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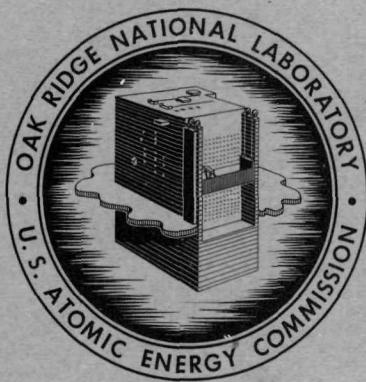
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C-44b – Nuclear Technology-Chemistry
and Chemical Engineering

MASTER

LABORATORY DEVELOPMENT OF CHLORIDE
VOLATILITY PROCESSES FOR THE RECOVERY
OF URANIUM DIRECTLY FROM SPENT ROVER
FUEL OR FROM ITS COMBUSTION ASH

T. A. Gens



OAK RIDGE NATIONAL LABORATORY
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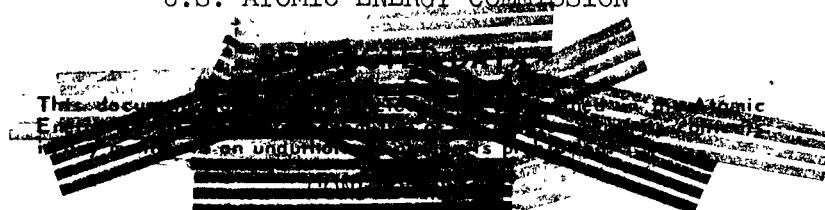
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LABORATORY DEVELOPMENT OF CHLORIDE VOLATILITY PROCESSES FOR THE RECOVERY OF URANIUM DIRECTLY FROM SPENT ROVER FUEL OR FROM ITS COMBUSTION ASH

T. A. Gens

ABSTRACT

Two chloride volatility processes for the recovery of uranium from the combustion ash from spent Rover fuel were studied in the laboratory. The fuel consists of graphite impregnated with uranium carbide. The cooling channels are of niobium carbide. In each method, the uranium is isolated as UCl_4 and it may be further processed by aqueous solvent extraction (Darex) or fluoride volatility methods. The combustion-chlorination process involves burning the fuel elements in oxygen at 700 to 900°C and then chlorinating the uranium and niobium oxide products with 15 vol % CCl_4 -85 vol % Cl_2 at 500°C . The volatilized uranium and niobium chlorides are collected at room temperature and then separated by selective volatilization of niobium chloride by controlled heating to 400°C .

Uranium recovery is quantitative, and less than 1% of the niobium remains with the uranium.

Corrosion rates for nickel or high-nickel alloys are expected to average about 0.5 mil/month through the cycle. The combustion-chlorination process should be reducible to large scale practice because the reactions proceed readily, and the corrosion problems are minor.

In the direct chlorination process, rough-crushed Rover fuel is treated with chlorinating and mixed chlorinating-oxidizing gases at 800°C . Uranium and niobium chlorides volatilize and are separated as in the combustion-chlorination process. Uranium recoveries are greater than 99%. About 40% of the graphite burns. Corrosion rates are excessive, more than 1 in./month for metal containers. Consequently, direct chlorination is not presently reducible to large-scale practice.

1. INTRODUCTION

The purpose of this work was to investigate the use of chlorination and chloride volatility methods for recovering uranium from spent graphite-base nuclear fuels. An efficient and simple process, preferably one in which common metals can be used as construction material, is desired.

A particularly important graphite-base fuel from which uranium must be recovered in the near future is the Rover fuel used in nuclear rocket research. The early Rover fuels, the KIWI A and B fuels, have a graphite matrix which is impregnated with uranium carbide.^{1,2} The work described in this report was performed with the KIWI B-1B fuel element, which is described in detail in reference 2. In later versions of the Rover fuel element, the use of uranium carbide particles, coated with pyrolytic graphite and dispersed through the graphite matrix, is planned. This modification is not expected to affect the combustion-chlorination process described below, but it will probably make it impossible to recover uranium by direct chlorination of the fuel element, the second process described in this work. Both the impregnated and coated-particle types of Rover fuels have cooling channels lined with niobium carbide. During manufacture of impregnated fuels, up to 5% of the uranium diffuses into the niobium carbide liner. The use of niobium in Rover fuel presents exceptionally troublesome chemical problems in aqueous solutions, and the presence of coated particles adds to the complexities.^{3,4} Therefore, there is considerable incentive for the investigation of advanced processing methods such as chloride-volatility, either as an independent method or as a head-end step for aqueous or fluoride volatility decontamination methods. Thus a conventional solvent extraction processing plant could process Rover fuel by the addition of combustion-chloride volatility equipment for head-end processing.

The more promising of the chloride volatility processes studied involves high-temperature, gas-phase chlorination of the metal oxide ash produced by burning the fuel in oxygen (most of the graphite is converted to CO₂). Quantitative recovery of uranium is achieved under conditions leading to corrosion rates of 1 mil/month or less. For Rover fuel, which

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contains about 18% uranium and 13% niobium, the combustion ash consists of about 44% uranium and 33% niobium. Simple methods of making practically quantitative separation of the chlorides of uranium and niobium were developed. In studies of the direct chlorination and volatilization of uranium from impregnated graphite matrix fuels, near-quantitative recovery of uranium was achieved, but the conditions required appear too drastic for containment of the process in metallic construction materials.

Other chloride volatility methods have been reported for recovering uranium from nuclear fuels containing zirconium, niobium, molybdenum, aluminum, and iron.⁵ An apparatus, called "The Torrefactor," is being built to demonstrate, on a large laboratory scale, the reprocessing of all these fuel types, as well as the processes for graphite fuels described in this work. Other processes being investigated for recovering uranium from Rover and other graphite-matrix fuels include combustion-hydrofluorination or combustion-fluorination,⁶ combustion followed by acid dissolution, disintegration-leaching, and grinding-leaching.^{3,4} A chloride volatility process is used in the industrial separation of niobium pentachloride from other chlorides by vapor-liquid distillation.⁷

Analyses were performed by W. R. Laing, G. R. Wilson, H. W. Dunn, E. I. Wyatt and co-workers of the Analytical Chemistry Division. Corrosion tests were planned by W. E. Clark of the Chemical Technology Division and performed by L. Rice and co-workers of the Reactor Chemistry Division.

2. FLOWSHEETS

2.1 Discussion of the Combustion-Chlorination Selective Volatilization Procedure

2.1.1 Basic Steps

The combustion-chlorination-selective volatilization process (Fig. 1 and Table 1) involves five operations requiring a total time of about 9 hr: burning the fuel elements; chlorinating the uranium and niobium oxide products, with volatilization of uranium and niobium chlorides; collecting of the chlorides at ambient temperature; separating the chlorides by the

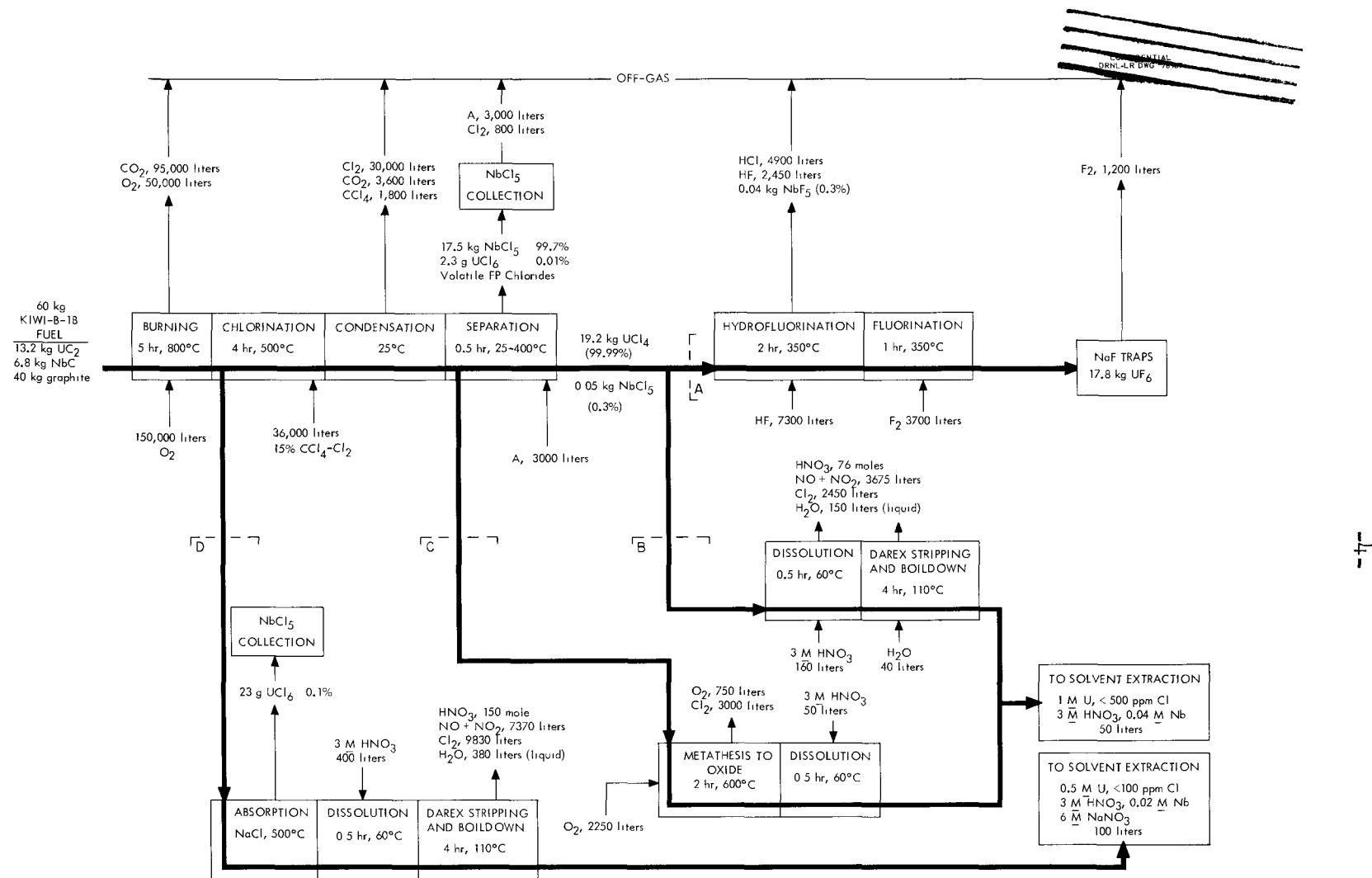


Fig. 1. Combustion-Chlorination Head-End Treatments for Four Subsequent Treatments: (A) Fluorination to UF_6 , (B) Aqueous Chloride Removal and Solvent Extraction, (C) Aqueous Solvent Extraction, and (D) Sorption of Uranium Chlorides on Sodium Chloride Before Aqueous Chloride Removal and Solvent Extraction. A 50% excess of all reagents was used.

