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Review of ORNL's MSR Technology and Status

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Abstract. The current status of molten salt reactor development is discussed with reference to the experience obtained from the Oak Ridge Molten Salt Reactor Experiment. The assessment of the future for this reactor system is reviewed with both consideration of advantages and disadvantages. Application of this concept to ADTT needs appears to be feasible by drawing on the experience gained with the MSRE. Key chemical considerations remain as: solubility, redox behavior, and chemical activity and their importance to ADTT planning is briefly explained. Priorities in the future development of molten salts for these applications are listed with the foremost being the acceptance of the $2\text{LiF}-\text{BeF}_2$ solvent system.

The molten salt reactor experiment, MSRE, was operated from 1965-1969 and was shut down by draining the homogeneous fuel from the reactor circuit into two drain tanks located at a lower level in the MSRE facility. The purpose of this review is to identify the ORNL position with respect to MSR's; review the pertinent MSR chemistry and the significant understanding gained since the MSRE operation era; and, finally, to relate these two elements to present accelerator driven transmutation technology, ADTT, interests.

If one surveys the current attitude at ORNL with regard to MSR's, he would observe that there is no official position. In parallel with the current national and DOE attitudes toward advanced nuclear programs, it is difficult to discern a definite position or proactive attitude toward the MSR status and technology. Rather, there is, at best, a "wait and see" attitude in spite of the fine history of development associated with this reactor concept and this attitude is consistent with the current DOE attitude toward all advanced reactor concepts. When viewed from outside, however, it is possible to become dismayed even though interaction with individuals or groups is still taking place.

The most recent expression of a ORNL interest in MSR's came in 1992 with documents written by F. J. Homan (then, director of reactor technology programs, ORNL) and U. Gat. While this expressed position is dated[1], it served to demonstrate the attitude toward MSR's that still prevails with some individuals. At that time, Homan and Gat identified the MSR advantages as:

(1) Simplicity: External cooling allows optimization of the core design to maximize efficiency. Molten salts have low vapor pressures at high temperatures, reducing the need for thick walled pipes and vessels.

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(2) Ease of fuel handling: Fluid fuel can be moved with pumps and pipes eliminating the need for complex fuel handling machinery.

(3) Simple fuel cycle: No head end preparation for reprocessing, or complex waste management. The fuel is in fluid form, amenable to chemical manipulation. Molten salts can be purified using the very simple fluoride volatility process.

(4) Simplified waste disposal: The waste which comes out of the reprocessing step contains little or no uranium or actinide elements. This simplifies waste management and results in better resource utilization than other reactor fuel cycles.

(5) Versatility: A single, basic design can be operated as modules, or in varying sizes; temperature control assures efficiency. One design can operate on any fuel. The MSR can burn actinides, burn plutonium from dismantled weapons, or breed.

(6) Ease of shutdown and maintenance: Fuel can be drained for maintenance, reducing occupational exposure.

(7) Economy: MSRs have been shown in various studies to have an excellent economic potential.

From today's standpoint we might qualify waste disposal and economy realizing that these issues are now seldom simple or economical. Relative to other reactor systems, however, these points could be valid.

On the negative side of the issue, Homan and Gat identified disadvantages and unresolved issues as:

- (1) Possible reactivity fluctuations due to density variation or bubble formation.
- (2) Necessity for a large external (to the core) fuel inventory,
- (3) High radiation levels in primary system due to presence of fuel throughout.
- (4) Reliability of components which contain and circulate the molten fuel.
- (5) A not fully integrated (combined) chemistry.
- (6) Lack of utility and industrial support.
- (7) Lack of licensing experience.

In addition to these listed issues, we might also add graphite swelling and undeveloped plutonium chemistry.

As a result of this analysis, Homan and Gat identified the following position reflecting the ORNL attitude of the time:

- (1) The MSR has promise.
- (2) The economic climate is not right to recommend the rebirth of MSR's.
- (3) A small program should be established to retain MSR experience lest retirement and/or death cause it to be lost.

(4) MSR's might even be more attractive than LMFBR's in today's climate.

