, however, considers escalation of costs during the construction period.

The Hastelloy N equipment in the MSBR is assumed to have a fabricated cost of USD 8 to USD 38 per pound, depending upon the complexity (cf. section 3.5.4.2). The reflector graphite is estimated to cost USD 9 per pound and the extruded core elements USD 11 per pound.

It is important to note that the MSBR construction cost estimates are not for a first-of-a-kind plant but assume that the station is of a proven design for an established molten-salt reactor industry in which development costs have been largely absorbed and in which manufacture of materials, plant construction and licensing are routine. However, recognition was taken of the fact that the MSBR cost estimate is based on conceptual designs rather than on actual construction experience, and a 15% contingency allowance was applied to reactor materials. A contingency factor of only 3% was used in the corresponding portion of the PWR estimate. This difference in contingency factors applied to the reactor materials adds about USD 8 million to the total MSBR cost estimate after indirect costs are included.

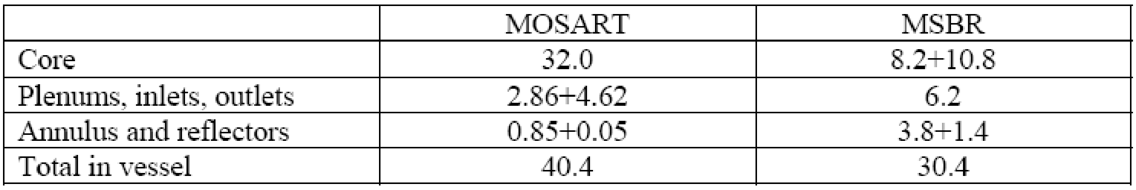
Clearly, those estimates, done in the 70's, require significant updating. The intrinsic cost of liquid salts is not specifically identified. More recent evaluations are provided in sections 3.5.4.2 and 3.5.4.3.

3.5.4.2 Evaluation of special materials inventories

Some economic evaluations have been performed in the frame of the ISTC-1606 project for MSBR and MOSART concepts [Zherebtsov,2008].

The distribution of fuel salt inventories in MOSART is given in Table 5.6.

Table 5.6: Fuel salt inventory in reactor vessel (m^3)



	MOSART	MSBR
Core	32.0	8.2+10.8
Plenums, inlets, outlets	2.86+4.62	6.2
Annulus and reflectors	0.85+0.05	3.8+1.4
Total in vessel	40.4	30.4

In Table 5.7, fuel salt inventories in primary circuit for ^{7}Li,Na,Be,An/F 2400 MWt MOSART system in comparison with the ^{7}Li,Be,Th,U/F MSBR, having thermal capacity 2250 MWt are presented. The fuel salt inventory in the primary circuit of MOSART system will make 56 m^3 at the given core volume of ~32 m^3. In the given estimation, the inventories of fuel salt concerning the processing system and drain pipeline are not taken into account.

Table 5.7: Fuel salt inventory in primary circuit (m^3)

	MOSART	MSBR
Reactor		
Core	32.0	19
Plenums, inlets, outlets	7.5	6.2
Annulus	In radial shield 1.8	3.8
Reflectors	0.1 (radial)	1.4
Heat exchangers		
Pipes	6.2	7.6
Inlets, outlets	0.6	0.8
Pumps	4.0	5.2
Pipes	3.4	4.1
Off gas bypass loop	0.3	0.3
Other	0.3	0.3
Total	56.2	48.7

Mass characteristics of special materials inventories to reactor vessel and primary system are given in Tables 5.8 and 5.9.

Table 5.8: Special materials inventory for reactor vessel in MOSART system

	Material	Density, g/cm^3	Inventory, t
Fuel salt in reactor vessel	NaF-LiF-BeF$_2$	2.14	85.9
Reactor vessel, including metal internals and nozzles	HN80MTY	8.71	90.3
Vessel cover+ shielding unit	HN80MTY	8.71	91.2
Radial vessel shielding	Steel	7.85	174.0
Upper vessel shielding	Steel	7.85	
Lower axial vessel shielding	Steel	7.85	
Radial reflector	Graphite	8.9	78.6
Upper axial reflector	Graphite	8.9	
Lower axial reflector	Graphite	8.9	18.1

Table 5.9: Mass and cost indexes of initial material inventories (MOSART and MSBR)

