Chapter

# Fast-Spectrum Fluoride Molten Salt Reactor (FFMSR) with Ultimately Reduced Radiotoxicity of Nuclear Wastes

*Yasuo Hirose*

## Abstract

A mixture of NaF-KF-$UF_4$ eutectic and NaF-KF-$TRUF_3$ eutectic containing heavy elements as much as 2.8 g/cc makes a fast-spectrum molten salt reactor based upon the U-Pu cycle available without a blanket. It does not object breeding but a stable operation without fissile makeup under practical contingencies. It is highly integrated with online dry chemical processes based on "selective oxide precipitation" to create a U-Pu cycle to provide as low as 0.01% leakage of TRU and nominated as the FFMSR. This certifies that the radiotoxicity of HLW for 1500 effective full power days (EFPD) operation can be equivalent to 405 tons of depleted uranium after 500 years cooling without Partition and Transmutation (P&T). A certain amount of U-TRU mixture recovered from LWR spent fuel is loaded after the initial criticality until U-Pu equilibrium but the fixed amount of $^{238}U$ only thereafter. The TRU inventory in an FFMSR stays at an equilibrium perpetually. Accumulation of spent fuel of an LWR for 55 years should afford to start up the identical thermal capacity of FFMSR and to keep operation hypothetically until running out of $^{238}U$. Full deployment of the FFMSR should make the entire fuel cycle infrastructures needless except the HLW disposal site.

**Keywords:** fast-spectrum fluoride molten salt reactor, high-level radioactive waste, structure of fuel salt, density of fuel salt, redox potential control, freezing behavior of fuel salt, selective oxide precipitation process, front-end processing dedicated to the MOX spent fuel, nuclear fuel cycle and associated wastes

## 1. Introduction

Almost but a few would recognize the relation between fossil fuel burning and the global greenhouse issue. However many of them tend to be in favor of expensive and inefficient but immediately harmless renewable energy than existing nuclear. A major barrier to persuade con-nuclear elements is the nuclear waste issue which should have directly associated with Pu production for the traditional strategy to close fuel cycle to ensure national energy security by using the liquid metal fast breeder reactor (LMFBR). In coping with this circumstance, resolutions to address both issues, i.e., decreasing radiotoxicity of the high-level radioactive waste

(HLW) and sustaining energy using the molten salt reactor (MSR) technology, have been expected.

The MSR technology was developed and culminated by successful operation of the molten salt reactor experiment (MSRE) and conceptual design of the molten salt breeder reactor (MSBR) in Oak Ridge National Laboratory (ORNL) by 1975 to make thorium as a naturally available fuel usable in addition to uranium.

Many attempts have been made to realize breeder reactors based on the U-Pu cycle using molten salt fuels; however such endeavors had been limited in the chloride salts, because of the feasibility to obtain high enough energy of neutron flux [1].

In addition to the predicted solubility data from thermodynamic calculations [2], recently actualized high solubility data of various fluorides of actinides and lanthanides specifically in the LiF-NaF-KF eutectic mixture (traditionally named as FLiNaK) [3–6] reportedly could allow utilizing the high enough energy neutrons for the U-Pu breeding cycle aided by a high heavy element inventory (2.8 t/$m^3$) and a small neutron moderating capability [7].

It was reported that a system nominated as a 3.2 GWt U-Pu fast-spectrum molten salt reactor (U-Pu FMSR) of 21.2 $m^3$ core volume (31.8 $m^3$ total primary system volume) starting from 68.5 tons of uranium with 15 tons of plutonium solving in FLiNaK to reach an equilibrium state after 10 years with an online chemical processing in which the conversion ratio (CR) became positive with inventory of 68.6 tons uranium, 20.9 tons plutonium, and 1.4 tons miner actinides did not need fissile material in feeding and consumed $^{238}U$ only [7].

It does not intend to reduce doubling time but can breed fissile to guarantee stable operation without a blanket. It does not deliberately decrease TRU but confines them into the reactor core and isolates them from improper uses indefinitely. It does continuously renew fissionable actinides by the metabolic function with an online processing and produce nearly actinide-free fission product streams to be wasted. This implies that fluoride molten salt reactor technology is being available based upon U-Pu breeding cycle to afford reasonable approach to global task addressed to sustaining natural resources, decreasing stockpile of plutonium as well as depleted uranium, relieving radioactive waste burden from the use of nuclear energy, achieving complete nonproliferation, inheriting safety characteristics of the liquid fuel, and establishing complete stand-alone system associating with only the waste disposal facility.

The author and associates have successfully performed a follow-up calculation not only for FLiNaK but also NaF-KF-$UF_4$ system as a matrix of the fuel salt [8, 9]. Their efforts have borne a fruit as a nuclear reactor plant using a mixture of NaF-KF-$UF_4$ fertile and NaF-KF-$TRUF_3$ fissile as the fuel salt incorporated with designated online chemical processes based upon the oxide selective precipitation process with extremely low heavy element released to the environment which was nominated as the fast-spectrum fluoride molten salt reactor (FFMSR) [10–12].

## 2. Preliminary survey and study

### 2.1 Is FLiNaK the best choice as the matrix for a liquid fuel?

Composing the fuel salt for a thermal reactor such as the Molten Salt Breeder Reactor (MSBR) had nothing to do with solubility. The fertile salt 0.72LiF-0.16$BeF_2$-0.12$ThF_4$ had a unique phase relationship in which liquidus was constant at 500°C during $ThF_4$ content was varied between 10 and 20 mol%. The fissile salt $^{233}UF_4$ was not dissolved in the fertile salt, but displaced $^{232}ThF_4$, as they had the same

monoclinic crystal structure. During the freezing process, almost 75% of the fuel salt was solidified at 500°C as the same composition as the liquid phase. Eventually 0.47LiF-0.515$BeF_2$-0.015$ThF_4$ containing very small amount of $^{233}UF_4$ solidified as eutectic at 370°C [13]. This freezing process was evaluated as nuclear criticality safety in the fuel salt drain tank, and it became as a basis of the technological feasibility.

In serious attempt to use hexagonal $PuF_3$ as a fissile instead of monoclinic $^{233}UF_4$ in 0.72LiF-0.16$BeF_2$-0.12$ThF_4$, it had been treated as the solubility of $PuF_3$. The term "solubility" has been used as a convenient synopsis of "liquefied fraction" on the phase diagram [14]. However they are not the same exactly because "solubility" is defined as the mole fraction of solute in solvent, while "liquefied fraction" is defined as the fraction in total mole value.

The elaborated solubility measurements in FLiNaK by Russian scientists [3–6] should have been more appropriately respected if they had made the chemical composition of alkali fluoride matrix of liquefied samples analytically quantified instead of their customary practice in which the matrix had been always assumed as FLiNaK, even if they have found no $UF_4$ or $PuF_3$ but 2KF-$UF_4$, 7KF-6$UF_4$, $KPu_2F_7$, $KPuF_4$, and $NaPuF_4$ in the solidified residue by the X-ray diffractometric analysis.

The author tries to interpret the solubility of $UF_4$ and $PuF_3$ in the FLiNaK by producing liquefied components at respective temperatures as shown in **Table 1** based upon the material balance referring from relevant phase diagrams in **Figure 1** [15] and **Figure 2** [16]. The red line in each ternary diagram which starts from the actinide fluoride corner, passes through the eutectic point, and ends in the alkali fluoride edge represents the actinide concentration in a fixed matrix composition.

The increasing process of liquefied fraction consists of two types, firstly composing compounds at the eutectic temperature and secondly increasing content of liquefied fraction according to rising temperature. Alkali fluoride compounds of $UF_4$ have a wider range of liquid zone than those of $PuF_3$ in the relevant phase diagrams.

| | Matrix | Melt Temp. °C | Compounds in Liquid Phase | Eutectic Temp. °C | Melt Temp. °C | $UF_4$ Mol% | $PuF_3$ Mol% |
|---|---|---|---|---|---|---|---|
| FLiNaK-UF4 | | | $UF_4$ | | 1035 | | |
| | | | 0.259LiF-0.259$UF_4$ | | 735 | 50.54 | |
| | | | 0.206NaF-0.115KF-0.260$UF_4$ | | 735 | 46.21 | |
| | 0.420KF | 865 | 0.420KF-0.503$UF_4$ | 735 | | 42.89 | |
| | 0.259LiF-0.420KF | 492 | 0.259LiF-0.096$UF_4$ | 490 | | 19.88 | |
| | 0.465LiF-0.115NaF-0.420KF | 454 | 0.206LiF-0.115NaF-0.152$UF_4$ | 445 | | 13.19 | |
| FLiNaK-PuF3 | | | $PuF_3$ | | 1396 | | |
| | | | 0.161LiF-0.044NaF-0.210$PuF_3$ | | 726 | | 36.35 |
| | | | 0.304LiF-0.420KF-0.340$PuF_3$ | | 726 | | 29.32 |
| | 0.07NaF | 900 | 0.071NaF-0.021$PuF_3$ | 726 | | | 19.80 |
| | 0.161LiF-0.115NaF | 760 | 0.161LiF-0.044NaF-0.058$PuF_3$ | 685 | | | 18.43 |
| | 0.465LiF-0.115NaF-0.420KF | 454 | 0.304LiF-0.420KF-0.168$PuF_3$ | 513 | | | 14.38 |
| FLiNaK-UF4-PuF3 | | | $PuF_3$ | | 1396 | | |
| | | | $UF_4$ | | 1035 | | |
| | | | 0.259LiF-0.259$UF_4$ | | 735 | 42.00 | |
| | | | 0.420KF-0.420$PuF_3$ | | 726 | | 36.10 |
| | | | 0.420KF-0.320$PuF_3$ | | 700 | | 26.11 |
| | | | 0.206LiF-0.115NaF-0.248$UF_4$ | | 666 | 28.64 | |
| | 0.420KF | 856 | 0.420KF-0.225$PuF_3$ | 619 | | | 18.36 |
| | 0.259LiF-0.420KF | 492 | 0.259LiF-0.096$UF_4$ | 490 | | 19.88 | |
| | 0.465LiF-0.115NaF-0.420KF | 454 | 0.206LiF-0.115NaF-0.152$UF_4$ | 445 | | 13.19 | |

**Table 1.**
*Interpretation of solubility upon accumulated liquefied compounds.*

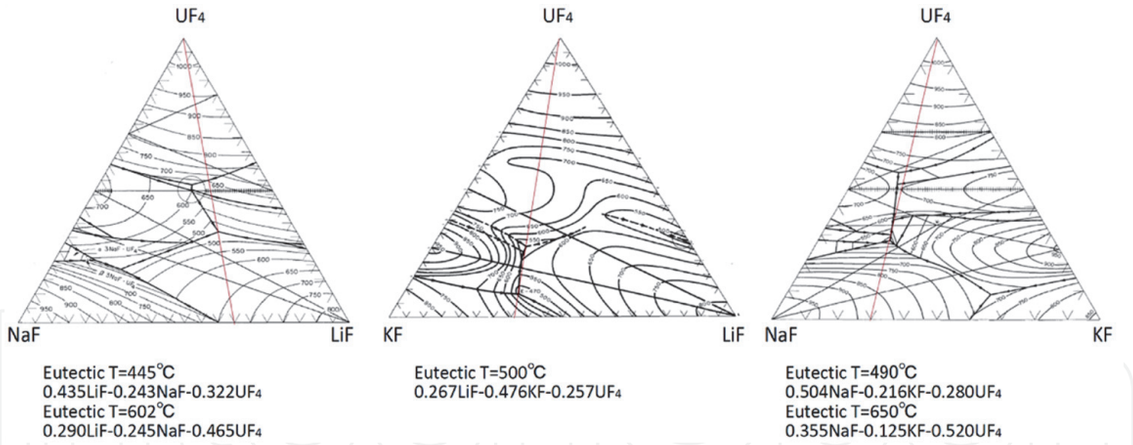



**Figure 1.**
*Phase diagrams for LiF, NaF, KF, and $UF_4$ system [15].*

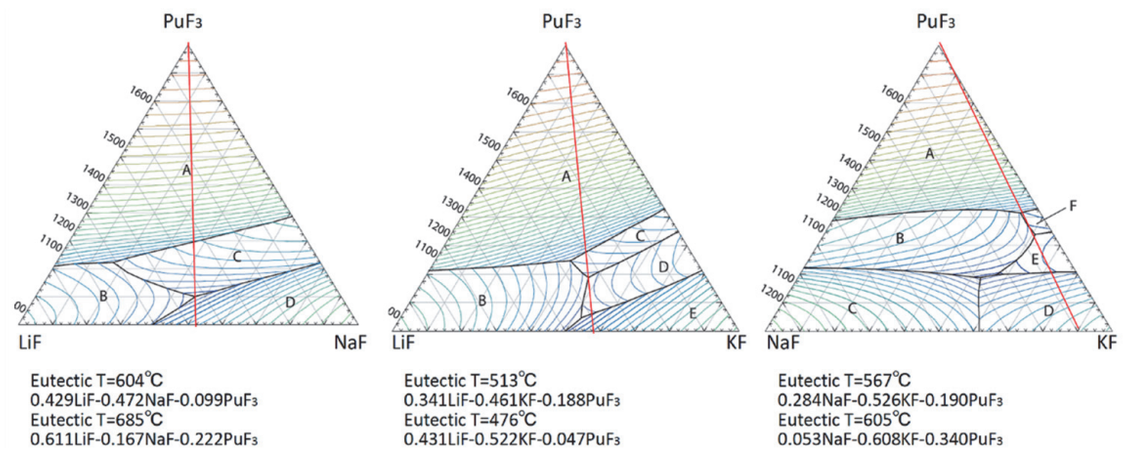



**Figure 2.**
*Phase diagrams for LiF, NaF, KF, and $PuF_3$ system [16].*

Coexistence of $UF_4$ and $PuF_3$ obviously competes each other in the first mechanism. The eutectic formation at lower temperature should have the priority.

