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ABSTRACT

Fused Salt--Fluoride Volatility Process. Corrosion tests indicated that nickel may be a suitable material of construction for a fluoride-melt dissolver.

The rate of dissolution of zirconium-uranium alloy in fused NaF-ZrF₄ at 600°C decreases as the ZrF₄ content increases. STR fuel element samples dissolved at 7-9 mg/min/cm² when the melt contained 35 mole % ZrF₄ and at 0.8-10. mg/min/cm² when the melt contained 60 mole % ZrF₄.

The reaction between F₂ and molten NaF-ZrF₄-UF₄ (50-50 NaF-ZrF₄ containing ~4 mole % UF₄) at 600°C appeared incomplete in batch equilibration tests, possibly as a result of inadequate salt agitation.

In fused salt fluorination tests with 4 and 2 mole % UF₄, recirculation of the product gas back to the fluorinator resulted in total solidification of the melt at 600°C. This did not occur with 0.4 mole % UF₄.

Measured rates of the decomposition of the UF₆·3NaF complex indicate that it is imperative that an adequate flow of F₂ gas be maintained through the NaF beds during the desorption cycle.

Zircex Process. The Zircex hydrochlorination product is primarily UCl₃.

In the hydrochlorination reaction, some decontamination of uranium from zirconium and niobium is obtained. Ruthenium, the rare earths, and strontium remain with the nonvolatile UCl₃. The cesium tends to divide evenly between the ZrCl₄ and the nonvolatile UCl₃.

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The hydrochlorination rate of 2% zirconium-98% uranium alloy increased from 0.172 mg/cm²/min at 300°C to 0.835 mg/cm²/min at 370°C.

A small amount of the material remaining in the hydrochlorinator vessel when zirconium-uranium alloy is hydrochlorinated is insoluble in dilute nitric acid. The insoluble residue contained 1 to 3% of the uranium, the amount retained apparently increasing as the hydrochlorination temperature increased.

The rate of hydrochlorination of a silicon-uranium alloy did not significantly change with composition and was about 0.1 mg/cm²/min.

The uranium-molybdenum core was leached from a zirconium-clad APDA fuel element by 8 M HNO₃.

The particle size of sublimed ZrCl₄ was increased by increasing the temperature at which it was condensed.

Calculations show that the removal of heat during hydrochlorination of zirconium-uranium fuels will be a major problem. An experimental unit to measure the temperature of the reaction and the heat transfer is being designed.

Hermex Process. The dissolution rates of uranium in 0.1 wt % magnesium amalgam was about twice that in mercury alone. The saturation solubility was 6.5 wt % uranium. The rate constants for the dissolution reaction were 2.52 g Mg(Hg)/cm²/min for a fast step and 1.05 for a subsequent slow step. Increasing the magnesium content of the solvent increased the dissolution rate and the saturation solubility.

A low rate constant of 0.02 g Bi(Hg)/cm²/min and a high saturation solubility of 9 wt % were obtained for the dissolution of uranium in bismuth amalgam.

General Dissolution Studies. Dissolution rates of Zircaloy-2 in aqueous FeCl₃ and FeCl₃-NaCl solutions were too low to be practicable. The rate in HCl was increased by boiling, and in aqua regia by boiling and adding concentrated nitric acid. The Zircaloy-2 cladding was removed from UO₂ cores with boiling 14 M H₂SO₄, with only 0.2% uranium loss. The zirconium cladding was removed from 10% molybdenum--90% uranium cores with only 0.014% uranium loss.

A sodium-bonded stainless steel--clad prototype APDA blanket element dissolved directly in aqua regia. While the sodium reacted violently, the amount exposed at any one time was small enough to prevent an eruption.

Mechanical De-jacketing and Handling Studies. A Mackintosh-Hemphill rotary straightener has been ordered for de-cladding experiments.

Feasibility proposals have been received from two companies on the use of spiral vibratory feeders as (1) countercurrent leachers and (2) trickle type dissolvers with continuous solids discharge. Both

proposals are encouraging. A spiral vibratory conveyor is being investigated.

Materials Evaluation. Tantalum and Pfaudler No. 53 glass-lined steel were satisfactorily resistant to aqua regia after 624 and 240 hr, respectively. Inconel was unaffected by 70% HNO_3 at room temperature for 240 hr. Sensitized type 302 stainless steel and type 304 L stainless steel Spraypak deteriorated in boiling nitric acid but was resistant where unsensitized.

1.0 FUSED SALT--FLUORIDE VOLATILITY PROCESS

In the fused salt--fluoride volatility process, fuel elements are dissolved in molten fluoride salts; the UF_4 formed is fluorinated to UF_6 , which volatilizes and is collected in NaF traps.

1.1 Dissolution Studies (R. G. Wymer)

Nickel appears to be resistant to corrosion under fluoride-melt dissolution conditions. In two separate experiments, nickel corrosion specimens placed in the lift-pump dissolver and exposed to flowing HF gas in NaF-ZrF_4 at 600°C showed no detectable weight loss after 3.5 hr. However, 0.024 mole of noncondensable gas, presumably hydrogen, was generated, indicating that the nickel dissolver and HF pump had collectively lost ~1.4 g.

