DEC 3 1963

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

ORNL-TM- 645

COPY NO. - 63

DATE - October 15, 1963

**LABORATORY DEVELOPMENT OF A COMBINED CHLORIDE VOLATILITY-AQUEOUS
PROCESSING METHOD FOR URANIUM-ZIRCONIUM NUCLEAR FUELS**

By

T. A. Gens

Technician: E. R. Johns

MASTER

ABSTRACT

The operations in a process proposed for recovering uranium from spent uranium-zirconium alloy fuels, including collecting the volatilized chlorination products (mainly zirconium tetrachloride and uranium pentachloride) in boiling water, concentrating the resulting solution, lowering the freezing point by removing chloride with hydrogen peroxide, and recovering uranium from the 5 M Zr product solution by solvent extraction with tributyl phosphate in Amsco diluent, were investigated in the laboratory and appeared to be reducible to large-scale practice. The high temperature chlorination equipment would also be adaptable for burning graphite matrix fuels and when combined with Darex equipment for processing fuels containing stainless steel, molybdenum, or aluminum may provide the basis for a feasible universal fuel processing system.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

Photostat Price \$ 2.60
Microfilm Price \$ 1.07
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

	Page
1. Introduction	1
2. Laboratory Studies	2
2.1 Conceptual Flowsheet and Brief Discussion of the Basic Operations	2
2.2 Collection of Zirconium Tetrachloride in Water	3
2.2.1 The Problem of Zirconium Oxide Formation	7
2.2.2 Recycle of Hydrogen Chloride	7
2.2.3 Concentrating by Boiling Off Hydrochloric Acid	8
2.3 Removal of Chloride from Solutions Containing Zirconium	10
2.4 Solvent Extraction of Uranium from Concentrated Solutions of Zirconium and Chloride	16
2.5 Corrosivity of Two Process Solutions	17
2.5.1 Four Molar Zirconium--Four Molar Chloride	17
2.5.2 Three Molar Zirconium--Nine Molar Chloride	18
2.6 Calcination of Raffinate	18
2.7 Conversion of Raffinate to Alkaline Waste	19
2.8 Chlorination of Mixed Uranium Oxide-Zirconium Oxide Fuel	20
3. Conclusions, Discussion, and Recommendations	22
4. Acknowledgments	24
5. References	25

1. INTRODUCTION

The work described in this report was undertaken to develop a head-end process for recovering uranium from uranium-zirconium alloy fuels which would be more economical than existing processes. An example of a uranium-zirconium alloy fuel is the Pressurized Water Reactor seed,¹ which is 93% Zr--7% U alloy clad in Zircaloy-2 (zirconium alloy containing about 1% tin and smaller amounts of iron, chromium, and nickel). Recently, Burn² estimated that, with improvements in existing aqueous processes, the uranium from the spent uranium-zirconium alloy fuels could be recovered at a cost of less than \$2 per gram of uranium, compared with \$11 per gram as the present Atomic Energy Commission price.³ Thus, recovery of this uranium is practical, but more economical processes are needed. For the present work the assumptions were made that, for a process to be practical for present use and also to effect significant cost reductions, it must (1) convert the fuels to an aqueous solution highly concentrated in zirconium, and (2) the uranium in the product must be recovered in a solvent extraction plant whose primary purpose is to recover uranium from the feed yielded by a second head-end process.

To achieve these goals, the possibility was explored of improving the Zircex process,^{4,5,6} in which fuels containing zirconium are treated with hydrogen chloride gas at 300°C or higher to remove the zirconium as volatile zirconium tetrachloride, and modifying the process to yield an aqueous solution from which uranium can be recovered by solvent extraction in a Darex⁷ plant. The Zircex process is primarily applicable to the uranium oxide blanket fuels clad in Zircaloy-2. Uranium-zirconium alloy fuels can also be processed by this method, but they present more difficult problems. Therefore, the new laboratory work described in this report deals only with the alloy fuels. In the Darex process, fuels containing stainless steel are dissolved in aqua regia in a titanium dissolver, the chloride is removed and recycled by distillation, and the uranium is recovered by solvent extraction in stainless steel equipment. The titanium dissolver can also be used for dissolving practically all other fuels of importance, except those containing zirconium or graphite in either aqua regia, nitric acid, or fluoride-catalyzed nitric acid.⁸ Alternatively, the chloride can be separated from the uranium during solvent extraction, if titanium extraction equipment is used, rather than

