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MASTER

LABORATORY DEVELOPMENT OF A PROCESS FOR RECOVERING URANIUM FROM ROVER FUEL BY COMBUSTION, LIQUID-PHASE CHLORINATION WITH HEXACHLOROPROPENE, AND AQUEOUS EXTRACTION

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Chemical Development Section B

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T. A. Gens T. B. Borne

ABSTRACT

The purpose of this work was to develop a process for recovering the uranium from spent Rover fuels. Only one reactor is used, and the process involves a 4-hr combustion of the fuel in oxygen at about 800°C, a 4-hr chlorination of the U_3O_8-Nb_2O_5 ash in refluxing hexachloropropene at 180°C, dissolution-extraction of the UCl_4 and $NbCl_5$ products at room temperature by dilute nitric acid, and extraction of the uranium from the resulting acid solution with 30% tributyl phosphate in Amsco diluent. The results indicate that an extract containing 50 g of uranium per liter can be produced in seven or eight extraction stages, with total uranium losses of less than 0.02%. Corrosion rates of several possible construction materials during chlorination are less than 0.1 mil/month.

Problems in the process involve handling about 10% of the niobium as a solid during the liquid-liquid separations, and handling solutions containing chloride.

The results of this laboratory-scale work indicate that the liquid-phase chlorination and subsequent extraction operations are reducible to large-scale practice, since these operations resemble the liquid-phase operations typically performed in radiochemical separation plants.

1. INTRODUCTION

This work was performed to investigate the chlorination with hot, liquid hexachloropropene (HCP) of the combustion ash from Rover fuels now being used in nuclear rocket research and the recovery of uranium from the chlorination product. The methods developed may also be applicable to graphite-matrix fuels other than the Rover fuels.

The Rover fuel chosen for the laboratory experiments and flowsheet calculations was the Kiwi-B-1B, which contains uncoated uranium carbide impregnated in graphite, with niobium carbide liners in the coolant channels.[1,2] In later fuels in the Rover series, the uncoated uranium

[redacted]

carbide is being replaced by uranium carbide particles that have been coated with pyrolytic carbon. This change in the Rover fuel should not have any major effect on the process developed in this work, in which the first step is combustion in oxygen. The combustion step is now being investigated on an engineering scale.[3,4] The fuel contains about 70% carbon; after burning, the ash contains about 50% uranium as U_3O_8, and 25% niobium as Nb_2O_5.

Chlorination by refluxing HCP is being investigated because high-temperature, gas-phase fluorination[2,4] and chlorination[5] of the Rover fuel combustion ash are inherently difficult. Also, aqueous dissolution of the combustion ash is complicated by the troublesome behavior of niobium in aqueous solutions.[6] Therefore, a process that avoids high-temperature gas-solid reactions, that permits the use of well-developed solution technology, that avoids excessive corrosion of the burner, and that leads to good uranium recoveries is desired. These requirements may possibly be met by the chlorination process described in this report. The chlorination products can be readily extracted to yield an aqueous solution from which the uranium may be recovered by extraction with tributyl phosphate--Amsco mixtures. Hexachloropropene has been used previously to convert uranium oxide to uranium tetrachloride on production-plant scale.[7]

The laboratory work involved experiments to determine the optimum volume of HCP, reflux time, and extraction procedure. Promising alternative methods for chlorinating and treating the chlorination product were investigated briefly and are discussed briefly, as is corrosion. Finally, conclusions and recommendations are given.

The help of G. R. Wilson, H. W. Dunn, C. A. Horton, and others of the Analytical Chemistry Division is gratefully acknowledged. Corrosion tests were performed by P. D. Newmann and co-workers of the Reactor Chemistry Division. Discussions with R. H. Rainey and A. D. Ryon of the Chemical Technology Division concerning solvent extraction were most helpful.

2. FLOWSHEET

The process (Fig. 1 and Table 1) involves five operations, besides solvent extraction, which require a total time of about 9 hr: burning of the fuel elements, chlorination of the product ash in HCP, extraction of the niobium chloride dissolved in the HCP with 3.6 $\underline{M}$ HNO_3, dissolution in water of the UCl_4 chlorination product, which is insoluble in HCP, and blending of the two aqueous solutions prior to extraction. A preliminary investigation of the efficiency of uranium extraction with 30% TBP--Amsco from the resulting 3 $\underline{M}$ HNO_3 solution indicated that the precipitation of about 10% of the niobium in the 3 $\underline{M}$ HNO_3 did not seriously interfere with extraction.

2.1 Combustion

The combustion step is being investigated on engineering scale, and results are reported elsewhere.[2-4] Pure oxygen is used, and carbon dioxide and nonvolatile uranium and niobium oxides are produced. About 4 hr at 800°C were required to burn completely the fuel samples in laboratory experiments. The temperatures inside the burning rods will exceed 800°C, and these high temperatures may cause sintering of the ash and make it necessary to leave a small heel after chlorination, as discussed below.

2.2 Chlorination and Preparation of Feed for the Solvent Extraction Step

Four liters of HCP per kilogram of ash are needed to produce nearly complete chlorination in one 4-hr treatment at the boiling point, which decreases from about 190°C initially to about 170°C after chlorination is complete. Longer chlorination is not recommended because the HCP and chlorocarbon reaction products, mostly trichloroacrylyl chloride (CAC), decompose with longer heating. The HCP is separated while still hot from the mostly insoluble UCl_4 product. About 98% of the niobium, which is soluble in hot HCP and only slightly soluble in cold HCP, stays in the HCP along with up to 10% of the uranium. These dissolved niobium and uranium chlorides are completely extracted from the HCP by a single treatment with 3.6 $\underline{M}$ HNO_3. (This molarity was chosen in order to produce

