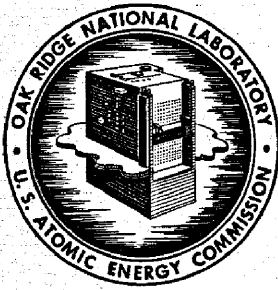


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DATE - June 20, 1968

**CHEMICAL FEASIBILITY OF FUELING
MOLTEN SALT REACTORS WITH PuF_3**

R. E. Thoma

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REACTOR CHEMISTRY DIVISION

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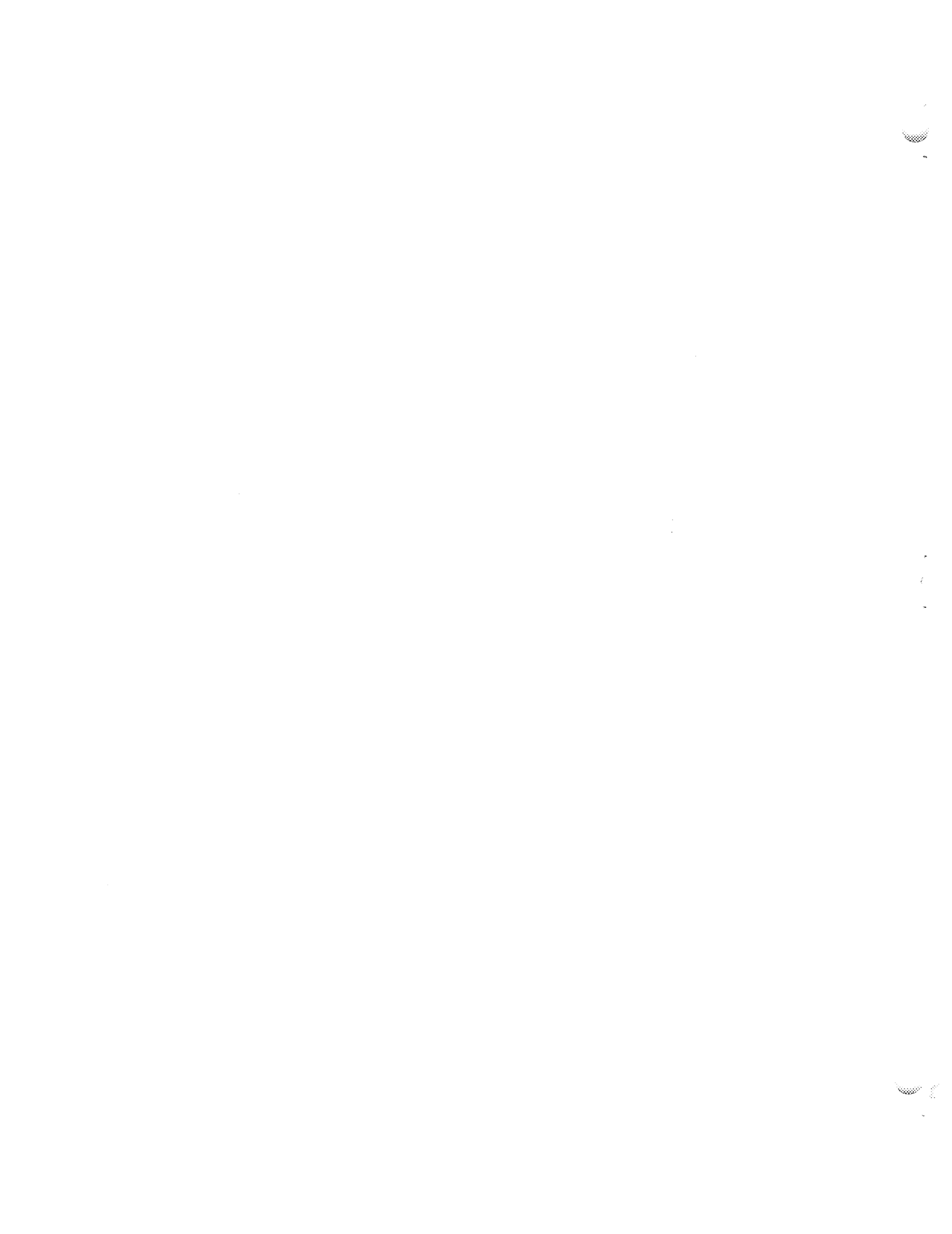
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CHEMICAL FEASIBILITY OF FUELING
MOLTEN SALT REACTORS WITH PuF_3

R. E. Thoma

ABSTRACT

The feasibility of starting molten salt reactors with plutonium trifluoride was evaluated with respect to chemical compatibility within fuel systems and to removal of plutonium from the fuel by chemical reprocessing after ^{239}Pu burnout. Compatibility within reactor containment systems is moderately well-assured but requires confirmation of PuF_3 solubility and oxide tolerance before tests can be made using the MSRE. Although separation of plutonium and protactinium in the chemical reprocessing plant, as would be desirable in a large breeder reactor, has not yet been demonstrated, conceptual designs of processes for effecting such separations are available for development.

INCENTIVES FOR FUELING MOLTEN SALT REACTORS WITH PLUTONIUM FLUORIDE

In a recent report, P. R. Kasten described the economic advantages of using plutonium as a startup fuel in molten salt reactors.¹ The following discussion summarizes his appraisal of the incentives which are derived from the use of plutonium in this manner. It is anticipated that large quantities of plutonium will be produced during the following decades by light water reactors fueled with slightly enriched uranium. Sale of the plutonium produced from these reactors at \$10/g of fissile material is an important consideration in the power cost of these systems. Recycle of plutonium in light water reactors does not lead to a fuel value of \$10/g for fissile material over many recycles.² Further, during the first few years when the fuel reprocessing industry associated with the light water reactors is developing, the costs of fabricating plutonium-fueled elements will be disproportionately high in comparison with cost for uranium fueled elements, and this will also tend to discourage recycle of plutonium. Thus, it appears that within the next several decades the net value of fissile Pu relative to its use in light water reactors will be less than \$10/g, probably about \$6/g.

In molten salt reactors the penalty of preparing plutonium fuels rather than uranium fuels does not appear to be economically significant. Also as shown¹ the value of plutonium in MSBR systems is about \$12/g. Thus, there is a differential of approximately \$6/g between the value of plutonium recycled

in light water reactors versus its value in MSBR's. A 1000 MW(e) MSBR requires about 1000 kg fissile plutonium during the startup period. At a differential of \$6/g, this corresponds to \$6 million. Presumably this \$6 million advantage for a 1000 MW(e) reactor would not be credited completely to MSBR's but would be split with light water reactors by using an intermediate Pu value.

One of the reasons for developing fast breeder reactors is that they can advantageously utilize plutonium as a fuel. If MSBR's are to serve as an alternative breeder system, it is desirable that they also utilize plutonium advantageously as a startup fuel. As indicated above, this appears to be possible if the technology is favorable. Further, the low specific inventory in MSBR's permits molten salt reactors to be built in relatively large numbers using plutonium product fuel from light water reactors. This feature permits MSBR's to contribute to improved fuel utilization since their operation would not be limited by the availability of uranium fuels.

