

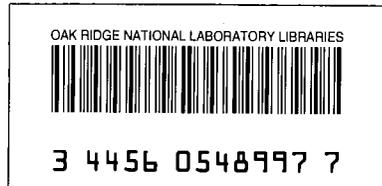
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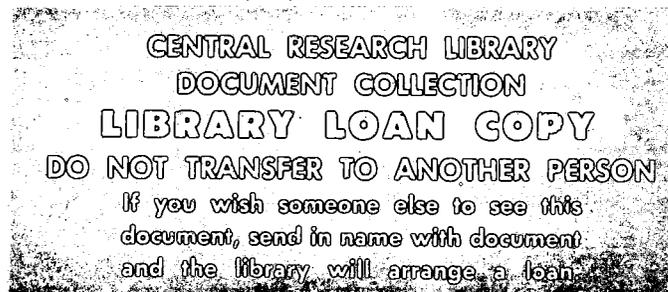
LABORATORY DEVELOPMENT OF A PROCESS FOR CHLORINATING THE COMBUSTION ASH FROM GRAPHITE FUELS CONTAINING ThC_2 AND UC_2 AND RECOVERING THE URANIUM BY SOLVENT EXTRACTION FROM A SOLUTION OF THE CHLORINATION PRODUCTS

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ABSTRACT

A process was investigated in the laboratory for recovering uranium from uranium carbide-thorium carbide-graphite fuels by burning, chlorinating the ash, dissolving the product in 6 N HCl, concentrating the chloride solution, and recovering the uranium by solvent extraction. The main objective of the work was to perform the combustion, chlorination, and dissolution in a single vessel, thereby avoiding a transfer of the combustion ash. The process appears adaptable to large-scale use only if corrosion rates of 20 mils/month are acceptable in the burner-chlorinator. Construction materials which do not corrode rapidly in chloride solutions must be used in the feed preparation and the first solvent extraction cycle.



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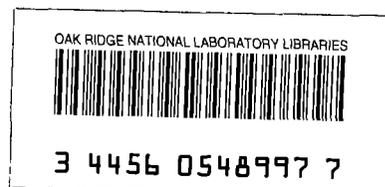
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1. INTRODUCTION

This work was undertaken to develop a method for converting the combustion ash from uranium carbide-thorium carbide-graphite reactor fuels to water soluble chlorides by treatment with a gaseous chlorinating reagent at high temperature and, in addition, to develop a method for recovering uranium by solvent extraction from an aqueous solution of the chloride products.

A practicable method for recovering uranium from graphite-base uranium-thorium carbide fuels will be needed when fuels of this type are discharged from reactors now being constructed (The High Temperature Gas Cooled Reactor, HTGR, at Peach Bottom, Pennsylvania,^{1,2,3} the Arbeitsgemeinschaft Versuch-Reaktor, AVR, in Germany,^{3,4} the Ultra High Temperature Reactor Experiment, UHTREX, at Los Alamos,² and the Organization of European Cooperative Development Dragon Reactor in England^{1,3}). During the past three years, a rapid development of coated-particle fuel technology has occurred,³ and the use of fuel particles coated with pyrolytic carbon is planned for all these reactors.

Other methods investigated for recovering uranium from graphite-base uranium-thorium carbide fuels include (1) simultaneous disintegration and leaching with boiling 21 M HNO₃,⁵ (2) combustion followed by dissolution of the ash in fluoride-catalyzed nitric acid,^{5,6} and (3) grinding to finer than 200 mesh and leaching with 16 M HNO₃.⁵ Only the latter two methods are applicable to the fuels containing particles with pyrolytic carbon. Disadvantages in methods 2 and 3 which stimulate the search for alternative processing methods are: (1) the incompatibility of fluoride-catalyzed nitric acid with materials of construction best suited for the burner and (2) engineering difficulties in fine-grinding, particularly with radioactive material.

The effect of temperature and length of treatment of the combustion ash with gaseous chlorinating agents on the fraction of ash converted to water-soluble chlorides was investigated. Both carbon tetrachloride and phosgene were used as chlorinating agents, with approximately equal results, and, because of the toxicity of phosgene, carbon tetrachloride was selected as the more desirable reagent. The recovery of

uranium from aqueous solutions of dissolved uranium and thorium chlorides containing 200 to 800 g of thorium per liter and 17 to 150 g of uranium per liter was investigated briefly using 15 or 30 vol % tributyl phosphate (TBP) or dibutyl-butyl phosphate (DBBP) in Amsco diluent. The effect of addition of nitric acid (to reduce the corrosion of titanium and allow extraction of the uranyl nitrate complex) and hydrogen peroxide (to oxidize chloride to volatile chlorine, thereby decreasing the viscosity and lowering the freezing point of the concentrated thorium chloride solutions) on solvent extraction was also investigated briefly.

Scouting studies were made in order to determine the boiling and freezing points of azeotropic solutions of thorium oxychloride and hydrochloric acid. More detailed studies of this system are being made. Results of corrosion studies of the combustion-chlorination cycle are reported. Finally, conclusions are presented.

If the process described in this work can be successfully developed on a large scale, the combustion-chlorination vessel might also be used in processing several other types of reactor fuels by closely related methods,^{7,8,9} now being developed on laboratory scale.