Since the 1969 shutdown of the MSRE, several evaluations of MSR technology have occurred[2,3,4]. While many evaluations have been and will continue to be made, the primary requirements for the molten salt in a homogeneous fluid-fueled reactor still remain as expressed earlier.[5]

The salt should have:

- (1) Low neutron cross section for the solvent components.
- (2) Thermal stability of the salt components.
- (3) Low vapor pressure.
- (4) Adequate solubility of fuel and fission product components.
- (5) Adequate heat transfer and hydrodynamic properties.
- (6) Chemical compatibility with container and moderator materials.
- (7) Radiation stability.
- (8) Low fuel and processing costs.

It is readily seen from Table 2 or Ref. 5 that several of the fluoride salts satisfy the characteristic properties of thermal stability, manageable melting point and low neutron cross section. To achieve lower melting temperatures, two or more salts are combined to produce still lower melting mixtures. The most developed fluoride solvents consist of LiF and BeF₂ in 2:1 mole ratio and melting at 452°C as shown in the phase diagram of Fig. 1 of Ref. 5. The 2LiF-BeF₂ solvent has acceptable viscosity, low vapor pressure and good thermal stability for use as the solvent system in a molten salt reactor.

In considering the application of these molten salts to a MSR situation, three important and interrelated chemical concepts must be controlled. These are solubility, redox chemistry, and chemical activity.

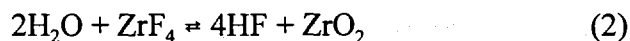
Solubility as applied to molten salts involves more than what we ordinarily understand for aqueous systems. In the case of the pure fluoride materials, solubility is determined by phase diagrams of the mixtures. These temperature versus composition determinations give the temperature at which components might fall from solution (as determined by the liquidus

line on the plot) and the identity of the salt phase which precipitates out. Because this information was of such vital importance to the control of the molten salt solution, much attention was given to the determination of phase diagrams in the early stages of the ORNL/MSR program. While much has been learned already about this phase diagram behavior, comparable information relating to PuF_3 is sorely lacking. For ADTT programs the determination of the $\text{LiF-BeF}_2\text{-PuF}_3$ phase diagram - especially in the region of 2LiF-BeF_2 with low concentrations of PuF_3 , is deemed as absolutely essential if PuF_3 fuels are to be used in the 2LiF-BeF_2 solvent.

In addition to concerns related to those of the pure materials, solubility has significance if impurities such as moisture react with the molten salts to produce metal oxides of much higher melting point and correspondingly lower solubility. For the case of the uranium fuel component, UF_4 , this reaction is written as:



where the very insoluble UO_2 could precipitate out. To prevent the loss of uranium from solution and possible accumulation of UO_2 precipitate in amounts large enough to pose criticality concerns, five mole percent of ZrF_4 was added to the solution to getter any oxide impurities through the reaction:



which is more favorable to reaction with moisture than the former.

Besides solubility concerns with respect to impurity reactions, one must prevent the liquid fuel component from reacting: (a) with the containment vessel and cause corrosion products plus structural weakening or (b) with the moderator graphite and leave behind insoluble fissionable materials. Reactions of the former such as:



and the latter:



were prevented by careful control of the solution redox chemistry which was accomplished by setting the UF_4/UF_3 ratio at approximately 100/1. Additions of metallic beryllium to the fuel salt to effect the reduction of UF_4 via:



to achieve the desired UF_4/UF_3 ratio. The routine adjustment of the redox chemistry was necessary to compensate for the net oxidizing effect of the fissioning uranium ; but since

much of this chemistry has been described in earlier reports[5], the reader is referred there for these details.

The significance of the redox control to ADTT systems is that in some cases where the fuel is PuF_3 , the Pu(III)/Pu(IV) redox couple is too oxidizing to present a satisfactorily redox "buffered" system. It is therefore proposed that redox control be accomplished by including an HF/H₂ mixture to the helium cover gas sparge which will not only set the redox potential, but will also serve as the redox indicator if the exit HF/H₂ stream is analyzed relative to the inlet. For a 7-10MWT reactor system similar to the MSRE but run with a PuF_3 , it is calculated that as little as 1 cc/min HF would be required to compensate for the net reducing effect of plutonium fission. (See the previous presentation[6] describing the difference in redox changes brought about by PuF_3 fission in comparison to UF_4 fission.)

