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# Extraction of uranium from solid waste containing uranium and fluorine

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ABSTRACT

A significant amount of waste residue and adsorbent containing uranium generated by uranium refining and conversion R&D activities has been stored at the Ningyo-toge Environmental Engineering Center of the Japan Atomic Energy Agency. The treatment of these materials is one of the most important tasks in the decommissioning of the plant. These solid wastes also contain significant quantities of fluorine, and it is important to separate this out in order to recover pure uranium as a resource.

As one method for separating fluorine from uranium, we have proposed the use of solvent extraction using tri-n-octylamine (TNOA), and silicofluoride ($Na_2SiF_6$) precipitation. The decontamination factor of fluorine for solutions, prepared by dissolving spent sodium fluoride (NaF) and uranium tetrafluoride ($UF_4$) residue into sulfuric acid, became 5.2 and 6.6 respectively when the TNOA solvent extraction process was performed. The $Na_2SiF_6$ process using $SiO_2$ is more effective in separating fluorine from a solution prepared by dissolving spent NaF and $UF_4$ residue using sulfuric and hydrochloric acid, with the decontamination factor of fluorine being 14 and 28. Uranium remaining in solution after removal of fluorine was recovered as uranium peroxide. The fluorine content of uranium recovered from $UF_4$ by $SiO_2$ treatment was as low as 0.012 wt%, and that of uranium recovered from NaF was below 0.0075%. This is in accordance with the target conditions defined by the ASTM standard.



## 1. Introduction

Uranium deposits were first discovered in the Ningyo-toge area in 1955. A test milling facility constructed in 1965 was used to establish the fundamental technology of the PNC process, producing uranium tetrafluoride directly from uranium ore. A Refining and Conversion Pilot Plant using this process was constructed in 1981 (Amamoto and Wakabayashi, 1993). A total of 385 t of $UF_6$ had been produced in the plant by 1991, when its operation was discontinued. A considerable amount of data on the design, construction, and operation of a commercial plant was obtained from this facility. However, as no promising overseas uranium deposits were discovered, the process has not been used for practical commercial purposes.

Small-scale reprocessed-uranium conversion testing was carried out at the Refining and Conversion Plant from 1982, in order to develop fundamental technologies for converting reprocessed $UO_3$ into $UF_6$. Thereafter, middle-scale testing and practical application testing was carried out. During demonstration testing, which continued until 2001, approximately 293 t of $UF_6$ was produced. Consequently, both the practical application and economic prospects for reprocessed-uranium conversion technology were successfully demonstrated (Amamoto, 2000).

On the other hand, as a result of the aforementioned tests a significant amount of scrap uranium, and adsorbent containing uranium, was generated. The treatment of scrap uranium and adsorbent is one of the most pressing issues in the decommissioning of the plant.

This waste totals approximately 1500 tons, and is presently stored in drums. The uranium concentration for some varieties of this waste exceeds 50 wt%. Hence, it is necessary to recover as much uranium as possible from the waste and scrap uranium, in order to be able to dispose of it more easily and to store the uranium as a resource (Japan Atomic Energy Commission, 2000).

### 1.1. Uranium recovery method

The production of yellow cake from ores is an essential step in the preparation of fuel for use in nuclear power plants. Sulfuric acid has been used for dissolving uranium ore, and this same method is expected to be applied to the recovery of uranium from scrap uranium (Litz and Coleman, 1979).

Wet chemical decontamination processes using inorganic or organic acids have also been developed as effective decontamination methods for metal wastes, and sludge-like uranium bearing wastes

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(Ikeda et al., 2002). On the basis of these previous studies, we have proposed using a combination of sulfuric acid and hydrochloric acid to obtain the highest dissolution of scrap uranium, as they not only have the requisite dissolving power but are also environmentally acceptable.

In uranium recovery processes for ore, uranium is generally recovered from the eluate by precipitation with either ammonia or hydrogen peroxide ($H_2O_2$). The method for recovering uranium as an ammonium diuranate precipitate is regarded as a cheap method. However, metal hydroxide impurities can co-precipitate with the uranium, as the reaction is carried out in a neutral pH range. In addition, ammonia is regarded as an environmental pollutant.

On the other hand, it has been reported that high purity uranium can be recovered from solution as uranium peroxide using $H_2O_2$, as this process is carried out under acidic conditions. The precipitation rate, specific gravity, and dewaterability of the slurry are important factors affecting precipitate production, with uranium peroxide offering benefits in all these areas.

Hydrogen peroxide hardly generates secondary waste, because it decomposes to water and oxygen. Thus, we selected the uranium peroxide method for the recovery of uranium from solution. The formula for the reaction between uranium and $H_2O_2$ can be written as: (Yan, 1990; Gurevich and Susorva, 1972; Mattus and Lopez, 1983).

$$UO_2^{2+} + H_2O_2 + xH_2O \rightarrow UO_4 \cdot xH_2O + 2H^+$$

Fig. 1 shows the points in the uranium conversion process where spent NaF adsorbents, sludge-like wastes, and residue wastes are generated. $UF_4$ was produced from a solution, in which yellow cake was dissolved as uranous ions in a reaction bath. A portion of $UF_4$, which could not be transported because of solidification, remained as a blockish residue waste in the reaction bath. NaF adsorbent was used for removal of hydrogen fluoride from the off-gas generated during the demonstration testing, which contains significant quantities of uranium and fluorine.