2. DISCUSSION OF FLOWSHEET

2.1 Type of Fuel to Which Process is Applicable

The type of fuel chosen for flowsheet calculations was one of the four types planned for use in the HTGR reactor.¹⁰ It contained 29.46 wt % Th, 1.4 wt % U, and 69.2 wt % C. This type contains approximately twice as much thorium and half as much uranium (weight percent basis) as the other three types of HTGR fuel, and it requires a longer chlorination treatment at higher temperatures than do the other types (see Sec 3). The only fuel samples available for laboratory work contained fuel particles that were not coated with pyrolytic carbon. The absence of the pyrolytic carbon coat is not expected to significantly affect the process investigated in this work, in which the first operation is burning, except that the problems caused by hydrolysis of the uranium and thorium carbides during storage and shipment (see Sec 2.4) are

thought to be serious only in the case of fuels that do not contain coated particles. The fuel samples used in the laboratory work, which resembled the HTGR fuel upon which the flowsheet (Fig. 1) is based, contained 28% Th and 2.4% U.

2.2 Operations

The proposed process (Fig. 1) involves five major operations, excluding solvent extraction, which require a total time of about 11 hr: burning the fuel in air or oxygen, chlorinating the ash with carbon tetrachloride vapor, dissolving the chloride products in water, boiling down to a concentrated solution, and adding hydrogen peroxide to lower the freezing point and reduce the viscosity of the solvent extraction feed solution. The last operation can be omitted when the solvent extraction feed solutions are as dilute as shown in the flowsheet (Fig. 1), but will be needed when more concentrated feed solutions are prepared. Burning, chlorination, and dissolution all take place in the burner. The aqueous solution of uranium and thorium chloride is transferred to a second vessel, where the boildown and freezing-point-lowering operations are carried out.

2.2.1 Burning the Fuel

The burning operation is completed within 4 hr at a furnace temperature of 800°C for fuel samples weighing about 30 g. The time required for burning on larger scale will probably be governed by the need for controlling the temperature of the burning fuel elements, to prevent both excessive corrosion of the reactor and sintering of the ash. Sintered ash would require more drastic chlorination conditions, with attendant corrosion problems. Air, air enriched with oxygen, or oxygen can be used to burn the graphite fuel. The major reaction products are uranium and thorium oxides and carbon dioxide, or carbon dioxide mixed with carbon monoxide if no excess oxygen is present. The burning of reactor fuels containing graphite is being investigated elsewhere.^{11,12}

2.2.2 Chlorinating to Convert Uranium and Thorium Oxides to Water-Soluble Chlorides

After burning, the furnace temperature is lowered to 550°C and nitrogen gas, saturated with carbon tetrachloride vapor at room temperature, is passed into the reactor for a period of 5 hr to convert the uranium and thorium oxide combustion products

