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URANIUM RECOVERY FOR SPENT FUEL BY DISSOLUTION IN
FUSED SALT AND FLUORINATION

by

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UNCLASSIFIEDABSTRACTURANIUM RECOVERY FOR SPENT FUEL BY DISSOLUTION IN
FUSED SALT AND FLUORINATION

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A promising non-aqueous process for the recovery of uranium from spent fuel elements is under development at Oak Ridge National Laboratory. This process consists of dissolution of the fuel element in a fluoride melt by hydrofluorination at 600 to 700°C, direct fluorination with fluorine for the production and volatilization of UF_6 , with further decontamination of the product UF_6 from fission product activity being secured in a NaF absorption-desorption step. Good decontamination is obtained in the fluorination step due to the low volatility of most of the fission product fluorides. An over-all decontamination factor of greater than 10^6 with adequate uranium recovery has been demonstrated in laboratory scale tests using a double bed procedure for the NaF step. A pilot plant has been constructed for testing the process with various heterogeneous fuel elements. The engineering and operational features of the pilot plant are described.

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INTRODUCTION

Chemical processing of nuclear power reactor fuels has the objective of recovering fissionable material in a reuseable form separated from fission product poisons. For many fuels the aqueous technology of solvent extraction, ion exchange or selective precipitation is not attractive since the fuel elements are resistant to aqueous dissolution. An alternative nonaqueous technology for processing uranium power reactor fuels is based on dissolution in a fluoride salt melt followed by fluorination to obtain UF_6 which is volatile and easily separated as a gas from most of the fission products. Further decontamination of the UF_6 from fission products is achievable in a NaF absorption step using gaseous chromatography principles. This approach shows promise as a means of avoiding the aqueous dissolution difficulty, and results in a fluoride product suitable either for recycle back to the diffusion cascade or for the production of more reactor metal. Such a nonaqueous process would be operated at atmospheric pressure and has promise of being relatively compact, with the radioactive waste being easily discarded in solidified fluoride salt.

A preliminary description of the volatility process was given in another article.¹ This paper is intended as a progress report on the results of further laboratory work on the process. Emphasis is placed on the treatment of zirconium-uranium fuel elements. In addition, a brief description of a pilot plant constructed for testing the process is given along with discussion of some of the engineering problems.

PROCESS STATUS

A schematic flowsheet for the proposed process for zirconium nuclear reactor fuels is given (Fig. 1). Hydrofluorination of the fuel element in molten fluoride salt, for example NaF-ZrF₄, results

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Fig. 1. Fused Salt-Volatility Recovery Process For Zirconium Fuel.

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in conversion of the metal to a fluoride, compatible with the salt system. For example, hydrofluorination of uranium produces UF_4 as a solute in the carrier solvent. The next step, fluorination, converts UF_4 to UF_6 which volatilizes out of the molten salt along with some fission products and excess fluorine. In order to further decontaminate the UF_6 from fission product activity, the gas mixture is passed into a bed of granular NaF at $100^\circ C$ resulting in the absorption of UF_6 . The UF_6 is then desorbed by raising the bed temperature to $400^\circ C$ in the presence of a flow of excess fluorine. Passage of the UF_6 through a second NaF bed held at the same temperature as the first bed in the desorption process, results in further decontamination before cold trapping of the product.

Laboratory studies have been carried out on the three steps involved as described in the following sections. This work has demonstrated the feasibility of each of the steps as well as the direction in which further work should be directed.

DISSOLUTION OF ZIRCONIUM AND ZIRCONIUM ALLOYS IN FUSED SALT

Two fluoride salt systems have been studied for use in the hydrofluorination dissolution step. The NaF- ZrF_4 system remains liquid at $600^\circ C$ over the composition range of 40-60 to 60-40 mole percent even with the addition of considerable UF_4 as a solute. The LiF-NaF system, with a liquidus temperature of $675^\circ C$ at a composition of 57-43%, has the advantage of being compatible with up to 55 mole percent zirconium. This permits dissolution with a higher fuel:salt ratio than in the NaF- ZrF_4 case since the ZrF_4 composition range in this case is only 20 mole percent. Although the LiF-NaF has to be operated initially at a temperature of $700^\circ C$, the dissolution of zirconium by forming ZrF_4 eventually allows decreasing the temperature to $600^\circ C$. The use of many other fluoride salt systems does not appear impossible.²

A summary of zirconium dissolution rates is given at typical salt compositions expected in the process (Table 1). The rates for

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Table 1. Dissolution of Zirconium in Fluoride Melts
by Hydrofluorination