The advantage of starting up on plutonium rather than ^{235}U arises from the fact that a lower concentration of Pu is required for criticality in the fuel, and also because after Pu burnout, the higher plutonium isotopes (neutron poisons) presumably can be separated from the uranium. This operation leads to slightly better nuclear performance over a 30-year reactor life when plutonium is the startup fuel than when

^{235}U is the startup fuel and the higher isotopes cannot be discarded (increase of about 0.01 in the breeding ratio).

The incentives described above form the basis for or justify evaluations of the feasibility of incorporating plutonium in molten salt reactors. An assessment was made of current information on chemical properties of PuF_3 in order to judge the feasibility of its incorporation in MSR fuel salts, and to estimate the character and extent of information which may be required to demonstrate chemical compatibility of PuF_3 in the multicomponent environment of fuel-fertile salt systems.

PREVIOUS EVALUATIONS OF PLUTONIUM-FLUORIDE FUELED REACTORS

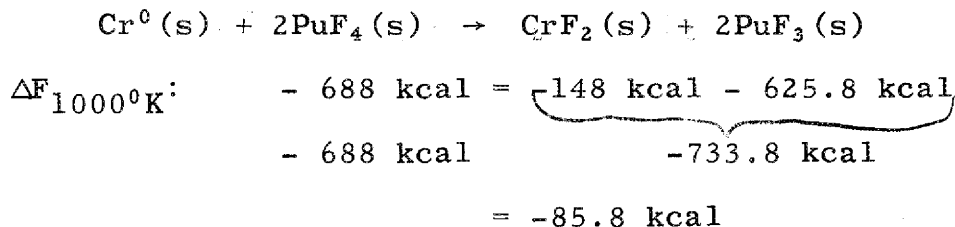
During the early stages of the Molten Salt Reactor Program, the fluorides of plutonium were considered for application in advanced versions of molten salt reactors. The results of one study³ showed that a PuF_3 fueled two-region homogeneous fluoride salt reactor was operable, although its performance was poor. Further development was not pursued for neither its chemical feasibility nor methods for improving performance was obvious. Although the thermochemical properties of the plutonium fluorides were not well established at that time, it was clear that the most soluble fluoride, PuF_4 , would be too strong an oxidant for use with available structural alloys. The solubility of PuF_3 , while sufficient for criticality even in the presence of fission fragments and non-fissionable isotopes of Pu, was

estimated to limit the amount of ThF_4 which could be added to the fuel salt.⁴ This limitation, coupled with the condition that the continuous use of ^{239}Pu as a fuel would result in poor neutron economy in comparison with that of ^{233}U -fueled reactors vitiated further efforts to exploit the plutonium fluorides for MSBR applications. Recent developments in fuel reprocessing chemistry and in reactor design have established the feasibility of a single-fluid MSBR. Consequently, it now appears that it will be possible to operate a $\text{LiF-BeF}_2\text{-ThF}_4\text{-PuF}_3$ single-fluid MSR with lower concentrations of thorium and plutonium than earlier considerations required, e.g., with thorium fluoride concentrations of 8 to 12 mole % and with a plutonium fluoride concentration of approximately 25% less than required for ^{233}U loading,⁵ i.e., $\cong 0.2$ mole %. Since the incentive to use $^{239}\text{PuF}_3$ in molten salt reactors applies exclusively to its temporary inclusion in the fuel stream, prior limitations concerning saturation of the fuel with respect to $^{241}\text{PuF}_3$ and $^{242}\text{PuF}_3$ do not seem to be relevant. If the chemical properties of plutonium trifluoride prove that its inclusion in molten salt reactor fuels is economically and technically feasible, its exploitation in this connection should be regarded as of significant advantage to the development of the United States AEC breeder reactor program.

CHEMICAL PROPERTIES OF PLUTONIUM FLUORIDE

One characteristic of the actinide elements is that

increasing instability of the higher oxidation states is observed with increasing atomic number. This property is evident among the compounds of plutonium, particularly the halides. Three stable fluorides of plutonium are known, whereas among the other halides, only the trivalent oxidation state is commonly exhibited. Since PuF_6 is a gas, only PuF_4 and PuF_3 can be considered for use in molten salt fuel mixtures. Plutonium tetrafluoride would exhibit higher solubility than PuF_3 in fluoride solvents, but would probably prove to be too strongly oxidizing to be compatible with Hastelloy-N. The free energy for the following corrosion reaction strongly favors oxidation of chromium containing alloys:



The above reaction also shows that it would not be possible to increase the concentration of plutonium in a fuel salt which was already saturated with respect to PuF_3 by addition of PuF_4 , since the corrosion reaction would proceed steadily and produce additional amounts of PuF_3 . Plutonium trifluoride is, therefore, regarded as the only suitable fluoride of Pu for application as a molten salt reactor fuel constituent. Current values of the thermochemical properties of PuF_3 and PuF_4 are compared with their uranium analogs and with thorium tetrafluoride and cerium trifluoride in Table 1. The values

listed here show that PuF_3 is more stable than UF_3 , and suggest as well that the solubilities of PuF_3 , UF_3 , and CeF_3 in fluoride solvents might be similar.

A. Solubility of PuF_3 in Fluoride Solvent Mixtures

1. $\text{LiF}-\text{BeF}_2$: The solubility of PuF_3 in $\text{LiF}-\text{BeF}_2$ solvents was measured by Barton⁶ for compositions ranging in BeF_2 from 28.7 to 48.3 mole % and from 450 to 650°C. Solubilities of PuF_3 in $\text{LiF}-\text{BeF}_2$ solvents are compared with those for CeF_3 in the same composition range in Figure 1. These results imply that the solubility of PuF_3 in $\text{LiF}-\text{BeF}_2$ solvents is markedly temperature- and composition-dependent. Extrapolation of these data to temperatures which are reasonable for the peritectic invariant point involving LiF , Li_2BeF_4 , and PuF_3 (Figure 2) indicates that the composition of the mixtures at this invariant point is $\text{LiF}-\text{BeF}_2-\text{PuF}_3$ (63-37-0.008 mole %), $T = 455^\circ\text{C}$, and that the $\text{Li}_2\text{BeF}_4-\text{BeF}_2-\text{PuF}_3$ eutectic occurs at the composition $\text{LiF}-\text{BeF}_2-\text{PuF}_3$ (48-52-0.01 mole %), $T = 358^\circ\text{C}$. The composition dependence of solubility appears to be related to the acid-base balance of the solvent, as is evident when the data are expressed as a function of the estimated fraction of "free" fluorides as contrasted to "bridging" fluorides. While PuF_3 solubility seems to be minimal in the "neutral" melt, $\text{LiF}-\text{BeF}_2$ (66.7-33.3 mole %) the minimum in the CeF_3 solubility curves seems to occur in mixtures which are slightly richer in BeF_2 (see Figure 3).

Barton investigated the effect of additional solutes on

Table 1. Comparison of the Properties of PuF₃ with ThF₄, UF₄, UF₃, and CeF₃.

	ThF ₄ (s)	UF ₄ (s)	PuF ₄ (s)	UF ₃ (s)	PuF ₃ (s)	CeF ₃ (s)
Free energy of formation at 1000°K (kcal/F atom)	-101 ^a	-95.3 ^b	-86.0 ^c	-99.9 ^b	-104.3 ^c	~118 ^a
m.p. (°C)	1111	1035	1037	1495	1425	1437
Crystal Structure	M ^d	M ^d	M ^d	H ^e	H ^e	H ^e
Density (g/cm ³)	5.71	6.72	7.0	8.97	9.32	6.16

^aL. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, ed., McGraw-Hill, New York, 1950, 76-192.

