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Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop

June 2006

Prepared by
D. F. Williams

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Nuclear Science and Technology Division

ASSESSMENT OF CANDIDATE MOLTEN SALT COOLANTS FOR THE NGNP/NHI HEAT-TRANSFER LOOP

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EXECUTIVE SUMMARY

This report provides an assessment of candidate salts proposed as the coolant for the loop that shuttles heat from the Next Generation Nuclear Plant (NGNP) to the Nuclear Hydrogen Initiative (NHI) hydrogen-production plant. The physical properties most relevant for coolant service were reviewed, and key chemical factors that influence material compatibility were also analyzed for the purpose of screening candidate salts. A preliminary assessment of the cost of the raw materials required to produce the coolant is also presented.

Salts that are suitable for use as the primary coolant in a high-temperature nuclear reactor were previously analyzed. Some of the fluoride salts identified in the previous study are also appropriate for consideration as the secondary coolant in a heat-transfer loop; therefore, results from the previous report are used in this document. However, alternative coolant salts (i.e., chlorides and fluoroborates) that were not considered in the previous report should be considered for service in the heat-transfer loop. These alternative coolants are considered in this report.

Table ES.1 presents a summary of the properties of the candidate coolants for the heat-transfer loop. Certain factors in this table, such as melting point and vapor pressure, can be viewed as stand-alone parameters for screening candidates. Heat-transfer properties are considered as a group in Sect. 3 in order to evaluate the combined effects of various properties. Deficiencies in the properties database were found in the same areas as were identified in the previous report: (a) thermal conductivity is the property with the greatest uncertainty and is the most difficult to measure, and (b) the heat capacity database can be improved with modern instruments and a modest effort.

The same trends in ranking coolant performance found in the previous report were also found in this report: lighter “low-Z” salts (salts containing elements with low atomic number) tend to exhibit better heat-transfer performance metrics. Ranking of salts based upon corrosion characteristics was again found to be inconclusive; however, some key factors were identified for further study. In particular, it appears that better preparative chemistry methods are needed to produce the high-purity chloride salts for corrosion studies. As in the case of fluoride salts, the identification and testing of redox buffers to suppress corrosion of the container alloy is highly desirable and may be absolutely necessary for operation of the heat-transfer loop at the highest temperatures with other halide salts.

Table ES.1. Summary of the properties of candidate coolants for the NGNP/NHI heat-transfer loop

Salt [a]	Formula weight (g/mol)	Melting point (ºC)	900ºC vapor pressure (mm Hg)	Heat-transfer properties at 700ºC			
				ρ, density (g/cm^3)	**ρ*Cp**, volumetric heat capacity (cal/cm^3-ºC)	**μ**, viscosity (cP)	**k**, thermal conductivity (W/m-K)
LiF-NaF-KF	41.3	454	~ 0.7	2.02	0.91	2.9	0.92
$NaF-ZrF_4$	92.7	500	5	3.14	0.88	5.1	0.49
$KF-ZrF_4$	103.9	390	1.2	2.80	0.70	< 5.1	0.45
$LiF-NaF-ZrF_4$	84.2	436	~ 5	2.92	0.86	6.9	0.53
LiCl-KCl	55.5	355	5.8	1.52	0.435	1.15	0.42
LiCl-RbCl	75.4	313	--	1.88	0.40	1.30	0.36
$NaCl-MgCl_2$	73.7	445	< 2.5	1.68	0.44	1.36	0.50
$KCl-MgCl_2$	81.4	426	< 2.0	1.66	0.46	1.40	0.40
$NaF-NaBF_4$	104.4	385	9500	1.75	0.63	0.90	0.40
$KF-KBF_4$	109.0	460	100	1.70	0.53	0.90	0.38
$RbF-RbF_4$	151.3	442	< 100	2.21	0.48	0.90	0.28

[a] Salt compositions are given in Table 1.

1. INTRODUCTION

The purpose of this report is to provide a review of relevant properties of candidate salts for use in the evaluation and ranking of coolants for the heat-transfer loop that shuttles heat from the Next Generation Nuclear Plant (NGNP) to the Nuclear Hydrogen Initiative (NHI) hydrogen-production plant. Considerable experience exists with molten salts; however, previous nuclear experience with molten salts was for reactor systems that contained fissile and fertile material in the primary fluid (which served as both fuel and primary coolant). The NGNP/NHI heat-transfer loop will use "clean" coolant salt and will operate at much higher temperatures than previous applications. The assumption for previous nuclear applications with molten salt was that the container alloy would need to last for 30 years. For the present heat-transfer-loop application, the system requirements and salt properties may be quite different than for previous applications. Therefore, a new assessment of coolant options is required.

High-temperature operation (>700ºC) and new compositions have been evaluated based on the open literature and internal reports available to the author and on use of the best available estimation techniques. Recommended estimation methods are identified when possible, and a brief discussion of measurement techniques is included when necessary. A number of fluoride salt compositions have been examined in detail in previous studies (e.g., eutectic compositions of $LiF-BeF_2$, $NaF-BeF_2$, LiF-NaF-KF, and $NaF-ZrF_4$). For applications that use molten salt outside of a neutron field, additional salts may be considered. Candidate coolants can include salts deemed unsuitable as a primary coolant but judged as acceptable for use in a heat-transfer loop. Familiar oxygen-containing salts (nitrates, sulfates, and carbonates) are excluded from consideration because they do not possess the necessary thermochemical stability at high temperatures. These salts are also incompatible with the use of carbon materials because they decompose at high temperatures to release oxygen, which rapidly reacts with the available carbon.

The screening logic for selecting secondary salt coolants requires that the elements constituting the coolant must form compounds that:

1. have chemical stability at T > 800ºC,
2. melt at useful temperatures (<525ºC) and are not volatile, and
3. are compatible with high-temperature alloys, graphite, and ceramics.

In addition to the fluoride salts considered in an earlier report, two families of salts fulfill these three basic requirements: (a) chloride salts and (b) alkali fluoroborates (MBF_4, M = alkali element). The properties of these two families of salts are reviewed and evaluated in this report. Other coolants (water, liquid metals, and fluoride salts) are included for the purpose of heat-transfer comparisons in Sect. 3.

2. REVIEW OF PROPERTIES

2.1 MELTING POINT AND VAPOR PRESSURE

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 is dependent, to some degree, on the system design. Because salt coolants possess high heat capacity, the temperature drop in a salt heat-transfer loop is typically smaller than for other high-temperature coolants. The previous generation of secondary coolant salts for use in a Molten Salt Reactor was expected to operate in a steam generator; thus, a secondary-salt freezing point less than 400ºC was required [1].

The situation for the NHI heat-transfer loop is different from that of primary or secondary salts identified for the Molten Salt Reactor. We do not know the exact demands that the heat-transfer loop will place on a molten salt coolant, nor do we know the demands that will be defined in the heat exchangers at each end of the loop. Thus, we cannot set the freezing point requirements for secondary coolant with confidence. However, a recent report [2] has used properties of typical salt coolants, some basic assumptions, and hypothetical heat exchanger designs in order to predict thermal profiles in both the heat-transfer loop and the heat exchangers at each process interface: (a) the intermediate heat exchanger at the reactor and (b) the process heat exchanger at the hydrogen plant. The previous report [2] considered the helium-cooled reactor that exchanged heat with a molten salt to be the heat-transfer agent in the loop. The peak helium temperature is assumed to be 900ºC, the salt is assumed to be supplied to the hydrogen plant at ~870ºC, and the working fluid in the hydrogen plant is assumed to be raised from an inlet temperature of 340ºC to 850ºC. Various loop/heat-exchanger configurations and cases were analyzed in this report. For the reference conditions analyzed, considerable thermal margin to freezing exists. The minimum steady-state temperature in the loop under reference conditions is ~680ºC, which represents a margin for freezing of 200ºC for $NaF\text{-}NaBF_4$ salt and 130ºC for FLiNaK salt. Grace periods for the onset of freezing were estimated to occur between 65–80 min for an off-site power loss and between 5–7 min for a loss-of-heat-sink transient. These times were deemed reasonable for taking actions to prevent the problems that would occur with substantial freezing of the salt. Therefore, the previous report [2] appears to indicate that the properties and freezing points associated with FLiNaK (454ºC m.p.) and $NaF\text{-}NaBF_4$ (385ºC) may be acceptable for use in the heat-transfer loop. Other options for heat-transfer agents are identified in this report.

An extensive database of phase diagrams exists for salt systems of all types [3]; therefore, there is very little need to pursue estimation techniques. Because no single-component salt freezes at a sufficiently low temperature, multicomponent 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 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 the freezing point (e.g., cost or some other physical or chemical property).

Salts that are useful as secondary coolants have been identified in previous reports [4–6]: (a) alkali-fluorides, (b) ZrF_4-salt mixtures, (c) fluoroborate salts, and (d) chloride salts. Beryllium fluoride-containing salts have been excluded from this list because of the potential toxicity of beryllium compounds and their high cost. Table 1 lists the primary eutectic compositions in each salt family in order of freezing point. Phase diagrams [5, 6] of the most important binary fluoroborate and chloride systems are included in Figs. 1–8. Discussion and analysis of phase diagrams and properties of the alkali fluorides and ZrF_4-salt mixtures were included in a previous report [7].