Melt	Composition (mole %)	Dissolution Rate (mg/min-cm ²)	
		600°C	700°C
LiF-NaF	57-43	---	13
LiF-NaF-ZrF ₄	35-27-38	5	9
LiF-NaF-ZrF ₄	26-19-55	0.1	4
NaF-ZrF ₄	65-35	8	---
NaF-ZrF ₄	50-50	4	5
NaF-ZrF ₄	40-60	0.8	---

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zirconium, zircaloy or zirconium-uranium alloy were not found significantly different. There is generally some increase of dissolution with temperature. The most important factor, other than salt composition, appears to be the rate at which anhydrous HF is passed through the melt. A high HF flow rate provides good agitation and minimizes retardation of the reaction by the rate of diffusion of gaseous HF into the melt, or the depletion of HF in the melt, particularly at the solid-liquid boundary layer. Although it is known that HF has some solubility in fluoride melts possibly due to interaction with NaF, its magnitude has not been determined exactly. The rate of dissolution generally decreases with increasing ZrF_4 content in the melt. This could be due to mass action or to the fact that ZrF_4 complexes the NaF, thus depressing the HF solubility.

FLUORINATION STUDIES

The volatilization of UF_6 from molten NaF- ZrF_4 is readily accomplished at $600^\circ C$ with elemental fluorine. The LiF-NaF case has not been examined. A typical uranium disappearance curve (Fig. 2) shows that it is possible to volatilize over 99.8% of the uranium from a melt initially containing 4 mole % with a F_2/U mole ratio of 4 or 5. The volatilization is rapid after an initial induction period. An alternate plot of the same data (Fig. 3) shows that a peak efficiency of about 30% was secured when 90% of the uranium had disappeared from the melt. The last 10% volatilized as the result of excess F_2 acting as a sweep gas. The efficiency accordingly decreased hyperbolically.

FISSION PRODUCT BEHAVIOR IN PROCESS

A summary of the more volatile fission product fluorides is given in comparison with UF_6 (Table 2). The problem of handling fission product activity mainly arises in and subsequent to the fluorination step. There is little fission product activity

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Fig. 2. Amount of Uranium Remaining in Fused Salt as a Function of Fluorine per Uranium Ratio. 400 g NaF-ZrF₄-UF₄ fluorinated at 600°C with F₂ flow rate of 100 ml/min.

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Fig. 3. Efficiency of UF_6 Volatilization as Function of Amount of F_2 Introduced.

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Table 2. Important Volatile Fission Product Fluorides

Fluoride	Boiling Point (°C)	Important Radio- active Isotopes	Half-life
RuF ₅	270	103	42 d
		106	1 y
NbF ₅	220	95	35 d
UF ₆	56	---	---
MoF ₆	35	99	67 h
IF ₇	4	131	8 d
TeF ₆	-38	127	110 d
		129	32 d

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volatilization in the hydrofluorination or dissolution step due to the lack of fluorinating potential. Typical uranium dissolution runs, with uranium having a short decay period, show that only a small fraction of any activity was volatilized (Table 3). The contamination in the waste HF in the use of long-decayed fuel is generally greater than 80% niobium. Although the volatilization of activity in the dissolution step is small, provision will have to be made in any process plant for handling the activity effluent with the HF-H₂ waste gas.

The behavior of fission product activity in the fluorination and NaF absorption steps has been extensively studied. The fluorination step results in good decontamination with respect to the nonvolatile fluorides of Cs, Sr and the rare earths (Table 4). Somewhat less decontamination is secured for Zr. The decontamination with respect to the volatile fluorides of Nb and Ru is small, necessitating the NaF decontamination step. No decontamination is secured for I, Te, and Mo in the fluorination step. The NaF absorption step, developed at the present time only for securing more Ru and Nb decontamination with long-decayed fuel (decay period of more than 120 days) results in a UF₆ product having less activity than natural uranium.

