

# MOLTEN-SALT REACTOR CHEMISTRY

## REACTORS

W. R. GRIMES *Oak Ridge National Laboratory,  
Oak Ridge, Tennessee 37830*

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*This document summarizes the large program of chemical research and development which led to selection of fuel and coolant compositions for the Molten-Salt Reactor Experiment (MSRE) and for subsequent reactors of this type. Chemical behavior of the  $\text{LiF-BeF}_2\text{-ZrF}_4\text{-UF}_4$  fuel mixture and behavior of fission products during power operation of MSRE are presented. A discussion of the chemical reactions which show promise for recovery of bred  $^{233}\text{Pa}$  and for removal of fission product poisons from a molten-salt breeder reactor is included.*

## INTRODUCTION

A single-fluid molten-salt thermal breeder (MSBR) of the type described by Rosenthal et al.,<sup>1</sup> Bettis and Robertson,<sup>2</sup> and Perry and Bauman<sup>3</sup> makes very stringent demands upon its fluid fuel.<sup>4-6</sup> This fuel must consist of elements having low capture cross sections for neutrons typical of the energy spectrum of the chosen design. The fuel must dissolve more than the critical concentration of fissionable material ( $^{235}\text{U}$ ,  $^{233}\text{U}$ , or  $^{239}\text{Pu}$ ), and high concentrations of fertile material ( $^{232}\text{Th}$ ) at temperatures safely below the temperature at which the salt leaves the MSBR heat exchanger. The mixture must be thermally stable, and its vapor pressure needs to be low over an operating temperature range (1100 to 1400°F) sufficiently high to permit generation of high quality steam for power production. The fuel mixture must possess heat transfer and hydrodynamic properties adequate for its service as a heat-exchange fluid. It must be relatively non-

aggressive toward some otherwise suitable material of construction and toward some suitable moderator material. The fuel must be stable toward reactor radiation, must be able to survive fission of the uranium (or other fissionable material) and must tolerate fission product accumulation without serious deterioration of its useful properties. We must also be assured of a genuinely low fuel-cycle cost; this presupposes a low-cost fuel associated with inexpensive turnaround of the unburned fissile material, and effective and economical schemes for recovery of bred fissile material and for removal of fission-product poisons from the fuel.

A suitable secondary coolant must be provided to link the fuel circuit with the steam-generating equipment. The demands imposed upon this coolant fluid differ in obvious ways from those imposed upon the fuel system. Radiation intensities will be markedly less in the coolant system, and the consequences of uranium fission will be absent. The coolant salt must, however, be compatible with metals of construction which will handle the fuel and the steam; it must not undergo violent reactions with fuel or steam should leaks develop in either circuit. The coolant should be inexpensive, possessed of good heat-transfer properties, and it should melt at temperatures suitable for steam cycle start-up. An ideal coolant would consist of compounds which would be easy to separate from the valuable fuel mixture should they mix as a consequence of a leak.

This report presents, in brief, the basis for choice of fuel and coolant systems which seem optimum in light of these numerous—and to some extent conflicting—requirements.

## CHOICE OF FUEL COMPOSITION

Compounds which are permissible major constituents of fuels for single-fluid thermal breeders

are those which can be prepared from beryllium, bismuth, boron-11, carbon, deuterium, fluorine, lithium-7, nitrogen-15, oxygen, and the fissionable and fertile materials. As minor constituents one might tolerate compounds containing the other elements in Table I.

Many chemical compounds can be prepared from the several "major constituents" listed above. Most of these, however, can be eliminated after elementary consideration of the fuel requirements.<sup>4-6</sup> No hydrogen- (or deuterium-) bearing compounds possess overall properties that are practical in such melts. Carbon, nitrogen, and oxygen form high melting binary compounds with the fissionable and fertile metals; these compounds are quite unsuitable as constituents of liquid systems. The oxygenated anions either lack the required thermal stability (i.e.,  $\text{NO}_3^-$  or  $\text{NO}_2^-$ ) or fail as solvents for high concentrations of thorium compounds (i.e.,  $\text{CO}_3=$ ). It quickly develops, therefore, that fluorides are the only suitable salts indicated in this list of elements.

Fluoride ion is capable of appreciable neutron moderation, but this moderation is by itself insufficient for good neutron thermalization. An additional moderator is, accordingly, required.