by distillation.³⁴ In the combination process proposed in this work, the fuels containing graphite would be burned in the same equipment used for chlorinating fuels containing zirconium, and the ash would be either dissolved directly in nitric acid, or, if necessary, chlorinated to produce water-soluble salts. Such processes for graphite-containing fuels are being developed^{9,10,11} but will not be described in this report. The proposed combination process, therefore, should be applicable to all of the important types of reactor fuels with only two head-end processes and one solvent extraction system.

A similar combination of high-temperature-chlorination head-end process for zirconium-containing fuels (Zircex process^{4,5}) with the Darex process was given serious consideration previously.¹² The major modifications to the Zircex process, described in this report, and the extension of the Darex process as described above, have made the proposal described here more attractive. Several workers in the reactor fuel processing field have pointed out the economic advantage of large plants capable of handling many types of reactor fuels.^{13,14,15}

In the rest of this report, the results of laboratory investigations of the operations involved in the proposed process for zirconium-containing fuels, and of preliminary corrosion tests, are described. Finally, recommendations and conclusions are given.

2. LABORATORY STUDIES

2.1 Conceptual Flowsheet and Brief Discussion of the Basic Operations

The conceptual process upon which the laboratory studies were based (top portion of Fig. 1) initially involves chlorination of the uranium-zirconium alloy fuel. The use of both hydrogen chloride and chlorine is indicated because the recycle of hydrogen chloride from a subsequent operation (see Sec 2.2.2) relieves the problems of handling an additional waste stream, and the use of chlorine is needed for the remainder (about three-quarters) of the chlorination step to produce the volatile uranium pentachloride and hexachloride. The volatilized zirconium and uranium chlorides are collected in boiling water. The solution is concentrated by a boildown, which can be performed either

simultaneously with the collection step or separately after collection. Chloride is removed to lower the freezing point of the concentrated solution, and uranium is recovered from the concentrated product by solvent extraction. It is estimated that the operations preceding solvent extraction would require about 12 hr per fuel element of the PWR seed type. Each of the above operations was investigated except the chlorination step, which had already been extensively investigated.⁴ In addition, calcination and conversion of the waste to alkaline solution were investigated briefly. No runs in which all operations were performed in sequence as outlined in Fig. 1 were made in the laboratory. Additional investigation of the process is planned on an engineering scale.¹⁶ What follows in this section is a discussion of important aspects of the proposed process. Some advantages of and problems in the proposed combination process are discussed in Sec 3.

2.2 Collection of Zirconium Tetrachloride in Water

During hydrochlorination (or chlorination) of uranium-zirconium alloys, the zirconium is converted to volatile zirconium tetrachloride:

The collection of the sublimed zirconium tetrachloride has presented some serious problems.⁴ Zirconium tetrachloride cannot be liquified at atmospheric pressure; it can be liquified at 25 atmospheres pressure at 437°C,¹⁷ but the use of pressurized equipment is undesirable with radioactive materials. The conventional method of collecting zirconium tetrachloride in zirconium production plants by condensation to form the solid,¹⁸ followed by mechanical or manual handling of the salt would not be satisfactory in radiochemical plants because of the radioactive fission products that would be associated with it. In addition, the possibility of operating a zirconium tetrachloride condenser remotely is made even more unlikely by the tendency of the condenser to plug in the area at which the zirconium tetrachloride vapor is cooled below the sublimation temperature, about 300°C.

