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DISSOLUTION OF BeO- AND Al_2O_3-BASE REACTOR FUEL ELEMENTS. PART I

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UNION CARBIDE CORPORATION
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Chemical Development Section B

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ABSTRACT

Aqueous methods for recovering uranium from BeO- and Al_2O_3-base gas-cooled-reactor fuel elements are being evaluated. Two methods for processing Hastelloy-X—clad pelletized BeO-base fuels containing 60-70% UO_2, such as the GCRE and MGCR, seem feasible. One method involves mechanical stripping or chopping of the cladding followed by leaching of the uranium from the fuel pellets with boiling 6-13 M HNO_3. In the other method the cladding and UO_2 are dissolved in boiling 2 M HNO_3--4 M HCl. In either case, most of the BeO matrix remains as an undissolved residue. Pellets containing 70% UO_2 dissolved completely in less than 20 hr in boiling 8 M HNO_3 containing either 2 M H_2SO_4 or 0.5 M HF, producing solutions containing 4 g of uranium per liter.

Fuels of high BeO content, e.g. BeO-5% UO_2, dissolved only slowly in boiling aqueous reagents. Highest initial rates were in sulfuric acid solutions, $\log(\text{Rate, mg min}^{-1}\text{cm}^{-2}) = 0.223\,(H_2SO_4,\ M) - 2.81$, and in HF-$NH_4F$ solutions. In boiling 5-8 M NH_4F the initial dissolution rate increased from 0.07 to 3.5 mg $\text{min}^{-1}\text{cm}^{-2}$ as the HF concentration increased from 0 to 20 M.

Leaching, with boiling 10 M HNO_3, of uranium from UO_2-Al_2O_3 fuel pellets was studied briefly. In 4 hr leaching uranium recoveries from pellets containing 10-μ grains of UO_2 dispersed in an Al_2O_3 matrix decreased from 99.99 to 11.6% when the Al_2O_3 content of the pellets increased from 3.7 to 61.1%. The uranium concentration was 1.0 M in the case of complete dissolution.

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1.0 INTRODUCTION

The objective of this study was to find aqueous systems suitable for the dissolution of BeO- and Al_2O_3-base gas-cooled-reactor fuel elements. Systems from which the uranium could be decontaminated and recovered by tributyl phosphate—nitric acid solvent extraction were of primary interest. BeO-base fuel elements are already in existence. Both the GCRE-I (core 2) and the ML-1 reactors, which went critical in October, 1960 and March, 1961, respectively, contain fuel elements comprised of pellets (70% UO_2-30% BeO) clad in Hastelloy-X (1,2). The MGCR fuel element will also be Hastelloy-X—clad BeO-UO_2 pellets (3,4), but the UO_2 content will be only about 53% (5). Alumina was considered earlier as the matrix material for the MGCR, but later designs favor the use of BeO. The fuel elements for reactors for nuclear ramjet propulsion, being developed under the Pluto program, are homogeneous dispersions of UO_2 and BeO (6). Fuel elements for the TORY-IIA reactor contained an average of 5.95 wt % UO_2. Both sintered Al_2O_3 and BeO are being considered as coatings for UO_2 or ThO_2-UO_2 fuel particles in graphite-base gas-cooled reactors (7).

This report summarizes laboratory work conducted prior to Aug. 15, 1961 on the dissolution of various UO_2-BeO fuel mixtures. Systematic scouting experiments involving various aqueous reagents indicated which systems offered the most promise for processing the fuels. The data consist chiefly of initial rates in the various reagents. Because of the low densities of the BeO-base fuels (3-5 g/cc) in comparison to those (7-10 g/cc) of the alloy, UO_2, and ThO_2 fuels considered in the past, an initial dissolution rate of 0.5 mg $min^{-1}cm^{-2}$ will probably be acceptable if other factors such as solubility and corrosion are not limiting. On this basis, the best dissolvent found for fuels containing >60% UO_2 was nitric acid containing about 0.5 M NaF while the most practicable reagent for fuels containing <10% UO_2 appears to be 5-10 M HF. Also included in this report are preliminary data on the dissolution of Hastelloy-X and the results of a brief study of the leaching of prototype UO_2-Al_2O_3 fuel pellets. Much of the information reported here supersedes that which has appeared in ORNL Chemical Technology Division, Chemical Development Section B, monthly and quarterly reports. Some of the data presented earlier were in error due to the difficulty in analyzing for beryllium in solution.

Selection of optimum processing conditions must await further development. Before process flowsheets can be devised, the solubilities of uranyl nitrate and uranium tetrafluoride in HNO_3-$Be(NO_3)_2$ and HF-BeF_2 solutions, respectively, must be determined. Dissolution of Hastelloy-X in dilute aqua regia must be studied more thoroughly, with emphasis on the off-gas composition. Studies on the dissolution of BeO-base fuels in nitric acid and hydrofluoric acid solutions need to be completed. In these studies the effects of particle size and uranium and beryllium concentrations on the dissolution rate should be evaluated and the stoichiometries of the respective reactions determined.

Chemical analyses were provided by the ORNL Analytical Chemistry Division, under the direction of G. R. Wilson, W. R. Laing, W. F. Vaughan, and C. Feldman.

2.0 LOW-BeO-CONTENT FUELS

Fuel elements in this category include those from the GCRE-I (core 2), ML-1, and MGCR. The fuel in each case is pelletized and clad in Hastelloy-X (Sect. 5.0). The fuel pellets (0.44 cm dia and 0.52 cm high) for the GCRE and ML-1 elements contain 70 wt % UO_2 and have a density of about 5.9 g/cc (96.7% of theoretical). The MGCR fuel pellets (5) are similar: 24 vol % UO_2 (53.4 wt %), 1.12 cm high, 1.05 cm dia, with a density of about 4.8 g/cc (98% of theoretical).