At 600°C and an HF flow rate of 56 mg/min, the dissolution rate of a high-zirconium alloy (STR specimens) in NaF-ZrF_4 melts varied with the melt composition:

NaF/ZrF_4 mole ratio of 40/60	0.8-1 mg/min/cm ²
50/50	4-5
65/35	7-9

At this temperature the first melt is saturated with ZrF_4 and the third is saturated with NaF .

1.2 Fluorination Studies (G. I. Cathers, M. R. Bennett, R. L. Jolley)

Fused Salt-Fluorination Equilibrium. In three batch equilibration tests, the reaction of F_2 with molten $\text{NaF-ZrF}_4\text{-UF}_4$ (50-50 NaF-ZrF_4 , containing 4 mole % UF_4), at 600°C , was incomplete apparently as a result of poor contact between the salt and gas phases. These runs were made in attempts to develop a satisfactory procedure for measuring the fused salt--fluorination equilibrium constant. The reactor containing the salt and F_2 gas was maintained for about 2 hr at 600°C and at atmospheric

pressure by feeding F_2 into the system to make up for any F_2 consumption. Two methods were used in analyzing the gas phase after the equilibration period. In the first run, the test reactor was cooled quickly to 100°C and the gas flushed through a NaF bed to trap UF_6 . The gas phase contained only 8.7 mole % UF_6 . Based on previous work, the equilibrium gas should be almost pure UF_6 , i.e., the equilibrium constant for the reaction is large. In the next two tests density determinations indicated the gas to be essentially pure F_2 . Although it seemed improbable that UF_6 redissolved in the molten salt during solidification, gas was sampled in the third run without prior solidification of the salt phase to check this point. The most probable explanation of the small amount of UF_6 found in these two runs is that there was not enough agitation of the molten salt to ensure complete equilibrium with the gas phase.

The density of the F_2 used in the above work was 1.72 g/liter (STP) in contrast to the theoretical density of 1.70, indicating that the F_2 was fairly pure.

When the UF_6 gas product stream was recirculated to a 50-50 NaF-ZrF₄ melt containing ~4 or 2 mole % UF_4 , the melt solidified. This did not occur when there was only 0.4 mole % UF_4 present. A high-melting insoluble precipitate may be involved. In the case where UF_4 was present, the solidified material did not melt even at 700°C . Analysis showed it to contain 8.51 wt % total uranium, of which 5.37 wt % was U(IV); the difference, 3.14 wt %, represents the amount present as U(VI).

Decomposition of $UF_6 \cdot 3NaF$ Complex. UF_6 is desorbed from the NaF bed by raising the temperature of the bed from 100°C to 400°C while sweeping with F_2 gas or a mixture of N_2 and F_2 . In laboratory studies in which the UF_6 was not completely desorbed, the amount retained by the bed was dependent on the temperature and partial pressure of the F_2 in the system. In these experiments, the NaF bed increased in weight at a rate ranging from 0.02% per minute at 245°C to 1.7% per minute at 365°C when the flow of sweep gas was stopped or when the desorbed UF_6 was held in contact with the bed because of plugging or other reason:

Temp. ($^\circ\text{C}$)	Time (min)	UF_6 Flow Rate (ml/min)	U in Residue (%)		Wt. Increase (%)		Wt. Increase Rate (%/min)
			U(IV)	Total	Found	Calc. ^a	
300	15	---	2.6	4.0	6.0	6.0	0.4
300	30	136	3.7	6.8	11.6	10.5	0.35
350	15	17	6.4	14.3	24.7	24.7	1.6
400	15	16	6.6	14.7	26.1	26.0	1.7

^aCalculation based on assumption that the residual uranium is U(V).

This effect is assumed to be due to decomposition of the $UF_6 \cdot 3NaF$ complex, forming a complex of nonvolatile UF_5 with NaF.

The first decomposition tests were made by passing UF_6 gas (100%) through a weighed 12-20 mesh NaF bed for various times, evacuating to eliminate excess UF_6 , and reweighing. Because of poor heat transfer in the vacuum, below $400^\circ C$ there was some difficulty in desorbing the excess UF_6 from the NaF bed at the end of the tests. Desorption with nitrogen required too much time at the flow rates feasible. Therefore the technique was adopted of analyzing the residues for total uranium and U(IV), and calculating the weight increase on the basis that the difference between the two values was due to U(V).

2.0 ZIRCEX PROCESS

In the Zircex process, uranium-zirconium fuel elements are treated with HCl, which converts the zirconium to $ZrCl_4$. This sublimes, leaving uranium chloride for further processing.

2.1 Chemical Studies on Hydrochlorination Reaction (J. E. Savolainen)

Nature of Uranium Compound. The Cl/U ratio in the uranium chloride residue was found to be 3.04/1, indicating that the uranium is present as UCl_3 . X-ray diffraction patterns showed there was no UCl_4 present. Since UCl_3 has a vapor pressure of only 3.5×10^{-3} mm Hg at $750^\circ C$ and does not melt until it reaches $842^\circ C$, operating temperatures of $700^\circ C$ probably can be safely used in the process.