Table 1. Useful salt compositions (mole percent) and eutectic temperatures for the NGNP/NHI heat-transfer loop

Alkali fluorides	ZrF_4 salts	Fluoroborate salts	Chlorides
	NaF-ZrF$_4$ (59.5-40.5) 500ºC		
LiF-NaF-KF (“FLiNaK”) (46.5-11.5-42) 454ºC	**LiF-NaF-ZrF$_4$** (42-29-29) 460ºC	**KF-KBF$_4$** (25-75) 460ºC	**NaCl-MgCl$_2$** (63-37) 475ºC (58-42) 445ºC
	LiF-NaF-ZrF$_4$ (26-37-37) 436ºC	**RbF-RbBF$_4$** (31-69) 442ºC	**KCl-MgCl$_2$** (68-32) 426ºC
	NaF-RbF-ZrF$_4$ (33-24-43) 420ºC		
			LiCl-KCl-MgCl$_2$ (9-63-28) 402ºC
	KF-ZrF$_4$ (58-42) 390ºC	**NaF-NaBF$_4$** (8-92) 384ºC	**NaCl-KCl-MgCl$_2$** (20-20-60) 396ºC
			LiCl-KCl (59.5-40.5) 355ºC
			LiCl-KCl-MgCl$_2$ (55-40-5) 323ºC
			LiCl-RbCl (58-42) 313ºC

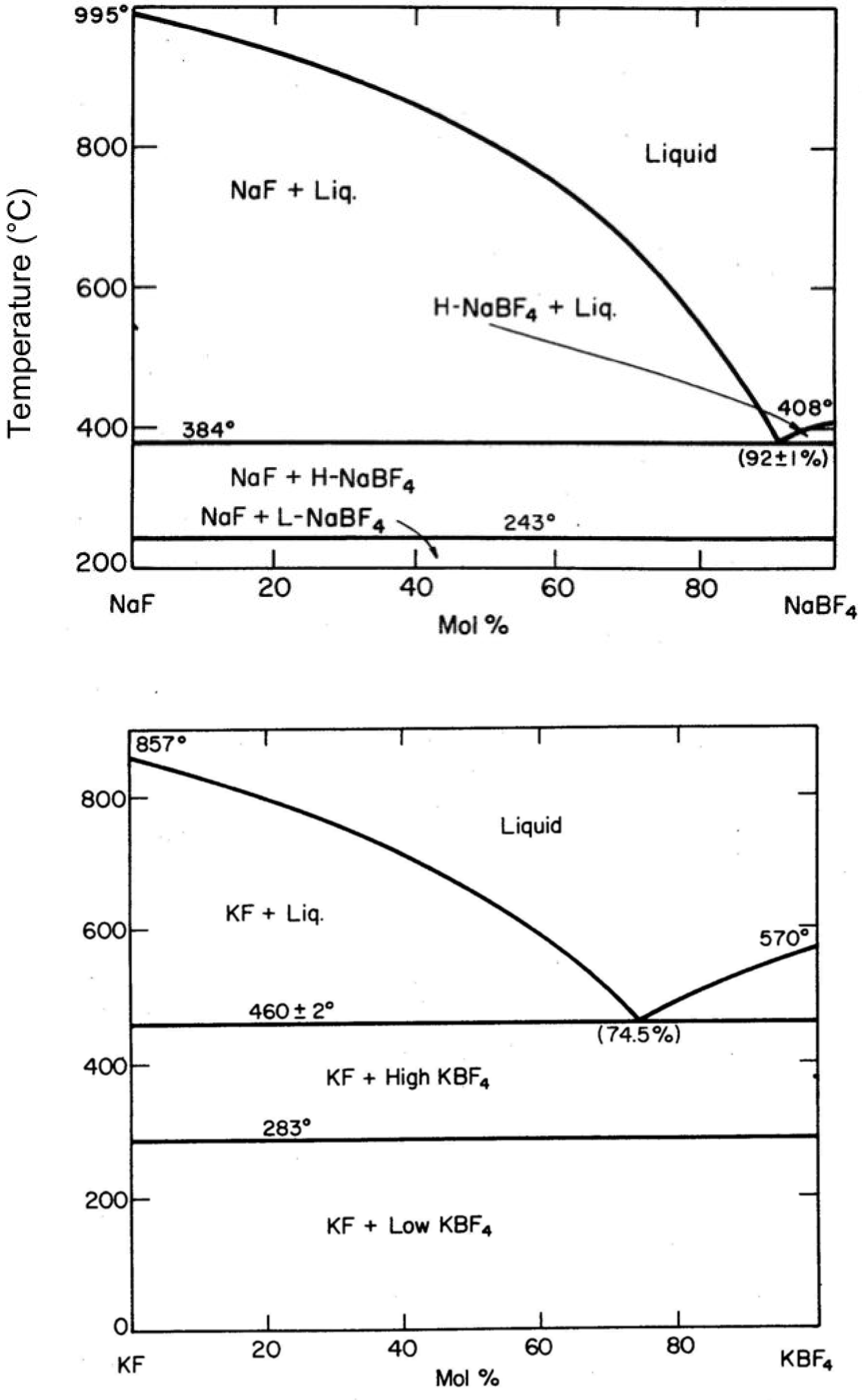

Fig. 1. Binary phase diagrams of NaF-$NaBF_4$ and KF-KBF_4 systems.

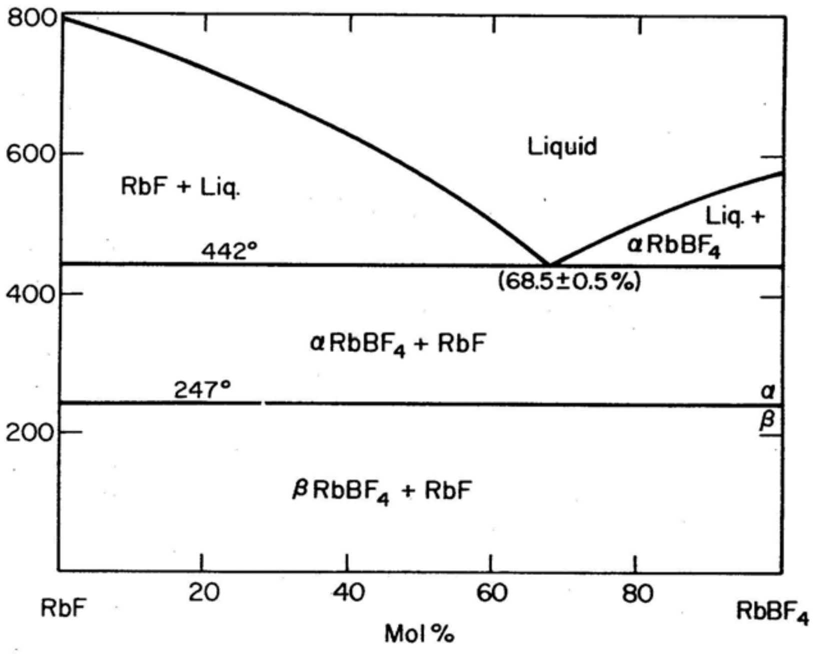

Fig. 2. Binary phase diagram of RbF-$RbBF_4$ system.

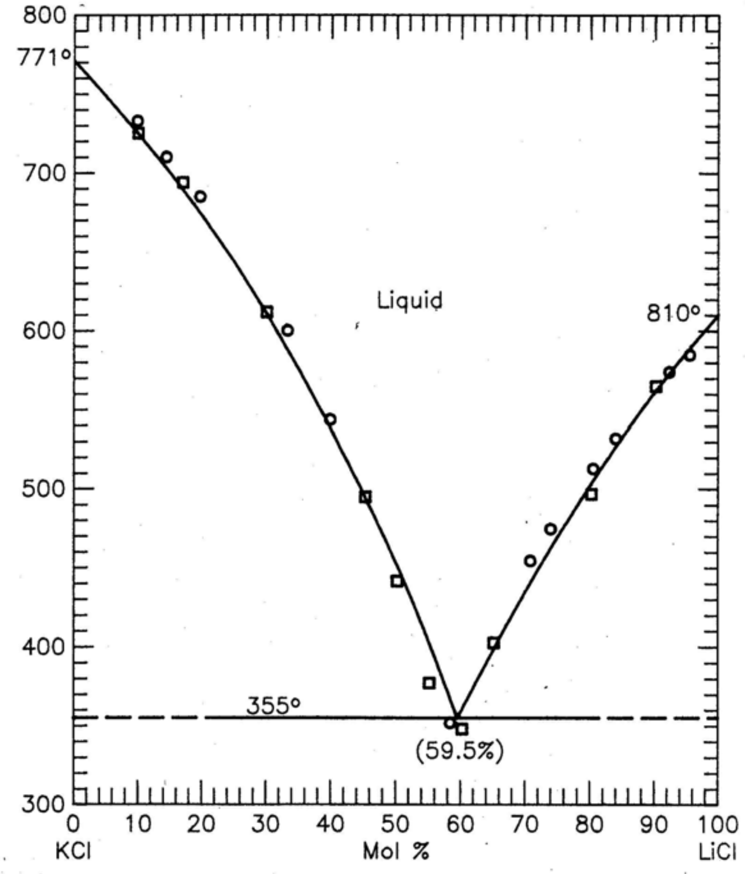

Fig. 3. Binary phase diagram of LiCl-KCl system.

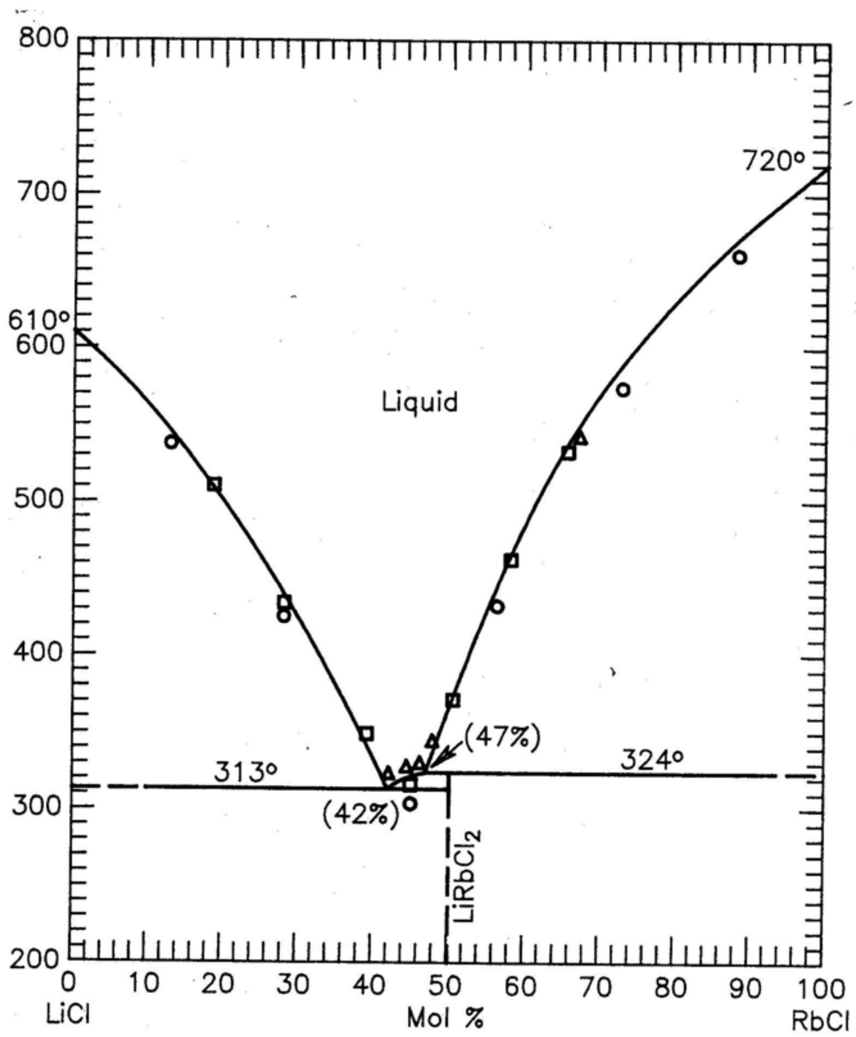

Fig. 4. Binary phase diagram of LiCl-RbCl system.

