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# New reprocessing system for spent nuclear reactor fuel using fluoride volatility method

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ABSTRACT

Our proposed spent nuclear fuel reprocessing technology named FLUOREX, which is a hybrid system using fluoride volatility and solvent extraction, meets the requirements of the future thermal/fast breeder reactors (coexistence) cycle. We have been done semi-engineering and engineering scale experiments on the fluorination of uranium, purification of $UF_6$, pyrohydrolysis of fluorination residues, and dissolution of pyrohydrolysis samples in order to examine technical and engineering feasibilities for implementing FLUOREX. We found that uranium in spent fuels can be selectively volatilized by fluorination in the flame type reactor, and the amount of uranium volatilized is adjusted from 90% to 98% by changing the amount of $F_2$ supplied to the reactor. The volatilized uranium is purified using $UO_2F_2$ adsorber for plutonium and purification methods such as condensation and chemical traps for fission products provide a decontamination factor of over $10^7$. Most of the fluorination residues that consist of non-volatile fluorides of uranium, plutonium, and fission products are converted to oxides by pyrohydrolysis at 600–800 °C. Although some fluorides of fission products such as alkaline earth metals and lanthanides are not converted completely and fluorine is discharged into the solution, oxides of U and Pu obtained by pyrohydrolysis are dissolved into nitric acid solution because of the low solubility of lanthanide fluorides. These results support our opinion that FLUOREX has great possibilities for being a part of the future spent nuclear fuel cycle system.

## 1. Introduction

### 1.1. Background

For future nuclear fuel cycle technologies, one of the most important factors to be considered is the flexibility of the technologies to fit various cycle scenarios. Nuclear energy produces electricity now by thermal reactors such as light water reactors (LWRs) and in the future, that will be done by fast breeder reactors (FBRs), which can enhance the utilization efficiency of uranium resources. The change from LWRs to FBRs will take a long time, so it is important for the near future to consider a reasonable and transparent LWR fuel cycle system which can recycle uranium and MOX (a mixture of plutonium and uranium oxides), holds no excess plutonium, and utilizes existing technologies.

Requirements for the future nuclear fuel cycle system may become different depending on progress from LWRs to FBRs (Fig. 1). In the first phase, nuclear power generation is dominantly done by LWRs, in the second, there is a co-utilization period of both LWRs and FBRs, and in the third the independent FBR fuel cycle will be established. In the first phase, the role of fuel reprocessing is mainly in the LWR fuel cycle in which Pu is reprocessed to produce MOX fuel for Pu-thermal utilization and U is separated for re-enrichment or storage. In this phase, a high decontamination factor (DF), which is defined by the ratio of radioactivity of materials before reprocessing to that of products after reprocessing, may be required for both U and Pu products. From late in the first phase to early in the second phase, fuel production for the initial fuel loading into FBRs will be added to the role of fuel reprocessing and a high DF may not be needed for MOX any more. The DF of U should still be high even in this period since excess U will be produced over that for utilization in MOX fuel production due to the difference in the Pu contents of the fuels for LWRs and FBRs. From late in the second phase to the third phase, fuel reprocessing will be done to recycle FBR fuels. Low DF fuels may be used in FBRs and thus a simplified fuel reprocessing system will be adopted in this era.

We have been developing flexible LWR fuel processing technologies applicable to different kinds of LWR and FBR cycle scenarios. The new LWR fuel cycle technology named FLUOREX, a

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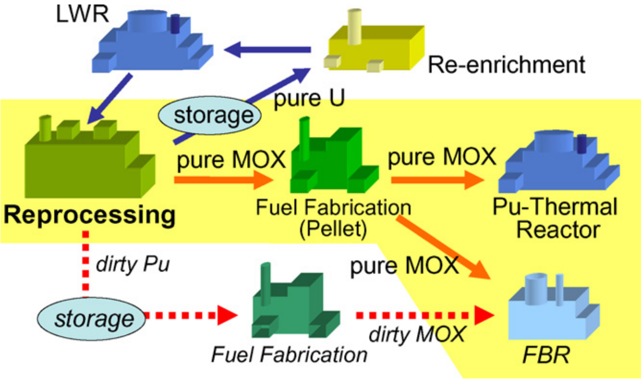

**Fig. 1.** Future nuclear fuel cycle flow in Japan.

hybrid process using fluoride volatilization and solvent extraction, is suitable for the above situation [1]. We have carried out semi-engineering and engineering scale experiments for the key elemental processes, and confirmed technical and engineering feasibilities for the FLUOREX reprocessing system. In this article, the FLUOREX concept is introduced, and the experimental results of key elemental processes, with special focus on the behavior of fluorides in FLUOREX, are described.

### 1.2. Concept of the FLUOREX reprocessing system

Spent fuel from LWRs contains about 93% uranium, 1% plutonium and 6% fission products (FPs) (Table 1). The key point of the cycle system is how to efficiently separate these elements into three parts: most of the uranium for re-enrichment, MOX for fuel fabrication, and FPs for waste. The FLUOREX reprocessing system adopts a fluoride volatility method to remove most of the uranium from spent fuel for easy treatment of residual plutonium and FPs. The mixture of plutonium and residual uranium is purified from FPs by solvent extraction.

The FLUOREX process flow is shown in Fig. 2. There are six main processes. Spent fuel from thermal reactors is sheared and the fuel is pulverized and separated from the cladding by a dry oxidation/reduction method. Fluorination of most uranium (ca. 90% of metals in spent fuel) to volatile uranium hexafluoride ($UF_6$) can be achieved by a fluoride volatility method using a compact facility. A small amount of plutonium and some FPs are also volatilized and they accompany $UF_6$ in the fluorination process, so the volatile $UF_6$ is purified to high DF (about $10^7$) by rectification and/or passing through adsorbents such as NaF. Pure $UF_6$ product is suitable for transferring directly to a re-enrichment process, or for storing for a certain period for future FBRs in simple storage facilities. Residues (ca. 10% of metals in spent fuel) including non-volatile fluorides of plutonium, residual uranium and FPs are converted to oxides by pyrohydrolysis and then dissolved into nitric acid solution in order to treat them in the well-established PUREX method. Pure Pu/U product can be obtained by a solvent extraction method without separating Pu and U, which is suitable for conventional MOX fuel fabrication and for interim storage. Behavior of elements in spent fuel in FLUOREX is also summarized in Table 1.