Distribution of Fission Products in Hydrochlorination of Zirconium-Uranium Alloy. Results of hydrochlorination of two samples of irradiated SFR fuel element at $330^\circ C$ indicated that the uranium is decontaminated from zirconium and niobium, and somewhat from cesium. The percentages of the various radioisotopes remaining with the nonvolatile product were:

Gross β	52, 59	Cs γ	56, 41
Gross γ	23, 35	TRE β	99, 99
Ru γ	98, 95	Sr β	100, 100
Zr γ	2, 12	Zr	1.4, 7.2
Nb γ	5, 42	U	99.8, 99.9

A small portion of the fuel specimen did not react in run 2. This incomplete reaction is reflected in the high zirconium and niobium activities.

The plutonium activity was too low to make a reliable analysis. The results indicate that the plutonium remains with the uranium.

Effect of Temperature on Hydrochlorination Rate of Zirconium-Uranium Alloy. The hydrochlorination rate of 97.89% uranium--2.11% zirconium alloy was shown to depend on the temperature:

$300^\circ C$	0.172 mg/cm ² /min
315	0.326
350	0.545
370	0.835

These rates were determined in a horizontal tube laboratory hydrochlorinator. The HCl flow rate was maintained sufficiently high that an excess of HCl was present at all times. A single small piece of alloy was used to prevent excessive heating during hydrochlorination. No increase in the temperature was observed with the thermocouple adjacent to the alloy specimen when the hydrochlorination started.

Effect of Hydrochlorination Temperature on Retention of Uranium by Insoluble Residue from Zirconium-Uranium Alloy. The dilute nitric acid--insoluble residue remaining after the hydrochlorinated uranium product was dissolved from an STR fuel element was identified by x-ray diffraction to be zirconium carbide and zirconium oxide. The oxide exists in both the cubic and monoclinic forms. The amount of uranium retained by the insoluble residue remaining after the uranium product was dissolved from an STR hydrochlorination run increased as the hydrochlorination temperature increased:

Temp. (°C)	Insoluble (% of total residue)	Uranium (% of total processed)	
		In Residue	Sublimed with $ZrCl_4$
330	1.96	1.35	0.048
370	1.34	3.03	0.039

The amount of uranium sublimed with the $ZrCl_4$ was not greatly affected by the increase in temperature.

Effect of Alloy Composition on Hydrochlorination Rate of Uranium. The presence of low concentrations of silicon did not materially change the hydrochlorination rate of uranium metal. At 330°C the observed hydrochlorination rate of uranium was 0.14 mg/cm²/min. At the same temperature, a 1% silicon--99% uranium alloy reacted at 0.1 mg/cm²/min and a 2% silicon alloy at 0.18 mg/cm²/min.

Hydrochlorination of APFA Fuels. The weight loss from a 2-cm-long section of an APFA fuel pin (zirconium-clad molybdenum-uranium alloy) on hydrochlorination at 330°C was 366 mg in 30 min. The zirconium cladding weighed about 165 mg. Presumably the 4-mil zirconium cladding is removed rapidly at the start of the hydrochlorination. Further hydrochlorination of the molybdenum-uranium core of the pin showed that 15 hr would be required for complete hydrochlorination of the core at 330°C, and 9 hr at 370°C.

Hydrochlorination of Thorium Metal. A specimen of thorium metal was hydrochlorinated at 330°C at a rate of 2.72 mg/cm²/min. The nonvolatile $ThCl_4$ product formed granules which fell free from the metal surface.

2.2 Recovery of Zirconium Tetrachloride Powder (L. A. Lee, M. A. Welt, MIT Practice School)

The particle size of zirconium tetrachloride condensed from the product vapor from a Zircex hydrochlorinator is increased by increasing the temperature

at which the condensation takes place. A simple cooler to condense the zirconium tetrachloride followed by two cyclone separators and a trap were sufficient to recover essentially all the zirconium tetrachloride. The particle size and distribution were obtained by measuring and counting photomicrographs of the product.

2.3 Heat Transfer in Hydrochlorination of Zirconium-Uranium Alloy (R. J. McNamee)

Calculations indicate that the most serious heat-transfer problem associated with hydrochlorination of zirconium-uranium alloys is the adequate transfer of heat from the fuel element as it reacts. Immediate experiments with 0.5-kg quantities of zirconium are planned to measure the temperature of the reaction and the resulting heat transfer. The calculation was based on hydrochlorination of one STR fuel assembly (17 fuel plates, two end plates). For simplification it was considered to be all zirconium; actually, it contains 1% uranium. For the reaction

$$\text{Heat of reaction} = -230 - (-88) = -142 \text{ kcal/mole Zr}$$

The fuel assembly weighs 27 kg which is 296 moles of zirconium. Therefore,

$$\text{Heat evolved in reaction} = (296)(142) = 42,032 \text{ kcal}$$

Heat will be removed in heating the product gases from the base reaction temperature, 25°C, to the maximum operating temperature, 500°C, and in vaporizing the ZrCl_4 .