^bC. F. Baes, Jr., "Thermodynamics," Vol. I, IAEA, Vienna, 1966, p. 409; and G. Long, ORNL-3789, January 31, 1965.

^cF. L. Oetting, Chem. Rev., 67, 61 (1967).

^dMonoclinic, space group C2/c.

^eHexagonal, space group P6/mcm.

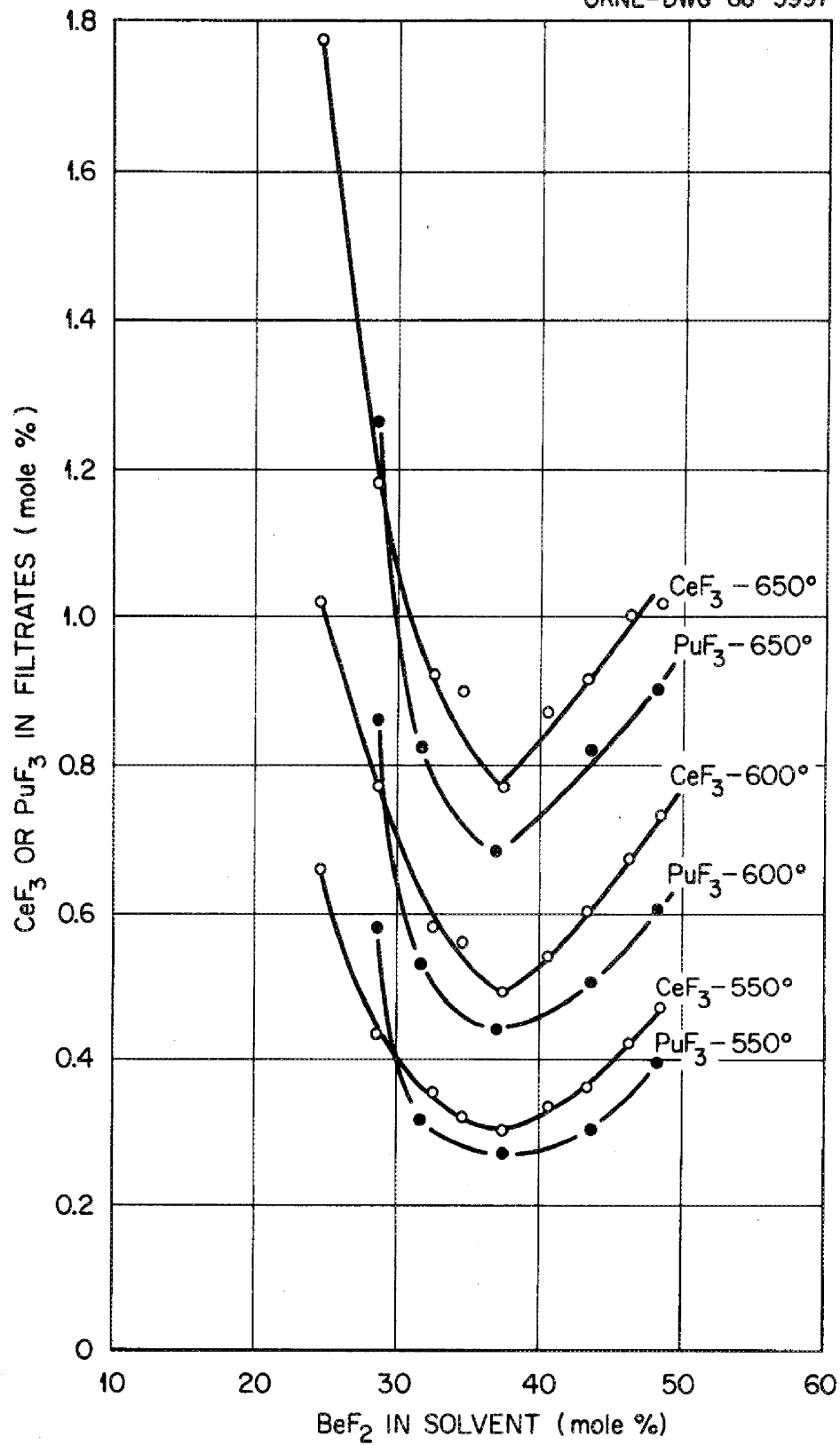


Fig. 1. Comparison of CeF_3 and PuF_3 Solubility in $LiF-BeF_2$ Solvent.