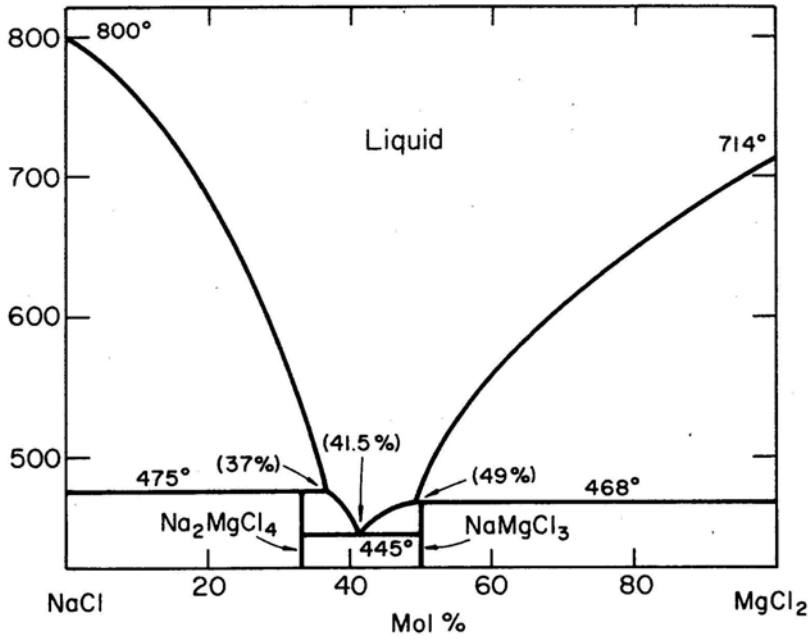

Fig. 5. Binary phase diagram of NaCl-$MgCl_2$ system.

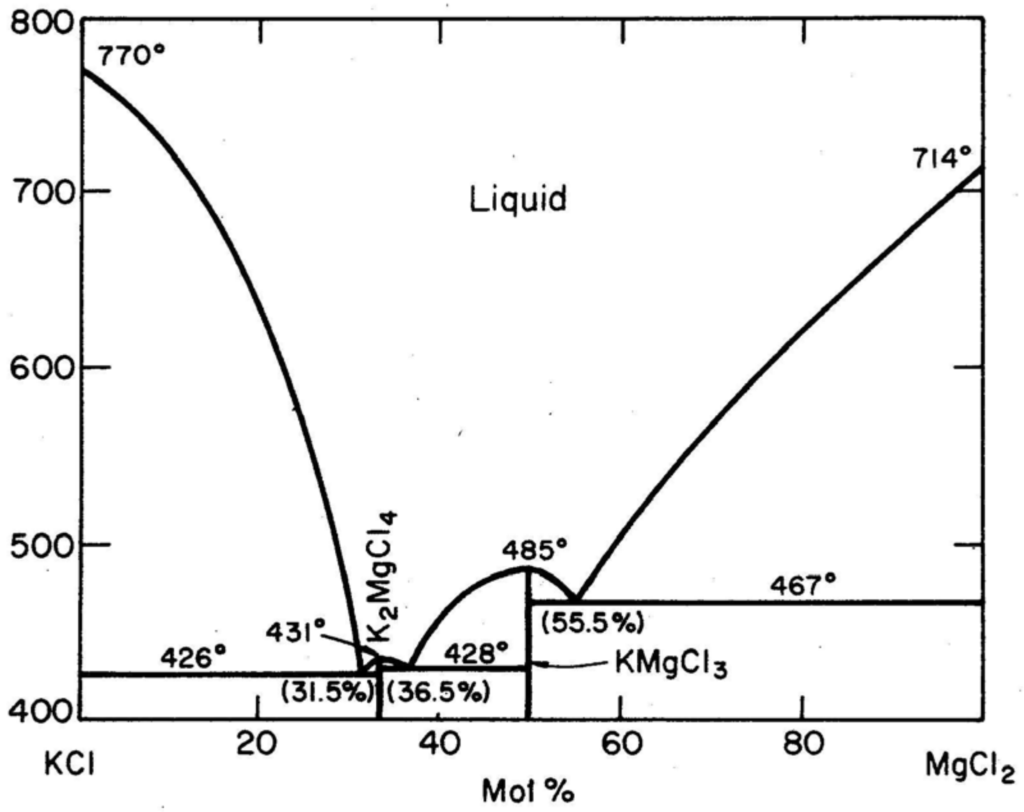

Fig. 6. Binary phase diagram of KCl-$MgCl_2$ system.

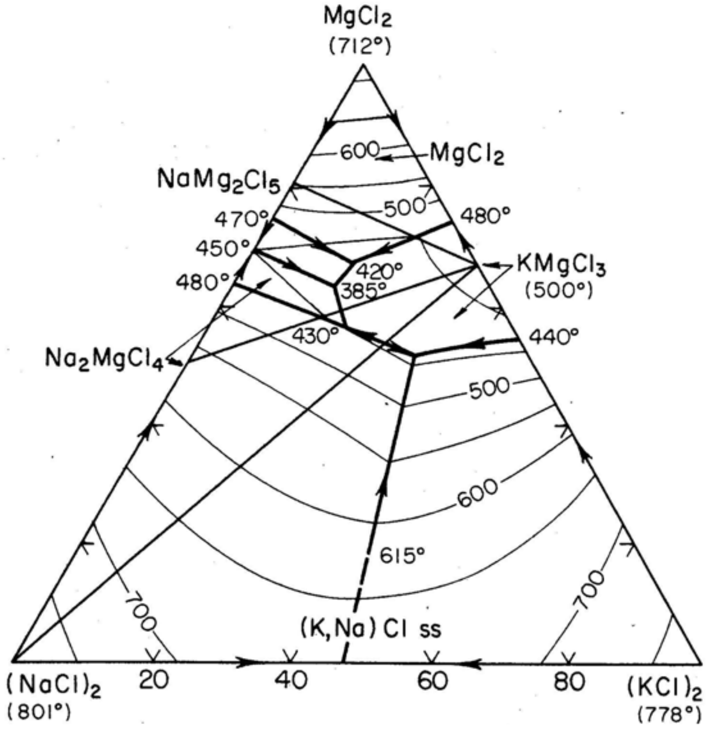

Fig. 7. Ternary phase diagram of NaCl-KCl-$MgCl_2$ system.

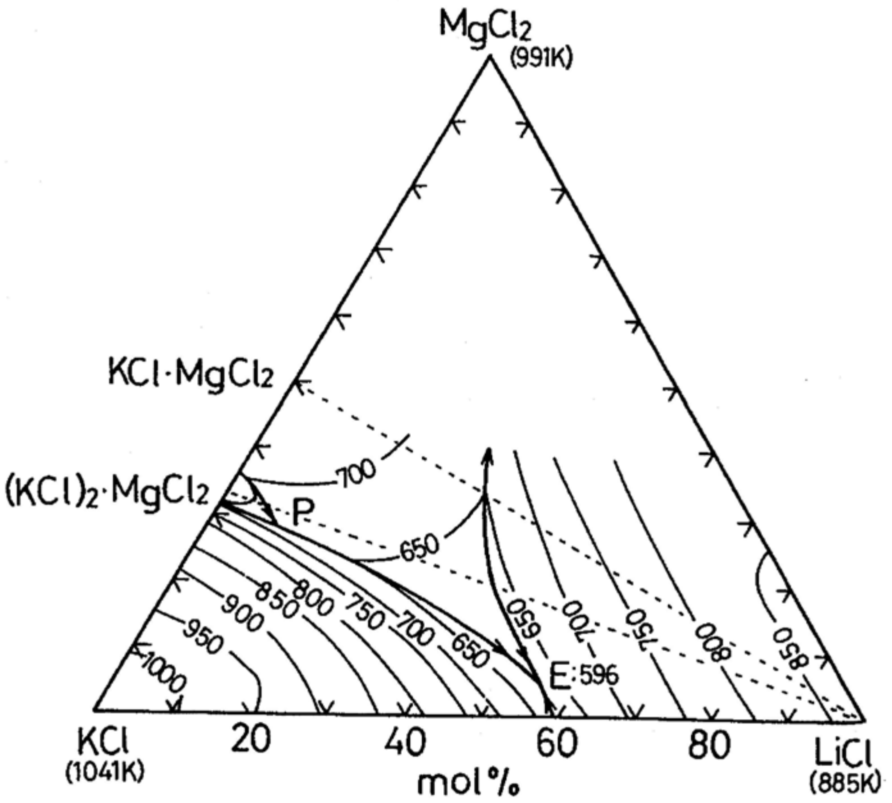

Fig. 8. Ternary phase diagram of LiCl-KCl-$MgCl_2$ system [6].
(Temperatures are expressed in degrees Kelvin.)

Many salts with reasonably low melting points have been excluded from the list in Table 1. The two primary reasons for exclusion are as follows: either the salts exhibit too high a vapor pressure (for example, $AlCl_3$, $ZrCl_4$, and $BeCl_2$ salts) or they are too corrosive for use at high temperatures [metal halides of Fe, Sn, Bi, Cd, Zn, and Tl, as well as oxygen-containing salts (nitrates, sulfates, and carbonates)]. Two classes of salts that meet the criteria in the previous list and are not necessarily too volatile or too corrosive have also been excluded from Table 1: (a) heavy halide salts containing bromine and iodine, and (b) mixed-halide salts with dissimilar halide anions (mixtures of chlorides, fluorides, bromides, and iodides). The poor heat-transfer metrics of heavy salts and the extra expense of bromine and iodine constituents argue against the use of these salts. The mixed-halide candidates do not offer compelling advantages over those salts identified in Table 1, and are considerably more complicated systems to prepare and understand. The discussion in Sect. 3 indicates that consideration of heavy halide salts (e.g., bromine) is likely to be prohibitive because chloride salts represent the lower limit of desirable heat-transfer performance for salts.