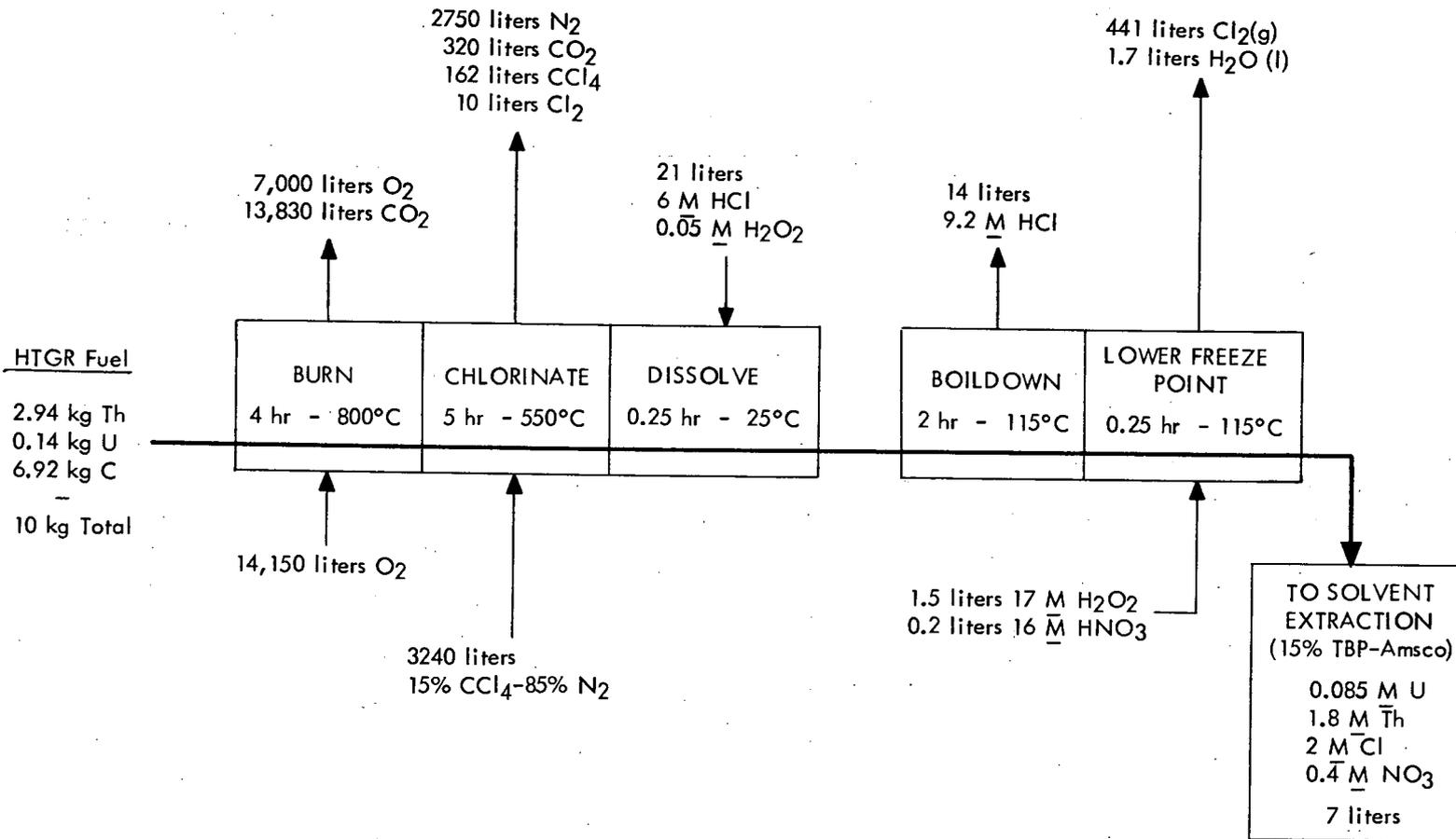


Fig. 1. Combustion-Chlorination-Aqueous Dissolution-Solvent Extraction Process for HGTR Type Fuels.

to water soluble chlorides. The other three types of HTGR fuel, which contain only 15 wt % Th, or half as much as the type used in the process demonstration runs, are expected to chlorinate more readily at only 500°C (see Sec 3). The longer chlorination time for the fuel used in the demonstration runs was also caused, in part, by hydrolysis of a portion of the uranium and thorium carbides before burning. Hydrolysis, which cannot be satisfactorily prevented in uncoated-particle fuel unless the fuel samples are stored in a very dry atmosphere, produces oxides that sinter during burning, and consequently chlorinate less readily (see Sec 2.4). About 10% of the uranium in the fuel converts to volatile uranium pentachloride during chlorination and collects on the cool exit of the reactor.

2.2.3 Dissolving the Chlorides

After chlorination, the uranium and thorium chlorides are dissolved in 6 N HCl at room temperature. Dissolution occurs readily without heating to yield a solution 0.6 M in Th and 0.028 M in U. Hydrochloric acid, rather than water, is used to prevent hydrolysis of uranyl chloride during the subsequent boildown. A low concentration of hydrogen peroxide (0.05 M) is present in the dissolvent to oxidize the slightly soluble tetravalent uranium to soluble uranyl chloride. To protect the dissolver against corrosion (see Sec 5), this peroxide could probably be added after the chloride solution is transferred out of the dissolver. In the latter case, either a portion of the uranium would be transferred as a slurry of uranium tetrachloride or a large volume of solution would be used to dissolve the uranium tetrachloride. The volumes of water or dilute hydrochloric acid needed to dissolve the uranium tetrachloride were not determined.

The best material of construction found for the combustion-chlorination was Inconel, but even with Inconel, corrosion rates were nearly 20 mils per month (see Sec 5).

2.2.4 Concentrating the Aqueous Solution

The solution of uranium and thorium chlorides is transferred to a second vessel, resistant to hydrochloric acid, heated to the boiling point and then concentrated by distilling off hydrochloric acid. The hydrochloric acid that is distilled off may be used to dissolve the chlorination product from the next run. The vessel used for the distillation must be constructed of a material resistant to hot concentrated hydrochloric acid,

such as zirconium, tantalum, or Hastelloy. The solution can be concentrated to over 3 M in thorium before the freezing point approaches 25°C (see Sec 4). However, the limiting critically safe U^{235} concentration in a solution in which the weight of U^{235} present is 4.8% of the weight of thorium, as in the case considered here, is about 22 g/liter.¹³ Therefore, concentration to only 20 g U/liter (1.8 M thorium) is recommended.

