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Oak Ridge, Tennessee

ORNL
CENTRAL FILES NUMBER
61 - 2 - 3

COPY NO. 34

DATE: February 13, 1961

SUBJECT: Processing of Beryllium Oxide Fuels

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ABSTRACT

Preliminary results from experiments on the dissolution of beryllium metal and sintered UO_2-BeO fuel pellets are reported. In all cases the pellets were fired in hydrogen at 1650-1800°C. Uranium, from UO_2-BeO pellets containing more than 60% UO_2, is readily leached with boiling 6-13 M HNO_3 in about 6 hr. The BeO in these pellets dissolves only slowly in nitric acid; however, in 8 M HNO_3-0.2 M NaF, it dissolves at about the same rate as the UO_2. Sintered pellets containing less than 10% UO_2 do not dissolve rapidly in common aqueous reagents. The highest rates are obtained in boiling acidic fluoride solutions; e.g., sintered BeO and BeO-8% UO_2 are dissolved initially at a rate of about 1.7 mg $min^{-1}cm^{-2}$ (13 mils/hr) in boiling 5.8 M NH_4HF_2.

Sintered BeO dissolved at an average rate of 5 mils/hr (0.64 mg $min^{-1}cm^{-2}$) by bubbling HF through molten 49 mol % NaF-40 mol % LiF-11 mol % BeF_2 at 600°C.

1.0 INTRODUCTION

The purpose of this memo is to summarize briefly the results of preliminary laboratory work relating to processing of nuclear reactor fuels containing beryllium metal or high-fired beryllia. To date, only dissolution experiments have been conducted; ultimately, however, processes by which the uranium contained in the irradiated fuels can be decontaminated and recovered either by solvent extraction from aqueous solution or by the Fluoride Volatility Process (1) will be evolved. These studies are part of the ORNL Chemical Technology Division's general program on processing of advanced reactor fuels. Techniques developed undoubtedly will be applicable to the reclamation of uranium from unirradiated fuel element scrap. Work on aqueous dissolution and Fluoride Volatility processing is still in the early stage; therefore, the results and conclusions given are necessarily preliminary and tentative. Extensive corrosion tests will ultimately be required; however, for each system being considered a material of construction is given which, based on past experience, might be suitable.

Chemical analyses were made by the groups of W. R. Laing and W. F. Vaughan, ORNL Analytical Chemistry Division.

2.0 MATERIALS

Two general classes of fuel materials are being studied: 1) UO_2-BeO mixtures in which the UO_2 content is greater than 60%, and 2) mixtures containing less than 10% UO_2. In each case, specimens were fired in hydrogen to 1650-1800°C.

Most of the aqueous dissolution experiments were performed with prototype GCRE and MGCR fuel pellets. The GCRE-I, core 2 fuel element probably will be sintered 70% UO_2-30% BeO pellets (0.52 cm high; 0.44 cm dia; density, 5.9 g/cc) clad in Hastelloy X (2). The MGCR fuel element will be similar; 61% UO_2-39% BeO pellets (1.12 cm high; 1.05 cm dia; density, about 4.8 g/cc) (3), probably clad in Hastelloy X (4).

Sintered BeO, used in most of the other experiments, was hot-pressed and fired at 1650°C. Its density was 2.87 g/cc, about 95% of theoretical. The samples of BeO-8% UO_2 had been fired at 1750°C and had a density of 3.1 g/cc. The theoretical density for pure BeO is 3.02 g/cc (5).

3.0 EXPERIMENTAL

3.1 Dissolution of Beryllium Metal

Beryllium metal is frequently mentioned as a cladding material for oxide fuel elements for gas-cooled reactors. Dissolution of the beryllium from such elements does not appear to be a problem. The metal dissolves rapidly in boiling sulfuric acid, dilute nitric acid containing traces

of fluoride ion, and in sodium hydroxide solution (Table 1). Vessels constructed of Ni-o-nel should be suitable for containment of these reagents.