These results would be summarized as:

1. The liquefied mixture of FLiNaK and heavy metal fluorides is not a solution.

2. KF (mp = 865°C) might have been temporally solidified prior to producing 0.445KF-0.555$UF_4$ (735°C) during the ascending temperature process in the solubility measurement of $UF_4$.

3. KF (mp = 865°C) and NaF (mp = 900°C) might have been temporally solidified prior to producing 0.651KF-0.349$PuF_3$ (619°C) or 0.772NaF-0.228$PuF_3$ (726°C) during the ascending temperature process in the solubility measurement of $PuF_3$.

4. The saturated FLiNaK solution of $UF_4$ and $PuF_3$ is elucidated as the mixture of three types of alkali fluoride compound assumed as 0.321 (0.435LiF-0.243NaF-0.322$UF_4$)-0.241 (0.730LiF-0.270$UF_4$)-0.438 (0.651KF-0.349$PuF_3$) with liquidus temperature of 619°C and solidus temperature of 445°C.

5. The liquidus temperature of the FLiNaK mixture might be substantially higher than that of solvent. Any physical favorable properties of FLiNaK should have not been directly attributed to the fuel salt.

## 2.2 Alternative choice to prepare the liquid fuel

Taking the lessons learned, the liquid fuel has to be a mixture of fertile salt and fissile salt both frozen into eutectic phases. Extensive numbers of phase diagram, which show the relationship between the variation of compositions and the liquidus temperature of mixtures, for alkali fluoride systems containing $UF_4$ and for those containing $PuF_3$ have been defined. The eutectic temperature means that nothing but liquid is stable over this temperature and that nothing but solid is stable under this temperature. The eutectic compositions and temperatures for the alkali fluoride systems containing $UF_4$ and $PuF_3$ are listed in **Table 2**.

There are various candidates for the combination of fertile salt and fissile salt as shown in **Table 3**. Technologically the liquidus temperature is preferably as low as possible. The lower heavy metal content of a component could imply higher liquidus temperature apart from the indicated eutectic temperature.

The author is particularly interested in the fuel system consisting of NaF-KF-$UF_4$ and NaF-KF-$PuF_3$ which do not contain enriched $^7$LiF for economic as well as technological reasons associated with tritium control and irradiation defects after being solidified. If there might be a particular reason to contain LiF in the fuel, it is decreasing viscosity.

It is revealed that this combination can provide 0.35NaF-0.29KF-0.28$UF_4$-0.08$PuF_3$ composed of mixing 0.762 (0.504NaF-0.216KF-0.280$UF_4$) and 0.238 (0.053NaF-0.608KF-0.340$PuF_3$) at the liquidus of 605°C and the solidus of 490°C. This means that nothing but liquid is stable at 605°C or higher and nothing but solid is stable at 490°C or lower according to the phase diagrams **Figures 1** and **2**.

| **Alkali fluoride with $UF_4$ [15]** | | | **Alkali fluoride with $PuF_3$ [16]** | | |
|---|---|---|---|---|---|
| **Compositions** | **Molecular ratio** | **ET*** | **Compositions** | **Molecular ratio** | **ET*** |
| LiF-$UF_4$ | 0.730–0.270 | 490 | LiF-$PuF_3$ | 0.798–0.212 | 745 |
| | | | LiF-$UF_4$-$PuF_3$ | 0.733–0.257–0.010 | 484 |
| NaF-$UF_4$ | 0.785–0.215 | 735 | NaF-$PuF_3$ | 0.779–0.221 | 726 |
| | 0.720–0.280 | 623 | | | |
| | 0.440–0.560 | 680 | | | |
| KF-$UF_4$ | 0.850–0.150 | 618 | KF-$PuF_3$ | 0.651–0.349 | 619 |
| | 0.615–0.385 | 740 | | | |
| | 0.460–0.540 | 735 | | | |
| LiF-NaF-$UF_4$ | 0.600–0.210–0.190 | 480 | LiF-NaF-$PuF_3$ | 0.429–0.472–0.099 | 604 |
| | 0.350–0.370–0.280 | 480 | | 0.611–0.167–0.222 | 685 |
| | 0.435–0.243–0.322 | 445 | | | |
| | 0.245–0.290–0.465 | 602 | | | |
| LiF-KF-$UF_4$ | 0.331–0.589–0.080 | 470 | LiF-KF-$PuF_3$ | 0.431–0.522–0.047 | 476 |
| | 0.267–0.476–0.257 | 500 | | 0.341–0.471–0.188 | 513 |
| NaF-KF-$UF_4$ | 0.293–0.622–0.085 | 650 | NaF-KF-$PuF_3$ | 0.285–0.528–0.187 | 567 |
| | 0.504–0.216–0.280 | 490 | | 0.053–0.607–0.340 | 605 |
| | 0.355–0.120-0.520 | 650 | | | |

**Eutectic temperature.*

**Table 2.**
*Alkali fluoride eutectic mixture containing $UF_4$ or $PuF_3$.*

| Case | Fertile salt (eutectic temp.) | Fissile salt (eutectic temp.) |
|---|---|---|
| Li | 0.730LiF-0.270$UF_4$ (490°C) | 0.788LiF-0.212$PuF_3$ (745°C) |
| Na | 0.720NaF-0.280$UF_4$ (623°C) | 0.779NaF-0.221$PuF_3$ (726°C) |
| K | 0.850KF-0.150$UF_4$ (618°C) | 0.651KF-0.349$PuF_3$ (619°C) |
| Li-Na | 0.435LiF-0.243NaF-0.322$UF_4$ (445°C) | 0.611LiF-0.167NaF-0.222$PuF_3$ (685°C) |
| Li-Na-K | 0.435LiF-0.243NaF-0.322$UF_4$ (445°C) | 0.341LiF-0.461KF-0.188$PuF_3$ (513°C) |
| Li-K | 0.267LiF-0.476KF-0.257$UF_4$ (500°C) | 0.341LiF-0.461KF-0.188$PuF_3$ (513°C) |
| Li-K-Na | 0.267LiF-0.476KF-0.257$UF_4$ (500°C) | 0.611LiF-0.167NaF-0.222$PuF_3$ (685°C) |
| Na-K | 0.504NaF-0.216KF-0.280$UF_4$ (490°C) | 0.053NaF-0.608KF-0.340$PuF_3$ (605°C) |

**Table 3.**
*Candidates for the combination of fertile salt and fissile salt.*

## 2.3 Density of alkali fluoride mixture with heavy metal fluoride

The density of a liquid mixture has been customarily obtained as a reciprocal of a weighted average of molecular volume of components; though this procedure worked satisfactorily during the MSRE and MSBR project in ORNL [17], concurrently it has been recognized that the results might be significantly erroneous without pertinent information about the respective components, e.g., liquid $UF_4$ or $PuF_3$. If the components would compose a complex compound, e.g., $2KF + UF_4 \rightarrow K_2UF_6$ or $3KF + PuF_3 \rightarrow K_3PuF_6$, it might cause a serious deviation from linearity.

Since most molten salt reactors considered during the early stages of MSR project in ORNL were thermal or epithermal, the fluorides of lithium, beryllium, sodium, and zirconium have been given the most serious attention for the carrier salt of liquid fuels. However some alkali fluoride mixtures including potassium with $UF_4$ were also investigated in ORNL during the earlier stage of MSR project although details had been classified [18]; however the density data were perceived as not from additivity calculation as listed in **Table 4**.

However it seems that the density of listed mixtures is approximately expressed by a couple of second-order approximate least square functions according to $UF_4$ molar concentration, one for binary systems and another for ternary (or pseudo-ternary) systems, regardless of alkali fluoride matrix as shown in **Figure 3**.

Based upon the density data for solid $UF_4$, $UF_3$, $PuF_4$, and $PuF_3$, i.e., 6.72, 8.97, 7.0, and 9.32 g/cm$^3$ at the room temperature [19], it is hypothetically assumed that $PuF_3$ can be substituted by 1.389 molecules of $UF_4$ and $UF_3$ by 1.335 molecules of $UF_4$ in the sense of density effect. The average temperature coefficients were reported as 0.0008/°C in the range of 0–4 mol% and as 0.0011/°C in the range higher than 22 mol% [18].

This procedure to estimate the density of fuel salts with substantially high concentration of actinides became a major breakthrough in the whole study; however it should be experimentally verified further (**Table 5** [19]).

## 2.4 Implication of density of the liquid fuel in the feasibility of reactor

### *2.4.1 Effect of density on conversion of inventories to concentrations*

The physical feasibility of the U-Pu FMSR was independently verified by us in the sense of heavy element inventory with small deviations [8]; however there have been drastic differences in mol% concentrations of $UF_4$ and $PuF_3$ to provide the

| Composition of salt | | | | MP | Liquid density | Liquid viscosity | Specific heat at 700°C | Thermal conductivity |
|---|---|---|---|---|---|---|---|---|
| Li | Na | K | U | °C | (g/cc)(T:°C) | (Cp) | (cal/g-deg) | (W/m-K) |
| | 60 | 40 | | 710 | 2.40-0.00060 T | – | – | – |
| 60 | 40 | | | 652 | 2.42-0.00055 T | 4.66 (600°C) | 0.58 | – |
| 50 | | 50 | | 492 | 2.46-0.00068 T | 4.75 (600°C) | 0.44 | – |
| 46.5 | 11.5 | 42 | | 454 | 2.53-0.00073 T | 4.75 (600°C) | 0.45 | 4.53 |
| 72.5 | | | 27.5 | 490 | 6.11-0.00127 T | 12.1 (700°C) | – | – |
| | 66.7 | | 33.3 | 623 | 5.51-0.00130 T | 16.3 (600°C)* | 0.21 | – |
| | 50 | | 50 | 680 | 6.16-0.00107 T | – | – | – |
| | | 45 | 55 | 735 | 6.07-0.00115 T | – | – | – |
| 38.4 | 57.6 | | 4 | 645 | 2.95-0.00770 T | 3.5 (700°C) | 0.53* | - |
| 33 | 45 | | 22 | 506 | 4.50-0.00101 T | – | 0.26 | – |
| 48 | | 48 | 4 | 560 | 2.75-0.00073 T | 3.2 (700°C) | 0.38 | – |
| | 48.2 | 26.8 | 25 | 558 | 4.54-0.00110 T | 9.8 (700°C) | 0.23 | – |
| | 46.5 | 26 | 27.5 | 530 | 4.70-0.00115 T | 17.3 (600°C) | 0.23* | 0.87 |
| | 50 | 20 | 30 | 575 | 4.78-0.00104 T | 10.0 (700°C) | 0.22 | – |
| | 35 | 20 | 45 | 708 | 5.60-0.00116 T | – | – | – |
| 44.5 | 10.9 | 43.5 | 1.1 | 452 | 2.65-0.00090T* | 4.61 (600°C)* | 0.44* | 4 |
| 45.3 | 11.2 | 41 | 2.5 | 490 | 2.67-0.00072 T | 5.10 (600°C)* | 0.38 | – |
| 44.7 | 11 | 30.3 | 4 | 560 | 2.80-0.00074 T | 5.35 (600°C) | 0.41 | – |

**Explicitly marked as experimental value.*

**Table 4.**
*Some physical properties of alkali fluorides containing $UF_4$ [18].*

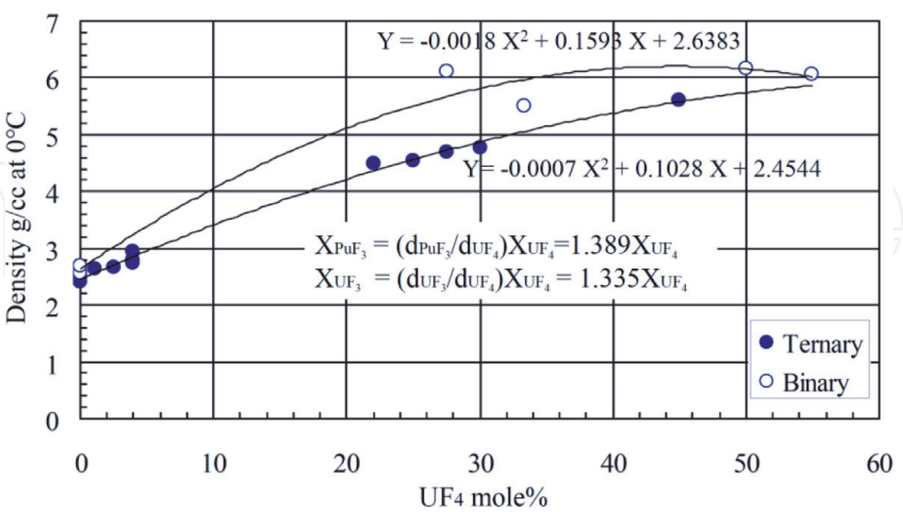



**Figure 3.**
*Density of alkali fluorides containing $UF_4$ [18].*

required inventory as shown in **Table 6**. We have learned that the reported work [7] have applied density of the fuel salt as 5.32 g/cc at 680°C derived from the weighted average process of molecular volume for 0.704 (FLiNaK)-0.21$UF_4$-0.067$PuF_3$-0.0045$MaF_3$-0.014FP [20], while it was 3.86 g/cc according to our procedure.