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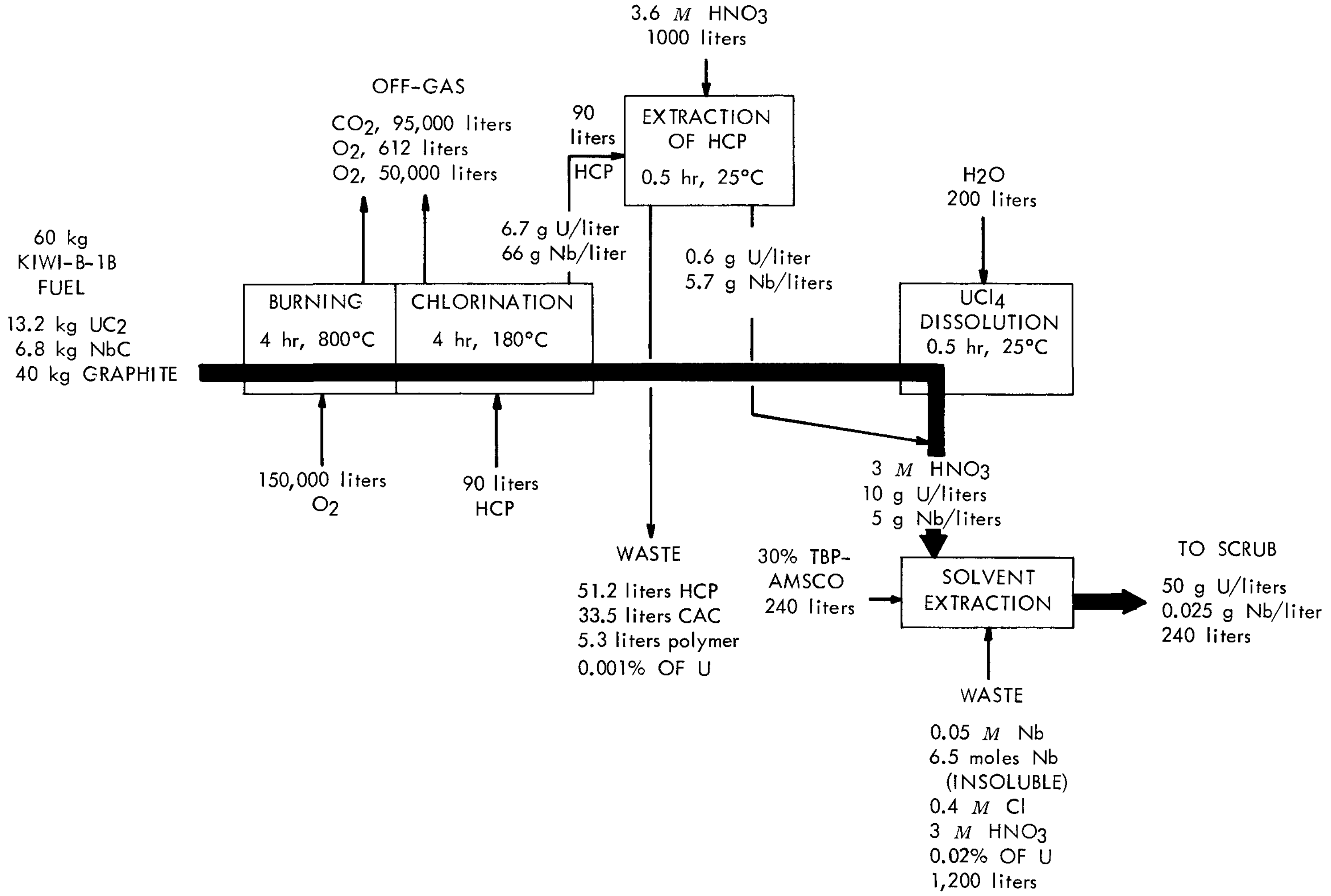

Fig. 1. Combustion-HCP Chlorination-Aqueous Extraction Process for Rover Fuel.

Table 1. Flowsheet Runs. Chlorination of 15.0 g of Rover fuel combustion ash in 60 ml of HCP, followed by extraction with 3 M HNO_3 and reextraction with 30% TBP-Amsco

Duration of HCP chlorination: runs 1-3, 4 hrs; 4-7, 3.5 hrs.

	Percent of Total U and Nb in Fractions													
	Run 1		Run 2		Run 3		Run 4		Run 5		Run 6		Run 7	
Fractions	U	Nb	U	Nb	U	Nb	U	Nb	U	Nb	U	Nb	U	Nb
3 M HNO_3 after TBP re-extraction	0.005	91.80	0.013	93.04	0.006	87.30	0.004	85.95	0.006	89.56	0.010	81.87	0.003	97.26
Material insoluble in 3 M HNO_3	0.194	4.75	0.007	3.20	0.098	10.67	0.130	12.30	0.153	7.70	0.274	15.78	0.132	2.36
3 M HNO_3 wash of insoluble material, 100 ml.	0.000	1.06	0.000	1.80	0.000	2.00	0.001	1.74	0.000	2.70	0.001	2.28	0.005[b]	0.36[b]
HCP after 3 M HNO_3 extraction	0.000	0.00	0.005	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00
1st TBP extract, 300 ml	89.59	1.48	84.41	0.94	85.80	0.04	90.72	0.04	85.50	0.04	87.24	0.07	90.00	0.02
2nd TBP extract, 200 ml	8.63	0.9	12.94	0.7	11.67	0.00	2.80	0.00	12.00	0.00	10.43	0.00	8.68	0.00
3rd TBP extract, 100 ml	1.16	0.0	1.96	0.0	1.68	0.00	5.88	0.00	1.79	0.00	1.47	0.00	0.933	0.00
4th TBP extract, 100 ml	.312	0.0	0.470	0.0	0.534	0.00	0.326	0.00	0.357	0.00	0.445	0.00	0.208	0.00
5th TBP extract, 100 ml	.077	0.0	0.133	0.0	0.156	0.00	0.110	0.00	0.148	0.00	0.104	0.00	0.053	0.00
6th TBP extract, 100 ml	.027	0.0	0.046	0.0	0.046	0.00	0.039	0.00	0.038	0.00	0.025	0.00	0.014	0.00
7th TBP extract, 100 ml	.006	0.0	0.015	0.0	0.014	0.00	0.007	0.00	0.010	0.00	0.007	0.00	0.004	0.00
8th TBP extract, 100 ml	--	--	0.005	0.0	0.004	0.00	0.002	0.00	0.003	0.00	0.003	0.00	0.002	0.00
9th TBP extract, 100 ml	--	--	0.002	0.0	0.002	0.00	0.001	0.00	0.000	0.00	0.001	0.00	0.001	0.00
	Concentrations in 3 M HNO_3 before TBP re-extraction, g per liter													
	11.6	3.5[a]	8.0	3.75	9.1	4.2	8.2	4.3	8.7	3.8	10.6	6.3	17.4	10.2

[a] Nb concentrations were calculated by dividing the total amount of Nb, including that insoluble in 3 M HNO_3 (data in 2nd row), by the volume of 3 M HNO_3 used.