Table 1. Initial Rates of Dissolution of Beryllium Metal in Various Boiling Reagents

Reagent	Initial, 10-min, Dissolution Rate, mg $min^{-1}cm^{-2}$
4 M HNO_3	0.02
15.8 M HNO_3	0.04
4 M HNO_3-0.05 M NaF	8
4 M HNO_3-0.1 M NaF	11
4 M H_2SO_4	63
6 M NaOH	2

3.2 Aqueous Processing of Fuels Containing 60-70% UO_2

Fuels which fall into this category generally will be clad in a metal such as Hastelloy X or stainless steel. Preliminary studies have shown that once the cladding is removed, either mechanically or chemically, the uranium can be leached almost quantitatively with boiling 6-13 M HNO_3 in about 6.5 hr to produce solutions containing about 6 g of uranium per liter (Fig. 1, Table 2). Losses to the BeO residue were less than

Table 2. Uranium Recoveries in Leaching GCRE Fuel Pellets (70% UO_2-30% BeO) with Boiling Nitric Acid

HNO_3 Conc., M	Leaching Time, min	Amount of Element in BeO Residue, %	
		Uranium	Beryllium
4	240	22.7	39.8
6	406	0.13	66.2
8	407	0.059	59.3
10	404	0.094	43.2
10	407	0.12	50.3
13	407	0.12	48.8