$$\text{Heat of sublimation} = (296 \text{ moles})(25.29 \text{ kcal/mole}) = 7,486 \text{ kcal}$$

$$\text{Sensible heat} = (296 \text{ moles } \text{ZrCl}_4)(22 \text{ cal/mole/}^\circ\text{C})$$

$$(475^\circ\text{C}) = 3,093 \text{ kcal}$$

$$(592 \text{ moles } \text{H}_2)(7 \text{ cal/mole/}^\circ\text{C})(475^\circ\text{C}) = 1,968 \text{ kcal}$$

$$\text{Total} \quad 12,547 \text{ kcal}$$

Net heat to be removed by cooling reaction vessel =

$$42,032 - 12,547 = 29,485 \text{ kcal}$$

Rate of attack (determined in laboratory-scale studies) = 3 mg/cm²/min

$$\frac{0.003 \text{ g/cm}^2/\text{min}}{6.4 \text{ g/cm}^3} = 0.000469 \text{ cm/min}$$

The fuel plates are 87 mils thick, or 0.22 cm. Therefore, since the attack

will be from both sides of the plate, the reaction will take

$$\frac{0.11 \text{ cm}}{0.000469 \text{ cm/min}} = 235 \text{ min, or 4 hr}$$

$$\begin{aligned} \text{Heat to be removed through wall of reaction vessel} &= \frac{29,485,000 \text{ cal}}{(4 \text{ hr})(252 \text{ cal/Btu})} \\ &= 29,251 \text{ Btu/hr} \end{aligned}$$

The amount of heat, q , that can be radiated from the fuel element at 500°C , the maximum allowable temperature, to the wall of the reaction vessel at 330°C is

$$q = \sigma F_e F_s A_1 (T_1^4 - T_2^4)$$

where σ is the Stefan-Boltzmann constant, F_s is the shape factor and equals 1 for a completely enclosed body such as that considered here, and F_e is a factor to allow for departure of radiating and receiving surfaces from complete blackness. The emissivities of the fuel element and the wall of the vessel, ϵ_1 and ϵ_2 , respectively, are related to these factors by

$$\epsilon_1 > F_e > \frac{1}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1}$$

The emissivity value for Inconel, the material of the vessel wall, is ~ 0.4 and for zirconium at 500°C is 0.18. Therefore

$$F_e = 0.16$$

It is assumed that only the outer plates will radiate to the wall; the inner plates will radiate to each other. The area of the assembly, A_1 , is

$$2(3.4 \text{ in.})(47 \text{ in.}) = 319.6 \text{ in.}^2$$

$$\begin{aligned} 2(2.5 \text{ in.})(47 \text{ in.}) &= 235.0 \\ &554.6 \text{ in.}^2 \end{aligned}$$

$$A_1 = 554.6/144 = 3.85 \text{ ft}^2$$

$$\begin{aligned} q &= (0.173 \times 10^{-8})(0.16)(3.85)[(1392^{\circ}\text{R})^4 - (1086^{\circ}\text{R})^4] \\ &= 2,510 \text{ Btu/hr radiated to reaction vessel wall} \end{aligned}$$

Since the ZrCl_4 will leave the vessel as a gas, rather than as a solid as considered in the equation, the heat that must be removed from the fuel element is

$$42,032 - 7,486 = 34,546 \text{ kcal}$$

$$\frac{34,546,000}{(4)(252)} = 34,272 \text{ Btu/hr}$$

Therefore, $2,510 \times 100/34,272 = 7.3\%$ of this heat will be removed by radiation

$29,251 - 2,510 = 26,741$ Btu/hr will have to pass through the gas film on the inner side of the reaction vessel wall.

From an empirical equation for natural convection, it is found that the gas-film heat-transfer (convection) coefficient, h_c , is equal to 2.4 Btu per hr/ft²/°F. The heat that must pass through the gas film on the inner wall of the reactor, Q , is given by

$$Q = h_c A \Delta t$$

where A is the heat transfer area required and Δt is the temperature difference across the gas film.

$$A = 26,741/2.4(500-330)(1.8) = 36.4 \text{ ft}^2$$

Since the gas film will be controlling, the flow of heat through it will determine the area necessary. The proposed reaction vessel 8 in. dia and 6 ft high would give 12.56 ft², so with fins or a slightly larger reaction vessel (i.e., 2 by 6 ft), the necessary area could be obtained. Therefore, the problem is not getting the heat out of the reactor, but rather getting it away from the fuel element.

Consider that for every mole of HCl which reacts, 0.25 mole of zirconium also reacts, producing

$$(142,000 \text{ cal/mole})(0.25 \text{ mole}) = 35,500 \text{ cal}$$

together with 0.25 mole of ZrCl_4 and 0.5 mole of H_2 . Assume that the reaction takes place at 300°C (the heat of reaction can be shown to be essentially constant with temperature) and that the limiting temperature of the zirconium and the gas is 500°C to prevent volatilization of UCl_3 . Let HCl enter at room temperature (25°C), and the zirconium be initially preheated to 300°C.

$$\text{Heat of sublimation} = (0.25 \text{ mole})(25,290 \text{ cal/mole}) = 6,322 \text{ cal}$$

Considering the ZrCl_4 leaving the reaction as a gas, the resultant heat produced by the reaction is 29,178 cal.