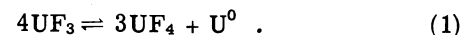
TABLE I  
Elements or Isotopes Which may be Tolerable  
in High-Temperature Reactor Fuels

Material	Absorption Cross Section (barns at 2200 m/sec)
Nitrogen-15	0.000024
Oxygen	0.0002
Deuterium	0.00057
Carbon	0.0033
Fluorine	0.009
Beryllium	0.010
Bismuth	0.032
Lithium-7	0.033
Boron-11	0.05
Magnesium	0.063
Silicon	0.13
Lead	0.17
Zirconium	0.18
Phosphorus	0.21
Aluminum	0.23
Hydrogen	0.33
Calcium	0.43
Sulfur	0.49
Sodium	0.53
Chlorine-37	0.56
Tin	0.6
Cerium	0.7
Rubidium	0.7

The only good moderator material truly compatible with molten-fluoride fuel mixtures is graphite.<sup>4-6</sup>

#### Phase Behavior Among Fluorides

Uranium tetrafluoride and uranium trifluoride are the only fluorides (or oxyfluorides) of uranium which appear useful as constituents of molten-fluoride fuels. Uranium tetrafluoride ( $\text{UF}_4$ ) is relatively stable, nonvolatile, and largely non-hygroscopic. It melts at  $1035^\circ\text{C}$  ( $1895^\circ\text{F}$ ), but this freezing point is markedly depressed by useful diluent fluorides. Uranium trifluoride disproportionates at temperatures above  $\sim 1000^\circ\text{C}$  by the reaction



It is unstable<sup>8,7</sup> at lower temperatures in most molten-fluoride solutions and is tolerable in reactor fuels only with a large excess of  $\text{UF}_4$  so that the activity of  $\text{U}^0$  is so low as to avoid appreciable reaction with moderator graphite or container metal.

Thorium tetrafluoride ( $\text{ThF}_4$ ) is the only known fluoride of thorium. It melts at  $1111^\circ\text{C}$  ( $2032^\circ\text{F}$ ) but fortunately its freezing point is markedly depressed by fluoride diluents which are also useful with  $\text{UF}_4$ .

Consideration of nuclear properties alone leads one to prefer as diluents the fluorides of Be, Bi,  $^7\text{Li}$ , Mg, Pb, and Zr in that order. Equally simple consideration of the stability of these fluorides<sup>8,9</sup> toward reduction by structural metals, however, eliminates the bismuth fluorides from consideration. This leaves  $\text{BeF}_2$  and  $^7\text{LiF}$  as the preferred diluent fluorides. Phase behavior of systems based upon  $\text{LiF}$  and  $\text{BeF}_2$  as the major constituents, has, accordingly, been examined in detail.<sup>10</sup> Fortunately for the molten fluoride reactor concept, the phase diagrams of  $\text{LiF}-\text{BeF}_2-\text{UF}_4$  and  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$  are such as to make these materials useful as fuels.

The binary system  $\text{LiF}-\text{BeF}_2$  has melting points below  $500^\circ\text{C}$  over the concentration range from 33 to 80 mole%  $\text{BeF}_2$ .<sup>10,11</sup> The phase diagram, presented in Fig. 1, is characterized by a single eutectic (52 mole%  $\text{BeF}_2$ , melting at  $360^\circ\text{C}$ ) between  $\text{BeF}_2$  and  $2\text{LiF}\cdot\text{BeF}_2$ . The compound  $2\text{LiF}\cdot\text{BeF}_2$  melts incongruently to  $\text{LiF}$  and liquid at  $458^\circ\text{C}$ .  $\text{LiF}\cdot\text{BeF}_2$  is formed by the reaction of solid  $\text{BeF}_2$  and solid  $2\text{LiF}\cdot\text{BeF}_2$  below  $280^\circ\text{C}$ .

The phase behavior of the  $\text{BeF}_2-\text{UF}_4$ <sup>10,11</sup> and  $\text{BeF}_2-\text{ThF}_4$ <sup>12</sup> systems are very similar. Both systems show simple single eutectics containing very small concentrations of the heavy metal fluoride.  $\text{ThF}_4$  and  $\text{UF}_4$  are isostructural; they form a continuous series of solid solutions with neither maximum nor minimum.