The proposed FLUOREX reprocessing system can recover both pure U and MOX with a DF of over $10^7$ and can drastically cut costs and waste generation compared with the conventional PUREX system, because the facility load in the solvent extraction process

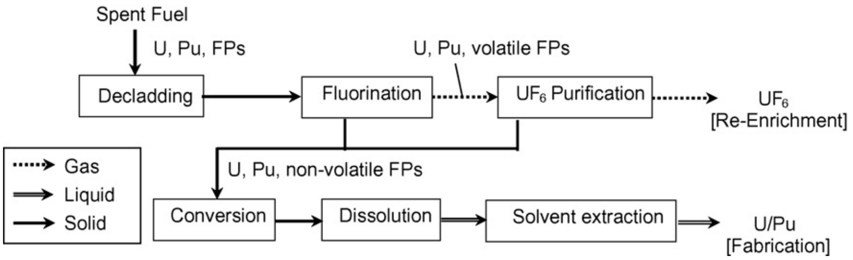

**Fig. 2.** FLUOREX reprocessing system for spent LWR fuel.

**Table 1**
Contents and behavior of the elements in spent fuels in FLUOREX

| Group | Elements | Contents in spent fuel (wt%)[a] | Behavior in the fluorination process | | |
|---|---|---|---|---|---|
| | | | Chemical form | Volatile/non-volatile | Branching after fluorination |
| Actinides | U | 92.9 | $UF_6$ | Volatile | $UF_6$ purification (90–98%) |
| | | | $UF_4$ | Non-volatile | Conversion (2–10%) |
| | Pu | 1.30 | $PuF_6$ | Volatile | $UF_6$ purification → conversion |
| | | | $PuF_4$ | Non-volatile | Conversion |
| | Np | 0.11 | $NpF_6$ | Volatile | $UF_6$ purification |
| | Am | 0.05 | $AmF_3$ | Non | Conversion |
| Alkali metals | Cs | 0.42 | CsF | Non-volatile | Conversion |
| Alkaline earth metals | Sr | 0.14 | $SrF_2$ | Non-volatile | Conversion |
| Transition metals | Zr | 0.60 | $ZrF_4$ | Non-volatile | Conversion |
| | Nb | $4.5 \times 10^{-7}$ | $NbF_5$ | Volatile | $UF_6$ purification |
| | Mo | 0.55 | $MoF_6$ | Volatile | $UF_6$ purification |
| | Tc | 0.12 | $TcF_6$ | Volatile | $UF_6$ purification |
| | Ru | 0.37 | $RuF_5$ | Volatile | $UF_6$ purification |
| Typical elements | Te | 0.08 | $TeF_6$ | Volatile | $UF_6$ purification |
| Lanthanides | La | 0.20 | $LaF_3$ | Non-volatile | Conversion |
| | Ce | 0.39 | $CeF_3$ | Non-volatile | Conversion |
| | Nd | 0.67 | $NdF_3$ | Non-volatile | Conversion |

[a] Calculated for PWR spent fuels, burnup rate of 55,000 MWD/t, 4-year cooling period [2].

will be about 1/10 that of the PUREX facility with the same capacity.

Up to now, we have examined the following subjects for each process in FLUOREX, from the viewpoint of engineering.

(1) *Fluorination process*: Applicability of the flame reactor, selective volatilization of U from spent fuel, and controls on the amount of volatilized U.
(2) *$UF_6$ purification process*: Development of a trapping system for volatile Pu and FPs from $UF_6$.
(3) *Conversion process*: Pyrohydrolysis behavior of non-volatile fluoride residues to obtain oxides.
(4) *Dissolution process*: Dissolution of oxides obtained by pyrohydrolysis, and effect of fluorine introduced into the process.

The results are shown in next section and characteristic experimental results of these subjects are described in last section.

## 2. Results and discussion

### 2.1. Fluorination process

In the fluorination process of FLUOREX, we plan to employ a flame type reactor because of its compactness and its high efficiency of fuel treatment. Most elemental technologies of the flame reactor have already been established [3]; however, the following subjects remain before realizing the conceptual design of the FLUOREX system: (1) selective fluorination and volatilization of U from spent fuel which is a mixture of U, Pu and FPs; and (2) the controls on the amount of volatilized U in the fluorination process [4].

#### 2.1.1. Selective fluorination and volatilization of U from spent fuel

Fig. 3 shows the experimental results for the fluorination of U and Pu mixture using a flame reactor coupled with $PuF_6$ decomposition chamber, as the amount of volatilized U/Pu plotted against the $F_2$ stoichiometric ratio. The $F_2$ stoichiometric ratio was defined as a ratio of supplied amount of $F_2$ to stoichiometric amount of $F_2$ calculated on the basis of reaction (1) in an experiment.

$$UO_2\,(\text{solid}) + 3F_2\,(\text{gas}) \rightarrow UF_6\,(\text{gas}) \qquad (1)$$

About 94–98% of U supplied into the combustion chamber was volatilized as $UF_6$. Less than 5% of Pu supplied was measured as $PuF_6$ in the reaction gas that passed through the decomposition chamber. Since it was confirmed that more than 90% of Pu supplied was fluorinated and volatilized as $PuF_6$ by reaction (2) in the combustion chamber from the analysis of chemical composition of reaction gas without passing through the decomposition chamber, almost all $PuF_6$ formed was decomposed to $PuF_4$ in the decomposition chamber by reaction (3). On the other hand, it appeared that a trace amount of Pu accompanied with $UF_6$ stream and a trapping and recovery system for gaseous Pu should be constructed.

$$PuO_2\,(\text{solid}) + 3F_2\,(\text{gas}) \rightarrow PuF_6\,(\text{gas}) \qquad (2)$$

$$PuF_6\,(\text{gas}) \rightarrow PuF_4\,(\text{solid}) + F_2\,(\text{gas}) \qquad (3)$$

The simulated FPs mixed with $UO_2$ and $PuO_2$ reacted with $F_2$ to form non-volatile FP fluorides, and they were detected at the wall of the combustion chamber, in the decomposition chamber, and at the filter. There was no effect by FPs on the fluorination and volatilization behavior of U and Pu observed in the experiments.

#### 2.1.2. The controls on the amount of volatilized uranium

In the FLUOREX reprocessing system, about 90–98% of U in spent fuels should be volatilized and separated from the mixture of residual U, Pu and FPs to control the Pu/U ratio in MOX. At first, we carried out $UO_2$ fluorination experiments to find out a key parameter to control the amount of U volatilized in the fluorination process.

The amount of U volatilized would depend on several factors such as $F_2$ stoichiometric ratio, $F_2$ concentration, $F_2$ feed rate, and grain size of fuel powder. We have studied the effect of $F_2$ stoichiometric ratio and $F_2$ concentration on the amount of U volatilized by measuring the temperature in the combustion chamber as an index of the amount of U reacted and volatilized. The inside temperature decreased about 100 °C with a decrease in $F_2$ stoichiometric ratio from 1.5 to 1.0; on the other hand, there was no significant change in the inside temperature when decreasing the $F_2$ concentration from 80% to 40% [5]. Thus, further experiments were performed to quantify the effect of $F_2$ stoichiometric ratio on the amount of U volatilized.

Fig. 4 shows the variation in the amount of U volatilized with $F_2$ stoichiometric ratio. The experimental results described in Section 2.1.1 are also plotted in Fig. 4. The amount of U volatilized in both experiments decreased with decreasing $F_2$ stoichiometric ratio, as was expected from the change of temperature in the combustion chamber described above. The results indicated that the amount of U volatilized could be adjusted by changing the $F_2$ stoichiometric ratio supplied to the combustion chamber.