It is useful to review the basic phase behavior of the pure components and mixtures that comprise Table 1. Table 2 contains a summary of freezing point, boiling point, and 900ºC vapor pressure for all pure-component constituents and most of the salt mixtures identified in Table 1.

Table 2. Selected phase transition properties of salt compounds and key mixtures

Salt constituent(s)	Freezing point (ºC)	Normal boiling point (ºC)	900ºC vapor pressure (mm Hg)
LiF	845	1681	0.1
NaF	995	1704	0.07
KF	856	1502	1.2
RbF	775	1408	0.75
ZrF_4	912	905 (sublimes)	722
BF_3	−126	−100	NA
$NaF-NaBF_4$	385	694	9500
$KF-KBF_4$	460	1070	100
$RbF-RbBF_4$	442	>1070	<100
LiCl	610	1382	7
NaCl	808	1465	2.5
KCl	772	1407	2.0
RbCl	717	1381	3.8
$MgCl_2$	714	1418	7
LiCl-KCl	355	~1400[a]	5.8
$NaCl-MgCl_2$	445	>1465	< 2.5
$KCl-MgCl_2$	426	>1418	< 2
LiF-NaF-KF (46.5-11.5-42)	454	1570[a]	0.5
$NaF-ZrF_4$ (59.5-40.5)	500	~1350[a]	6
$KF-ZrF_4$ (58-42)	390	~1450[a]	1.2

[a] Estimated by extrapolation of lower-temperature data (~1100ºC) or assumption of ideal mixture behavior.

In nearly ideal mixtures of the alkali halides, each component exerts its own pressure, shown in Fig. 9, in proportion to its molar composition. For mixtures of alkali halides with polyvalent elements or with BF_3, a dramatic depression of the native vapor pressure of the pure components (i.e., ZrF_4) is noted, due to formation of coordination complexes, as described in an earlier report and illustrated in Fig. 10. This depression of native vapor pressure also occurs for the same reasons in the fluoroborate system and the chloride salts and displays the same trends as described in the previous report (more effective halide-ion donation/complex formation for the heavier alkali halides). Thus, the mixture of BF_3 with heavier alkali fluorides results in a lower-vapor-pressure salt. The data are not as extensive for the chloride salts; however, a significant drop in vapor pressure was measured in the KCl-$MgCl_2$ system as compared with pure $MgCl_2$ and pure KCl [8]. Figure 10 demonstrates that, in general, optimized compositions of fluorides have the lowest vapor pressure, followed by chlorides, and then fluoroborates.

A previous report on the heat-transfer-loop application [2] considered two salt options for the heat-transfer loop: LiF-NaF-KF eutectic (i.e., “FLiNaK”) and (b) the sodium fluoroborate (NaF-$NaBF_4$) eutectic. Table 2 and Fig.10 indicate that the estimated vapor pressure [actually a decomposition pressure of $NaBF_4 \rightarrow NaF + BF_{3(g)}$] of sodium fluoroborate at 900ºC is extremely high (~13 atm) and will likely exclude this salt from consideration. Potassium fluoroborate has a much lower vapor pressure at 900ºC (~0.13 atm) and is a better choice for the heat-transfer-loop application. The pressure of potassium fluoroborate at 900ºC is approximately equal to the vapor pressure of sodium fluoroborate at 620ºC [the temperature proposed for use of NaF-$NaBF_4$ in the Molten Salt Breeder Reactor (MSBR)]. The vapor pressure of the rubidium fluoroborate eutectic has not been measured, but it will certainly be somewhat less than the value for the potassium fluoroborate eutectic.

In a previous report [7], the importance of the identity and behavior of the vapor species was highlighted for the ZrF_4-containing salts. The recommendation was to consider ZrF_4 salts that exhibited very low vapor pressures (i.e., salts with 20–45 mol % ZrF_4, depending on the alkali fluoride present and the temperature) to avoid the problems associated with the sublimation and transport of ZrF_4. A similar situation may apply to $MgCl_2$-containing salts, and it is likely that a chloride salt composition that minimizes the vapor pressure of $MgCl_2$ (~20–45% $MgCl_2$) will be preferred. This composition range coincides with the location of the low-temperature eutectics containing $MgCl_2$ and alkali halides. Salt mixtures containing BF_3 in the form of a fluoroborate anion (BF_4^-) present some special features that merit additional discussion.

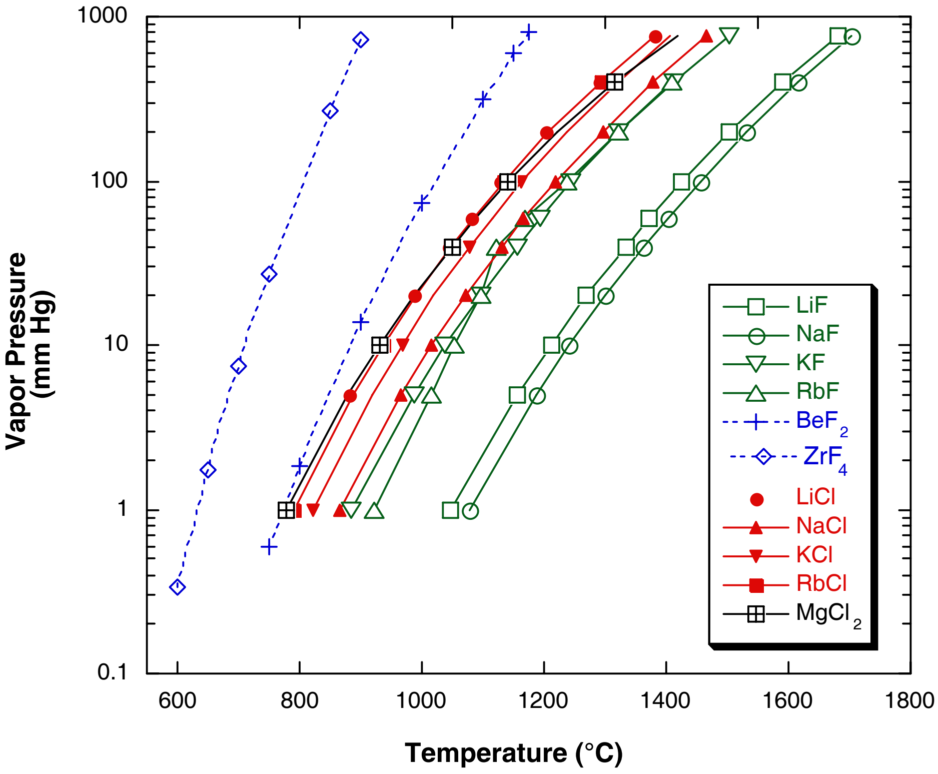

Fig. 9. Vapor pressure of constituents of candidate coolant salts.

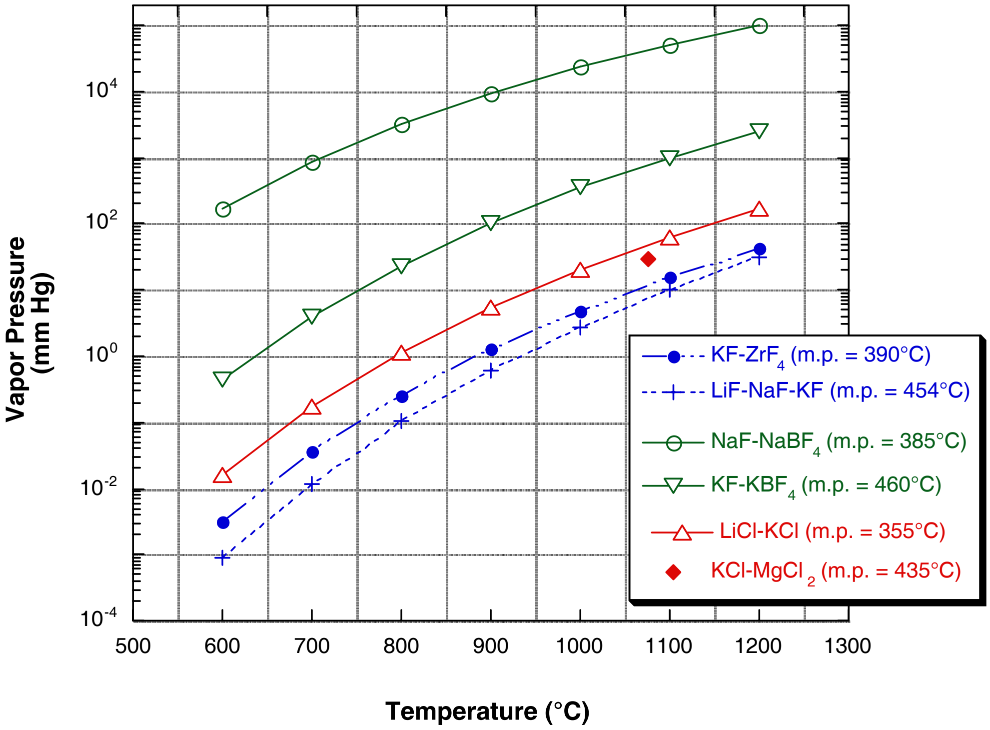

Fig. 10. Vapor pressure of selected candidate coolant salts.

Consideration of fluoroborate salts as the secondary coolant for the MSBR was driven by the need for a low-cost coolant that exhibited superior heat-transfer properties. Fluoroborates met these requirements, but they also imposed some additional constraints, often referred to as "nuisance" factors, that should be recognized. Most of these nuisance factors do not affect the fundamental viability of the fluoroborate coolant option and are due to the significant pressure (>0.5 atm) of BF_3 that exists over a fluoroborate salt at useful temperatures.

Work at Oak Ridge National Laboratory (ORNL) identified some of the practical issues that must be addressed when using fluoroborates [9, 10]. In order to maintain the eutectic salt composition, it is necessary to monitor and control the BF_3 pressure of the cover gas. There are inevitably purge gas streams, for example, those associated with shaft seals and bearings on pumps or other machinery. Therefore, the exhaust from these systems must include a means to trap BF_3 or to recycle it.