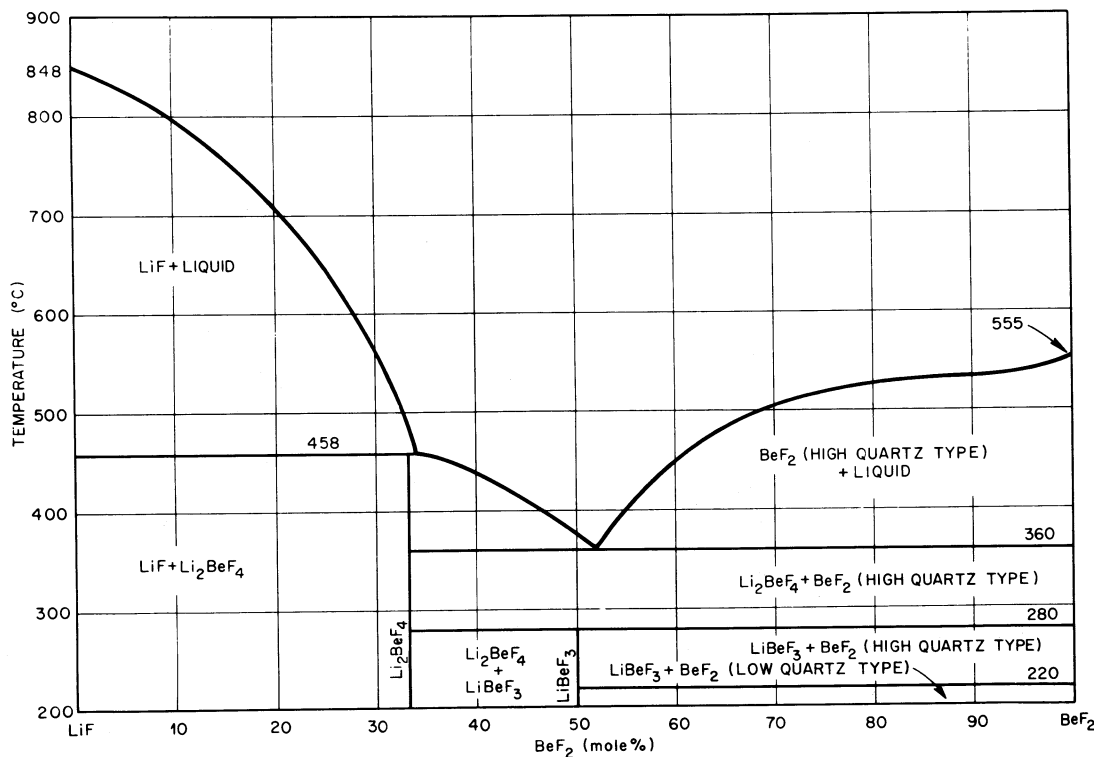


Fig. 1. The system LiF-BeF<sub>2</sub>.

The binary diagrams LiF-UF<sub>4</sub><sup>13</sup> and LiF-ThF<sub>4</sub><sup>14</sup> are generally similar and much more complex than the binary diagrams discussed immediately above. The LiF-UF<sub>4</sub> system shows three compounds (none are congruently melting) and a single eutectic, at 27 mole% UF<sub>4</sub>, melting at 490°C. The LiF-ThF<sub>4</sub> system contains four binary compounds, one of which (3LiF·ThF<sub>4</sub>) melts congruently, with two eutectics at 570°C and 22 mole% ThF<sub>4</sub> and at 560°C and 29 mole% ThF<sub>4</sub>.

The ternary system LiF-ThF<sub>4</sub>-UF<sub>4</sub>,<sup>15</sup> shown in Fig. 2, shows no ternary compounds and a single eutectic freezing at 488°C with 1.5 mole% ThF<sub>4</sub> and 26.5 mole% UF<sub>4</sub>. Most of the area on the diagram is occupied by the primary phase fields of the solid solutions UF<sub>4</sub>-ThF<sub>4</sub>, LiF·4UF<sub>4</sub>-LiF·4ThF<sub>4</sub>, and LiF·UF<sub>4</sub>-LiF·ThF<sub>4</sub>. Liquidus temperatures decrease generally to the LiF-UF<sub>4</sub> edge of the diagram.