$$\text{Heat used in heating HCl to } 300^\circ\text{C} = (1 \text{ mole})(6.58 \text{ cal/mole}/^\circ\text{C})(300-25^\circ\text{C}) = 1,809 \text{ cal}$$

$$\text{Heat used in heating } \text{ZrCl}_4 \text{ to } 500^\circ\text{C} = 0.25 \times 22 \times 200 = 1,100$$

$$\text{Heat used in heating } \text{H}_2 \text{ to } 500^\circ\text{C} = 0.5 \times 7 \times 200 = 700$$

$$\text{Total } 3,609 \text{ cal}$$

Thus, only about 12% of the heat can be removed by the stoichiometric reaction gases. Unless radiation is considerably greater than calculated above, large quantities of an inert gas will have to be added to remove the heat from the fuel element. Otherwise, the temperature will rise considerably above 500°C. A 6-in.-dia hydrochlorinator is being designed to investigate this problem.

3.0 HERMEX PROCESS

The Hermex process is a means of processing uranium by dissolving it in mercury and separating the uranium from the amalgam thus formed by physical methods such as distillation and pressing.

4.1 Dissolution Studies (O. C. Dean, E. Sturch)

Magnesium Amalgam Solvent. Uranium dissolved in boiling 0.1 wt % magnesium amalgam about twice as fast as in mercury alone. The saturation solubility was about 6.5 wt %. When the magnesium concentration of the amalgam was increased to 0.3 wt %, the dissolution rate increased and the saturation solubility was >16%. The dissolution rate decreased with time:

Mg in Amalgam (%)	Amount Dissolved (g)			
	5 min	1 hr	7 hr	24 hr
0.1	1.4	2		
0.3		3	16	22

The runs were made with 10 ml of boiling magnesium amalgam and 15-20 cm² uranium wafers. Attempts to dissolve uranium in 0.5 wt % magnesium amalgam indicated both increased saturation solubilities and increased dissolution rates, but frothing on heating interfered with the experiments. The uranium-magnesium amalgam solidified on cooling. There was no excessive oxidation during the dissolution.

The dissolution reaction appeared to be a composite of two first-order reactions. Data indicated a rate constant of 2.52 g Mg amalgam/cm²/min for the faster step and of 1.05 for the slower step in the equation

$$\frac{dC}{dt} = \frac{kS}{m} (C_s - C)$$

where C is the uranium concentration, in grams per kilogram of mercury; t is the time in minutes; S is the surface area in square centimeters; m is the mass of the mercury in grams; C_s is the uranium saturation concentration in grams per kilogram of mercury; and k is the specific rate constant.

Bismuth Amalgam Solvent. In boiling 1.5 wt % bismuth amalgam the uranium dissolution rate was about one-fourth that in mercury, and slightly less than that in sodium amalgam. The dissolution rate constant was 0.02 g Bi(Hg)/cm²/min. The saturation solubility was about 9 wt % uranium. The dissolutions were made with 10 ml of bismuth amalgam and a uranium wafer with a surface area of about 22 cm². The uranium dissolved completely in 24 hr. The stability of uranium-bismuth-amalgam is greater than that of uranium amalgam, and is comparable to that of uranium-sodium amalgam. There appears to be an oxide-film-like protective coating formed at the amalgam-air interface in the case of uranium-bismuth amalgam.

4.0 GENERAL DISSOLUTION STUDIES

Since nitric acid solutions are readily processed by solvent extraction methods, the aim of dissolution studies is, in general, to find a satisfactory means of obtaining a nitric acid solution of the material to be processed. This may involve jacket removal prior to dissolution of the fissionable material.

4.1 Dissolution of Zirconium (J. E. Savolainen, A. H. Kibbey)

Ferric Chloride. Dissolution rates of Zircaloy-2 in aqueous FeCl₃ and FeCl₃-NaCl solutions were too low for ferric chloride to be considered as a solvent. Ferric chloride has been reported (C. B. Golden et al., Ind. Eng. Chem. 44: 1930, 1952) to be an embrittling agent for zirconium. Two specimens of Zircaloy-2 were pickled with HF to a bright finish. One was then treated 4 hr with boiling (105°C) 30 wt % FeCl₃, the other with boiling (108°C) 30 wt % FeCl₃--10 wt % NaCl. Both reagents slightly dulled the bright finish. Both specimens were then treated with boiling 8.6 M HCl--2.9 M HNO₃ for 24 hr, which dulled the finish further. Dissolution rates were:

<u>Specimen</u>	<u>Reagent</u>	<u>Rate</u> <u>(mg/cm²/min)</u>	<u>Reagent</u>	<u>Rate</u> <u>(mg/cm²/min)</u>
1	30 wt % FeCl ₃	0.0043	8.6 M HCl --2.9 M HNO ₃	0.021
2	30 wt % FeCl ₃ --10 wt % NaCl	0.0074	Same	0.0057

Concentrated HCl and Aqua Regia. The rate of dissolution of Zircaloy-2 in concentrated HCl was increased by boiling under reflux:

12 M HCl, 25°C	4 x 10 ⁻⁵ mg/cm ² /min
12 M HCl, boiling under reflux	8 x 10 ⁻⁴ mg/cm ² /min

The dissolution rate in aqua regia (5 M HCl--9 M HNO₃) was increased by boiling and adding small amounts of concentrated HCl or HNO₃ to a total of 100 ml, over a 1-hr period:

5 M HCl--9 M HNO ₃	25°C	4×10^{-5} mg/cm ² /min
5 M HCl--9 M HNO ₃ ; adding conc. HNO ₃	Boiling	1.5×10^{-2}
5 M HCl--9 M HNO ₃ ; adding conc. HCl	Boiling	1.4×10^{-1}

Hydrofluoric Acid Systems. The possibility of dejacketing fuel elements having thin zirconium or Zircaloy-2 cladding by hydrofluoric acid prior to core dissolution in nitric acid was studied. Room temperature dissolution rates for zirconium in 1 M HF and in 1 M HF--1 M HNO₃ solutions were ~0.2 mg/cm²/min. When the dissolvent was 1 M HF--1 M HNO₃--1 M HCl, the rate was qualitatively observed to be rapid, and the reaction proceeded until the amount of zirconium dissolved was approximately stoichiometrically equivalent to the amount of fluoride present.

Sulfuric Acid. Sulfuric acid may be used to dissolve zirconium or Zircaloy-2 cladding from UO₂ fuel elements. A 5.85-g specimen of PWR fuel (Zircaloy-2-clad UO₂) was dissolved in a large excess (~1800%) of boiling 14 M H₂SO₄ under reflux. Initially finely divided black zirconium metal and free sulfur formed in the dissolver solution. However, after 4.5 hr digestion, all the finely divided metal had dissolved and the solution was pale yellow-green and water clear; the free sulfur had sublimed off and was solidified in the condenser. Analysis of the solution for zirconium and uranium indicated that the uranium loss to the dissolver solution was ~0.18%. The cladding solution contained 0.0356 mg of uranium per milliliter.

Sulfuric acid also appears suitable for dissolving the zirconium cladding from 10% molybdenum--90% uranium cores. The proposed APDA fuel element has a 0.150-in.-dia 10% molybdenum--90% uranium alloy core, and a 0.004-in.-thick zirconium metal cladding. The thin zirconium cladding was removed by dissolution in 900% excess 14 M H₂SO₄, assuming the formation of ZrOSO₄, or 100% excess 10 M HF, assuming formation of ZrF₄. The core was subsequently dissolved in 8 M HNO₃ and would be adjusted to 2 M HNO₃ prior to solvent extraction. The gray insoluble residue contained approximately 1/2 and 1/4, respectively, of the molybdenum and zirconium present, but only 0.014% the total uranium. The amounts of the various reagents required per kilogram of fuel and the adjusted solvent extraction feed composition calculated for each system are:

Cladding Dissolution System	Amount of Reagent (liters/kg feed)			Solvent Extraction Feed Composition
	Cladding Dissolution	Core Dissolution (8 M HNO ₃)	Feed Adjustment (16 M HNO ₃)	
900% excess 14 M H ₂ SO ₄	0.288	4.386	0.688	Free NO ₃ ⁻ = 2.0 M SO ₄ ²⁻ = 0.75 M Zr ⁴⁺ = 0.075 M UO ₂ (NO ₃) ₂ = 0.678 M Mo = 0 M
100% excess 10 M HF	0.322	4.386	0.672	Free NO ₃ ⁻ = 2.0 M F ⁻ = 0.60 M Zr ⁴⁺ = 0.075 M UO ₂ (NO ₃) ₂ = 0.676 M Mo = 0 M

The 900% excess 14 M H_2SO_4 is the optimum amount, determined at Idaho (IDO-14035). Molybdenum precipitated quantitatively, as molybdic acid, in the solvent extraction feed. A concentration of 0.75 M sulfate in the solvent extraction feed is high but is permissible. The fluoride ion concentration of 0.30 M, not complexed by zirconium, is undesirable from the standpoint of corrosion. Dilution of these feeds with more nitric acid to minimize the deleterious effects of the sulfate or the addition of $Al(NO_3)_3$ to reduce the corrosive effect of fluoride would not only dilute the uranium, but would also increase the volumes of aqueous waste to be stored.

In laboratory experiments in which the zirconium cladding was removed from BTR fuel elements with 450% excess of 14 M H_2SO_4 , assuming the formation of $Zr(SO_4)_2$, free sulfur (crystalline and amorphous), SO_2 , and H_2S were obtained as end-products of the reaction. This indicates the need for a fairly complicated off-gas system if H_2SO_4 is used as the dissolvent for removing the zirconium cladding from fuel elements.

Leaching of Cores. Mechanical chopping of AFDA fuel pins into 3/8- to 1/2-in. lengths would make possible the selective dissolution of the core material. Pieces of zirconium-clad AFDA fuel (10% Mo-U core) 2 to 3 times as long as their diameters (0.15 in.) were boiled in 8 M HNO_3 for 13 to 93 min. At 13, 30, and 45 min, the dissolution rates of the core material were, respectively, 85.9, 95.3, and 108.0 mg/cm²/min. At the end of 93 min, the core was completely disengaged from the cladding. Deposits of molybdic acid, which would hinder dissolution of the alloy, did not form.