	MOSART, t	MOSART, $	MSBR, t
AnF$_x$	7.32 (9.35)*	-	(1.47 +68)**
^{7}LiF-NaF-BeF$_2$	120	3 000 000	162
NaF-NaBF$_4$	456	2 240 000	456
Graphite	20	600 000	304
Hastelloy NM	1280	64 000 000	1377
Steel	3028	15 000 000	2840

*) TRU's for scenarios 1 and 2 respectively; **) UF$_4$ + ThF$_4$

Total mass inventory of LiF-NaF-BeF$_2$ in the primary system will make, approximately, 120 t (from them the reactor vessel will contain approximately 86 t of salt). Thus, for primary system is required 71.4 t NaF, 11.4 t ^{7}LiF (3.1 t of ^{7}Li metal) and 37.2 t BeF$_2$. In case of enrichment ^{7}Li up to 99.99 %, the cost of the salt solvent inventory will make 3 M$ at the price 170 $/kg on ^{7}LiF and will increase up to 10.7 M$ at cost 800 $/kg on ^{7}Li. It shall be reminded that only initial inventory of fuel salt in MSBR and DMSR demanded accordingly, more than 50 t and 113 t ^{7}LiF, respectively. Thus, transition from the ^{7}LiF-BeF$_2$-based salt used in MSBR to ^{7}LiF-NaF-BeF$_2$ mixture used in MOSART, allows essentially to decrease the cost of initial solvent inventory due to minimization of expensive ^{7}Li amount.

To assure the MOSART operation, it is necessary to have an opportunity to feed the reactor by fresh fuel, to remove the neutron poisons from the fuel salt and to keep redox potential in the system at an acceptable level. It will demand the additional charge of chemical reagents to primary system, including Li, Be, HF etc., during its operation.

Estimations show that the main contribution in operational annual consumption of account materials will make charge of Li in the fuel salt processing system of MOSART. For 50 years of operation, the amount of TRUs loaded in 2400 MWt MOSART system, with removal time for soluble fission products of 300 efpd, will make about 42-44 t. The amount of lanthanides removed from the fuel salt for same period will be about one order less. Then the total charge ^{7}Li for 50 years of reactor operation, using reductive extraction in bismuth for actinide recycling and lanthanides removal, will make more than 5 t. In case of ^{7}Li enrichment up to 99.99%, its cost, required for processing system, will make from 3 M$ up to 15 M$. Once again, it shall be noted that cost of ^{7}Li for the fine sets used in PWR is given. Almost for certain, if there will be a need for large amounts of ^{7}Li, its cost may fall more than in 5 times.

Some alternatives to reduce the amount of lithium flow in MOSART fuel processing system are available. For example, to replace lithium with the sodium dissolved of bismuth in reductive extraction stage of actinides recycling. In this case, lithium will be used only for fuel salt clean-up from lanthanides, and its mass flow rate in the processing system will decrease on the order. Replacement of a reductive extraction process by electro-deposition for actinides recycling is also possible. In this case, lithium in processing system practically is not required.

The cost of the secondary coolant is accepted equal 5 $/kg. At total volume of the secondary coolant in the system 240 m^3, its cost will make near 2.3 M$.

The greatest dimensions among components of equipment in MOSART correspond to the reactor vessel (height of 11.2 m, diameter of 4.5 m, mass ~180 t), a little bit smaller for drain tanks and heat exchangers (height of 9 m, diameter of 1.5 m, mass of ~ 50 t). It is close to the sizes of similar components of a 1000 MWe PWR design. The MOSART reactor vessel made from nickel-molybdenum alloy, in the collected condition, will have its own mass 538 t.

As can be seen from Table 5.9, MOSART system will demand 1280 t of Hastelloy NM for components of the primary and secondary circuits, approximately 100 t less than in the MSBR. Thus consumption on Hastelloy NM in the primary and secondary circuits of MOSART is approximately equal. Taking 50 $/kg for the specific cost of Ni-Mo alloy chosen for MOSART (6-8 times higher than cost of products made of stainless steel), for 1280 t, the cost of materials for components of the primary and secondary circuits in MOSART system will make about 64 M$. The price of this alloy was determined roughly on the basis of ratio between the average cost of sheet and high-quality hire from Hastelloy N in conditions of US manufacture in 1969-1970, making then for a sheet of 22 $/kg, 55 $/kg for nozzles and covers, and 66 $/kg for heat exchanger tubes.