The single-fluid molten-salt breeder fuel will need a concentration of ThF<sub>4</sub> much higher than that of UF<sub>4</sub>. Accordingly, the phase behavior of the fuel will be dictated by that of the LiF-BeF<sub>2</sub>-ThF<sub>4</sub> system. Figure 3 gives the ternary system LiF-BeF<sub>2</sub>-ThF<sub>4</sub>; this system shows a single ternary eutectic at 47 mole% LiF and 1.5 mole% ThF<sub>4</sub>, melting at 360°C.<sup>10,11</sup> The system is complicated to some extent by the fact that the compound

3LiF·ThF<sub>4</sub> can incorporate Be<sup>2+</sup> ions in both interstitial and substitutional sites to form solid solutions whose compositional extremes are represented by the shaded triangular region near that compound. Liquidus temperatures < 550°C (1022°F) are available at ThF<sub>4</sub> concentrations as high as 22 mole%. The maximum ThF<sub>4</sub> concentration available at liquidus temperatures of 500°C (932°F) is seen to be just above 14 mole%. Inspection of the diagram reveals that a considerable range of compositions with > 10 mole% ThF<sub>4</sub> will be completely molten at or below 500°C.

As expected from the general similarity of ThF<sub>4</sub> and UF<sub>4</sub>—and especially from the substitutional behavior shown by the LiF-UF<sub>4</sub>-ThF<sub>4</sub> system (Fig. 2)—substitution of a small quantity of UF<sub>4</sub> for ThF<sub>4</sub> scarcely changes the phase behavior. Accordingly, and to a very good approximation, Fig. 3 represents the behavior of the LiF-BeF<sub>2</sub>-ThF<sub>4</sub>-UF<sub>4</sub> system over concentration regions such that the mole fraction of ThF<sub>4</sub> is much greater than that of UF<sub>4</sub>.

#### Oxide Fluoride Equilibria

Phase behavior of the pure fluoride system LiF-BeF<sub>2</sub>-ThF<sub>4</sub>-UF<sub>4</sub>, as indicated above, is such that adequate fuel mixtures seem assured. The

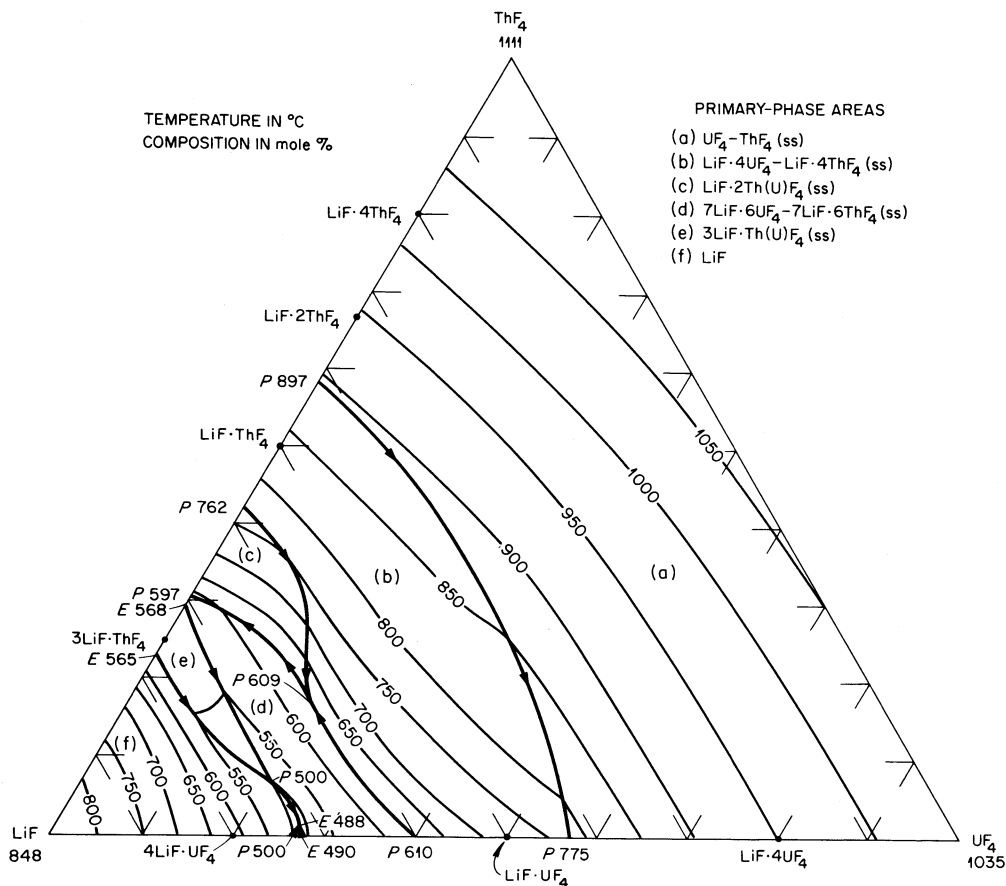


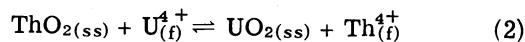
Fig. 2. The system LiF-ThF<sub>4</sub>-UF<sub>4</sub>