The chemical activity of the molten fluoride solute components and the influence of molten salt solution composition on activity coefficients were actively considered during the MSRE era but the significance of solvent changes on these solute chemical equilibria was not strongly emphasized. The solvent system in the MSRE is, essentially, 2LiF-BeF₂ which is "neutral" in a Lewis acid/base terminology with regard to the free fluoride ion concentration as determined by:



Further emphasis of this important characteristic is valuable to ADTT because departure from the 2LiF-BeF₂ composition has been contemplated in future concepts. One such system is NaF-ZrF₄ which is attractive because it does not present the health hazard of BeF₂. However, the eutectic composition of NaF-ZrF₄ is highly acidic (ie., fluoride deficient) much like the LiF-BeF₂ eutectic composition the vapor pressure of the acidic component is significant. It was high enough in pre-MSRE days at Oak Ridge, that ZrF₄ was found to distill from the melt and condense on cooler surfaces in the containment system. Control of the ZrF₄ mass transport was considered too difficult to ensure, so the 2LiF-BeF₂ solvent system was chosen.

Figure 1 shows the effect of solvent changes on the equilibrium quotient for the hydrogen reduction of UF_4 :



It can be readily seen that there is a significant change in the equilibrium quotient in going from the (Lewis) basic LiF-BeF₂-ThF₄(72-16-12 mol %) to the acidic LiF-BeF₂(48-52 mol %). Take for example the equilibrium quotients at 600°C for Lines B and D which are 5.62×10^{-6}