Unless fluorine is removed from the solution in which the NaF and $UF_4$ residues described above are dissolved, a significant amount of fluorine may become mixed with the uranium precipitate.

There is a variety of techniques available to remove fluorine from acidic solutions, for example, it has been reported that fluorine can be removed as $Na_2SiF_6$ (Kumar et al., 2010). The technique to separate uranium in a sulfuric acid ($H_2SO_4$) and hydrochloric acid (HCl) solution from other metal elements, specifically solvent extraction with amine, has also been investigated (Sato, 1966; Metwally et al., 2005; Lee et al., 1984). Amine extractant can be disposed more easily in comparison with organophosphate extractant, because it decomposes to nitrogen and oxygen.

Consequently, it is expected that pure uranium can be recovered from solution when fluorine is removed by using one of these methods.

Fig. 2 shows the proposed process flowsheet. In this study, we investigated the dissolution behaviors of NaF and $UF_4$ residue in HCl and $H_2SO_4$, as well as the precipitation and extraction behaviors of fluorine from aqueous HCl and $H_2SO_4$ solutions.

## 2. Experimental

### 2.1. Materials

The concentration of major elements in the $UF_4$ residue, and spent NaF, were investigated. Samples were dissolved in concentrated nitric acid, with the concentrations of cations and anions

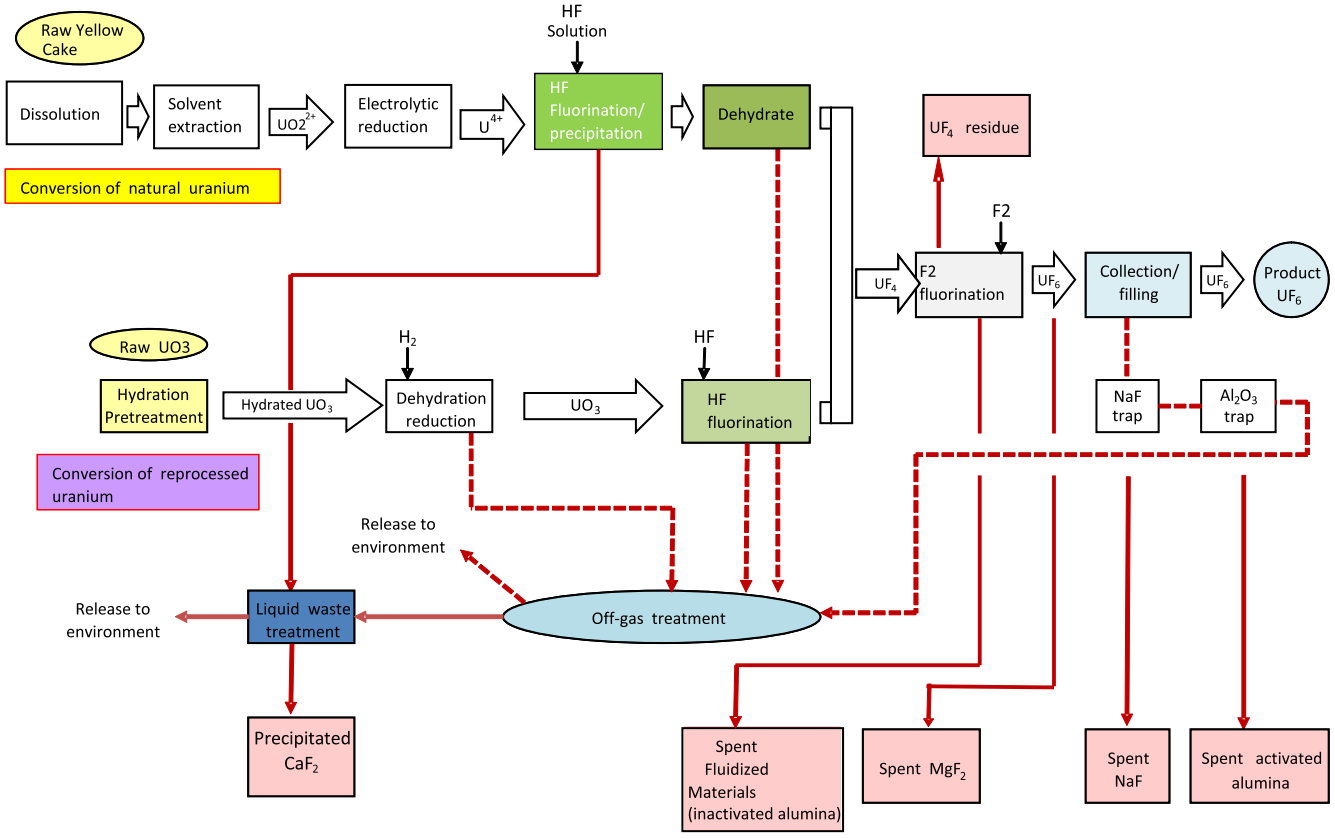


**Fig. 1.** The points in the uranium conversion process where adsorbents and sludge-like wastes are generated.