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NEW LABORATORY DEVELOPMENTS IN THE ZIRCEX PROCESS

T. A. Gens
R. L. Jolley

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

A new Zircex flowsheet is proposed in which the nonvolatile products from hydrochlorination of uranium-zirconium alloys are chlorinated with carbon tetrachloride, thereby avoiding the loss of 1-6% of the uranium observed in engineering development studies of the older flowsheet for STR fuel in which the hydrochlorination residue was dissolved in nitric acid. Other potential advantages of the new flowsheet include decreased corrosion and elimination of possible explosions between uranium-zirconium alloys and nitric acid. The uranium may be recovered by aqueous dissolution and solvent extraction or by gas-phase fluorination at 200-400°C of uranium chlorides.

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1.0 INTRODUCTION

The Zircex process is based on the use of hydrogen chloride gas at 350-800°C to convert uranium-zirconium alloys to volatile zirconium chloride and relatively nonvolatile uranium trichloride (1,2). The outstanding advantage of the process over aqueous dissolution is the separation of zirconium from uranium during hydrochlorination. The purpose of the work reported here was to attack three unsolved problems that were apparent in the Zircex process after analysis of a series of engineering-scale demonstration runs (1): (a) 1-6% uranium loss to the nitric acid--insoluble residue that remained after leaching the products of hydrochlorination of Submarine Thermal Reactor (STR) fuel (1% uranium-97% zirconium-2% tin)in nitric acid; (b) excessive corrosion in the hydrochlorinator of all materials of construction tested (3), caused by the cyclic use of hydrogen chloride gas at temperatures of up to 600°C and boiling nitric acid; and (c) the possiblility of explosive reactions resulting from the contact of nitric acid with certain uranium-zirconium alloys if hydrochlorination should be incomplete. The use of carbon tetrachloride to chlorinate and volatilize all the products, including uranium chloride, remaining in the reactor after hydrochlorination was investigated as a method of attacking simultaneously these three problems, and a new flowsheet is proposed.

Chlorination of zirconium oxide with carbon tetrachloride gas at 550-600°C was found to be superior to other methods of chlorination in a study at the Oak Ridge Y-12 plant (4). Oxides of uranium and plutonium have also been converted to chlorides with carbon tetrachloride (5-7). The use of carbon tetrachloride gas has been recommended previously as a method of recovering uranium from the residue remaining after leaching the Zircex hydrochlorination products in nitric acid (2). The conversion of uranium chloride in the Zircex hydrochlorination product to uranium hexafluoride with fluorine gas at 160-300°C has been demonstrated previously (8).

Further work will be required to test the process on a larger scale, to develop a satisfactory method for removing and disposing of the zirconium tetrachloride from the off-gas stream,to outline the conditions for a suitable uranium solvent extraction procedure, and to determine the distribution of fission products in the process. Extensive corrosion tests are underway to find a material of construction sufficiently resistant to carbon tetrachloride vapor at high temperatures.

The laboratory work was performed by G. E. Woodall, D. M. Helton, and E. R. Johns. Analytical work was performed by W. Laing, G. Wilson, and A. D. Horton of the Analytical Chemistry Division. Corrosion tests were planned by W. E. Clark of the Chemical Technology Division and run by E. S. Snavely, L. Rice, and co-workers of the Reactor Experimental Engineering Division. Equipment constructed of metal was designed and procured by J. W. Brown and T. A. Arehart of the Chemical Technology Division.

2.0 FLOWSHEET

Several changes were introduced in the Zircex flowsheet (1,2) by the use of carbon tetrachloride to convert all products remaining in the reactor after hydrochlorination to volatile chlorides from which >99.9% of the uranium is recoverable (Fig. 2.1). An alloy resembling the PWR seed (6.3% uranium-93.7% Zircaloy) (9) was used in this work, rather than an alloy of the STR composition (1% uranium-99% Zircaloy) used in previous larger scale work, to permit more accurate uranium determinations. The results of several flowsheet runs are listed in Table 2.1.

The first operation is hydrochlorination at about 600°C (fuel element temperature) as in the previous Zircex flowsheet. This portion of the new flowsheet is based on previous work (1), in which it was observed that hydrochlorination removed about 97% of the zirconium from the reactor in the case of STR fuel and that 1-10% of the uranium chloride was sublimed or entrained in the off-gas. The residual zirconium was in the form of nonvolatile zirconium oxide or oxychloride. The amount of nonvolatile zirconium compounds produced will vary with the amount of oxygen or oxygen-containing impurities introduced with the hydrogen chloride or dissolved in the fuel alloy.

The products remaining in the reactor after hydrochlorination are completely volatilized from the reactor during chlorination with carbon tetrachloride in nitrogen carrier gas at 500-600°C (10). Uranium chloride gas from both hydrochlorination and chlorination is selectively condensed at 300°C and removed from the condenser by dissolution in water or nitric acid or by fluorination to form uranium hexafluoride. Since nitric acid is not introduced into the reactor, the corrosion problem is decreased and potential explosions with unreacted alloy in the reactor are avoided. Over 97% of the zirconium passes through the 300°C condenser and is condensed and disposed of separately. A uranium loss of less than 0.1%, occurring by passage of some uranium chloride through the 300°C condenser, was observed.

A brief burnoff with air of the carbon deposited during chlorination may be necessary (Table 2.1 and Sect. 4.1). In the flowsheet runs (Table 2.1), air was admitted for 5 min halfway through and again after chlorination. After these runs no carbon was found in the reactor or the condenser, but a small amount of carbon was observed mixed with zirconium chloride at the cool exit from the condenser (Fig. 4.1).