2.2.5 Using Hydrogen Peroxide to Remove Chloride and Lower the Freezing Point

After the uranium-thorium chloride solution is evaporated to the desired concentration, 2 moles of hydrogen peroxide per mole of dissolved thorium are added, at 80 to 115°C. Each mole of hydrogen peroxide causes about 1.5 moles of chloride to be volatilized from the solution, mostly in the form of chlorine. Very little volume change occurs. The removal of chloride lowers the viscosity and freezing point of the solution to form a suitable feed solution for solvent extraction. The peroxide addition-freezing point lowering operation might be omitted if the solutions are as dilute as shown in the flowsheet (Fig. 1), where the uranium concentration was limited by criticality considerations to 20 g/liter. However, the use of geometrically safe vessels to permit further concentration beyond that recommended in the flowsheet might be desirable to reduce the volumes of the solvent extraction feed and waste solutions. Further concentration, to beyond 20 g of uranium per liter, would be particularly desirable for the other three types of HTGR fuels, where the uranium content is 20 wt % of the thorium content, rather than 4.8%, as in the case chosen for demonstration of the process. Removal of chloride from the solvent extraction feed solution also reduces the chloride content in the wastes and therefore the corrosion problems in storing the wastes. In addition, during the freezing-point-lowering operation, the thorium in solution is converted to a species which does not extract as readily into TBP-Amsco (see Sec 2.5). Experiments to determine the maximum thorium concentrations that can be achieved after the freezing-point-lowering operation (Sec 4) indicate that solutions containing as much as 5 moles of thorium per liter (1160 g/liter) would be satisfactory solvent extraction feed. The solubility of uranium in such concentrated thorium solutions has not been determined, but in a scouting run in which the solvent extraction feed solution (Fig. 1) was concentrated to 5 M in thorium, the uranium also remained in solution.

The solvent extraction feed solution was made 0.4 M in nitric acid on the assumptions that a solvent extraction column constructed of titanium would be used and that nitric acid is needed to protect the titanium against corrosion.

2.3 Process Demonstration Runs

A series of three demonstration runs (Table 1) were performed to investigate briefly the extractability of uranium and thorium with 15 and 30% TBP in Amsco diluent. In all runs, the fuel was burned, the combustion ash was chlorinated under flowsheet (Fig. 1) conditions, and the chlorination product was completely dissolved in cold 6 N HCl. Hydrogen peroxide was added in the amounts and under the conditions shown in Fig. 1, and the product solutions were made 1 M in HNO₃ before solvent extraction.

In scouting runs (Sec 2.5), it was found that 30% TBP-Amsco could not be used satisfactorily to extract uranium from solutions containing as much as 80 g of uranium per liter because a uranium-rich third phase separated from the organic phase. Therefore, a run was made (run 1) in which 30% TBP-Amsco was used to extract uranium from a solution containing 40.5 g of uranium and 305 g of thorium per liter, which is approximately the highest concentration of uranium which can be extracted with 30% TBP without forming a third phase. Over 99.99% of the uranium and about 4% of the thorium was extracted in five batch extractions. When 15% TBP-Amsco was used as the extractant, five batch extractions were required (run 3) to achieve a comparable uranium recovery from a solution containing only 16.8 g of uranium per liter, which is approximately the uranium concentration shown in the flowsheet (Fig. 1). In the latter run, 8% of the thorium also extracted. When 15% TBP-Amsco was used as the extractant for a more concentrated solution containing 68.5 g of uranium per liter and 799 g of thorium per liter (run 2), eight batch extractions were required to recover 99.99% of the uranium, and in this case, 12% of the thorium was also extracted. Therefore, it appears advantageous to extract with 30% TBP-Amsco from as concentrated a solution as possible without encountering third-phase formation. No attempts were made to separate the extracted uranium and thorium.

Table 1. Demonstration Runs with UC₂-ThC₂-Graphite Fuels

Combustion with O₂, 4 hr - 800°C
 Chlorination with 15% CCl₄-N₂, 5 hr - 550°C
 Solvent volume equals aqueous volume
 5 to 8 batch extraction

Run	wt g	Sample Composition, wt %		Solvent, TBP in Amsco, %	Aqueous Feed, g/l		Raffinate	
		U	Th		U	Th	U, %	Th, %
1	31	1.5	7.0	30	40.5	305	0.003	95.61
2	7	1.2*	14.0*	15	68.5	799	0.002	77.64
3	27	1.2*	14.0*	15	16.8	197	0.01	91.60

*Samples 2 and 3 were approximately one-half fuel containing 2.4 wt % U--28 wt % Th, and one-half graphite core.

2.4 Major Problems

A serious problem is encountered in burning fuels in which the uranium and thorium carbides have hydrolyzed to an appreciable extent through exposure to air and moisture during storage or shipment. During the hydrolysis of the uranium and thorium carbides, both volatile and nonvolatile hydrocarbons are formed.^{14,15} Unless hydrolyzed fuels are handled carefully during burning, violent explosions can occur. In the laboratory work, a quartz reaction tube was destroyed by such an explosion. In other runs, explosions were avoided by passing air over the fuel as it was heated from room temperature to 800°C, and then introducing oxygen in place of the air. The ash produced by burning hydrolyzed fuel is sintered and much less readily chlorinated than is the ash produced by burning the carbide fuel that has not hydrolyzed. A sample of fuel, hydrolyzed through exposure to air in the laboratory to the extent that the cylindrical fuel element had crumbled into a powder, was burned and then chlorinated under flowsheet (Fig. 1) conditions. Fifteen percent of the uranium and 6% of the thorium in the ash remained in the form of oxide which would not dissolve in water. The portion of ash which did not chlorinate dissolved within 12 hr in refluxing 15 M HNO₃-0.1 M HF. The ash could probably have been fully chlorinated at a higher temperature, but the corrosion rates of metallic construction materials become excessive at higher temperatures. Fortunately, the thorium and uranium carbide fuel particles, when coated with pyrolytic carbon, will probably be protected against hydrolysis to the extent that the problems caused by hydrolysis will not be encountered. At present, use of the pyrolytic carbon coat is planned in all reactors using thorium-uranium carbide fuels.¹⁶ Burning the fuel at too high a temperature might also produce sintering and an oxide product that would not chlorinate readily.