[b] In run 7, the 3 M HNO_3 wash actually involved a 1-hr treatment at reflux, rather than a cold wash as in the other runs.

a solvent extraction feed solution that was 3 M in nitric acid.) If enough 3.6 M HNO_3 were used to yield a product containing about 2 g of niobium per liter, all the uranium and niobium would dissolve. However, under the flowsheet conditions (Fig. 1 and Table 1), in which a more concentrated solution containing about 10 g of uranium and 5 g of niobium per liter is needed to keep the volumes of 3 M HNO_3 and TBP-Amsco low, about 10% of the niobium precipitates as the hydrous oxide.

The UCl_4 residue is removed from the burner-chlorinator by dissolution in cold water. Water is used, rather than nitric acid, to prevent rapid corrosion of the vessel, which would probably be made of nickel or a nickel-base alloy. This product solution is blended with the nitric acid used to extract uranium and niobium from the HCP, either before or after the HCP extraction. Early runs (Sec 4.1) indicated that complete chlorination of the combustion ash could be achieved and that no unchlorinated residue should be found after the UCl_4 dissolution. However, a small amount of unchlorinated ash, containing about 0.1% of the total uranium, was found in the flowsheet runs (material insoluble in 3 M HNO_3, second row, Table 1). This unchlorinated residue was carried along with the niobium precipitate through the extraction with TBP-Amsco in the flowsheet runs, but the 0.1% of the uranium in the residue may be too large to be discarded to waste. No significant amount of uranium was recovered by washing or leaching the precipitate, after solvent extraction, in 3 M HNO_3 (see third row in Table 1). The unchlorinated residue could be left in the burner-chlorinator as a heel to be chlorinated during the next run. The separation of the unchlorinated residue from the UCl_4 solution is not difficult; the residue is a dense solid. The behavior of the unchlorinated residue through several cycles of the process cannot be predicted from laboratory experiments since the residue is probably the result of sintering the ash during burning, and the amount of sintering will depend on the conditions of burning. In exploratory runs with large lumps of ash that had fused during burning, the surface chlorinated rapidly, but reaction was very slow after the surface became coated with UCl_4. Careful temperature control during burning is, therefore, required.

2.2.1 Results of Batch Solvent Extractions

Because about 10% of the niobium was present as a precipitate in the 3 M HNO_3 solution going to solvent extraction, it was necessary to make some preliminary batch solvent extraction tests. The results, expressed in Table 1 as percentages of total uranium and niobium in each extract, showed that uranium extracted well, that only about 1% of the niobium extracted, and that the niobium precipitate did not significantly hinder the uranium recovery. Over 99% of the niobium, including 10% as precipitate, remains in the 3 M HNO_3 and is discarded to waste. A McCabe-Thiele diagram based on these results (see Sec 4.2) indicates that 7 or 8 theoretical solvent extraction stages would be needed to produce an extract containing 50 g of uranium per liter with less than 0.02% loss to the raffinate, starting with a 3 M HNO_3 feed containing 10 g of uranium per liter.

If desired, about 50% of the HCP can be recovered by distillation from the chlorocarbon waste (Sec 4.3). Hexachloropropene costs about $10 per lb in research quantities. At this price, with no HCP recovery, the HCP used in the process shown in Fig. 1 would cost about $0.30 per g of uranium recovered.

2.3 Major Operating Problems

The major operating problem appears to be handling of solid hydrous niobic oxide during liquid-phase separations. During the extraction of uranium and niobium from HCP with 3.6 M HNO_3, the aqueous phase floats on the HCP, and the niobic oxide collects above the interface in the aqueous phase. Because this extraction is unusually efficient, as evidenced by the small amount of uranium and niobium remaining in the HCP (fourth row in Table 1), only one extraction stage is needed. However, a clean separation of the HCP is desirable because the HCP is soluble in TBP-Amsco and would soon build up to undesirable concentrations in the TBP-Amsco if the separation of HCP from the 3 M HNO_3 were not complete. Two HCP solvents, chloroform and carbon tetrachloride, which are immiscible with water and easier to remove than HCP from TBP, were used in the laboratory work to wash HCP from the 3.6 M HNO_3, without any detectable uranium losses to the solvents. Methods for handling the solids in bottom-interface extraction columns have been developed at the Hanford Atomic Products Operations, and solvent extraction of uranium from slurries containing up to 20 wt % solids has been accomplished.[8] Corrosion is not a major problem during burning or chlorination by HCP. Titanium may be used for the nitric-hydrochloric acid solutions[9] during solvent extraction. The waste can be neutralized to form an alkaline sodium chloride solution. The problems involved in storing this solution are not known. It may be possible to use inexpensive materials of construction such as concrete or mild steel, rather than expensive metals such as titanium, zirconium, or Hastelloy C, for the storage tanks.

3. CHEMISTRY OF THE CHLORINATION PROCESS

The main reaction in chlorination of uranium trioxide in liquid HCP reportedly[7,10] is:

$$UO_3 + 3\ C_3Cl_6 \longrightarrow UCl_4 + 3\ C_3Cl_4O + Cl_2, \tag{1}$$

where C_3Cl_4O is trichloroacrylyl chloride (CAC). However, the chlorine produced in Eq. (1) apparently is not lost, but is consumed in further chlorination of uranium oxide, since off-gas studies[10] revealed no appreciable chlorine. Thus, the overall reaction was considered, for flowsheet calculations, to be:

$$UO_3 + 2\ C_3Cl_6 \longrightarrow UCl_4 + 2\ C_3Cl_4O + 0.5\ O_2, \tag{2}$$

although some chlorine is probably used up in secondary reactions

$$C_3Cl_6 + Cl_2 \longrightarrow CCl_4 + C_2Cl_4 \tag{3}$$

and

$$C_3Cl_6 + Cl_2 \longrightarrow C_3Cl_8, \tag{4}$$

since appreciable amounts of the products of Eq. (3) and (4) are found in the chlorination products.[7,11] The major organic product, CAC, produces skin burns and severe damage to the eyes but has no detectable harmful effects on the liver.[12] The type of organic products obtained varies with experimental conditions. For example, prolonged heating produces a large amount of dissolved polymers. The uranium chloride product has very little solubility in either hot or cold HCP. The presence of a small amount of soluble uranium chloride in the organic reaction products is probably due to the solubility of uranium pentachloride in CAC.[13] Uranium pentachloride could form by the reaction:

$$UO_3 + 3\ C_3Cl_6 \longrightarrow UCl_5 + 3\ C_3Cl_4O + 0.5\ Cl_2, \qquad (5)$$

which is quite similar to the reaction shown in Eq (1).