Some additional factors should be recognized that do not require special process systems but that change the character of operations when compared with more conventional low-vapor-pressure halide salts. In fluoroborate systems the cover gas contains a significant quantity of toxic BF_3 gas that will hydrolyze to form HF and hydroxyfluoroborate upon contact with moist air (or in the lung). Any leakage of moisture into the coolant system will rapidly generate highly corrosive HF and hydroxyfluoroborate. Even simple operations, such as bubbling an inert gas (e.g., helium) in molten fluoroborates, can cause plugging problems because of the local depletion of BF_3 from the salt (and the resulting increase in melting point). Potential solutions were found for all of these problems at ORNL, but it is not clear that one would choose fluoroborates if a simpler salt system could meet the requirements for the coolant. The nuisance factors associated with the use of fluoroborates can be summarized as follows:

1. Purge-gas streams in contact with the salt must provide for trapping and/or recycle of the considerable pressure of BF_3.
2. Exclusion of traces of moisture to the cover-gas supply and purge-gas exhaust system is of paramount importance because of the rapid generation of HF from mixing of moisture and BF_3. Purged sealing surfaces and bearings are especially vulnerable to moisture-induced corrosion.
3. Because of the rapid hydrolysis when BF_3 encounters moisture, safety systems associated with leakage of fluoroborate salts from process piping will be more complex to design, analyze, and construct.
4. Gas-salt contacting operations must be carefully designed to avoid local depletion of the BF_3 content of the salt. This will require control systems to monitor and adjust the BF_3 content of the gas supply.

None of these nuisance factors were encountered when a simple halide salt with manageable vapor pressure characteristics, such as $2LiF\text{-}BeF_2$, was used for coolant service. At the end of the MSBR program, studies of alternate coolants were under way to determine if a salt other than a fluoroborate could meet all the requirements [4].

Many of the candidates listed in Table 1 were nominated for study in previous work at ORNL, but the salts containing rubidium and magnesium were not included. Although rubidium options may have been considered to be expensive or unusual, the exclusion of the magnesium chloride salts appears to have been an oversight. The $MgCl_2$-containing salts were considered in previous fast-reactor studies as a fuel salt, and there appears to be no reason to exclude them from consideration as a coolant for the NGNP/NHI loop.

2.2 DENSITY

The densities of many of the salt mixtures in Table 1 have been measured. The method of additive molar volumes for estimating the density of salt mixtures has also been found to be fairly accurate for many salt mixtures over a wide temperature range. This estimation method and a tabulation of reference molar volumes for fluoride and fluoroborate mixtures were presented in the previous report [7]. It is expected that the method of additive molar volumes will also prove useful in chloride-salt systems in the event that reliable experimental information is not available. The density equations for most of chloride salts in Table 1 have been determined experimentally and are summarized along with those of fluorides and fluoroborates in Table 3.

Table 3. Salt density equations developed from experimental studies or the method of additive molar volumes

Salt constituents	Molar composition	Density equation[a]
LiF-NaF-KF	(46.5-11.5-42)	2.530 − 0.00073 × T (ºC)
$NaF-ZrF_4$	(59.5-40.5)	3.584 − 0.000889 × T (ºC)
$KF-ZrF_4$	(58-42)	3.416 − 0.000887 × T (ºC)
$LiF-NaF-ZrF_4$	(26-37-37)	3.533 − 0.000517 × T (ºC)
LiCl-KCl	(59-41)	1.8772 − 0.00087 × T (ºC)
LiCl-RbCl	(58-42)	2.7416 − 0.000689 × T (ºC)
$NaCl-MgCl_2$	(58-42)	2.2971 − 0.000507 × T (ºC)
$KCl-MgCl_2$	(67-33)	2.25458 − 0.000474 × T (ºC)
$NaF-NaBF_4$	(8-92)	2.2521 − 0.000711 × T (ºC)
$KF-KBF_4$	(25-75)	2.258 − 0.0008026 × T (ºC)[b]
$RbF-RbBF_4$	(31-69)	2.946 − 0.001047 × T (ºC)[b]

[a] Equations derived from references [11–16] unless otherwise noted.
[b] Equation derived from method of additive molar volumes [17].

2.3 HEAT CAPACITY

The heat capacities of all salt constituents (i.e., compounds) have been measured, and many of the heat capacities for salt mixtures have also been measured. For cases in which experimental determinations are not available, the molar heat capacity is estimated based upon pure-component heat capacities weighted according to mole fraction and any mixing-enthalpy information that is available. Table 4 contains predictions based on the empirical equation of Dulong-Petit [7] for comparison with experimentally determined, or derived, values of heat capacity. When possible, heat capacity values were evaluated at 700ºC. In some instances no accurate temperature dependence was available from the experimental database. In general, the variation of heat capacity of molten salts with temperature is small.

Table 4. Salt heat capacity from experiments and prediction

Salt constituents	Molar composition	Heat capacity (cal/g-ºC)	
		Measured [a]	Predicted
LiF-NaF-KF	(46.5-11.5-42)	0.48	0.387
NaF-ZrF_4	(59.5-40.5)	0.28	0.275
KF-ZrF_4	(58-42)		0.251
LiF-NaF-ZrF_4	(26-37-37)		0.296
LiCl-KCl	(59-41)	0.287	0.289
LiCl-RbCl	(58-42)	0.213	0.212
NaCl-$MgCl_2$	(58-42)	0.258	0.262
KCl-$MgCl_2$	(67-33)	0.276	0.229
NaF-$NaBF_4$	(8-92)	0.36	0.435
KF-KBF_4	(25-75)	0.312	0.367
RbF-$RbBF_4$	(31-69)	0.218	0.258

[a] Values based upon references [11, 12, 18–22].

2.4 VISCOSITY

Chloride salts and fluoroborates are, in general, very low viscosity melts. They do not exhibit large changes in viscosity with salt composition (as BeF_2 mixtures do) and are less viscous than most fluoride salt mixtures. It is difficult to measure small values of viscosity at high temperatures, and special methods have been developed for this purpose. However, it should be noted that the difference between low-viscosity systems rarely controls the choice of the particular salt system; rather, certain compositional regions of highly viscous systems (such as BeF_2 salts) are identified as forbidden regions [7]. The viscosities of the salt mixtures in Table 1, or mixtures very similar in composition, have been measured. These results, summarized in Fig. 11, reflect the general trends cited above.

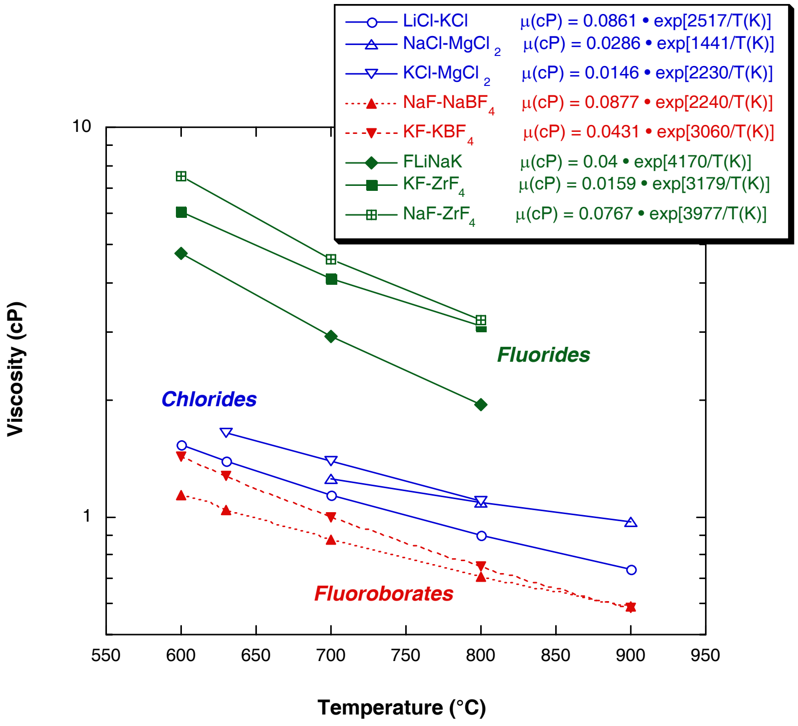

Fig. 11. Salt viscosity based upon experimental measurements [11–13, 16, 24–26].

For some of the salt mixtures in Table 1, there are no experimental measurements of viscosity. For these mixtures, estimates based upon values for pure components and an ideal-mixture viscosity estimation were made using the following equation [23]:

$$\mu_{\text{ideal-mix}} = \{ \sum (x_i \bullet \mu_i^{1/3}) \}^3 \quad , \qquad (1)$$

where: μ_i is the dynamic viscosity (cP) of component i, and

x_i is the mole fraction of component i.

The ideal-mixture viscosity of the eutectic of LiCl-RbCl is predicted by Eq. (1) to be very close to the viscosity of the LiCl-KCl eutectic. For the purposes of heat-transfer estimates, the viscosity of the LiCl-KCl eutectic can be used in estimates of viscosity for the LiCl-RbCl eutectic. Most of the other ternary mixtures in Table 2 are very slight modifications of binary systems displayed in Fig. 11, and the value of the binary system can be used for the purposes of heat-transfer calculations.

2.5 THERMAL CONDUCTIVITY

A discussion in a previous report indicated the difficulties and inaccuracies that have plagued the measurement and our understanding of thermal conductivity of high-temperature molten salts. These metrological difficulties also apply to high-temperature chloride and fluoroborate salts, and corrections similar to those made in fluoride systems have also been necessary for the chloride and fluoroborate systems. Improvements in the measurement of thermal conductivity of high-temperature salts have consistently led to a lower estimate of the actual value. The recent (and more accurate) measurements also indicate a very weak dependence of thermal conductivity on temperature. The general trend that lighter salts (with lower-atomic-number atoms) have higher thermal conductivities has been confirmed by many investigators [27, 28]. It also appears that families of salt compounds fall onto a single correlating curve, based upon the average ionic weight (formula weight divided by number of ionic species), as indicated in Fig. 12.