It will be necessary to condense volatilized uranium chloride from the off-gas and dissolve this volatilized chloride in water which can then be added to the solution of nonvolatile chlorides. In laboratory chlorinations under flowsheet conditions (Fig. 1), about 10% of the uranium in the ash was converted to volatile chlorides and collected on the cool exit of the reactor tube. To prevent entrainment of condensed uranium chloride, it will be necessary to filter the off-gas.

The use of chlorinating reagents introduces corrosion problems, both before and after dissolution of the chloride products. There has been little previous experience with chlorides or gaseous chlorinating agents in reactor fuel reprocessing plants. Early corrosion tests (see Sec 5) indicate that no entirely satisfactory materials of construction exist for the vessel in which the fuel is burned, chlorinated, and dissolved in water, and, to use the process, corrosion rates of 20 mils/mo would have to be accepted in this vessel. Alloys of high nickel content, such as Inconel, Hastelloy, or Nichrome, exhibited the lowest corrosion rates. A chloride-resistant construction material, such as titanium, will be required for the solvent extraction equipment. After the first extraction column, use of stainless steel equipment is possible, since nearly all chloride contamination can be scrubbed out of TBP-Amsco solvent.¹⁷ The chloride-containing raffinate can be made alkaline to permit storage in tanks made of inexpensive materials.

2.5 Scouting Runs

A series of scouting runs (Table 2) was made to investigate the effect of nitric acid, the use of hydrogen peroxide to lower the freezing point (last operation before solvent extraction, see Fig. 1), chlorination reagent and conditions, choice of solvent [tributyl phosphate (TBP) or dibutyl butylphosphonate (DBBP) in Amsco] and concentrations of solvent and of uranium and thorium in the aqueous feed on the efficiency of solvent extraction. The only variables that had no apparent effect on the efficiency of the solvent extraction were the chlorination reagent and conditions. The chlorination products were dissolved in 6 N HCl, as shown in Fig. 1. In runs 1-3, Table 2, hydrogen peroxide was added as shown in Fig. 1; in run 4 this operation was omitted. In runs 2 and 4, nitric acid was added before solvent extraction; in runs 1 and 3, nitric acid was not added.

A comparison of runs 2 and 3 with runs 1 and 4 (Table 2) shows that while DBBP extracts uranium at least as efficiently as TBP, it extracts much more thorium than does TBP (71 and 54% vs 8 and 25%, respectively). Dibutyl butylphosphonate was investigated primarily because it is known to be useful for extracting uranium from nitrate-free chloride solutions,¹⁸ but TBP appears to effect a better uranium and thorium separation

Table 2. Results of Scouting Runs with UC₂-ThC₂-Graphite Fuels

Combustion with O₂ 4 hr - 800°C

Solvent volumes equal aqueous feed volumes

5 to 8 batch extractions

Fuel Composition: Runs 1-3, 1.5% U--7% Th

Run 4, 2.8% U--28% Th

Fuel Sample Sizes: 9-25 g

All chlorination products 100% water-soluble

Run	Chlorination		Time, hr	Solvent (in Amsco)	Aqueous Feed			Raffinate, %	
	Reagent	T°C			HNO ₃ , M	g/liter		U	Th
						U	Th		
1	COCl ₂	500	3	30% TBP	0	121	563	0.001	91.82
2	15% CCl ₄ -N ₂	500	1	30% DBBP	2	76	354	0.000	28.80
3	15% CCl ₄ -N ₂	500	1	15% DBBP	0	151	706	0.001	45.90
4*	15% CCl ₂ -N ₂	550	3	15% TBP	2	20	223	0.001	75.05

* H₂O₂ addition (see Fig. 1) omitted.

in all solutions used in this work. A solvent not investigated in this work, but which is known to be useful for separating uranium and thorium, is di-sec-butyl phenyl phosphonate.¹⁹

A comparison of runs 1 and 4 shows that only 8% of the thorium was extracted by TBP when peroxide was added, but 25% was extracted when no peroxide was used. The addition of hydrogen peroxide converts the thorium oxychloride to a species containing only one chloride atom per thorium atom (see composition of solvent extraction feed in Fig. 1), which apparently is less readily extractable by TBP.

The use of 30% TBP and 30% DBBP in Amsco led to the separation of a third, uranium-rich phase from the organic phase during the first batch extractions, when the uranium concentration in the aqueous phase was 121 (run 1) and 76 (run 2) g/liter, respectively. However, a solution containing 151 g of uranium per liter (run 3) was extracted with 15% DBBP without third-phase formation. A 30% TBP solvent was used (see run 1, Table 1) to extract a solution containing 40 g of uranium per liter without third-phase formation. Apparently, only 15% TBP or DBBP should be used with solutions containing over 40 g of uranium per liter, to avoid formation of a third phase.

Surprisingly, the absence of nitric acid in run 1 did not appear to seriously hinder the extraction of uranium. It was thought that the presence of nitric acid would cause formation of uranyl nitrate, which would be extracted more readily by TBP than would uranyl chloride. A more detailed study of the uranium extraction coefficients is needed in these solutions to determine the effect of nitric acid on extraction efficiency.