We concluded that the flame reactor was suited to application in the fluorination process of FLUOREX, and the selective

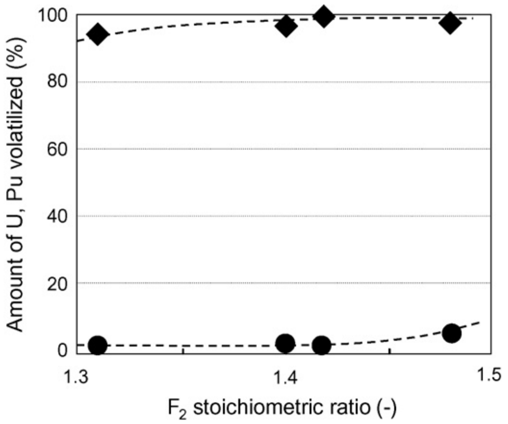

**Fig. 3.** Amount of U and Pu volatilized plotted against $F_2$ stoichiometric ratio: diamonds, U; circles, Pu.

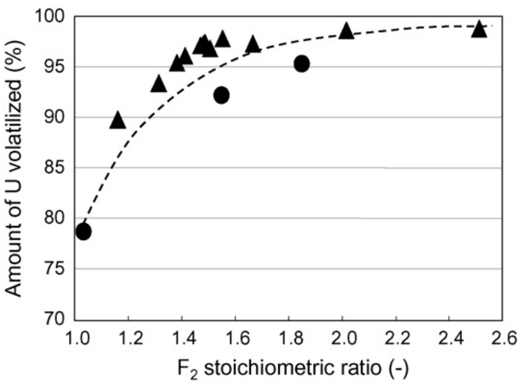

**Fig. 4.** Relationship between the amount of U volatilized and $F_2$ stoichiometric ratio: triangles, obtained in the $UO_2 + PuO_2$ + simulated FPs fluorination experiments (Section 4.1.1); circles, obtained in the $UO_2$ fluorination experiments (Section 4.1.2).

volatilization of U and the control of the amount of U volatilized could be achieved.

### 2.2. $UF_6$ purification process

Uranium volatilized as $UF_6$ in the fluorination process is fed into the $UF_6$ purification process and purified to high DF (about $10^7$) in order to transfer it directly to a re-enrichment process or to store it in simple storage facilities. Gaseous $UF_6$ includes the volatile FP fluorides listed in Table 1 as impurities, and in addition, a small amount of Pu ($PuF_6$) accompanies the $UF_6$ as mentioned in Section 2.1.1. Thus the trapping system for $PuF_6$ and volatile FP fluorides from gaseous $UF_6$ should be installed for the $UF_6$ purification process in FLUOREX.

We have studied the trapping system for $PuF_6$, and uranyl fluoride ($UO_2F_2$) was focused on as an alternative trapping material for $PuF_6$ [6]. The idea for using $UO_2F_2$ as the trapping material for $PuF_6$ has been presented in the literature [7], and the reaction in which $PuF_6$ was collected on $UO_2F_2$ was demonstrated according to reaction (4).

$$UO_2F_2\,(\text{solid}) + 2PuF_6\,(\text{gas}) \rightarrow UF_6\,(\text{gas}) + 2PuF_4\,(\text{solid}) + O_2\,(\text{gas}) \qquad (4)$$

We have carried out trial examinations on the preparation and conditions for using $UO_2F_2$ and on the trapping behavior of $IrF_6$, which is a substitute for $PuF_6$ and has very similar physico-chemical properties to those of $PuF_6$, and the typical volatile FP fluorides, Ru and Nb.

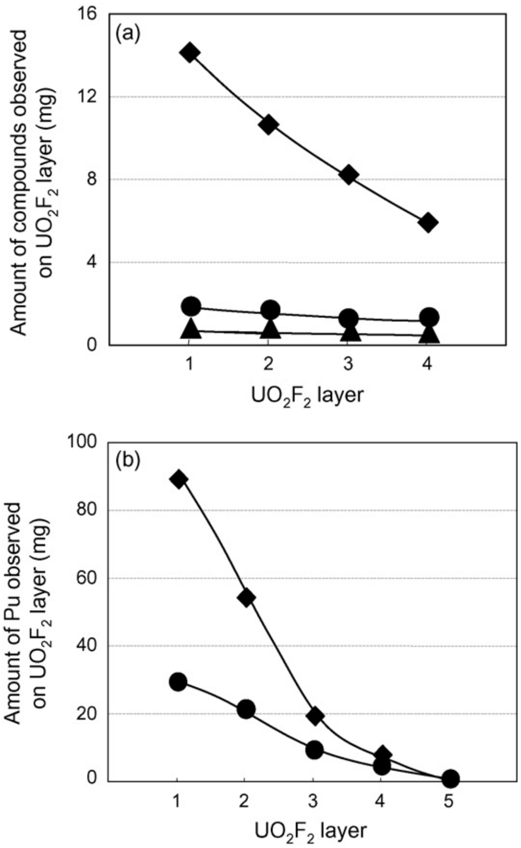

**Fig. 5.** Distribution of fluorides through the $UO_2F_2$ layers in the adsorber: (a) Ir, Nb and Ru at 150 °C: diamonds, $IrF_6$; circles, $NbF_5$; triangles, $RuF_6$; (b) $PuF_6$: diamonds, at 160 °C: circles, at 106 °C.

Fig. 5(a) shows the distributions of Ir, Nb and Ru through the $UO_2F_2$ layers in the adsorber. The amount of Ir detected on the $UO_2F_2$ layers decreased on passing through the layers, and amounts of Nb and Ru were nearly constant through the layers. Total amount of Ir on the $UO_2F_2$ was about 6 times larger than those of Nb and Ru. On the other hand, the trapping ratio, which is defined as the ratio of the amount of Ir, Nb and Ru detected on $UO_2F_2$ to that provided to the adsorber, was 29% for Ir, 6% for Nb, and 86% for Ru. The trapping ratio of Ir increased to 73% as the temperature of the adsorber increased to 200 °C, and those of Nb and Ru showed no dependency on the temperature. The larger amount of Ir trapped on $UO_2F_2$ and the higher trapping ratio of Ir, which was used as a substitute for Pu, led us to expect that the $UO_2F_2$ would be promising to remove Pu from the $UF_6$ stream in FLUOREX. Furthermore, it is also attractive to apply the $UO_2F_2$ adsorber for the Pu trapping system since $UO_2F_2$ and $PuF_4$ trapped by reaction (4) can be transferred directly to the conversion process and converted to oxides easily. In the present experiment, we observed that Ru had a larger trapping ratio on the adsorber; however, the amount of Ru that would actually reach the $UO_2F_2$ adsorber would be small in the FLUOREX system because the Ru fluoride is not stable below 200 °C [8], and decomposes on the wall of the equipment or is trapped by the particle filter which is set between the fluorination process area and the $UO_2F_2$ adsorber.