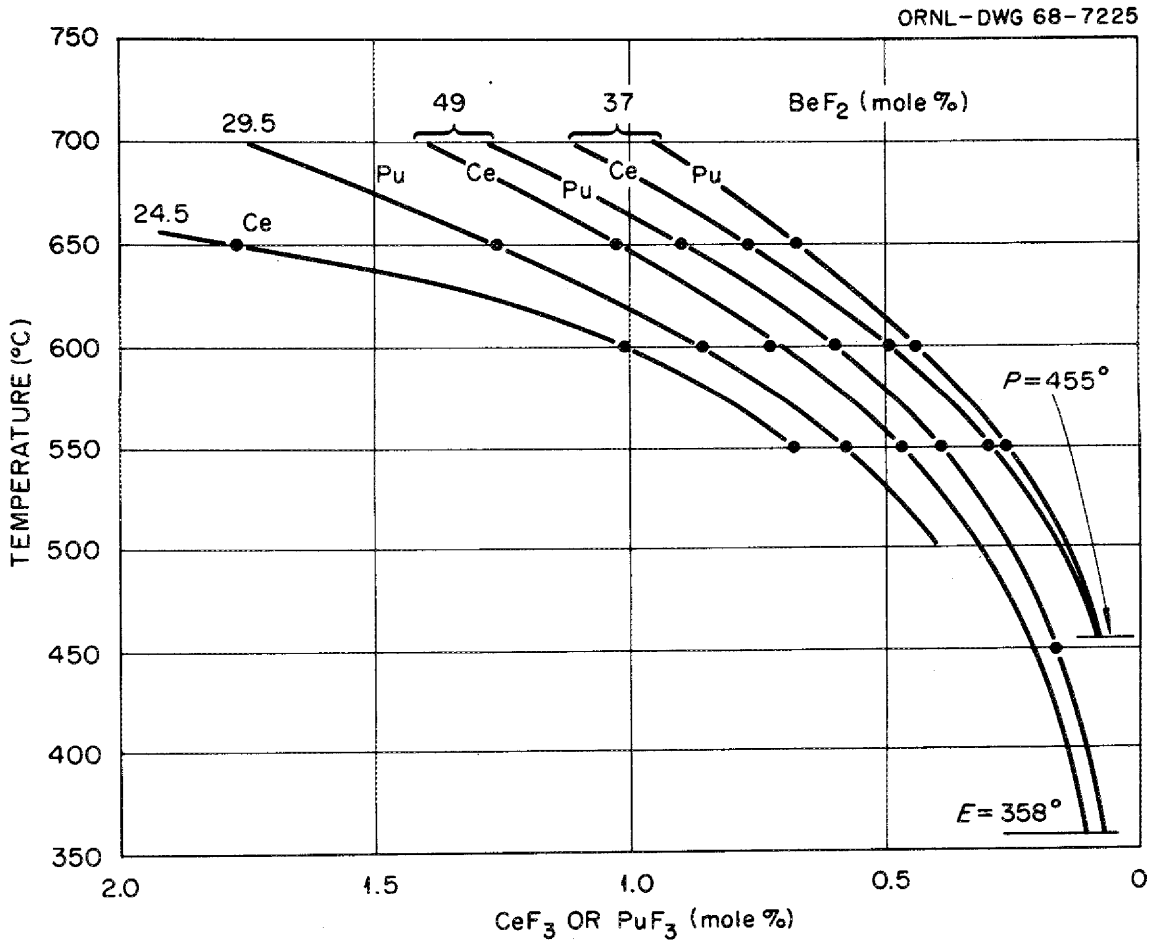


Fig. 2. Solubility of CeF₃ and PuF₃ in LiF-BeF₂ Solvents Extrapolated to LiF-BeF₂-MF₃ Invariant Equilibrium Points. 455° = the peritectic, LiF-Li₂BeF₄-MF₃, 358° = the eutectic, Li₂BeF₄-BeF₂-MF₃.

the solubility of PuF_3 in $\text{LiF}-\text{BeF}_2$ mixtures,⁶ using low (≈ 1 mole %) concentrations of ThF_4 , BaF_2 , and CeF_3 , and high concentrations (20 mole %) of UF_4 . His results showed that at 1 mole %, ThF_4 had very little effect on the solubility of PuF_3 in this solvent. The same amount of BaF_2 diminished the solubility of PuF_3 in a manner not clearly understood. Barton speculated that the saturating phase in these experiments was quite possibly not pure PuF_3 , but rather was a solid solution of BaF_2 and PuF_3 . As the molar ratios of BaF_2 and PuF_3 were varied in these experiments the optical properties of the precipitating phase also varied, such as to indicate that the solid phase in equilibrium with liquid was a BaF_2 - PuF_3 solid solution. The magnitude of the effect indicated that the concentration of divalent fission products anticipated in reactor operation would probably not significantly affect the solubility of PuF_3 .

Data obtained with CeF_3 - PuF_3 solute mixtures in the solvent $\text{LiF}-\text{BeF}_2$ (63-37 mole %) are shown in Figure 4. The theoretical curves for CeF_3 - PuF_3 mixtures shown in Figure 4 were calculated from the equation $N_{\text{PuF}_3}(\text{d}) = S_{\text{PuF}_3}^0 N_{\text{PuF}_3}(\text{ss})$, where $N_{\text{PuF}_3}(\text{d})$, is the mole fraction of PuF_3 in solution $S_{\text{PuF}_3}^0$, the mole fraction (solubility) of PuF_3 in the solvent at a specified temperature (shown labeled " PuF_3 only" in Figure 4) while $N_{\text{PuF}_3}(\text{ss})$ is the mole fraction of PuF_3 in solid solution. Agreement between experimental and calculated solubility values indicates that PuF_3 and CeF_3 form solid solutions.

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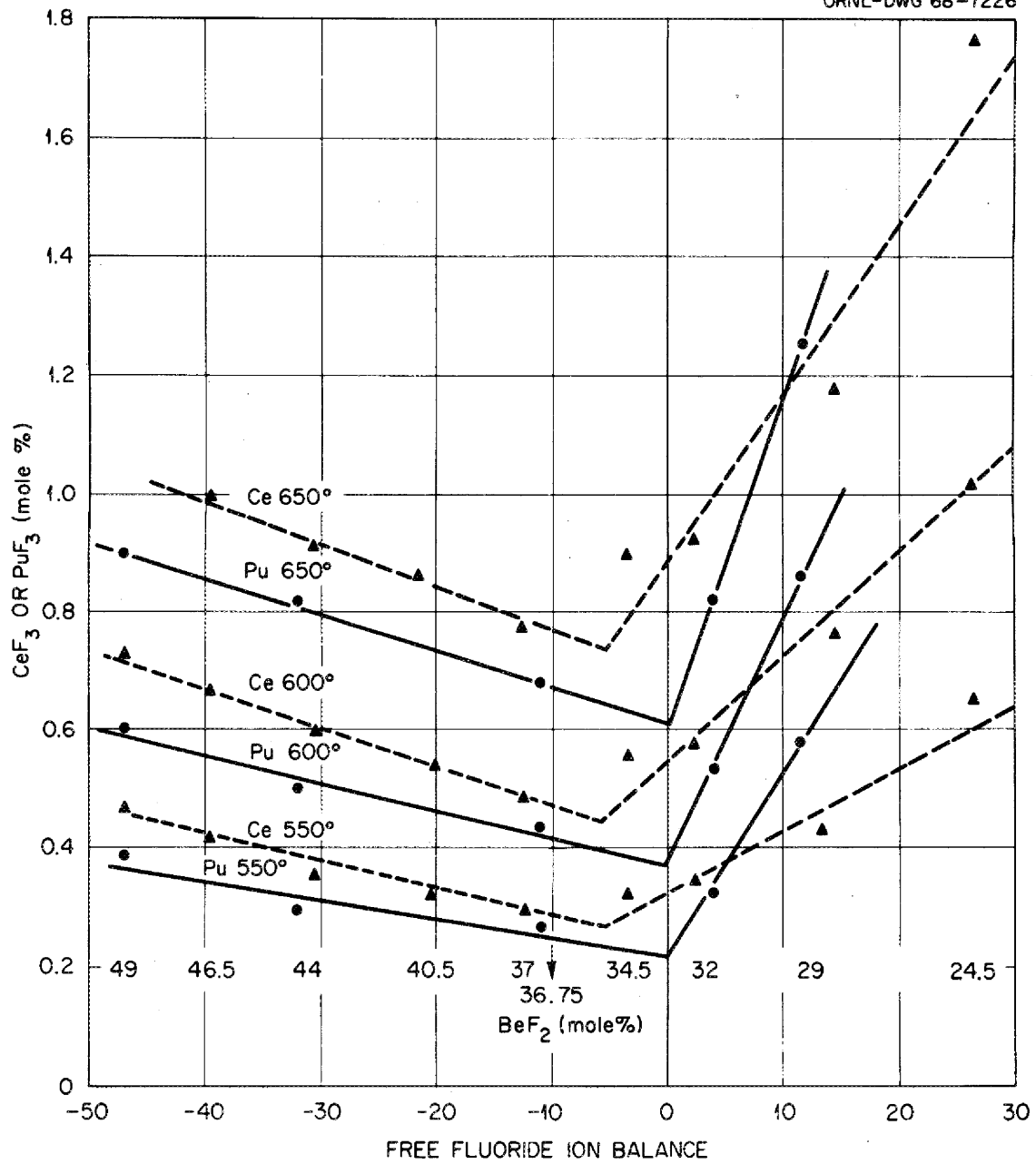


Fig. 3. Effect of LiF- BeF_2 Solvent Composition on the Solubility of CeF_3 and PuF_3 .