UNCLASSIFIED
ORNL-LR-DWG. 74827

Fig. 1. Combination of High Temperature Chlorination and Darex Processes.

To avoid these problems, collection of the zirconium tetrachloride was attempted by leading the off-gas from the hydrochlorination reaction into the vapor above a refluxing zirconium chloride solution. A schematic drawing of the experimental system is shown in Fig. 2. The zirconium tetrachloride reacts with water vapor to form zirconyl chloride:

which is then sorbed into the aqueous solution as a highly soluble hydrated salt. This reaction occurs as the zirconium tetrachloride leaves the heated inlet line, at a temperature between the line temperature of 300°C and the water-vapor temperature of about 100°C. Although reaction occurs below the sublimation temperature of zirconium tetrachloride, no condensation was observed because of the speed of the hydrolysis and sorption processes. Thus, the gaseous zirconium tetrachloride is removed from the off-gas, into the solution where it forms a very soluble zirconyl salt, and the problem of handling solids is avoided. This new collection method appears to be readily adaptable to continuous operation.

In two laboratory demonstrations of this method of collecting zirconium tetrachloride in boiling water, which were carried out in glass equipment over periods of 6.5 and 4 hr, the product solutions contained 1.8 M zirconium--7.3 M chloride and 0.8 M zirconium--7.1 M chloride, respectively. No plugging occurred, although in both experiments a small amount of salt deposit was observed on the wall downstream from the point at which the heated gas entered the sorption vessel. This deposit was visible as long as zirconium tetrachloride was entering the vessel, but the amount of deposit was kept very small by increasing the solution boilup rate. No condensation of zirconium tetrachloride was observed in the vapor phase. A small amount of zirconium oxide was produced by the undesired reaction:

Of the zirconium collected in the two experiments, 2% and 1.4%, respectively, were collected as water-insoluble zirconium oxide, and the

UNCLASSIFIED
ORNL DWG. 63-4898

Fig. 2. Sorption of ZrCl_4 from Chlorination Off-Gas into Boiling Water.

balance was collected as water-soluble zirconyl chloride. The zirconium oxide did not remain in the sorption vessel (Fig. 2) but passed out through the condenser and caustic off-gas scrubber as a white smoke which was finally captured only by passing the off-gas through two large settling chambers in series. From these experiments it was concluded that the continuous operation of the zirconium tetrachloride sorption process was practical and that zirconium concentrations in the product solution at least as high as 1.8 M can be achieved.

2.2.1 The Problem of Zirconium Oxide Formation

The formation of zirconium oxide by the reaction shown in Eq. 3 is probably not a serious problem since the amount formed is small and probably can be reduced further by proper design of the heated inlet line and by the addition of an inert diluent gas to accelerate the flow of the zirconium tetrachloride vapor at the point that it leaves the heated line (see Fig. 1), thereby causing the vapor-phase hydrolysis to occur at a temperature as close to the water vapor temperature (about 100°C) as possible. At the water-vapor temperature, hydrolysis proceeds according to Eq. 2, which is the desired reaction. With excess water vapor at temperatures as high as 300°C, a temperature which has been used to produce zirconium oxide,¹⁹ the hydrolysis probably proceeds only by the reaction shown in Eq. 3, and the only product is the undesirable zirconium oxide. In the second demonstration run described above, an estimated 30% of the zirconium oxide produced was captured from the sorption off-gas and returned to the boiling solution by adding a vapor trap below the condenser. This zirconium oxide dissolved within 3 hr in the boiling solution.

2.2.2 Recycle of Hydrogen Chloride

By cooling the top of the condenser on the zirconium tetrachloride sorption vessel to -80°C, or slightly below -80°C (see Fig. 2), and providing a column with several plates in the temperature range between -80°C at the top and about 100°C at the bottom, it should be possible to keep water from escaping with the off-gas (which is mainly water

vapor, hydrogen and hydrogen chloride; see Eqs. 1 and 2). Hydrogen chloride and water form a maximum-boiling azeotrope containing 20.2 wt % hydrogen chloride having a normal boiling-point of 108.6°C, and pure hydrogen chloride has a normal boiling point of -83.7°C. If the top of the condenser were cooled to -80°C or lower, anhydrous hydrogen chloride could be removed from the top of the condenser and recovered by passing the off-gas through a cold trap. Recycle of this hydrogen chloride might be desirable to avoid having to neutralize and store it.

