MOLTEN SALT CHEMISTRY - PART I. PREPARATION OF CeF₃, PuF₃, ThF₄ AND PURIFICATION OF LiF-BeF₂-ThF₄ MIXTURE

by

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1973
Equipment set up for the preparation of CeF$_3$, PuF$_3$ and ThF$_4$ and purification of LiF-BeF$_2$-ThF$_4$ mixture for the determination of solubility of CeF$_3$ and PuF$_3$ in ternary mixtures of LiF-BeF$_2$-ThF$_4$ and binary mixtures of LiF-ThF$_4$ are described. Using these equipment the preparation of 75 g of CeF$_3$ tagged with $^{144}$Ce and 60 g of PuF$_3$ and purification of 1.2 kg of LiF-BeF$_2$-ThF$_4$ mixture have been carried out. The analysis of compounds for fluoride by pyrohydrolysis and the estimation of Li, Be and Th in the salt mixture has been reported.
1. INTRODUCTION

Indian Nuclear Power Programme is well under way with the commissioning of Tarapur Atomic Power Station and the construction of Rajasthan Atomic Power Project and Madras Atomic Power Project in progress. As the next step in the reactor programme, various breeder concepts have been evaluated from the point of view of economy and fuel utilisation and fast breeder reactor is one of them. The Department of Atomic Energy is building a Fast Breeder Test Reactor at Madras. Another concept which looks promising is that of Molten Salt Breeder Reactor. It was decided in 1967 to investigate the feasibility of using such a reactor for Indian Nuclear Power Programme with particular emphasis on the use of plutonium.

The molten salt reactors are attractive on account of their good potential for the utilisation of thorium and plutonium provided PuF₃ is sufficiently soluble in the salt matrix. Enriched uranium, ²³³U and plutonium are the possible start up fissile materials for these reactors. A molten salt reactor utilising ²³³U as the fissile material can have a conversion ratio greater than unity and it is termed a Molten Salt Breeder Reactor (MSBR). The reactors utilising enriched uranium or plutonium as the start-up materials act as converters (conversion ratio less than 1) but change over to breeders with the ²³³U-²³²Th fuel cycle.

Conceptual Molten Salt Breeder Reactors are thermal spectrum reactors which use fluorides of fissile materials dissolved in a suitable molten salt mixture as fuel. Graphite is used as the moderator. For the salt matrix, fluorine, lithium-7 and beryllium have been chosen as
major constituents because of their low neutron absorption cross-sections and also because of the reasonable solubility of fissile and fertile fluorides in mixtures of lithium and beryllium fluorides at temperatures of practical interest. The fertile thorium as the tetrafluoride is dissolved in the fluoride salt matrix to form a separate blanket stream or directly added to the core salt itself. The reactor is termed as a two-fluid reactor or single-fluid reactor accordingly. Currently the single-fluid, two region concept is being preferred at ORNL because it leads to comparable breeding and eliminates the necessity of using graphite as a plumbing material to separate salt streams. These reactors operate at about 1300°F and at atmospheric pressure. Heat is transferred from the fuel salt to coolant salt in an intermediate heat exchanger. A eutectic mixture of sodium fluoroborate and sodium fluoride is selected as the coolant salt. The coolant salt passes through a stream generator where supercritical steam is generated for power generation. Another side stream of the core fuel is continuously passed through a chemical processing system for the separation of protactinium and fission products. As there is no excess reactivity built in the reactor, provision for continuous on-line refuelling is made.

Molten Salt Breeder Reactors have a number of advantages over the other reactor systems. These are

I. Low specific inventory (approximately 1 kg/MWe) as compared to other breeder reactor designs,
II. Absence of material handling problems such as fuel fabrication etc.,
III. Possibility of in-line fuel reprocessing,
IV. High negative temperature coefficient of reactivity and
V. Absence of positive excess reactivity in the reactor.

Some of these features have been brought out by the operation of a 8 MW(t) Molten Salt Reactor Experiment at ORNL.

There are of course a number of drawbacks also in this reactor system. Some of these are
1) Need to pre-heat the equipment and to keep the equipment above the melting point of the salt mixture at all times,

ii) Problem of long-term containment and recirculation of fuel,

iii) Necessity for techniques of remote maintenance,

iv) Problem of graphite damage at high power densities to be used in the reactor and

v) Rigid requirement of leak tightness and component reliability.

Extensive research and development work on all the aspects of Molten Salt Reactor Technology has been in progress at Oak Ridge National Laboratory for more than 25 years and a recent review summarises the present status of this concept(1).

The idea of using fused-fluorides as reactor fuel originated at ORNL and has been extensively studied since 1950. The basic feasibility of such a reactor system was demonstrated by the Aircraft Reactor Experiment (ARE) in 1954 where NaF-ZrF₄-UF₄ (53.1 - 40.7 - 6.2 mole pct) was used as fuel(2). Enriched uranium containing 93.4 pct ²³⁵U was used. To test the types of fuels and equipment that would be used in an MSBR the 8 MW(t) Molten Salt Reactor Experiment (MSRE) was built and operated from June 1965(3). This reactor operated at 1200°F and at atmospheric pressure. The initial fuel charge contained LiF-BeF₂-ZrF₄-UF₄ of composition 65 - 29 - 5 - 0.9 m/o and the uranium was about 33% ²³⁵U. The melting point of the salt is 840°F. Operation with ²³⁵U as fuel was terminated in March 1968. Uranium from the salt was removed by fluoride volatility techniques and the reactor was recharged with ²³³U as fuel(4) and operated from October 1968 to December 1969. The MSRE was the first reactor in the world to operate on ²³³U fuel. During the last phase of MSRE operation about 300 g of PuF₃ was also added to demonstrate the suitability of PuF₃ as a make up fuel for MSRE(5).