Chloride may be removed from the Zircex product solution, by dissolving the anhydrous chlorides in 13 M HNO_3, by methods developed in the Darex process (2) which involve chloride distillation from concentrated nitric acid solution (Sect. 4.4).

The small volume of the Zircex product solution may make it necessary to take special precautions to remove fission product heat. For example, 3 kw of heat, which is approximately the heat absorption expected from fission product decay, could raise the temperature of the Zircex product solution 10°C per hour and evaporate 5 liters of water per hour at the boiling point. Nearly all the fission products will probably be

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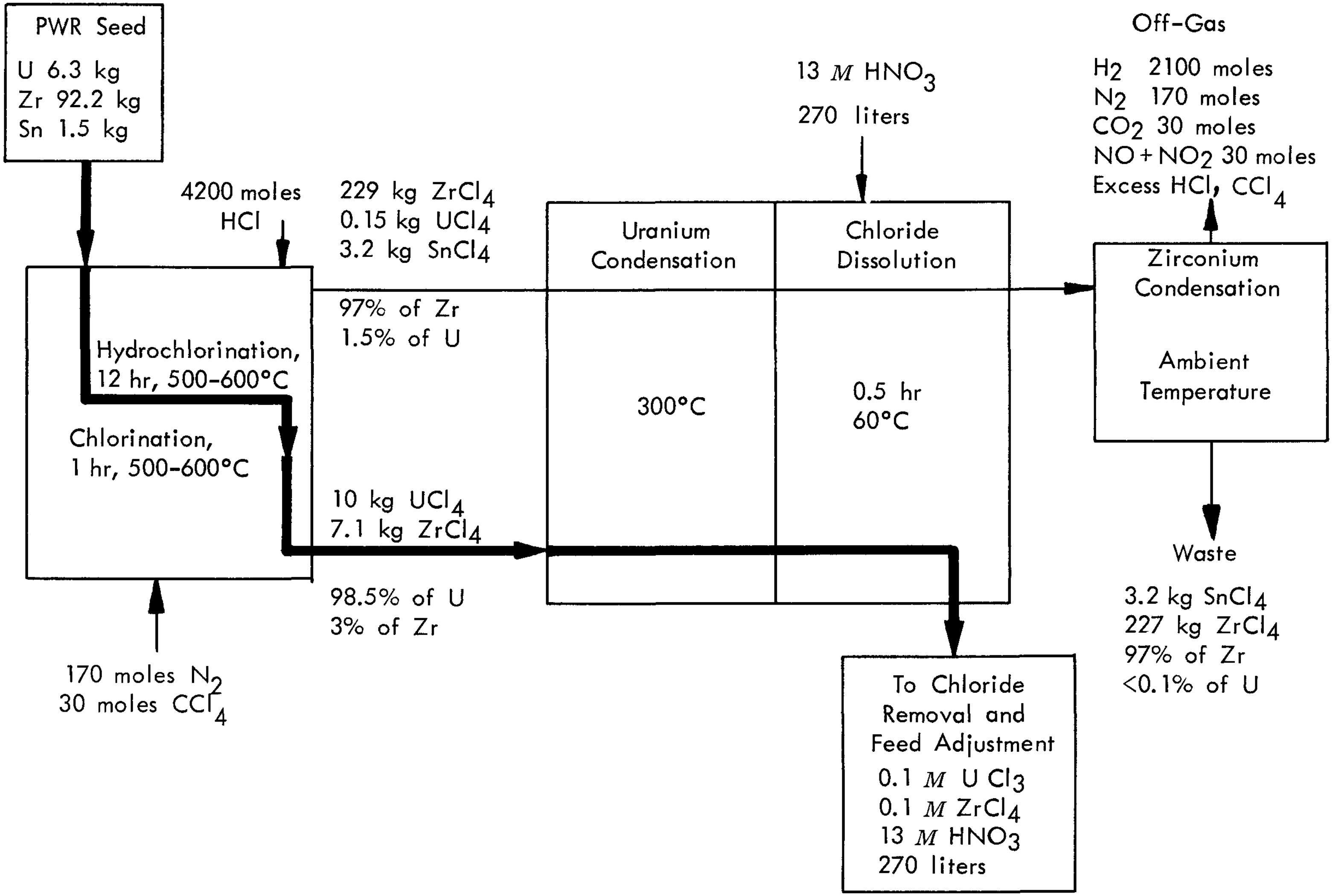

Fig. 2.1. Modified Zircex process: gas phase hydrochlorination of PWR seed followed by chlorination with carbon tetrachloride.

moved from the reactor to the uranium condenser and some, such as niobium and zirconium, to the zirconium condenser by vaporization or entrainment. Experiments with irradiated uranium-zirconium alloys will be required to determine the distribution of fission products, and, particularly, whether any fission products remain in the reactor.

Table 2.1 Zircex Flowsheet Runs with CCl_4

Sample weights: 2-4 g (70 mils thickness)
Alloy composition: 7% uranium—93% zirconium
Condenser temperature: 300°C
Times: hydrochlorination, 2 hr at 600°C; chlorination, 1 hr at 600°C; air oxidation, 0.2 hr at 600°C

Run No.	U Condenser Packing	Percent Found in U Condenser[b]		Percent Found in Zr Condenser[b]	
		U	Zr	U	Zr
6	Glass wool[a]	99.9	2.5	0.1	97.5
11	Copper turnings	99.99	1.1	0.01	98.9
15	Copper turnings	99.99	0.1	0.01	99.9
20	Nickel wire	99.9	0.15	0.1	99.85

[a] Glass wool may be used only when nitric acid is used (Fig. 2.1) to dissolve the chlorides in the uranium condenser. Copper and nickel were investigated primarily for uranium recovery by fluorination but might prove satisfactory if water, rather than nitric acid, is used to dissolve the chlorides in the uranium condenser.