2.2.3 Concentrating by Boiling Off Hydrochloric Acid

Concentration of the solution containing zirconyl chloride and hydrogen chloride by boiling off hydrochloric acid is possible and desirable in order to reduce the costs of solvent extraction and waste storage. During the boildown, the hydrogen chloride-water azeotrope is affected by the presence of the zirconyl ion, which decreases the hydrogen chloride and water concentration and also associates with the water and hydrogen chloride to form weakly-bonded hydrates. Thus, at any point during boildown, the composition of the solution is that of a complex hydrate-type compound containing zirconyl chloride, hydrogen chloride and water, or a mixture of these complex hydrate compounds. The compounds are not stable enough to distill; distillation removes only hydrogen chloride and water.

The effect of this behavior on the concentration operation was investigated briefly. Zirconyl chloride-hydrogen chloride solutions were prepared by dissolving $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in hydrochloric acid and distilling until the boiling point remained constant for 10 min. Melting points of the product were determined from inflections in the time-vs-temperature curve upon cooling. After the melting point determinations, the volumes at the melting points were measured, and the salt was dissolved in water and analyzed for zirconium.

The results (Fig. 3) showed that, during the distillation of zirconyl chloride-hydrogen chloride solutions, a series of compounds

Fig. 3. Freezing Points of Zirconyl Chloride-Hydrogen Chloride Solutions Made by Distilling Off Hydrochloric Acid.

are obtained with melting points increasing as the zirconium content increases. The practical effect of this behavior on the operation of such a process to concentrate the product is that a product solution containing more than 1 M zirconium will solidify upon cooling to room temperature. In addition, at about 4.3 M zirconium, the melting point (about 105°C) is almost as high as the boiling point (about 110°C), so that the maximum zirconium concentration that can be practically achieved without the formation of solid at the boiling point is about 4 M. In the range of 3 to 4 M zirconium, the product solution contained about three atoms of chlorine per atom of zirconium. A more detailed laboratory study of this system is being made.

Therefore, by collecting zirconium tetrachloride in water and boiling off hydrochloric acid, a product containing 360 g of zirconium per liter, which would be solid at room temperature, can be obtained. This concentration of zirconium is almost equivalent to that which would be achieved by condensing the zirconium tetrachloride as a solid, if a solid with a density of 1 were obtained. The collection and concentration steps could probably be carried out simultaneously. By removing and recycling anhydrous hydrogen chloride and refluxing the water during sorption of zirconium tetrachloride, as discussed in Sec 2.2.2, less water would be used to reach any desired zirconium concentration in the product, and the problem of disposing of waste hydrochloric acid might be avoided.

2.3 Removal of Chloride from Solutions Containing Zirconium

Instead of separating uranium and zirconium chloride by a process based on the low vapor pressure of uranium trichloride as previously proposed (Zircex process^{4,5,6}), it is possible, by using chlorine rather than hydrogen chloride as the chlorinating agent, to volatilize uranium, as the penta- and hexachlorides, together with the zirconium tetrachloride. Since uranium chlorides, particularly the higher valent chlorides, are highly soluble in hydrochloric acid solutions, it is possible to sorb both uranium and zirconium chlorides into water from the chlorination off-gas. Recovery of uranium from the resulting

aqueous solution might then be achieved by solvent extraction. This new concept avoids the problem in the hydrochlorination process of having to filter the off-gas to prevent the loss of uranium by volatilization with the zirconium tetrachloride. However, some method of lowering the melting point of the $\text{ZrOCl}_2\text{-HCl-H}_2\text{O}$ salt (Fig. 3) would be necessary before solvent extraction could be undertaken, since the organic solvents useful for extracting uranium are not sufficiently stable in the 50 to 100°C temperature range needed to keep the salt molten. Dilution with water would lower the melting point, but is undesirable because it would increase the volume of the solution to be solvent extracted.