Table 1. Data for the Chlorination of Rover-Fuel Combustion Ash in 15% CCl_4 --85% Cl_2

Run No.	Weight of Combustion Ash or Intact Fuel Element (g)	Chlorination Step Time (hr)	T ($^{\circ}\text{C}$)	Uranium-Niobium Separation Step		Results (%)			
				Time (hr)	T ($^{\circ}\text{C}$)	Volatile U	Nb	Non-volatile U	Nb
(a) Followed by Selective Volatilization of NbCl_5 in a Stream of Argon									
VA 5	1.2, ash	3	450	1	100	0.11	80.6	99.89	19.5
VA 6	1.0, ash	3	450	2	100-200	0.022	47.4	99.98	52.6
VA 7	1.2, ash	3	450	3	100-350	0.010	90.6	99.99	9.4
VA 9	1.0, ash	3	450	1	25-400	0.012	98.4	99.99	1.6
VAFS 5 ^a	31.9, fuel element	5	580	0.5	25-400	0.013	99.6	99.99	0.4
VAFS 6	30.3, fuel element	2.5	500	0.5	25-400	0.039	99.99	99.96	0.01
VAFS 7	33.1, fuel element	3	550	0.5	25-400	0.003	99.7	99.99	0.3
VAFS 8	32.2, fuel element	6	450	0.5	25-400	0.007		99.99	
VAFSO 2	25.6, fuel element	4.1	480	0.5	25-400	0.066	99.86	99.93	0.14
VAFSO 4	35.0, fuel element	3.3	500	0.5	25-400	0.006	99.93	99.99	0.07
(b) Using an NaCl Bed to Collect Uranium Chloride									
VA 8	1.1, ash	4.5	450		450	0.14	99.8	99.87	0.2
VAFS 2	32.2, fuel element	6	450		450	0.25	99.6	99.75	0.4
VAFS 3 ^b	37.0, fuel element	5.5	450		500	2.12	99.7	97.88	0.3
VAFS 4 ^b	31.1, fuel element	6	450		300-500	0.14	92.0	99.86	8.0

^a In this and subsequent runs, 98% H_2SO_4 was added to the CCl_4 bubbler.

^b Vertical salt beds; plugging occurred below 500 $^{\circ}\text{C}$.

selective volatilization of niobium pentachloride or oxychloride; and collecting of the niobium chloride. Collection of the mixed uranium and niobium chlorides and of the separated niobium pentachloride is carried out simultaneously with the chlorination and separation steps, respectively.

Pure oxygen is used in the burning step, and carbon dioxide and non-volatile uranium and niobium oxides are produced. About 5 hr at 800°C is required. (The burning of the graphite is discussed in detail elsewhere.)^{6,8} Chlorinating the uranium and niobium oxides to produce volatile chlorides requires about 3 hr at 500°C in 15% CCl_4 -85% Cl_2 . The burning and the chlorinating are quantitative, and nothing remains in the reactor with un-irradiated specimens. These operations are conducted in a single vessel made of nickel or high nickel alloys. Laboratory corrosion tests (see Sec 5) indicate corrosion rates as low as 0.0 and 1 mil/month during burning and chlorination, respectively, and 0.2 mil/month in sequential operation. (The oxide skin on the reactor protects it from attack by chlorinating agents.) An occasional flushing of the reactor, perhaps with water, would be necessary to remove nonvolatile fission products.

The volatilized chlorides are condensed as solids in a second vessel at room temperature. The Cl_2 , CO_2 , and CCl_4 off-gases pass through this vessel for disposal or recycle of Cl_2 and CCl_4 . The uranium and niobium chlorides are separated rapidly by raising the temperature to 400°C over a 0.5-hr period in order to volatilize niobium chloride in a stream of inert gas. About 0.01% of the uranium is lost by volatilization with the niobium, and the rest remains as nonvolatile uranium tetrachloride, which can be converted to uranium hexafluoride [route (a), Fig. 1] or dissolved in water or nitric acid in preparation for chloride removal and subsequent solvent extraction [route (b), Fig. 1]. These routes are discussed in the next subsection. The volatilized niobium chloride is condensed in a third vessel at room temperature. The niobium chloride might be removed by dissolving it in potassium fluoride solution or hydrofluoric acid, or perhaps by melting (m.p. of pure NbCl_5 , 194°C) and allowing it to flow out as a liquid. Several of the more important fission products, such as zirconium, niobium, and molybdenum have volatile chlorides that should follow the niobium chloride.

It is important in the chlorination and separation steps to keep oxygen-containing impurities, such as water, out of the system, because such chemicals lead to the production of nonvolatile niobium oxide.

Corrosion in the collection and separation steps should be relatively minor compared with corrosion in the burning and chlorination steps. However, either hydrogen fluoride and fluorine or water must be introduced to further process the uranium chloride by routes (a) or (b), respectively. In either case, the corrosion of materials such as nickel or Nichrome V should be low, and Haynes 25 should serve well as a collection vessel in preparation for route (b) (see Sec 5).

2.1.2 Routes that May Be Taken After the Chlorination Step

Details of the Fluoride Volatility process [route (a), Fig. 1] and the Darex process [route (b)] are reported elsewhere.^{9,10} The volatilized uranium and niobium chlorides from the chlorination step can also be separated at about 500°C by passage through a sodium chloride bed, which retains all the uranium chlorides but less than 1% of the niobium chlorides [Fig. 1 (d) and Table 1 (b)]. The bed is dissolved in nitric acid and further processed by procedures developed in the Darex process. The problems of sintering and plugging attending the use of salt beds at high temperatures, particularly when heavily loaded, makes the use of this procedure more attractive as a cleanup or safety measure for route (a) of Fig. 1, rather than as a method of uranium recovery. Other disadvantages that attend the use of a salt bed are the need for the removal of large amounts of chloride from and the inclusion of large amounts of sodium nitrate in the solvent extraction feed [Fig. 1 (d)].

The gas-phase removal of chloride from the UCl_4 , followed by HNO_3 dissolution of the resulting oxide [Fig. 1 (c) and Table 2] appears to offer the advantages of simplicity and smaller amounts of nitrate waste over the previously developed aqueous (Darex) chloride removal process. Of several variations in metathesis reagents and temperatures tried, oxygen at 600°C appeared most attractive. Oxygen causes little corrosion, even at 800°C (Sec 5), and reduces the chloride content, based on 0.1 M uranium solutions, to levels comparable to those obtained in the Darex chloride-removal process.

Table 2. Chlorination of Rover Fuel Combustion Ash in 15% CCl_4 -- Cl_2 ^a
at 500°C Followed by Chloride Removal in Oxygen at 600°C

Run	Chloride Removal Time (hr)	Results (% of Volatile or Nonvolatile Chlorides)				Concentration of Chloride in 0.1 M U Product (ppm)	
		Volatile in Argon		at 400°C			
		U	Nb	U	Nb		
VAFSO 1	2	0.06	99.9	99.94	0.1	77	
VAFSO 2	1	0.003	99.9	99.997	0.1	84	
VAFSO 3	5	0.04	99.9	99.96	0.1	<38	

^a All gas mixtures reported in this report are on a volume-percentage basis.

2.1.3 Possibilities for Decontaminating the Uranium

The burning, chlorination, condensation, and separation procedures outlined in Fig. 1, with little modification, might, in themselves, without the further treatments a, b, c, or d, lead to the efficient separation of fission products as well as niobium from the uranium chloride product. Demonstrations with irradiated fuel are planned. The chlorination temperature of 500°C is needed only to obtain rapid reaction, not for the volatilization of uranium chlorides. The uranium and niobium chlorides could be passed in a stream of chlorine through a chamber at about 300°C to remove the fission products that volatilized during chlorination at 500°C but which are not volatile at 300°C. Subsequent treatment of the solid chlorides, after condensations, with an inert gas stream at 400 to 500°C should remove by volatilization the fission products chlorides that were volatile enough to pass through the 300°C chamber.

2.2 Discussion of the Direct Chlorination Process (Not Preceded by Burning in Oxygen)

The direct chlorination process (Fig. 2 and Table 3) involves the treatment of ground or rough-crushed graphite fuel at 800°C with a series of four chlorinating reagents and requires a total time of about 9 hr. Collection of the mixed uranium and niobium chlorides and selective re-volatilization of niobium chloride is performed as shown in Fig. 1.

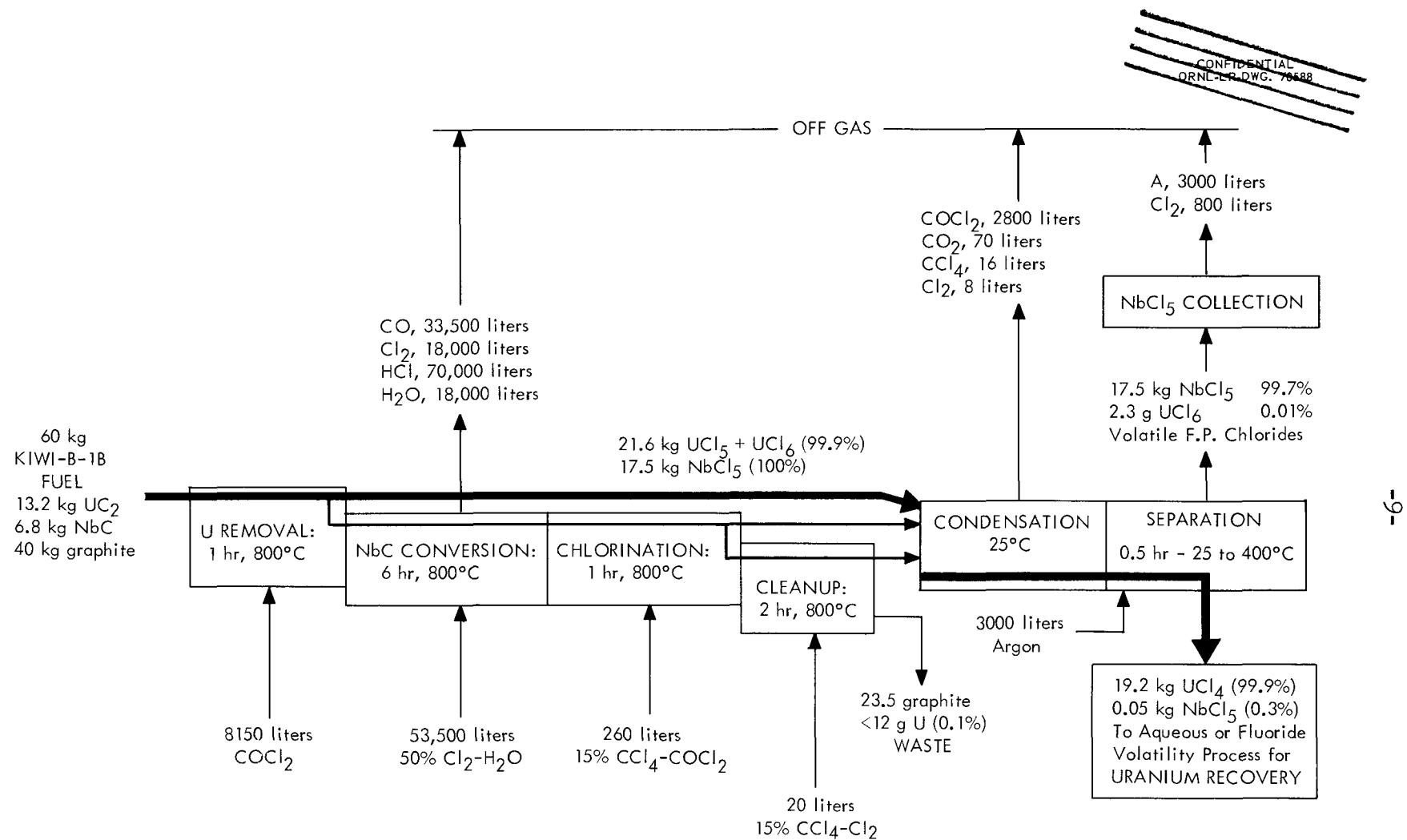


Fig. 2. Direct Chlorination Head-End Treatment for Fluoride Volatility or Darex--Solvent Extraction Process. A 50% excess of all reagents was used.