MOSART reactor vessel will contain up to 20 t of the graphite reflector demanding replacement of every 4 years, and about 175 t of steel shielding. For comparison, the graphite initial inventory in MSBR makes 304 t, and the central part of core is subject to replacement every 4 years. It demands the additional charge of graphite 44 t/year. Thus, after 30 years of MSBR operation, about 1200 t of irradiated graphite will be collected, in comparison with 160 t for MOSART system. The total cost of graphite (at specific cost 30 $/kg) required for 30 years MOSART operation will not exceed 5 M$.

The carried out estimations of capital making cost of MSBR included significant uncertainty because of uncertainties in design. From them, in particular, followed that cost of primary and secondary salt carriers was insignificant compared to the total capital investments in the NPP, whereas expenses for components made from Hastelloy NM (29%) and graphite (6%) made about 35% from the total capital investments. In cost of components made of Hastelloy NM cost of an alloy itself made about 33%, and 67% of cost concern to expenses for manufacturing of the main components of primary system. It is now obvious that relative cost of a graphite reflector in MOSART capital making cost will make less than 1% valid essentially smaller amount of a used material and less strict requirements to its gas permeability.

The basic contribution to capital cost of MOSART, as well as in project MSBR, will bring the equipment made of alloy Hastelloy NM. As the weight and sizes of the main circulation pumps (hence, and their cost) not so strongly depend on capacity, transition from MSBR to MOSART conditions will not change the situation significantly. Transition from the LiF-BeF$_2$-ThF$_4$ fuel salt used in MSBR to LiF-NaF-Be$_4$ system, used in MOSART, will allow due to the better transport properties of last a little to improve specific heat removal (to lower metal consumption) in intermediate heat exchanger by 10%.

The analysis allows planning a number of the actions directed on reduction of cost for the equipment of MOSART primary and secondary systems. First of all, it is represented expedient instead of shell-tube heat exchanger to use the plate type heat exchanger, made of offered sheets with 1 mm thickness. Higher specific heat removal in such heat exchangers and cheaper sheet material (instead of pipes) will allow to lower their cost considerably.

High cost of Ni-base alloys, basically, may impose restriction on MSR development. Therefore it is very important to develop coating technology of Ni-free high temperature materials by Hastelloy NM films. In particular, the use of plate-type heat exchangers make easy coatings of heat exchange surface in comparison with coating of tubes with small diameter in the shell- tube heat exchanger.

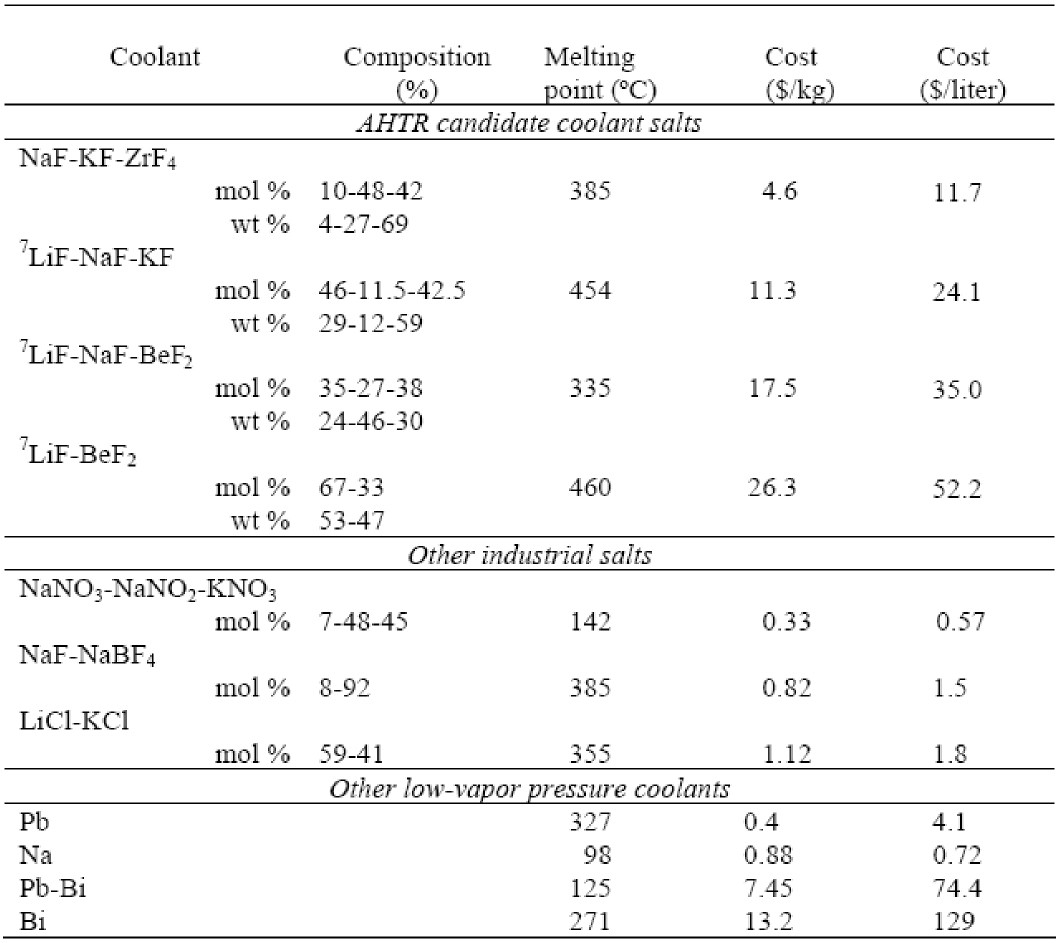
3.5.4.3 Cost of the salts as primary coolant in AHTR