We have also confirmed the trapping behavior of $PuF_6$ on $UO_2F_2$ by preliminary experiments. In the experiments, $PuF_6$ gas was synthesized not by the fluorination of $UO_2 + PuO_2$ powers using the flame reactor, but by the fluorination of U/Pu alloys using a fixed bed reactor. Samples of U/Pu alloy (containing about 0.6 wt% of Pu) placed in the reactor was treated with $F_2$ (80 vol%) at 800 °C, and $UF_6$ and $PuF_6$ volatilized were introduced into the $UO_2F_2$ adsorber (a 50 mm thickness of the $UO_2F_2$ layer). The temperature of the adsorber was set at 160 and 106 °C to study the effect of the temperature on the trapping behavior of Pu. The $UO_2F_2$ in the adsorber was divided into five parts from the inlet to the outlet, and each section was analyzed to determine the amount of Pu trapped on the $UO_2F_2$ after the adsorption experiments.

Distribution of Pu through the $UO_2F_2$ layers is plotted in Fig. 5(b). The results showed that Pu was well adsorbed onto the $UO_2F_2$, and the efficiency of adsorption was higher at 160 °C. A trace amount of Pu (less than 1%) was observed in the gas passed through the adsorber, and it should be attributed to the channeling effect of the adsorber used in this experiment. The effectiveness of $UO_2F_2$ adsorber in trapping Pu volatilized was ensured, and we are planning to do detailed investigations on the adsorption mechanism of $PuF_6$ onto $UO_2F_2$, the adsorption capacity for $PuF_6$ onto $UO_2F_2$, and the optimum design of the $UO_2F_2$ adsorbent and the adsorber.

Some purification system for FP fluorides should be installed in the $UF_6$ purification process of the FLUOREX after the $UO_2F_2$ adsorber for trapping of Pu. Many kinds of purification systems for FP fluorides, such as rectification [9], condensation [10], and chemical sorption [11], have been studied previously. We have carried out a detailed examination of the literature to assist on constructing a purification system suitable for the FLUOREX reprocessing system. The fluorination equipment shown in Fig. 6 includes condensers and chemical traps such as NaF, $MgF_2$ and $BaF_2$, and the trapping ability of these purification systems is now under study.

### 2.3. Conversion process

After fluorination and volatilization of U in the fluorination process, residues (ca. 10% of metals in spent fuel) including non-volatile fluorides of Pu, residual U, and FPs are removed from the

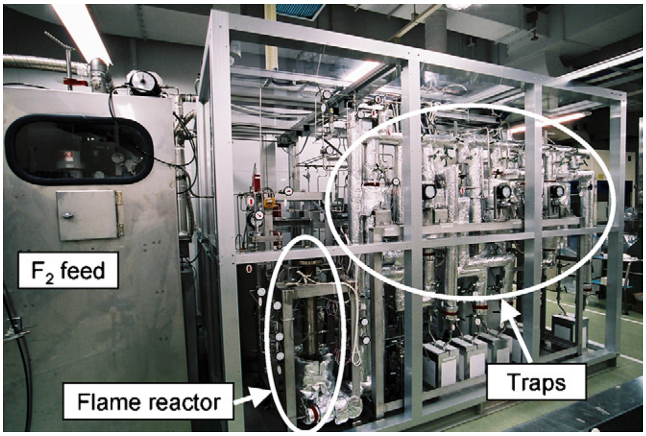

**Fig. 6.** Exterior photo of the fluorination equipment used for the $UO_2$ fluorination experiments.

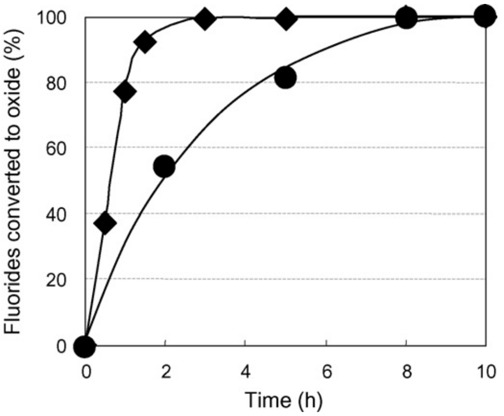

**Fig. 7.** Percentage of conversion of $UF_4$ and $PuF_4$ to oxides at 550–600 °C as a function of time: diamonds, $UF_4$ to $UO_2$; circles, $PuF_4$ to $PuO_2$.

fluorination equipment and introduced into the conversion process. Fluorides of U, Pu, and some FPs included in the residues are less soluble in nitric acid solution, and their conversion to oxides is needed. The conversion process has a role in making insoluble fluorides soluble in nitric acid, and in addition, this process has the purpose of removing fluorine from the residues to avoid its transfer into the dissolution and solvent extraction processes.

We plan to convert these fluorides into acid-soluble oxides by pyrohydrolysis, which is a well-established method for re-conversion of $UF_6$ into uranium oxides. Experimental studies of pyrohydrolysis conversion of uranium tetrafluoride ($UF_4$) into $UO_2$ have been reported [12], but information about pyrohydrolysis behavior of Pu [13] and FPs [14,15] is limited. We have performed some experiments on the pyrohydrolysis conversion of $PuF_4$ and FP fluorides to clarify the pyrohydrolysis behavior of these compounds and to determine the operation conditions of the conversion process.

The pyrohydrolysis reactions of $UF_4$ and $PuF_4$ are expressed as reactions (5) and (6).

$$UF_4\,(\text{solid}) + 2H_2O\,(\text{gas}) \rightarrow UO_2\,(\text{solid}) + 4HF\,(\text{gas}) \quad (5)$$

$$PuF_4\,(\text{solid}) + 2H_2O\,(\text{gas}) \rightarrow PuO_2\,(\text{solid}) + 4HF\,(\text{gas}) \quad (6)$$

The percentage of converted amount of $UF_4$ and $PuF_4$ to oxide is plotted against time in Fig. 7. Both $UF_4$ and $PuF_4$ were converted to oxides within 5 h. The reaction rate at the initial stage of conversion was calculated as 1.5 g/h for $UF_4$ and 0.5 g/h for $PuF_4$. Although the reaction rate of $PuF_4$ was about three times smaller than that of $UF_4$, we considered that these reaction rates would be enough for the conversion process in FLUOREX.

Conversion behavior of non-volatile FP fluorides was investigated by thermodynamic evaluation and experiments. The thermodynamic evaluation was done by calculating the $\Delta G$ value (change of Gibbs free energy) of each pyrohydrolysis reaction, and the results are listed in Table 2. Fluorides of transition metals such as zirconium are expected to convert to oxides because of the negative $\Delta G$ value of the reaction. On the other hand, the conversion reaction of fluorides into oxides will not progress for alkali metal, alkaline earth metal and lanthanide elements.