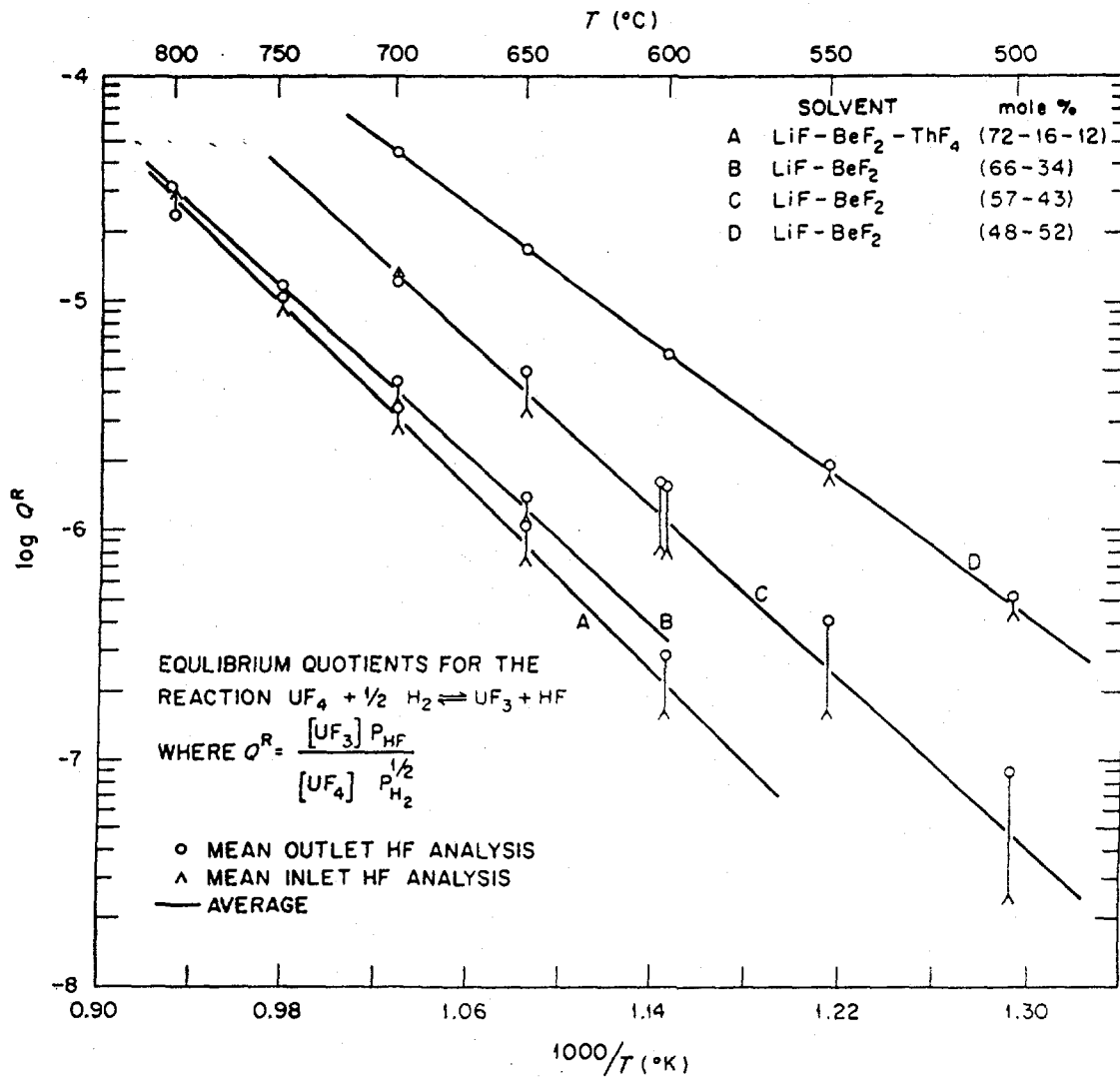


Fig. 1. Equilibrium quotients[7] for the H_2 reduction of UF_4 . Activity coefficient effect from solvent changes shown by shift in Q values.

and $3.47 \times 10^{-7} \text{ atm}^{1/2}$, respectively. This gives an equilibrium quotient ratio of 16.2. The practical significance of this difference is that one finds the UF_3 equilibrium concentration is considerably higher in the acidic (Line D) case. The change is due solely to the change in activity coefficients which is brought about by fluoride ion coordination equilibria as shown in Eq. 6.

Figure 2 shows how the activity coefficients of the mono-di-tri and tetrapositive fluoride salts vary with LiF composition at 600°C . From these activity coefficients, one can calculate the expected change in the equilibrium quotient for changes in the solvent composition. However, these activity coefficient data are often limited and the prediction of their values at other temperatures is difficult because the coefficients are expected to vary considerably, depending on the complexation differences of the ions as a function of temperature.

In ADTT applications these activity coefficient variations are important because changes in their values with solvent composition and temperature variations will have a profound effect on the equilibrium chemistry which controls redox potential, corrosion and fission product behavior. For example, in the more acidic NaF-ZrF₄ system, the chemistry of these processes will be much different from that experienced for the LiF-BeF₂ solvent and consequently should be carefully evaluated if it were to be selected.

As has been stated previously[6], fuel processing to remove fission products needs further development. Krypton and xenon removal by gas sparge is an obvious necessity and easily achievable. Inclusion of a H₂/HF mixture for redox control could provide a compatible combination to solve both objectives. Nevertheless, removal of other fission products must be considered if long-term operations are anticipated. It has been stressed several times already and bears repeating here --- on line processing to remove fission products should be considered only after having developed a satisfactory batch processing mode. Otherwise, coupling the complexities of a slip-stream processing operation to an operating accelerator-driven system would compromise the reliability of the overall system by adding a yet-proven process.

Priorities that should be given in future molten salt development with regard to ADTT applications are, first, selection of 2LiF-BeF₂ as the basic solvent system with lowest possible ZrF₄ oxide getter to minimize problems associated with reductive processing of the fuel salt and the associated reduction of ZrF₄. Next most important is the consideration of PuF₃