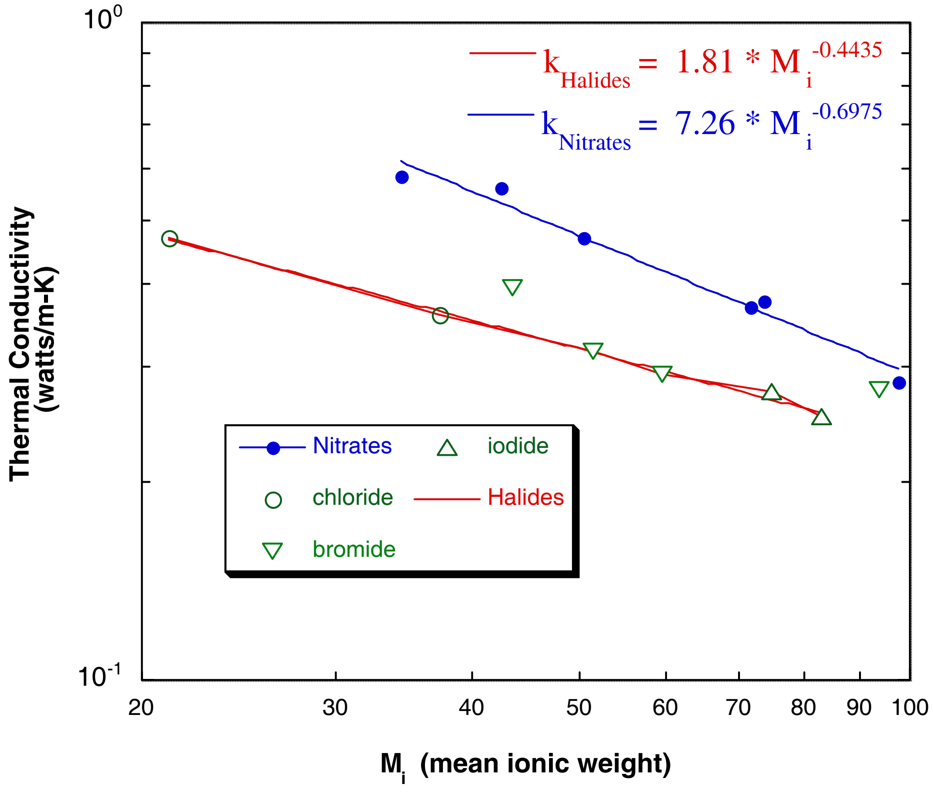

Fig. 12. Thermal conductivity correlation in one-component nitrate and halide salts [27, 28].

It has been suggested by a number of investigators that mixtures of salt compounds (such as binary or ternary eutectics) should display some type of nonideal behavior and that the conductivity is not characterized by a simple mole-fraction-weighted average of pure-component values. One investigator [27] has interpreted the addition of a second salt compound as a disruption of the order of the pure-compound quasi-crystalline lattice, thus representing an increase in disorder, which will then decrease the amount of heat transferred by the natural vibrational modes. However, the most reliable measurements indicate that the conductivity of a mixture of salt compounds is very close to the mole-fraction average of the pure-compound values [29]. For coolant salt mixtures with no reliable measurements, a mole fraction average has been used to estimate the conductivity in Table 5.

Table 5. Comparison of measured and predicted thermal conductivities [a]

Salt composition (mol %)	Formula weight (g/mol)	Melting point (ºC)	Temp (ºC)	Measured conductivity (W/m-K)	Conductivity-based pure-compound values (W/m-K)
LiF-NaF-KF	41.3	454	500	0.60	0.68
NaF-ZrF_4	92.7	500	700	--	0.36
KF-ZrF_4	103.9	390	700	--	0.32
LiF-NaF-ZrF_4	84.2	436	700	--	0.36
LiCl-KCl	55.5	355	355	0.69	0.43
			538	0.28	
			700	0.38	
LiCl-RbCl	75.4	313	700	--	0.39
NaCl-$MgCl_2$	76.1	450	700	--	0.43
KCl-$MgCl_2$	81.4	435	800	--	0.39
NaF-$NaBF_4$	104.4	385	621	0.4	
KF-KBF_4	109.0	460	621	--	< 0.4
RbF-$RbBF_4$	151.3	442	621	--	< 0.4

[a] Measured values and pure compound values from [1, 20, 27–32].

3. HEAT-TRANSFER COMPARISONS

It is useful to compare the heat-transfer performance of the NGNP/NHI loop candidate coolants with those of other coolants that we have experience with or would like to consider for related applications. 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 6 lists the properties of the additional coolants identified in this report to be used in the heat-transfer comparisons. Properties of fluoride salts and other comparison coolants were examined in detail in a previous report [7] and are summarized in the Executive Summary of this report.

Table 6. Estimates of properties for additional secondary coolant candidates

Salt	Melting point (ºC)	FW[a] (g/mol)	Density (g/cm^3)	Heat capacity (cal/g-ºC)	ρ*Cp (cal/cc-ºC)	Viscosity (cP)	Thermal conductivity (W/m-K)
LiCl-KCl	355	55.47	1.515	0.287	0.435	1.15	0.42
LiCl-RbCl	313	75.37	1.883	0.213	0.401	1.30	0.36
NaCl-MgCl$_2$	450	76.09	1.677	0.262	0.439	1.36	0.50
KCl-MgCl$_2$	435	81.44	1.664	0.276	0.459	1.40	0.40
NaF-NaBF$_4$	385	104.38	1.754	0.360	0.632	0.90	0.40
KF-KBF$_4$	460	108.96	1.696	0.312	0.529	0.90	0.38
RbF-RbBF$_4$	442	151.26	2.213	0.218	0.482	0.90	0.28

[a] Formula weight.

Generalized heat-transfer metrics are a useful tool to group coolant performance in the absence of more detailed system designs. Bonilla [33] has provided general figures of merit (FOMs) based on minimal pumping power for a given coolant temperature rise as the objective function for forced convection:

$$\textbf{FOM}\text{ (forced convection, turbulent)} = \mu^{0.2} / (\rho^2\, C_p^{2.8}) \ , \qquad (2)$$

where

μ = viscosity,

ρ = fluid density,

C_p = heat capacity.

For natural convection cooling, Bonilla also provide the following groups for passive cooling:

$$\textbf{FOM}\text{ (natural convection, turbulent)} = [\ \mu^{0.2} / \beta\, \rho^2\, C_p^{1.8}]^{\,0.36} \ , \qquad (3)$$

and

$$\textbf{FOM}\text{ (natural convection, laminar)} = [\ \mu / \beta\, \rho^2\, C_p]^{\,0.5} \ , \qquad (4)$$

where

β = volume expansivity = $1/\rho \bullet d\rho/dT$ [1/ºC] .

During evaluation of secondary coolants for the MSBR, Sanders [1] proposed an FOM related to the area required for the primary heat exchanger:

$$\textbf{FOM}\text{ (heat exchanger area)} = \mu^{0.2} / [\rho^{0.3} C_p^{0.6}\, k^{0.6}] \ . \qquad (5)$$

Sanders recommends that this FOM be used only for comparisons within a coolant group type (salts, metals, or other). All of these FOMs are “golf scores”—that is, lower numbers correlate with better performance. Tables 7 summarizes the various FOMs for the comparison and candidate coolants.

In general, we can conclude 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 many passive cooling situations, the turbulent natural convection component is of primary importance.

Table 7. Heat-transfer ranking of secondary coolant candidates at 700ºC[a]

NATURAL CONVECTION				TURBULENT FORCED CONVECTION			
Laminar		Turbulent		Pumping factor		Area factor	
Water (300ºC)	0.63	Water (300ºC)	4.84	Water (300ºC)	0.20	Na	1.6
Na	3.51	LiF-NaF-KF	13.30	2LiF-BeF$_2$	0.70	Pb	5.4
RbF-RbBF$_4$	4.22	2LiF-BeF$_2$	13.91	NaF-BeF$_2$	0.91	Water (300ºC)	13.0
NaF-NaBF$_4$	4.31	LiF-NaF-ZrF$_4$	13.92	LiF-NaF-BeF$_2$	1.02	2LiF-BeF$_2$	21.5
KF-KBF$_4$	4.60	LiF-ZrF$_4$	14.46	LiF-NaF-KF	1.13	LiF-NaF-KF	21.6
Pb	5.36	**NaF-NaBF$_4$**	14.71	LiF-NaF-ZrF$_4$	1.42	LiF-NaF-BeF$_2$	22.6
LiF-NaF-KF	6.61	NaF-ZrF$_4$	14.72	LiF-ZrF$_4$	1.82	NaF-BeF$_2$	25.2
LiCl-RbCl	6.86	LiF-NaF-BeF$_2$	15.64	NaF-ZrF$_4$	1.98	**NaF-NaBF$_4$**	28.0
LiF-NaF-RbF	7.11	**KF-KBF$_4$**	15.93	**NaF-NaBF$_4$**	2.20	LiF-NaF-RbF	31.8
LiCl-KCl	7.15	NaF-BeF$_2$	16.48	KF-ZrF$_4$	3.39	*NaCl-MgCl$_2$*	35.1
KCl-MgCl$_2$	7.74	**RbF-RbBF$_4$**	16.59	**KF-KBF$_4$**	3.53	**KF-KBF$_4$**	35.4
NaCl-MgCl$_2$	7.81	KF-ZrF$_4$	16.74	LiF-NaF-RbF	3.79	LiF-NaF-ZrF$_4$	35.9
LiF-ZrF$_4$	7.90	LiF-NaF-RbF	17.37	RbF-ZrF$_4$	4.82	NaF-ZrF$_4$	37.4
NaF-ZrF$_4$	7.90	RbF-ZrF$_4$	17.62	*KCl-MgCl$_2$*	5.66	*LiCl-KCl*	37.5
RbF-ZrF$_4$	8.89	Na	20.33	**RbF-RbF$_4$**	5.67	LiF-ZrF$_4$	37.5
LiF-NaF-ZrF$_4$	9.01	*LiCl-KCl*	20.83	*LiCl-KCl*	5.88	*KCl-MgCl$_2$*	39.7
KF-ZrF$_4$	9.05	*KCl-MgCl$_2$*	21.08	*NaCl-MgCl$_2$*	6.40	KF-ZrF$_4$	42.5
2LiF-BeF$_2$	10.12	*LiCl-RbCl*	21.26	*LiCl-RbCl*	8.99	*LiCl-RbCl*	44.5
LiF-NaF-BeF$_2$	10.66	*NaCl-MgCl$_2$*	21.70	Na	13.15	**RbF-RbBF$_4$**	45.4
NaF-BeF$_2$	13.45	Pb	28.53	Pb	33.63	RbF-ZrF$_4$	48.7

[a] Red bold typeface denotes fluoroborate salts. Blue italics typeface denotes chloride salts.

It is expected that the turbulent-forced-convection metrics are the most important for the purposes of the NGNP/NHI loop application.

4. COST OF SALTS

Many important economic factors must be considered with respect to selection of coolant. However, at this stage of the NGNP/NHI loop design, it is most useful to focus on the acquisition cost of the salt coolant. The cost of the salt associated with a significant deployment of the heat-transfer loops is the most important value. Unfortunately, at present, we cannot predict this cost for all salts, because some of the constituents of candidate salts are not commodity chemicals and the cost associated with the deployment of significant numbers of heat-transfer loops would “swamp” the existing markets and would change the price that is offered.