Based on the results of the thermodynamic evaluation, we studied the behavior of the main fission products by pyrohydrolysis experiments using a thermogravimetric analyzer and a horizontal reactor. The experiments were performed at a temperature from 200 to 1000 °C under the atmosphere in which the partial pressure of water vapor was 0.3 atm. Progress of the pyrohydrolysis reaction was confirmed by weight changes for the thermogravimetry and chemical analysis of reaction residues for the horizontal reactor. Table 2 summarizes the results. Fluorides of alkali metals (e.g. Cs) were volatilized above 600 °C, and no conversion reaction to oxides was observed. Fluorides of alkaline earth metals (e.g. Sr) could be converted to oxides but the temperature at which the reaction occurs was too high (over 1000 °C) to adopt as the operating temperature in the conversion process by reason of equipment structural materials. For fluorides of lanthanides (e.g. Nd), the conversion reaction began to form oxyfluorides at about 600 °C, and conversion to oxides was finished above 1000 °C. We plan to operate the conversion process at a moderate operating temperature of 600–700 °C, but the results of experiments suggested that fluorides of alkaline earth metals and most lanthanides would not be converted to oxides at that condition.

Warf et al. [15] have shown that the conversion reaction of fluorides such as alkali metals and alkaline earth metals into oxides was accelerated in the presence of $U_3O_8$. In the conversion process of FLUOREX, FP fluorides will coexist with uranium compounds such as $UF_4$, $UO_2$, and $UO_2F_2$ from the $UF_6$ purification process, so it

**Table 2**
Pyrohydrolysis behavior of elements contained in fluorination residues

| Group | Elements | Thermodynamic evaluation ($\Delta G$ at 600 °C) | Results of experiments | | |
|---|---|---|---|---|---|
| | | | 600–800 °C | 1000 °C | Mixed with $U_3O_8$ at 600–800 °C |
| Alkali metals | Cs | No reaction (positive) | No reaction (volatilized) | No reaction (volatilized) | Converted to oxides ($Cs_2U_4O_{13}$) |
| Alkaline earth metals | Sr | No reaction (positive) | No reaction | Converted to oxide (SrO) | Converted to oxides ($SrUO_4$) |
| Transition metals | Zr | Will react (negative) | Converted to oxide | Converted to oxide ($ZrO_2$) | – |
| Lanthanides | Nd | No reaction (positive) | Converted tooxyfluoride (NdOF) | Converted to oxide ($Nd_2O_3$) | Converted to oxyfluoride and oxide (NdOF + $Nd_2O_3$) |
| Actinides | U | Will react (negative) | Converted to oxide ($UO_2$) | Converted to oxide ($UO_2$) | – |
| | Pu | Will react (negative) | Converted to oxide ($PuO_2$) | Converted to oxide ($PuO_2$) | – |

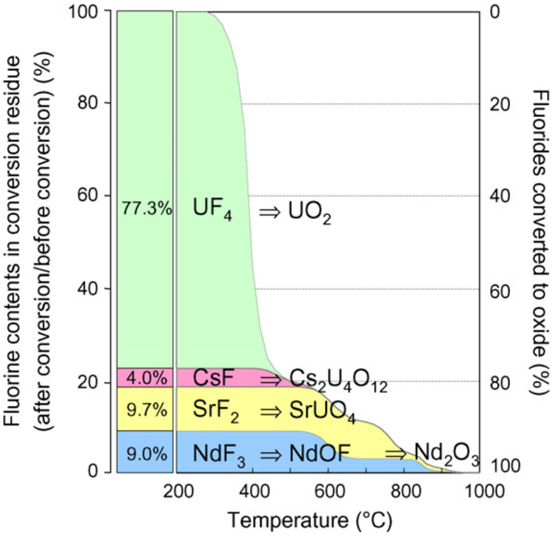

**Fig. 8.** Temperature dependence of the conversion behavior of fluorides into oxides in the conversion process (schematic view).

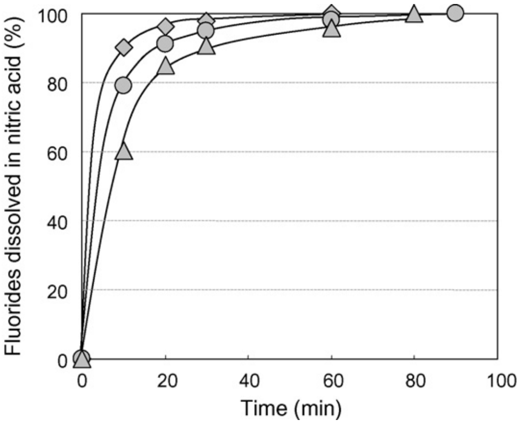

**Fig. 9.** Dissolution behavior of pyrohydrolysis samples: diamonds, pyrohydrolysis samples from $UF_4$; circles, from $PuF_4$; triangles, from mixture of $UF_4$, $PuF_4$ and FP fluorides.

seems likely that fluorides of alkali metals and alkaline earth metals will be converted to oxides in the actual conversion process. Thus we performed additional experiments on the pyrohydrolysis reaction of FP fluorides mixed with uranium compounds. Fluorides of Cs, Sr, and Nd were separately mixed with $U_3O_8$, $UO_2$, or $UF_4$, and their pyrohydrolysis behavior was examined in the same manner as described above. In the case of Cs mixed with $U_3O_8$, no volatilization of cesium fluoride occurred and a complex of U and Cs, $Cs_2U_4O_{13}$, was formed at 600–800 °C. Formation of a complex, $SrUO_4$, was also observed for Sr with $U_3O_8$, $UO_2$, and $UF_4$. The percentage of the Sr fluoride changed to the complex in the experiment with $U_3O_8$ was about 70% at 800 °C for 1 h, which was larger than that in the $UO_2$ and $UF_4$ cases (40–50% for the same conditions). The result suggested that mixture of Sr fluoride and $U_3O_8$ was more effective in removing fluorine from Sr fluoride in comparison with the mixture of Sr with $UO_2$ and $UF_4$, which will be present in the actual conversion process in FLUOREX; however, we considered it adequate for removal of fluorine from Sr fluoride in the case of coexistence with $UO_2$ and $UF_4$. For Nd with $U_3O_8$, oxyfluoride began to form at 600 °C and oxide at 1000 °C as observed in the experiment without $U_3O_8$, and acceleration of the reaction was confirmed in the case with $U_3O_8$. These results of additional experiments with U compounds, summarized in Table 2 and Fig. 8, indicated that a substantial amount of fluorine in the fluorination residues would be removed in the conversion process considering the coexistence of FP fluorides with U compounds.

### 2.4. Dissolution process

The conversion residues from the conversion process are led to the dissolution process and dissolved in nitric acid for provision to the extraction process. We have recognized two subjects to be confirmed in the dissolution process: dissolution of U and Pu oxides obtained by pyrohydrolysis in the conversion process and effect of fluorine introduced into the dissolution process.

The dissolution percentage of pyrohydrolysis product is plotted against the dissolution duration in Fig. 9. The results showed that the pyrohydrolysis samples of U and Pu could dissolve into nitric acid without complications in a reasonable time, even in the case of a mixture of U, Pu and FPs.