[b] No measurable quantities of uranium or zirconium were found in the reactor.

3.0 CHEMISTRY OF THE PROCESS

In hydrochlorination 4 moles of hydrogen chloride is required per mole of zirconium and 3 per mole of uranium:

$$Zr + 4\ HCl \longrightarrow ZrCl_4 + 2\ H_2 \qquad (1)$$

$$U + 3\ HCl \longrightarrow UCl_3 + 1.5\ H_2 \qquad (2)$$

Some uranium tetrachloride is also produced (1). Since a large amount of hydrogen is also produced (2100 moles/100 kg of fuel), precautions must be taken against explosions. Carbon tetrachloride is used to chlorinate the zirconium oxide or oxychloride (4) residue, and any uranium oxide (5-7) that may be present:

$$ZrO_2 + CCl_4 \longrightarrow ZrCl_4 + CO_2 \qquad (3)$$

$$ZrOCl_2 + 0.5\ CCl_4 \longrightarrow ZrCl_4 + 0.5\ CO_2 \qquad (4)$$

Uranium trichloride is thought to be converted to the more volatile uranium tetrachloride by the reaction

$$UCl_3 + 0.25\ CCl_4 \longrightarrow UCl_4 + 0.25\ C \qquad (5)$$

Reaction 5 may have produced the deposit of carbon that was burned off with air (Table 2.1). The major reaction of carbon tetrachloride and uranium dioxide reportedly (6) is

$$UO_2 + 2\ CCl_4 \longrightarrow UCl_4 + 2\ COCl_2 \qquad (6)$$

and it is probable that some phosgene is produced by a similar reaction of carbon tetrachloride with zirconium oxide or zirconyl chloride. Decomposition of phosgene,

$$COCl_2 \text{ ——— } CO + Cl_2 \qquad (7)$$

has been observed and is favored by high temperatures (6). Reaction 7 probably leads to production of a large amount of carbon monoxide, relative to the uranium present, during chlorination. The uranium chloride in the condenser always appeared to be brown uranium trichloride rather than green uranium tetrachloride (11), probably because the following reaction occurs in the condenser:

$$UCl_4 + 0.5\ CO \longrightarrow UCl_3 + 0.5\ COCl_2 \qquad (8)$$

The formation of higher molecular weight decomposition products of carbon tetrachloride, which can occur in liquid phase chlorinations (5,7), was not observed in this work even when pure carbon tetrachloride vapor undiluted by carrier gas was introduced into the reactor.

4.0 LABORATORY STUDIES

The main part of the equipment used in the laboratory studies consisted of two sections of 1-in.-i.d. Inconel pipe connected by Swagelok fittings (Fig. 4.1). The reactor was heated to 600°C by a clam-shell resistance furnace and the uranium chloride condenser was heated to 300°C by a second clam-shell furnace which butted against the 600°C furnace. The reactor held a porcelain boat in which the alloy specimens were placed and the condenser contained copper turnings, nickel wire, or glass wool packing to provide surface area and to filter out the uranium chlorides. Auxiliary equipment included a manifold and heater for mixing and preheating the reagent gases and an off-gas scrubber for recovering in water uranium and zirconium chlorides that passed through the condenser. Materials recovered in the 300°C area and the scrubbers were analyzed. The only material found in the 600°C area after a run was a trace of nickel chloride.

In the chlorination of products from engineering-scale hydrochlorinations (Sect. 4.1), the equipment was simplified in that the condenser was removed and a 1-in.-i.d. quartz reactor was used to permit visual observation. The uranium and zirconium chloride products were captured together at room temperature on the cool exit of the quartz tube.

Mathieson hydrogen chloride gas was used as received for the hydrochlorinations. For chlorination, a mixed gas was prepared by bubbling nitrogen or hydrogen chloride through liquid carbon tetrachloride at 25°C [vapor pressure = 116 mm (12)].

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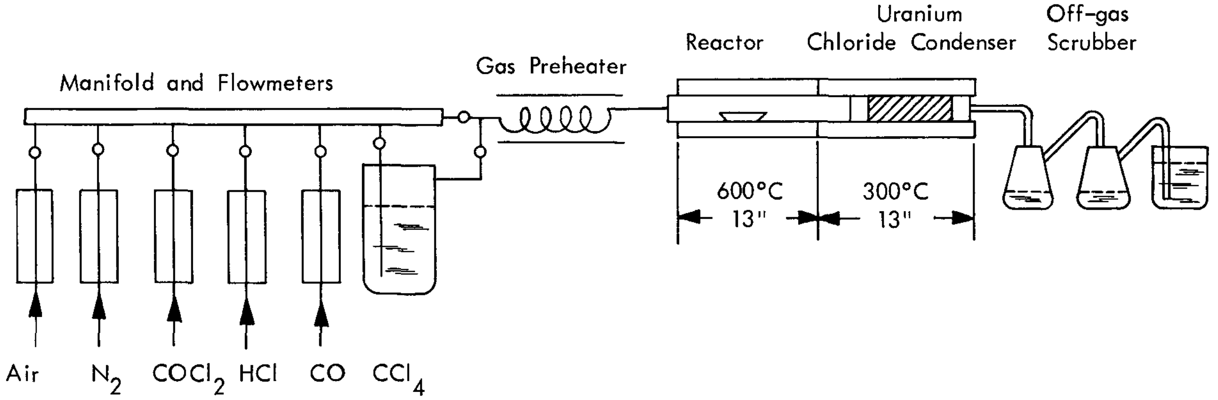

Fig. 4.1. Laboratory equipment used in Zircex hydrochlorination-chlorination experiments.