| | $ThF_4$ | $UF_4$ | $PuF_4$ | $UF_3$ | $PuF_3$ | $CeF_3$ |
|---|---|---|---|---|---|---|
| Free energy of formation at 1000 K (kcal/F atom) | −101 | −95.3 | −86.0 | −99.9 | −104.3 | −118 |
| Melting point (°C) | 1111 | 1035 | 1037 | 1495 | 1425 | 1637 |
| Crystal structure* | M | M | M | H | H | H |
| Density (g/cc) at 20°C | 5.71 | 6.72 | 7.0 | 8.97 | 9.32 | 6.16 |

*M, monoclinic; H, hexagonal.*

**Table 5.**
*Comparison of properties of $PuF_3$ with $ThF_4$, $UF_4$, $PuF_4$, $UF_3$, and $CeF_3$ [19].*

| | U-Pu FMSR [7] | Our work [8] | | |
|---|---|---|---|---|
| **Fuel salt** | **$UF_4$-$PuF_3$ in FLiNaK** | **$UF_4$-$PuF_3$ in FLiNaK** | **$PuF_3$ in NaK-KF-$UF_4$** | **$TRUF_3$ in NaF-KF-$UF_4$** |
| Power, MWth | 3200 | 3200 | 3200 | 3200 |
| Reactor core H/R ratio, h/r | 1.85 | 1.85 | 1.85 | 1.85 |
| Reactor core volume, $m^3$ | 21.2 | 21.2 | 21.2 | 21.2 |
| Specific power, $W/cm^3$ | 150 | 150 | 150 | 150 |
| Average neutron flux, $cm^{-2}\ s^{-1}$ | $\sim 10^{15}$ | | | |
| Initial fuel loading, U/Pu/MA, ton | 68.5/15/− | 72.1/16.1/− | 71.3/15.6/− | 71.3/17.1/2.1 |
| Equil. fuel loading, U/Pu/MA, ton | 68.6/20.9/1.4 | 71.9/20.3/1.2 | 71.2/19.2/1.3 | 71.2/19.6/1.2 |
| Fuel salt density, g/cc, at 680°C* | 5.32 | | | |
| Fuel salt density, g/cc, at 680°C** | 3.862 | 4.442 | 4.343 | 4.358 |
| $k_{eff}$ in equil. state | 1.008 | 1.008 | 1.008 | 1.008 |
| $k\infty$ in equil. state | 1.044 | 1.054 | 1.051 | 1.052 |
| Temperature coefficient | $-2.4–10^{-5}$ | $-8.0–10^{-5}$ | $-7.6–10^{-5}$ | $-7.3–10^{-5}$ |

*Weighted average of molecular volume.*
*Interpolated from the ORNL data.*

**Table 6.**
*Results of the follow-up calculations.*

The calculated molar concentration of the heavy elements in the fuel salt is inversely proportional to the density of the fuel salt for the identical inventories. The nuclear characteristics rely on the heavy metal inventory; however the phase relationship and chemical/hydrothermal characteristic solely rely on molecular concentration of heavy metal fluorides. Accordingly the fuel composition for which we have to examine the technological feasibilities should be 0.612 (FLiNaK)-0.290$UF_4$-0.098$TRUF_3$ instead of 0.704 (FLiNaK)-0.21$UF_4$-0.067$PuF_3$-0.0045$MaF_3$-0.014FP.

Establishing the standard process to evaluate reliable density value of the fuel salt is an indispensable step of research and development work of the molten salt reactor technology particularly when it is across multiple research parties.

### *2.4.2 Deviation of density due to $UF_3$ formation*

The physical calculations up to now for the FFMSR are performed for the fuel salt having chemical composition as.

$$0.350\mathrm{NaF} - 0.290\mathrm{KF} - 0.280\mathrm{UF_4} - 0.080\mathrm{PuF_3}\ (d_{928\mathrm{K}} : 4.684\,g/\mathrm{cc}) \qquad (1)$$

However if $[UF_3]/[UF_4]$ ratio should have been kept at 5% for the redox buffer control as will be discussed in Section 2.5.2, the chemical composition might have been altered as.

$$0.350\mathrm{NaF} - 0.290\mathrm{KF} - 0.267\mathrm{UF_4} - 0.013\mathrm{UF_3} - 0.080\mathrm{PuF_3}\ (d_{928\mathrm{K}} : 4.714\,g/\mathrm{cc}) \quad (2)$$

This unique temperature unrelated factor (±0.06% of fuel density) on the reactivity should be evaluated accordingly.

## 2.5 Challenges for realization of FFMSR

### *2.5.1 Characteristic arrangement for the unmoderated MSR*

The authors have never dared to realize molten salt fast reactors for burning TRU, unless we could have seen a tank-within-tank layout proposed by Forsberg [21] and reproduced in **Figure 4**, to ensure characteristic safety of the unmoderated MSR based on the technology for the fluoride high-temperature reactor (FHR).

A unique criticality safety challenge associated with unmoderated MSR is that criticality can occur if the fissile materials leak from the system and come near the neutron moderators, such as concrete. This has to exclude the "catch pan" arrangement to transfer gravitationally the spilled fuel material into the drain tank, which has been traditionally adapted by graphite-moderated MSR.

The combination of the direct reactor cooling system (DRACS), the pool reactor auxiliary cooling system (PRACS), and the buffer-salt pool which includes drain tanks in the bottom and is located in the underground silo can accommodate the decay heat removal and criticality issues under the design basis as well as the beyond-design-basis accident, even including the outer vessel failure.

### *2.5.2 Redox control of FFMSR*

$UF_4$ molecule in a liquid fluoride mixture intrinsically oxidizes to dissolve Cr as the most vulnerable constitution of the specifically developed structural material Hastelloy N to result in $CrF_2$ and to form $UF_3$ molecule. This challenge to be

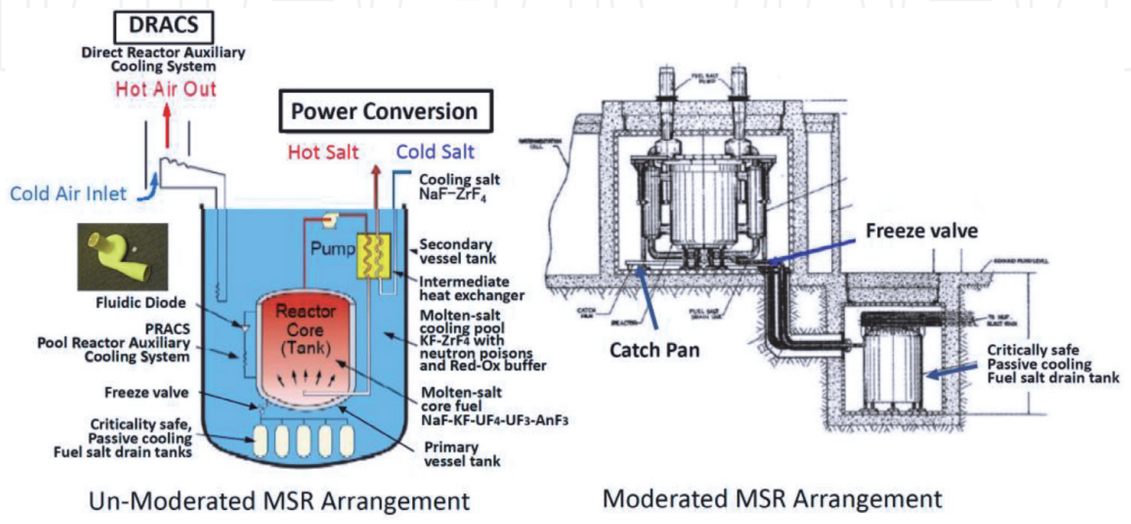



**Figure 4.**
*Comparison between unmoderated and moderated arrangement [21].*

addressed for a $UF_4$-fueled molten salt reactor was overcome by keeping U(IV)/U(III) ratio no less than 100 with constant monitoring of $CrF_2$ concentration [22].

From 1965 to 1969, a successful operation of the MSRE proved that the fission of $^{235}UF_4$ as well as of $^{233}UF_4$ made the fuel salt moderately oxidizing as previously suggested and proven that the absence of metallic uranium deposition or uranium carbide formation incidence due to successive fissioning. The U(IV)/U(III) ratio could be maintained within the projected range by periodic dissolution of beryllium metal bar suspended in the pump bowl. During the post-MSRE work, it was found that the significant intergranular cracks due to the presence of fission product tellurium could be suppressed by adjusting the U(IV)/U(III) ratio no higher than 70 [22].

In 1968, Thoma [19] described that no significant differences were believed to exist in the yield or chemistry of the principal species of fission products which would result from the incorporation of $PuF_3$ in MSR fuels and then the use of a tri-fluoride solute should result in a cation excess and should cause the fuel solution to generate a mild reducing potential, because he had confirmed that the fission of $^{235}UF_4$ fuel consuming ~0.8 is equivalent to $UF_3$ per gram atom of fissioned uranium.

In 1994 Toth [23] ratified Thoma's perception [19] made in 1968 regarding the effect of $PuF_3$ fission on redox potential of the fuel salt however with strong warning that further investigations should be required if Pu fuels were used in future designs.

In November 2017, the ORNL has made an official presentation to the US-NRC staff [24] that the fission of $PuF_3$ releases three fluorine ions, while the fission products require more than three, and thus there will be a fluorine ion deficit with net reducing conditions without showing fission product yield data or chemical status of fission products. The ORNL traditionally has ignored the fact in which fission of $^{239}Pu$ yields much more rare metals and much less zirconium than those of $^{235}U$ or $^{233}U$ which could decrease the required fluorine ions substantially.

The author solicited Dr. Shimazu [25] to take a positive approach to certify the new redox potential control paradigm using the newest computation practice and elucidated free fluorine yield data for $^{233}UF_4$, $^{235}UF_4$, and $^{239}PuF_3$ per unit fission as well as per unit power output under both thermal neutron (MSRE) and fast neutron (FFMSR) environment assuming that the chemical behavior of fission product in molten fluoride environment is identical as evaluated for $^{235}U$ fission by Baes [26] as shown in **Table 7**.

It was informed by the study [27] with molten LiF-$BeF_2$-$ThF_4$ (75-5-20 mol%) salt mixture fueled by 2 mol% of $UF_4$ and containing additives of $Cr_3Te_4$, including 250-h tests with exposure of nickel-based alloy specimens at temperatures from 700 to 750°C and under mechanical loading, that there were no traces of tellurium intergranular cracking on specimens in the fuel salt with [U(IV)]/[U(III)] ratio from 20 to 70 and no nickel-uranium intermetallic film on the specimens with fuel salts characterized by the ratio larger than 3, as shown by the acceptable redox voltage range in **Figure 5** [27, 28].

| Fissionable Materials | Mole-F/Fission | | Mole-F/MWt-y | |
|---|---|---|---|---|
| | Fast | Thermal | Fast | Thermal |
| $^{233}UF_4$ | 0.65 | 0.80 | 1.13 | 1.14 |
| $^{235}UF_4$ | 0.80 | 0.80 | 1.35 | 1.36 |
| $^{239}PuF_3$ | 0.60 | 0.60 | 1.02 | 1.09 |

**Table 7.**
*Free fluorine production rate per fissioning in liquid fluoride fuel [25].*

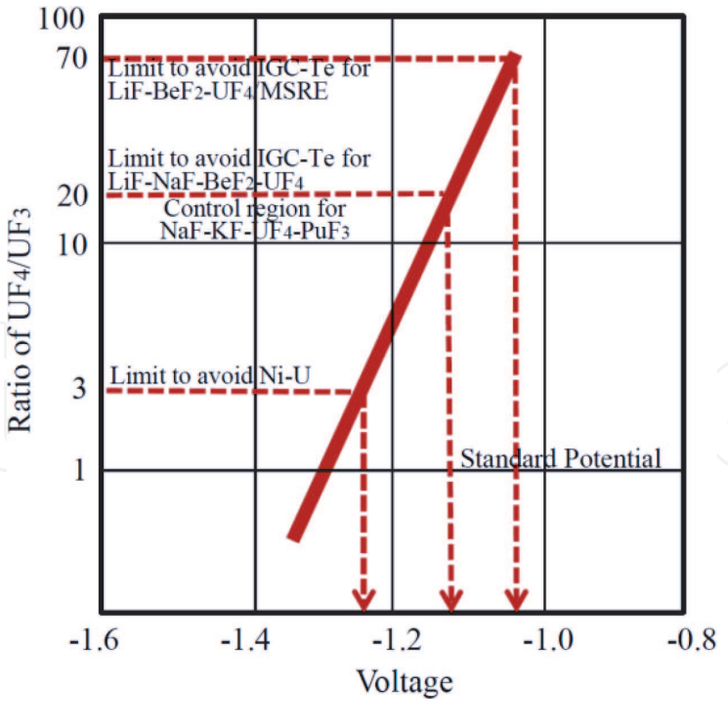



**Figure 5.**
*Dependence of the redox potential on $UF_4/UF_3$ ratio [27, 28].*

NaF-KF-$UF_4$ compound might be less Lewis basic than LiF-$BeF_2$-$ThF_4$; however it will require to make the [U(IV)]/[U(III)] ratio at least 20. This means that $UF_3$ has to be kept as the redox buffer at 1.33 mol% while total uranium fluoride at 28.1 mol%.

## 2.6 Operational behavior of FFMSR

### *2.6.1 Effect of U inventory on reactor physical properties*

Neutronic calculations were made taking originally proposed configurations of the reactor (core height/radius ratio, 1.85; core volume, 21.2 $m^3$; primary circuit volume, 31.8 $m^3$) and the power output (3.2$GW_{th}$) the same as Ref. [7], but other factors, such as the actinide isotopic composition (45,000MWD/t-U in BWR, 5 years cooling), neutron leakage (with 30 cm steel reflector), the fuel temperature (627°C), the salt cleanup and makeup condition, etc., were discretely specified to give verified number of heavy element masses and concentrations in the fuel salt to give designated reactivity ($k_{eff}$ = 1.007) from the start up to the equilibrium state (40 years).