behavior of systems such as this, however, is markedly affected by appreciable concentrations of oxide ion.

When a melt containing only LiF, BeF<sub>2</sub>, and UF<sub>4</sub> is treated with a reactive oxide (such as H<sub>2</sub>O) precipitation of transparent ruby crystals of UO<sub>2,00</sub> results.<sup>6,7</sup> If the melt contains, in addition, an appreciable concentration of ZrF<sub>4</sub> the situation is markedly altered. ZrO<sub>2</sub> is less soluble than is UO<sub>2</sub> in such melts, and the monoclinic ZrO<sub>2</sub> (the form stable below ~1125°C) includes very little UO<sub>2</sub> in solid solution. Thus, inadvertent oxide contamination of a LiF-BeF<sub>2</sub>-ZrF<sub>4</sub>-UF<sub>4</sub> melt yields monoclinic ZrO<sub>2</sub> containing 250 ppm of UO<sub>2</sub>.<sup>16</sup> Precipitation of cubic UO<sub>2</sub> (containing a small concentration of ZrO<sub>2</sub>) begins only after precipitation of ZrO<sub>2</sub> had dropped the ZrF<sub>4</sub> concentration to near that of the UF<sub>4</sub>.

Slow precipitation of UO<sub>2</sub> followed by a sudden entrance of this material into the reactor core could result in undesired increased reactivity. This possibility was assumed to represent a danger to the Molten-Salt Reactor Experiment. Accordingly, the MSRE fuel was chosen to contain 5 mole% of ZrF<sub>4</sub> to eliminate such a possibility.

When a mixture of LiF and BeF<sub>2</sub> containing ThF<sub>4</sub> and UF<sub>4</sub> is treated with a reactive oxide a homogeneous cubic phase is produced; this phase is a solid solution of UO<sub>2</sub> and ThO<sub>2</sub> which is very rich in UO<sub>2</sub>.<sup>17</sup> Careful studies have shown that the reaction



[where the subscripts (ss) and (f) indicate the solid-phase solid solution and the molten-fluoride solution, respectively] approaches equilibrium with reasonable speed. Values for the equilibrium quotient *Q* for this reaction

$$Q = \frac{N_{\text{UO}_{2(ss)}} \cdot N_{\text{Th}_{(f)}^{4+}}}{N_{\text{ThO}_{2(ss)}} \cdot N_{\text{U}_{(f)}^{4+}}} \quad (3)$$

increase with UO<sub>2</sub> concentration of the oxide phase and decrease markedly with temperature. Since values of *Q* for mixtures similar to those chosen as fuel compositions are typically 300 to 1000, it is clear that oxide contamination of such salts will selectively precipitate the uranium.