With the successful operation of MSRE the studies are now directed towards development of MSBR. A number of designs for power reactor systems of this type have been proposed and evaluated at ORNL. Some of
the designs are as follows:

A. Two-region two-fluid MSBR $^{235}\text{U} - ^{233}\text{U}$

In this design the fissile and fertile streams pass through separate graphite tubes within the reactor core. Some of the basic data for this reactor is as follows:

<table>
<thead>
<tr>
<th>Power</th>
<th>1000 MW(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel composition</td>
<td>Blanket stream composition</td>
</tr>
<tr>
<td>mol pct</td>
<td>mol pct</td>
</tr>
<tr>
<td>LiF</td>
<td>LiF</td>
</tr>
<tr>
<td>63.60</td>
<td>71</td>
</tr>
<tr>
<td>BeF$_2$</td>
<td>BeF$_2$</td>
</tr>
<tr>
<td>32.1</td>
<td>2</td>
</tr>
<tr>
<td>ThF$_4$</td>
<td>ThF$_4$</td>
</tr>
<tr>
<td>0.00</td>
<td>27</td>
</tr>
<tr>
<td>UF$_4$</td>
<td></td>
</tr>
<tr>
<td>0.22</td>
<td></td>
</tr>
</tbody>
</table>

Breeding ratio - 1.05
Specific inventory 0.77 Kg/MW(e)

B. Two-region two-fluid MSBR with protactinium removal

Composition of fuel and blanket is same as in (A)
Breeding ratio 1.07
Specific inventory 0.68 KG/MW(e)

C. One-fluid two-region MSBR $^{235}\text{U} - ^{233}\text{U}$

In (A) and (B) the use of graphite tubes in the reactor core posed serious problems and led to this concept. In this design the fissile and fertile materials are combined in one stream. Two regions are obtained by having different fuel-salt to moderator ratios in the inner and outer regions of the reactor. The central region is graphite-moderated and is critical, whereas the outer region does not have any graphite and is sub-critical. The basic design data is as follows:

<table>
<thead>
<tr>
<th>Power</th>
<th>1000 MW(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel-cum-fertile salt composition</td>
<td></td>
</tr>
<tr>
<td>mole pct</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>71.7</td>
</tr>
<tr>
<td>BeF$_2$</td>
<td>16.0</td>
</tr>
<tr>
<td>ThF$_4$</td>
<td>12.0</td>
</tr>
</tbody>
</table>
The concept (C) is the present favourite because it is technologically simpler than the other two concepts. Though this design concept is the best from the point of view of breeding gain and fuel inventory requirements, it envisages on-line reprocessing (which is not yet developed on an engineering scale) for the removal of protactinium and fission products and also requires replacement of core graphite every four years.

As the high performance MSBR's suffer from the above disadvantages, as an intermediate stage towards development of MSBR, large MSRE type converters of 300 MW(e) and 1000 MW(e) are being considered. These intermediate type of reactors envisage batch reprocessing for recovery of fissile material and discard of the salt matrix with fission products and a core graphite life of 30 years. With addition of on-line reprocessing these reactors become breeders. The basic design data for a plutonium fuelled MSR with batch processing every 8 years and 30 year graphite life has been published recently(8) and is given below:

**Power**
300 MW(e)

**Salt composition**

<table>
<thead>
<tr>
<th>Salt Composition</th>
<th>Mole Pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>72</td>
</tr>
<tr>
<td>BeF₂</td>
<td>18</td>
</tr>
<tr>
<td>ThF₄</td>
<td>10</td>
</tr>
</tbody>
</table>

**Breeding ratio** 0.84

**Specific inventory** 1.9 Kg/MW(e)

Indian nuclear power programme envisages the use of $^{233}\text{U}/^{232}\text{Th}/^{233}\text{U}$ cycle for the utilisation of thorium. It appears that MSBR concept is suitable for this purpose from various considerations. The principal amongst these are:

<table>
<thead>
<tr>
<th>Salt Composition</th>
<th>Mole Pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>72</td>
</tr>
<tr>
<td>BeF₂</td>
<td>18</td>
</tr>
<tr>
<td>ThF₄</td>
<td>10</td>
</tr>
</tbody>
</table>

Breeding ratio 0.84

Specific inventory 1.9 Kg/MW(e)
i) Conversion ratio for a $^{233}$U/$^{232}$Th/$^{233}$U cycle is higher in thermal reactors

ii) Nuclear homogenity of the system helps in achieving low specific inventory in thorium cycle reactors

iii) Removal of protactinium by continuous reprocessing helps in conservation of the fissile U-233 which is the decay product of $^{233}$Pa.