Operational features are characterized by annual feed/breed balance of fissile material as TRU over four zones under a constant U inventory which can be maintained by an appropriate makeup. The effect of U inventory in three levels on TRU feed/breed balance is evaluated in which fuel salt cleaning started after 300 effective full power days (EFPD) with an interval of 300 EFPD and illustrated in **Figure 6**. The larger inventory of U requires larger amount of initial fissile inventory but smaller amount of supplement; however the peak annual supplement is less dependent on the initial U charge. U inventory of 61.4 tons is the lowest threshold limit to make breeding break-even possible, while that of 71.5 tons can provide as much as 100 kg TRU of annual breeding; however it is the highest threshold limit by U content acceptable by a relevant fuel salt.

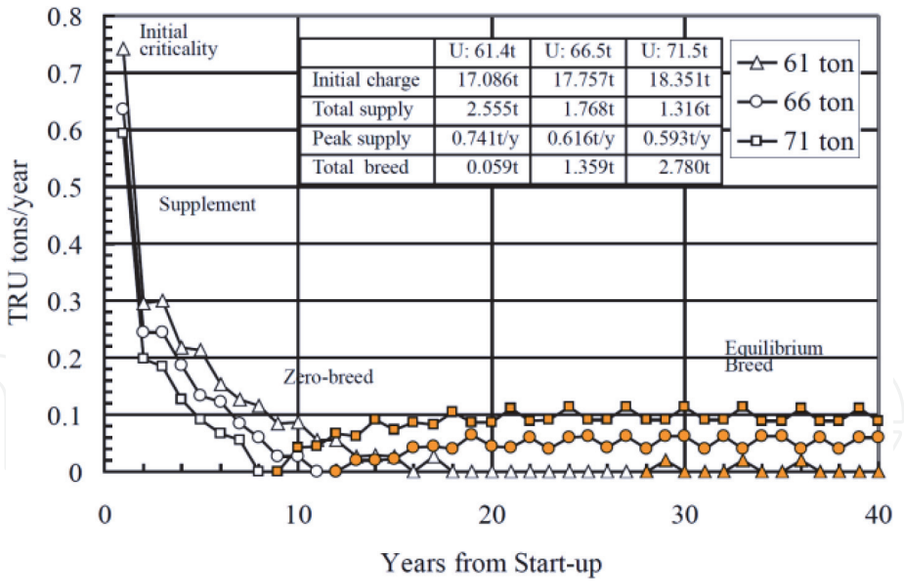



**Figure 6.**
*Effect of initial U charge on the feed/breed balance.*

### *2.6.2 Effect of fuel salt cleaning interval on reactor physical properties*

Three hundred EFPD and 1500 EFPD of the fuel salt cleaning interval are evaluated both for an identical initial charge of the fuel salt composition (U: 71 t) as shown in **Figure 7**. No chemical cleaning but only makeup of TRU was made during the designated initial interval. The longer interval requires larger amount of fissile material supplement; however the peak annual supplement is less dependent on the extension of cleaning interval. A longer interval makes the cleaning volume smaller but nevertheless total makeup larger; however the cost of facility is specifically determined by the peak annual makeup value.

The operation of an FFMSR with 1500 EFPD of fuel salt cleaning interval is assumed as barely providing a steady and sustaining operation with an appreciable breeding (10 kg TRU/year) in equilibrium.

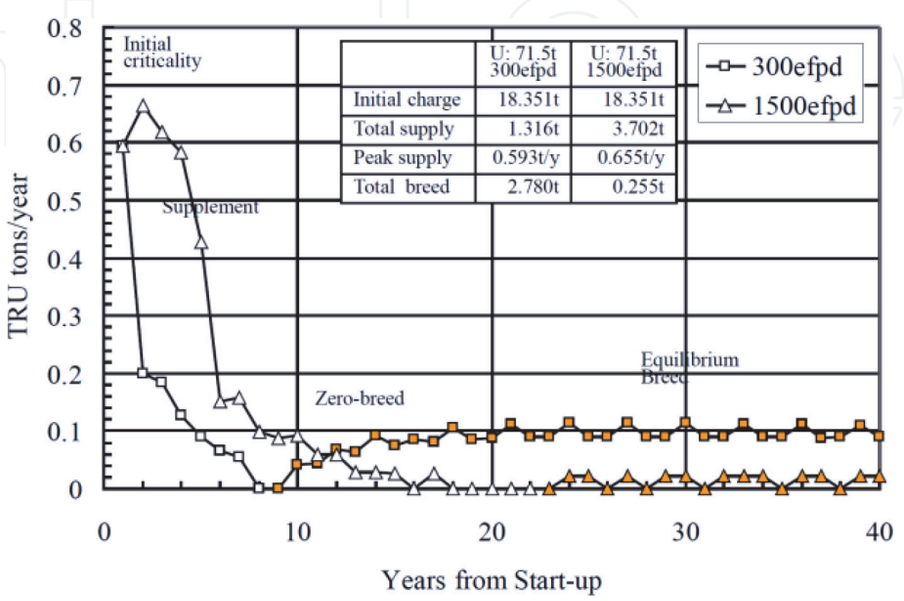



**Figure 7.**
*Effect of fuel salt cleaning interval on the feed/breed balance.*

### *2.6.3 Effect of initial fissile isotope composition*

The effect of isotopic composition of initial feed TRU was evaluated for BWR-UOx fuel and ABWR-MOX fuel as shown in **Figure 8**. The isotopic compositions of each feed TRU are shown in **Table 8**.

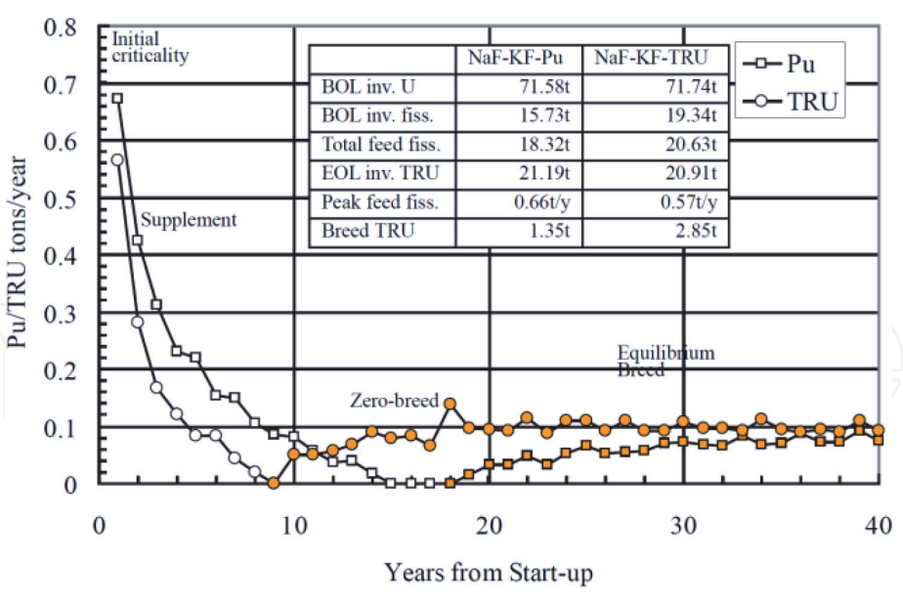
It is revealed that the breeding performance of an FFMSR applied on the ABWR-MOX spent fuel is much better than that on the BWR-UOX spent fuel though they can be comparable after the equilibrium state.

What is more drastic is the capability of accumulated TRU to support deployment of the FFMSR. It is assumed that a 3.3 GWt (1.0 GWe) BWR yields annually 20.4 t of spent nuclear fuel (SNF) (50 GWd/t-U) containing 0.27 t of TRU; meanwhile a 3.93 GWt (1.38 GWe) full MOX ABWR yields annually 34.8 t of SNF (33 GWd/t-HM) containing 1.28 t of TRU. The accumulated SNF from a BWR for 54.6 years will support an FFMSR-UOX, and that of an ABWR's SNF for 17.8 years will support an FFMSR-MOX, with equivalent power output the same as the respective reactor. This means that a full MOX ABWR can be a breeding reactor with 17.8 years doubling time by the combination of FFMSR deployment.

## 2.7 Evolution of TRU constitution

The TRU inventory is almost kept at a constant through FFMSR operation with specific trends of isotopic evolution as shown in **Figures 9** and **10**.

The high content of Np is distinct in the TRU from LWR; however it is transmuted effectively. The content of Pu isotopes is getting saturated in both cases. Am isotopes are slowly decreasing until 40 years. The buildup of Cm is over a factor of 3.5; however it tends to be saturated after 20 years. This is a characteristic feature compared with the case of MOSART [29] in which non-fissionable Cm isotopes

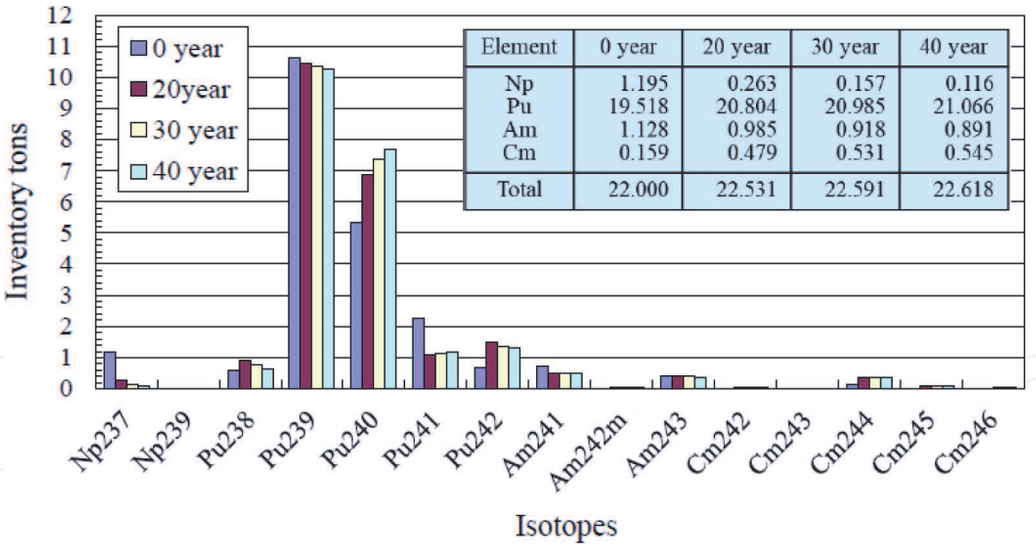



| | NaF-KF-Pu | NaF-KF-TRU |
|---|---|---|
| BOL inv. U | 71.58t | 71.74t |
| BOL inv. fiss. | 15.73t | 19.34t |
| Total feed fiss. | 18.32t | 20.63t |
| EOL inv. TRU | 21.19t | 20.91t |
| Peak feed fiss. | 0.66t/y | 0.57t/y |
| Breed TRU | 1.35t | 2.85t |

**Figure 8.**
*Effect of initial fissile isotope composition on the feed/breed balance.*

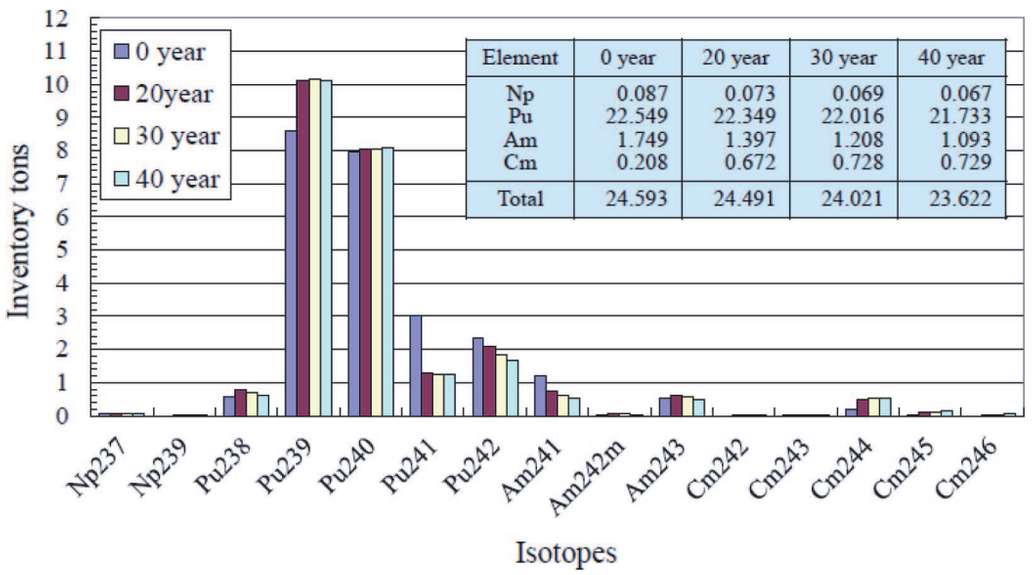
| Source of TRU | Np/Pu/Am/Cm (wt.%) | $^{238/239/240/241/242}$Pu (wt.%) |
|---|---|---|
| BWR-UOX-45GWd/t-U | 5.19/89.22/4.90/0.69 | 2.80/51.77/25.98/11.07/8.38 |
| ABWR-MOX-33GWd/t-HM | 0.35/91.69/7.11/0.85 | 2.62/38.17/35.33/13.49/10.39 |

**Table 8.**
*Isotopic composition of initial feed TRU.*




| Element | 0 year | 20 year | 30 year | 40 year |
|---|---|---|---|---|
| Np | 1.195 | 0.263 | 0.157 | 0.116 |
| Pu | 19.518 | 20.804 | 20.985 | 21.066 |
| Am | 1.128 | 0.985 | 0.918 | 0.891 |
| Cm | 0.159 | 0.479 | 0.531 | 0.545 |
| Total | 22.000 | 22.531 | 22.591 | 22.618 |

**Figure 9.**
*Evolution of TRU isotopic composition during burnup (BWR-UOX).*




| Element | 0 year | 20 year | 30 year | 40 year |
|---|---|---|---|---|
| Np | 0.087 | 0.073 | 0.069 | 0.067 |
| Pu | 22.549 | 22.349 | 22.016 | 21.733 |
| Am | 1.749 | 1.397 | 1.208 | 1.093 |
| Cm | 0.208 | 0.672 | 0.728 | 0.729 |
| Total | 24.593 | 24.491 | 24.021 | 23.622 |

**Figure 10.**
*Evolution of TRU isotopic composition during burnup (ABWR-MOX).*

build up remarkably. Generally favorable features of fast neutron irradiation are represented, though further assessments for several hundred years are inevitable.