2.1 GCRE Fuel (70% UO_2-30% BeO)

2.1.1 Leaching with Nitric Acid

Two aqueous processes for recovering uranium from GCRE-type fuels are being developed. The first is leaching of the fuel pellets with nitric acid after mechanical disengagement (stripping or chopping) of the cladding. To simulate this process, integral pellets were leached with boiling nitric acid solutions to determine the rate at which uranium and beryllium were solubilized. With boiling 6-13 M HNO_3, the UO_2 was almost completely leached in 6-7 hr, leaving about half the BeO as an undissolved residue (Table 1 and Fig. 1). Uranium losses to the BeO residue were about 0.1%. The resulting solutions contained about 4 g of uranium per liter. The BeO residue was dissolved only after an additional 30-50 hr of reflux.

Table 1. Uranium Losses on Leaching GCRE Fuel Pellets (70% UO_2-30% BeO) with Boiling Nitric Acid

0.4-0.5 g pellet, 100 ml acid

HNO_3 Conc, M	Leaching Time, hr	Amount Remaining in BeO Residue, % U	Amount Remaining in BeO Residue, % Be
4	4.0	22.7	39.8
6	6.8	0.13	66.2
8	6.8	0.059	59.3
10	6.7	0.094	43.2
10	6.8	0.12	50.3
13	6.8	0.12	48.8

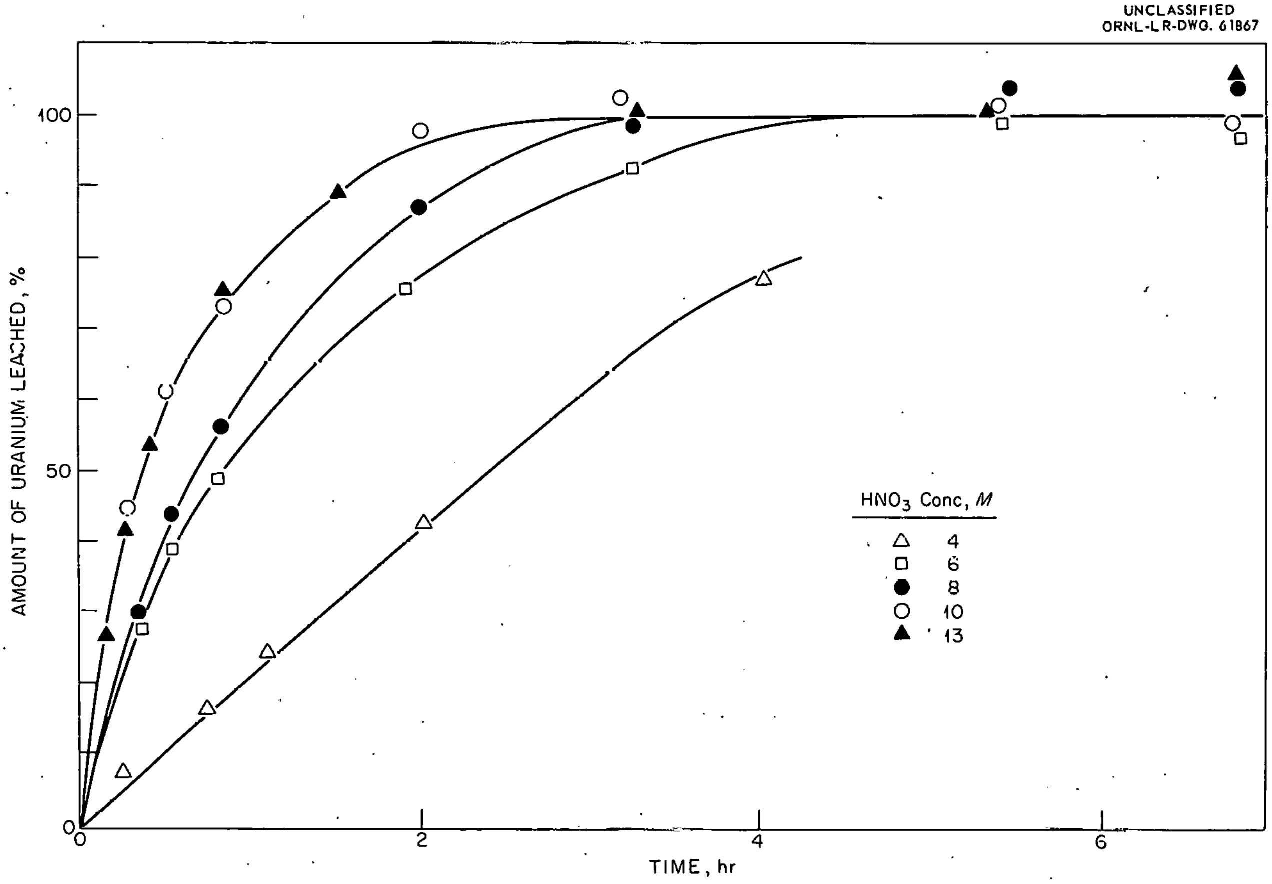

Fig. 1. Effect of nitric acid concentration on the rate of leaching of UO_2 from GCRE (70% UO_2-30% BeO) fuel pellets. Boiling solution used in each experiment. Uranium concentration in resulting solution: ~4 g/liter.

2.1.2 Modified Darex Process

The alternative process involves dissolution of the Hastelloy-X cladding in dilute aqua regia (Sect. 5.0) and subsequent leaching of UO_2 with the resulting solution. Leaching of GCRE fuel pellets for 4 hr with a typical decladding solution, 25 g of Hastelloy-X per liter, 4.1 N hydrogen ion, 3.4 M Cl^-, recovered essentially all the uranium. The final solution contained about 4 g of uranium per liter. Most of the BeO remained as an undissolved residue. The GCRE fuel pellets are attacked rapidly by aqua regia solutions so that decladding of the fuel with this reagent without loss of uranium to the solution is not feasible.

2.1.3 Leaching with HNO_3-HCl Solutions

In HNO_3-HCl solutions, the rate at which uranium and beryllium were leached from GCRE pellets was determined mainly by the hydrogen ion concentration. For example, rates were about the same in 6 M HNO_3 and in 2 M HNO_3—4 M HCl (Fig. 2). The UO_2 and BeO dissolved completely in ~10 and 30 hr, respectively, regardless of the HCl concentration to produce solutions containing about 4 g of uranium per liter.