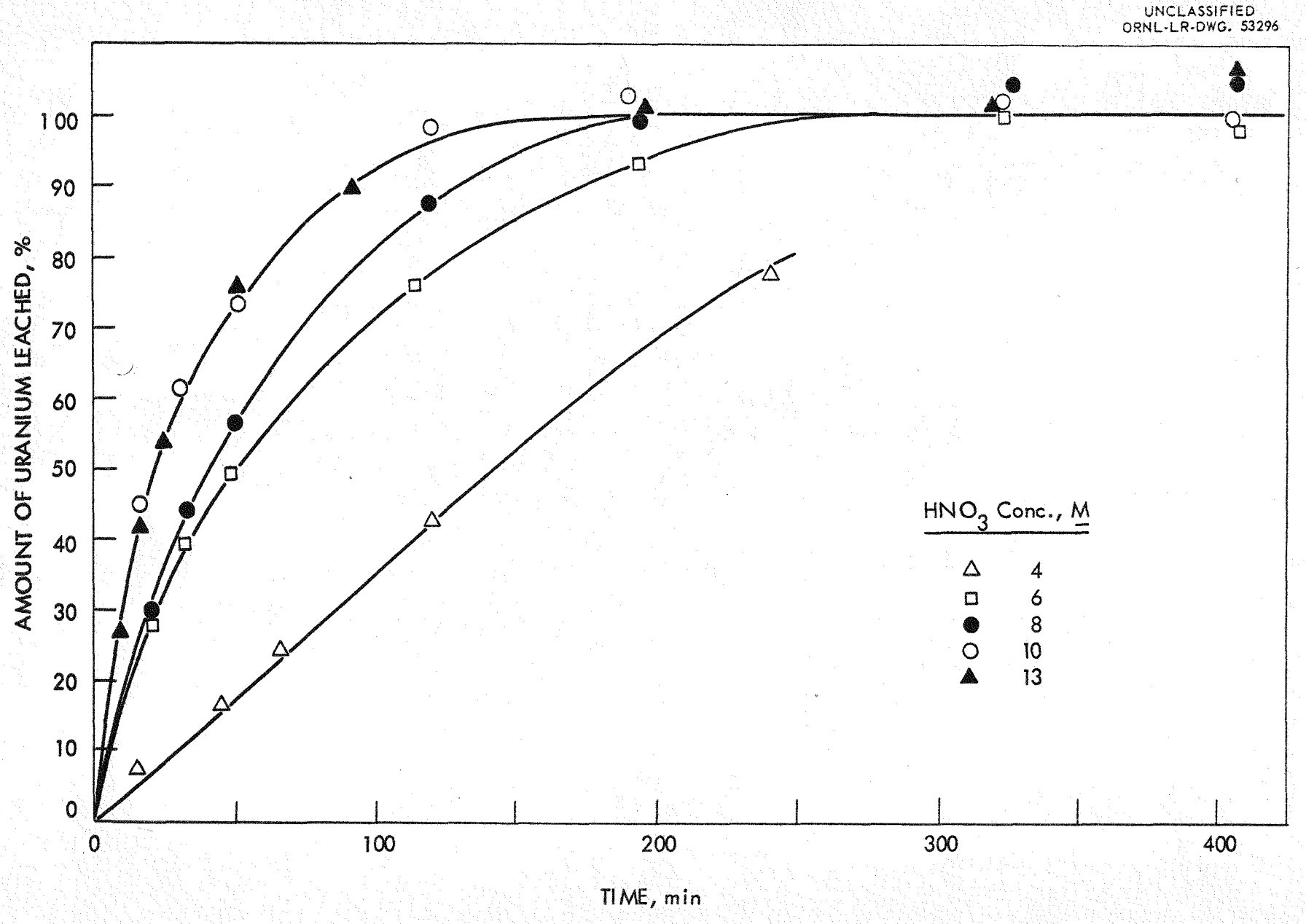

Fig. 1. Effect of nitric acid concentration on the rate of leaching of UO_2 from GCRE (70% UO_2-30% BeO) fuel pellets. Boiling solution used in each experiment.

0.2% after about 5 hr of leaching (Table 2). Although only about 50% of the BeO dissolved in 5 hr, its solution was complete in about 40-50 hr. Similar studies with pellets containing 66% UO_2 indicated that leaching of the uranium was also complete in about 5 hr (Fig. 2).

Preliminary experiments indicated that, in boiling 8 M HNO_3 containing 0.2 M NaF, the BeO dissolved at a rate which was nearly equal to that of the uranium (Fig. 2). Additional experiments are in progress to determine the minimum effective fluoride concentration.

Since both the GCRE and MGCR fuels will be clad in metal, preliminary experiments were conducted to determine the feasibility of dissolving both the cladding and core. The preferred cladding materials, Hastelloy X and, possibly, 316 stainless steel, can be dissolved in dilute aqua regia. The stainless steel could also be dissolved in 4 to 6 M H_2SO_4. The uranium can probably be leached out of the fuel pellets with either mixed nitric acid-sulfuric acid or nitric acid-hydrochloric acid (Table 3). Although the BeO dissolved only very slowly in either reagent, its rate of solution was higher in solutions containing sulfuric acid (Table 3). Ultimately, dissolution of the cladding and leaching of the uranium in the resulting solution must be demonstrated. Methods for ensuring complete dissolution of the BeO must be devised. Vessels constructed of titanium probably would contain the aqua regia and nitric acid solutions. If a process involving use of sulfuric acid were adopted, materials such as Ni-o-nel would be required.

Table 3. Leaching of GCRE Fuel Pellets (70% UO_2-30% BeO) with Boiling Acid Mixtures

Reagent	Time, min	Amount Dissolved, %		Material Balance, %
		Uranium	Beryllium	
5 M HNO_3-2 M HCl	15	33	2	92
	30	57	2	98
	60	74	4	101
	90	81	6	103
3 M HNO_3-3 M H_2SO_4	18	25	3	92
	35	32	7	95
	60	64	18	96
	120	73	23	103
	245	94	44	101