The niobic oxide in the combustion ash is thought to chlorinate slowly in HCP as follows:

$$Nb_2O_5 + 5\ C_3Cl_6 \longrightarrow 2\ NbCl_5 + 5\ C_3Cl_4O. \qquad (6)$$

This assumed reaction has not yet been verified. The fraction chlorinated increases with time and with increasing amounts of HCP (see Sec 4.1). The niobium pentachloride product is soluble in hot HCP, but precipitates as large white crystals upon cooling. The slow chlorination of tantalum[14] and plutonium[15] oxides in refluxing HCP has also been observed.

The volume of HCP needed to satisfy the stoichiometry of Eqs. (2) and (6), assuming a density of 1.75 for HCP, is 1.8 ml per gram of ash. Therefore, the use of 4 ml of HCP per gram ash should lead to reaction of less than half of the HCP, and over half of the HCP should be recoverable from the product. Since a possible recovery of slightly less than half of the HCP when the ratio is 4 ml per gram of ash was indicated from the laboratory work (Sec 4.3), the HCP probably enters into some side reactions, such as that shown in Eq (4), or perhaps reacts with UO_3 according to Eq (1) or (5) rather than Eq.(2).

4. LABORATORY STUDIES

Studies of the effect of reflux time and the ratio of the volume of the HCP to the weight of the ash indicated the best ranges of these variables and also suggested possible variations in the process. Extraction of uranium with 30% TBP--Amsco from the nitric acid extraction product was investigated to determine if the dissolved and precipitated niobium would interfere or would itself extract.

The recovery of HCP by distillation from the mixed chlorocarbon solution after chlorination was investigated. Extraction of uranium from HCP with glycol and re-extraction with di-2-ethyl-hexyl phosphoric acid was also tried and seemed promising, particularly because the solubility of niobium pentachloride in glycol is high. Chlorination of Rover fuel combustion ash with phosphorous pentachloride and oxychloride was briefly investigated as an alternative to HCP chlorination.

4.1 Effect of Reflux Time and HCP-to-Ash Ratio

Early observations showed that, in contrast to the uranium chlorination product which was only slightly soluble in HCP, the niobium chlorination product dissolved in the hot HCP. All the niobium that dissolved in the hot HCP was also soluble in dilute nitric acid to the extent of 2 g of niobium per liter. Therefore, the extent of chlorination was determined at any time by filtering the hot HCP-chlorination mixture, extracting the niobium from the HCP with dilute nitric acid, dissolving the HCP-insoluble material in mixed hydrofluoric-nitric acid and analyzing for niobium in the two aqueous fractions. From this study, it was apparent that the use of 2 or 3 ml of HCP per gram of ash would lead to less than 80% chlorination in 4 hr at reflux and less chlorination at shorter reflux times (Fig. 2). After 3 hr with 4 ml of HCP per gram of ash, about 98% of the niobium was found in the HCP. The remaining 2% was either very slow to chlorinate or had chlorinated but was sorbed on the insoluble UCl_4, since a longer reflux time of 4 hr did not improve the separation. It was concluded that at least 4 ml of HCP per gram of ash and 3 hr of reflux time are needed for complete chlorination.

This conclusion was further confirmed by a series of runs (Table 2) in which the reflux time or volume of HCP used per gram of ash was less than recommended in the flowsheet (Fig. 1). These runs showed that the amount of unchlorinated residue varied inversely with the reflux time and the volume of HCP. After the ash was refluxed in HCP, water or nitric acid was introduced into the reaction vessel to remove all extractable uranium and niobium from both the UCl_4 precipitate and the HCP. The material that did not extract in three passes of the water or acid