Table 3. Recovery of Uranium from Crushed Rover Fuel (KIWI-B-1B) by Direct Chlorination at 800°C.

Treatments: 1 hr, COCl_2 ; 6 hr, 50% $\text{Cl}_2\text{-H}_2\text{O}$; 1 hr 15% $\text{CCl}_4\text{-COCl}_4$;
2 hr, 15% $\text{CCl}_4\text{-Cl}_2$

Run	Mesh Size	Volatile	Percentage of Uranium:	
			Leachable in 3 M HNO_3	Lost to Graphite
1	4-12	99.91	0.011	0.083
2	RC ^a	99.93	0.008	0.066

^a Rough crushed; fuel channels exposed.

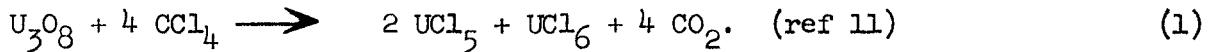
Over 95% of the uranium and part of the niobium, estimated at 50% for flowsheet calculations, is removed in a 1-hr treatment with phosgene gas at 800°C. Mixed chlorine--carbon tetrachloride gas may be used, but the rate of reaction with this reagent is lower. The remaining niobium is converted to the pentoxide by a 6-hr treatment with 50% $\text{Cl}_2\text{-H}_2\text{O}$ at 800°C. This step is actually a slow "burning" operation, and 40% of the carbon is also converted to the oxide (carbon monoxide was assumed for flowsheet calculations). Any uranium that had been trapped in the niobium carbide is also converted to oxide. This uranium oxide is chlorinated to UCl_5 and UCl_6 and volatilized by a 1-hr treatment at 800°C with 15% $\text{CCl}_4\text{-85% COCl}_2$. This mixture is preferred because the production of stable and less-volatile uranyl chloride is thereby avoided. A further treatment for 2 hr at 800°C with 15% $\text{CCl}_4\text{-85% Cl}_2$ converts nearly all the remaining uranium to volatile pentavalent and hexavalent chlorides. Uranium remaining in the graphite amounts to less than 0.1%, with 10% of this loss recoverable by leaching the graphite in dilute, hot nitric acid. The moisture-containing off-gas from the second chlorination step, the niobium carbide conversion, has to be routed around the vessels that are used to collect and separate uranium and niobium chloride from the exit gases from the other three steps, because moisture would convert the uranium and niobium chlorides to oxides and thereby prevent the subsequent separation of niobium by volatilization as the pentachloride or oxychloride. Corrosion studies indicate that (Sec 5) the reactor for the direct-chlorination process must be made of a ceramic in order to be sufficiently corrosion resistant, although the condensation,

separation and niobium chloride collection could all be performed in metal vessels. Consequently, it was assumed that direct chlorination is probably not practical for large scale use at the present time.

3. CHEMISTRY OF THE CHLORINATION PROCESSES

The major combustion products from Rover fuel are U_3O_8 , Nb_2O_5 , and CO_2 . Unless excess oxygen is present during burning, carbon monoxide is also produced. There is also some possibility of a rapid reaction between carbon monoxide and oxygen to produce carbon dioxide.⁶

An approximate equation may be written for the chlorination of U_3O_8 with carbon tetrachloride vapor:



The value of ΔH at 25°C for this reaction is only -27 kcal per mole of uranium. Although the reaction goes approximately as shown in Eq. (1), the instability of and the rapid rate of interconversion between higher uranium chlorides makes it impossible to define the valence state of the uranium exactly.

The vapor pressure data in Fig. 3, taken from ref 12, show the effect of the uranium valence state on the volatility of uranium chlorides. It is necessary for the vapor pressure to reach only a small fraction of 1 atm for rapid volatilization in a stream of gas or under vacuum, and the vapor pressures at the melting points are sufficient for volatilization. For example, the vapor pressure of UCl_6 at 200°C has been measured as 32 mm Hg,¹³ while the melting point of UCl_6 is about 180°C . Thus UCl_6 , UCl_5 , and UCl_4 can be volatilized readily at temperatures above 200, 300 and 550°C , respectively.

It can be seen from the excellent separation of uranium and niobium chlorides achieved by the selective volatilization of niobium chloride in argon between room temperature and 400°C [Fig. 1 and Table (1a)] that the decomposition of volatile higher uranium chlorides to nonvolatile uranium tetrachloride,



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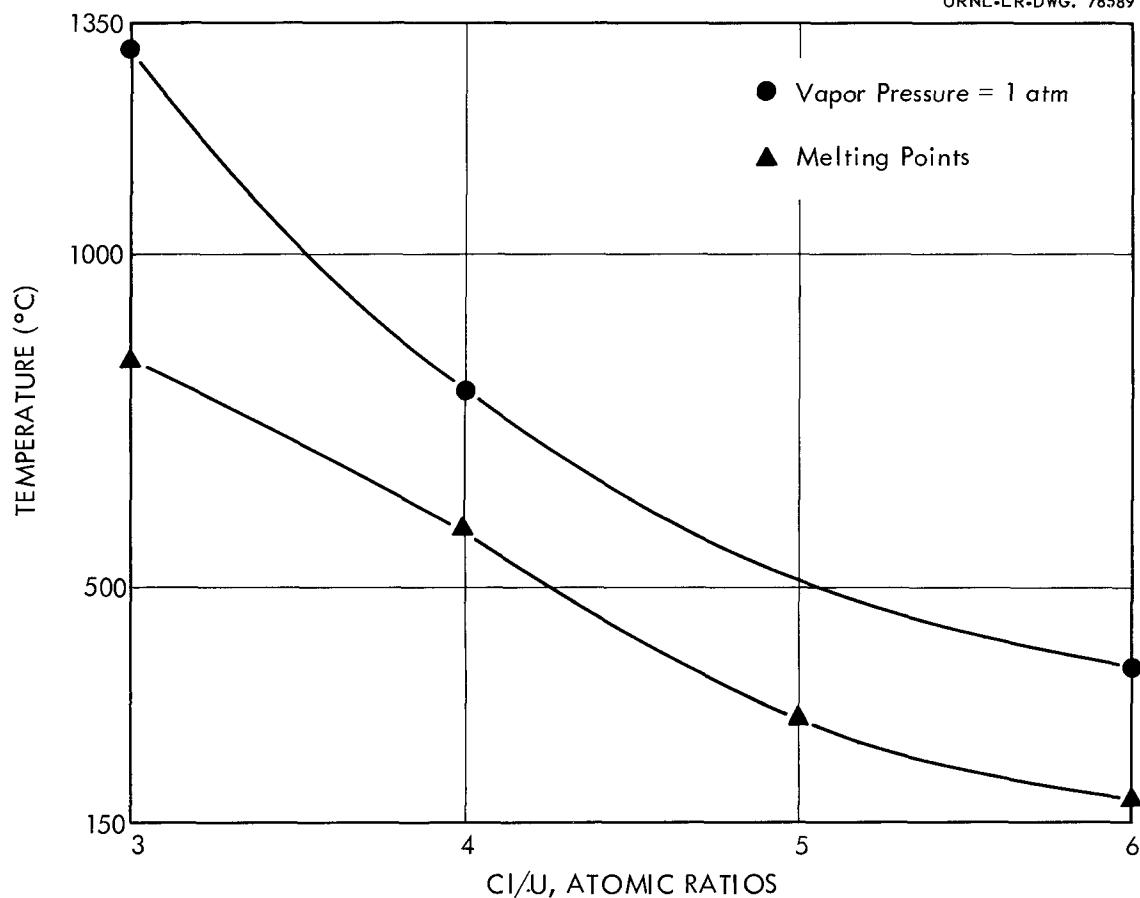


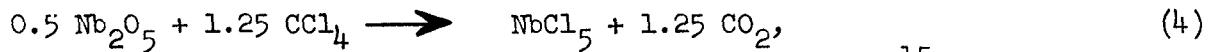
Fig. 3. Vapor Pressure and Melting Points of Uranium Chlorides.

and



occurs very rapidly. It is also apparent that reactions (2) and (3) would prevent the volatilization of uranium as the penta- or hexachloride at moderate temperatures such as the 500°C used in the chlorination step, unless a large excess of chlorine were present to drive the reactions in the reverse direction. Thus, the function of chlorine during the chlorination step is to maintain uranium in the volatile penta- or hexavalent state, thereby ensuring the complete removal of uranium from the reactor and greatly increasing the reaction rate (see Sec 4).

The chlorination of niobium oxide involves the following reaction with carbon tetrachloride:¹⁴



although some niobium oxychloride, which is very stable¹⁵ and is volatile at the chlorination temperature,^{16,17} may form.

Only carbon tetrachloride is consumed during chlorination, and the chlorine and unused carbon tetrachloride could probably be recovered in a trap cooled by dry ice and then recycled. Efficient recovery of chlorine could lead to the recovery of more chlorine than is introduced, since part of the chlorine supplied by carbon tetrachloride (Eq. 1) is released by reactions 2 and 3 during the separation step. Small amounts of carbon monoxide and phosgene are also expected in the chlorination products.^{11,18,19} The phosgene would be captured in the chlorine cold trap and should cause no problems if recycled to the chlorinator, and the carbon monoxide would pass through with the carbon dioxide.