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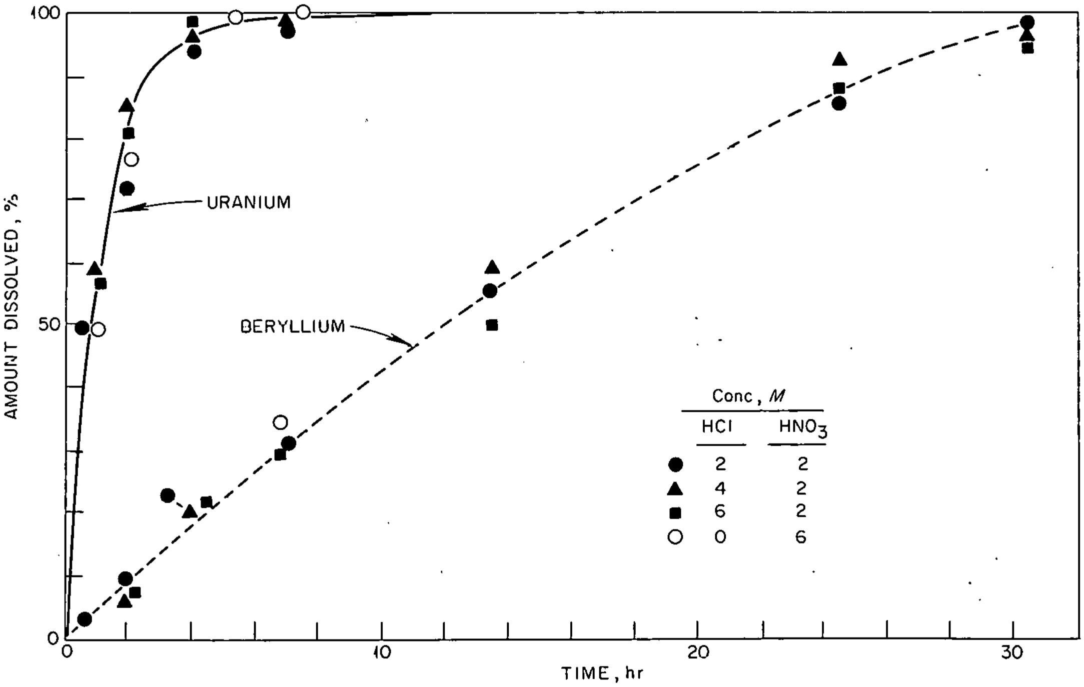

Fig. 2. Dissolution of GCRE fuel pellets (70% UO_2—30% BeO) in boiling HNO_3-HCl. Solutions contained about 4 g of uranium per liter when all uranium was leached.

2.1.4 Leaching with HNO_3-H_2SO_4 Solutions

In HNO_3-H_2SO_4 solutions with total hydrogen ion concentrations in the range 8-24 N, the rate of leaching of UO_2 from GCRE fuel pellets decreased with increasing sulfuric acid concentration regardless of the HNO_3 concentration. For example, the UO_2 dissolved in 3 hr was about 98, 92, 75, and 60% in solutions containing 0.2, 3, 5, and 6 M H_2SO_4, respectively (Fig. 3a). However, the dissolution rate of the BeO matrix (in 5 hr) increased from about 25 to 70% with the addition of H_2SO_4 from 0 to 3 M (Fig. 3b). The BeO rate did not increase further when the H_2SO_4 concentration was increased to 7 M. Dissolution was complete in about 15 hr in boiling 8 M HNO_3 containing 1-2 M H_2SO_4, but required at least 30 hr in the absence of sulfuric acid. The final solution contained about 4 g of uranium per liter.