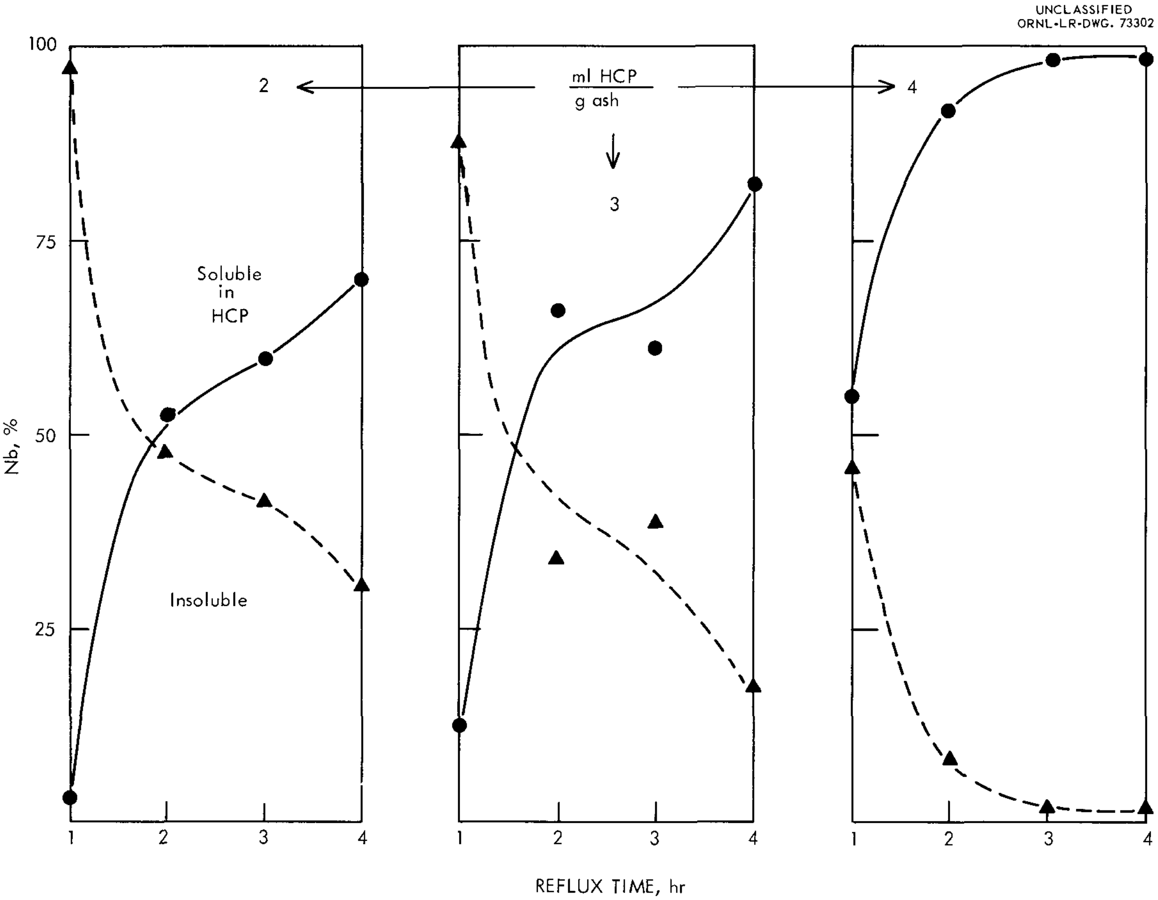

Fig. 2. Percent of Niobium Soluble in HCP as a Function of Reflux Time and ml HCP/g Ash.

Table 2. Chlorination of Rover Combustion Ash Under Non-Flowsheet Conditions, and Recovery of Uranium in Aqueous Solution

Volume of Extractant: equal to volume of HCP used
% U or Nb in HCP: <0.01%, all runs

Run	ml HCP per g ash	Reflux Time (hr)	Extractant	1st Extraction U (%)	1st Extraction Nb (%)	2nd Extraction U (%)	2nd Extraction Nb (%)	3rd Extraction U (%)	3rd Extraction Nb (%)	Unchlorinated Residue U (%)	Unchlorinated Residue Nb(%)
1	4	1.5	3 M HNO_3	99.41	81.4	0.40	0.11	0.07	0.15	0.119	18.4
2	3	1.5	3 M HNO_3	99.80	83.4	0.06	0.09	0.001	0.00	0.13	16.5
3	1.5	3	3 M HNO_3	98.20	1.2	0.002	0.00	0.001	0.00	1.79	98.8
4	2.8	2.8	3 M HNO_3	99.07	85.6	0.094	0.11	0.02	0.01	0.84	14.3
5	4	3	8 M HNO_3	99.57	77.6	0.010	0.00	0.002	0.00	0.43	22.4
6	5	3	1 M H_2O_2	98.45	45.4	0.010	0.00	0.001	0.00	1.55	54.6
7	3	2	H_2O	99.07	77.4	0.010	0.00	0.001	0.00	0.92	22.6
8	3	3	H_2O	99.58	97.1	0.030	0.00	0.003	0.00	0.37	2.9
9	3	3	3 M HNO_3	99.50	79.3	0.010	0.55	0.001	0.23	0.53	19.9
10	3	3	3 M HNO_3	96.80	78.7	0.010	0.01	0.000	0.00	3.2	21.3
11	3	3	3 M HNO_3	99.67	95.4	0.011	0.01	0.000	0.00	0.32	4.6
12	3	3	3 M HNO_3	100.00	97.8	0.000	0.00	0.000	0.00	0.00	2.2

solution was considered to be unchlorinated ash. The formation of an intermediate niobium oxychloride was also considered likely, in which case the ash might be broken up but dissolution of niobium in HCP as the pentachloride still would not occur. Since the uranium in the oxide ash chlorinates rapidly,[7,16] conversion of the ash to water-soluble UCl_4 and HCP-insoluble $NbOCl_3$ might occur, and good uranium recoveries might be possible without complete chlorination of the niobium in the ash. Some runs, such as No. 2, in which the uranium in the unchlorinated residue was reduced to 0.13% after only 1.5 hr of reflux, while 16.5% of the niobium remained in the residue, showed that the uranium oxide was being preferentially chlorinated. However, in other runs such as 9-11, 0.3 to 3% of the uranium remained in the unchlorinated residue, presumably trapped inside unchlorinated niobium oxide. These runs show, in agreement with the related study described above, that at least 4 ml of HCP per gram of ash and 3 hr of reflux are needed to chlorinate and dissolve the niobium and ensure chlorination of 99.9% of the uranium.

A comparison of run 8, in which water was used as the extractant, with the runs in which 3 $\underline{M}$ HNO_3 was used, shows that water is as satisfactory as 3 $\underline{M}$ HNO_3. When nearly complete chlorination was achieved (run 12), only one extraction of the HCP was needed. The carryover of uranium and niobium into the second extraction in other runs apparently is caused by leaching of the unchlorinated residue, rather than by additional extraction from the HCP. Strong nitric acid (run 5) or hydrogen peroxide solutions (run 6) converted much of the water-soluble niobium compound into insoluble niobium oxide, which retained some of the uranium in an insoluble form.

The solubility of niobium in the mixed nitric acid--chloride solutions, up to 30 g/liter, was surprising in view of the reportedly low solubilities of niobium in nitric acid[17] and in hydrochloric acid.[18] Apparently a mixture of the two acids under proper conditions can dissolve large amounts of niobium. The presence of some α-hydroxychlorocarbon acid was also detected by infrared spectroscopy in the aqueous HCP extract, and this acid could have complexed some niobium in a water-soluble form. Although concentrated niobium solutions were found in some cases, the variables effecting the niobium solubility are not yet understood, and several hours are required to approach the equilibrium solubility. Therefore, under the flowsheet conditions of Fig. 1, a niobium solubility of less than 5 g/liter is usually observed.

The maximum amount of uranium found in the HCP fraction following the chlorination step was 10% of the total. The yellow color of the HCP indicated that the uranium which dissolved in the HCP was not the green, tetravalent uranium. This HCP-soluble uranium was probably pentavalent and soluble in the CAC reaction product rather than in HCP itself.[13]

4.2 Solvent Extraction

Because about 10% of the niobium was present as a precipitate in the 3 M HNO_3 solution going to solvent extraction, it was necessary to make batch solvent extraction tests, using 30% TBP--Amsco, to determine if this precipitate would interfere with the uranium recovery. The results, expressed in Table 1 as percentages of total uranium and niobium in each extract, showed that uranium extracted well. Little niobium extracted, and the precipitate did not significantly hinder the uranium recovery. About 99% of the niobium, including 10% as a precipitate, remained in the 3 M HNO_3 and was discarded to waste. The results of runs 2 and 7, in which the uranium concentrations in the 3 M HNO_3 were 8 and 17 g/liter, respectively, when plotted on a McCabe-Thiele diagram (Fig. 3), indicated that about ten and seven solvent extraction stages, respectively, would be needed to produce an extract containing 50 g of uranium per liter with less than 0.02% loss to the raffinate, at an assumed operating ratio of 1 liter of 30% TBP-Amsco to 5 liters of 3 M HNO_3.