CHEMISTRY OF NaF ABSORPTION STEP

The separation of UF₆ from fission products secured in the NaF absorption step may be described as gaseous chromatography. A summary of the activity distribution in several runs (Table 5) shows that a three-way split occurs between U, Ru and Nb. A large part of the Ru activity passes through the first NaF bed when the UF₆ is being absorbed at 100°C. The Nb is also absorbed. Desorption of the UF₆ at 100-400°C, however, results in essentially all of the Nb remaining on the first bed. The second bed serves to remove any activity carried from the first bed in the UF₆ stream. The effectiveness of the NaF in removing particulate matter in the gas stream is illustrated by the rare earth decontamination

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Table 3. Volatility of Fission Product Activity in Hydrofluorination
Step

6 g uranium (decay period 21 days) dissolved in 67 g NaF-ZrF₄ (50-50 mole %)
HF flow rate 1.2 g/hr for 12 hr

	Activity in HF (% of Initial)	
	Run 1	Run 2
Gross β	10^{-4}	10^{-2}
I β	0.03	0.4
Te β	2	---
Mo β	0.2	---
Ru β	0.005	0.03
Nb β	---	0.7

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Table 4. Decontamination of Uranium in Fluorination and NaF
Absorption Steps

Feed: natural uranium, cooled 120 days

Process Step	Decontamination Factor						
	Gross β^a	Gross γ^a	Ru	Nb	Zr	Cs, Sr and Rare Earths	I, Mo, Te
Fluorination	10^2	10^2	10	10	10^3 - 10^4	$>10^4$	1
NaF absorption	$>10^4$	$>10^4$	10^3	10^4	$>10^3$	10^3	Unknown
Over-all	$>10^6$	$>10^6$	10^4	10^5	$>10^7$	$>10^7$	Unknown

^aFor case of long decay period. Gross decontamination is less in presence of I or Te in case of short decay period.

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Table 5. Distribution of Activity in NaF Absorption-Desorption StepPercentage of total activity^a

	After 4 Consecutive Runs			After 1 Run		
	NaF Bed #1	NaF Bed #2	Ru Cold Trap	NaF Bed #1	NaF Bed #2	Ru Cold Trap
Ru γ	1.6	1.1	97	18	0.9	81
Nb γ	98	0.04	2	99	0.04	0.4
Rare Earth β	92	4	4	97	0.1	3

^aActivity found in product, NaF beds and Ru cold trap.

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in the first bed.

A chemical complex of UF_6 and NaF , first reported by Martin, Albers and Dust, is the basis for the NaF absorption step.³ The reaction is described by equation (1):

This reaction is reversible in that an equilibrium partial pressure of UF_6 exists over the complex. The dependence of the equilibrium partial pressure on temperature over the range of 80 to 350°C was studied by the transpiration method for a better understanding of the process operation (Fig. 4). The effectiveness of NaF at 100°C in absorbing UF_6 is due to the small equilibrium pressure of about 10^{-3} mm Hg. This corresponds to a cold trap temperature for UF_6 of less than -80°C.⁴ At 360°C the equilibrium pressure is approximately atmospheric, this accounting for the relative ease of desorption.

PROCESS TEST EQUIPMENT

A pilot plant has been constructed for testing the operation of the fused salt volatility process, and for studying some of the more unusual chemical engineering and mechanical requirements in handling fused salts and radioactive gases. This plant, located in a heavily shielded cell at Oak Ridge National Laboratory, will be capable of processing uranium at high irradiation levels. A picture of the fluorination vessel, designed to handle 300 to 400 pounds of fused salt, indicates the plant scale (Fig. 5). Control of the process is maintained from the graphic part of the panel board (Fig. 6).

All of the salt process vessels are constructed from nickel or high nickel base alloys since such materials have been shown resistant to fluoride materials at high temperatures if sulfur embrittlement effects are avoided. The gas transfer lines are monel to provide for the contingency that an aqueous decontamination procedure will be necessary in maintenance of the equipment. The monel lines and remote

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Fig. 4. Equilibrium Partial Pressure of UF₆ Over UF₆ · 3NaF Complex as a Function of Temperature.

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Fig. 5 Fused Salt-Fluorination Process Reactor

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Fig. 6 Control Panel Board for Fused Salt Volatility Process

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control valves in the gas transfer system are located in a heated duct system maintained above the triple point of UF_6 .

The problem of transferring fused salt between process vessels and preventing any gas leakage is a major one in the process. Unit operations studies were made to demonstrate the feasibility of using auto-resistance electrical heating of 1/2 in inconel pipe, and to show that a vented loop in the line would serve as a freeze valve. The three small electrical furnaces, evident in Fig. 5, serve in heating the vent lines into the three freeze valves connected to the fluorinator vessel.

The over-all feasibility of both the chemical and chemical engineering features of the process pilot plant was demonstrated on a small scale in a laboratory test unit, designed to handle 50-g-batches of uranium (Fig. 7) at high irradiation levels. The unit, as photographed, was partly disassembled.

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Fig. 7 Shielded Laboratory Test Unit for Study of Fused Salt
Volatility Process