## 2.8 Freezing behavior of fuel salt

The molten salt reactor is feasible as long as the liquidus temperature of the fuel salt is kept at least 50°C lower than the reactor core inlet temperature. According to the classic design principle of molten salt reactors, the fuel salt should be composed of a single eutectic mixture, and all components of the fuel salt should congruously solidify at the eutectic point.

In the case of the FFMSR, the phase change is incongruous manner as the fuel salt should be composed of a pair of independent eutectic mixtures. It should be qualified by freezing behavior down to the solidus temperature in order to justify any engineering effort particular to the molten salt reactor such as the freeze valve, the fuel drain tank, and the reactor safety evaluation.

The freezing of NaF-KF-$UF_4$-$PuF_3$ system is dictated by the eutectic point of fissile salt (605°C) to give eutectic of NaF-KF-$PuF_3$ irrespective of the concentration of $UF_4$ as shown in **Table 9**. These values of liquidus temperature are substantially higher than that of the classic fuel salt such as 0.72LiF-0.16$BeF_2$-0.12$ThF_4$ (500°C) for thermal neutron molten salt reactors based upon the Hastelloy N technology however near to that of the revised MSFR (594°C) [30].

The solidified fuel salt eventually produces a specific stratified structure, a lighter fissile salt on a heavier fertile salt. The density of solidified salt is assumed as 8% higher than that of liquid at the same temperature.

Feasibility of the freeze valve can be controversial because it has originally been developed on the assumption that the fuel salt was a single eutectic mixture which solidified congruously.

## 2.9 Effect of burnup and tri-fluorides on freezing behavior

If the U(IV)/U(III) ratio in the system is fixed at 20 as a redox buffer medium, 71.4 tons-U (300,000 moles) of the total U inventory should consist of 285,700 moles of $UF_4$ and 14,300 moles of $UF_3$. The concentration of $UF_3$ is 1.33 mol% when that of $PuF_3$ is 8.10 mol%. Meanwhile, $UF_4$ inventory is reduced to a factor of 0.952 by chemical reduction to $UF_3$.

It has been suggested thermodynamically that tri-fluorides of fission product lanthanide behave as $PuF_3$ as well as those of minor actinide in the phase relationship and would interfere the freezing behavior.

Calculations are made to evaluate the effect of reduction of $UF_4$ to $UF_3$ and buildup of fission product lanthanide tri-fluorides in NaF-KF-0.281$UF_4$-0.081$PuF_3$ fuel salt according to chemical processing intervals for two cases of fissile salt arrangement and shown in **Tables 10** and **11**.

It is revealed that the effect of $UF_4$ reduction to $UF_3$ does not affect liquidus temperature of fuel salt meaningfully irrespective of fissile salt.

| Temp. °C | Liquid Composition mole ratio | Wt. % | Density g/cc | Solid Composition mole ratio | Wt. % | Density g/cc |
|---|---|---|---|---|---|---|
| ~605 | 0.354NaF-0.290KF-0.275$UF_4$-0.081$PuF_3$ | 100.00 | 4.700 | | | |
| 605 | 0.341NaF-0.146KF-0.275$UF_4$ | 76.81 | 4.585 | 0.013NaF-0.144KF-0.081$PuF_3$ | 23.19 | 5.443 |
| 580~ | 0.341NaF-0.146KF-0.189$UF_4$ | 57.80 | 4.156 | 0.086$UF_4$ | 19.00 | 6.72* |
| 490 | | | | 0.341NaF-0.146KF-0.189$UF_4$ | 57.81 | 4.595 |
| ~605 | 0.349NaF-0.289KF-0.281$UF_4$-0.081$TRUF_3$ | 100.00 | 4.727 | | | |
| 605 | 0.336NaF-0.145KF-0.281$UF_4$ | 77.95 | 4.624 | 0.013NaF-0.144KF-0.081$TRUF_3$ | 22.93 | 5.580 |
| 590~ | 0.336NaF-0.145KF-0.173$UF_4$ | 53.47 | 4.049 | 0.108$UF_4$ | 23.60 | 6.72* |
| 490 | | | | 0.336NaF-0.145KF-0.173$UF_4$ | 53.47 | 4.491 |

* at 25°C

**Table 9.**
*Liquid and solid components of fuel salt during freezing.*

| Chem. Process Interval (EFPD) | $UF_3$ mole % | Fuel Salt (NaF-KF)-$UF_4$-$TRUF_3$ | | | | | Fertile Salt (NaF-KF)-$UF_4$ | | | | | Fissile Salt (NaF-KF)-$TRUF_3$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Composition (mole%) | | | | liq.[a] °C | mole % | Composition (mole%) | | | liq.[a] °C | mole % | Composition (mole%) | | | liq.[a] °C |
| | | NaF | KF | $UF_4$ | $XF_3$[b] | | | NaF | KF | $UF_4$ | | | NaF | KF | $XF_3$[b] | |
| 0 | 0 | 34.62 | 28.88 | 28.10 | 8.10 | 605 | 76.18 | 44.18 | 18.94 | 36.88 | 590 | 23.82 | 5.3 | 60.7 | 34.0 | 605 |
| 0 | 1.33 | 33.33 | 30.49 | 26.75 | 9.43 | | 72.26 | 44.09 | 18.89 | 37.02 | 600 | 27.74 | | | | |
| 300 | | 33.12 | 30.59 | 26.75 | 9.54 | | 71.94 | 43.97 | 18.85 | 37.18 | 600 | 28.06 | | | | |
| 600 | | 32.91 | 30.69 | 26.75 | 9.65 | | 71.62 | 43.86 | 18.80 | 37.34 | 605 | 28.38 | | | | |
| 900 | | 32.68 | 30.80 | 26.75 | 9.77 | 610 | 71.26 | 43.73 | 18.74 | 37.53 | 610 | 28.74 | | | | |
| 1200 | | 32.47 | 30.90 | 26.75 | 9.88 | 620 | 70.94 | 43.60 | 18.69 | 37.71 | 620 | 29.06 | | | | |
| 1500 | | 32.26 | 31.00 | 26.75 | 9.99 | 625 | 70.62 | 43.48 | 18.64 | 37.88 | 625 | 29.38 | | | | |
| 1500 | 0 | 33.85 | 29.39 | 28.10 | 8.66 | 620 | 74.53 | 43.62 | 18.70 | 37.68 | 620 | 25.47 | | | | |

*liq[a], liquidus temperature; $XF_3$[b]: $PuF_3$ + $UF_3$ + $LaF_3$ + if any.*

**Table 10.**
*Option (a): to keep eutectic freezing at 605°C of fuel salt, 0.053NaF-0.607KF-0.340$PuF_3$.*

| Chem. Process Interval (EFPD) | $UF_3$ mole % | Fuel Salt (NaF-KF)-$UF_4$-$TRUF_3$ | | | | | Fertile Salt (NaF-KF)-$UF_4$ | | | | | Fissile Salt (NaF-KF)-$TRUF_3$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Composition (mole%) | | | | liq.[a] °C | mole % | Composition (mole%) | | | liq.[a] °C | mole % | Composition (mole%) | | | liq.[a] °C |
| | | NaF | KF | $UF_4$ | $XF_3$[b] | | | NaF | KF | $UF_4$ | | | NaF | KF | $XF_3$[b] | |
| 0 | 0 | 35.29 | 28,51 | 28.10 | 8.10 | 610 | 76.79 | 44.39 | 19.02 | 36.59 | 580 | 23.21 | 5.2 | 59.9 | 34.9 | 610 |
| 0 | 1.33 | 33.76 | 30.06 | 26.75 | 9.43 | | 72.98 | 44.34 | 19.00 | 36.66 | 590 | 27.02 | | | | |
| 300 | | 33.56 | 30.15 | 26.75 | 9.54 | | 72.66 | 44.23 | 18.96 | 36.81 | 590 | 27.34 | | | | |
| 600 | | 33.36 | 30.24 | 26.75 | 9.65 | | 72.35 | 44.12 | 18.91 | 36.97 | 590 | 27.65 | | | | |
| 900 | | 33.14 | 30.35 | 26.75 | 9.77 | | 72.01 | 44.00 | 18.86 | 37.14 | 600 | 27.99 | | | | |
| 1200 | | 32.93 | 30.44 | 26.75 | 9.88 | | 71.69 | 43.88 | 18.81 | 37.31 | 605 | 28.31 | | | | |
| 1500 | | 32.72 | 30.54 | 26.75 | 9.99 | | 71.38 | 43.76 | 18.76 | 37.48 | 610 | 28.62 | | | | |
| 1500 | 0 | 34.25 | 28.99 | 28.10 | 8.66 | | 75.19 | 43.84 | 18.79 | 37.37 | 605 | 24.81 | | | | |

*liq[a], liquidus temperature; $XF_3$[b]: $PuF_3$ + $UF_3$ + $LaF_3$ + if any.*

**Table 11.**
*Option (b): to allow liquidus at 610°C of fuel salt, 0.052NaF-0.599KF-0.349$PuF_3$.*

The buildup of lanthanide tri-fluorides does affect the liquidus temperature of fertile salt up to 625°C for the case (a); meanwhile it does not exceed 610°C using the fissile salt (b).

Option (a) should allow 900 EFPD of the chemical process interval if the liquidus temperature of fertile salt at 610°C is acceptable.

Option (b) should allow 1500 EFPD of the chemical process interval if the liquidus temperature of fertile salt at 610°C is acceptable. Option (b) however is against the rule in which no free fissile material is deposited before eutectic freezing. The choice of alternatives is depending upon less than 3% of difference of designated molar composition of tri-fluoride in the fissile salt. Not only the phase behavior of stable tri-fluoride such as $PuF_3$ and $LnF_3$ but also that of fluctuated $UF_3$ should be examined carefully.

## 3. Chemical processing

### 3.1 How fission product stream be free from TRU

It has been evaluated that the radiotoxicity of the PWR-UOX-SNF of 50GWd/t-U decreases to the reference level represented by that of annually transmuted natural uranium (7.83 t-$U_{nat.}$) after 130,000 years from discharge. If the HLW contains absolutely no TRU, the radiotoxicity decreases to the reference after 270 years mainly dominated by that of alkali and alkali earth elements ($FP_{alk}$: Rb, Cs, Sr., Ba) as shown in **Figure 11** [31].

The radiotoxicity of HLW from a reprocessing of UOX fuel with a nominal Pu loss rate of 0.5% and with removing minor actinides (MA; viz., Am and Cm) with a loss rate of 1% will decrease at the reference level in 500 years. It is assumed that the period will decrease to 370 years if Pu and MA are removed simultaneously from the HLW as TRU at the overall loss rate of 0.5%. This represents that the permissible TRU content in the finally disposed fission product ($FP_{alk}$: Rb, Cs, Sr., Ba) is 65.9 g-TRU/8461 g-$FP_{alk}$ (0.78%) as shown in **Table 12**.