4.1 Chlorination of Products from Engineering-scale Hydrochlorinations

Samples of hydrochlorination products from three engineering-scale runs (1) were converted to volatile zirconium and uranium chlorides by treatment with carbon tetrachloride—hydrogen chloride or carbon tetrachloride—nitrogen at 550-600°C (Table 4.1) (10). Two of the products (HC76 and HC79) were from unirradiated STR fuel and one (HC82) was from unirradiated EBWR fuel. The chlorides, which collected on the cool exit of the quartz tube, dissolved completely and rapidly in warm nitric acid. In run 1, 1% of the hydrochlorination product was not converted to volatile chlorides. Spectrographic analysis indicated that the nonvolatile material contained mostly silicon and a maximum of 10^{-3}% of the total uranium. Very little reaction occurred when no carbon tetrachloride was added to the hydrogen chloride gas (run 2) or when air was used as a carrier gas (run 3). In all chlorinations except runs 5 and 8, a deposit of carbon collected on the reaction surface and appeared to inhibit the reaction slightly. It burned off immediately when oxygen was passed into the quartz tube. The residues that had not been leached in nitric acid (runs 5-8) were chlorinated in about one-third the time required to chlorinate residues that had been leached (runs 1 and 4), probably because the temperature was 600°C rather than 550°C.

4.2 Off-gas

Hydrochlorination. During hydrochlorination, the off-gas, after the zirconium chloride has been removed, will be almost completely hydrogen (eq. 1, Sect. 3.0) and unused hydrogen chloride. Some tin chloride will also be present, since its vapor pressure is high (normal boiling point, 114°C), as well as the rare gas fission products.

Chlorination. Chlorination of oxides with carbon tetrachloride is known to produce various amounts, depending on the reaction conditions, of the highly volatile gases carbon dioxide, carbon monoxide, oxygen, phosgene, and chlorine (4-7). Gas chromatographic analysis of an off-gas sample obtained midway through a chlorination of hydrochlorination product showed the following composition of the portion of the off-gas that was not carrier gas:

CO_2	63%	CO	2.8%
O_2	8%	Unknown	26%

The unknown 26% was probably carbon tetrachloride, chlorine, and/or phosgene.

4.3 Variations in Procedure, Equipment, and Reagents

The flowsheet presented in Fig. 2.1 represents the best experimental conditions developed in the laboratory work. Some variations that were investigated are described below.

Condensation. The flow rate in all experiments described above was about 4 ft/min. By using a larger (4-in.-i.d.) condenser, the effect of a flow rate of 0.2 ft/min

Table 4.1 Recovery of Uranium from Zircex Hydrochlorination Products by Chlorination with Carbon Tetrachloride

Maximum amount of uranium not recovered by chlorination was 10^{-3}% of that in sample of hydrochlorination product

Run No.	Temp, °C	Residue Sample Wt, g	Carrier Gas	Total Time, hr	% of Sample Remaining in Boat	No. of Times Carbon Burned off During Run	Amount of CCl_4, multiple of stoichiometric	Source[a] of Hydrochlorination Product, Zircex Run No.
Sample leached in 7 M nitric acid before chlorination								
1	550	2.9422 (13.4% U)	HCl	3.0	1.1	2	-	HC76
2	550	2.9422 (13.4% U)	HCl (no CCl_4)	0.2	100	0	-	HC76
3	550	2.9422 (13.4% U)	Air	0.2	100	0	-	HC76
4	550	1.0067 (13.4% U)	N_2	4.0	0.3	1	49	HC76
Sample not leached in 7 M nitric acid before chlorination								
5	600	1.0948 (13.4% U)	N_2	0.8	0.03	0	20	HC76
6	600	1.9446 (13.4% U)	HCl	1.0	0.02	1	11	HC76
7	600	1.2904 (2.77% U)	N_2	1.0	0.2	1	48	HC79
8	600	4.4183	N_2	1.1	0.0	0	7.4	HC82

[a] STR fuel (1% uranium, 97% zirconium, 2% tin) was used in Zircex runs HC76 and HC79; EBWR fuel (93.5% uranium, 5% zirconium, 1.5% niobium) was used in Zircex run HC82.

was investigated. No packing was used, and no other experimental conditions were changed. The uranium loss to the zirconium chloride sublimate increased to 0.9% and the amount of zirconium remaining in the condenser increased to 8%.

In another vain attempt to avoid the use of packing, four baffles that closed off three-quarters of the 1-in.-i.d. condenser were placed at 1-in. intervals. The uranium loss was 50%.

When a porous nickel filter (1/16 in. thick, 5 μ mean pore size) was used instead of packing in the condenser, 3.6% of the uranium was lost. Use of two 30- by 250-mesh Ni-o-nel screens resulted in a 7% uranium loss. Introducing carbon monoxide (20 cc/min) into the condenser (to reduce uranium tetrachloride to uranium chloride, eq. 8) during the run did not decrease the uranium loss in a duplicate run with the Ni-o-nel screens.

Chlorination. Carbonyl chloride (phosgene) was used in one run in place of carbon tetrachloride, with the hope that carbon deposition would be avoided. Chlorination proceeded smoothly, but the carbon deposit formed as before.