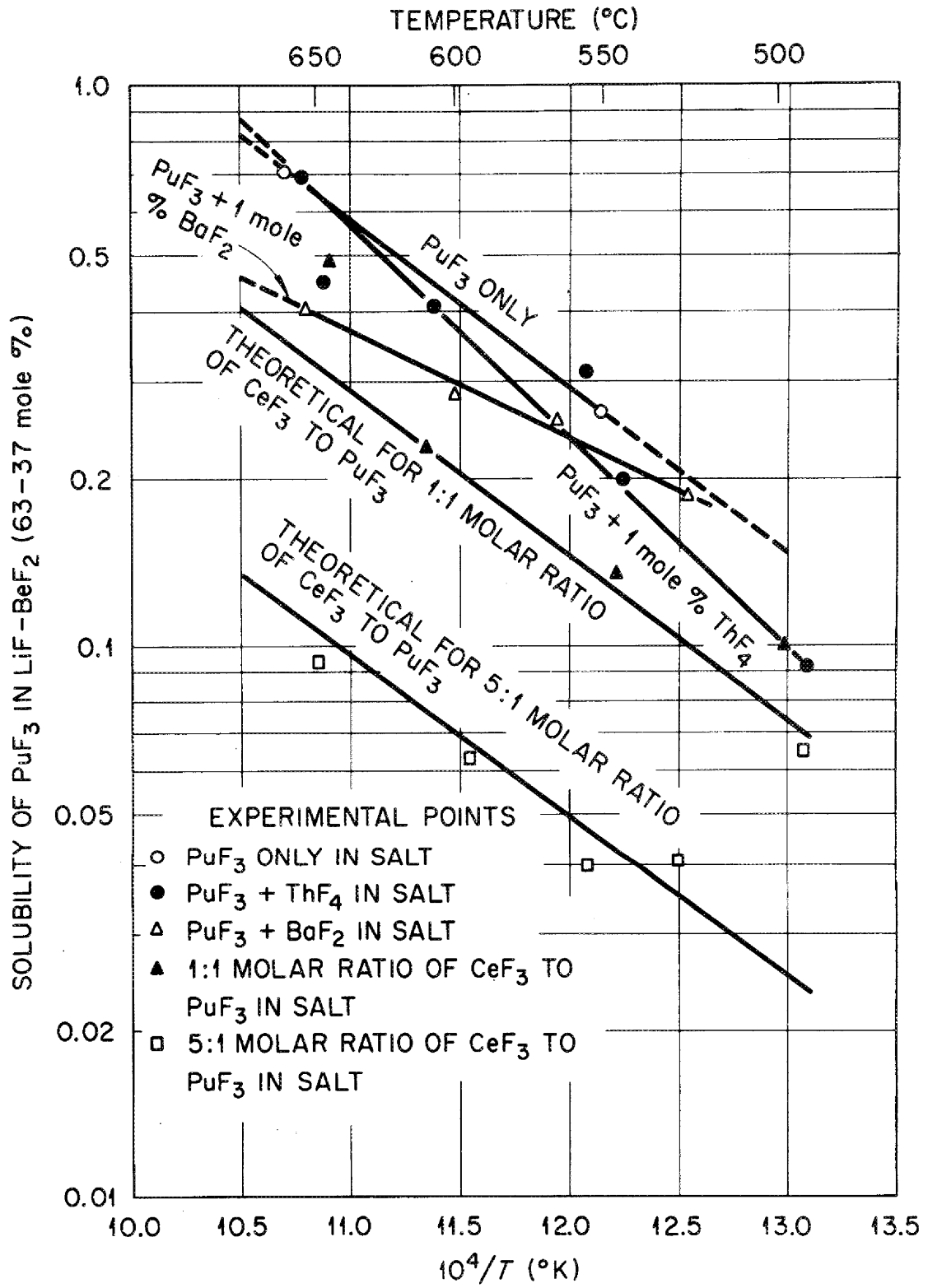


Fig. 4.

The solutes were found combined in single-phase materials with optical properties intermediate between those of CeF_3 and PuF_3 .

2. $\text{LiF}-\text{BeF}_2-\text{UF}_4$: Barton⁶ measured the solubility of PuF_3 in a $\text{LiF}-\text{BeF}_2-\text{UF}_4$ melt of the composition 70-20-10 mole %. The results which he obtained comprise the only available information on the solubility of PuF_3 in melts which contain more than 1 mole % of metal tetrafluorides. The values for the solubility of PuF_3 in the $\text{LiF}-\text{BeF}_2-\text{UF}_4$ solvent fall on a straight line when plotted as logarithm of concentration vs. reciprocal temperature. Considered in terms of "free fluoride" ions available, the ion balance in the solvent may vary from -10 to -30 depending on whether one assumes the predominant anionic association of uranium ions to be UF_5^- or UF_3^{3-} in the melt. Tetravalent uranium does not form stable phases of the stoichiometries Li_2UF_6 , Li_3UF_7 , or Li_4UF_8 . Of these, only Li_4UF_8 exists as an equilibrium crystalline phase, and its temperature range of stability extends only over 30°C . It seems most probable that the uranium ions in the solvent exist principally as UF_5^- . If so, the solubility data from Table 2 fit closely with those shown in Figure 3. Since ${}^7\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ single fluid fuels are likely to be more neutral on the negative side, we must presume that the solubility will be near the lowest values. The results of all the measurements which have been made suggest however that the solubility of PuF_3 in MSR solvent systems will not be lower than 0.25 mole % at temperatures of 550°C or higher.

Table 2. Solubility of PuF_3 in $\text{LiF}-\text{BeF}_2-\text{UF}_4$
(70-10-20 mole %)

<u>Filtration Temperature</u> (°C)	<u>Concentration of Pu in Filtrate</u>	
	(wt. %)	(mole %)
558	3.43	1.27
600	4.57	1.70
658	6.50	2.48

The data in Figure 3 indicate that if the "free fluoride" ion balance is negative, the differences in solubilities of CeF_3 and PuF_3 are essentially constant. Therefore, the solubility of PuF_3 in solvents similar in composition to the MSBR carrier and MSRE fertile carrier salt mixtures can be deduced from the results of CeF_3 solubility measurements, which in respect to those for PuF_3 , can be accomplished with comparative ease.

B. Segregation of PuF_3 on Crystallization of Fuel Salts

The principal components of MSR fuel mixtures do not form intermediate compounds with PuF_3 . From the solubility data cited above, it can be inferred that if it is employed in fuel mixtures at concentrations of a few tenths mole percent, PuF_3 will tend to crystallize from such mixtures as the primary phase and in solid solution with UF_3 and/or the rare earth trifluorides. The ${}^7LiF/BeF_2$ ratio in ${}^7LiF-BeF_2-ThF_4-PuF_3$ fuel mixtures could be adjusted to insure that at saturation other fluorides, such as ${}^7Li_3(Th,U)F_7$ would coprecipitate with PuF_3 at the liquidus. It is anticipated therefore that in the concentrations at which PuF_3 would probably be employed, it would not be deposited preferentially from the bulk salt during the inadvertent freezing, nor at locations such as in freeze valves where repeated thawing and freezing would take place.