The nuclear fuel of a 3.2 GWt FFMSR supported by 93.6 t-HM reaches the burnup of 51.3 GWd/t-HM in 1500 EFPD by consuming depleted uranium (4.33 t-$U_{dep.}$/50 GWd/t-HM), which might have been discarded as a radioactive waste somehow. If the radiotoxicity of 4.33 t-U instead that of 7.83 t-U is assumed as the reference for the HLW of FFMSR, the period to decrease to the revised reference value might be extended to 500 years after discharge. In order to keep TRU/$FP_{alk}$ at 0.78%, the permissible loss rate of the TRU into the $FP_{alk}$ should be less than 0.036% due to the specific TRU concentration in an FFMSR fuel as high as in an equivalent LMFBR fuel, as shown in **Table 11**. The required loss rate is far less than

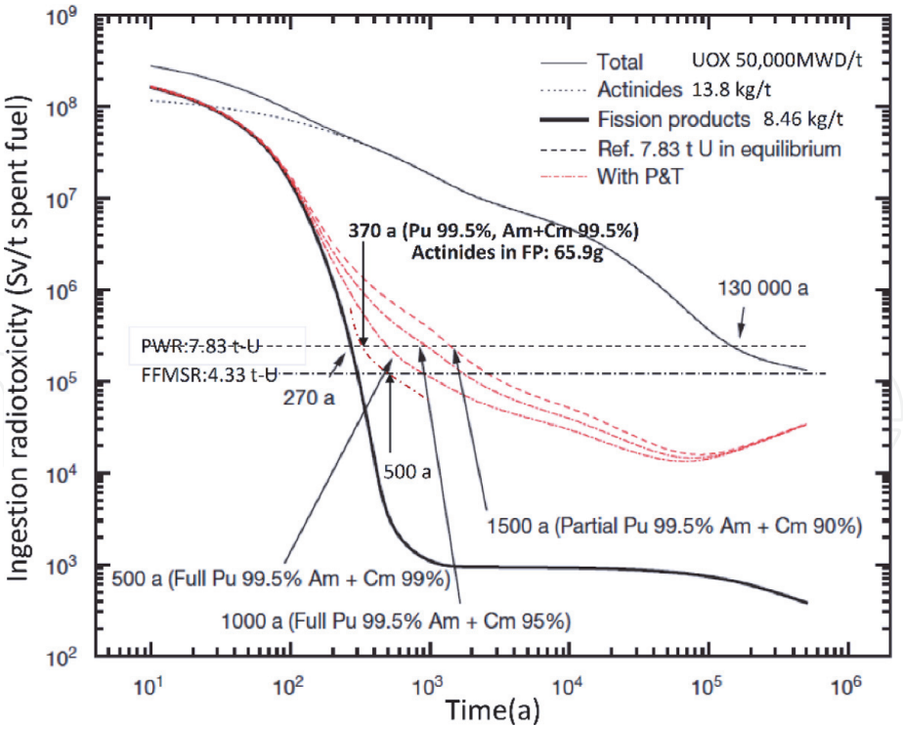



**Figure 11.**
*Ingestion radiotoxicity of 1 t of spent nuclear fuel [31].*

| | PWR-UOX 50GWd/t-U | | | FFMSR 51.3 GWd/t-HM* | | |
|---|---|---|---|---|---|---|
| **Element** | **Mass g/t-U** | **Permissible TRU (g)** | **Required loss rate** | **Mass g/t-U** | **Permissible TRU (g)** | **Required loss rate** |
| Uranium | 935,245 | | | 730,300 | | |
| TRU | 13,179 | | | 212,100 | | |
| Halogens | 358 | | | 741 | | |
| Rare gases | 8388 | | | 7533 | | |
| Noble and semi-noble metals | 13,306 | | | 18,594 | | |
| Alkali and alkaline earths | 8461 | 65.9 | 0.5% | 9665 | 75.3 | 0.036% |
| Lanthanides | 15,621 | | | 16,655 | | |
| Zirconium | 5442 | | | 4559 | | |
| FP total | 51,576 | | | 57,624 | | |

**Burnup at the end of the first 1500 EFPD and thereafter.*

**Table 12.**
*Comparison of required loss rate.*

0.1% of the target to be achieved by the pyro-processes such as electrochemical refining or liquid metal extraction currently under development [31].

The chemical processing in the FFMSR should be efficient to remove fuel material from the fission product streams but not necessarily efficient to remove fission products to become as neutron poisons if it were operated under the thermal neutron from the fuel stream.

To perform this new and perpetual mission, a processing interval of 1500 EFPD is sufficiently long and provides a small throughput in other words. The online chemical processing facility of α-β-γ-n remote operable capability collocated with

the FFMSR would be the most expensive auxiliary part of the plant to be constructed as well as to be operated. Such cost should be depending upon the nature of process, i.e., process complexity, material compatibility, process wastes, and capacity in particular.

### 3.2 Requirements to be concerned

The crucial point in the fuel cleanup process is not the complete removal of neutron-absorbing material such as lanthanides from the fuel but keeping any leak of actinides into waste streams as low as possible. This could justify the use of the selective oxide precipitation process as an absolutely simple choice compared with other pyro-processes such as the electrochemical or the reductive extraction [32].

The fluoride volatile process of $UF_6$ had been perceived as the most practical since the successful operation in MSRE during switch over the fissile from $^{235}U$ to $^{233}U$; however it has been overlooked the fact that metallic Zr scrap in addition to the fuel should be followed by a prolonged $H_2$ sparge to remove metallic corrosion products (Ni, Fe, Cr) caused by $F_2$ treatment. The presence of a certain amount of Pu should require applying a reducing process from $PuF_4$ to $PuF_3$ in order to avoid accidental precipitation of $PuO_2$ and severe material corrosion. Any absence of such treatment after the final removal of $^{233}UF_6$ might have resulted MSRE remediation in a fruitless and endless trouble by undisclosed reasons of line clogging of the fuel drain tank.

### 3.3 Selective oxide precipitation process

In the very early stage of the Molten-Salt Reactor Program (MSR Program) started at ORNL, experimental studies on selective precipitation of oxides had been carried out because it might have been a suitable scheme for the reprocessing of molten salt reactor fuels, though it was abandoned after the discovery of the reductive extraction and metal transfer process associated with the $UF_6$ volatile process, which, though complex and material incompatible, involved handling only liquids and gases. However the ultimately small throughput may allow us to select a solid handling process if the process is simple, fast, and material compatible.

A successful attempt was made to precipitate mixed uranium, plutonium, minor actinides, and rare earths from LiF-NaF molten salt solution by fluor-oxide exchange with other oxides (e.g., CaO, $Al_2O_3$) at temperatures 700–800°C. It was found that the following order of precipitation in the system is U-Pu-Am-Ln-Ca. Essentially all U and TRU were recovered from the molten salt till to rest concentration $5 \times 10^{-4}$%, when 5–10 mol% of rare earths are still concentrated in solution [33, 34].

An optional process to be applied to the DMSR fuel was suggested as follows. Treat the melt with a strong oxidant to convert $UF_3$ to $UF_4$, $PaF_4$ to $PaF_5$, and $PuF_3$ to $PuF_4$. Precipitate the insoluble oxides using water vapor diluted in helium. The oxides $UO_2$, $Pa_2O_5$, $PuO_2$, $CeO_2$, probably $NpO_2$, and possibly $AmO_2$ and $CmO_2$ should be obtained. Recover the oxides by decantation and filtration. Hydrofluorinate the oxides into the purified melt of LiF-$BeF_2$-$ThF_4$, and reduce the melt with $H_2$ and reconstitute fuel with the desired $UF_4/UF_3$ ratio [35].

This could justify the use of the selective oxide precipitation process as an absolutely simple choice compared with other pyro-processes such as the electrochemical or the reductive extraction [36].

### 3.4 Customization of the process

Based upon the survey, it is concluded that the application of the selective oxide precipitation process with alkali or alkali earth metal oxides ($K_2O_2$; melt at 490°C

and CaO; solid) as the oxidizer can be feasible under special cautions about selectivity to the FFMSR technology relying on NaF and KF as major constitutes of fuel solvent, as shown in **Figure 12**.

If it can reduce TRU concentration to $5 \times 10^{-4}$ mol% in liquid phase from 8 mol %, the available loss rate will be $6.25 \times 10^{-5}$. The permissible loss rate of $3.6 \times 10^{-4}$ is six times larger than the available loss rate.

Intense increase of liquidus temperature should be taken into account during actinide removal treatment from 605°C up to 800°C. Using $K_2O_2$ as a precipitator can modify Na/K ratio from 0.55/0.45 to nearly 0.40/0.60 to give eutectic mixture at 710°C.

Elemental fluorine freed from $UO_2$ precipitation reaction would react with $TRUF_3$ to oxidize them into $TRUF_4$ which can be eventually precipitated as $TRUO_2$ by succeeding the use of CaO as a precipitator no more than ca. 20 mol% which may give stable ternary eutectic at ca. 700°C of the final waste salt.

As actinides are extremely abundant than lanthanides, the separation efficiency of actinides from lanthanides should not be good enough in a practical application; repeated treatments might be required to reduce actinide concentration in the lanthanide stream until permissible level is attained, even though moderate amount of lanthanides are permitted in the actinide stream. Up to 10% of lanthanides would be allowed to leave in the fuel salt stream, but lower than 0.01% of actinide leak into the waste stream is anticipated.

The process is a small batch scale (e.g., 21.2 l/day) in a pure Ni-made vessel facilitated to eliminate solid handling but performed by liquid phase handling only. The relevant fuel batch contains 12.9 kg of TRU which substantially exceed the significant mass of 8 kg; however it is always accompanied with 47 kg of chemically inseparable uranium. It is anticipated that the heat generation rate of a fuel batch will be 13.4 kW and the radioactivity will be 6MCi at 2 days after being drained.

The process is incorporated with He sparge to purge rare gases and halogens as well as noble and semi-noble metal fission products and electroreductive removal of zirconium developed for the MSRE remediation [37] as shown in **Figure 13**. Accumulation of fission product zirconium tetrafluoride in the fuel system would

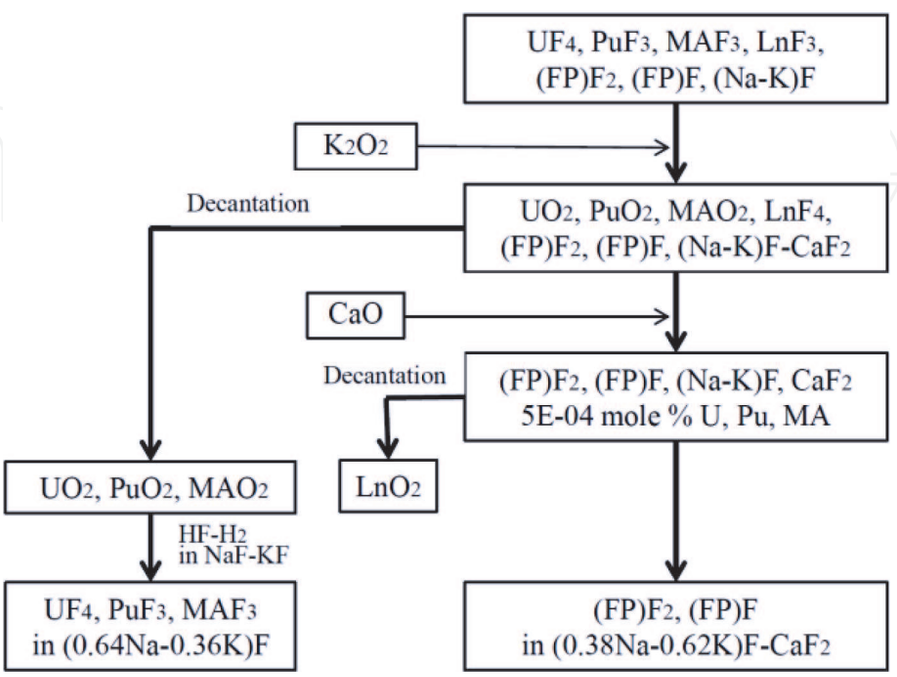



**Figure 12.**
*Process flowsheet of the oxide selective precipitation.*

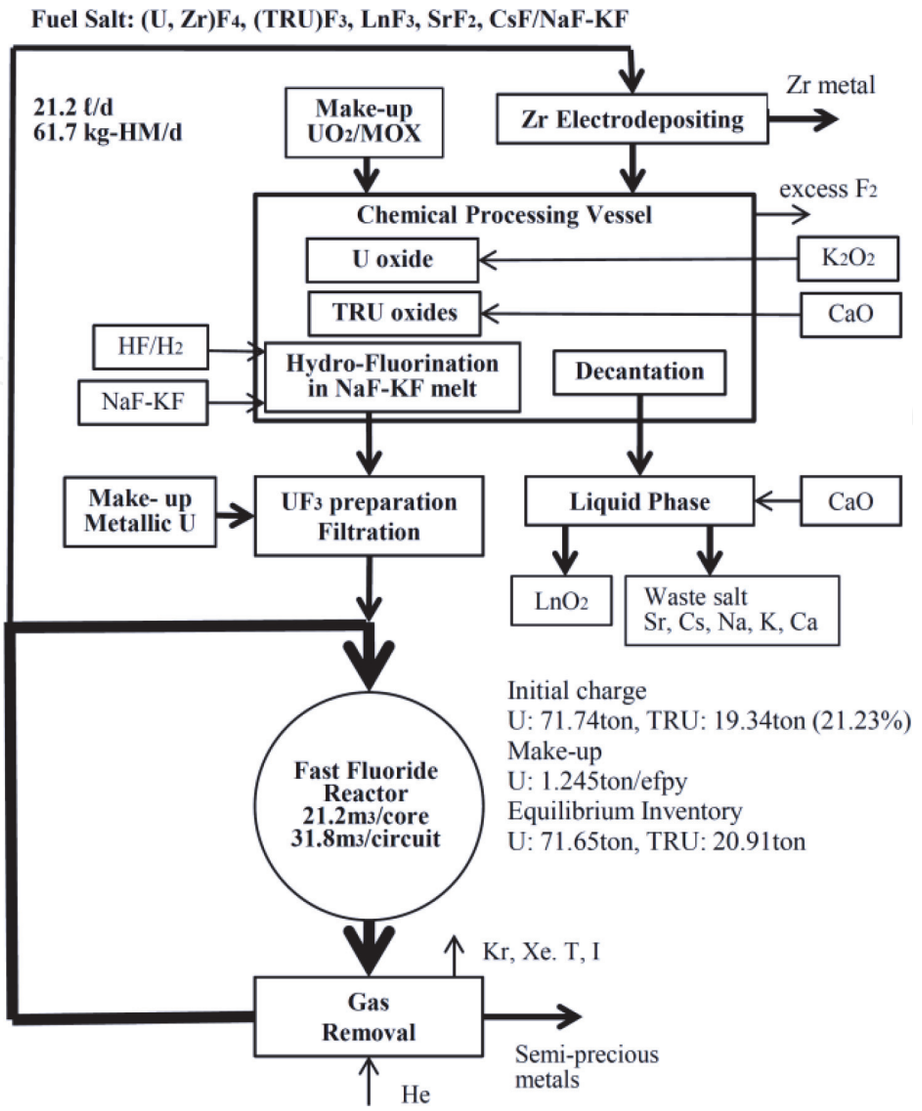



**Figure 13.**
*Online chemical process in a typical 3.2 GWt FFMSR.*

| Fuel-in mole% | | $K_2O_2$ 26.52 mole% | CaO 19.14 mole% | Decant -ation | Hydro-fluorination in NaF-KF | Fuel-out U make-up | | CaO 2.08 mole% | Waste solution mole% | |
|---|---|---|---|---|---|---|---|---|---|---|
| $UF_4$ | 26.67 | $UO_2$ | $UO_2$ | | $UF_4$ | $UF_4$ | 27.27 | | | |
| $UF_3$ | 1.33 | | | | | $UF_3$ | 1.40 | | | |
| $NpF_3$ | 0.03 | $NpF_4$ | TRU-$O_2$ | | $NpF_3$ | $NpF_3$ | 0.03 | | | |
| $PuF_3$ | 7.63 | $PuF_4$ | | | $PuF_3$ | $PuF_3$ | 7.63 | | | |
| $AmF_3$ | 0.26 | $AmF_4$ | | | $AmF_3$ | $AmF_3$ | 0.26 | | | |
| $CmF_3$ | 0.17 | $CmF_4$ | | | $CmF_3$ | $CmF_3$ | 0.17 | | | |
| $LnF_3$ | 1.04 | $LnF_4$ | | $LnF_4$ | | | | $LnO_2$ | | |
| RbF CsF $SrF_2$ $BaF_2$ | 0.31 | RbF CsF $SrF_2$ $BaF_2$ | | RbF CsF $SrF_2$ $BaF_2$ $CaF_2$ | | | | | RbF CsF $SrF_2$ $BaF_2$ $CaF_2$ | 15.65 |
| NaF | 43.79 | NaF | | | | | 44.27 | | NaF | 32.05 |
| KF | 18.77 | KF | | | | | 18.97 | | KF | 52.30 |