Some considerations and data are available in [Williams,2006].

There are many important economic factors to be considered with respect to selecting coolant. However, at this stage of the AHTR design, it is most useful to focus on the cost of acquiring the salt coolant. The most important “salt cost” is that associated with a significant deployment of the AHTR. Unfortunately, this cost cannot be predicted because many of the constituents of candidate salts are not commodity chemicals, and the cost associated with deploying significant numbers of AHTRs would swamp the existing markets and change the price that is offered.

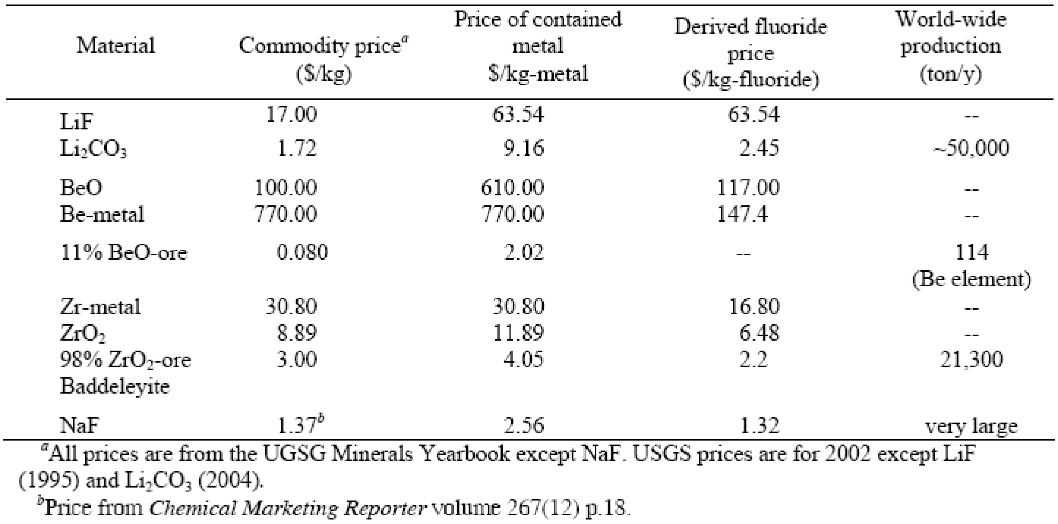
However, there are some basic trends and facts that can be used to help understand the classification and costs of various salt constituents. In 1971, ORNL conducted a survey of potential coolants that could be used as the secondary coolant in the MSBR design [Sanders,1971]. In the context of this survey, solicitations were made to vendors to provide prices for candidate salts. The goal was to establish an estimate of the unit prices required for supplying the coolant inventory (~280,000 liters) for a 1000-MWe MSBR plant. Some vendors could not supply estimates for an order this large, and extrapolation methods were employed to refine the estimates when possible. The results of these 1971 price estimates are shown in Table 5.10. A more recent survey of commodity pricing for relevant salt constituents is included as Table 5.11.