3. EFFECT OF THORIUM CONTENT AND CHLORINATION TIME AND TEMPERATURE ON RATE OF ASH CHLORINATION

The time required to convert the combustion ash to water-soluble chlorides by use of 15% $\text{CCl}_4\text{-N}_2$ is inversely dependent on the thorium content of the fuel and directly dependent on the temperature (Fig. 2). The ash from fuel samples containing only 7% Th was completely converted to water-soluble chlorides in 3, 2 and 1 hr at 425, 450 and 500°C, respectively, while a temperature of 550°C and a 4-hr treatment was required for fuel samples containing 28% Th. At temperatures as low as 400 and 500°C,

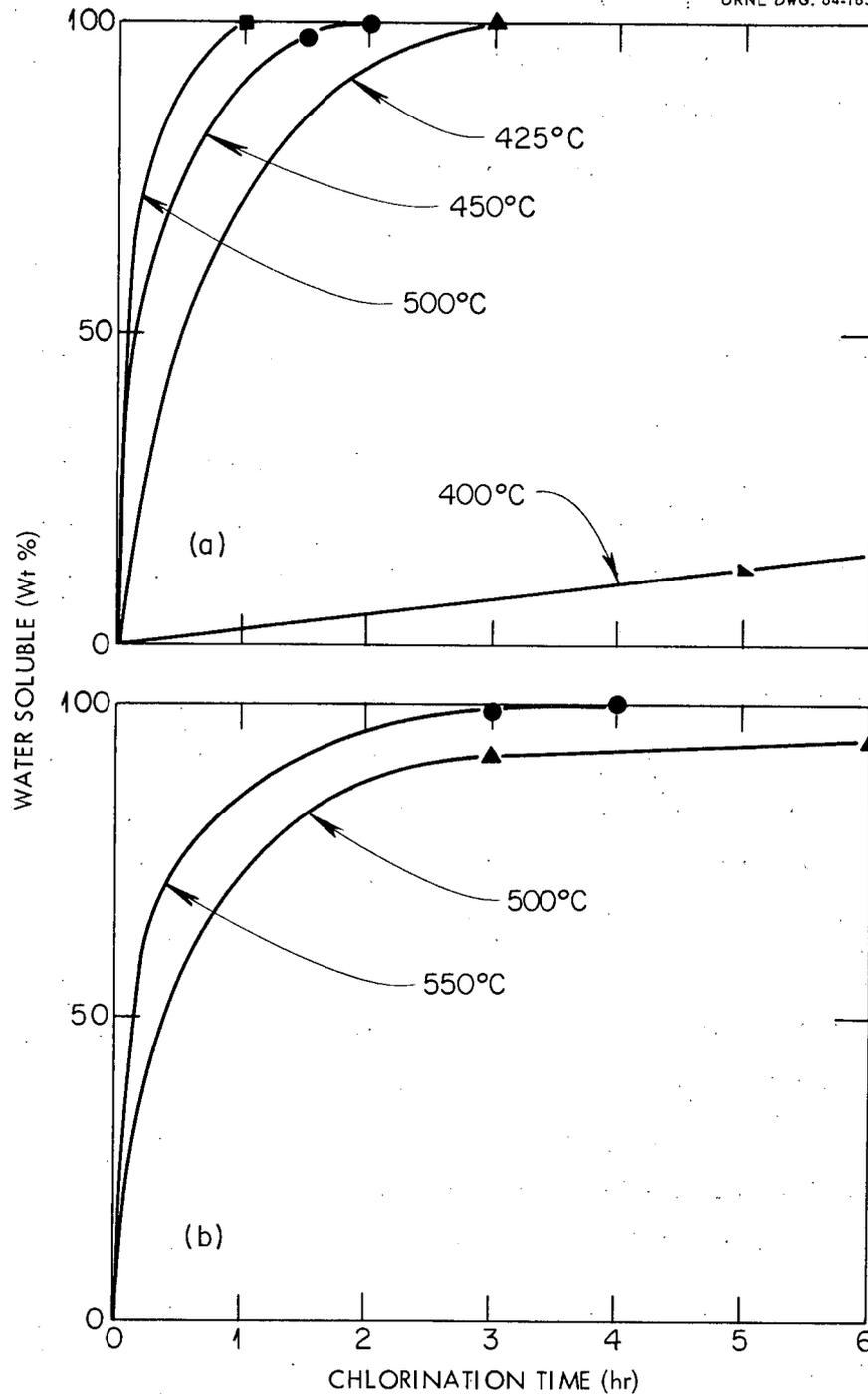


Fig. 2. The Combustion Ash from 7% Th--1.5% U--91.5% C Fuels (a) was Converted Rapidly to Water Soluble Chlorides at Temperatures as Low as 425°C. Fuels Containing 28% Th--2.4% U--69.6% C (b) Required a Chlorination Temperature of 550°C. Ash samples weighing 1.5 g (bed depth, 1 cm) were chlorinated with 500 cc/min of 15% CCl_4 --85% N_2 in a 5 cm ID quartz tube.

respectively, the time required for 100% conversion became excessive for the 7 and 28% Th fuel samples. The time required to achieve 100% conversion of the ash to soluble chlorides was also probably affected adversely by hydrolysis of part of the uranium and thorium carbides prior to the burning step (see Sec 2.4), and the minimum chlorination time of ash from fuels in which no hydrolysis has occurred may be less than that indicated in Fig. 2.