However, there are some basic trends and facts that can be used to help understand how to classify and evaluate the 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 [1]. In the context of this survey, solicitations were made to vendors to provide prices for candidate salts. The desire was to establish an estimate of the unit prices required for supplying the coolant inventory (~280,000 L) for a 1000-MW(e) MSBR plant. Some vendors could not supply estimates for an order this large, and extrapolation methods were employed to refine the estimates whenever possible. The results of these 1971 price estimates are shown in Table 8. A more recent survey of trade-journal pricing for relevant salt constituents is included as Table 9.

Based on the 1971 study and the more recent trade-journal values, it is evident that the constituents of candidate coolants fall into two categories: (a) relatively inexpensive commodity chemicals (NaF, NaCl, KCl, and $MgCl_2$) and (b) moderately expensive specialty materials produced on a large scale (zirconium metal, LiF, and LiCl). The zirconium prices in Table 8 and 9 do not reflect the cost associated with hafnium removal.

Table 10 shows the costs of the raw materials associated with the various candidate salt mixtures. Based on these raw material costs, it is clear that many of the chloride salts are the least expensive, followed by fluoroborate salts, and then fluoride salts. It is possible that this classification could change for some constituents based upon market factors not yet considered. For example, there exist two alternative raw material sources for obtaining ZrF_4: (a) recovery of irradiated cladding and fuel element hardware and (b) recovery of ZrF_4 from spent pickling solution streams (from HF 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 rubidium and potassium minerals that currently 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 (the 16th most abundant metal). Rubidium is more abundant than copper, lead, and zinc—and much more abundant than lithium or cesium.

Table 8. Price estimate of salt coolants (1971 U.S. dollars)

Coolant		Composition (%)	Melting point (ºC)	Price ($/kg)	Price ($/L)
NGNP/NHI loop candidate coolant salts					
LiF-NaF-KF					
	mol %	46-11.5-42.5	454	11.3	24.1
	wt %	29-12-59			
NaF-KF-ZrF_4					
	mol %	10-48-42	385	4.6	11.7
	wt %	4-27-69			
NaF-$NaBF_4$					1.5
	mol %	8-92	385	0.82	
LiCl-KCl					1.8
	mol %	59-41	355	1.12	
Other industrial salts					
$NaNO_3$-$NaNO_2$-KNO_3					0.57
	mol %	7-48-45	142	0.33	
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 9. Commodity prices for selected materials

Material	Commodity price ($/kg)	Price of contained metal ($/kg-metal)	Source
LiF	17.00	63.5	*USGS Minerals Yearbook* 1995
LiCl	11.00	67.2	*USGS Minerals Yearbook* 2000
Li_2CO_3	1.72	9.16	*USGS Minerals Yearbook* 2004
NaF	1.37	2.56	*Chemical Marketing Reporter* **267**(12) (2005)
NaCl	0.122	0.310	*Kirk-Othmer Encyclopedia* 2003
$NaBF_4$	5.00		*Kirk-Othmer Encyclopedia* 1993
KF	4.54	6.74	*Chemical Marketing Reporter* **267**(12) (2005)
KCl	0.125	0.238	*Chemical Marketing Reporter* **267**(12) (2005)
KBF_4	3.55		*Kirk-Othmer Encyclopedia* 1993
$MgCl_2$	0.36	1.41	*Chemical Marketing Reporter* **267**(12) (2005)
Zr metal	30.80	30.80	*USGS Minerals Yearbook* 2000
ZrO_2	8.89	11.89	*USGS Minerals Yearbook* 2000
98% ZrO_2 ore (baddeleyite)	3.00	4.05	*USGS Minerals Yearbook* 2000

Table 10. Estimated raw material costs for various salt mixtures[a]

Salt mixture	Composition (mol %)	Composition (wt %)	Raw material cost ($/kg–salt mixture)	Cost/volume ($/L at 700ºC)
		Lowest cost $MgCl_2$-containing salts		
$KCl-MgCl_2$	68-32	62-38	0.21	0.35
$NaCl-MgCl_2$	58-42	46-54	0.25	0.42
$NaCl-KCl-MgCl_2$	20-20-60	14-18-68	0.28	0.50
$LiCl-KCl-MgCl_2$	9-63-28	5-61-34	0.74	1.13
		Moderate cost fluoroborate and chloride salts		
$KF-KBF_4$	25-75	13-87	3.68	6.26
$LiCl-KCl-MgCl_2$	55-40-5	40.5-51.5-8	4.52	7.01
LiCl-KCl	59.5-40.5	45.5-54.5	5.07	7.71
$NaF-NaBF_4$	8-92	3-97	4.88	8.55
		Higher cost fluoride salts		
$NaF-ZrF_4$	59.5-40.5	27-73	4.02	12.63
$KF-ZrF_4$	58-42	32.5-67.5	4.85	13.58
LiF-NaF-KF	46.5-11.5-42	29-12-59	7.82	15.79

[a] Costs are based on values in Table 9.

5. CHEMICAL CONSIDERATIONS

A previous report [7] presented a review and discussion of chemical factors related to the selection of fluoride salts for primary coolant applications. The most important chemical factor concerns the maintenance of acceptably small levels of corrosion for the materials to be used in piping, tanks, and components. Alloy corrosion is the key materials-compatibility issue that is influenced by salt chemistry. The same basic principles discussed in the previous report govern the chemical behavior of chloride salts and, to some extent, fluoroborate salts. The corrosion database applicable to coolant applications for chloride and fluoroborate salts is not as extensive as that established for fluoride salts. The chloride and fluoroborate database is also populated by salts with relatively large and often unquantified levels of corrosive impurities; thus, it is more difficult to draw conclusions from this body of work. Because of this fact, this section highlights the preparative chemistry of chloride and fluoroborate salts. A review of the thermodynamics of the chloride and fluoroborate salt systems relevant to corrosion chemistry is first provided, followed by a consideration of preparative chemistry, and finally a discussion of the relevant corrosion database.

5.1 THERMODYNAMIC FACTORS

Many useful analogies can be drawn between chloride and fluoride salts. Both halide salts are excellent fluxes and generally preclude the use of passive layers to provide corrosion protection. The electrochemical sequence in both systems ranks elements in a similar order. However, there are also some important differences with respect to thermodynamic stability and coordination behavior. For example, the most stable form of uranium in fluorides is UF_4, whereas the most stable form of uranium in chlorides is UCl_3. These differences in the coordination chemistry and the thermodynamic stability affect the speciation of transition-metal solutes, and are relevant to the corrosion chemistry in chloride and fluoroborate systems.

The thermodynamics of corrosion in fluoride salts was examined in considerable detail at ORNL. This work included treatment of salt-solution nonideality and was not based solely on the thermodynamics of simple compounds in an ideal thermodynamic mixture. Extensive consideration of corrosion by oxygen-containing impurity constituents was not necessary for the fluoride system because of the highly effective purification methods that were developed. Previous work on corrosion in chloride systems has been most often discussed in terms of the thermodynamics of pure solid compounds and has been dominated by effects of oxygen-containing impurities. Different thermodynamic conventions have also evolved for analysis of each salt system. The most straightforward comparison can be made based upon the free-energy of formation of the salt constituents and the corresponding metal-halide products that result from corrosion of a container alloy. Table 11 indicates that there appears to be somewhat less inherent thermodynamic stability in the chloride system than in the fluoride system (i.e., the difference in free energy between salt fluorides and alloy fluorides is larger for the fluoride system than it is for chloride system).

Table 11. Comparison of free energies of constituents in chloride and fluoride systems

	Free energy of formation of halide compound at 1000 K[a] (kcal/mol–halide-element)	
Cation species	Fluoride	Chloride
	Coolant salt constituent	
Mg^{2+}	–	124.0
Li^{+}	125	84.0
Na^{+}	112	81.6
K^{+}	109	87.4
Zr^{4+}	96.9	
	Corrosion-product halide constituent	
Cr^{2+}	75.2	71.4
Fe^{2+}	66.4	58.2
Ni^{2+}	55.3	49.9

[a] Based upon values in [34, 35].

Many additional factors will influence the corrosion of alloys in contact with salts, but it is useful to keep in mind that the fundamental thermodynamic driving force for corrosion appears to be slightly greater in chloride systems than it is in fluorides. This treatment ignores a number of important salt-solution effects, especially for salt mixtures that exhibit large deviations from ideal thermodynamic behavior. Additional study in the laboratory will be needed in order to understand whether chloride salts are fundamentally more corrosive toward alloys than fluorides are and whether corrosion control strategies can be devised that can be used with, or favor, chloride salt systems.

The fluoroborates under consideration are not conventional salt systems that share a common anion (i.e., chlorides, fluorides). Rather, they are reciprocal salt mixtures that contain identical alkali cations (Na^+, K^+, or Rb^+) but a mixture of dissimilar anions (F^- or BF_4^-). The predominant anion in the fluoroborate eutectic mixture is the BF_4^- anion. The BF_4^- anion has an ionic radius similar to that of I^- and an electronic polarizability slightly higher than that of Cl^-. Phase diagrams of analogous systems with BF_4^- replaced by I^- often have a similar character. It has also been noted that the BF_4^- anion is similar in size and shape to the perchlorate ion (ClO_4^-) and shares the property of not forming coordination compounds with transition metals. The solubility of alloy-metal halides (e.g., CrF_3 or Na_3CrF_6) in fluoroborates is much smaller than in simple halide salt systems and displays a dramatic decrease with decreasing temperatures. This limited solubility (0.46, 0.046, and 0.01 mol % Na_3CrF_6 at 700, 500, and 385ºC, respectively) presented a potential problem in steam-cycle heat exchangers, because of the likelihood of deposition of corrosion products in the cold spot of the heat exchanger (and plugging the flow channel).

The interaction of trace amounts of oxides, air, or moisture (either in the salt or cover gas) with fluoroborates often controls alloy corrosion, but these chemical interactions are complex and are not completely understood. The hydrolysis of BF_3 in the presence of any moisture in the cover gas above the salt is rapid and generates HF that is intensely corrosive to the system, especially when it is absorbed into molten salt. Some of the actual oxygen- and hydrogen-containing species that result from hydrolysis of BF_3 in the salt have been identified. However, our understanding of this chemistry is not complete [36], and more work is needed before preparative chemistry and online purification requirements can be defined with confidence.

The behavior of hydrogen- and oxygen-containing species in fluoroborates is also important because it provides a means to sequester tritium in the salt, and thus an intermediate fluoroborate loop could serve as an effective tritium barrier. The species that is likely responsible for holding tritium in the salt was identified by Maya [37], and an engineering-scale experimental program was conducted that proved the effectiveness of sodium fluoroborate in sequestering tritium [38].