The complex compounds $\text{NaCl} \cdot \text{UCl}_4$ and $2 \text{NaCl} \cdot \text{UCl}_4$ are known,²⁰ and mixtures of these compounds are probably the final products obtained from the sorption of uranium chloride on a sodium chloride bed. The eutectic of these compounds, which melts below 500°C , may cause the sintering and plugging observed in salt beds below 500°C . Above 500°C , diffusion through the bed is probably rapid enough to ensure the formation of complex compounds richer in sodium chloride and therefore of higher melting point. Some of the uranium captured in the sodium chloride bed probably has a valence higher than four, since the uranium-containing portion of the bed is red so long as chlorine gas flows. In the absence of chlorine, the bed color changes to the green of tetravalent uranium. A complex compound of niobium pentachloride and sodium chloride is known,^{21,22} but the decomposition temperature is about 287°C (ref 22), and the niobium chloride cannot be captured on sodium chloride beds at temperatures as high as 400°C .²³

The gas-phase removal of chloride from uranium chloride is based on the reactions shown below, depending on whether oxygen or water vapor is used:

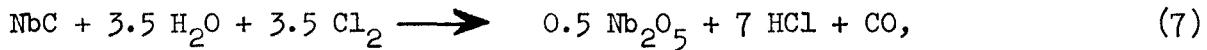


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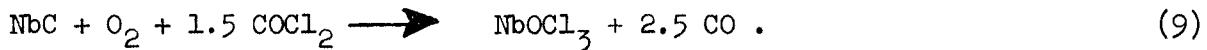


Some of the stable intermediate compound UO_2Cl_2 was produced by reaction (5) at 300 to 500°C , and good chloride removal could not be achieved in a practical time period at these temperatures. The hydrolysis reaction (6) proceeds rapidly in moist air even at room temperature but the moist chloride off-gas from the reaction can cause excessive corrosion, particularly at low temperatures and on alloys containing large amounts of nickel. Therefore, oxygen rather than water was used to achieve chloride removal (Fig. 1). In practice, some inert diluent gas should be mixed with the oxygen to prevent uranium volatilization through the reverse of reactions (2) and (3) when chlorine is liberated rapidly at the beginning of the chloride removal operation.

The direct chlorination process involves chemical reactions very similar to those already discussed. However, the niobium carbide conversion step involves reactions which, for the flowsheet calculations, were assumed to proceed as follows:



The treatment of niobium carbide with oxygen-phosgene or oxygen-chlorine mixtures converts most of the carbide to the volatile oxychloride:



Reaction (9) proceeds slowly unless the reagent gas contains 40% O_2 , enough to satisfy the stoichiometry of the reaction and prevent a buildup of carbon on the reaction surface. At 700°C or higher, niobium carbide ignites and burns rapidly in 40% O_2 -- COCl_2 . Only a small amount of nonvolatile Nb_2O_5 forms, and none forms in the presence of excess carbon. Reaction (7) was chosen for the process (Fig. 2) because, although the niobium reacts and is volatilized from the graphite surface, it hydrolyzes to form nonvolatile Nb_2O_5 in the vapor phase and remains in the reactor. If niobium were volatilized from the reactor during the NbC conversions, two waste streams containing niobium would result, since the off-gas from the niobium carbide conversion cannot be passed through the chloride collector. Passage of

this off-gas, containing moisture or oxygen, through the chloride collector would convert uranium and niobium chlorides to oxides and thereby prevent the separation of niobium chloride by volatilization. When either oxygen or water vapor was mixed with chlorine or phosgene to effect the conversion of niobium carbide to either oxide or oxychloride, it was impossible to avoid the undesirable "burning" of carbon, as illustrated in Eqs. (8) and (9), since the complete conversion of niobium carbide could not be achieved without attacking and volatilizing the carbon arising from niobium carbide. Attempts to completely convert the niobium carbide to oxide by hydrolysis, $\text{NbC} + 3.5 \text{ H}_2\text{O} \longrightarrow 0.5 \text{ Nb}_2\text{O}_5 + \text{CO} + 3.5 \text{ H}_2$, (10) were unsuccessful, probably because hydrogen competes with carbon as a reducing agent at the high temperatures required for rapid hydrolysis. Incomplete conversion of the niobium carbide always resulted in excessive uranium losses.

4. CHLORINATION EXPERIMENTS AND RESULTS

4.1 Chlorination of Combustion Ash

Studies of chlorination of combustion ash had two major objectives: (1) achievement of rapid rates at temperatures low enough for easy containment of the reagents in metal equipment, and (2) complete volatilization of the ash. Both goals were achieved by mixing chlorine in the reagent gas to maintain uranium as the volatile penta- or hexavalent chloride (see Eqs. (2) and (3), Sec 3).

The addition of 30 vol % Cl_2 to a 15 vol % CCl_4 --85 vol % N_2 gas stream increased the volatilization rate of UCl_4 at 500°C over tenfold (Fig. 4). It was necessary to achieve rapid volatilization at about 500°C because uranium tetrachloride melts below 600°C (Fig. 3) and because corrosion rates increase rapidly in this temperature range (Sec 5).

The chlorination and volatilization of ash (Fig. 5) did not occur as rapidly as the volatilization of UCl_4 (Fig. 4), apparently because chlorination is the slower and rate-limiting step, rather than volatilization. Analysis of the residue after partial chlorination (Table 4) showed that niobium was being removed from the ash much more rapidly than uranium;

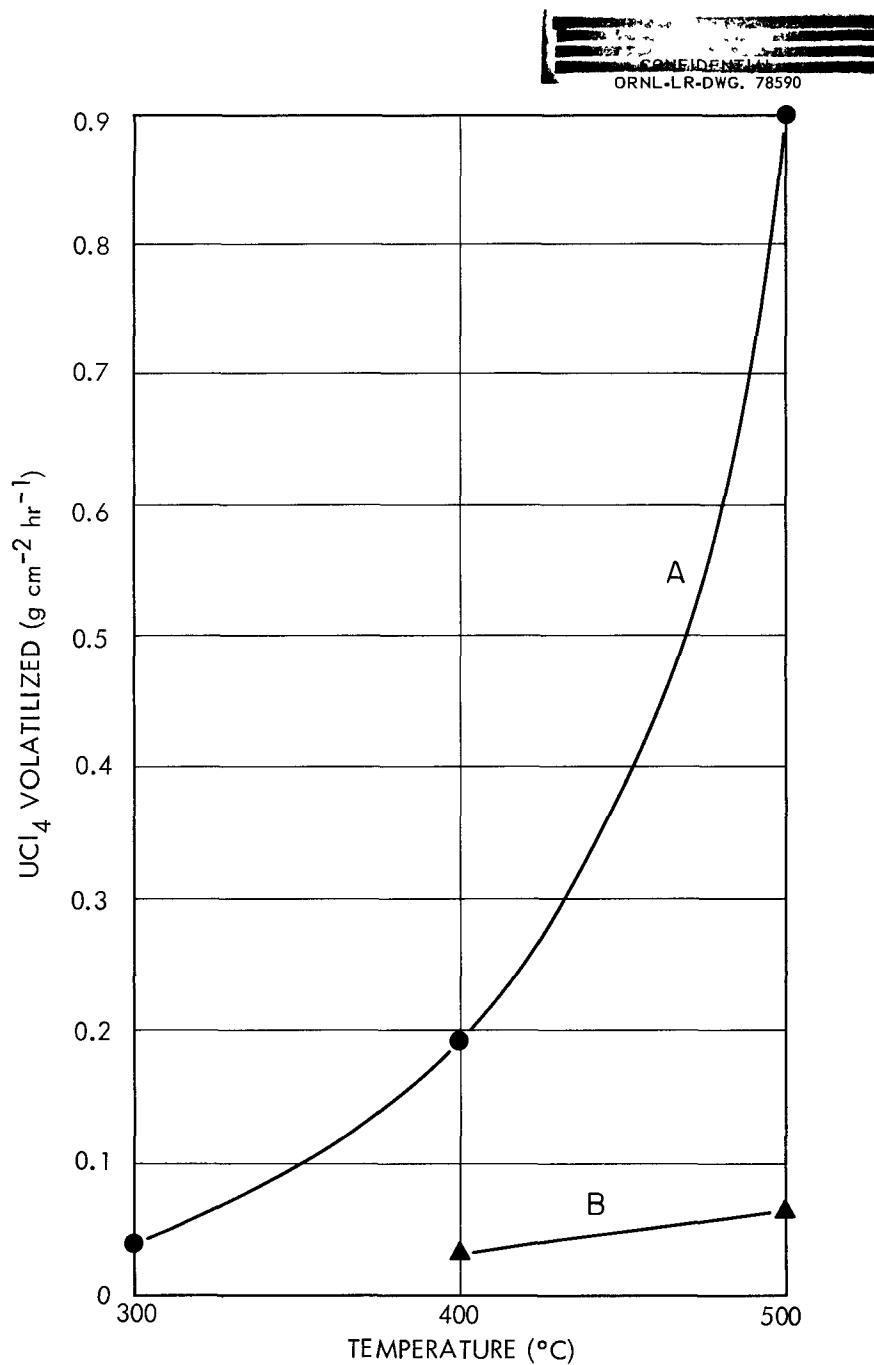


Fig. 4. Volatilization of Uranium Chloride in Flowing
(A) 30% Cl₂--15% CCl₄--55% N₂ and (B) 15% CCl₄--85% N₂.
Flow rate, 300 cc/min; inner-diameter of tube, 1 in.