4. FREEZING AND BOILING POINTS OF THORIUM OXYCHLORIDE-HYDROGEN CHLORIDE SOLUTIONS

A brief study was made to determine the boiling points and the freezing points of evaporated (at boiling point.) solutions of thorium oxychloride and hydrogen chloride and similar solutions in which the chloride content had been decreased by the addition of hydrogen peroxide.

Solutions of thorium oxychloride and hydrogen chloride were prepared, and the hydrochloric acid was distilled off until the boiling point appeared to be constant. The solutions were then cooled slowly to determine the freezing point from inflections in the cooling curve. The products were analyzed and the freezing and boiling points plotted as a function of thorium oxychloride composition (Fig. 3). The boiling points increased from 110° to 140°C as the thorium oxychloride content increased from 0 to 8 M. The freezing points were below room temperature up to thorium oxychloride concentrations of nearly 4 M, and increased to about 140°C as the thorium oxychloride concentration increased from 4 to 8 M. It should be possible to handle $\text{ThOCl}_2\text{-HCl}$ solutions that have been evaporated to nearly 4 M in thorium without encountering the problem of formation of solid thorium compounds at room temperature.

Even more concentrated thorium solutions, which are stable at room temperature, can be prepared by adding hydrogen peroxide to hot $\text{ThOCl}_2\text{-HCl}$ solutions that have been evaporated to thorium concentrations at which solids would ordinarily form upon cooling. For example, the addition at 80°C of 1.5 moles of H_2O_2 (as 50% H_2O_2) per mole of thorium to a solution which had been evaporated to 5 M in thorium lowered the freezing point from about 60°C to -20°C. No measurable volume change occurred.