Thermodynamic free energies that drive corrosion in the fluoroborate system were developed for the actual NaF-$NaBF_4$ solvent system and are shown in Table 12.

Table 12. Relevant free energies of constituents in the NaF-$NaBF_4$ system

	Free energy of formation of halide compound at 1000 K (kcal/mol–halide element)
Cation species	Fluoride/Fluoroborate
	Coolant-salt constituent
Na^+ (as $NaBF_4$)	122 [a]
Na^+ (as NaF)	112
	Corrosion-product constituent
Cr^{3+} (as Na_3CrF_6)	~100
Fe^{2+} (as $NaFeF_3$)	84.3
Ni^{2+} (as $NaNiF_3$)	78.9

[a] This value for formation was derived from the difference of free energy between $NaBF_4$ and BF_3.
Source: References [39–41].

Because of the potential for coherent metal borides to form on the surface of the container alloy, additional factors must be considered in the fluoroborate system. The oxidation of metal alloy constituent (usually chromium) during a redox-driven corrosion process must be accompanied by reduction of a salt constituent. It is possible to reduce B^{3+} in the fluoroborate salt to form a metal boride (e.g., Cr_xB or TiB_x) or elemental boron. Boron deposits have been identified on the alloy surface during numerous corrosion tests. The analytical tests performed at the time did not uncover the chemical identity of the deposited boron. It has been suggested that if the deposited boron exists as a boride, it could possibly confer some corrosion resistance as a resistant surface layer. Borides are one of the few classes of ceramics that exhibit stability in the presence of fluoride salts and do not fall victim to a fluoride flux by dissolving into the salt. However, all tests with fluoroborate salts containing large amounts of impurity oxides and moisture have demonstrated intense corrosion and no evidence of passivation of the alloy surface in contact with fluoroborates.

5.2 PREPARATIVE CHEMISTRY

The first step in molten salt work is acquisition of raw components, which are then combined to produce a melt mixture that has the desired properties when melted. However, most suppliers of halide salts do not provide materials that can be used directly. To prevent severe corrosion of the container metal, major impurities must be removed in addition to moisture/oxide contaminants. Hydrofluorination has proven to be a very effective method for the removal of oxygen-containing impurities from fluoride salts [7]. Removal of oxygen-containing impurities from chloride and fluoroborate salts is considerably more difficult, because fluoride ion more readily displaces oxygen from most compounds than does chloride ion and because borate and hydroxyborate impurities are difficult to fluorinate with HF.

Nearly all of the chloride salts prepared for corrosion studies have contained relatively high levels of oxygen-containing impurities. The typical salt preparation for these studies involved treatment of reagent chlorides by drying the solid salt under vacuum, followed by prolonged treatment with dry HCl gas, and finishing with an inert gas purge of HCl from the salt. This treatment is not effective in removing the last portion of bound oxygen from the salt. Depending on the salt composition, oxygen contents of up to a few percent may remain. A more effective method for removing oxygen is needed if the basic corrosion mechanism in pure chloride salts is to be investigated; otherwise, the effects of oxygen-containing species will dominate the apparent corrosion response. The use of carbochlorination has been recommended by Cherginets [42] for removal of oxygen, and it has been claimed that salts with very low levels of oxygen content (~3ppm) can be produced by this method [43].

A similar type of purification improvement is needed for fluoroborates. Previous treatments with HF and BF_3 (to avoid loss of BF_3 from the melt) were not as effective as desired. A carbofluorination treatment for fluoroborate purification was recommended at the end of the Molten Salt Reactor Program [44], but it does not yet appear to have been developed for fluoride or fluoroborate salts. There is also a need for accurate analytical methods for determination of oxygen in melts, and in certain cases it is necessary to identify the oxygen-containing species (oxide type, hydroxyl, etc).

For both chloride and fluoroborate salts, it is possible to consider the addition of a redox buffer to confer a more reducing environment in the loop and prevent alloy corrosion, as discussed in a previous report [7]. The redox buffers suitable for chlorides and fluoroborates will likely be different or act differently from the buffers suitable for fluoride salts.

5.3 REVIEW OF CORROSION DATABASE

The corrosion database for fluoride salts was reviewed in a previous report [7]. The corrosion-relevant database for chloride and fluoroborate salts is much smaller than the fluoride database, especially for temperatures above 650ºC. The most relevant corrosion results for chloride salts for the purposes of comparisons are displayed in Table 13. These results do not conform to any expected or predictable trends. For example, the effect of chromium content in the alloy does not seem to be an important factor, and the effect of temperature is not clear. Unexpected variability in the tests very likely reflects variability in the purity of the starting materials and the degree to which impurities were excluded from the loop during operation. The corrosion rates are rather high for these salts at a relatively low

Table 13. Summary of Brookhaven loop corrosion tests for chloride salts

Loop ID[a]	Loop material	%Cr-Ni-Mo in Fe-alloy	Duration (h)	T_{max} (°C)	ΔT (°C)	Corrosion rate (mil/y)
Tests with LiCl-KCl eutectic salt						
TCL F	347 SS	17.5-1.4-0.2	5500	575	155	0.5
TCL L-1	410 SS	12.4-0.2-0.1	2200	570	160	2.1
TCL L-3	2.25Cr-1Mo	2.25-0 -1	697	550	150	High[b]
Tests with NaCl-KCl-$MgCl_2$ eutectic salt (30-20-50 mol %)						
TCL L-5	347 SS	17.5-11.4-0.2	2467	500	45	3.9
TCL L-6	410 SS	12.4-0.2-0.1	3971	494	42	3.3
FCL-M1	347 SS	17.5-11.4-0.2	1034	520	0	1.3
FCL-M2	347 SS *roughened*	17.5-11.4-0.2	656	515	0	10.7

[a] TCL refers to natural (thermal) convection loop, FCL refers to a pumped (forced convection) loop.

[b] No specimen corrosion depth was reported, but salt analysis showed 0.11% iron.

Source: Reference [45].

temperature (~550ºC). These rates are similar to those experienced with fluoride salts in contact with stainless steels and Inconel at ~800ºC and are much higher than those experienced with Hastelloy-N in contact with fluoride salts at temperatures as high as 815ºC.

The corrosion database for fluoroborates is shown in Table 14. The improvement in fluoroborate salt purity during the MSBR program was responsible for a steadily decreasing level of corrosion in tests. The level of corrosion, ~1 mil/year, was much higher than that seen in comparable tests with fluoride salts but was judged acceptable for going forward with the MSBR designs. No experience exists with loop corrosion tests using chlorides or fluoroborates at temperatures approaching the levels anticipated in the NHI loop. The database for fluorides contains tests in the 800–900ºC temperature range with both Inconel and Hastelloy-N (INOR-8) alloys.

Table 14. Summary of Hastelloy-N corrosion loops with $NaF-NaBF_4$ eutectic salt

Loop ID[a]	Duration (h)	T_{max} (ºC)	ΔT (ºC)	Corrosion rate (mil/y)
NCL 13A	30,627	607	125	0.66
NCL 14	39,202	607	150	0.55
NCL 17	24,865	607	100	1.0
NCL 20	19,928	688	250	1.0
FCL-1	17,000	621	167	1.2
FCL-2	5,300	621	167	0.94

[a] NCL refers to natural convection loop, FCL refers to a pumped (forced convection) loop.

Source: Reference [46].

6. SUMMARY AND RECOMMENDATIONS

The key finding of this report is that each class of salt—fluoride, fluoroborate, and chloride—possesses some feature that recommends it for consideration as the NGNP/NHI-loop heat-transfer fluid. However, certain factors are of overriding importance and permit us to rank candidates in an orderly fashion. Certain factors that are important (corrosion performance) remain to be determined.

With respect to basic viability as a heat-transfer-loop fluid, $NaF-NaBF_4$ can be ruled out on the basis of a prohibitively high decomposition pressure of BF_3. Both $KF-KBF_4$ and $RbF-RbBF_4$ have acceptable BF_3 decomposition pressures at 900ºC but also have much poorer heat-transfer metrics. Even these heavy fluoroborate salts may prove to be impractical because of various nuisance factors described in Sect. 2.1 of this report.

With respect to turbulent-forced-convection heat-transfer performance, the FLiNaK eutectic (454ºC) is clearly the best salt in Table 1. As a class of salts, fluorides tend to be the best heat-transfer fluids, followed by fluoroborates, and finally by chlorides. The other obvious fluoride salt choice, the $KF-ZrF_4$ eutectic (390ºC), has roughly the same heat-transfer performance as the $KF-KBF_4$ eutectic (460ºC). All chloride salts display poorer heat-transfer performance than fluorides (and most fluoroborates). There is not a great deal of difference in heat-transfer performance between the different chloride salt options.

With respect to raw materials cost, chloride salts that contain $MgCl_2$ are by far the least expensive. All fluoroborates, fluorides, and lithium-containing salts have much larger raw material costs. This factor alone motivates additional work on chlorides if their inferior heat-transfer metrics do not exclude them from consideration.

There is a reasonable expectation (based upon prior experience) that careful alloy design and intelligent salt-chemistry control will permit a 900ºC peak temperature loop to operate with fluoride salts with a tolerable level of corrosion. Our experience with fluoroborates and chlorides at these temperatures is much more limited, and a large degree of uncertainty exists about whether 900ºC loop operation can be achieved with these salts. Such performance must be demonstrated.

The preceding observations lead to the following recommendations:

1. The NGNP/NHI loop design study should exclude the previous choice of $NaF\text{-}NaBF_4$ as a coolant option and replace this choice with (a) a chloride salt evaluation or (b) evaluation of $KF\text{-}KBF_4$.
2. Because FLiNaK is clearly superior in heat transfer to all other salts in Table 1, there is little reason to consider other moderately expensive fluoride salts (e.g., $KF\text{-}ZrF_4$), unless a lower melting point is required or a more economical option is identified.
3. If a single salt had to be recommended for additional study, the ternary eutectic $LiCl\text{-}KCl\text{-}MgCl_2$ (402ºC, 9-63-28 mol %), appears to be the best compromise between raw material cost, performance, and melting point.
4. There is a need to demonstrate and recommend an improved method for purification of chloride salts to be used in corrosion tests. This new method should become a purification standard to be used in conjunction with corrosion tests.
5. High-temperature corrosion tests with properly purified chloride salts should be conducted to confirm the possibility of using chloride salts in the NGNP/NHI loop. These tests should include both batch exposures and loop tests and will probably also require the innovative use of redox buffers to minimize corrosion.

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