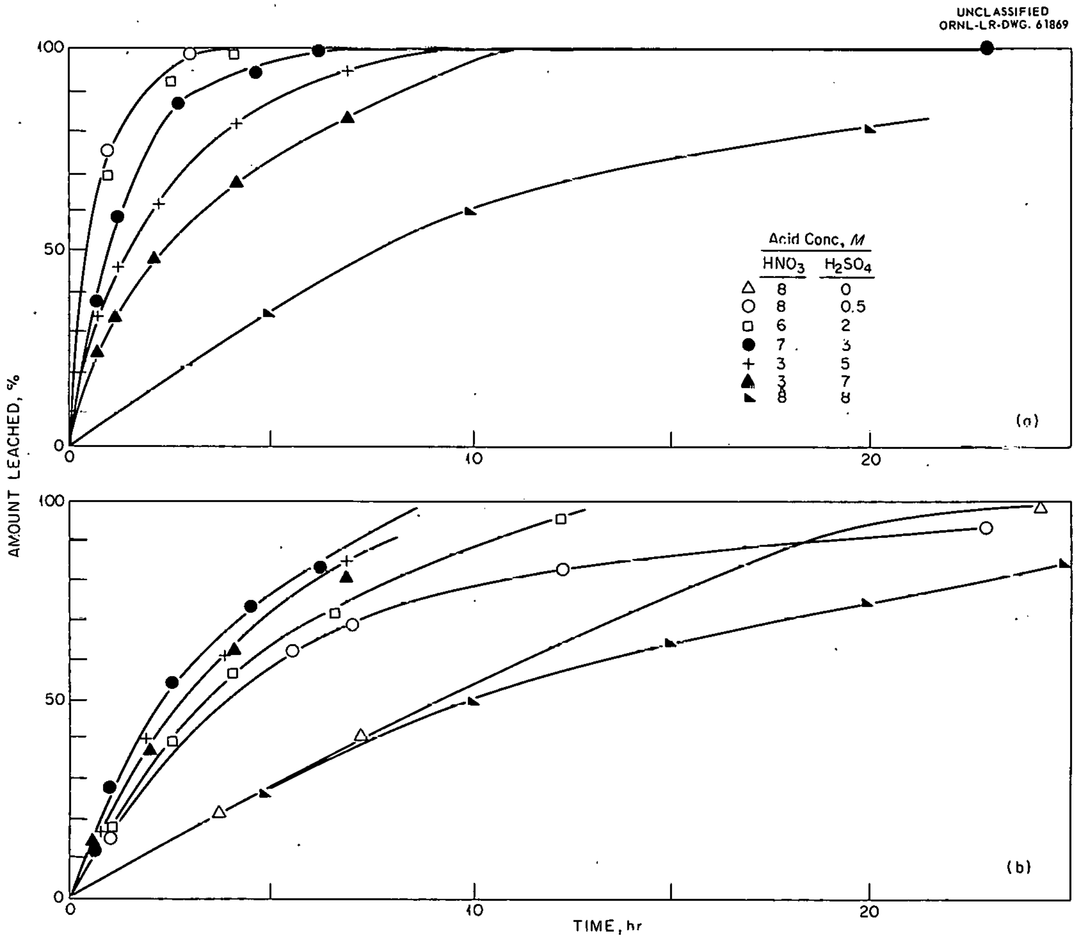

Fig. 3. Effect of H_2SO_4 concentration on the rate of leaching, with HNO_3-H_2SO_4 of (a) UO_2 and (b) BeO from GCRE (70% UO_2-30% BeO) fuel pellets. Solutions contained 4 g of uranium per liter when all uranium was leached.

2.1.5 Leaching with HNO_3-NaF Solutions

GCRE fuel pellets dissolved completely in <12 hr in boiling 8 M HNO_3 containing 0.5-0.8 M NaF. Uranium dissolved completely in 6-8 hr regardless of the NaF concentration (Fig. 4a), although the initial dissolution rate was slightly lower in the presence of NaF. The final solutions in each case contained about 4 g of uranium per liter. The initial rate of attack on the BeO matrix was not markedly affected by changes in the NaF concentration (Fig. 4b); however, even after 47 hr digestion in solutions containing 0.05, 0.1, and 0.2 M NaF, respectively, 20, 15, and ~4% of the BeO remained undissolved.

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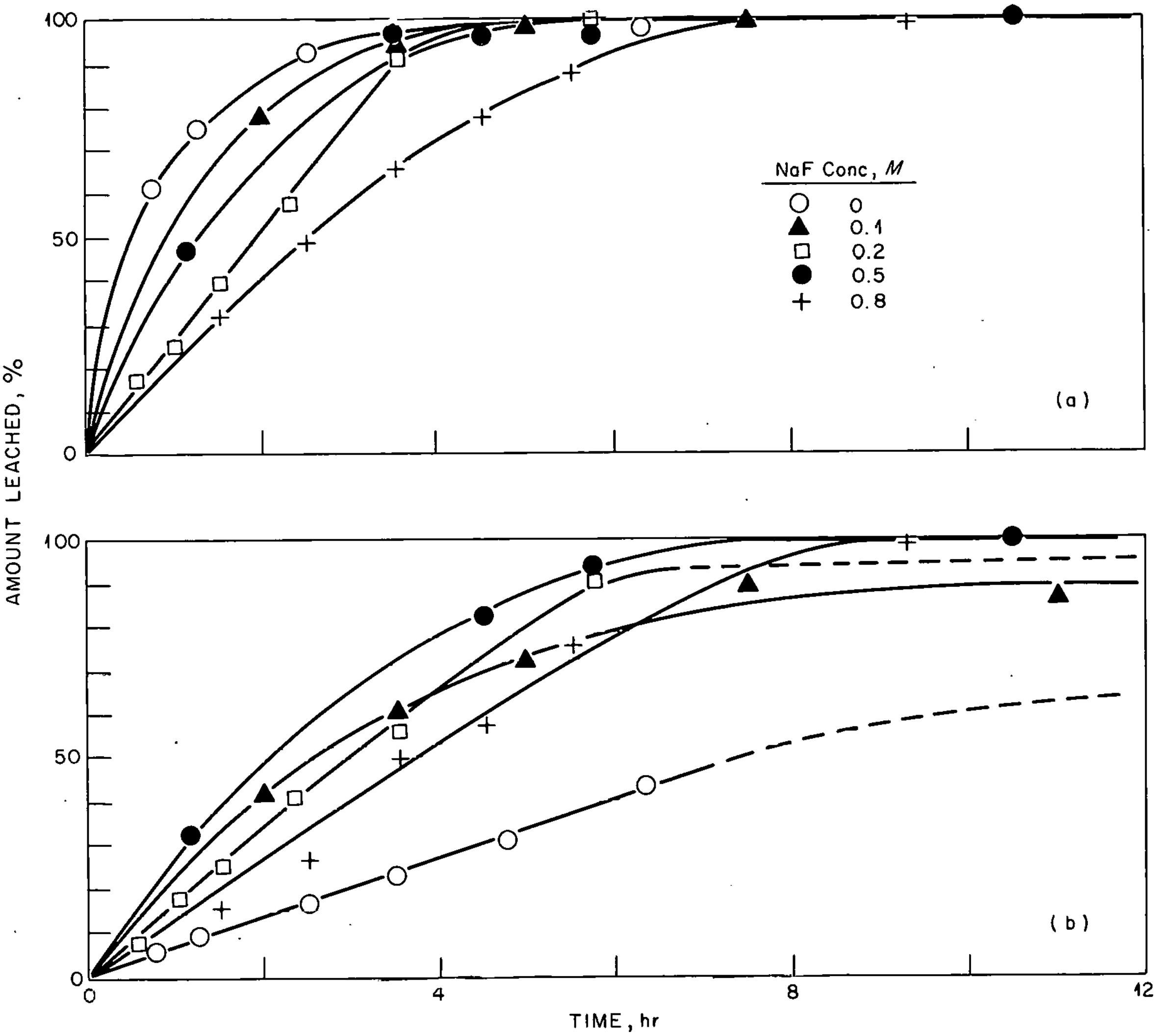

Fig. 4. Effect of NaF concentration on the rate of dissolution of (a) UO_2 and (b) BeO in GCRE fuel pellets (70% UO_2-30% BeO) in boiling 8 M HNO_3--NaF solutions.