However, India does not have enriched uranium and uranium-233 will not be available till the Fast Breeder Reactors operate for a sufficiently long time. Indian interest lies in the possibility of starting up a molten salt reactor using plutonium with ultimate switch over to uranium-233. In order to assess the chemical feasibility of a plutonium start-up molten salt reactor, it is necessary to establish the solubility of plutonium trifluoride in the solvent composition of interest which is expected to be a mixture of LiF, BeF$_2$, and ThF$_4$. It was estimated that the minimum solubility of plutonium trifluoride required for the start-up of a molten salt reactor is about 0.24 m/o in the ternary mixture of LiF-BeF$_2$-ThF$_4$ based on the assumption that the fissile plutonium content is about 70%($^{240}$Pu is the principal fuel, its high neutron absorption cross section tends to depress the thermal flux, and thus increase the critical loading of fissile material. It is estimated that this may be as high as two to three times the value reported earlier($^{8a}$). The study of plutonium start-up reactors is being continued with the object of reducing the initial fissile loading. One method suggested for this is to increase the LiF-BeF$_2$-ThF$_4$ to moderator ratio by lowering the thorium concentration in the reactor.

As no data on the solubility of PuF$_3$ in ternary mixtures existed, it was decided as a first step in the chemical investigations to determine the solubility of plutonium trifluoride in LiF-BeF$_2$-ThF$_4$ mixtures in the temperature region of interest for a molten salt reactor.

Solubility of PuF$_3$ in binary fluorides of alkali metals and beryllium...
has been reported by Barton. Based on the similarity between Ce(III) and Pu(III) Thoma pointed out that CeF$_3$ should serve as a convenient stand-in for the determination of the solubility of PuF$_3$ and Barton determined the solubility of CeF$_3$ in ternary mixtures of LiF-BeF$_2$-ThF$_4$. In order to initiate the investigation of the solubility of PuF$_3$, it was necessary to prepare fluorides like CeF$_3$, PuF$_3$ and ThF$_4$ and purify the LiF-BeF$_2$-ThF$_4$ from mixture and oxide impurities as the tolerance level for oxide impurities is of the order of only a few hundred ppm. This report describes the method of preparation of CeF$_3$, PuF$_3$, ThF$_4$ and purification of LiF-BeF$_2$-ThF$_4$ mixtures for the determination of the solubility of PuF$_3$. The experimental facilities set up for the solubility determination, the solubility of CeF$_3$ as a stand-in for PuF$_3$ and the solubility of PuF$_3$ in LiF-BeF$_2$-ThF$_4$ and LiF-ThF$_4$ melts are given in Part II and Part III of this series.

2. PREPARATIVE AND PURIFICATION METHODS FOR FLUORIDES REPORTED IN LITERATURE

The fluorides of the lanthanide elements are generally prepared by three methods all of which are essentially similar. These methods are

i) Direct hydrofluorination of the oxide

$$M_2O_3 + 6HF \xrightarrow{700^\circ C} 2MF_3 + 3H_2O \quad \quad \cdots \quad (1)$$

ii) Reaction of the oxide with ammonium bifluoride

$$M_3O_3 + 6NH_4HF_2 \xrightarrow{300^\circ C} 2MF_3 + 6NH_4 + 3H_2O \quad \quad (2)$$

iii) Dehydration of the hydrated trifluoride obtained by precipitation from aqueous solution

Spedding and Daane found that direct hydrofluorination of oxides yields superior grade trifluorides and that the most reactive oxides are obtained by the decomposition of the lanthanides (III) oxalates at 700-800$^\circ$C. They also found that static bed apparatus is quite satisfactory for the preparation of the trifluoride up to 1 kg. The same authors
first reported the ammonium bifluoride method for the preparation of the trifluorides. However, this method produces the trifluoride with a higher oxygen content than the product obtained by hydrofluorination. Although the reaction between ammonium bifluoride and the rare earth oxide is suitable for the preparation of small amounts of the trifluorides, complete removal of the excess ammonium bifluoride is difficult when larger amounts are employed.

The main disadvantage associated with lanthanide trifluoride hydrate appears to be the difficulty in obtaining it in an easily filterable form and the slightly higher oxygen content of the anhydrous trifluorides. However, this method has been frequently used and the trifluoride hydrates, usually obtained by the addition of hydrofluoric acid to solutions of the trivalent lanthanides can be dehydrated by vacuum drying above 1000°C, by heating in anhydrous hydrogen fluoride at 600°C or heating in helium at 400°C.

Plutonium trifluoride requires only mild reducing conditions for its formation; for example, the reaction of the dioxide with a mixture of hydrogen and hydrogen fluoride goes to completion at about 500°C. Plutonium trifluoride has also been prepared by heating other compounds of plutonium such as plutonium(III) oxalate in hydrogen-hydrogen fluoride mixtures, by reacting plutonium(III) and (IV) oxalates with Freon-12 at 400-450°C and by thermal decomposition of PuF₄·2.5 H₂O in vacuum.