Temperature. Because carbon tetrachloride vapor at 600°C proved highly corrosive to most materials of construction (Sect. 4.6), experiments were made at a lower temperature. Samples of residues from engineering-scale STR and EBWR hydrochlorinations (runs HC76 and HC82, respectively; see Table 4.1) were chlorinated for 0.25-1 hr at various temperatures and weight losses were compared.

The initial weight loss with high-zirconium (STR) hydrochlorination product at 350°C was found to be approximately one-third that at 600°C (Fig. 4.2), indicating that a lower chlorination temperature might be feasible. However, with high-uranium (EBWR) product, no reaction was observed at 400°C and the reaction rate increased rapidly when the temperature was increased to 500°C or higher (Fig. 4.2). Since it will probably be possible to decrease the amount of nonvolatile zirconium compounds produced during Zircex hydrochlorination of zirconium content fuels by carefully purifying the hydrogen chloride before use (1), the products should be high in uranium content, and a chlorination temperature of 500°C or higher will probably be required to produce satisfactory initial rates.

An unsuccessful attempt was made to quantitatively recover the uranium from a sample of the high-zirconium STR hydrochlorination product at 375°C. Chlorination with carbon tetrachloride in hydrogen chloride carrier gas was continued for 5 hr, after which 79 wt % of the sample had volatilized. Passage of an inert gas over the remainder of the sample for 1 hr at 600°C, to remove the uranium chloride produced but not volatilized at 375°C, removed all but 1.8 wt % of the original residue. A leach of the remaining material in boiling 5 M nitric acid recovered an additional 5.4% of the uranium present in the hydrochlorination product. The insoluble residue contained 0.3% of the uranium present in the hydrochlorination product.

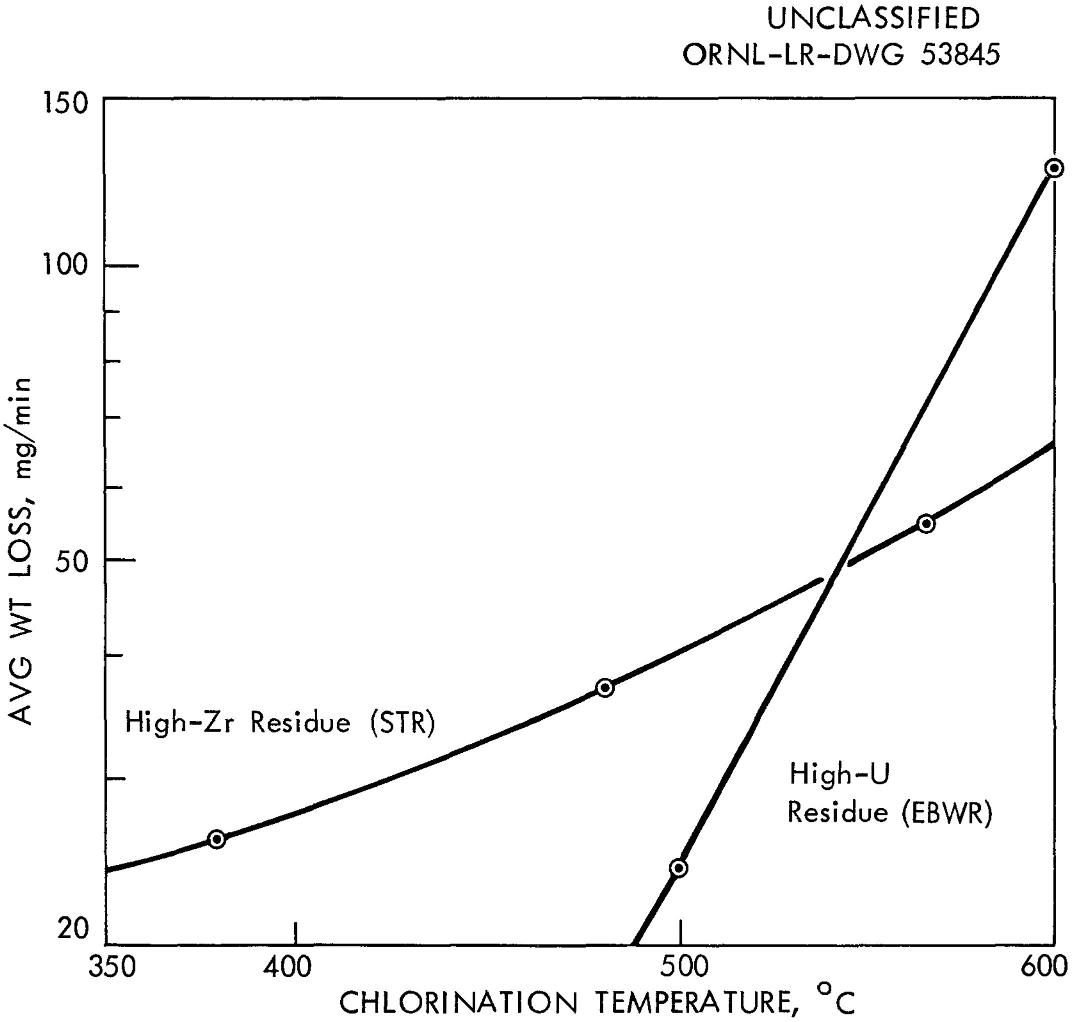

Fig. 4.2. Initial chlorination rates of products from Zircex hydrochlorination with carbon tetrachloride (vapor pressure 120 mm Hg) in hydrogen chloride carrier gas. Flow rate 300 cc/min; 1-in.-i.d. tube; 2- to 4-g samples; 0.25- to 0.5-hr runs.