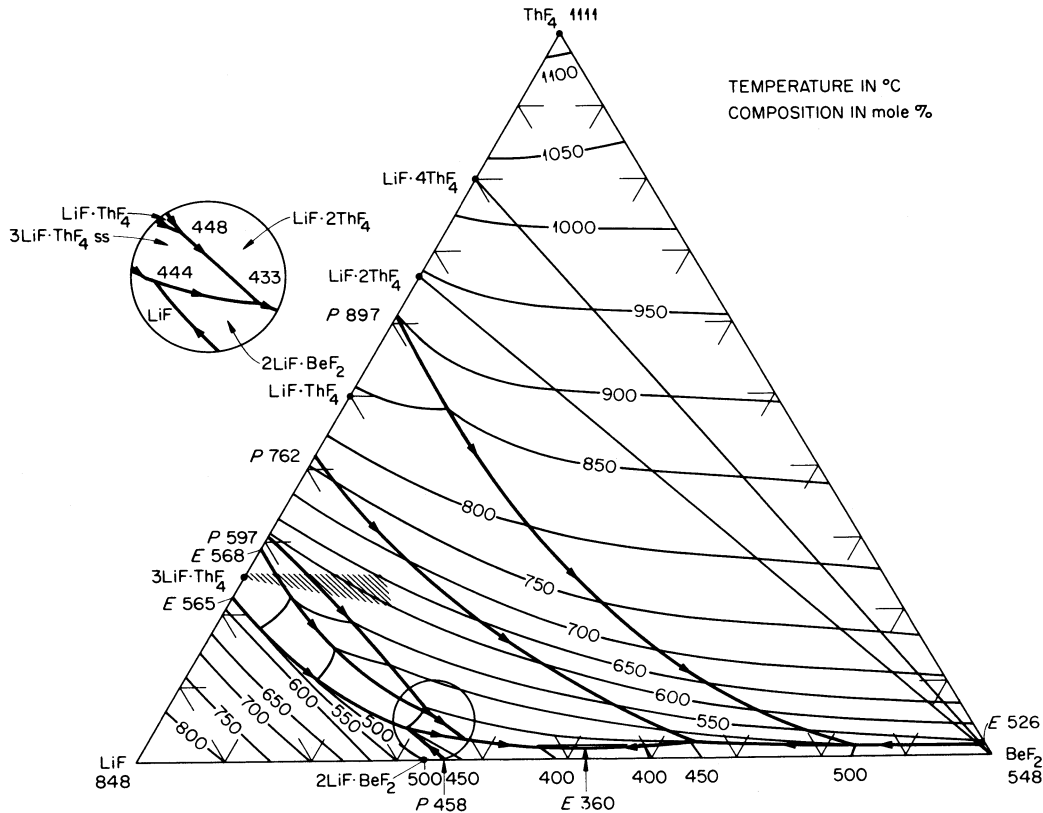


Fig. 3. The system  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ .

It is likely, though not certain, that addition of some  $\text{ZrF}_4$  would afford protection of the sort obtained with the MSRE fuel. Such addition is undesirable, however, since the presence of  $\text{ZrF}_4$  would certainly complicate the separation processes described later in this paper and elsewhere in this series.

The successful operation of the MSRE over a three year period (discussed later) lends confidence that oxide contamination of the fuel system can be kept to adequately low levels. This confidence, when added to the prospect that the breeder fuel will be reprocessed (and its oxide level reduced) at regular intervals, suggests very strongly that successful operation can be achieved without added "oxide protection."

Tolerance levels for oxide concentration in  $\text{LiF}-\text{BeF}_2-\text{UF}_4$  and  $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{UF}_4$  systems have been studied in detail and are relatively well understood.<sup>16,18-20</sup> Analogous values for the  $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$  system are still largely lacking. It is known, however, that processing of these quaternary melts with anhydrous  $\text{HF}$  and  $\text{H}_2$  serves to remove oxide to a level below that required for precipitation of the solid solutions. There seems little doubt, therefore, that initial processing of

the type used for MSRE fuels can be successfully applied on a large scale to the  $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$  system.

#### MSRE and MSBR Fuel Compositions

The fuel chosen for operation of MSRE (with a  $^{235}\text{U}-^{238}\text{U}$  isotopic mixture containing 33% of the fissionable isotope) was a mixture of  $^7\text{LiF}$ ,  $\text{BeF}_2$ ,  $\text{ZrF}_4$ , and  $\text{UF}_4$  consisting of 65, 29.1, 5, and 0.9 mole%, respectively. The uranium concentration was fixed at  $\sim 1\%$  so that there was less possibility of fissile U precipitating ( $\sim 0.3$  mole%  $^{235}\text{U}$  was necessary to achieve criticality and to provide a small excess of fissionable material for power operation of the machine). The  $\text{ZrF}_4$  was added, as indicated above, to preclude possible inadvertent precipitation of  $\text{UO}_2$ . Beryllium fluoride is an extremely viscous material; its viscosity is markedly lowered by addition of  $\text{LiF}$ . The ratio of  $\text{LiF}$  to  $\text{BeF}_2$  in the MSRE fuel was chosen to optimize the conflicting demands for low viscosity and a low liquidus temperature for the molten fuel.

The single-fluid breeder requires a high concentration of  $\text{ThF}_4$ ; concentrations near 12 mole% seem to be reasonable for good reactor