Hydrated thorium tetrafluoride is precipitated from aqueous solutions of thorium by the addition of hydrofluoric acid. The dehydration of the tetrafluoride can be successfully achieved by heating the solid above 500°C in anhydrous hydrogen fluoride. A simplest and satisfactory method of preparation of thorium tetrafluoride is by heating ThO₂ in anhydrous hydrogen fluoride. Highly reactive forms of the dioxide can be obtained by the thermal decomposition of the oxalate at 400°C. The combination of a preliminary decomposition followed by hydrofluorination is superior to the direct conversion of the oxalate.
As it was reported by Spedding and Daane that the direct hydro-
fluorination of the oxide at high temperatures gives superior grade
trifluoride with the minimum amount of oxide impurity this method was
chosen for the preparation of both CeF\textsubscript{3} and PuF\textsubscript{3} in the present work.
As thorium fluoride was obtained from the Chemical Engineering Division
as hydrated fluoride, this was dehydrated by heating in a current of
anhydrous hydrogen fluoride at a temperature of 600\textdegree C as has been
reported by Katz and Rabinowitch\textsuperscript{(27)}.

At ORNL\textsuperscript{(30)} the purification of LiF-BeF\textsubscript{2} salt mixture from oxide,
moisture and sulphur containing impurities is done by sparging the
molten mixture at high temperature with hydrogen and HF followed by further
hydrogen sparging. The treatment with hydrogen reduces the sulphur
containing impurity to \(S^2\)\textsuperscript{-}, and oxidants (for example Fe\textsuperscript{3+}) to lower
valence states. The HF treatment volatalises \(H_2S\) and \(HCl\) and converts
the oxides and oxyfluorides of beryllium into fluorides. The subsequent
treatment with hydrogen reduces any nickel fluoride formed during HF
treatment to nickel and other lower valence fluoride like \(Fe^{+2}\) into
insoluble metals. The molten salt is filtered through a porous nickel
filter to remove these metallic impurities. As the solubility of plutonium
trifluoride has to be determined in the ternary mixture of LiF-BeF\textsubscript{2}-ThF\textsubscript{4},
it was decided to carry out the purification of these by the same
procedure as that used at ORNL.

3. EQUIPMENT

3.1 High purity hydrogen and argon lines

Two gas manifolds of the type shown in Figure 1 were constructed
for the supply of high purity argon and hydrogen necessary for most of
the preparation of fluorides and purification of salt mixtures. In both
the assemblies the gas (Ar or \(H_2\)) from the cylinder passes through a flow-
meter to the purification unit consisting of a drier and a high
temperature getter for oxygen and nitrogen. Linde molecular sieves type 4A
are used for removal of moisture from the gases. For the getter assembly,
uranium turnings heated to 750\textdegree C are used for the purification of argon,
and titanium sponge heated at 900°C for purification of hydrogen.
The drying towers are made from 2" Sch 40 stainless steel pipe. The
getter towers are made from 4" Sch 40 stainless steel pipe and are lined
with molybdenum to prevent reaction of the getter with stainless steel
at high temperature. The flanges on this 4" pipe are water cooled to pre-
vent overheating of the neoprene 'O' rings. The gas enters the getter
bed through a tantalum tube which has been fitted onto the top flange
with a swagelok coupling. The purified gas goes to the manifold through
the second opening on the cover flange. The getter temperature is moni-
tored with the help of a thermocouple fitted inside the tantalum tube.
Split unit furnaces of 2 KW capacity are used for heating the getters.
The temperature of the titanium getter is controlled by an on-off
temperature indicator-cum-controller. The temperature of uranium getter
is read on a temperature indicator. The gas manifolds are fitted
with vacuum and pressure gauges and 1/4" brass valves having stainless
steel diaphragm seals. Piping has been provided from these gas manifolds
to the HF manifold.

3.2 Hydrogen fluoride gas manifold

A hydrogen fluoride gas manifold was constructed for distribution
of hydrogen fluoride gas mixed with high purity argon and hydrogen into
the reaction vessels used for the preparation and purification of fluorides.
The manifold is shown in Figure 2. It is constructed mainly of 3/8" O.D.
nickel tube and Hoke HF control needle valves or 1/4" diaphragm valves.
All the connections between the valves and nickel tubes is made by back
brazing with low melting silver solder and various sections of the
piping are connected with 1/4" or 3/8" standard monel teflon gasketed flare
fittings and brass flare nuts. The manifold is isolated from the high
purity argon and hydrogen lines with the help of a monel check valve
which prevents the back diffusion of HF into these high purity gas lines.
The HF pressure or total line pressure can be read on a helicoid gauge.
The manifold is connected to an HF cylinder of 3" diameter and length 16"
through a gas mixer of 1" O.D. and 6" length filled with nickel turnings.
The HF cylinder has two monel needle valves, one of which is used for
evacuating and filling the cylinder with HF, while the other is used for
supplying HF to the gas manifold. For filling the cylinder with HF, it is
cooled in dry ice and connected to the outlet of a standard HF cylinder through an outlet valve (Matheson valve type No.56A-570) and pipe fittings. Because of the difference in temperature and pressure of the cylinders the smaller cylinder gets filled up with HF. The cylinder is connected to the manifold after filling. The HF manifold is connected to the fluoride preparation and purification vessels in the glove box through 3/8" O.D. monel piping. The waste HF emerging from the reaction vessel is let out through a water trap and monel line filter and finally led into NaF traps or NaOH bubbler kept in a separate glove box for disposal.