4.3 Recycle of HCP

The chlorocarbon products, from a run in which 3 ml of HCP per gram of ash and 3 hr reflux were used and the uranium and niobium were extracted with 3 M HNO_3, were distilled and the volume percent distilled as a function of temperature was determined (Table 3). Chloroform was used to wash all chlorocarbons from the 3 M HNO_3.

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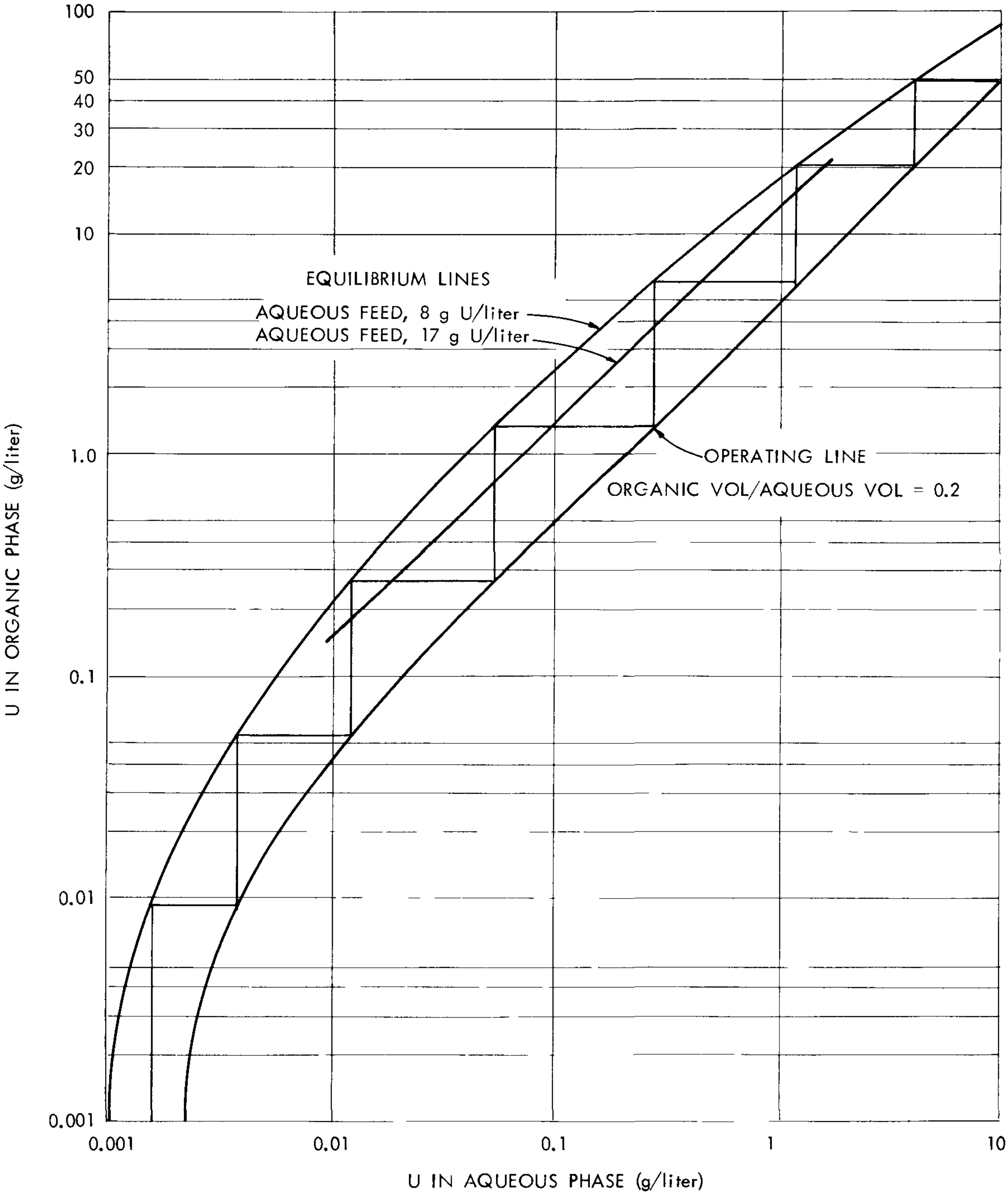

Fig. 3. Stage-Concentration Diagram for Extracting Uranium from the Hexachloropropene Extract with Tributyl Phosphate-Amsco Mixture.

Table 3. Single-Plate Distillation of Chlorocarbon Product

Distillation Range (T^oC)	Volume % Distilled	Material Suspected
<100	--	$CHCl_3$
100-160	16.8	$CHCl_3$ + CAC[a]
160-170	28.2	CAC
170-190	19.5	CAC + HCP
190-250	25.7	HCP
>250 (residue)	10.2	polymer

[a] CAC is trichloroacrylyl chloride, $CCl_2=CCl-COCl$.

The experiment shows that a single-plate distillation would recover about 26% of the HCP for recycle. Assuming most of the mixed CAC-HCP cut is HCP, multiplate distillation would recover a maximum of about 45% of the HCP. Using 4 ml of HCP per gram of ash, and assuming no degradation of the extra HCP, single-plate distillation would recover about 45% of the HCP. A recovery of about 50% of the HCP would be predicted on the basis of Eqs. (2) and (6) (Sec 3) under the flowsheet (Fig. 1) conditions, and in practice it appears that approximately this recovery can be achieved.

Trichloroacrylyl chloride apparently does not hydrolyze upon contacting water; the largest cut of distillate had the boiling point of this compound, about 160°C.[19] This conclusion is also supported by chloride analyses of the aqueous product. These analyses agree well with the calculated amounts of chloride that should be present as a result of the dissolution of uranium and niobium chlorides.