Table 5.10: Price estimate of salt coolants in 1970 (US $)



Coolant		Composition (%)	Melting point (°C)	Cost ($/kg)	Cost ($/liter)
AHTR candidate coolant salts					
NaF-KF-ZrF$_4$					
	mol %	10-48-42	385	4.6	11.7
	wt %	4-27-69			
^{7}LiF-NaF-KF					
	mol %	46-11.5-42.5	454	11.3	24.1
	wt %	29-12-59			
^{7}LiF-NaF-BeF$_2$					
	mol %	35-27-38	335	17.5	35.0
	wt %	24-46-30			
^{7}LiF-BeF$_2$					
	mol %	67-33	460	26.3	52.2
	wt %	53-47			
Other industrial salts					
NaNO$_3$-NaNO$_2$-KNO$_3$					
	mol %	7-48-45	142	0.33	0.57
NaF-NaBF$_4$					
	mol %	8-92	385	0.82	1.5
LiCl-KCl					
	mol %	59-41	355	1.12	1.8
Other low-vapor pressure coolants					
Pb			327	0.4	4.1
Na			98	0.88	0.72
Pb-Bi			125	7.45	74.4
Bi			271	13.2	129

Table 5.11: Commodity prices for selected materials



Material	Commodity price[a] ($/kg)	Price of contained metal $/kg-metal	Derived fluoride price ($/kg-fluoride)	World-wide production (ton/y)
LiF	17.00	63.54	63.54	--
Li_2CO_3	1.72	9.16	2.45	~50,000
BeO	100.00	610.00	117.00	--
Be-metal	770.00	770.00	147.4	--
11% BeO-ore	0.080	2.02	--	114 (Be element)
Zr-metal	30.80	30.80	16.80	--
ZrO_2	8.89	11.89	6.48	--
98% ZrO_2-ore Baddeleyite	3.00	4.05	2.2	21,300
NaF	1.37[b]	2.56	1.32	very large

[a] All prices are from the UGSG Minerals Yearbook except NaF. USGS prices are for 2002 except LiF (1995) and Li_2CO_3 (2004).

[b] Price from *Chemical Marketing Reporter* volume 267(12) p.18.

Based on [Sanders,1971] and the more recent commodity values, it is evident that the constituents of candidate coolants fall into three categories: (a) relatively inexpensive commodity chemicals (NaF); (b) moderately expensive specialty materials produced on a large scale (Zr metal, LiF); and (c) very expensive specialty materials (^{7}LiF, Be). For the 1971 study, the price of 99.995% ^{7}Li was assumed to be $120/kg-LiF. Some of the values for Zr-prices in Tables 5.10 and 5.11 do not reflect the cost associated with hafnium removal.

It is possible that this classification could change for some constituents based on market factors not yet considered. For example, there are two alternative raw material sources for obtaining hafnium-free ZrF_4 (a) recovery of irradiated cladding and fuel-element hardware, and (b) recovery of ZrF_4 from spent pickling-solution streams (from hafnium cleaning of Zircalloy). It is also possible that the market could change the specialty prices associated with RbF and KF compounds. Alkali ores possess considerable amounts of Rb and K minerals that remain unused and accumulate in tailing piles. Rubidium has an unusual position with respect to markets. While the world market for rubidium is extremely small (4 tons/year), it ranks as the 23rd most abundant element on earth (16th most abundant metal), more abundant than copper, lead, and zinc, and much more abundant than lithium or cesium.

3.5.5 Non-proliferation considerations

The fuel cycle of MSR working as actinide burner (incinerating transuranium fuel) brings no exceptional requirements regarding to proliferation resistance – the standard care has to be paid to the front-end processing of transuranium fuel. The circulating fuel subjected to on-line reprocessing contains the wide mixture of plutonium isotopes, together with other minor actinides, and is not a potentially nuclear weapon-usable material.

However, the MSR working as Th-breeder requires special vigilance dedicated to the ^{233}U non-proliferation. As pure ^{233}U can be generated from separated ^{233}Pa, the only way how to increase proliferation resistance of the fuel cycle is via denaturing the separated protactinium by the “dirty” uranium from the MSR fuel circuit containing, in addition to ^{233}U, also ^{232}U and ^{234}U which decrease the proliferation risk by increasing the radiation barrier caused by their fission products. Theoretically, the uranium in the MSR could also be denatured by ^{238}U, which could generate all known products of U–Pu fuel cycle. However, this way of denaturing destroys a great advantage of the MSR systems – minimized production of radioactive wastes, mainly higher actinides.