3.3 Reaction vessel for the preparation of the fluorides

The reaction vessel used for the preparation of high purity fluorides is shown in Figure 3. This consists of 3" I.D. 15" long nickel tube extended by a 1" I.D. 6" long nickel tube. One end of the cylinder is provided with a teflon gaasketed flanged opening and the other end is provided with a gas outlet. The material to be fluorinated is placed in a nickel boat and introduced into the reaction vessel through the flanged opening. The flange is closed leak-tight and the material is heated in a stream of H₂ + HF to the desired temperature by means of a split-unit heater of 3 1/2" I.D. and 16" length surrounding the vessel. The temperature of the reaction vessel is measured by means of a chromel-alumel thermocouple placed between the furnace wall and reaction vessel. The thermocouple is connected to a calibrated indicating pyrometer for reading the temperature directly. The whole equipment is mounted in a glove box used for the preparation and purification of salts.

4. Salt purification assembly

As the salt to be purified contained beryllium fluorides, it was decided to set up the salt purification assembly in a glove box. Continuous monitoring of the atmosphere was carried out by the Health
Physics Group to detect any abnormal release or spread of beryllium during operations. The beryllium concentration either in the atmosphere or on the working surfaces did not exceed or reach the maximum tolerance set by the Industrial Hygiene Section.

The apparatus constructed for the purification of salt mixture by sparging with $\text{H}_2$ and HF is shown in Figure 4. It consists of two 3" I.D nickel cylinders one 14" and the other 10" long. Each of these has a nickel liner made from 1/16" nickel sheet, to contain the molten salt. On the top of the larger cylinder a gas outlet tube and 1" O.D., 12" long charging port have been welded. The smaller cylinder is provided with a flange so that a mating cover flange can be tightened on to it. This cover flange is provided with a gas inlet tube and a porous nickel filter. The two cylinders are interconnected through the porous nickel filter by 1/2" O.D., nickel tubing. This whole assembly can be lowered into a 10" I.D. stainless steel drum welded to the bottom of the glove box and can be heated by heating the stainless steel drum by split-unit heaters. The top of the stainless steel drum is water-cooled to prevent excessive heating of the glove box. A pulley block arrangement fixed inside the glove box is used for raising or lowering the assembly in the stainless steel drum.

4. CHEMICALS

For the preparation of the trifluorides, $\text{CeO}_2$ obtained from the Chemistry Division and $\text{PuO}_2$ obtained from the Fuel Reprocessing Division were used. For the preparation and purification of thorium fluoride, hydrated thorium fluoride obtained from the Chemical Engineering Division was used. $\text{LiF}$ obtained from M/s. National Fluorine Corporation and $\text{BeF}_2$ obtained from M/s. Brush Beryllium Co. were used for the preparation of the mixture, purified by hydrogen and HF sparging.

5. PREPARATION

5.1 Preparation of $\text{CeF}_3$ Tagged with $^{144}\text{Ce}$
As it is convenient to determine the solubility of CeF\(_3\) in LiF-BeF\(_2\)-ThF\(_4\) by the radiometric assay of the equilibrated and filtered samples, about 75 g of CeF\(_3\) containing \(^{144}\)Ce tracer was prepared. For this about 75 g of CeO\(_2\) were dissolved in conc HNO\(_3\) and a few drops of HF. The solution thus obtained was evaporated to dryness repeatedly to remove the HF with conc HNO\(_3\). The residue was dissolved in 0.5N HNO\(_3\). To this solution, 500 ul or \(^{144}\)Ce solution (1.7 m Ci) was added. Ce\(_2\)(C\(_2\)O\(_4\))\(_3\) was precipitated from this solution by the addition of a saturated oxalic acid solution. The precipitate was filtered, washed four times with distilled water and finally with alcohol and dried. The dried oxalate was transferred to a silica crucible and ignited for about 4 hours. The CeO\(_2\) thus obtained was transferred to a nickel boat and charged into the nickel reaction vessel in the glove box. The vessel was then flushed with high purity argon and heated to 600\(^\circ\)C. At this stage a constant flow of hydrogen (500 ml/min) and HF (1500 ml/min) was maintained and the furnace temperature was raised to 725\(^\circ\)C. The reaction was carried out for a period of 4 hours. The furnace was switched off and the hydrogen and hydrogen fluoride flow was replaced by high purity argon.

The product obtained was analysed by pyrohydrolysis for the fluoride and the cerium oxide left after pyrohydrolysis was weighed as CeO\(_2\). The analysis indicated a complete conversion of CeO\(_2\) to CeF\(_3\) (see Table I).

5.2 Preparation of PuF\(_3\)

As the plutonium obtained from the Fuel Reprocessing Division was in the form of plutonium dioxide, it was decided to prepare the plutonium trifluoride by the same method as that used for CeF\(_3\). Sixty grams of PuO\(_2\) were weighed into the nickel boat. The procedure for the preparation of PuF\(_3\) was essentially the same as that described for CeF\(_3\). An HF flow of 100 ml/min and hydrogen flow of 300 ml/min were maintained for 8 hours at a temperature of 500\(^\circ\)C. The product obtained was analysed for Pu and F, which showed complete conversion of the oxide to the trifluoride (Table I).