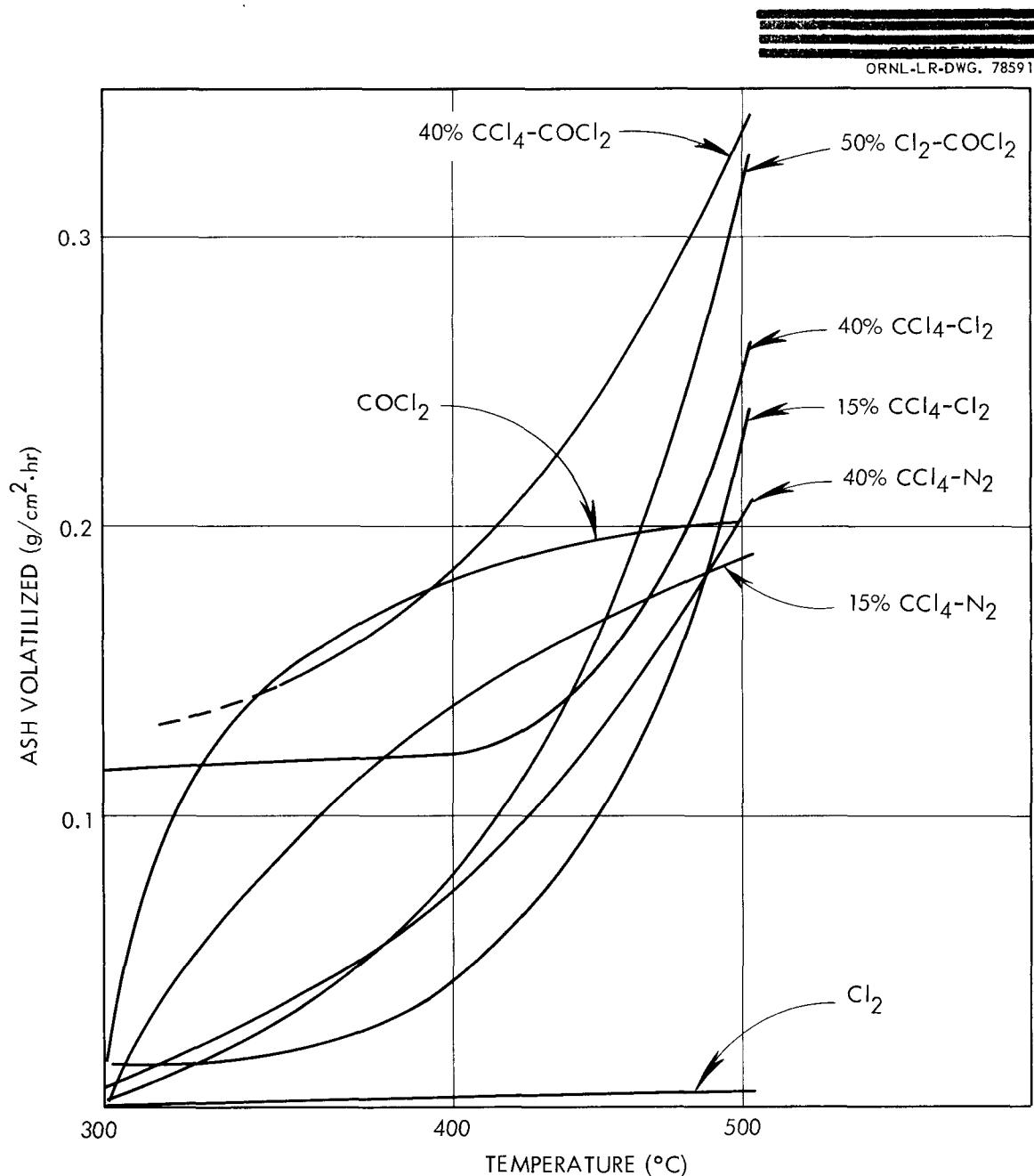


Fig. 5. Chlorination and Volatilization of Graphite-Fuel Combustion Ash in Flowing Chlorinating Gas. Flow Rate, 500 cc/min; tube internal diameter, 1-in.; time, 30 min.

Table 4. Chlorination of Rover Fuel Combustion Ash in Various Chlorinating Reagents and Reagent Mixtures

Temperature: 500°C
 Tube: 1-in. ID
 Ash Weight: 0.4-0.9 g
 Gas-Flow Rate: 300 cc/min
 Time: 30 min

Reagent	U/Nb Mole Ratio in Residue	Reagent	U/Nb Mole Ratio in Residue
None	1.3	Cl ₂	No reaction
15% CCl ₄ --N ₂	7.6	COCl ₂	69
40% CCl ₄ --N ₂	12	50% Cl ₂ --COCl ₂	6.8
40% CCl ₄ --Cl ₂	33	40% CCl ₄ --COCl ₂	77

thus the presence of niobium oxide in the ash does not slow the chlorination reaction. Since the chlorination rate is not limited by the rate of volatilization of uranium, which depends on the partial pressure of chlorine, it appears that chlorine aids carbon tetrachloride in the chlorination of uranium oxide, since the replacement of nitrogen by chlorine in the carbon tetrachloride vapor (Fig. 5) resulted in higher chlorination rates. The highest chlorination-volatilization rates were obtained with phosgene mixed with carbon tetrachloride vapor or chlorine. Pure chlorine did not react with the ash at 500°C. Phosgene or phosgene--carbon tetrachloride vapor probably chlorinate niobium oxide rapidly, because the residues after partial chlorination were mainly uranium salts (Table 4). Because of (1) the hazards associated with phosgene, (2) the need for the introduction of chlorine toward the end of a chlorination with phosgene to ensure complete volatilization of uranium, and (3) the simplicity of preparing a chlorine--carbon tetrachloride reagent by bubbling chlorine through liquid carbon tetrachloride, the use of chlorine--carbon tetrachloride vapor was recommended in the flowsheet (Fig. 1). Since the rates achieved with 40% CCl₄--60% Cl₂ were only slightly higher than those obtained with 15% CCl₄--85% Cl₂, the reagent containing 15% CCl₄ was used.

To determine the optimum temperature for chlorination, several flowsheet runs were made in which the combustion ash was chlorinated at various temperatures between 450 and 580°C. The time required for complete reaction

was excessive — more than 6 hr — at temperatures less than 450°C and was at a minimum of 2.5 to 3 hr at about 500°C. The reaction time increased at temperatures above 500°C because of the reduction in surface area caused by the melting of the uranium chlorides and the attendant sintering of the mixed ash--chloride residue (Fig. 6).

4.2 Direct Chlorination of Graphite Fuels

4.2.1 Uncoated Fuels

In experiments in which graphite fuel impregnated with uranium carbide, the type used in the Turret reactor, was treated with chlorine gas, it was found that a temperature of over 750°C was required for the rapid removal of uranium (Fig. 7). After 2 hr at 750°C, the graphite retained 1.5% of the total uranium. Since this was not coated graphite, the 1.5% uranium retention must be due to either the slow diffusion of uranium compounds through the smaller graphite pores at 750°C or to the formation of uranyl chloride (UO_2Cl_2) that becomes trapped in larger pores near the surface. The presence of water-soluble but nonvolatile uranium on the graphite after chlorination in experiments described below supports the latter postulate. Thus, it is necessary to use both high temperatures and reagents other than chlorine which are capable of attacking or avoiding the formation of uranyl chloride in order to achieve the rapid removal of uranium from uncoated uranium carbide--graphite fuels.

4.2.2 Problems Presented by Fuels Coated with Niobium Carbide

The niobium carbide coating on Rover fuel that does not contain coated fuel particles complicates the direct chlorination procedure for removing the recovering uranium, since the niobium coating must be destroyed in order to recover contained uranium. As discussed in Sec 3, it is necessary to burn a large fraction of the graphite in order to obtain the complete reaction of the niobium carbide, which can be attacked only by reagents that simultaneously burn the carbon. Should the niobium carbide coating of future Rover fuels be free of uranium, a direct chlorination process might be more attractive than at present. However, as discussed in the introduction to this report, while the use of coated fuel particles may

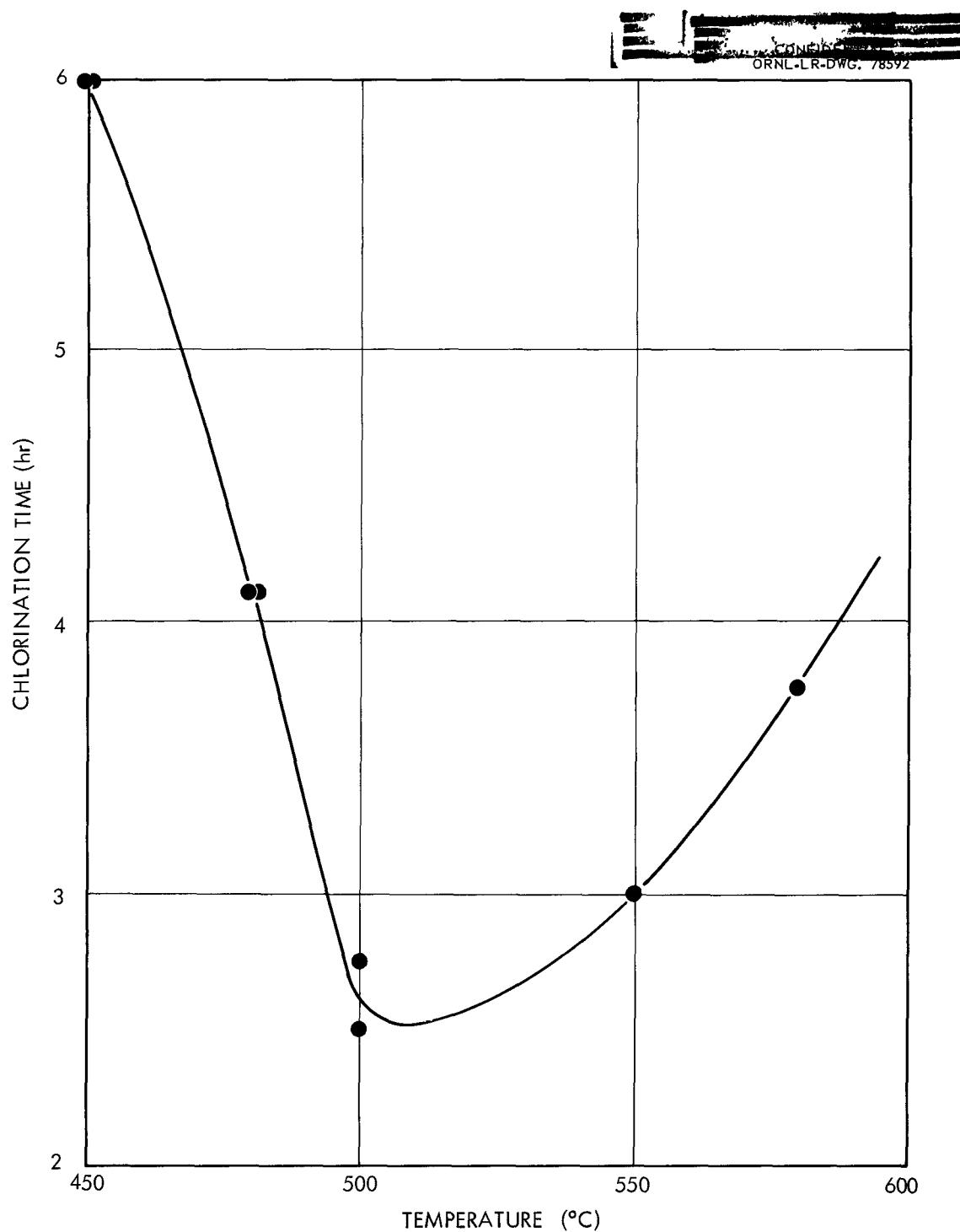


Fig. 6. Time Required for Complete Chlorination of Combustion Ash from 30 to 33 g Rover Fuel Rods in 15% CCl_4-Cl_2 . Flow rate, 1 liter/min; inner diameter of tube, 2 in.