An attempt to quantitatively recover the uranium from a sample of the high-zirconium STR hydrochlorination product by chlorination at 500°C for 1.5 hr was successful. After admitting air for 5 min at 500°C to burn off carbon upon completion of the chlorination, the temperature had to be raised to 600°C for 0.1 hr to remove a very small amount of less volatile material thought to be copper chloride. A chlorination temperature of 500°C results in rapid and almost quantitative conversion of the hydrochlorination product to volatile chlorides, and apparently will permit quantitative uranium recovery.

4.4 Demonstration of Chloride Removal

Chloride removal from nitric acid solution of the uranium chloride product was demonstrated because it was not known previously whether zirconium was sufficiently soluble and stable in solutions containing uranium and concentrated nitric acid to permit extensive boiling. It was not intended to determine the optimum conditions of temperature, reflux rate, etc., which have been examined in detail in related systems (2).

Chloride removal to below 100 ppm in the solvent extraction plant feed solution is needed because of the high rate of attack of acidic chloride solutions on iron-base alloys such as stainless steel, the major construction material used in solvent extraction plants.

A 100-ml sample of Zircex product solution (0.095 $\underline{M}$ uranium tetrachloride--0.090 $\underline{M}$ zirconium tetrachloride--13 $\underline{M}$ nitric acid) was prepared by dissolving the anhydrous chlorides in 13 $\underline{M}$ nitric acid. As mentioned in Sect. 3.0, the chief uranium chlorination product is probably the trichloride rather than the tetrachloride, but the form of the product is of little significance as regards the chloride removal experiment. The solution was placed in a distilling flask equipped with a downdraft condenser and brought to boiling with 100 cc/min of nitrogen gas bubbling into the solution. The distillate was collected and the exit gas was passed through a series of three 5 $\underline{M}$ sodium hydroxide scrubbers. Approximately every 0.5 hr, the distillate and scrubber flasks were removed for chloride determinations and replaced with fresh flasks, and enough 13 $\underline{M}$ nitric acid was added to the Zircex product solution to bring the volume up to 100 ml.

The rate of chloride removal was rapid. The chloride content of the Zircex product solution approached 5 ppm after a volume of distillate equal to 80% of the volume of the product solution had been collected (Fig. 4.3). The first point on the left in Fig. 4.3 represents the chloride initially in the product solution. To achieve the accuracy desired, the second and third points were obtained by analyzing the distillate for chloride and subtracting the resulting quantity of chloride from that present in the product solution initially; thus the second and third points also reflect the holdup of chloride in the condenser. The last two points were obtained by direct analysis of the Zircex product solution. Chloride holdup in the condenser was of minor importance in the latter points, since the chloride concentration of the distillate was only 50 ppm after the first hour. The smooth curve indicates good agreement between the two sets of chloride determinations.

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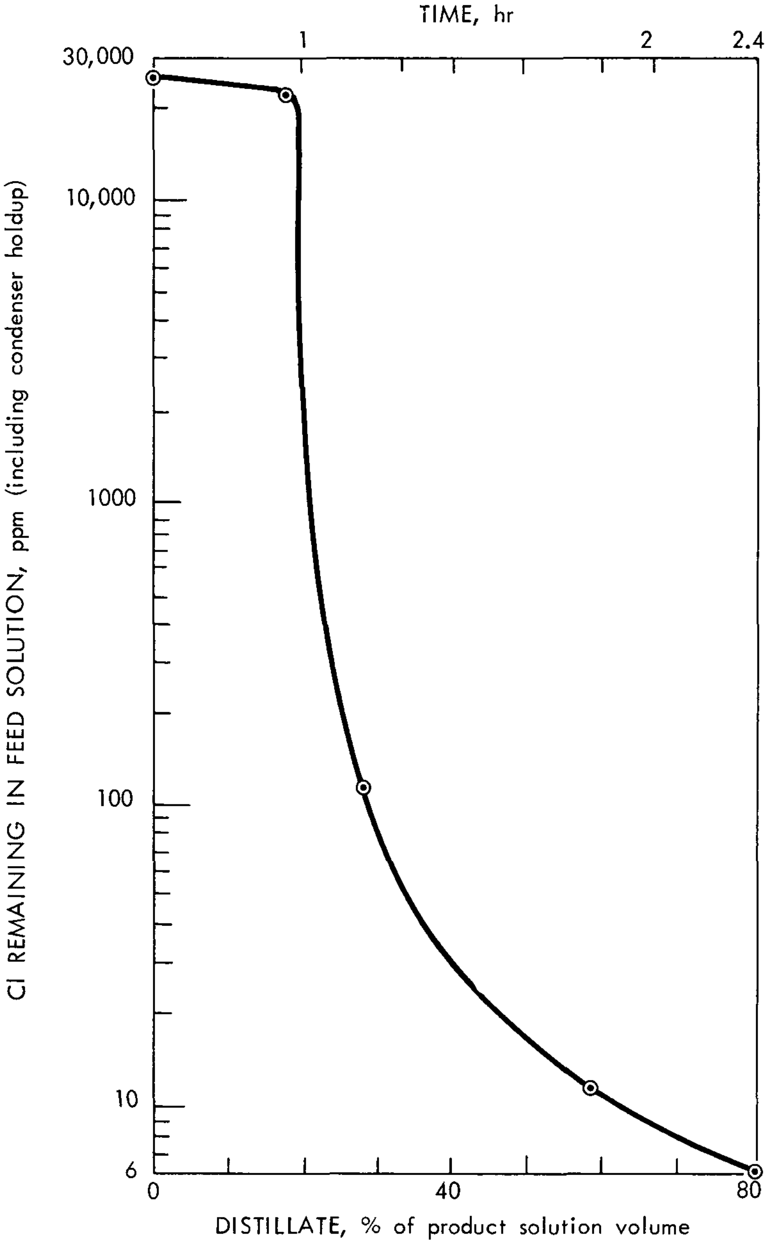

Fig. 4.3. Darex chloride removal from boiling Zircex product solution (0.1 *M* uranium tetrachloride—0.1 *M* zirconium tetrachloride—13 *M* nitric acid). Solution volume kept constant at 100 ml by addition of 13 *M* HNO_3; purge gas: N_2 (100 cc/min).