5.3 Dehydration of Thorium Fluoride:

As the thorium fluoride obtained from the Chemical Engineering Division was
in the hydrated form, it was decided to dehydrate it in a stream of HF rather than direct conversion of ThO$_2$ to ThF$_4$. A reaction vessel similar to that used for the preparation of PuF$_3$ and CeF$_3$ was set up in a fume hood with the necessary piping. An HF flow of 500 ml/min was maintained using high purity argon as carrier gas for HF. A dehydration temperature of 700°C was used and the reaction was carried out for a period of 4 hours. A total of about 400 grams of ThF$_4$ was dehydrated by this method in four batches. The product was analysed for ThO$_2$ and F$^\text{-}$. This ThF$_4$ was used for the adjustment of ThF$_4$ composition in LiF-BeF$_2$-ThF$_4$ salt mixture for the determination of the solubility of PuF$_3$.

6. PURIFICATION OF LiF-BeF$_2$-ThF$_4$ MIXTURE

To check the performance of the salt purification assembly at high temperature the apparatus, after complete assembly, was lowered into the 10" I.D. S.S. drum welded to the bottom of the salt purification box. A 6 KW split-unit furnace was installed around this drum. The gas inlet and outlet lines were connected to the apparatus and it was flushed with hydrogen. The equipment was then heated to 650°C while hydrogen continued to flow through at 500 ml/min. This exercise, besides providing a high temperature check of the whole assembly also removed the oxide film from the inner surface of the apparatus. After cooling the apparatus, the charging port was opened and LiF, BeF$_2$, and ThF$_4$ were added into the apparatus so as to have 1.2 kg of LiF-BeF$_2$-ThF$_4$ of approximate composition 70:18:12 m/o. The apparatus was sealed back, checked for leak tightness and then heated to 900°C to melt the salt. The flow of H$_2$ and HF could not be maintained during this operation because of high resistance of well packed salt powder in the apparatus. The temperature after melting was brought down to 650°C and the sparging of the salt with HF + H$_2$ (450 ml/min + 500 ml/min) was started. In the initial melt-down operation the water present in most of these salts will react with fluoride to give oxide as shown by equation (3)

$$H_2O(g) + 2F^-(d) \rightarrow O^{2-}(d) + 2HF(g) \quad \cdots \quad (3)$$
Pure hydrogen used for sparging the salt in the temperature range of 900 to 650°C was actually found to contain appreciable quantities of HF. The extent of oxide formation is not actually known. However, it was suspected that the melt could have been saturated with metal oxide leading to precipitation of beryllium or thorium oxide, by the reaction indicated by equation (4)

\[ 2 \text{H}_2\text{O}(g) + \text{ThF}_4(d) \rightarrow \text{ThO}_2(s) + 4\text{HF}(g) \]  ... (4)

In order to calculate roughly the amount of HF required for the oxide removal it was assumed that up to 10% of the salt charged was converted to oxide. There was no way to actually assess the amount of oxide as there was no provision for taking molten salt samples in this apparatus. It was however felt that 10% may be the upper limit for oxide concentration when the slightly hydrated fluorides are melted in a closed container. To remove this oxide the equilibrium of the reactions indicated by equations (3) and (4) has to be shifted to the left. This was achieved by sparging the melt with HF gas. HF gas alone would however lead to extensive corrosion of the nickel container vessel. The reaction for this is given by equation (5).

\[ 2 \text{HF}(g) + \text{Ni}(s) \rightarrow \text{NiF}_2(d) + \text{H}_2(g) \]  ... (5)

In order to limit the attack on the container vessel the HF was mixed with hydrogen. HF at the rate of 450 ml/min and hydrogen at the rate of 500 ml/min were used for purification of the melt.

The HF-H\(_2\)O equilibria in molten LiF-BeF\(_2\)-ThF\(_4\) melts have not been studied and it is very difficult to assess the percentage HF utilization in such melts. In the case of LiF-BeF\(_2\) melts the equilibrium HF utilization is up to 70% at 600°C and even higher at lower temperatures\((31)\). However, in a dynamic system and in the simple apparatus used for purification the HF utilization efficiency may be only 40-50%. In case of LiF-BeF\(_2\) melts saturated with ZrO\(_2\) the efficiency at 600°C drops down to 15-25%\((31)\). For purification in the present set up a HF utilization efficiency of 12% was assumed. Based on this, about 550 litres of HF was required for purification of the 1.2 kg of...
salt having 10% oxide. So the HF + H₂ sparging was continued for 20 hours to get a total HF flow of 540 litres. It was felt that the oxide impurity in the salt will be less than 50 ppm. In this process appreciable quantity of nickel is dissolved into the melt as NiF₂. To get rid of this, the reaction indicated by equation (5) had to be reversed to reduce NiF₂ to particulate Ni which could be filtered off. For this, the temperature of the furnace was raised up to 825°C, the HF flow was stopped and the hydrogen flow increased to 1.5 litres/min. Standard free energy change for the reduction of nickel fluoride with hydrogen, assuming a unit activity for NiF₂/solution is -14 Kcal/mole. As the rate of this reaction is not known, the hydrogen sparging was continued for 24 hours. After about 20 hours no HF could be detected in the outlet gas either visually or with the help of a pH paper. The temperature was increased to 860°C for the last hour to reduce any left over traces of NiF₂. The salt after this operation was pressure transferred to the purified salt container through the nickel filter. The salt was analysed for Li, Be, Th and total fluoride and the results are given in Table II.