Furthermore, the MSR on-line reprocessing technology represents an extremely difficult process to master, the technology has to be directly connected with the MSR primary circuit and finally the breeding factor of the reactor is relatively low. These features contribute to increase the proliferation technical difficulty and improve the safeguardability of MSR systems.

4 Pre-selection of reference salts for the different applications and compilation of properties in a database

As summarised in Tables 4 and 5 (cf. section 3), different applications of molten salts in nuclear systems have been identified, for fuel salts and coolant salts. Various aspects of their applications and properties have been discussed in this report, leading to the following pre-selection.

The $^7LiF-BeF_2$ (66:34 in mol%) salt is the selected fuel carrier for the moderated (thermal) molten salt thorium breeder, giving as fuel salt $^7LiF-BeF_2-ThF_4-UF_4$. From neutronic as well as chemical point of view, there are no alternatives for this salt that do not penalise the breeding capacity of the reactor.

$^7LiF-ThF_4$ (78:22 or even 71:29 in mol%) is the reference fuel solvent composition for the non-moderated (fast) molten salt thorium breeder reactor. The neutronic analysis of the TMSR concept has demonstrated the feasibility of the concept, but it must still be clarified whether the physico-chemical properties (melting temperatures, solubility for the actinide trifluorides, density, expansivity, viscosity, thermal conductivity, heat capacity) of this salt fuelled by significant amount of UF_4 (2-4% of the total heavy nuclei in the moderated and 12-18% in the non-moderated systems) or AnF_3 (up to 25% of the total heavy nuclei in the non-moderated concept) are consistent with safe operation of the reactor and fuel salt clean-up unit. To tune these properties, addition of other components is possible. The most obvious is BeF_2 but there is an incentive to keep the content of this material low (e.g. $71LiF-2BeF_2-27ThF_4$ or $75LiF-5BeF_2-20ThF_4$ in mole%) or even zero. Alternatives are NaF and possibly CaF_2. Therefore, the $^7LiF-NaF-ThF_4$ system must be further analysed, whereas scoping studies of the $^7LiF-CaF_2-ThF_4$ system are required to assess the feasibility of this composition, including suitability for fuel salt processing.

The molten salt actinide burner is a non-moderated system also. The carrier salt for this application must have good solubility for the actinide trifluorides and this can be achieved using $^7LiF-NaF$ as solvent or $^7LiF-(NaF)-BeF_2$. Again, the goal is to keep the content of BeF_2 low or even zero. An interesting alternative is the use of plutonium and minor actinides as start-up for the thorium cycle in the MSR, leading to $^7LiF-NaF-ThF_4$ carrier salt.

In summary, it is clear that the $^7LiF-(NaF)-AnF_4-AnF_3$ salt (where An represent actinides) is the key system to be investigated in parallel to the $^7LiF-(NaF)-BeF_2-AnF_4-AnF_3$ system. Optimisation of the fractions of the components is still needed with respect to mentioned-above physico-chemical properties, corrosion behaviour in the Ni-Mo alloys and fuel salt processing.

For coolant salts, one has to make a distinction between salt for in-core use (primary coolant) and salts for out-of-core use (secondary or intermediate coolants). For primary coolants in thermal reactors, the requirements are very similar to thermal breeder reactors and $^7LiF-BeF_2$ (66-34 with Tm=460℃) is the main candidate, with $^7LiF-NaF-KF$ (46-11.5-42.5 with Tm=454℃), LiF-NaF-RbF (46.5-6.5-47 with Tm=426℃) and $^7LiF-NaF-BeF_2$ (30.5-31-38.5 with Tm=316℃) as alternatives. Note that the last alternative molten salt mixture has the lowest liquidus temperature.

For secondary coolant applications, neutronic considerations nor actinide solubility play a role and a wider choice of materials is possible. For MSRs in which tritium control is the main concern, the $NaF-NaBF_4$ (8:92 with Tm=385℃) system is the prime candidate, mainly because of its satisfactory tritium trapping. A ternary salt $LiF-NaF-BeF_2$ should be considered in future studies as alternative secondary coolant because a freezing temperature range of about 315-335℃ would be a practical value for engineering consideration.