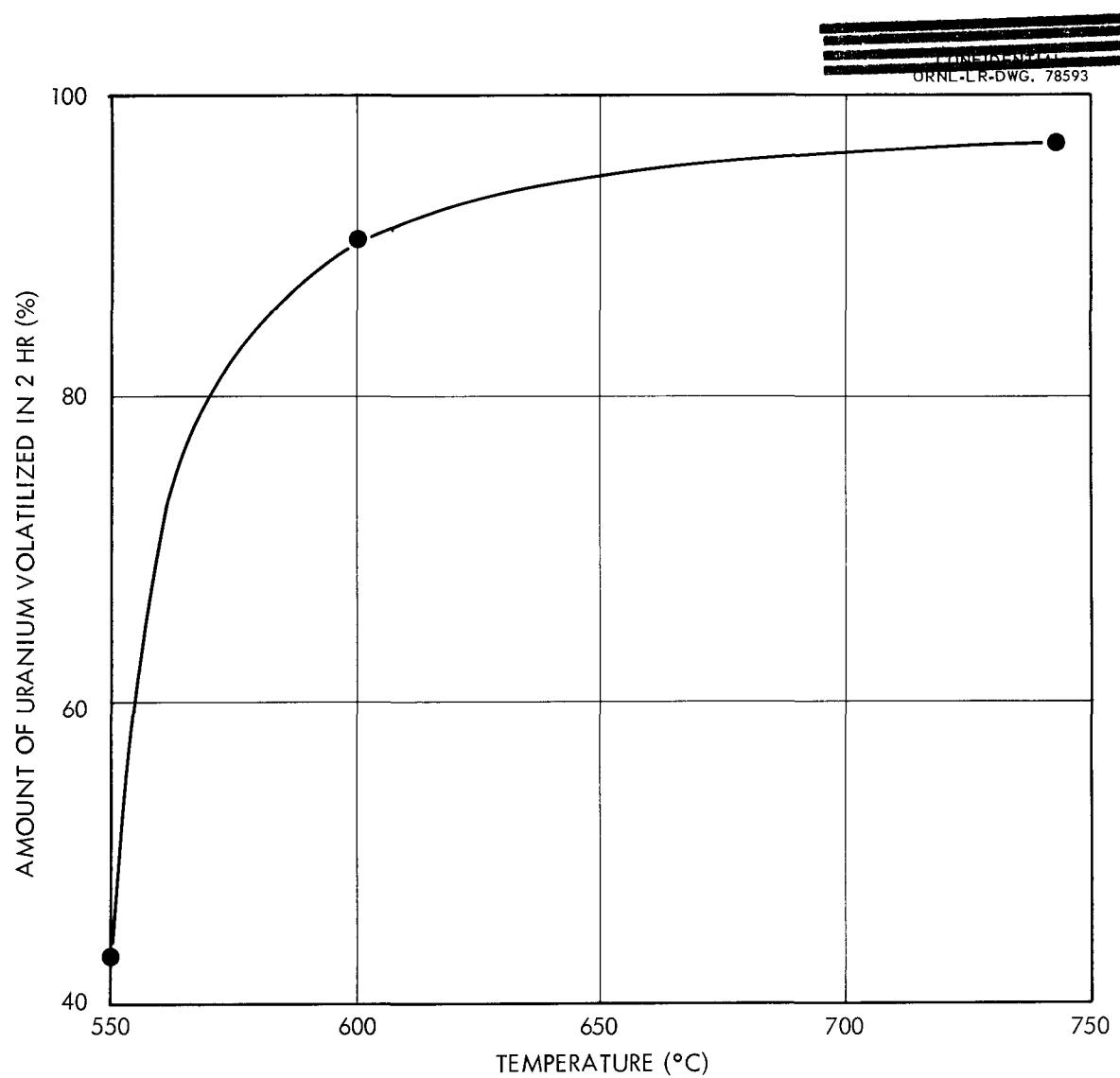


Fig. 7. Volatilization of Uranium Chloride from Turret Uranium Carbide-Graphite (7% U) Reactor Fuel by Treatment with Gaseous Chlorine.

prevent diffusion of uranium into the niobium carbide liner, it may also make it impossible to recover the uranium by direct chlorination, since this method of recovery is dependent on rapid diffusion of uranium chloride out of the fuel element.

The rate of attack of niobium carbide by hydrogen chloride, chlorine, or phosgene at 700 to 800°C was excessively slow. The addition of a small amount of oxygen to chlorine at 700°C increased the reaction rate greatly, with the maximum niobium volatilization occurring at about 50% oxygen (Table 5). The products are thought to be only nonvolatile niobium oxide and volatile niobium oxychloride. The nonvolatile niobium oxide residue did not form when the niobium carbide was in contact with graphite, and the only product was volatile niobium oxychloride. The addition of oxygen to phosgene produced a slightly different effect in that the attack on niobium carbide was relatively very slow with reagents containing less than 40% oxygen, the stoichiometric quantity required for reaction (9) (see Sec 3). At this point the niobium carbide ignited, and the rate of attack was more rapid than that for the analogous chlorine reagent.

In a series of runs in which uranium recovery was attempted by the direct chlorination of ground KIWI B-1B Rover fuel (Table 6), the recovery exceeded 99% if the preliminary treatment with mixed chlorine-oxygen was extensive enough to completely burn the niobium carbide. Variations in the length of the subsequent treatments with chlorine and chlorine--carbon tetrachloride had a minor effect on the recoveries in comparison with that of the chlorine--oxygen treatment. Raising the temperature from 625 to 800°C at a 0.25-hr contact time in 25% O₂--Cl₂ increased the uranium recovery from 95 to 97%, while the percentage of graphite weight loss increased from 17.5 to 20%. About 10% of the graphite weight loss occurs through desorption of absorbed vapors, and the balance occurs through burning. Both an increase in contact time to 0.5 hr at 800°C and an increase in the amount of oxygen in the chlorine from 25 to 33% improved uranium recoveries while also increasing the amount of graphite burnt.

It appears that excellent uranium recoveries are possible at 800°C if there is enough burning to effect a weight loss of more than 30% for

Table 5. Data for the Chlorination of Niobium Carbide in Chlorine or Phosgene Mixed with Oxygen

Time: 1 hr Flow: 300 cc/min	Temperature: 700°C NbC wts: ~0.5 g
Percentage of O ₂ in Either Cl ₂ or COCl ₂	Nb Remaining in Residue, %
% O ₂ in Cl ₂	
20	72
30	14 ^a
50	29 ^a
70	29 ^a
% O ₂ in COCl ₂	
0	99
25	87
40	7 ^b

^a As Nb₂O₅.

^b As Nb₂O₅, reaction complete in 10 min.

Table 6. Preliminary Data on the Recovery of Uranium from Ground Rover Fuel (12- to 25-mesh) by Direct Chlorination; Removal of Niobium Carbide with Chlorine-Oxygen Mixtures

Treatments: 0.25-0.5 hr, COCl₂; 2 hr, Cl₂; 0.25-1 hr,
15% CCl₄--85% Cl₂

Runs, Averaged Results	Temp. (°C)	% of O ₂ in Cl ₂	O ₂ -Cl ₂ Contact Time (hr)	Graphite Weight Loss (%)	Percentage of Uranium:		
					Volatile	in 3 M HNO ₃	Lost to Graphite
31-33	625	25	0.25	17.5	95.29	3.04	1.67
23-25,27	800	25	0.25	20.2	96.78	2.05	1.17
26,28,29	800	25	0.5	21.3	97.49	2.28	0.23
35,47	800	33	0.5	32.1	99.16	0.36	0.48

the graphite. Major disadvantages in the use of chlorine-oxygen mixtures are the rapid burning as well as the uneven burning. The fuel that contacts fresh reagent gas as it enters the reactor burns faster than fuel farther

from the reagent inlet. Because of these disadvantages, chlorine--water vapor mixtures were also investigated. This reagent burns carbon slower at 800°C and thus it is easier to control the amount of graphite burning.

In the use of 50% $\text{Cl}_2\text{--H}_2\text{O}$, as in the case of chlorine-oxygen, the major variable affecting uranium recoveries is the completeness of the reaction with niobium carbide, as indicated by the amount of graphite burned. In a series of runs made according to the flowsheet conditions (Fig. 2) with ground (4- to 12-mesh) Rover fuel in which the temperature was varied, excellent uranium recoveries (99.9%) were achieved at 800°C, but the recoveries decreased regularly with temperature to less than 98% at 650°C (Fig. 8). Very little additional uranium was recoverable by leaching the graphite product in hot nitric acid. The recoveries are directly correlatable with the graphite weight losses, which increase from 39% at 650°C to 47% at 800°C.

In similar experiments with rough-crushed Rover fuel, which was crushed only enough to break the fuel into long splinters and expose the coolant channels, the uranium recoveries were again directly correlatable with the amount of graphite burnt. However, in this case, both the uranium recoveries and the graphite weight losses were greater at 675 than at 725°C (Fig. 9). The same result might have occurred with the 4- to 12-mesh material (Fig. 8) without having been observed because the range between temperatures was greater in the experiments with 4- to 12-mesh particles. In either case, a temperature of about 800°C was needed for the best uranium recoveries. The amount of uranium recoverable by leaching the rough-crushed fuel product was also smallest for the material that had been chlorinated at 800°C.

Since the uranium loss was still excessive (nearly 1%) with the 4.8-hr treatment of rough-crushed fuel with 50% $\text{Cl}_2\text{--H}_2\text{O}$, the effect of varying the period of the treatment was studied. Uranium recoveries increased from 98.5% to more than 99.9% as the time was increased from 4 to 6 hr (Fig. 10). The graphite weight loss also increased from 38 to 58%, indicating that as much carbon is burned by equivalent treatments of rough-crushed fuel as with 4- to 12-mesh fuel. The amount of uranium remaining in the graphite and recoverable by leaching in dilute nitric acid decreased