2.1.6 Ignition Studies

All the above studies were made with integral fuel plates, and rates would undoubtedly be higher with crushed or ground pellets. As an alternative to mechanical grinding, the effect of igniting three types of UO_2-BeO pellets at red heat in air was determined. Two samples containing 66 and 70% UO_2, respectively, slowly crumbled to powder during heating (Table 2), but a sample containing only about 8% UO_2 was virtually unaffected. Leaching of the disintegrated pellets with 3 M HNO_3—3 M H_2SO_4 at room temperature for 16 hr completely recovered the uranium. Although little BeO dissolved at room temperature, it dissolved completely in about 1 hr at the boiling point.

Table 2. Ignition Experiments with UO_2-BeO Pellets

0.4- to 0.5-g pellets heated in air to red heat;
residue leached with 3 M HNO_3—3 N H_2SO_4

Pellet Composition, %		Ignition Time,	Wt Gain,	Leaching[a]		Amount Leached, %	
UO_2	BeO	min	%	Time, hr	Temp	U	Be
70.4	29.6	46	2.4[a]	16	Room	100	0
				1	Reflux	100	100
66.2	33.8	45	2.4[a]	3	Room	63.8	0
				1.25	Reflux	100	85.7
				18	Reflux	100	100
8.0	92.0	210	0[b]				

[a] Pellet disintegrated to powder when heated.

[b] Sample did not disintegrate on ignition; no leaching conducted.

A GCRE fuel pellet (70% UO_2—30% BeO) mechanically ground to pass a 100-mesh screen required 18 hr for complete dissolution in boiling 8 M HNO_3. This corresponds to about a 50% increase in dissolution rate over that with integral pellets. The final solution contained ~4 g of uranium per liter.

2.2 MGCR Fuel (61% UO_2-39% BeO)

The 61% UO_2 pellets used to simulate MGCR fuel behaved similarly to GCRE pellets except that the uranium was leached more slowly, probably due to the larger size of the MGCR pellets and/or the lower uranium content. In a single experiment, 97.8% of the uranium and 35% of the beryllium were leached from a 4.76-g pellet in 24 hr with 100 ml of boiling 8 M HNO_3. The weight loss was 74.4%.

3.0 HIGH-BeO-CONTENT FUELS

Fuels in this category, such as the TORY-IIA (6), contain only 5-10% UO_2 and are very resistant to the common aqueous dissolvents. Dissolution rates were highest (~3.5 mg $min^{-1}cm^{-2}$) in concentrated sulfuric acid or fluoride systems.

3.1 Dissolution in Sulfuric Acid

Sintered beryllia (density 2.87 g/cc, about 95% of theoretical) and BeO-5% UO_2 dissolved at about the same rates in boiling sulfuric acid solutions, the initial rates* increasing from about 0.01 to 3.5 mg $min^{-1}cm^{-2}$ as the acid concentration was increased from 4 to 16 M (Fig. 5). Approximate values for the initial rates can be calculated from the equation

$$\log (\text{Rate, mg min}^{-1}\text{cm}^{-2}) = 0.223\ (H_2SO_4,\ \underline{M}) - 2.81$$

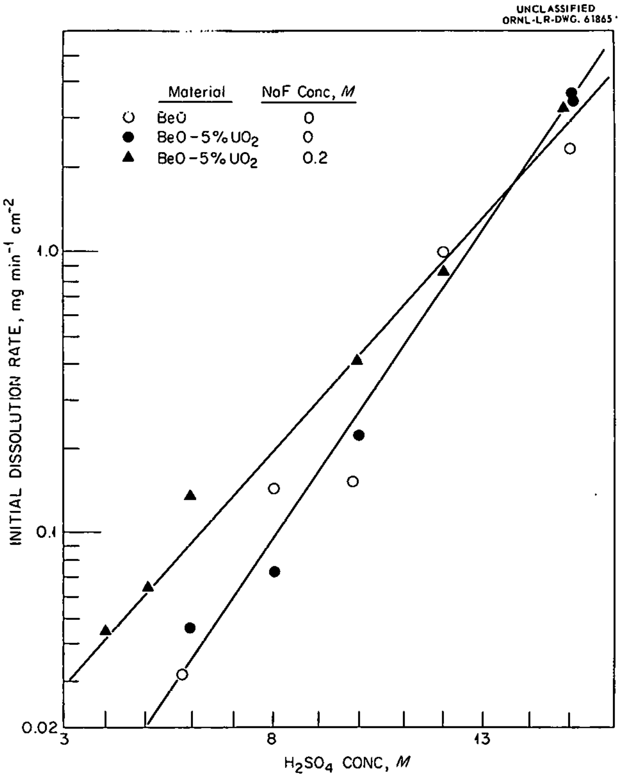

Fig. 5. Initial dissolution rates of BeO and BeO-5% UO_2 in boiling H_2SO_4 and H_2SO_4—0.2 M NaF solutions.

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*Initial dissolution rates were calculated from weight changes when less than 10% of the specimen had dissolved.

Dissolution rates of BeO-5% UO_2 were increased slightly by the addition of 0.2 M NaF to 4-14 M H_2SO_4 (Fig. 6). The BeO-5% UO_2 initial rates in H_2SO_4—0.2 M NaF solutions can be calculated from the relation

$$\log (\text{Rate, mg min}^{-1}\text{cm}^{-2}) = 0.168\ (H_2SO_4,\ M) - 2.043.$$

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

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

3.2 Dissolution in HF-NH_4F Solutions

Sintered BeO-5% UO_2 dissolved in boiling HF or HF-NH_4F solutions. In HF solutions, the initial dissolution rate increased from 0 to 1.4 mg $min^{-1}cm^{-2}$ as the HF concentration increased from 0 to 20 M; however, the rate varied only slightly with HF concentration between 5 and 20 M (Fig. 6a). In mixed solutions containing 0-5 M HF, the initial rate of dissolution was virtually unaffected when the NH_4F concentration was varied over the range 0-8 M. In more concentrated HF solutions, however, the initial rate increased as the NH_4F concentration increased from 0 to 5 M. For example, in 15 M HF solutions, the initial rate increased from about 1.2 to 2.8 mg $min^{-1}cm^{-2}$ as the NH_4F concentration increased from 0 to 5 M. Solutions with NH_4F concentrations greater than 5 M did not yield higher rates. Sintered BeO-5% UO_2 did not dissolve in NH_4F solutions; initial rates in 0-8 M NH_4F were 0.07 mg min^{-1} cm^{-2} or less.