For solid fuel fast reactors, no salt has been clearly identified as prime candidate in this study. However, recent studies at MIT have identified $NaCl-KCl-MgCl_2$ as a promising candidate.

Finally, heat transfer applications require a cheap and stable salt. $NaNO_3-KNO_3$ possibly with addition of $NaNO_2$ is the main candidate identified at this stage.

5 Identification of first priority needs in salt properties determination

The salt properties are very important for the assessment of the feasibility of the various nuclear applications of molten salts. As discussed, a distinction must be made for fuel salts and coolant salts, although many common aspects can be identified. In general one can group the properties in (a) melting temperature, (b) physico-chemical properties, and (c) actinide solubility.

The melting temperatures of most binary and ternary salts are reasonably well known, and reliable thermodynamic models have been developed to predict melting points of ternary and quaternary mixtures.

Exceptions are salts containing significant amount of transuranium actinides of relevance to burner reactors. In this field, a significant effort is needed in the near future. The main needs are thus (i) measurements on plutonium and other actinide trifluorides (ii) verification measurements in ternary and quaternary systems to check and improve thermodynamic models.

Physico-chemical properties (density, viscosity, heat capacity, thermal conductivity) are poorly known for most of the salts that have been identified. An exception is the ^{7}LiF-BeF$_2$-ThF$_4$-UF$_4$ system that was extensively studied in the 1960s. Of these properties, the density (or molar volume) follows ideal behaviour and can be easily obtained from the pure compounds. This is not true for the other properties, but there is generally lack of data. Systematic experimental studies are needed here, especially on composition with actinides. Especially thermal conductivity is poorly known, and also theoretical models are poorly developed. In this field, the benefits from atomistic calculations must be explored, in combination with local structure determination techniques (NMR, Raman, EXAFS) to create the fundamental basis for the understanding of the molten salt properties.

Actinide solubility is a key issue for transmutation or burner fuels, but only a limited number of studies on PuF$_3$ solubility exist and none on the solubility of NpF$_4$/NpF$_3$, AmF$_3$ or CmF$_3$. Solubility determinations in the systems with proper redox potential are therefore of prime importance. A prerequisite for such measurements is the availability of the pure actinide tri- and tetrafluorides in significant quantities, for which dedicated synthesis facilities are needed.

6 Conclusions

MSR concepts (TMSR) offer alternative options for breeding and waste reduction with the added value of liquid fuel (intrinsic safety features, fuel cycle flexibility, on-line fuel processing, no fuel refabrication required, in-service inspection). For breeding, MSR is especially well fitted to thorium cycle.

The newly developed TMSR-NM concepts combine the assets of high temperature operation (cf. VHTR), breeding capability together with good intrinsic safety parameters in fast spectrum (unique among fast spectrum systems, SFR, LFR), high efficiency for waste minimization or reduction, and competitive economics. Attractive MSR designs are available for breeding (TMSR in thermal and fast spectrum) and for MA burning (MOSART). They are robust reference configurations (with significant improvement compared to MSBR), allowing to concentrate on remaining R&D issues.

In a broader sense, the development and commercialization of a new coolant technology and its use in multiple reactor concepts is a major challenge. However, the increasing demands for high-temperature heat, the ability to convert such heat efficiently to electricity, and the interests in advanced reactors for breeding and waste management are creating the incentives to develop this family of technologies. The development and commercialization of such a coolant technology opens several new frontiers for nuclear energy.

The development of liquid salts is significantly impeded by the complexity of their behaviour, as a result of their multi-component nature, in contrast to mono-specific coolants. This is a long term perspective to understand the behaviour and properties of liquid salts and to proceed towards a predictive approach making easier the selection of the appropriate salt composition for every given application.

The ALISIA project is a concrete step towards this objective. In the frame of the project, candidate salt compositions have been re-assessed for the different applications envisioned to liquid salts. The interest of FLiBe (with or wo Be) has been confirmed (TMSR, TMSR-NM, and MOSART). Exact compositions are still to be optimized but ALISIA has conducted to a real screening.

There is an active European network on liquid salts and MSR, successful at harmonizing R&D programs .in Europe. The effort is to be continued in further projects (SUMO in the 7th Euratom FWP, ISTC-3749).

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