4.2 Silicon-Uranium Alloy (J. E. Savolainen, A. H. Kibbey)

The boiling point dissolution rates of 2% silicon-uranium alloy in 6 M and 14 M H_2SO_4 and in 8 M HNO_3 were determined to be 0.052, 0.11, and 22.95 mg/cm²/min, respectively. These results, together with data previously reported (ORNL CF No. 56-6-101, p. 15) for 0.5 and 1% silicon-uranium alloys are:

Si in Alloy (%)	Dissolution Rate (mg/cm ² /min)		
	6 M H_2SO_4	14 M H_2SO_4	8 M HNO_3
0	0.032	0.258	---
0.5	0.043	---	58.15*
1	0.064	---	76.74*
2	0.052	0.11	22.45

* Decreased rapidly owing to adherent SiO_2 deposit on the surface.

A 6-g sample of 2% silicon-uranium alloy was completely dissolved in boiling 8 M HNO_3 under reflux. The insoluble silica residue which was removed and washed by centrifugation contained 0.011% of the total uranium present.

4.3 Stainless Steel--containing Fuel (J. E. Savolainen, A. H. Kibbey)

Aqua Regia. A prototype AFDA blanket element of stainless steel--clad--stainless steel core bonded with sodium metal dissolved rapidly in excess 2 M HCl--5 M HNO₃ at 60-80°C. The 17.3-g sample dissolved completely in less than 24 min. The cladding was penetrated in approximately 1 min, after which time a series of brilliant flashes occurred as the sodium was exposed to the aqueous solution. The dissolver solution was orange-brown rather than green, indicating that the dissolved chromium was being oxidized to the hexavalent state; the color obtained in previous similar runs had indicated the presence of trivalent chromium. The reaction is not considered to be so violent as to prohibit processing of this type of material by dissolution in acid.

4.4 Removal of Chloride from Aqua Regia Dissolver Solutions

Continuous Chloride Removal (J. E. Savolainen, M. L. Hyman). If a process for dissolution of stainless steel fuel elements in aqua regia is to be feasible, a method must be devised to remove the chloride from the dissolution product prior to solvent extraction. This removal is necessary to prevent corrosion of the stainless steel processing equipment and to avoid the adverse effect which chloride exerts on uranium extraction in the nitrate system.

A continuous distillation column was successfully used to strip chloride from a synthetic APPR dissolver solution originally containing 70 g of stainless steel and 16.8 g of uranium per liter and 2.4 N in HCl.

The column feed was diluted fourfold and fed into the top of the column at D/F = 2. The stripping vapor, which was 15.2 M HNO₃, was generated in an external reboiler. The stripped feed, collected as the column bottoms in a separate receiver, contained <10 ppm chloride and all the uranium in the feed. The distillate recovered 90% of the chloride in the feed. A second run, using the same feed solution, but with a D/F = 3, again gave complete recovery of the uranium in the stripped bottoms. However, in this case only 81% of the chloride was recovered in the distillate.

There was no evidence of "denitration" of the UO₂(NO₃)₂ even at the 115-120°C temperatures encountered in the column.

Proposed Chloride Removal Flowsheet (C. D. Watson, F. G. Kitts, H. F. Johnson). A proposed removal scheme (Fig. 1) would allow recovery and recycle of the concentrated acids. In order to design a distillation system for the separation of hydrochloric acid from the aqua regia solution, vapor-liquid equilibrium data for the ternary aqua regia system are necessary. Such data have recently been obtained by an MIT Practice School group, and are being correlated. The data will apply to the aqua regia separation column. The effect of salts on the data is not known, but will be determined before the initial separation column is designed.

Fig. 1. Proposed Flowsheet for Aqua Regia Dissolution of Stainless Steel-containing Fuel Elements, Showing Removal of Chloride from Dissolver Solution.

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5.0 MECHANICAL DEJACKETING AND HANDLING STUDIES

5.1 Mechanical De jacketing Studies (C. D. Watson, G. A. West, F. G. Kitts)

Methods of mechanically decladding spent power reactor fuels are being investigated to (1) expose spent fuel cores soluble in nitric acid, (2) prevent solids buildup in dissolvers, and (3) eliminate storage of diluent materials as aqueous waste.

A Mackintosh-Hemphill model AXY rotary straightener machine (Fig. 2) has been ordered to demonstrate jacket removal by a rolling operation. This machine is capable of handling cylindrical fuels from 3/8 to 1 in. o.d. and 18 in. in length and longer. These diameters cover the range of the proposed fuel rods, including the Na-K bonded fuels. This machine has three top and three bottom rolls, which are offset. The jacket is expanded by an offset cross-roll pass between two fixed cross-roll passes.

5.2 Discharging Solids from a Dissolver (G. A. West, F. G. Kitts, C. D. Watson)

Present processing plants cannot process stainless steel-- or zirconium-clad uranium unless a method is developed for discharging the solids from the dissolver. Three methods are being considered: (1) continuous removal with spiral vibratory conveyors, (2) batch basket removal, and (3) batch fluidization. The spiral vibratory conveyor is currently being investigated. The Carrier Conveyor Corp. and the Syntrol Company are submitting proposals of their units for (1) continuous trickle dissolution (Fig. 3) with constant or intermittent discharge of solids and (2) countercurrent leacher (Fig. 4), either trickle or flooded, with constant discharge of solids. Removal of solids by a perforated basket in batch operations would require shutdown and breaking of process lines and dissolver openings and then effecting a leaktight seal in assembly.