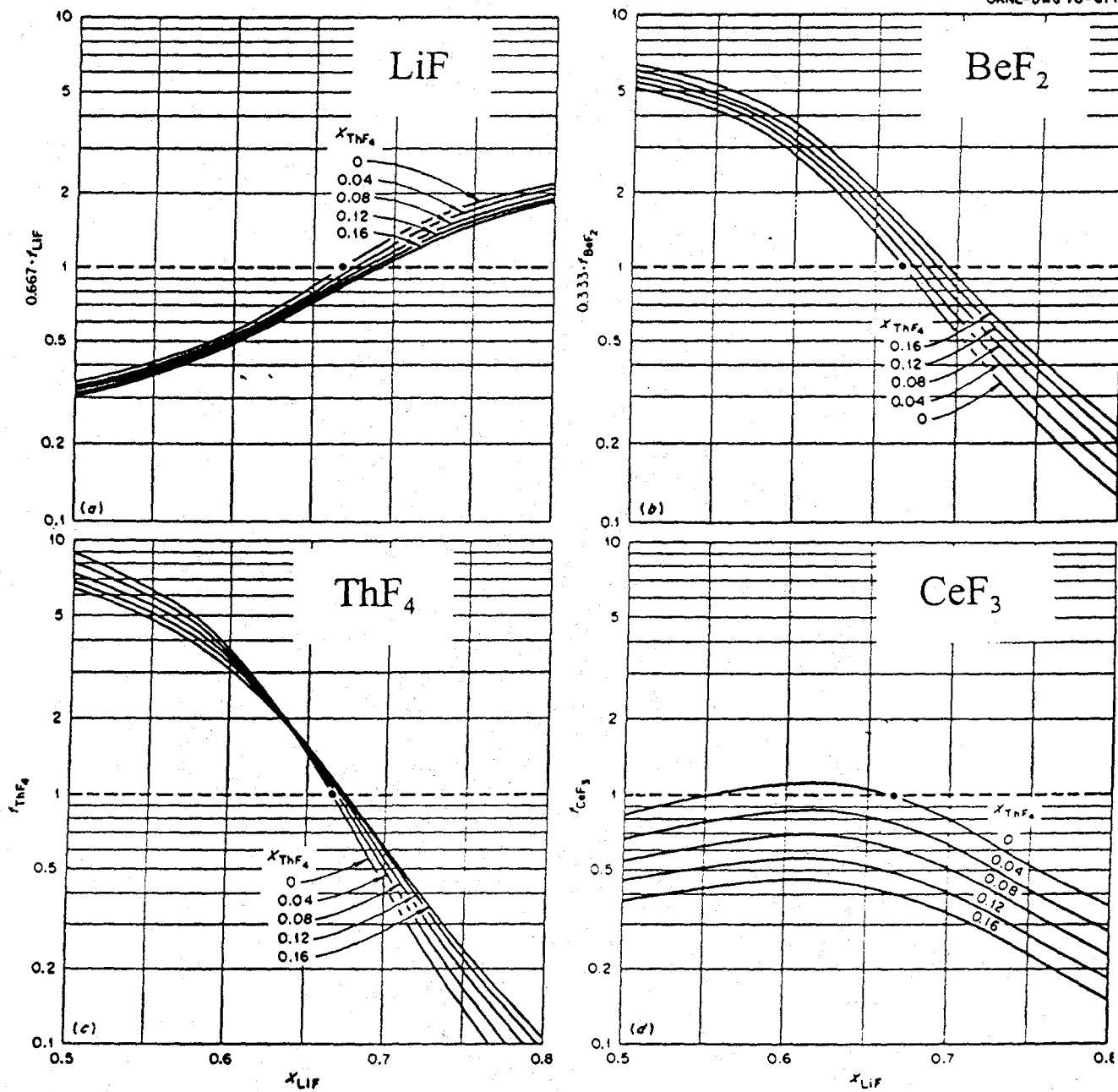


Fig. 2. Activity coefficients[8] in the LiF-BeF₂-ThF₄ mixtures at 600°C.

chemical behavior in this solvent system: PuF_3 solubility, the phase diagram behavior of the ternary PuF_3 - LiF - BeF_2 system in the region of low (<5 mole percent) PuF_3 , and the redox effects of the fission process. Analytical chemical support must be also included in the list of priorities as a key infrastructure element. Next in priority should be processing chemical development; first the establishment of the degree necessary with batch processing carrying the needs while continuous processes are developed over a longer time period. Finally, fission product chemistry behavior should be addressed with tellurium and noble metals as key points of concern. However, a full understanding of their chemical behavior could be deferred until the later stages of technology development since the other priorities hold a greater degree of preeminence.

CONCLUSIONS

Molten salt reactors are a proven concept and merit future development for ADTT applications. The molten fluoride chemistry for the 2LiF - BeF_2 system is well established and can be applied with great confidence. However, other less understood solvent systems must be considered with caution lest subtle solvent effects such as those presented here cause severe problems with process operations. The chemistry of plutonium, as PuF_3 , needs further study and testing, especially in corrosion loop studies for redox control. Processing of the fuel salt needs further development with continuous on-line processing as the ultimate objective. Nevertheless, the future for systems utilizing this high-temperature fluid can be very promising based on the fine record established over the past several decades.

ACKNOWLEDGMENTS

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