3.3 Dissolution in KF-HF Solutions

Dissolution rates in KF-HF solutions were lower than those in the corresponding NH_4F-HF solutions. In 3.2 M KF, the initial rate was 0.0061 mg $min^{-1}cm^{-2}$, and in 3.2 M KF—5 M HF it was 0.36 mg $min^{-1}cm^{-2}$, about one-fourth the corresponding values in NH_4F-HF solutions.

3.4 Dissolution in HNO_3, HNO_3-H_2SO_4, and HNO_3-HCl Solutions

Boiling 4-16 M HNO_3 did not dissolve BeO or BeO-5% UO_2. Initial rates ranged from 0.003 to 0.016 mg $min^{-1}cm^{-2}$ (Table 3). Dissolution in nitric acid containing up to 0.2 M NaF was not appreciably faster. Nitric acid solutions containing up to 8.6 M H_2SO_4 or 6 M HCl also left the fuel specimens virtually unaffected.

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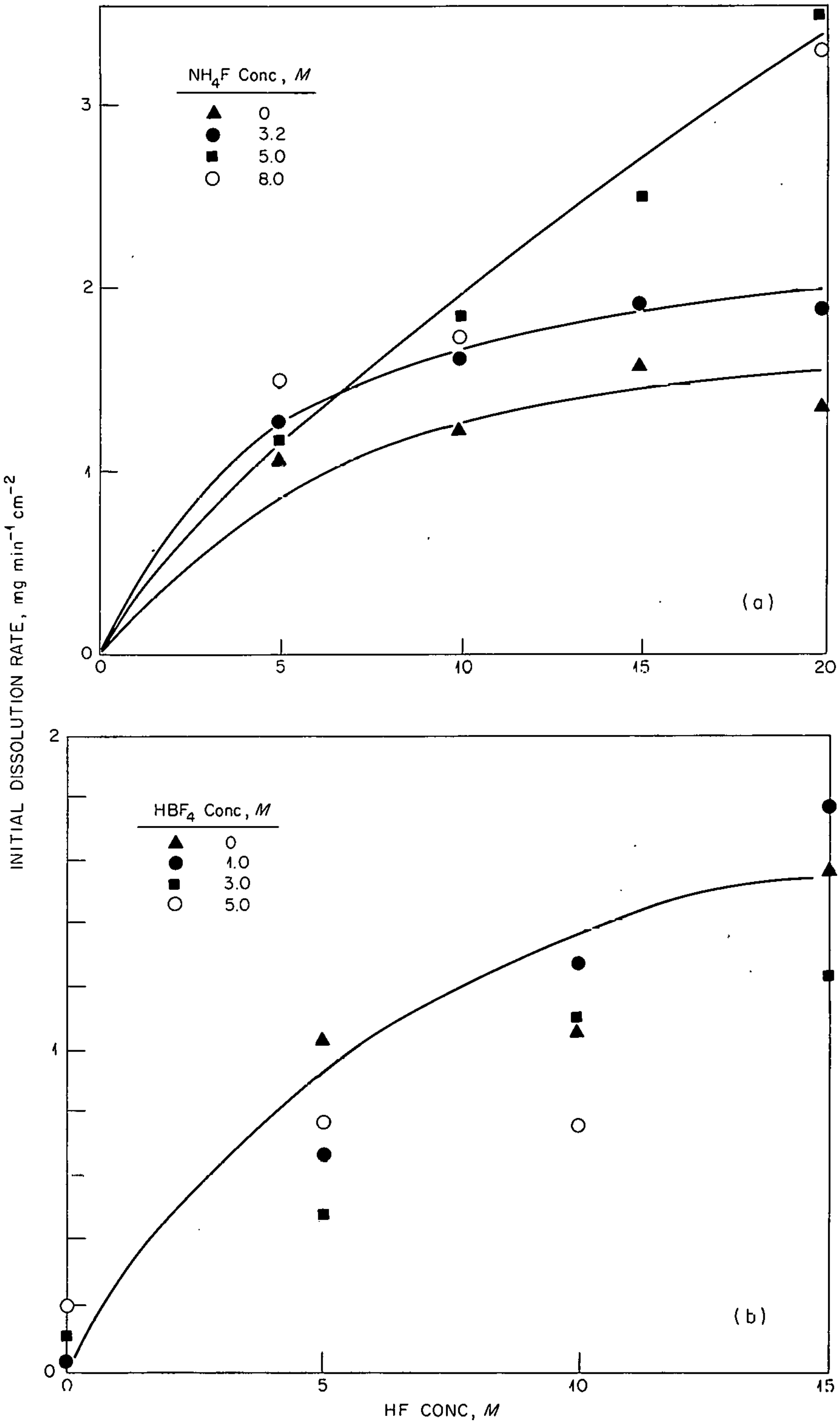

Fig. 6. Effect of (a) NH_4F and (b) HBF_4 concentrations on initial dissolution rates of BeO-5% UO_2 in boiling mixtures with HF.

Table 3. Initial Dissolution Rates of BeO and BeO-5% UO_2 in Boiling Nitric Acid, HNO_3-H_2SO_4, and HNO_3-HCl Solutions

Density of 0.4- to 0.5-g specimens: about 95% of theoretical
Vol of reagent: 100 ml
Less than 10% of specimen dissolved

Acid Conc, M			Initial Dissolution Rate, mg min^{-1} cm^{-2}	
HNO_3	H_2SO_4	HCl	BeO	BeO-5% UO_2
4.0	0	0	0.003	-
8.0	0	0	0.005	0.014
12.0	0	0	0.011	0.016
15.7	0	0	0.010	0.016
5.0	5.0	0	0.026	0.036
8.63	4.32	0	0.033	0.048
8.61	8.61	0	0.011	0.026
8.0	0	1.0	0.011	0.012
4.0	0	2.0	0.007	0.016
2.0	0	4.0	0.003	0.013
2.0	0	6.0	0.003	0.023

3.5 Dissolution in HF-HBF_4 Solutions

Addition of HBF_4, in concentrations up to 5 M, to boiling HF solutions had little effect on the initial rate of dissolution of sintered BeO-5% UO_2. The initial rate increased from about 0 to 1.4 mg min^{-1} cm^{-2} as the HF concentration increased from 0 to 15 M regardless of the HBF_4 concentration (Fig. 6b). In boiling HBF_4 solutions containing no HF, the initial rate increased only to 0.2 mg $min^{-1}cm^{-2}$ as the HBF_4 concentration increased to 5 M.