7. ANALYSIS

7.1 Analysis of fluoride by fusion pyrohydrolysis

This method of estimation of F⁻ in fluorides is based on the fact that when a stream of moist oxygen, air or helium is passed over heated metal fluorides (either with or without accelerator like U₂O₈, UO₃ and flux like sodium tungstate depending on the type of fluorides to be analysed), they undergo hydrolytic reaction

\[
\text{MF}_x + x \text{H}_2\text{O} \rightarrow \text{M(OH)}_x + x \text{HF} \quad \cdots \quad (6)
\]

This reaction will go to completion if the hydrogen fluoride is removed continuously, if no water vapour is allowed to condense and if no reaction occurs with other decomposition products that remove the hydrogen fluoride from the effluent gas stream. The evolved HF gas
is passed through a solution of 1N NaOH, which absorbs the HF completely. By titrating the excess NaOH with standard acid, the HF evolved and hence the F⁻ content of the fluoride is calculated.

The pyrohydrolysis apparatus used for the estimation of F⁻ in the fluoride samples is shown in Figure 5. It consists of a fused silica tube of 20" length and 1.1/4" diameter, closed with standard 34/35 ground silica joint through which the apparatus is connected to the gas supply. A 10" long and 3/8" diameter delivery tube of fused silica is fused to the reactor tube at right angles to the exit end of the tube. A heavy duty nichrome wound furnace surrounds the reactor tube for heating the sample. A chromel-alumel thermocouple with hot junction is located in the centre of the furnace at the external wall of the reactor tube. A calibrated pyrometer is used for the indication of the temperature. Cylinder oxygen is connected to the inlet of the pyrohydrolysis tube through a calibrated flowmeter and bubbler filled with distilled water containing glass beads for saturating the oxygen with water. The assembly, apart from the bubbler and flow meter, is set up inside a glove box.

For the estimation of fluorine in fluorides about 100 to 150 mg of the sample to be analysed is weighed into a tared platinum boat. The apparatus is heated to a temperature of 500°C with moist oxygen flowing at the rate of 2 litres/minute. When the temperature has reached 500°C the sample is quickly inserted into the centre of the reaction tube through the ground silica joint. After inserting the sample the tube is quickly closed and the temperature is raised to 800°C and maintained there for 45 minutes while moist oxygen flows at the rate of 2 litres/min. The delivery tube of the reaction tube is immersed in standard solution of NaOH kept in a 100 ml measuring cylinder. The HF liberated by the reaction is absorbed in NaOH and the excess NaOH is titrated against standard acid. A blank experiment without the fluoride sample is carried out and subtracted from the NaOH consumed. The blank correction is usually about 1%. From the volume of the standard NaOH consumed the fluoride content of the sample is calculated. The fluoride content in CsF₃, PuF₃ and ThF₄ obtained from duplicate analysis is given in Table 1 together with the weight of the oxide found after pyrohydrolysis. It may be seen that
there is good agreement between the calculated values of fluoride and oxide content to the experimentally determined values.

7.2 Estimation of Total Fluoride in Purified LiF-BeF$_2$-ThF$_4$ Mixtures

As it has been reported$^{30}$ that the fluorides of alkali and alkaline earth metals are particularly difficult to decompose without an accelerator material, about 2.5 g of U$_3$O$_8$ (accelerator) is mixed with a weighed quantity of the salt mixture and the pyrohydrolysis is carried out at a temperature of 1000°C. The rest of the procedure for analysis is the same as that used for the estimation of fluoride in CaF$_3$ etc. The estimated fluoride content together with the calculated value on the basis of Th, Be and Li analyses is given in Table II.

7.3 Analysis of the Salt Mixture LiF-BeF$_2$-ThF$_4$ for Li and Be and Th

About one gram of the salt mixture was brought into solution by repeated digestion with perchloric acid. After the salt has dissolved, the bulk of the acid was removed by fuming and the residue was made up to a volume of 100 ml with water. Suitable aliquots were taken for the estimation of Th, Be and Li.

7.4 Estimation of Th

7.5 Volumetric method

A 10 ml aliquot was diluted to a volume of 50 ml with water and the pH of the solution was adjusted to 2.8. The solution was titrated with M/20 EDTA solution using xylenol orange as indicator. Near the end point when the acidity of the solution increased it was adjusted to pH 2.8. The end point was the first change from pink to yellow.