Some amount of fluorine from the reaction intermediates of alkaline earth metals and lanthanides, as shown in Fig. 8, will be introduced into the dissolution process as fluoride ion, although most of the elements in the conversion residues are in the form of oxides. Existence of fluoride ion in the process should cause some issues: formation and re-precipitation of Pu as $PuF_4$ that has a low solubility, corrosion of equipment, and influence on the solvent extraction behavior of U and Pu. The amount of fluoride ion in the dissolution process is determined by the solubility of the fluorides introduced into the process. Information about the solubility of fluorides to nitric acid solution is limited, so we have evaluated the solubility products, $K_{sp}$, of fluorides in nitric acid solution [16]. Solubilities of the fluorides of Sr, Ce, La and Nd were measured by both the dissolution method and the precipitation method, details of which were described in the literature [16]. It is found that the Sr fluoride, $SrF_2$, dissolves easily into nitric acid solution. The lanthanide fluorides, $CeF_3$, $LaF_3$ and $NdF_3$ are less soluble in nitric acid solution; however, the solubility products of lanthanide fluorides in nitric acid solution are about $10^1$ to $10^2$ times larger than those in water. Table 3 summarizes $pK_{sp}$ ($=-\log K_{sp}$) for lanthanide fluorides in 6 mol/L $HNO_3$ solution, and also includes $pK_{sp}$ in water [17] for comparison. We assumed that the $K_{sp}$ values for lanthanide fluoride in nitric acid solution are so small that not all lanthanide fluorides will dissolve in the dissolution process.

The behavior of Pu, whether it will dissolve or precipitate, in the dissolution process would be presumed by calculations based on the concentration of fluoride ion in the dissolution process and the solubility products of $PuF_4$. Fluorine in acidic solution forms hydrofluoric acid and fluoride ions, and the acid dissociation constant ($K_a$) is described as Eq. (7):

$$K_a = \frac{[H^+][F^-]}{[HF]} \tag{7}$$

The solubility product of $PuF_4$, $K_{sp}$, can be expressed by Eqs. (8) and (9):

$$K_{sp} = [Pu^{4+}][F^-]^4 \tag{8}$$

**Table 3**
Solubility products ($K_{sp}$) of lanthanide fluorides

| Elements | $pK_{sp}$ in 6 mol/L $HNO_3$ at 80 °C [16] | $pK_{sp}$ in water at 25 °C [17] |
|---|---|---|
| Ce | 16.7 (±2.6) | 19.2 |
| La | 18.0 (±1.9) | 18.9 |
| Nd | 17.6 (±1.8) | 18.6 |

$$[Pu^{4+}] = \frac{K_{sp}}{[F^-]^4} \tag{9}$$

From Eqs. (7) to (9), we can calculate the maximum concentration of Pu ions, that is, the maximum amount of Pu soluble in the solution, when concentrations of nitric acid and fluoride ion are given. Although we considered that re-precipitation of Pu would be avoidable based on the results of the dissolution test using the pyrohydrolysis samples described above, further study on the solubility product of $PuF_4$ in nitric acid solution is required to accomplish the design of the dissolution process.

Fluorine is known as one of the elements that accelerate corrosion of metals and alloys. In the nuclear industry field, corrosion behavior of metals and alloys in $HNO_3$–HF solution has been studied for the purpose of dissolution of spent nuclear fuel [18]. Based on surveys of the literature, we focused on Ni–Cr alloys as corrosion resistant materials which are suitable for use in the dissolution process of FLUOREX. We have been doing corrosion tests not only for well-know alloys but also for newly developed alloys under conditions of the dissolution process, with the expectation to adopt them as structural materials for equipment in the process.

Influence of fluorine on the solvent extraction behavior of U and Pu has been studied by a preliminary experiment, and we observed no significant effect on the distribution coefficient of U and Pu in the TBP/dodecane system. Detailed studies are needed in the future.

It is also desirable to remove fluorine from the solution of the dissolution process for controlling the above issues, i.e. the re-precipitation of Pu, corrosion of materials, and effect on the solvent extraction behaviors of U and Pu. The “masking reagent”, a compound in which a metal ion has the ability to form a complex with fluoride ions, has been investigated for the purpose of decreasing the amount of fluorine in $HNO_3$-HF solution [19]. Some promising masking reagents are compounds of Zr, and we have been studying some of their fundamental aspects, such as the efficiency of fluorine removal and effects on corrosion and solvent extraction.

## 3. Conclusion

Our new nuclear fuel reprocessing system named FLUOREX, which is a hybrid system using fluoride volatility method and solvent extraction, has been confirmed to be feasible from technical and engineering aspects based on engineering scale experiments. We reached the following conclusions for each process of FLUOREX.

(1) *Fluorination process*: Selective volatilization of U from spent fuels is possible by using the flame reactor, and the controls on the amount of volatilized U can be achieved by controlling $F_2$ stoichiometric ratio in the flame reactor.
(2) *$UF_6$ purification process*: $UO_2F_2$ adsorber is adequate for removal of volatile Pu accompanying the $UF_6$ stream. The purification system for FPs will be constructed by combination of known purification methods.
(3) *Conversion process*: Most of the fluorides in the fluorination residues are converted to oxides by pyrohydrolysis, and some of the alkaline earth metals and lanthanides are introduced into the next process as fluorides or oxyfluorides.
(4) *Dissolution process*: Pyrohydrolysis products of U and Pu are soluble in nitric acid solution, and re-precipitation of Pu in the process is avoidable by an appropriate design choice in which the solubility of $PuF_4$ and lanthanide fluorides is taken into consideration. Application of corrosion-resistant materials and masking reagent is also effective to decrease the effects of fluorine in the process.

Very recently, we have performed a small-scale fundamental experiment on the fluorination process using spent LWR fuel. We plan in the near future to do a further study in order to obtain engineering data for detailed design of the FLUOREX plant.

## 4. Experimental

### 4.1. Experimental for fluorination process

#### 4.1.1. Experimental for selective fluorination and volatilization of U from spent fuel

For explanation of selective fluorination of U, experiments were performed using a simulated spent fuel which was a mixture of $UO_2$, $PuO_2$ and simulated FPs [4]. A schematic drawing of the flame reactor used in the experiments is shown in Fig. 10. The simulated spent fuel powder, the chemical composition of which is listed in Table 2, was charged in the feeder funnel and provided into the combustion chamber at the feed rate of about 300 g/h with Ar gas. Fluorine gas was supplied into the combustion chamber surrounding the feed of simulated spent fuel. The concentration of $F_2$ gas in the chamber was about 80%, and the flow rate of $F_2$ gas was 1.2 to 2.0 times larger than the stoichiometry for the reaction (1).

$$UO_2\,(\text{solid}) + 3F_2\,(\text{gas}) \rightarrow UF_6\,(\text{gas}) \tag{1}$$

Reaction (1) was started easily in the combustion chamber which had been preheated to 600 K and continued without addition of heat from outside, since reaction (1) was exothermic and the temperature at the center of the reaction reached about 1500 K. Due to the high temperature of the reaction reached, the reaction area looked like it was “burning with a flame”. Stable thermal conditions of the flame burning were established within several minutes.