C. Chemical Compatibility with Fuel Circuit Materials

A considerable amount of theoretical and experimental

evidence exists which indicates that as a component of fluoride fuel mixtures PuF_3 will be chemically compatible with container alloys and graphite. Of the actinide fluorides which may be used to constitute molten salt reactor fuel mixtures, plutonium trifluoride is the most chemically stable. Unlike UF_3 , it shows no tendency to disproportionate to the tetrafluoride and metal.

Fluoride melts containing PuF_3 were contained in nickel vessels in many of the experiments conducted by C. J. Barton and co-workers. Nickel proved to be an entirely satisfactory container material for this use. In the nickel based alloy, Hastelloy-N, the corrosion reaction which is intrinsic to uraniferous fluoride salt systems is $\text{Cr}^0 + 2\text{UF}_4 \rightleftharpoons 2\text{UF}_3 + \text{CrF}_2$, a reaction which has no analog in PuF_3 fuel systems. The role of PuF_3 in corrosion of Hastelloy-N container vessels may therefore be nil. The possibility that some unidentified reaction might cause mass transfer in a temperature gradient cannot be ruled out. Since such corrosion is limited by the diffusion of chromium in Hastelloy-N to liquid-solid boundaries,⁷ the rate of mass transfer could only be extremely low.

The compatibility of PuF_3 with MSR fuel circuit environment has, to an extent, already been demonstrated in the MSRE, where some 100 ppm of plutonium was generated and remained entirely in the fuel salt. Its stability there was established by the results of routine chemical analysis which were in good agreement with the anticipated values during ^{235}U operations.

It appears highly unlikely that the carbides of plutonium can form in molten salt reactors which employ PuF_3 in the fuel stream. The free energy of formation of the plutonium carbides is quite low, ~ 20 kcal/mole at 1000°K .⁸ While the uranium carbides have comparably low free energies of formation, the possibility of carbide formation with moderator graphite exists only if the activity of U^0 , formed in disproportionation, is permitted to rise $\geq 5 \times 10^{-7}$. Since disproportionation of PuF_3 does not occur, the driving force for the formation of plutonium carbides is entirely absent.

Thermodynamic data suggest that if graphite were to react with MSR fuel mixtures containing UF_3 , the most likely reaction would be $4\text{UF}_4 + \text{C} \rightleftharpoons \text{CF}_4 + 4\text{UF}_3$, which should come to equilibrium at CF_4 pressures of or below 10^{-8} atm. It has been shown by mass spectrometric analysis⁹ that the concentrations of CF_4 over graphite systems which were maintained for long periods at elevated temperatures did not exceed the lower detection limits (< 1 ppm) for this compound. Reduction of PuF_3 by a similar reaction appears to be very improbable.

From consideration of the thermochemical properties of PuF_3 and from its chemical behavior in the MSRE as described above, we can anticipate that the compatibility of PuF_3 with MSR graphite moderator and containment alloys will be excellent.

D. Solubility of Pu₂O₃ in Fluoride Mixtures

Initial demonstration of the application of PuF₃ in molten salt reactors would come appropriately from its inclusion in MSRE fuel salt. Before embarking on such a demonstration, it would be necessary to have accurate information about the solubility of Pu₂O₃ in the MSRE fuel and flush salts. C. F. Baes appraised the thermochemical data for PuF₃ and Pu₂O₃ recently¹⁰ and concluded that there is a distinct possibility of precipitating Pu₂O₃ if PuF₃ is introduced into the MSRE fuel salt at a concentration of as high as 0.2 mole % and if the oxide level should approach the value for ZrO₂ saturation (~500 ppm). In our previous experience with the MSRE, the total concentration of oxide in the fuel salt has remained less than 100 ppm. Although it seems improbable that saturation of the MSRE fuel salt with Pu₂O₃ could occur at such low oxide concentrations, the oxide tolerance of such mixtures is currently inestimable because of the uncertainties which may be present in the thermochemical data. Laboratory experience with PuF₃ melts has not suggested that Pu₂O₃ exhibits unusually low solubility in fluoride mixtures, i.e., that its solubility is lower than ZrO₂ or UO₂. However, since the possibility exists that Pu₂O₃ precipitation might occur, the oxide chemistry of Pu³⁺ in molten fluorides should be determined experimentally if the MSRE were to be used to demonstrate the potential application of PuF₃-based fuels.

ESTIMATION OF EFFECTS OF CHEMICAL REPROCESSING

One of the anticipated advantage of starting molten salt reactors on plutonium rather than on ^{235}U is that slightly improved nuclear performance (increase of about 0.01 in the breeding ratio) over a 30-year reactor life would result from its temporary presence in the reactor. The maximum economic advantage would result from removal of the higher isotopes of plutonium (neutron poisons) after plutonium burnout. The incentives for using PuF_3 to start up molten salt reactors are to some extent enhanced or diminished relative to the simplicity (economy) of the fuel reprocessing methods which are employed in conjunction with its use. For the economic advantage of employing plutonium in the fuel-fertile salt to be very significant, the reprocessing costs associated with removal of ^{241}Pu and ^{242}Pu should not add appreciably to the fuel cycle costs. In order to achieve such economy, it will probably be necessary to remove plutonium via the same chemical processes which are to be employed for the ^{233}U -Th fuel-fertile stream. At the current stage of MSBR fuel reprocessing development, it is anticipated that reductive extraction methods would be employed. As is shown below, the available electrochemical data for plutonium and protactinium compounds do not permit us to deduce whether protactinium is separable from plutonium on a short cycle, ~ 3 days, when plutonium is the fuel. Further, removal of ^{241}Pu and ^{242}Pu after ^{239}Pu burnout involves separation of plutonium from thorium. This separation appears to

be more tractable than the former, but also cannot be assured at this point. If separation coefficients for plutonium are found to lie between those for protactinium and the rare earths, little or no plutonium would be removed concurrent with protactinium.

Unlike the lanthanides, the actinides exhibit trends in chemical properties which reach minimum or maximum values among the first members of the series. Such a trend is shown in Cunningham and Wallman's values¹¹ of the formal potentials for the reaction $M(s) \rightarrow M^{3+}$ in aqueous solution. (See Figure 5)

A similar trend is suggested in the reduction potentials for Th^{4+} , U^{3+} , and Pu^{3+} in the fluoride solvent, $LiF-BeF_2$ (66-34 mole %) (Figure 5). These trends might imply that the ϵ_0' for the reduction of plutonium into a bismuth alloy will be nearly identical to that for protactinium. We have no means available at present for estimating ϵ_0' for plutonium reduction with the accuracy required to indicate its position in the reduction sequence of the actinides Th to Pu.

Moulton¹² has recently evaluated the possibilities of removing Pu from molten salt reactor fuels by reductive extraction into bismuth. His conclusions are summarized as follows. The stability of Pu-Bi intermetallic phases is not predictable quantitatively. The similarities of the Th-Bi, U-Bi, and Pu-Bi phase diagrams indicate that the activity of plutonium will be substantially lower in bismuth.