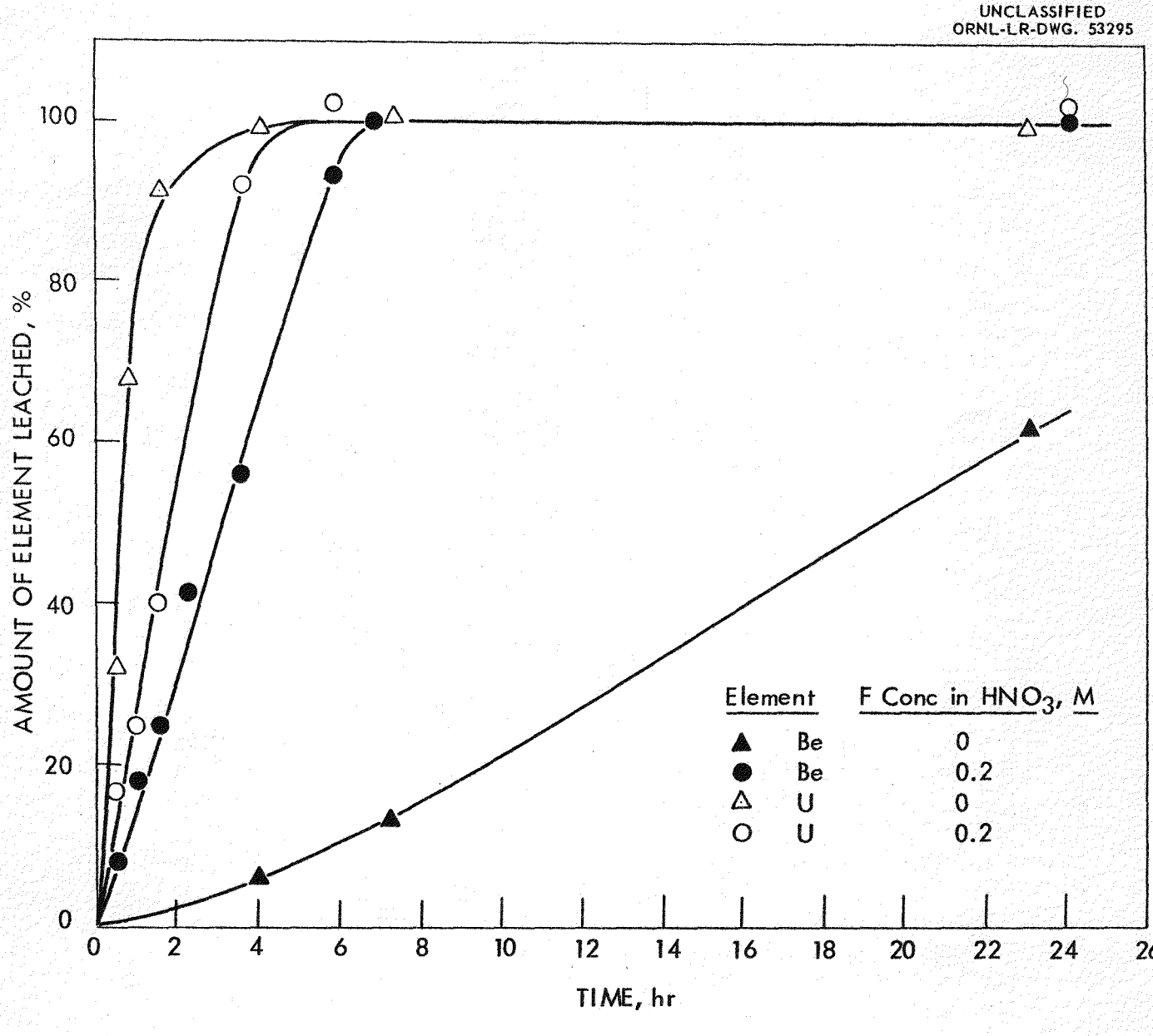

Fig. 2. Leaching with boiling 8 M HNO_3 and 8 M HNO_3--0.2 M NaF of sintered UO_2-BeO fuel pellets containing 65-70% UO_2. Composition of pellets: △ , ▲ , 66.2% UO_2; ○ , ● , 70% UO_2.

Crushing or grinding the fuel pellets would undoubtedly render them more soluble. As an alternative to mechanical grinding, the effect of ignition at red heat in air on 4 types of UO_2-BeO pellets was determined. Two samples containing 66 and 70% UO_2, respectively, slowly crumbled to powder during heating (Table 4). Conversion of the UO_2 to a higher oxide, with an attendant change in molar volume, is probably responsible for the disintegration. Pellets containing 61% UO_2 did not disintegrate on heating, but did increase slightly in weight. The disintegrated pellets were leached with 3 M HNO_3-3 M H_2SO_4. Uranium was completely leached in 16 hr at room temperature from pellets containing 70% UO_2. Although essentially no beryllium dissolved at room temperature, its solution was complete in about 1 hr at the boiling point (Table 4). Similar results were obtained with pellets containing 66% UO_2; however, complete dissolution of the BeO in boiling dissolvent occurred somewhere between 1 and 18 hr.