A decomposition chamber with the temperature at 650 K was set at the bottom of the combustion chamber in order to collect Pu volatilized as $PuF_6$ (reaction (2)) by thermal decomposition reaction (reaction (3)).

$$PuO_2\,(\text{solid}) + 3F_2\,(\text{gas}) \rightarrow PuF_6\,(\text{gas}) \tag{2}$$

$$PuF_6\,(\text{gas}) \rightarrow PuF_4\,(\text{solid}) + F_2\,(\text{gas}) \tag{3}$$

Small coils made by Ni were installed in the decomposition chamber to increase the solid surface area on which reaction (3) occurred. The decomposed $PuF_4$ and non-volatile FP fluorides

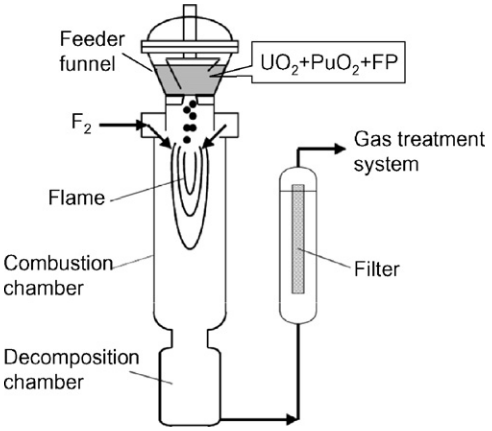

**Fig. 10.** Schematic of the flame reactor for fluorination of simulated spent fuels.

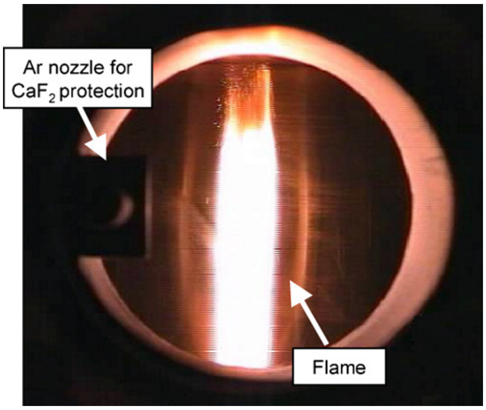

**Fig. 11.** Flame of $UO_2$ fluorination observed through the $CaF_2$ window.

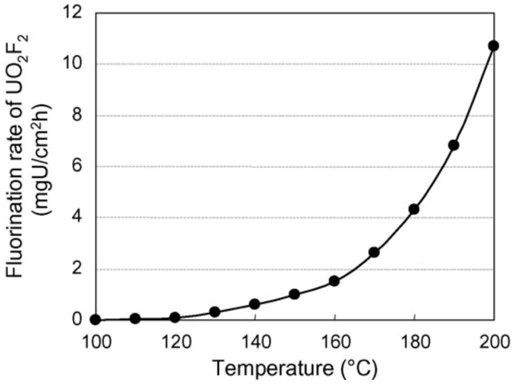

**Fig. 12.** Dependence of temperature on fluorination rate of $UO_2F_2$.

collected in the decomposition chamber, and a gas stream including $UF_6$ and volatile FP fluorides was passed through a filter and introduced into a gas treatment system. Chemical composition of the gas stream was measured for sampled portions.

### 4.1.2. Experimental for the controls on the amount of volatilized uranium

An exterior photo of the newly constructed equipment used in the volatilization efficiency the control experiments is shown in Fig. 6. The equipment was divided into four parts: sample ($UO_2$, $F_2$, Ar) feeders, the flame reactor, the $UF_6$ purification system consisting of several chemical traps and condensers, and the $F_2$ recovery system. Details of the equipment have been reported elsewhere [5]. The flame reactor used in the experiments has the ability to produce $UF_6$ at a rate up to 1000 g/h, and includes a $CaF_2$ window located in the upper part of the combustion chamber through which the flame burning in the chamber can be observed. An example photo of an observed flame is shown in Fig. 11.

Experimental conditions were as follows: $UO_2$ powder was fed to the combustion chamber at the rate of 500 gU/h, and $F_2$ gas was supplied with the $F_2$ stoichiometric ratio of 1.0, 1.5 or 1.83. The $F_2$ concentration in the chamber was set to about 80%. After a fluorination experiment for a certain fixed time was done, residues in the bottom of the combustion chamber were collected, and the amount of U in the residues was analyzed to determine the amount of U volatilized.

### 4.2. Experimental for $UF_6$ purification process

Uranyl fluoride used in the experiments was synthesized by hydrolysis of $UF_6$, and dried in vacuum at about 180 °C. The $UO_2F_2$ was obtained as flakes and the water content was less than 0.1 wt%. The filter shown in Fig. 10 was exchanged to an adsorber that was filled with the $UO_2F_2$. Powdered $UO_2$ mixed separately with metal powder of Ir, Ru, or Nb was fluorinated by the reaction with $F_2$, and the reaction gas was passed through the adsorber. The $UO_2F_2$ in the adsorber was divided into four sections from the inlet to the outlet of the reaction gas, and each section was checked by X-ray diffraction and chemical analyses to determine the amount of Ir, Ru, and Nb trapped after the adsorption experiments.

The conditions for using $UO_2F_2$ adsorber were determined before the adsorption experiments. $UO_2F_2$ will react with $F_2$ to form volatile $UF_6$ at a certain temperature, so temperature selection is important when using $UO_2F_2$ as a trapping material. We performed an experiment in which we treated $UO_2F_2$ with $F_2$ (80 vol%) at a temperature from 100 to 200 °C to measure the fluorination rate of $UO_2F_2$. The results shown in Fig. 12 indicated that the fluorination rate of $UO_2F_2$ was slow enough to use it as the trapping material below 200 °C. Thus the temperature of the adsorber was set as 150 °C in the adsorption experiments described above.

In the preliminary experiments, $PuF_6$ gas was synthesized not by the fluorination of $UO_2 + PuO_2$ powers using the flame reactor, but by the fluorination of U/Pu alloys using a fixed bed reactor. Samples of U/Pu alloy (containing about 0.6 wt% of Pu) placed in the reactor was treated with $F_2$ (80 vol%) at 1100 K, and $UF_6$ and $PuF_6$ volatilized were introduced into the $UO_2F_2$ adsorber (a 50 mm thickness of the $UO_2F_2$ layer). The temperature of the adsorber was set at 160 and 106 °C to study the effect of the temperature on the trapping behavior of Pu. The $UO_2F_2$ in the adsorber was divided into five parts from the inlet to the outlet, and each section was analyzed to determine the amount of Pu trapped on the $UO_2F_2$ after the adsorption experiments.