The activity of a metal in bismuth can be referred to the pure metal by the use of an activity coefficient γ_M which is $\ll 1$ and more or less constant at this value from infinite dilution up to saturation where the saturating phase is the solid intermetallic. Then $\epsilon = \epsilon_0' - \frac{RT}{nF} \ln \gamma_M/\gamma_S$. (γ_S , the ion activity coefficient, goes to 1 at infinite dilution and can be considered as 1 to a first approximation.) Literature values of γ_{Th} and γ_U are 5.7×10^{-8} and 1.3×10^{-4} (13,14) which would give $\epsilon_{0Th}' = -1.58$ and $\epsilon_{0U}' = -1.27$ with respect to the H_2 -HF electrode at $\epsilon_0 = 0$. The results of experiments conducted by Moulton and Shaffer show that ϵ_0' for Pu is about 0.05V more negative than ϵ_0' for U. If $\gamma_{Pu} = \gamma_{Th}$, then $\epsilon_0' = -1.20$, while if $\gamma_{Pu} = \gamma_U$, $\epsilon_{0Pu}' = -1.40$. One can be reasonably sure that ϵ_{0Pu}' will fall somewhere within these limits. Since ϵ_0' for the rare earths lie about -1.50, it is likely that Pu can be separated from them and from thorium. Its position relative to U and Pa is not so clear.

An argument can be made that γ_{Pu} will be nearly the same as γ_M for either U or Th. The solubility of $PuBi_2$ in Bi is greater at any temperature than that of UBi_2 or $ThBi_2$, and its congruent melting point is lower (830 vs. 1010 and 1230°C) which suggests that γ_{Pu} is not very small. On the other hand, the metal itself melts lower (640 vs. 1132 and 1750°C) so that of the three systems only $PuBi_2$ melts higher than the metal. There is some correlation between electro-negativity and stability of actinide intermetallic compounds

with bismuth. Plutonium and thorium both have a value of 1.3 (Pauling scale) while uranium is 1.7. The Pu intermetallic will therefore probably exhibit comparable stability.

If plutonium comes out before or with uranium in the reduction extraction process, it can be concluded that the utilization of PuF_3 in molten salt reactors would have little or no effect on fuel reprocessing costs. It would be necessary to separate the uranium and plutonium, probably by fluorination, but this step should not increase overall fuel processing costs appreciably.

If it is found that the separation coefficients for plutonium in reductive extraction processes are unfavorable, alternative methods for its removal could be devised. One possible method would involve fluorination of the fuel first at 550°C to remove uranium as UF_6 , then at higher temperatures, $\geq 700^\circ\text{C}$ to remove plutonium as PuF_6 , leaving any undecayed protactinium with the carrier salt. This procedure would utilize the increase in stability of PuF_6 with increasing temperature¹⁵ and the fact that protactinium does not form volatile fluorides. Such a method would, of course, not be applicable during operation of a reactor with PuF_3 fuel, but rather is a possible means of final removal of plutonium.

The chemical feasibility of incorporating PuF_3 in molten salt reactor fuels, as demonstrated by operating the MSRE with a PuF_3 fuel, would not be impaired by the incomplete development of a chemical process for its separation from

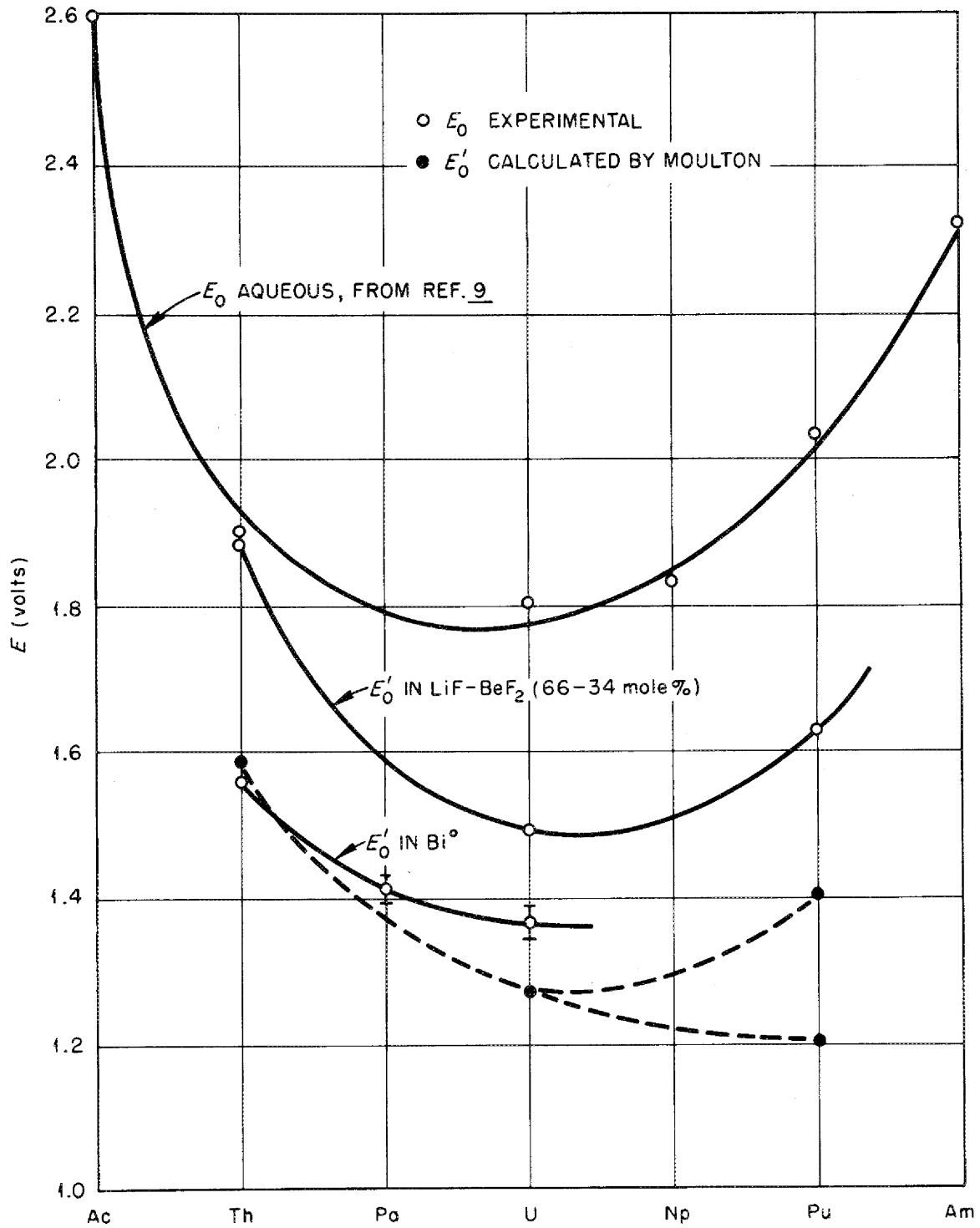


Fig. 5. Standard Reduction Potentials for Some Actinides in Aqueous, Molten Salt, and Metallic Solvents.

protactinium. It should be inferred therefore that while a flowsheet for its separation cannot now be devised, the research and development efforts are readily identifiable and are experimentally tractable.

FISSION PRODUCTS

In one of the important continuing investigations within the MSRP, we are attempting to establish experimentally the chemical identities and modes by which a number of the fission products, notably those of the near noble metals, are distributed, partly as a means for predicting the behavior of spent fuel in the chemical reprocessing plant and partly to establish its corrosion potential accurately with increasing burnup. No significant differences are believed to exist in the yields or chemistry of the principal species of fission products which would result from incorporation of PuF_3 in MSR fuels. The feasibility of using PuF_3 in startup operations of an MSR does not therefore appear to require a separate research program relative to fission products from plutonium.