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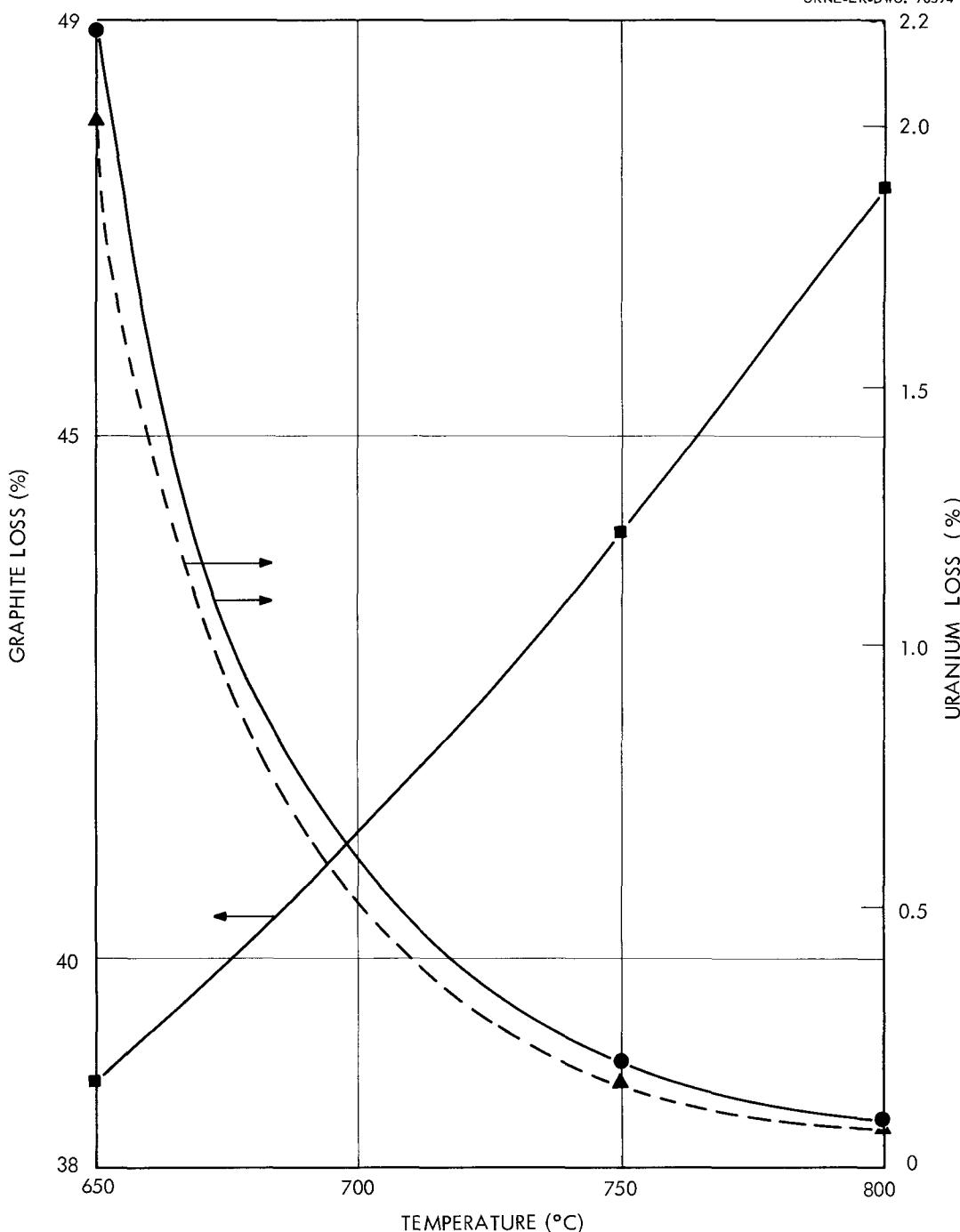


Fig. 8. Graphite Weight and Percent Uranium Losses from Ground (4-12 mesh) Rover Fuel as a Function of Temperature of Treatment in 50% $\text{Cl}_2\text{--H}_2\text{O}$. Treatments: 1 hr, COCl_2 , 6 hr, 50% $\text{Cl}_2\text{--H}_2\text{O}$; 1 hr, 15% $\text{CCl}_4\text{--COCl}_2$; 2 hr, 15% $\text{CCl}_4\text{--Cl}_2$. Dashed line shows the uranium loss not recoverable by leaching in 3 M HNO_3 . About a 10 wt % loss in graphite was caused by vapor desorption.

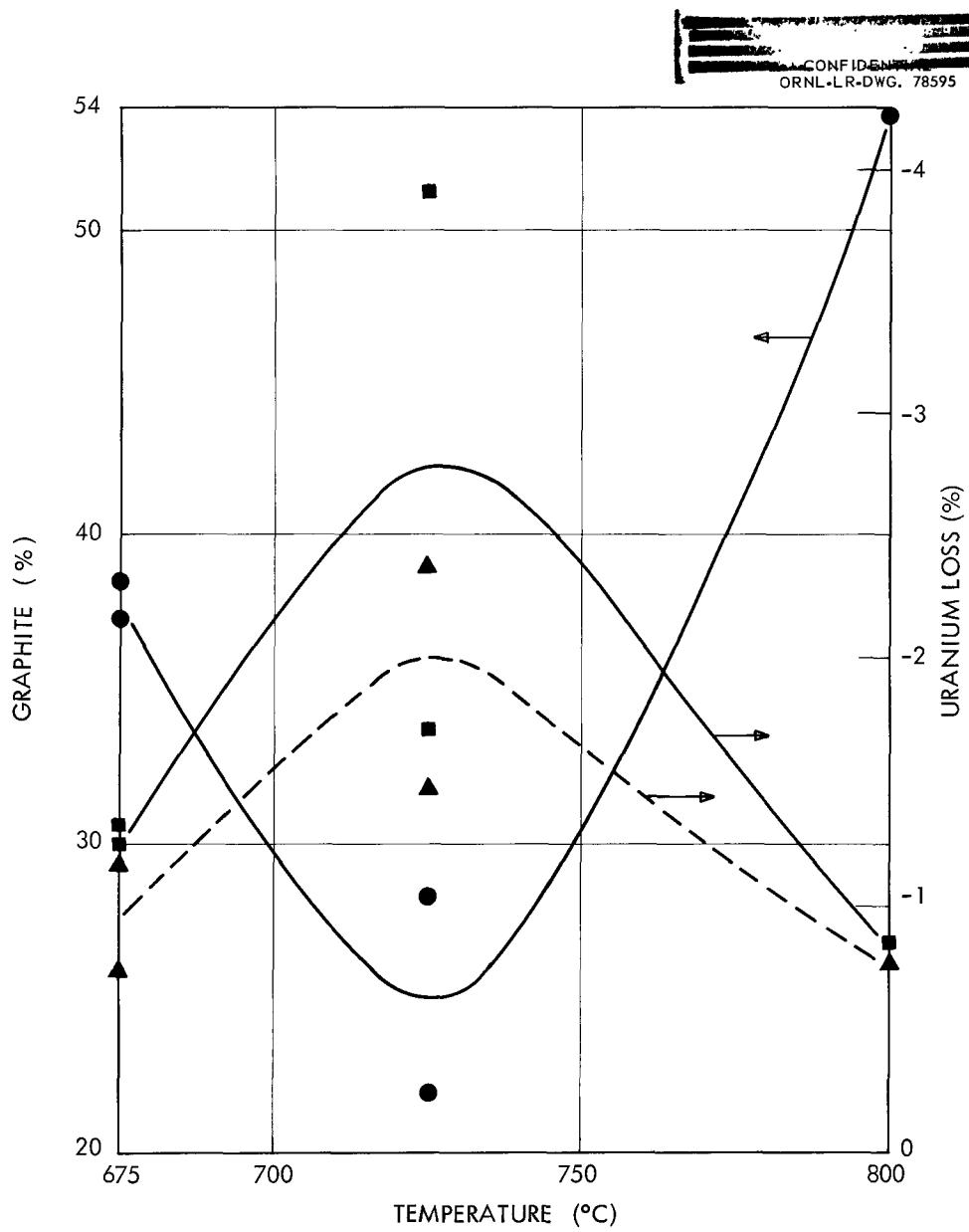


Fig. 9. Graphite Weight and Percent Uranium Losses from Rough-Crushed Rover Fuel as a Function of Temperature of Treatment in 50% $\text{Cl}_2-\text{H}_2\text{O}$. Treatments: 1 hr, COCl_2 ; 4.8 hr, 50% $\text{Cl}_2-\text{H}_2\text{O}$; 1 hr 15% $\text{CCl}_4-\text{COCl}_2$; 2 hr, 15% CCl_4-Cl_2 . Dashed line shows uranium losses not recoverable by leaching in 3 M HNO_3 .

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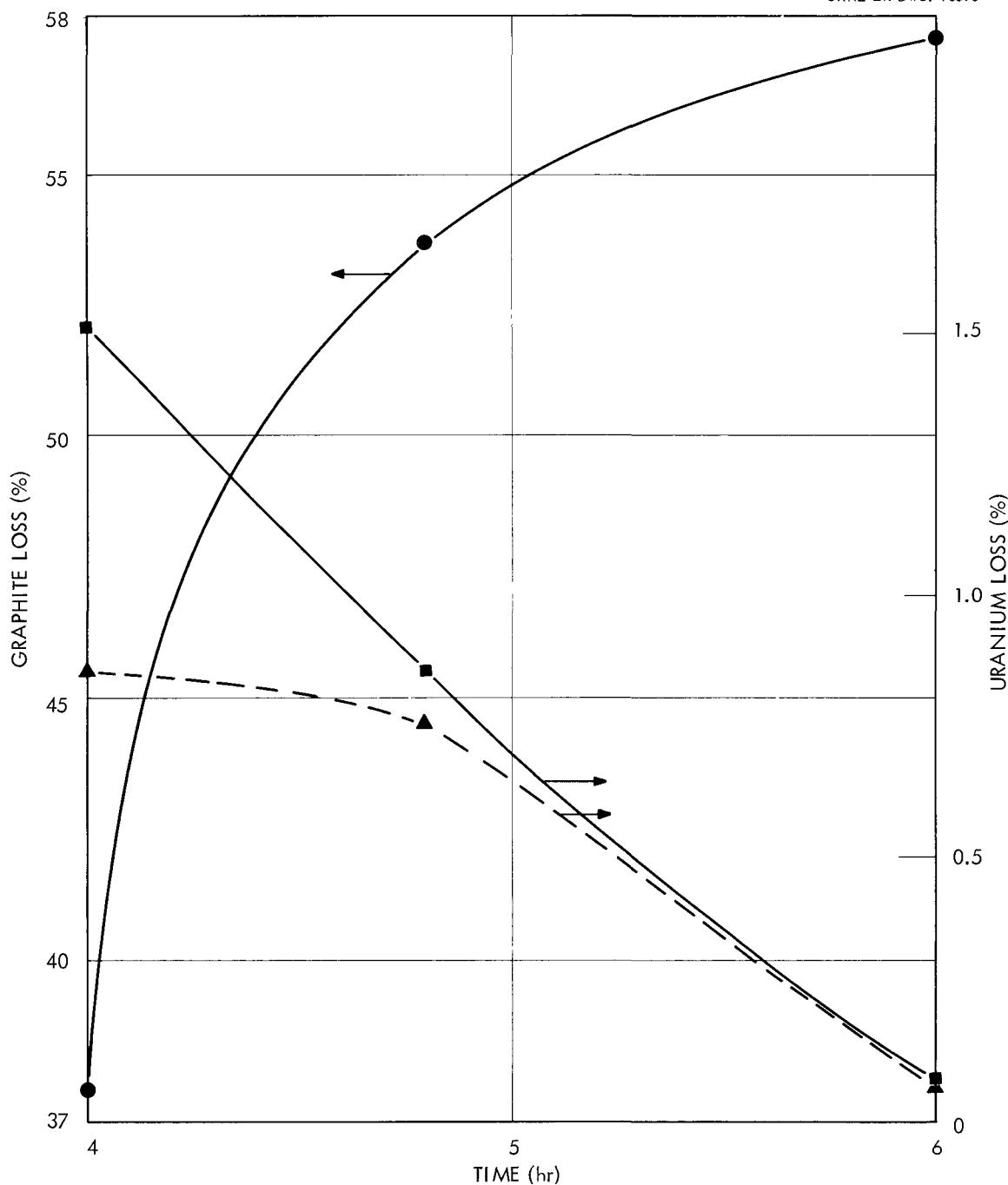


Fig. 10. Graphite Weight and Percent Uranium Losses from Rough-Crushed Rover Fuel as a Function of Duration of Treatment in 50% $\text{Cl}_2\text{--H}_2\text{O}$. Treatments: 1 hr, COCl_2 ; 4-6 hr, 50% $\text{Cl}_2\text{--H}_2\text{O}$; 1 hr, 15% $\text{CCl}_4\text{--COCl}_2$; 2 hr, 15% $\text{CCl}_4\text{--Cl}_2$; Temperature, 800°C. Dashed line shows uranium loss not recoverable by leaching in 3 M HNO_3 .

from about 50% of the total loss after the 4-hr treatment to essentially none after the 6-hr treatment.