**Table 13.**
*Process parameters of oxide selective precipitation.*

give an adverse effect in the fuel storage tank due to its reducible nature under gamma radiation as well as sublimation. Some detail process parameters are shown in **Table 13**.

## 4. Chemical engineering of FFMSR

### 4.1 Initial fuel charge

An institutional restriction imposed to our task is the fact that no separated plutonium is tolerable in Japan to secure proliferation resistance under the international agreement. Japanese reprocessing plant cannot produce anything but U-Pu mixed oxide.

In the case of the FFMSR, the preparation work of initial charge does not require a high gamma facility if the source materials come from a conventional reprocessing plant. The oxide precipitation process incorporated with the hydro-fluorination process makes solid mixed oxide as makeup material feasible.

A typical 3.2 GWt FFMSR requires U-21.23% TRU mixed compound of 90 tons for the initial charge and 3.41 kg-U/EFPD (1245 kg-U/EFPY) of makeup in the equilibrium state compared with the 47.8 kg-U/EFPD of projected throughput of the chemical processing.

The FFMSR requires several tons of TRU supplement according to the nuclear characteristics until it reaches to equilibrium. This system is capable of making up 0.92 kg-TRU/EFPD (336 kg-TRU/EFPY), if the same U-TRU mixed compound as the initial charge is applied.

According to the specific nucleonic characteristics, the minimum U makeup is 1115 kg-U/EFPY, and the peak TRU supplement is 720 kg-TRU/EFPY. This means that as high as 39.2% U-TRU mixed compound should be temporally required in this occasion.

### 4.2 Redox buffer control and burnup effect

The nuclear reaction in the FFMSR consists of transformation of $UF_4$ into $TRUF_3$ and fission of $TRUF_3$ into fission products. The annual free fluorine production of 3.2 $GW_{th}$ FFMSR at the equilibrium is 1308 moles (0.25/0.238 mol/kg-U $\times$ 1245 kg-U/EFPY) from the transmutation of $UF_4$ and 3264 moles from the fission of $TRUF_3$ based on 1.02 mole-F/MWt/y times 3200 according to **Table 6**. The annual consumption of $UF_3$ is 4572 moles (1088 kg-U). This can be compensated by dissolution of 1524 moles uranium metal (363 kg-U) in the fuel salt containing $UF_4$ as a part of annual U makeup (1245 kg-U), though any side stream hydro-fluorination is also available.

Taking into account uranium inventory as much as 71.65 tons (28 mol%), assumed U[IV]/U[III] = 20 ratio represents 3.41 tons of U[III] inventory and 1.33 mol% of $UF_3$ concentration. Since the daily supply of U[III] is 3 kg/EFPD, very stable control of U[IV]/U[III] ratio is available. On the other hand, steadiness of $UF_3$ concentration as high as 1.33 mol% represents 26.67 mol% of the $UF_4$ and 9.33 mol% of the total tri-fluoride concentration instead of 8.0 mol% of $TRUF_3$.

It should be assumed that the inventory of fission product lanthanide tri-fluoride at the burnup of 50,000 MWd/t-HM is 6.9% (0.55 mol%) of TRU tri-fluorides. Any effect of fluctuation as high as ~1.33 mol% in $UF_4$ or ~1.88 mol% in total tri-fluoride upon the liquidus temperature of fuel salt should be carefully examined.

### 4.3 Back-end process and radioactive wastes

In the FFMSR, the inventory ratio of fission products to that of TRU is the key factor to guarantee an effectively low concentration of TRU in the waste stream

with a given TRU leak rate. The inventory of fission product is equal to that of accumulation during 1500 EFPD (51GWd/t-HM).

The waste stream consists of gases (He, Kr, Xe, and $^{3}H$), spent charcoal filter absorbing I, solid elements (Zr, rare metals, and semi-rare metals such as Zn, Ga, Ge, As, Se, Nb, Mo, Ru, Rh, Pd, Ag, Tc, Cd, In, Sn, Sb, and Te), lanthanide oxides, and NaF-KF-$CaF_2$ matrix salt containing alkali/alkali earth fission product fluorides.

Storage of fission product gases in high-pressure cylinders and then transfer to the repository was a standard practice in the MSBR design; however it is impractical in Japan, because of regulative requirement of annual pressure proof test of high-pressure cylinders.

Though the fission yield of $^{85}Kr$ from the FFMSR system is assumed as about 1/3 of that from the graphite-moderated thorium molten salt reactors, special attention was suggested such as underground disposal by geological hydro-fracturing should be paid for radioactive Kr [38] if releasing from a high stack as currently applied in the spent fuel reprocessing plant will not be allowed in the future.

The spent iodine filter such as silver-impregnated matrix is a universal issue in every molten salt reactor as well as in spent solid fuel reprocessing plants.

Zr is electrochemically separated from the fuel salt prior to the oxide precipitation. Zr compounds are not desirable in the waste salt tank because of their reducibility in addition to sublimation capability [34].

Rare and semi-rare metals could possibly be industrially utilized after appropriately separated because they are virtually alpha activity free. They include various very long-lived fission products, such as $^{99}Tc$, $^{126}Sn$, $^{79}Se$, and $^{107}Pd$, which are to be disposed in a very compact form.

NaF-KF mixture containing soluble and major heat-generating fission product fluorides (CsF, $SrF_2$, etc.) and the process reagent (KF and $CaF_2$) is the main process waste as far as the online chemical processing is concerned.

Composition of fuel salt is assumed as 0.348NaF-0.284KF-0.280$UF_4$–0.082TR$UF_3$-0.006$LnF_3$ ($T_{liq.}$ = 605°C), and that of waste salt is assumed as 0.356NaF-0.580KF-0.060$CaF_2$-0.004$FPF_{1.5}$ ($T_{liq}$ = 700°C).

Storage of the waste salt as liquid phase at higher than 700°C should be unpractical. It might be cooled to solidify in a tank shortly after being transferred.

The inventories are assumed as fuel salt, 147.87 tons; HM fluoride, 120.54 tons; and matrix salt, 27.33 tons. The high-level waste salt originated from a 1.5 GWe FFMSR system for 1500 EFPD operation (51.3 GWd/t-HM) is 46.26 tons (20.12 $m^3$ at 2.3 g/cc of density), and the radiotoxicity of this amount of waste is equivalent to 405 tons of depleted uranium after 500 years cooling.

The throughput of high-level waste salt mixture from the vitrified high-level waste of 1.5 GWe PWR (50 GWd/t-U) after 99.5% Pu by reprocessing and 99% MA removal by P&T is probably 59 tons, and the radiotoxicity of this amount of waste is equivalent to 1163 tons of natural uranium after 500 years cooling.

The selection of the fuel matrix without $^{7}Li$ economically allows a direct disposal of the waste matrix salt without recycle; nevertheless the bulk mass is comparable to that of vitrified waste of LWR though public utilization of decay heat before immobilization of cooled waste salt might be feasible.

Furthermore the incomparably favorable fact that the FFMSR system does not produce any fuel cycle-associated wastes, starting from uranium mine tailing all through to alpha-contaminated HEPA filters of MOX fuel fabrication plant, should be taken into account.

The characteristic capability of the oxide selective separation process enables to retrieve alpha contamination-free metals as well as lanthanide oxides without

elaborating partitioning processes. Effective technologies to utilize such recovered resources are sincerely expected.

Full deployment of the FFMSR should make the entire fuel cycle infrastructures from the uranium mining to the spent fuel reprocessing including P&T needless except the HLW disposal site.

### 4.4 Contingency plan

The annual loss of TRU due to fuel salt chemical cleaning is 6 kg based upon the assumption 1500 EFPD of interval and 0.1% of nominal loss rate for 22.6 tons-TRU inventory. This can be accounted for in the equilibrium phase indefinitely because the annual TRU surplus is 10 kg. However if a flushing procedure should be required at the maintenance work according to 0.43% of the transfer rate in the MSRE operation experience [34], 97 kg of TRU may be transferred to the flushing salt even if it will be recovered efficiently later. How much TRU should have been given as a dowry at the deployment of a stand-alone FFMSR is a question. The reactivity swing by the chemical process unit outage (halt of the makeup and FP separation) should also be evaluated.

### 4.5 Dedicated front-end process for the ABWR

The dedicated front-end plant might produce U-TRU mixed fluoride from the MOX spent fuel of ABWR for which the Rokkasho Reprocessing Plant cannot deal with technical reasons as shown in **Figure 14**.

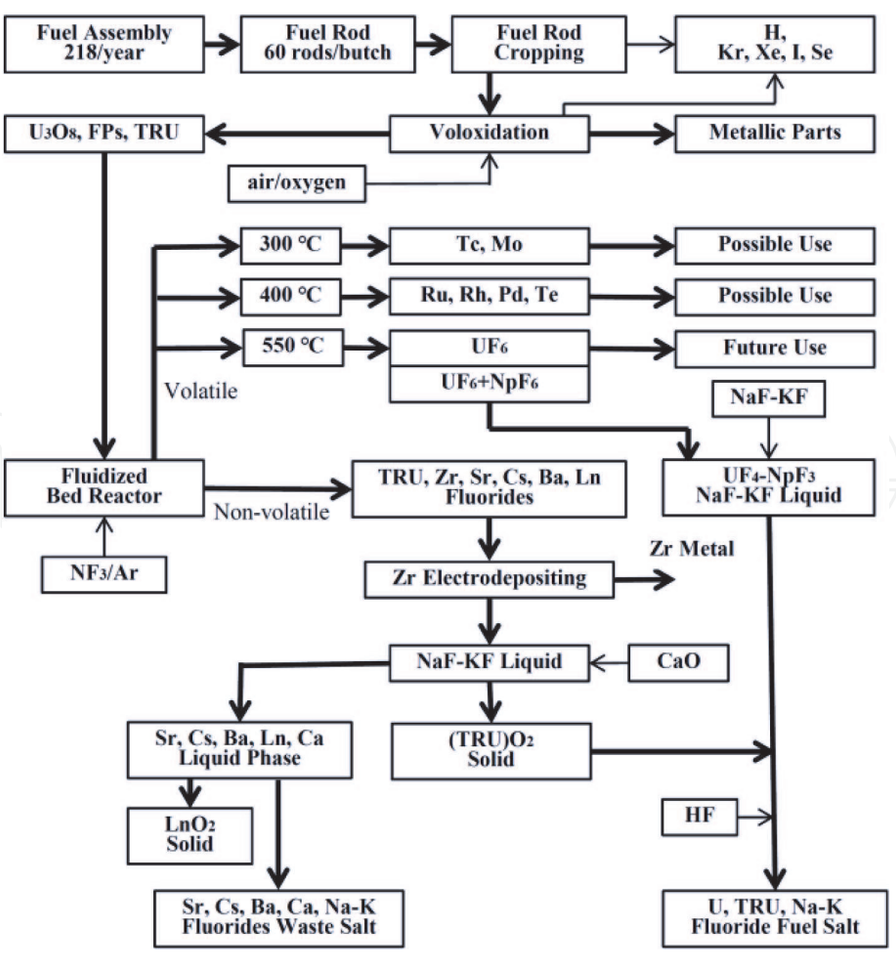



**Figure 14.**
*Dedicated front-end process for the ABWR-MOX fuel.*

The original fluoride volatility process converts all components into volatile fluorides by using fluorine flame reactor and then separates them into fractions according to their properties [39]. However we were rather interested in the recently developed innovative process using $NF_3$ as a thermally sensitive reagent; it would react with different compounds at different temperatures [40]. For example, $NF_3$ reacts with Tc and Mo oxide near 300°C and Ru and Rh near 400°C, while U oxides required near 500°C to form a volatile fluoride. This process eventually yields the nonvolatile fraction containing all TRU fluorides. Then we intended to apply the oxide selective precipitation process, to provide TRU stream not so much cleaned from fission products but to result very clean fission product stream from TRU contamination.