The Zircex product solution was boiled for a total of 12 hr after chloride removal without precipitation, either at the boiling point or upon cooling, and concentrated by evaporation of nitric acid to 0.106 M uranium--0.10 M zirconium before precipitation started after long standing at 25°C and to 0.123 M uranium--0.12 M zirconium before precipitation started at the boiling point. The precipitates redissolved when water was added. At 25°C, the solubility of zirconium exceeded 3 M in less than 2 M nitric acid and decreased to 0.3 M in 6-9 M nitric acid. Since zirconium is not extracted as readily as uranium from nitric acid into the organic phase during solvent extraction (13), the aqueous phase during second-stage solvent extraction would probably be a uranium—nitric acid solution, which can be concentrated as desired.

4.5 Niobium and Thorium in the Zircex Process

Niobium reacted with hydrogen chloride gas at 600°C at 3 mg/sq cm.min and with chlorine gas at 300 and 400°C at 11 and 40 mg/sq cm.min (Fig. 4.4). The product is volatile niobium pentachloride. In one run with hydrogen chloride, reaction ceased after 5 min due to formation of a protective coating, probably Nb_2O_5, on the niobium. Formation of the coating was prevented by saturating the hydrogen chloride gas with carbon tetrachloride at 25°C, and an average rate of 0.5 mg/sq cm.min was obtained in a 1-hr run. A carbon deposit on the niobium surface probably prevented higher rates.

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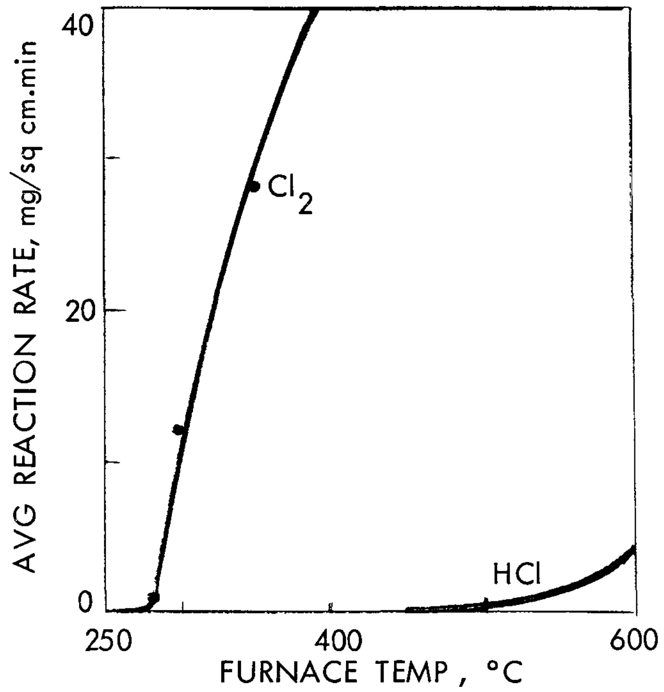

Fig. 4.4. Reaction rate of niobium with hydrogen chloride and chlorine gas. Flow rates: 300 cc/min. Time: 30 min. Sample sizes: 1.6 g (25 mils).

Thorium metal reacted with hydrogen chloride gas at 700°C at a rate of 12.7 mg/sq cm.min. Much nonvolatile material, probably thorium dioxide, collected on the thorium but did not appear to hinder the reaction. The thorium tetrachloride reaction product remained in the reactor, mostly on the exit, which was at approximately 600°C.

Pure hydrogen chloride gas at 600°C did not react with lead or molybdenum metal.

4.6 Corrosion

Only a few scouting tests have been made in the search for a material of construction for a flowsheet of the type in Fig. 2.1. Several potential construction materials were subjected to the following series of treatments at 600°C.

a) Hydrogen chloride for 11 hr

b) Carbon tetrachloride in nitrogen carrier gas for 1 hr

c) Oxygen for 5 min

d) Repeat of (b)

The most resistant alloy tested was Chlorimet-2 with corrosion rates of 5-18 mils/month (Table 4.2). Pyroceram, a ceramic material, was far superior to the alloys tested. The severest corrosion probably occurs during the portion of the cycle in which carbon tetrachloride is used. Inconel or Nichrome V appears satisfactory under these conditions. Since lowering of the temperature from 600°C to 500°C (Sect. 4.3) during chlorination with carbon tetrachloride would probably decrease the corrosion rate greatly, further tests of the Zircex cycle are being made at 500°C.

4.7 Alternative Fluorination Procedure

The oxide impurity in the products obtained from hydrochlorination of uranium-zirconium alloy, which prevented quantitative recovery of uranium in nitric acid (1), also impeded the quantitative recovery of uranium as uranium hexafluoride by treatment with fluorine gas (8). However, uranium chloride captured on the off-gas filter was easily and quantitatively recovered by fluorination at 256°C (8). Since the flowsheet proposed in Fig. 2.1 involves collecting all uranium as chlorides in a separate chamber, the 300°C condenser, these chlorides should be quantitatively converted to uranium hexafluoride easily at relatively low temperatures. An advantage of the Zircex fluorination procedure with enriched fuels is the direct production of relatively pure uranium hexafluoride, which can probably be passed directly into the gaseous diffusion cycle for re-enrichment of U-235. An experiment to determine if uranium chloride collected in the 300°C condenser could be converted to uranium hexafluoride indicated that quantitative recovery of uranium is readily accomplished at 200°C.