7.6 Gravimetric method

A 20 ml aliquot was diluted to 150 ml with water. The solution was heated to boiling after addition of 1.5 ml conc HCl. To the boiling solution 5 ml of saturated oxalic acid was added dropwise followed by vigorous stirring. The mixture was kept on a hot plate for an hour. When the precipitate settled, it was filtered after cooling to room temperature and
the precipitate was washed several times with 0.1 N HCl. Thorium oxalate was ignited at 800°C and weighed as ThO₂. The filtrate was used for the estimation of beryllium.

### 7.7 Estimation of Beryllium

The filtrate from thorium oxalate was evaporated to a small volume. 10 ml of conc HNO₃ was added and the evaporation continued. This process was repeated five times to destroy bulk of the oxalic acid remaining in the solution after thorium precipitation. The solution was then heated till HClO₄ remaining in it started fuming and this destroyed any oxalic acid remaining in the solution. The solution was then cooled and made up to a volume of 50 ml with water. Two aliquots, one containing 25 ml and the other 20 ml were taken for the estimation of beryllium.

Each aliquot was diluted to about 200 ml with water and after adjustment of pH to 4-5 the solutions were heated to about 60°C and to these 12 ml of ethanolic solution of N-Benzylphenyl hydroxylamine (0.33 g) was added with stirring. The beryllium complex Be(BPHA)₂ was quantitatively precipitated by dropwise addition of dil NH₄OH to bring the pH to 5.5-6.5. This was then digested on a hot plate for 15 min with occasional stirring, filtered through a weighed medium-porosity sintered glass crucible, washed with warm water and finally dried at 110°C to constant weight.

### 7.8 Estimation of Lithium

25 ml aliquot of the salt solution was diluted to about 150 ml and then heated to boiling. To the vigorously stirred solution NH₄OH solution was added dropwise till it was in a slight excess (pH 7.5-8.5). To the precipitated thorium and beryllium hydroxide about 1 g filter pulp was added and the mixture was allowed to boil for 2-3 min. This was then filtered and the residue washed several times with 2% NH₄NO₃ solution. The combined filtrate was evaporated to about 10 ml volume, cooled and 5 ml conc H₂SO₄ was added and the solution was heated to fuming. This operation was repeated three times, then it was dissolved in water and quantitatively transferred to a 30 ml tared platinum crucible.
All the \( \text{H}_2\text{SO}_4 \) and \( (\text{NH}_4)_2\text{SO}_4 \) was removed from the solution by heating it to 400°C. The crucible was heated to dull redness (600-700°C) for 5 min., cooled and two drops of conc \( \text{H}_2\text{SO}_4 \) were added and the process repeated till a constant weight was reached and the weight of \( \text{Li}_2\text{SO}_4 \) was obtained. The composition of the salt mixture on the basis of analysis of Th, Be and Li is presented in Table II.

ACKNOWLEDGEMENT

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REFERENCES


**Table I**  
ANALYSIS OF FLUORIDE BY PYROHYDROLYSIS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$F^-$ found w/o</th>
<th>$F^-$ Calc w/o</th>
<th>Oxide found w/o</th>
<th>Oxide calculated w/o</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CeF}_3$</td>
<td>28.76</td>
<td>28.94</td>
<td>87.42</td>
<td>87.30</td>
</tr>
<tr>
<td>$\text{PuF}_3$</td>
<td>19.38</td>
<td>19.26</td>
<td>91.00</td>
<td>91.56</td>
</tr>
<tr>
<td>$\text{ThF}_4$</td>
<td>24.70</td>
<td>24.67</td>
<td>85.86</td>
<td>85.70</td>
</tr>
</tbody>
</table>

**Table II**  
ANALYSIS OF LiF-BeF$_2$ SALT MIXTURE

<table>
<thead>
<tr>
<th>Salt</th>
<th>Weight percent</th>
<th>Mole percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>24.4</td>
<td>66.5</td>
</tr>
<tr>
<td>BeF$_2$</td>
<td>12.6</td>
<td>19.0</td>
</tr>
<tr>
<td>ThF$_4$</td>
<td>63.2</td>
<td>14.5</td>
</tr>
<tr>
<td>$F^-$</td>
<td>47.8 (47.55)*</td>
<td>-</td>
</tr>
</tbody>
</table>

* Calculated $F^-$ content on the basis of assayed LiF, BeF$_2$ and ThF$_4$ contents
GAS INLET
FLOW METER

TO VACUUM

TO SUPPLY

PRESSURE GAUGE

VACUUM GAUGE

THERMOCOUPLE

WATER INLET
TANTALUM TUBE

DRIYING TOWER

GAS (H₂, Ar) PURIFICATION LINE

FIGURE - 1
HELICOID GAUGE
H₂ + Ar INLET
CHECK VALVE.

HF CMOMEL} (T.
METERfNG TO PU.F3 PORTFICATION TO SALT PURIFICATION BOX MONEL NEEDLE VALVE
MONEL DIAPHRAGM VALVE
FLARE FITTING.

HYDROGEN FLUORIDE GAS LINE
FIGURE-2
FIGURE-3. FLUORIDE PREPARATION VESSEL
GENERAL ARRANGEMENT FOR SALT PURIFICATION UNIT

FIGURE - 4.
FIGURE-6. APPARATUS FOR PYROHYDROLYSIS