With $^{235}\text{UF}_4$ fuel, the fission reaction is mildly oxidizing, resulting in the oxidation of ~ 0.8 equivalent⁴ of UF_3 per gram atom of fissioned uranium. The oxidation potential results from the anion-cation imbalance which develops as the fission products reach thermodynamic equilibrium. With UF_4 as the fissile solute, a slight excess of

fluoride ions develops. Use of a trifluoride solute, however, should result in a cation excess, and should cause the fuel solution to generate a mild reducing potential.

The yield of ^{135}Xe from plutonium fission is somewhat greater than from ^{235}U , and in turn, is less than from ^{233}U . The relative poison fraction of ^{135}Xe in the fuel would be at a minimum at initiation of power operations with PuF_3 fuel and would increase as ^{233}U was generated within the system.

USE OF THE MSRE TO DEMONSTRATE FEASIBILITY OF OPERATION OF MSR'S WITH PuF_3

Consideration of several developments in molten salt reactor chemistry within recent years suggests that the most appropriate and earliest demonstration of the applicability of PuF_3 in molten salt reactors would come from its use in the MSRE. Sufficient basic chemical information exists to conclude that it is neither necessary nor important to demonstrate chemical compatibility with metal alloys in engineering laboratory scale tests. Laboratory scale tests with plutonium should be restricted to the minimum number necessary to establish stabilities because of the inhalation hazard of plutonium-239. Plutonium-239 is, in fact, regarded as one of the most toxic substances known to the experimentalist.

The fact that plutonium-beryllium mixtures are neutron

sources also complicates laboratory and engineering scale experiments in which ${}^7\text{LiF}-\text{BeF}_2-\text{PuF}_3$ mixtures are used. Some typical values¹⁶⁻¹⁸ of the neutron energies produced from actinide-beryllium α, n reactions are listed in Table 3.

Tate and Coffinberry¹⁹ have computed theoretical neutron yields of plutonium-beryllium alloys employing calculations which include a term from the experimental stopping power of the matrix elements for alpha particles. The available data suggest that in a dilute Be^{2+} solution, such as in a MSRE fuel mixture, e.g., ${}^7\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{PuF}_3$ (64-28-5-3-0.2 mole %) the neutron yield would not be so great as to require special shielding of salt lines, drain tanks, or fuel sample transport containers.

The possible criticality problems associated with storage of PuF_3 -bearing fuel salt have been considered qualitatively and do not seem to be ominous. Whereas fission multiplication factors hold for ${}^{233}\text{U}$ into the epithermal neutron range, they do not do so in the case of plutonium. Further, more energetic α, n reactions will accompany ${}^{233}\text{U}$ operation of the MSRE²⁰ than are likely with PuF_3 , primarily because of the presence of ${}^{232}\text{U}$ in the charge which is to be used. Accordingly, the potential radiation problems associated with α, n reactions in fuel salt will have been faced before PuF_3 is used in the MSRE. Although radiation from fuel-fertile salt in storage tanks does not seem to be serious, detailed scrutiny of the possible problems which

Table 3. Typical Values of Neutron Energies Produced
From Actinide-Beryllium α, n Reactions

α Source	$t_{\frac{1}{2}}$	Q(Mev)	Neutron Energy (Mev)	Neutron yield/ 10^6 disintegrations
^{210}Pu	138.4d	5.3	≤ 11 , av. 4	80
^{222}Rn	3.83d	5.48	≤ 11	460
^{226}Ra	1.62×10^3 y	5.65	≤ 13	460
^{233}U	1.63×10^5 y	4.82		
^{235}U	7.07×10^8 y	4.80		
^{239}Pu	2.43×10^4	5.15	≤ 10 , av. 4	

might arise from α, n reactions would be necessary before the PuF_3 were to be used in the MSRE.

Except for a few data on solubility of the fluorides and oxides, which are obtainable in laboratory measurements, chemical compatibility in reactor containment systems is reasonably assured. If the solubilities of Pu_2O_3 and PuF_3 in $\text{LiF}-\text{BeF}_2-\text{ZrF}_4$ melts are found to be in excess of 300-400 ppm and 0.2 mole %, respectively, a test in the MSRE would be virtually assured of success with respect to the chemical behavior of the plutonium-bearing salt.

CHEMICAL DEVELOPMENT REQUIREMENTS

It appears that the chemical feasibility of employing PuF_3 in molten salt reactors will be assured if two general properties, solubility of the oxides and fluorides in $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4$ solvents are suitably high, and the extractability of Pu metal from fluoride melts into bismuth amalgams is sufficiently discrete to be economic. As noted above, only the absence of solubility data obviates the conclusion that PuF_3 could be incorporated in the MSRE fuel salt at our earliest convenience.

In order to establish that it is chemically feasible to fuel molten salt reactors with PuF_3 , a program of chemical development should include the following items:

- a. Determination of the solubility of PuF_3 in $\text{LiF}-\text{BeF}_2-\text{ZrF}_4$ and $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4$ solvents. It should be adequate to carry out most of the necessary measurements with CeF_3 as a proxy for PuF_3 . Thereafter, only a few experiments with PuF_3 would be required to confirm the conclusions based on CeF_3 solubilities.
- b. Determination of the solubility of Pu_2O_3 in $\text{LiF}-\text{BeF}_2-\text{ZrF}_4-\text{ThF}_4-\text{UF}_4$ solvents. The lanthanide oxides do not serve adequately as proxies for estimation of actinide oxide solubilities. It will be necessary therefore to determine the oxide tolerance of fuel salts directly with plutonium oxide in alpha-laboratory facilities.
- c. Establishment of the standard reduction potentials and separation coefficients for plutonium in Bi-Th alloys.
- d. Solubility of Pu in Bi-Th alloys.

Items c. and d. should become a part of the existing programs in chemical and chemical engineering development. It may be unnecessary to initiate experimental work in this part of the program until it is first demonstrated that PuF_3 fuels perform satisfactorily in a molten salt reactor.

It is likely that some 15 to 20 years will pass before plutonium trifluoride is incorporated in a full scale power reactor. If a demonstration that molten salt reactors are operable with PuF_3 fuels is regarded as desirable, it can probably be realized with the MSRE. Since molten salt fuel processing technology will require a period of years to evolve,

the ambiguous fate of plutonium in fuel reprocessing should not at this point be considered a deterrent to a continuing evaluation of the chemical feasibility of employing PuF_3 as an MSR fuel.

SUMMARY

A definite economic advantage is associated with startup of molten salt breeder reactors with PuF_3 -based fuel. If the solubilities of plutonium oxide and plutonium trifluoride are confirmed as exceeding a few hundred ppm and ≈ 0.2 mol %, respectively, the chemical feasibility of fueling molten salt reactors with PuF_3 will be essentially assured. Separation of protactinium and plutonium during operation of a PuF_3 -fueled reactor, and removal of ^{241}Pu and ^{242}Pu after two years of operation, as would be desirable in a large breeder reactor from an economic standpoint, has not yet been demonstrated, although conceptual designs of processes for effecting such separations are available for development.

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