One test was carried out with boiling 3 M HNO_3—0.5 M HBF_4—0.3 M $(NH_4)_2Cr_2O_7$, a solution which is being tested as a dissolvent for zirconium in titanium vessels (8). Beryllium oxide—5% UO_2 dissolved in this mixture at an initial rate of only 0.03 mg $min^{-1}cm^{-2}$, which is essentially the rate in 0.5 M HBF_4 alone.

3.6 Dissolution in Other Reagents

Attempts were made to dissolve BeO in a variety of aqueous and organic reagents. None of the reagents tested dissolved BeO rapidly enough to warrant further interest (Table 4).

Table 4. Initial Dissolution Rates of BeO in Various Boiling Reagents

Conditions same as in Table 3

Reagent	Rate, mg $\min^{-1}$ cm^{-2}
HI, 47%	Wt gain
glacial acetic acid	Wt gain
Dimethyl sulfoxide	0
HBr, 48%	0
6 M HCl—0.24 M oxalic acid	0
Trichloroacetic acid, 2.5 M	0.002
Resorcinol	0.003
Fuming sulfuric acid, 30%	0.007
Hypophosphorous acid, 31%	0.009
Ammonium silicofluoride	0.009
7.37 M H_3PO_4	0.093
7.37 M H_3PO_4—0.25 M NaF	0.18
Fluosilicic acid, 30%	0.70

4.0 BERYLLIUM METAL AND BERYLLIDES

Beryllium metal is frequently mentioned as a cladding material for oxide fuel elements for gas-cooled reactors, particularly the EGCR (9). Dissolution of the metal 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 sodium hydroxide solution (Table 5).

Several uranium and thorium beryllides, prepared by the ORNL Metallurgy Division,were also subjected to dissolution tests. UBe_{13} rapidly dissolved in boiling 4 M H_2SO_4 and in 4 M HNO_3—0.05 M NaF. $ThBe_{13}$ dissolved rapidly in 4 M HNO_3, but only slowly in 4 M H_2SO_4. A composite containing both UBe_{13} and $ThBe_{13}$ dissolved readily in 4 M HNO_3—0.05 M NaF.

Table 5. 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

5.0 DISSOLUTION OF HASTELLOY-X

Hastelloy-X, the cladding material for the GCRE-I (core 2), ML-1, and MGCR reactors, is approximately 45% Ni, 22% Cr, 22.5% Fe, 9.3% Mo, with traces of Si, Mn, and W. It can be dissolved in dilute aqua regia solutions containing 1-5 M HNO_3 and 4 or 5 M HCl. The initial dissolution rates are in the range 6-28 mg $min^{-1}cm^{-2}$ (Table 6). Standard Darex (5 M HNO_3—2 M HCl) and Sulfex (4-6 M H_2SO_4) dissolvents (10) proved unsatisfactory for the dissolution of Hastelloy-X, initial dissolution rates being 0.2 and 0.1 mg $min^{-1}cm^{-2}$, respectively.

Dissolution of Hastelloy-X in boiling 2 M HNO_3—4 M HCl is described approximately by the equation

$$0.494\ Ni + 0.25\ Cr + 0.195\ Fe + 0.061\ Mo + HCl + 4\ HNO_3 \longrightarrow 0.494\ Ni(NO_3)_2 + 0.25\ Cr(NO_3)_3 + 0.195\ Fe(NO_3)_3 + 0.061\ Mo(NO_3)_6 + NOCl + 5/2\ H_2O + 0.156\ NO + 0.156\ NO_2$$

This equation was derived from the following data:

Run No.	Wt. of Alloy Dissolved, g	Moles of Alloy Dissolved[a]	Moles Consumed per mole of alloy: H+	NO_3^-	Cl⁻
1	3.19	0.051	5.2	1.0	1.6
2	2.99	0.047	3.7	0.82	0.74

[a] 1 mole = 59 g = 0.494 mole Ni, 0.25 mole Cr, 0.195 mole Fe, and 0.061 mole Mo.

Table 6. Initial Rates of Dissolution of Hastelloy-X[a] in Boiling Dilute Aqua Regia Solutions

Dissolution time: 10 min

HNO_3 Conc, M	HCl Conc, M	Dissolution Rate, mg $min^{-1}cm^{-2}$
0	3	0.05
1	3	7.7
3	3	0.6
5	3	0.4
0	4	0.05
1	4	26
3	4	26
5	4	5.9
0	5	0.05
1	5	27
3	5	28
5	5	13

[a] 46% Ni, 22.5% Cr, 17.2% Fe, and 9.3% Mo.

Off-gas analyses will be required if a more exact stoichiometry is to be determined.

Solutions containing 50 g of alloy per liter, which were stable at 25°C, could be prepared by dissolution in boiling 2 M HNO_3—4 M HCl.

6.0 ALUMINA-BASE FUELS

Another ceramic fuel, UO_2-Al_2O_3, was suggested for the MGCR (4). The fuel, in the shape of pellets, would be clad in stainless steel or Hastelloy-X. Uranium oxide can be leached from such fuels if the Al_2O_3 content is less than about 10%.