The distinguished feature of this process is the capability to separate useful metallic fission products as well as lanthanide oxides free from alpha contamination from other residual materials of fluorination process effectively, without laborious partitioning.

A suite of processes are shown as the flowsheet specifically for the ABWR spent fuel processing; however it can be reasonably modified to the original LWR spent fuel or LWR-MOX spent fuel.

## 5. Experimental test plans

### 5.1 Clarify phase relationship in NaF-KF-$UF_4$-$UF_3$-$PuF_3$ system for the FFMSR

It is perceived that experimental confirmation of density assessment procedure of molten salt mixtures is inevitable to establish any MSR technology. The liquid fuel of the FFMSR contains $UF_4$, $UF_3$, and $PuF_3$. Currently any performance of experimental activity on the specimens containing Pu as the special nuclear material is not available other than in the Russian Research Laboratories.

We plan the experimental procedure using NaF-KF-$^{nat.}UF_4$ containing in situ prepared $^{nat.}UF_3$ to simulate NaF-KF-$^{nat.}UF_4$-$PuF_3$ taking advantage of identical crystal structure as well as similarity of density between $PuF_3$ and $UF_3$.

Furthermore, the phase relationship (freezing behavior) will be experimentally evaluated in order to justify that the feasibility of the phase structure should be understood.

The plan includes:

1. Confirmation of synthetic process of heavy element fluoride.
2. Confirmation of recovery process of heavy element as $UO_2$.
3. Confirmation of synthetic process of NaF-KF-$UF_4$-$UF_3$.
4. Density measurement of liquid NaF-KF-$UF_4$-$UF_3$ to clarify the dependency of heavy element content with different solid densities on density of the liquefied salt.
5. Investigation of the phase diagrams of NaF-KF-$UF_4$-$UF_3$ to clarify the dependency of $UF_3$ collocation in the NaF-KF-$UF_4$ phase diagram using the solubility measuring practice. Effect of trivalent fission products on the phase diagram using $CeF_3$ as a surrogate of $UF_3$ and $PuF_3$.

### 5.2 Experimental confirmation of chemical effects of TRU fissioning

The chemical effects of $UF_4$ fissioning in a fluoride molten salt reactor were confirmed by the successful operation of the MSRE during the end of the 1960s. However any experimental confirmation of the chemical effect of $PuF_3$ fissioning in

a fluoride molten salt reactor has not yet been undertaken in spite of a strong warning made by the ORNL scientist in the end of the last century [23].

In spite of the continued effort by the author to try to stimulate academic discussion on the chemical effect of TRU fissioning controversial against the ORNL since 2015, it seems to the author to become "an inconvenient truth" for which no one dares to discuss. The author seriously concerns that the present situation might jeopardize the technological development of plutonium burning technology in the immediate future.

The author plans to propose a capsule irradiation test of NaF-KF-$TRUF_3$ specimens under the fast neutron flux ($3.9 \times 10^{19}$ $m^{-1}$ $s^{-1}$) during liquid Na cooling in an experimental fast reactor (JYOYO) located in Oharai, Japan. It plans to measure the freed fluorine ions per a fission of fissile Pu and compare with that of $^{235}U$ by the weight loss of the pure Zirconium metal specimen immersed in the fuel salt.

The proposed specimens are:

1. 0.053NaF-0.608KF-0.340$TRUF_3$ eutectic mixture (liquidus: 605°C) 2.56 g-TRU/cc as the subject.

2. 0.053NaF-0.608KF-0.340$CeF_3$ eutectic mixture (liquidus: 605°C) as the reference.

3. 0.528NaF-0.285KF-0.188$^{235}UF_4$ eutectic mixture (liquidus: 490°C) 2.52 g-U/cc as the comparative.

The nominal sample temperature in the test region is at least 600°C; however it is assumed that the gamma heat of capsule structure should enable to heat the specimen up to 750°C.

## 6. Conclusions

The study on our FFMSR was started from the review of the reference technology and based upon the comprehension of immaturity of the TRU burning technologies using the MSR due to the prejudice of the original design principle of ORNL in which the use of $PuF_3$ had been an exclusively temporary issue.

The various aspects but restricted in chemical technology discussed in this work should be taken into account and reviewed carefully in the imminent future activity although they are in limited scope and hypothetical nature to be verified experimentally. The present neutron physical calculations are preliminary nature in which the direct fission fraction of $^{238}U$ is not quantified, taking for instances. The system has not yet been optimized, in various factors.

FFMSR should provide us with a tool to stimulate immediate use of existing LWR by making values to the spent fuel as well as to the depleted uranium and to create nuclear fission energy not relying on the existing fuel cycle infrastructure with the ultimate safety owing to the absence of and eliminating fuel cycle wastes and the simplicity for an indefinitely long term.

One of a price in return for these efforts is exclusive challenges to overcome increased reactor core inlet temperature up to 660°C (50°C higher than the liquidus temperature of fuel) however it might deserve.

## Acknowledgements

The author would like to express his thanks to Prof. Dr. Koshi Mitachi and Prof. Dr. Yoichiro Shimazu for their volunteer dedication to the entire physical

calculations in this work, Prof. Dr. L.I. Ponomarev for the courtesy of personally introducing his work, and Standard Power, Co. Ltd. for publishing this chapter. He would like to dedicate this paper to the late Prof. Dr. Yoich Takashima for his guidance in initiating the work associated with MSR technology.





## Author details

Yasuo Hirose
Standard Power, Inc., Tokyo, Japan

*Address all correspondence to: yahirose@mint.ocn.ne.jp

## References

[1] Mourogov A, Bokov P. Potentialities of the fast spectrum molten salt reactor concept: REBUS-3700. Energy Conversion and Management. 2006;**47**: 2761-2771

[2] Benes O, Cabet C, Deloech S, Hosnedl P, Ignatiev V, Kornings R, et al. Review report on liquid salts for various applications. In: ALISIA Project. 2009. p. 15/64

[3] Lizin A, Tomilin S, Gnevashov O, Gazizov A, Osipenko A, Kormilitsin V. $PuF_3$, $AmF_3$, $CeF_3$, $NdF_3$ solubility in LiF_NaF_KF melt. Atomic Energy. 2013; **115**(1):11-17

[4] Lizin A, Tomilin S, Gnevashov O, Gazizov A, Osipenko A, Kormilitsin M. $UF_4$ and $ThF_4$ solubility in LiF_NaF_KF melt. Atomic Energy. 2013;**115**(1):22-25

[5] Lizin A, Tomilin S, Ignatiev V. Joint solubility of $CeF_3$ and $PuF_3$ in ternary melts of lithium, thorium and uranium fluorides. Radiochemistry. 2015;**57**(1): 32-37

[6] Lizin A, Tomilin S, Naumov S, Ignatiev V, Nezgovorov N, Baranov A. The study of joint solubility of $UF_4$ and $PuF_3$ in molten fluorides of lithium, sodium and potassium. Radiochemistry. 2015;**57**(5):425-429

[7] Degtyarev A, Pnomarev L. Molten salt fast reactor with U-Pu fuel cycle. Progress in Nuclear Energy. 2015;**82**: 33-36

[8] Hirose Y, Mitachi K, Shimazu Y. Feasibility of molten salt fast reactor for emerging national tasks. In: Proc. 2015 ANS International High-Level Radioactive Waste Management (IHLRWM 2015), Charleston, SC; April 12–16; ANS. 2015. pp. 608-617

[9] Hirose Y, Mitachi K, Shimazu Y. Operation control of molten salt U-Pu fast breeder reactor. In: Proc. ICAPP 2016, San Francisco, CA, April 17-20. 2016. p. 16124

[10] Hirose Y. Feasibility of using (Li, Na, K)F-$UF_4$-$TRUF_3$ fuels for U-Pu fast-spectrum molten-salt reactors. In: Proceedings of ICAPP 2017, Kyoto, Japan, April 28. 2017. p. 17107

[11] Hirose Y. Some chemical aspects of molten-salt reactors specifically in TRU burning applications. In: Proc. ICAPP 2018, Charlotte, NC, US, April 8-11. 2018. pp. 787-798

[12] Ponomarev L, Lizin A, Tomilin S, Fedorov Y, Hirose Y. Fast spectrum, liquid fueled reactors. In: Dolan T, editor. Molten Salt Reactors and Thorium Energy. Cambridge, MA, USA: Wood Head Publishing of Elsevier; 2017. pp. 376-433

[13] Grimes W, Cuneo R, Blankenship F, Keilholtz G, Poppendick H, Robinson M. In: MacFerson H, editor. Fluid Fuel Reactors. Reading, Mass, USA: Addison-Wesley Pub. Co.; 1958. pp. 569-591

[14] Benes O. Thermodynamics of molten salts for nuclear applications [thesis]. In: JRC Technical Notes, JRC-ITU-TN-2008/40. Prague: Institute of Chemical Technology; 2008

[15] Thoma R, editor. Phase Diagrams of Nuclear Reactor Materials, ORNL-2548; 1959

[16] Benes O, Kornings R. Actinide burner fuel: Potential compositions based on the thermodynamic evaluation of $MF–PuF_3$ (M = Li, Na, K, Rb, Cs) and $LaF_3$-$PuF_3$ systems. Journal of Nuclear Materials. 2008;**377**:449-457

[17] Canter S. Density and viscosity of several fluoride mixtures. In: ORNL-TM-4308; 1973

[18] Grines W, Cuneo D. Molten salt as reactor fuels. In: Tipton C, editor. Reactor Handbook. Vol. I. New York: Wiley (Interscience); 1960. pp. 425-473. Chap. 17

[19] Thoma R. Chemical Feasibility of Fueling MSR with PuF3. In: ORNL-TM-2256; 1968

[20] Ponomarev L. Private communication. November 26 2015

[21] Forsberg C. Accident criticality safety for fast spectrum molten salt reactors. In: Transactions of the 2007 ANS Annual Meeting, June 24–28 2007

[22] Grimes W. Molten-salt reactor chemistry. Nuclear Applications & Technology. 1970;**8**:137-155

[23] Toth LM, Del Cul G, Dai S, MetCalf G. Molten fluoride fuel salt chemistry. In: International Conference on ADTTA, Las Vegas, NV, AIP Conference Proceedings 346. 1994. pp. 617-619

[24] Holcomb D. Overview of fuel and coolant salt chemistry and thermal hydraulics. In: Presentation for US Nuclear Regulatory Commission Staff, November 7-8, 2017, Washington, DC. 2017. ML17331B115

[25] Shimazu Y, Hirose Y. Evaluation of redox environment in fluoride molten salt reactors based on ENDF-VII. In: Proceedings of AESJ 2015 Autumn Meeting, Shizuoka, Japan, September 10–12. 2015. B-20

[26] Baes C Jr. The chemistry and thermodynamics of molten salt reactor fuels. Journal of Nuclear Materials. 1974; **51**:149-162

[27] Ignatiev V, Feynberg OI, Gnidoi I, Merzlyakov A, Surenkov A, Uglov V, et al. Molten salt actinide recycler and transforming system without and with Th–U support: Fuel cycle flexibility and key material properties. Annals of Nuclear Energy. 2014;**64**:408-420

[28] Williams D. REDOX control of MSR fuel. In: GEDEON-Practis Workshop, Cadarache, France, June 19–20. 2002

[29] Ignatiev V, Feynberg O, Gnidoi I, Merzlyakov A, Smirnov V, Surenkov A, et al. Progress in development of Li,Be, Na/F molten salt actinide recycler & transmuter concept. In: Proceedings of ICAPP 2007, Nice, France, May 13–18. 2007. p. 7548

[30] EVOL (Project no.249696) Final Report. Available from: http://cordis.europa.eu/docs/results/249/249696/final1-final-report-f.pdf#search=%27EVOL%28Project+no.249696%29Final+Report%27

[31] IAEA. Implications of partitioning and transmutation in radioactive waste management. In: Technical Reports Series No. 435. 2004. p. 5

[32] Shaffer J. Chemical reactions of oxides with fluorides in LiF-KF. In: ORNL-2474. 1958. pp. 99-101

[33] Shaffer J, Watson G, Grime W. Chemical reprocessing of reactor fuels by oxide precipitations. In: ORNL-2931. 1960. pp. 84-90

[34] Gorbunov V. Experimental studies on interaction of plutonium, uranium and rare earth fluorides with some metal oxides in molten fluoride mixtures. Radiochimija. 1976;**17**:109-224

[35] Engel J, Grimes W, Bauman H, McCoy E, Dering J, Rhoades W. Conceptual design characteristics of a denatured molten-salt reactor with once-through fueling. In: ORNL-TM-7207. 1980

[36] Ignatiev V, Gorbunov V, Zakirov R. Fuels and fission products clean up for molten salt reactor of the incinerator type. In: ISTC Task #1606. 2007

[37] Peretz J. Identification and evaluation of alternatives for the disposition of fluoride fuel and flush salts from the MSRE at ORNL. In: ORNL-ER-380. 1996

[38] Messenger S, Forsberg C, Massie M. Gaseous fission product management for molten salt reactors and vented fuel system. In: ICAPP-2012, Chicago, USA, June 24–28. 2012. p. 12097

[39] Uhlir J, Marecek M. Fluoride volatility method for reprocessing of LWR and FR fuels. Journal of Fluorine Chemistry. 2009;**130**:89-93

[40] McNamara B, Casella A, Scheele R, Kozelisky A. Nitrogen trifluoride-based fluoride-volatility separations process: Initial studies. In: PNNL-20775. 2011