**Table 4**
Chemical composition of samples used in the experiments

| Group | Fluorination test (Section 4.1.1) | | Dissolution test (Section 4.4) | |
|---|---|---|---|---|
| | Compounds used for fluorination | Content (wt%) | Compounds before pyrohydrolysis | Content (wt%) |
| Actinides | $UO_2$ | 95.3 | $UF_4$ | 40.0 |
| | $PuO_2$ | 1.37 | $PuF_4$ | 10.0 |
| Alkali metals | $Cs_2O$ | 0.52 | RbF | 9.75 |
| Alkali earth metals | SrO | 0.18 | $SrF_2$ | 3.60 |
| Transition metals | $ZrO_2$ | 0.86 | – | – |
| Lanthanides | $La_2O_3$ | 0.26 | $LaF_3$ | 5.15 |
| | $CeO_2$ | 0.52 | $CeF_3$ | 9.80 |
| | $Nd_2O_3$ | 0.91 | $NdF_3$ | 21.2 |
| | $Y_2O_3$ | 0.10 | $GdF_3$ | 0.52 |

### 4.3. Experimental for conversion process

Experiments on pyrohydrolysis of $UF_4$ and $PuF_4$ were carried out using a horizontal furnace in which an $Al_2O_3$ tube was installed [4]. Each fluoride sample (2 g) was loaded into a platinum boat and placed in the center of the furnace. The sample was heated to 550–600 °C, and then water vapor saturated at the temperature of 94–96 °C was supplied to the $Al_2O_3$ tube. The reaction gas that passed through the tube was collected by condensation, and the content of fluorine in the condensate was analyzed to determine the amounts of $UF_4$ and $PuF_4$ converted to oxides.

### 4.4. Experimental for the dissolution process

Dissolution behavior of pyrohydrolysis products have been studied by a dissolution test [4] of samples obtained in the pyrohydrolysis experiment of $UF_4$ and $PuF_4$ described above. The pyrohydrolysis samples of $UF_4$, $UF_4$ and $PuF_4$ (10:1), and the mixture of $UF_4$, $PuF_4$ and FP fluorides, for which composition is shown in Table 4, were dissolved into 3 mol/L nitric acid solution at 370 K (the ratio of solid to liquid was about 1/10).

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## References

[1] O. Amano, F. Kawamura, A. Sasahira, H. Tagawa, Y. Kani, V.N. Prusakov, Therm. Nucl. Power 54 (2003) 46–54.
[2] Y. Ando, H. Takano, JAERI-Research 99–004 (1999) 270 p.
[3] For example:
  (a) M. Mareček, F. Lisý, J. Uhlíř, in: Proceedings of the International Workshop on P&T and ADS Development 2003, Mol, Belgium, PA, October, (2003), p. 19;
  (b) S.H. Smily, D.C. Brater, C.C. Littlefield, J.H. Pashley, USAEC Report K-1518, 1966, 38 p.
  (c) A. Level, Energie Nucl. 6 (1964) 225–232;
  (d) S.H. Smiley, D.C. Brater, in: Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September, (1958), pp. 153–164;
  (e) C.A. Powell, Ibid (1958) 165–171.
[4] O. Amano, F. Kawamura, M. Aoi, K. Hoshino, A. Sasahira, Y. Kani, V.N. Prusakov, in: Proceedings of the GLOBAL 2003, New Orleans, Louisiana, November, (2003), pp. 718–723.
[5] A. Sasahira, Y. Kani, K. Iino, K. Hoshino, F. Kawamura, in: Proceedings of the GLOBAL 2007, Boise, Idaho, September, (2007), pp. 1477–1483.
[6] A. Sasahira, Y. Kani, F. Kawamura, K. Hoshino, V.N. Prusakov, O. Amano, in: Proceedings of the GLOBAL 2005, Tsukuba, Japan, October, (2005), p. 395.
[7] T. Tsujino, S. Sugikawa, E. Yagi, JAERI-M 6393 (1976) 17–27.
[8] (a) D.L. Hildenbrand, K.H. Lau, J. Chem. Phys. 89 (1988) 5825–5828;
  (b) T. Sakurai, A. Takahashi, J. Nucl. Sci. Technol. 15 (1978) 574–579, and the references therein.
[9] For example:;
  (a) L.J. Anastasia, E.L. Carls, A.A. Chilenskas, J.E.A. Graae, A.A. Jonke, N.M. Levitz, M.J. Steindler, L.V.E. Trevorrow, US Patent 3,753,920 (1973).
  (b) Á. Bragança Jr., P.C.C. Sibinelli, O.J.M. Peixoto, Trans. ANS 71 (1994) 79–80;
  (c) F. Lisý, in: Proceedings of the 3rd International Conference on Accelerator Driven Transmutation Technologies and Applications, Praha, Czech Republic, June, (1999), p. P-G5.
[10] (a) J.C. Bresse, P.R. Larson, I & EC 49 (1957) 1349–1354;
  (b) E. Yagi, M. Maeda, H. Kagami, K. Miyajima, JAERI-M 7064 (1977) 115.
[11] For example:
  (a) S. Katz, G.I. Cathers, Nucl. Appl. 5 (1968) 206–210;
  (b) M.J. Stephenson, J.R. Merriman, H.L. Kaufman, USAEC Report K-1713 (1967) 55 p.
  (c) S. Katz, Inorg. Chem. 5 (1966) 666–668;
  (d) W.R. Golliher, R.A. ReDoux, S. Bernstein, V.A. Smith, TID-18290 (1960) 14.
[12] (a) J.O. Hbbits, Anal. Chem. 29 (1957) 1670–1672;
  (b) M. Iwasaki, N. Ishikawa, J. Nucl. Sci. Technol. 20 (1983) 400–404.
[13] Centre d'Etude de l'Energie Nucleaire, EURAEC-1069, R-2289 (1964) 33 p.
[14] A.I. Popov, G.E. Knudson, J. Am. Chem. Soc. 76 (1954) 3921–3922.
[15] J.C. Warf, W.D. Cline, R.D. Tevebaugh, Anal. Chem. 26 (1954) 342–346.
[16] O. Amano, A. Sasahira, Y. Kani, K. Hoshino, M. Aoi, F. Kawamura, J. Nucl. Sci. Technol. 41 (2004) 55–60.
[17] G. Adachi, Science of Rare Earths, Kagakudojin, Tokyo, 1999, p. 312 [in Japanese].
[18] For example:;
  (a) R.S. Ondrejcin, B.D. Mclaughlin, US DOE Report DP-1550 (1980) 46 p.
  (b) D.C. Agarwal, B.D. Anderson, in: Proceedings of the Corrosion 98, San Diego, CA, March, (1998), pp. 164/1–1164/11;
  (c) E.M. Horn, P.E. Manning, M. Renner, Werkst. Korros. 3 (1992) 191–200.
[19] (a) B.C. Norby, US DOE Report WINCO-11787 (1992) 15 p.
  (b) O.K. Tallent, J.C. Mailen, D.O. Campbell, S.R. Buxton, Nucl. Technol. 60 (1983) 395–405.