A spiral vibratory conveyor mounted vertically could be operated as a continuous countercurrent leacher or a continuous trickle type dissolver (Fig. 5). An immediate problem in the operation of such a piece of equipment is a heat-, acid-, and radiation-resistant, vapor-tight flexible connector for process lines. A stationary vapor-tight outer housing with process lines welded through and extending into the leacher itself through slots large enough to allow the necessary vibratory motion is being studied for this purpose.

5.3 Experimental Handling Mechanical Facility (C. D. Watson, F. G. Kitts)

The facility (ORNL CF. No. 56-6-101, Fig. 2) to demonstrate the removal of auxiliaries, de jacketing and shearing of various fuel elements has been redesigned. Major changes are the inclusion of a traveling saw

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Fig. 2. Diagram of Mackintosh-Hemphill Machine

Fig. 3. Continuous Trickle Dissolver

Fig. 4. Countercurrent Leacher.

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Fig. 5. Vibratory Dissolver with Solids Discharge

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complete with feed and delivery tables, and the in-line arrangement of the machines (Fig. 6). End portions of rods up to 12 ft long can be removed by the saw and rods of any length can be run through the derodder, the limiting factor being the clearance at the ends of the machine. Entry and delivery tables will be provided which will accommodate rods up to 10 ft long. Continuous tabling will be used to facilitate transfer of materials from one machine to another with a minimum of stress on the manipulators. The area will be serviced by a pair of Argonne Model 8 manipulators mounted on carriers rolling atop the 3-ft-thick simulated shielding wall.

6.0 MATERIALS EVALUATION

(C. D. Watson, G. A. West)

Corrosion tests are in progress to evaluate materials of construction for the reprocessing of power reactor fuels by the aqua regia and the hydrochlorination dissolution systems. Materials selected for the aqua regia corrosion test are titanium, tantalum, durichlor, hastalloy F, and glass-lined steel. The test specimens were placed in the vapor phase, interface, and liquid of the aqua regia which is 2 N HCl--5 N HNO₃ at boiling (110°C). It is planned to spike the solution with stainless steel and uranium as the second and third phase of the test program. The current test with straight aqua regia indicates tantalum to have superior resistance. Titanium and glass-lined steel were mildly attacked and durichlor was severely attacked by the vapor. Inconel showed practically no corrosion with 70% HNO₃ at room temperature (27°C) in over 600 hr. This test is being conducted to determine the effect of adding HNO₃ to the hydrochlorination system. (see table).

A "side" test was conducted to determine the corrosion of sensitized and unsensitized types 302 and 304 stainless steel spraypak material. The spraypak was sensitized 1 hr at 1250°F. The corrosion rates by the ASTM boiling 60% HNO₃ test on the sensitized types 302 and 304 stainless steel were 64.8 and 30.4 mils/month, respectively. The unsensitized types 302 and 304 stainless steel corrosion rates were 1.24 and 1.13 mils/month, respectively.

MWG:jgh

NOTE: A preliminary report on this subject, CF 56-5-48, (35¢) and progress for May, CF 56-5-101, (25¢) and June, CF 56-6-101 (30¢) have been issued. Progress for August will be reported in CF 56-8-101 (30¢).

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Fig. 6. Experimental Handling Facility

Corrosion of Materials of Construction for Power Reactor Fuel Reprocessing

Conditions: Test specimens (a) disks 1 in. dia x 1/4 in. thick with 3/16 in. dia hole in center (b) plates 1 in. wide x 2 in. long x 1/8 in. thick; contained in 2-liter pyrex flasks with reflux condensers; new solution added each 48 hr period and specimens electrolytically defilmed with a Na_2CO_3 solution before weighing.

Material	Specimen Position	Corrosion Rate (mils/month)		No. of 48-hr Periods
		Max	Avg	
Boiling (109°C) 2 N HCl--5 N HNO ₃				
Titanium 55-A	Vapor	1.18	0.54	11
	Interface	2.24	1.59	11
	Liquid	3.77	2.35	11
Tantalum	Vapor	0	0	13
	Interface	0	0	13
	Liquid	0	0	13
Durichlor	Vapor	447	206	1
	Interface	7.42	2.52	5
	Liquid	3.34	2.07	5
Pfaudler No. 53 Glass-lined steel	Liquid	2.36	0.78	5
Hastelloy F	Vapor	191	127.8	1
	Interface	23	18.9	1
	Liquid	12.8	11.4	5
70% HNO ₃ at 27°C				
Inconel	Liquid	0.86	0.28	5
Boiling 60% HNO ₃ (119°C)				
302 stainless steel				
Sensitized	Liquid	67.5	64.8	2
Unsensitized	Liquid	1.32	1.24	5
304 stainless steel				
Sensitized	Liquid	30.7	30.4	2
Unsensitized	Liquid	1.32	1.13	5

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