5. DISCUSSION OF CORROSION RATES AND SUITABLE MATERIALS OF CONSTRUCTION

Corrosion tests in chlorine and carbon tetrachloride vapor indicate an activation energy of about 20 kcal/mole with all materials tested (Fig. 11). The strong dependence of corrosion rates on temperature necessitates careful wall temperature control and explains why excessive corrosion rates have sometimes been observed when wall temperatures were allowed to rise during chlorination. On the other hand, the strong dependence of corrosion rates on temperature makes the use of chlorinating agents attractive at temperatures of 500°C or lower for nickel or Nichrome V, or at 600°C for INOR-8 (INOR-8 corroded at a lower rate in chlorine than in either $\text{CCl}_4\text{-N}_2$ or $\text{CCl}_4\text{-Cl}_2$, differing in that respect from the other metals or alloys). The corrosion tests were generally run for 24 hr, but at temperatures near 700°C, the testing period was shortened because of catastrophic corrosion rates. Brief corrosion tests with type 304 stainless steel at 600 and 625°C indicated corrosion rates about a hundred times faster than those observed with the best high-nickel alloys tested.

Preliminary corrosion tests were made with Haynes 25 and "A" nickel for the burning-chlorination cycle shown in Fig. 1 (data shown in Table 7). These tests resulted in corrosion rates for "A" nickel in Cl_2 -15 vol % CCl_4 about threefold higher (3 to 4 mils/month) than in N_2 -15 vol % CCl_4 (Fig. 11). This was the only case in which the corrosion rates in $\text{Cl}_2\text{-CCl}_4$ differed significantly from the rates in $\text{N}_2\text{-CCl}_4$. The "A" nickel specimens fortunately were protected from chlorinating reagents by the oxide coat that they picked up during the oxygen portion of the cycle, and the overall corrosion rate was less than 1 mil/month. Haynes 25 did not behave this way, and the overall cycle corrosion rate of 3 to 5 mils/month was nearly as high as the 5 to 6 mils/month corrosion rate observed in $\text{Cl}_2\text{-CCl}_4$ (Fig. 11).

Corrosion rates during Darex²⁶ and Fluoride Volatility⁹ operations have been reported in detail elsewhere. The Darex corrosion data also

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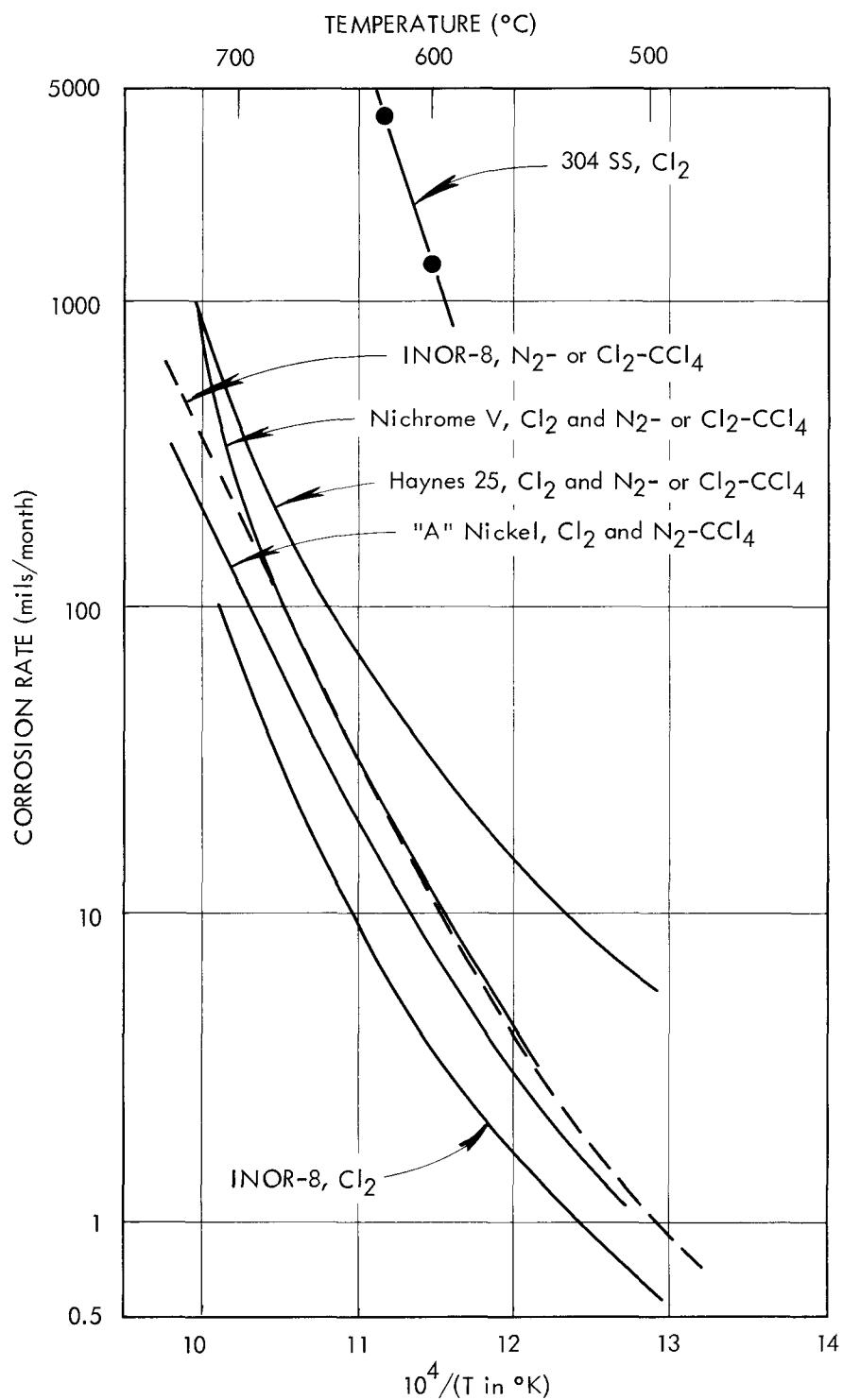


Fig. 11. Corrosion Rates of Metals in Chlorine and Carbon Tetrachloride Vapor as a Function of Temperature. (See ref 25).

Table 7. Corrosion of Haynes 25 Alloy and "A" Nickel in 10-Hr Cyclic Tests^a
(From ref 24)

Alloy	Specimen Temperature (°C)	Test Atmosphere	Test Period (hr)	Corrosion Rate (mils/month)		
				Oxygen	Cl ₂ + CCl ₄	10-hr Cycle
Haynes 25	800	Oxygen	5	b	b	3.1
	499	Cl ₂ + CCl ₄	5			
Haynes 25	799	Oxygen	5	b	b	4.2
	496	Cl ₂ + CCl ₄	5			
Haynes 25	c	Oxygen	5	b	b	4.3
	c	Cl ₂ + CCl ₄	5			
Haynes 25	787	Oxygen	5	Wt gain	6.0	3.0
	521	Cl ₂ + CCl ₄	5			
Haynes 25	775	Oxygen	5	1.82	8.5	5.2
	501	Cl ₂ + CCl ₄	5			
Haynes 25	780	Oxygen	5	Wt gain	7.5	3.7
	501	Cl ₂ + CCl ₄	5			
Haynes 25	730	Oxygen	24	0.7		
"A" Nickel	771	Oxygen	5	b	b	Wt gain
	497	Cl ₂ + CCl ₄	5			
"A" Nickel	766	Oxygen	5	b	b	0.5
	503	Cl ₂ + CCl ₄	5			
"A" Nickel	771	Oxygen	5	b	b	0.2
	502	Cl ₂ + CCl ₄	5			
"A" Nickel	526	Cl ₂ + CCl ₄	5		3.6	
"A" Nickel	499	Cl ₂ + CCl ₄	5		4.2	
"A" Nickel	502	Cl ₂ + CCl ₄	5		3.1	

^a Cycle was 5-hr in oxygen at ~800°C and 5-hr in Cl₂ + CCl₄ at ~500°C.

^b Rate calculated from weight lost during entire 10-hr cycle.

^c No temperature recorded.

includes some high-temperature chlorination tests that indicate that Haynes 25 should serve well under the cycle shown in routes b, c, or d, shown in Fig. 1.

6. CONCLUSIONS AND RECOMMENDATIONS

The combustion-chlorination process is more attractive than the other process, direct chlorination. The very favorable chemical kinetics and equilibria involved in the combustion-chlorination process, in the separation of uranium and niobium (and possibly fission products) by volatilization of niobium chloride (or perhaps by use of a salt bed) and in the high-temperature chloride-removal steps show the practicality of the development of a uranium recovery process for Rover fuel under conditions such that nickel or high-nickel alloys are suitable construction materials.

Chlorination processes, such as the combustion-chlorination process, are versatile. For example, the combustion-chlorination process described here is probably compatible with other high-temperature gas-solid chlorinations, especially the chlorination or hydrochlorination of zirconium alloy fuels. It may even be possible to conduct both of these processes in the same reactor.

Selection of the best of the several alternative processing routes discussed will depend mostly on engineering considerations, none of which has been given more than cursory attention as yet, as well as the particular circumstances influencing the processer. For example, the high-temperature chloride-removal operation might appeal to a processer who already has a TBP--nitric acid solvent extraction plant.

Early evaluation of one important engineering problem would be helpful in establishing the value of the combustion-chlorination process. On the basis of laboratory observations, the most difficult operation to engineer (with the exception of burning, which is receiving an independent study)⁶ will be the collection of volatilized chlorides, particularly niobium chloride. The sublimed niobium chloride is, under most circumstances, a low-density crystalline material which collects as masses of fluffy needles. This fluffy product may cause entrainment problems and make it necessary to use large collection vessels. On the other hand, entrained niobium chloride should be easily captured by simple, coarse filters because of its tendency to crystallize in long needles. In contrast to zirconium chloride for example, it might be possible to collect niobium chloride as a liquid.

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