Table 4.2[a] Corrosion of Various Alloys in the Zircex Cycle

Gas flow rate: 1 ft/min

Alloy	Corrosion Rate, mils/month		
	400°C	500°C	600°C
In Zircex Cycle			
S-816			38, 20
Chlorimet-2			18, 5
316 stainless steel			19, 21
Pyroceram 9608	0.9	1.3	1.0
Nitrogen Gas Saturated with Carbon Tetrachloride at 25°C			
Nichrome V	0.2	1.8	5.5
Inconel	1.6	6.5	18
Chlorimet-2	2.4	6.4	32
Pyroceram 9608	0.9	1.3	1.0

[a] Data obtained by E. S. Snavely, L. Rice, and co-workers of the Reactor Experimental Engineering Division.

A 4-cm section of an Inconel condenser (1 in. i.d.) was packed with 70 g of 40 gauge nickel wire and 139 mg of uranium, as uranium chloride, collected at 300°C (Fig. 4.1). The condenser was cooled, detached, capped, and placed in a fluorination train of equipment. Two fluorinations were made. The first consisted of 50 min heating from room temperature to 190°C (25% fluorine, 75% helium), 10 min heating from 190 to 195°C (50% fluorine, 50% helium), 5 min heating from 195 to 200°C (75% fluorine, 25% helium), and 30 min at 200°C with pure fluorine. The second fluorination consisted of 40 min heating from 200 to 395°C (25% fluorine, 75% helium), 10 min heating from 395 to 400°C (50% fluorine, 50% helium), 10 min at 400°C (75% fluorine, 25% helium), and 30 min at 400°C with pure fluorine. The flow rate in all experiments was 100 ml/min (STP). In both fluorinations, the uranium hexafluoride was trapped at room temperature on 12- to 20-mesh sodium fluoride. In the first fluorination at 200°C, 98.0% of the uranium was collected on the sodium fluoride. In the second at 400°C, an additional 0.9% was collected. A maximum of 1.1% of the uranium remained in the condenser. Some uranium was expected to remain in the condenser since the contents were exposed to air, and the moisture in air rapidly converts uranium tetrachloride to uranium oxide, necessitating a higher temperature for fluorination.

The significant result of the fluorination experiments is the large percentage (98%) of uranium recovered as uranium hexafluoride at 200°C. This result confirms previous observations (8) that relatively low-temperature fluorination can be used to quantitatively convert uranium chlorides, purified by sublimation, to uranium hexafluoride.

Attempts to fluorinate uranium chlorides captured on copper turnings in the 300°C condenser were not successful because the copper ignited in the fluorine.

Further fluorination work is needed in larger scale equipment where hydrochlorination, chlorination, and fluorination may be carried out in a single run without dismantling and introducing air. It will also be necessary to determine the fission product distribution and find methods of removing and disposing of nonvolatile fission products and zirconium fluoride, which collect in the condenser.

5.0 REFERENCES

1. J. J. Perona, J. B. Adams, J. E. Savolainen, and T. A. Gens, "Status of the Development of the Zircex Process," ORNL-2631 (March 1959).

2. J. E. Savolainen and R. E. Blanco, "Preparation of Power Reactor Fuels for Aqueous Processing," Chem. Eng. Prog: 53 (2): 78-F (1957).

3. P. D. Miller, C. L. Peterson, E. L. White, and F. W. Fink, "Evaluation of Container Materials for Zircex and Darex Nuclear-fuel-recovery Processes," BMI-1242 (December 1957).

4. L. P. Twichell, "Chlorination of Purified Zirconium Oxide," Y-574 (March 1950).

5. R. S. Lowrie and C. E. Larson, "Factors Affecting the Chlorination of Uranium Compounds with Liquid Carbon Tetrachloride," C-0.350.24 (November 1946).

6. I. V. Budayev and A. N. Volsky, "The Chlorination of Uranium Dioxide and Plutonium Dioxide by Carbon Tetrachloride," P/2195, Proc. 2nd Internatl. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 28, p. 316, UN, New York.

7. J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," NNES-VIII-5, McGraw-Hill, New York, 1951, pp. 464-467.

8. P. R. Ammann, D. A. Madden, and D. L. Swift, "Zircex-Fluoride Volatility Combination," KT-339 (March 1958).

9. "The Shippingport Pressurized Water Reactor," Addison-Wesley Publishing Co., Reading, Mass., 1958, p. 586.

10. T. A. Gens, "Recovery of Uranium from Residues Produced in Hydrochlorination of Nuclear Fuel Alloys," ORNL-CF-59-4-9 (April 1959).

11. J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Wiley, New York, 1957, p. 416.

12. B. Pesce and V. Evdokimoff, "Equilibrium between Vapor and Liquid in Binary Mixtures. I. Method of Measuring Partial Vapor Pressure," Gazz. chim. ital., 70: 712 (1940).

13. C. Buck, G. R. Howells, T. A. Parry, B. F. Warner, and J. A. Williams, "Chemical Processes at U.K. Atomic Energy Authority Works, Dounreay," P/82, Proc. 2nd Internatl. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 17, p. 28, UN, New York.

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