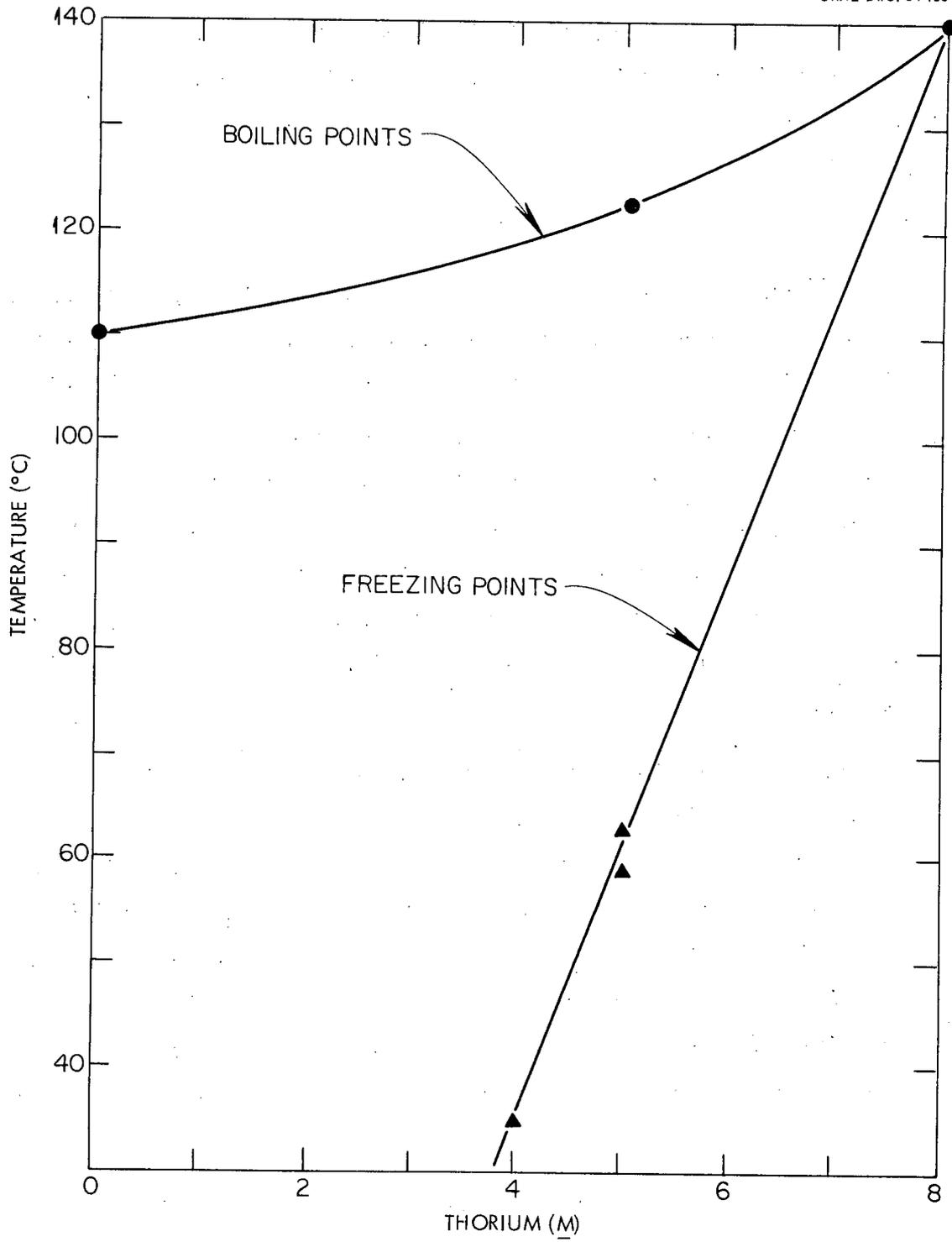


Fig. 3. Boiling Points and Freezing Points of Boiled Thorium Oxychloride-Hydrochloric Acid Solutions Increase with Thorium Concentration.

The product solution was also stable at the boiling point and after standing several weeks at room temperature. Hydrogen peroxide lowers the freezing point by reacting with chloride to produce chlorine, which volatilizes out of the solution. A similar use of hydrogen peroxide to lower the freezing point of $ZrOCl_2$ -HCl solutions has been described previously.⁹

5. CORROSION

A series of corrosion tests²⁰ were made in which several alloys, known to be resistant to oxygen and chlorinating reagents at elevated temperatures, were exposed to combustion-chlorination aqueous-dissolution cycles resembling the cycle shown in Fig. 1. The chlorination temperature and reagent, and the dissolution temperature and reagent were varied to determine their effect on corrosion rates. In all tests, the welded corrosion specimens were first exposed to oxygen at 800°C for 4 hr. The chlorination and dissolution portions of the cycle lasted 5 hr and 0.25 hr, respectively. Several materials, including Nichrome V, the Hastelloys N and B, Inconel, Corronel 230, and type "A" nickel corroded at rates of about 20 to 30 mils/month (Table 3). Haynes-25 and Carpenter 20 corroded at higher rates.

Increasing the chlorination temperature from 500 to 550°C caused no appreciable increase in the corrosion rates of Nichrome V, but caused about a 100% increase from 20 to over 40 mils/month in the corrosion rates of Hastelloy N. The use of Cl_2 --15% CCl_4 rather than N_2 --15% CCl_4 caused no detectable increase in corrosion rates. The addition of 0.05 M H_2O_2 to 6 M HCl during the aqueous dissolution steps caused roughly a 50% and 25% increase in the corrosion rates of Nichrome V and Hastelloy N, respectively. Increasing the temperature of the aqueous dissolution step from 25 to 50°C caused no detectable change in corrosion rates.

6. CONCLUSIONS

The process proposed for HTGR-type fuels, involving burning in oxygen at about 800°C, chlorinating the ash with carbon tetrachloride vapor at 550°C, dissolving the

Table 3. Corrosion Rates (mils/month) of Welded Specimens in Chlorination-Hydrochloric Acid Dissolution Cycles²⁰

Each test preceded by 4 hr of exposure to O₂ at 800°C

Metals	(1) ^a 5 hr, N ₂ --15% CCl ₄ , 500°C (2) 0.25 hr, 6 M HCl, 25°C			(1) 5 hr, Cl ₂ --15% CCl ₄ , 500°C (2) 0.25 hr, 6 M HCl, 50°C			(1) 5 hr, N ₂ -- 15% CCl ₄ , 550°C (2) 0.25 hr, 6 M HCl, 50°C		(1) 5 hr, N ₂ -- 15% Cl ₄ , 550°C (2) 0.25 hr, 6 M HCl--0.05 M H ₂ O ₂ , 50°C	
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 1	Cycle 2
Nichrome V	23.6	23.3	20.9	28.0	28.3	25.0	18.1	14.8	30.9	23.8
Hastelloy N	--	--	23.6	19.4	20.3	18.8	39.8	49.4	40.6	57.3
Hastelloy B	--	--	36.6	23.2	23.5	24.1	--	--	--	--
Inconel	--	--	13.2	17.6	17.7	18.5	--	--	--	--
Corronel 230	--	23.0	21.7	22.9	25.0	22.4	--	--	--	--
"A" Nickel	--	--	--	38.2	36.4	27.6	--	--	--	--
Haynes 25	53.5	50.2	--	51.4	50.2	51.1	--	--	--	--
Carpenter 20	115.8	--	--	--	--	--	--	--	--	--

^aIn each cycle, steps (1) and (2) represent the sequence of operations.

chlorides in aqueous solution, feed adjustment, and recovering uranium by solvent extraction was demonstrated on a laboratory scale. A major problem in large scale use lies in finding a suitable construction material for the combustion-chlorination reactor. This problem is intensified by the introduction of water into the vessel to dissolve the chlorination products. The corrosion tests described in Sec 5 indicate that average corrosion rates in the combustion-chlorination aqueous-dissolution cycle will be about 20 mils/month. Nickel, or several alloys of a high-nickel content, all corroded at about the same rate. Because of these high corrosion rates no further work on this process is recommended unless satisfactory alternative methods cannot be found for recovering the uranium from the UC_2 - ThC_2 -graphite fuels.

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