3.3 Aqueous Processing of Fuels Containing Less Than 10% UO_2

Sintered BeO-UO_2 fuel bodies containing less than 10% UO_2 did not dissolve rapidly in common aqueous reagents. The highest rates were obtained in boiling acidic fluoride solutions; e.g. sintered BeO and BeO-8% UO_2 dissolved initially at rates of about 1.7 mg $min^{-1}cm^{-2}$ in boiling 5.8 M NH_4HF_2 (Table 5). Other workers (6) obtained similar rates in boiling 11.5 M HF-7.5 M NH_4F containing 3% H_2O_2. At present, no suitable alloy has been found which will contain the acidic fluoride solutions.

Molten ammonium bifluoride reacts with beryllia according to the equation (7):

$$BeO + 2\ NH_4HF_2 \longrightarrow (NH_4)_2BeF_4$$

The rate of dissolution of sintered BeO in molten NH_4HF_2 increased from about 0.08 to 1.7 mg $min^{-1}cm^{-2}$ when the reaction temperature was increased from 135 to 228°C (8).

Dissolution rates of BeO expressed in mg $min^{-1}cm^{-2}$ may be converted to rates in mils/hr by the following equation:

$$\text{Rate (mils/hr)} = 7.85\ \text{Rate (mg min}^{-1}\text{cm}^{-2}\text{)}$$

3.4 Fluoride Volatility Processing

The Fluoride Volatility Process (1) involves dissolution of fuels in molten fluoride salts and subsequent recovery of the uranium by volatilization as UF_6. Laboratory work on this process with sintered BeO fuels is directed by G. I. Cathers, ORNL Chemical Technology Division. Initial experiments were conducted with 1650°C-fired, hot-pressed BeO. In two runs, of 2- and 5-hr duration, this material was attacked at an

Table 4. Ignition Experiments with UO_2-BeO Pellets

Pellets heated in air to red heat

Pellet Composition, %		Ignition	Weight	Leaching Conditions[a]		Amount Leached, %	
UO_2	BeO	Time, min	Gain, %	Time, hr	Temperature	Uranium	Beryllium
70.38	29.62	46	2.4[b]	16	Room	100	0
				1	Reflux	100	100
66.2	33.8	45	2.4[b]	3	Room	63.8	0
				1.25	Reflux	100	85.7
				18	Reflux	100	100
60.97	39.03	70	0.6	(c)			
8.0	92.0	210	0	(c)			

[a]Residual powders leached with boiling 3 M HNO_3-3 M H_2SO_4.

[b]Pellet disintegrated to powder when heated.

[c]Sample did not disintegrate upon ignition; no leaching experiments were conducted.

Table 5. Initial Rates of Dissolution of Sintered BeO and BeO-8% UO_2 in Various Boiling Reagents

Material	Reagent	Initial, 10-min Dissolution Rate, mg $min^{-1}cm^{-2}$
BeO	4 M HNO_3	0.003
BeO-8% UO_2	4 M HNO_3	0.02
BeO-8% UO_2	4 M HNO_3-0.1 M NaF	0.07
BeO	4 M HNO_3-0.2 M NaF	0.04
BeO	12 M HNO_3-0.2 M NaF	0.02
BeO	15.8 M HNO_3-0.2 M NaF	0.03
BeO	4 M H_2SO_4	0.05
BeO	6 M H_2SO_4	0.03
BeO	8 M H_2SO_4	0.26
BeO-8% UO_2	8 M H_2SO_4	0.05
BeO	6 M HCl	0.008
BeO	15% HBF_4	0.07
BeO	50% HBF_4	1.6
BeO	5 M NH_4F	0.05
BeO-8% UO_2	5 M NH_4F	0
BeO	5.8 M NH_4HF_2	1.7
BeO-8% UO_2	5.8 M NH_4HF_2	1.5
BeO	5 M NH_4HF_2-2 M NH_4NO_3	1.9

average rate of 5 mils/hr by bubbling HF through molten 49 mol % NaF-40 mol % LiF-11 mol % BeF_2 at 600°C. Volatilization of uranium from melts containing BeF_2 has also been demonstrated. These preliminary experiments, in light of past experience, indicate that beryllium oxide fuels (containing any amount of UO_2) can be processed by this method providing that stainless steel and Hastelloy claddings have been removed. It might be possible to dissolve the cladding material if another solvent or technique (such as allowing a sludge to accumulate) were used. The construction material of primary interest is INOR-8 (Hastelloy N).

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