4.4 Possible Modifications in the HCP Process

The high solubility of the niobium and the low solubility of the uranium chlorination products in HCP suggested a possible method of separation. Distillation of the HCP and $NbCl_5$ away from the UCl_4 product offered a possible method of removing the troublesome niobium before dissolution of the UCl_4 in water. Chlorination of the combustion ash with PCl_5-$POCl_3$ mixtures offers a means of selective volatilization of niobium chloride. Investigation of these modifications revealed disadvantages that caused them to be less attractive.

4.4.1 Separation of Uranium and Niobium by Differences in Solubility in HCP

Fifteen grams of combustion ash were chlorinated under the flowsheet conditions. The products were filtered while hot. The precipitate (1st, Table 4) on the filter, mostly UCl_4, was dissolved in a mixture of nitric and hydrofluoric acids and analyzed. Twenty percent of the chlorocarbon product was removed by distillation in order to decrease the uranium chloride solubility,[13] and the HCP was refiltered while hot (2nd precipitate). The material on the filter was dissolved in hydrofluoric-nitric acid and analyzed. The HCP was cooled, and the crystals which formed (3rd precipitate) were filtered, dissolved in hydrofluoric-nitric acid and analyzed. The HCP and CAC were also analyzed. The distillation to remove CAC did not produce complete precipitation of the uranium; 0.34% remained in the hot HCP and precipitated with niobium upon cooling (Table 4). In other runs (Sec 4.1), less than 2% of the niobium remained with the UCl_4 precipitate from hot HCP under similar conditions, and the presence of 10% in this fraction in the present run was due to some cooling of the HCP during filtration. The separation was not considered complete enough for practical use, since a 0.5% uranium loss would have to be tolerated and some niobium would remain in the uranium fraction.

Table 4. Separation of Uranium and Niobium by Difference in Solubility in HCP

Fraction	U (%)	Nb (%)
First precipitate (from hot HCP)	99.52	10.12
Second precipitate (from hot HCP after distilling off CAC)	0.11	13.81
Third precipitate (from HCP at 25°C)	0.34	65.35
CAC distillate	0.00	3.27
HCP	0.03	7.45

4.4.2 Evaporation of HCP and $NbCl_5$ with Chlorine or Argon Carrier Gas, and Aqueous Dissolution of the Residue

Three runs were made in which approximately 15-g samples of combustion ash were chlorinated in HCP for 3 hr at 3, 5, and 6 ml of HCP per gram of ash, and the liquid products and part of the $NbCl_5$ were evaporated off in chlorine carrier gas (300 cc/min). The evaporated products contained 76, 63, and 36%, respectively, of the niobium, and the amount of the total uranium lost with the volatilized niobium was 0.005, 0.01, and 0.4%, respectively. These results were unsatisfactory, since a large uranium loss had to be accepted to achieve volatilization of an appreciable amount of niobium.

Because the volatilization of uranium may have been caused by the formation of volatile chlorides (UCl_5 or UCl_6) by reaction of UCl_4 with the chlorine carrier gas, an experiment was performed with argon carrier gas. Uranium hexachloride reportedly has a vapor pressure of about 30 mm Hg at 200°C.[20] Chlorination of a 15-g sample of ash in HCP was performed under flowsheet (Fig. 1) conditions, and the HCP and $NbCl_5$ were evaporated in a stream of argon gas (300 cc/min). The evaporated fraction contained 93% of the niobium and only 0.001% of the uranium; thus, it is apparent that chlorine carrier gas causes the volatilization of some uranium and does not improve the volatilization of niobium, and that argon carrier gas is preferable.

Evaporation of the $NbCl_5$ and HCP in argon carrier gas before dissolution of the UCl_4 residue in nitric acid offers an operable method of reducing the amount of niobium in the solvent extraction feed, but use of this method would introduce problems in addition to the added operation of evaporation. Part of the volatilized $NbCl_5$ collects in the condenser as a solid, and part washes down into the condensate. The $NbCl_5$ in the condenser could probably be removed satisfactorily by melting (m.p., 194°C) after the run, and it also dissolves readily in cold dilute hydrofluoric acid or concentrated hydrochloric acid. Another problem is introduced by the pyrolysis of chlorocarbons that remain in the residue during evaporation. The pyrolysed material hinders dissolution of the UCl_4 residue in nitric acid. This material can be removed by steam stripping from nitric acid, and a 1 or 2 hr treatment in boiling nitric acid is needed to completely dissolve the UCl_4 residue. Despite these problems, this modification is a possible alternative if the niobic oxide precipitate that forms during the process outlined in Fig. 1 proves too difficult to handle. A treatment with strong boiling nitric acid to remove chloride previous to solvent extraction (Darex process[21]) would simultaneously remove these pyrolysis products.

4.4.3 Extraction of Chlorinated Products from HCP with Glycol

The problem caused by the low solubility of niobium in 3 $\underline{M}$ HNO_3 (Sec 2) might be avoided if an efficient solvent could be found for extracting uranium and niobium chlorides from the HCP. The solvent should be immiscible with HCP, and the uranium should be re-extractable with one of the conventional uranium solvents so that it would be further processed by methods already developed. Glycol appears to satisfy most of these requirements. Unfortunately, TBP-Amsco does not extract uranium from glycol efficiently, and it was necessary to use an extractant used previously mainly in the uranium ore processing industry, 10% di-2-ethylhexyl phosphoric acid (Di-2-EHPA) in Amsco.[22]

A 15-g sample of combustion ash was chlorinated under the flowsheet conditions. After cooling, the uranium and niobium were batch extracted at room temperature from the 60 ml of HCP with five 60-ml passes of glycol. The HCP-insoluble residue (UCl_4) was dissolved at room temperature in 500 ml of glycol, and the glycol fractions were combined into one 800-ml sample. The uranium and niobium were batch extracted from the glycol at room temperature with 10% di-2-EHPA--Amsco (Table 5). Essentially all the uranium and niobium were extracted in seven batch extractions. There was no appreciable uranium loss in the HCP after glycol extraction, but 0.7% of the uranium remained in an unchlorinated residue. This residue would remain as a heel to be recovered on the next cycle of the process, as discussed in Sec 2. No other solids were observed during either extraction operation. During a scouting run in which 100% chlorination was achieved, the HCP-insoluble fraction dissolved completely in glycol. A major disadvantage of this extraction procedure over that proposed in Fig. 1 is

Table 5. Chlorination of 15 g of Combustion Ash for 3 hr in 60 ml of HCP, Dissolution of and Extraction from HCP of the Uranium and Niobium Chlorides with Glycol, and Re-extraction of Uranium and Thorium from Glycol with 10% Di-2-EHPA--Amsco