Two types of high-density unirradiated pellets, "homogeneous" and "heterogeneous," containing from 4 to 75% Al_2O_3 were used in the studies. The "homogeneous" pellets consisted of 10-μ grains of UO_2 dispersed in an Al_2O_3 matrix while the UO_2 particles were much larger (about 150 μ) in the "heterogeneous" pellets. The pellets were leached with boiling 10 M HNO_3 (the solutions would have been 1 M in uranium if dissolution had been complete) for 4 hr and the uranium loss to the undissolved portion was determined. Losses were different with different types of pellet but always increased with increasing Al_2O_3 content. For example, losses from "homogeneous" pellets increased from about 0.002 to 88% as the Al_2O_3 content of the pellet increased from 4 to 61% (Table 7). In general, losses from "heterogeneous" pellets were about half those from the "homogeneous" pellets, other conditions being the same. In all cases, less than 1% of the Al_2O_3 was dissolved. Extended leaching (72 hr) or addition of 0.2 M HF to the nitric acid did not appreciably increase uranium recovery. Boiling 5 M HNO_3—5 M HCl was also ineffective in leaching either uranium or aluminum from the pellets.

Table 7. Leaching with Boiling 10 M HNO_3 for 4 hr of Unirradiated MGCR Prototype UO_2-Al_2O_3 Fuel Pellets

Run No.	Type of Pellet[a]	Al_2O_3 in Pellet, %	U Loss to Residue, %
1	Homogeneous	3.7	0.002
2		13.7	3.30
3		16.6	15.7
4		28.4	23.0
5		35.4	55.1
6		47.3	81.4
7		61.1	88.4
1	Heterogeneous	4.4	0.05
2		9.5	0.16
3		11.2	0.15
4		18.9	0.74
5		25.9	3.28
6		33.0	10.8
7		41.7	24.5
8		70.1	48.3
9		75.6	48.3

[a] Pellets described in text.

7.0 TOXICITY OF BERYLLIUM COMPOUNDS

Exposure to beryllium and its compounds gives rise to dermatitis, acute pneumonitis, and chronic pneumonitis. Dermatitis of the skin develops from handling compounds such as beryllium sulfate and beryllium chloride. The introduction of these compounds into a cut or wound produces ulcerations which require excision for proper healing. A more serious, and frequently fatal, class of beryllium poisoning derives from exposure of a worker to beryllium-containing dusts. The eyes and respiratory tract become seriously inflamed, chest pains render breathing difficult, and cyanosis may result. The third class, and the most insidious, is known as chronic pneumonitis, a slowly progressive lung condition which may result in death. Apparently this disease resembles the miners' disease "silicosis" in some ways, being basically a granulomatous reaction, characteristic of a chronic allergic reaction. The gradual loss of oxygen exchange space in the lungs reduces the individual's ability to ward off infection. There are no good methods for treatment; the fatality rate approaches 35%. The toxic effects of beryllium are summarized in a recent book by Darwin and Buddery (11).

The ORNL Chemical Technology Division beryllium laboratory, designed for the safe execution of the experimental work, was described previously (12). Limits of exposure under three different conditions were based upon prior experience:

1949 Toxicity Limits for Beryllium Compounds

	Be Conc, $\mu g/m^3$ of air
Eight hour maximum working exposure, air-borne	2
Maximum momentary exposure, air-borne	25
Average monthly concentration in air near plant	0.01

These limits were recommended by the Beryllium Advisory Committee of the U. S. Atomic Energy Commission (13).

Floors (14) should not exceed 20 $\mu g/ft^2$ as measured by filter paper smears, and equipment that might be touched should not exceed 5 $\mu g/ft^2$. A bibliography of articles covering all aspects of beryllium toxicology was issued recently (15).

8.0 OTHER DISSOLVENTS FOR BeO AND Al_2O_3

Ceramic beryllia (density 2.7-3.0 g/cc) is nearly inert to all materials except hydrogen fluoride (16). The reactivity of BeO is greatly dependent on the temperature to which it has been fired. Low-fired BeO is readily dissolved in boiling mineral acids.

As the results of the present study show, concentrated aqueous fluoride systems were the best dissolvents tested for ceramic BeO. Similar studies were conducted previously at the Y-12 plant on dissolution of BeO-9% UO_2 specimens (density 3.14 g/cc) in boiling HF-NH_4F-H_2O_2 solutions (17). In solutions where the NH_4F and H_2O_2 concentrations were constant at 1 M and 3%, respectively, the rate increased from 0.09 to 1.2 mg $min^{-1}cm^{-2}$ as the HF concentration increased from 1 to 26 M. In 11.5 M HF solutions containing 3% H_2O_2, the rate was not markedly affected when the NH_4F concentration was increased from 1 to 7.5 M.

Workers at Brookhaven National Laboratory dissolved beryllium metal and sintered BeO in 18 mole % NO_2—82 mole % HF (18). Sintered BeO dissolved at a rate of 2.1 mg $min^{-1}cm^{-2}$ at $50^\circ C$. Neither beryllium metal nor BeO dissolved in anhydrous HF at temperatures up to $100^\circ C$.

Both sintered BeO and Al_2O_3 dissolved slowly in molten NH_4HF_2 (19,20). At the boiling point, about $225^\circ C$, Al_2O_3 and BeO dissolved at rates of 0.35 and 1.7 mg $min^{-1}cm^{-2}$, respectively (20).

The optimum temperature for reacting BeO with gaseous HF appears to be about $225^\circ C$ (21). At higher temperatures the reaction apparently is stifled by hydrolysis of the BeF_2 formed. However, sintered BeO was dissolved by HF at an average rate of 0.64 mg $min^{-1}cm^{-2}$ (5 mils/hr) in the presence of molten 49 mole % NaF—40 mole % LiF—11 mole % BeF_2 at $600^\circ C$ (22). Recovery of uranium from such melts by fluorination has also been demonstrated.

Chlorine reacts with beryllia at temperatures above $600^\circ C$ (16). Russian investigators (23,24) concluded that the optimum temperature range for reacting carbon-BeO mixtures with chlorine or BeO with carbon tetrachloride was $900\text{-}1000^\circ C$.

Beryllium oxide reacts with water vapor, presumably to form volatile $Be(OH)_4$, but the rate of reaction is low at temperatures below about $1300^\circ C$ (25).

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