Fraction	Vol (ml)	U (%)	Nb (%)
HCP	60	0.000	0.00
Glycol	800	0.033	0.24
Unchlorinated Residue (in HF)	---	0.699	3.58
1st di-2-EHPA extraction	800	67.79	44.27
2nd di-2-EHPA extraction	800	26.32	48.10
3rd di-2-EHPA extraction	400	3.16	2.60
4th di-2-EHPA extraction	400	1.43	0.72
5th di-2-EHPA extraction	200	0.46	0.23
6th di-2-EHPA extraction	200	0.08	0.13
7th di-2-EHPA extraction	200	0.03	0.12

that di-2-EHPA has been used mainly for recovery of uranium from ore concentrates, and new problems introduced by the presence of highly enriched uranium have not been investigated. However, di-2-EHPA has proved satisfactory for use in extracting strontium from radioactive solutions.[23]

4.4.4 Chlorination with PCl_5 and $POCl_3$

Chlorination of the Rover fuel combustion ash can be accomplished with conventional chlorinating agents such as PCl_5. Because it would not be practical to intimately mix the solid PCl_5 with the radioactive ash, it was necessary to add liquid $POCl_3$ to transform the mixture into a viscous mass so that nearly complete chlorination could be achieved. The formation of the low-melting complex product $NbCl_5 \cdot POCl_3$ probably helped achieve nearly complete chlorination and may also have aided in the volatilization of the niobium. The normal boiling point of $NbCl_5 \cdot POCl_3$ is 263°C,[24] while that of $NbCl_5$ is 247.4.[25]

Five grams of ash were slurried with 30 g of PCl_5 and 10 ml of $POCl_3$, and then heated. Reaction started at 40°C. The temperature was increased over 0.5 hr to 300°C, then argon was passed over the melt for 1 hr at 300°C. The nonvolatile fraction contained 99.6% of the uranium in a water-soluble form, and 2% of the niobium. The nonvolatile niobium was in the form of oxide that had not chlorinated. In practice, the volatile fraction (containing 98% of the niobium) would have to be revolatilized to recover 0.4% of the uranium lost to this fraction. Although this procedure was rapid and did not require excessively high temperatures, and the separation achieved in the single stage evaporation was fair, it was not investigated further.

5. CORROSION

Preliminary corrosion tests indicated that several metals or alloys, including nickel and type 304 stainless steel, would serve well as containers for refluxing HCP (Table 6) or HCP containing dissolved U_3O_8 (Table 7). Despite this compatibility with many metals, refluxing HCP dissolves U, Al, Zr, and Ti rapidly. On the other hand, other metals ordinarily attacked by chlorinating agents, Th, Nb, Mo, and W, are not attacked by refluxing HCP.

Table 6. 48-hr Corrosion Rates in Refluxing HCP[26]
For all materials, there was no measurable corrosion in the liquid phase

Material	Vapor-phase Corrosion Rate (mil/month)
Haynes-25	0.1
Nichrome-V	0.2
INOR-8	0.1
Nimonic 75	0.1
304L SS	0.2

In 5-hr exposures to oxygen at 800°C, three "A" nickel sample showed small weight gains. Nickel is reportedly especially useful in oxygen atmospheres at temperatures up to 1200°C.[27] Nickel also is resistant to alternating treatment with fluorine at 400°C and oxygen at 700°C.[28]

Corrosion tests that simulate the entire process in the reactor (burning, chlorination, and dissolution of UCl_4 in water) are being made. Since the corrosion rates during burning and chlorination are very low, and since the UCl_4 dissolution involved only a brief contact with cold water, corrosion in the reactor does not appear to present a significant problem.

Table 7. Cumulative Corrosion Rates (mils/month) in Refluxing HCP in which 280 g of U_3O_8 per liter Have Been Dissolved

Material	24 hr		72 hr		96 hr		120 hr		168 hr		264 hr	
	V[a]	L	V	L	V	L	V	L	V	L	V	L
"A" Nickel	0.00	0.28	--	--	0.06	0.09	0.07	0.08	0.04	0.06	0.04	0.05
Haynes-25	0.03	0.00	--	--	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01
Nichrome-V	0.15	0.14	--	--	0.14	0.05	0.06	0.04	0.11	0.03	0.08	0.03
Inor-8	0.06	0.05	--	--	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01
304L SS	0.37	0.16	--	--	0.19	0.07	0.22	0.06	0.18	0.05	0.12	0.05
Niobium	0.50	0.85	0.45	0.75	--	--	--	--	0.23	0.95	--	--
Tantalum	0.00	0.09	0.00	0.06	--	--	--	--	0.01	0.05	--	--

[a] V = vapor; L = liquid .

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6. CONCLUSIONS AND RECOMMENDATIONS

Chlorinating the Rover fuel combustion ash for 4 hr with refluxing HCP (180°C, 4 ml per gram of ash) is an attractive method for converting the uranium in the ash to a water-soluble form in preparation for solvent extraction with TBP-Amsco. The process is rapid and nearly quantitative.

The unchlorinated residue containing about 0.1% of uranium in the original charge can be left for recovery on subsequent cycles, so that the only uranium losses are about 0.001% to the HCP and less than 0.02% to the raffinate from solvent extraction.

Corrosive and unfamiliar high-temperature operations are avoided; corrosion rates of less than 0.1 mil/month during chlorination are predicted from laboratory data for many materials, including type 304 stainless steel and nickel.

Problems in the process involve handling of solid niobic oxide during liquid-liquid separations, and the presence of chloride in the solvent-extraction feed. The solids did not cause emulsions or uranium losses in laboratory tests. The mixed chloride-nitrate system would probably require titanium solvent extraction equipment. The waste chloride solution would be neutralized prior to storage.

Recommendation: Test the process with Rover fuel on a scale large enough to produce enough chlorination product to (1) permit the evaluation of the efficiency of countercurrent extraction of the HCP with 3 $\underline{M}$ HNO_3 and of the resultant 3 $\underline{M}$ HNO_3 solution of uranium and niobium with TBP-Amsco; (2) to permit the investigation of the effect of the solid niobic oxide on these operations. The tests should be carried through several cycles to permit investigation of the effect of ash sintering on the amount of and behavior of the unchlorinated residue. The variables affecting the solubility of niobium in mixed nitric-hydrochloric acid should be determined more exactly.

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