The small amount of uranium present in the uranium-zirconium alloys¹ did not appear to change the freezing points of the $\text{ZrOCl}_2\text{-HCl-H}_2\text{O}$ product solutions. (This fact was established only for 4 M zirconium solutions, the concentration used for the experiments described below).

It was observed early in this work that the melting point of these hydrate compounds was highly dependent on the chloride content of the compounds. The addition of a small amount of concentrated hydrochloric acid to the azeotropic solution containing hydrochloric acid and ZrOCl_2 caused a sharp increase in the temperature at which solidification occurred. Therefore, a method of decreasing the chloride content of the azeotropic solution was sought. Ideally, this method should remove enough chloride from the azeotropic hydrochloric acid containing 4 M zirconium (the practical upper limit for the solution produced by sorbing zirconium tetrachloride in water, see Sec 2.2.3) to lower the freezing point of this solution from about 100°C to below room temperature, and should add no materials that would interfere with removal of uranium by solvent extraction.

Hydrogen peroxide, under the proper conditions, removed chloride rapidly and efficiently from hydrochloric acid solutions by the reaction:

The escaping chlorine also carries off hydrogen chloride and water vapor, and therefore calculations based on reaction 4, under certain conditions, will indicate efficiencies greater than 100%. For example (Fig. 4) the addition of 98°C of 50% of the stoichiometric amount of peroxide needed to remove all chloride from an 11 M HCl--1.33 M zirconium--3 M HNO_3 solution resulted in the removal of over 75% of the total chloride,

UNCLASSIFIED
ORNL-LR-DWG. 66416

Fig. 4. Removal of Chloride from HCl-Zirconium Solutions by the Reaction: $2\text{HCl} + \text{H}_2\text{O}_2 \longrightarrow \text{Cl}_2 (\text{g}) + 2\text{H}_2\text{O}$.

and the peroxide was 160% efficient, based on reaction 4. This calculated efficiency decreased uniformly with larger additions of peroxide. For example, in this solution described above, 150% of the stoichiometric amount of hydrogen peroxide led to an efficiency of 65%, based on the same reaction. In this case the chloride concentration was reduced from the initial value of 11 M to 0.07. Because of this decrease in efficiency with the quantity of peroxide added, complete removal of the last traces of chloride is not possible by this method.

A temperature higher than 60°C is needed to prevent the reversal of reaction 4 or side reactions, which are favored by lower temperatures.^{20,21} However, a temperature of 75°C led to efficiencies as high as achieved at 98°C (Fig. 4).

The presence of 3 M HNO_3 in the solution discussed above appeared to increase the efficiency of the hydrogen peroxide over that in similar solutions containing no nitric acid (Fig. 4). However the efficiency, with 3 M HNO_3 present, decreased more rapidly with increasing amounts of hydrogen peroxide. This was due to the reaction between hydrogen peroxide and nitric acid. However, the reaction with nitric acid is slow, and the presence of up to 3 M HNO_3 does not appear to hinder the chloride removal process.

A study similar to that described in connection with Fig. 4 was made to further investigate the effect of hydrogen chloride concentration and to compare the efficiency of chloride removal from pure hydrochloric acid to that from solutions containing zirconium (Fig. 5). These experiments, done at 98°C, showed clearly that, while chloride removal is efficient by reaction 4 in concentrated hydrochloric acid, the efficiency decreases with initial chloride concentration. For example, only about 10% of the peroxide enters into reaction with chloride in 3.1 N HCl to produce volatile chlorine. Comparison of the curve for 12 M HCl to the curves for 1.33 M zirconium--11 N chloride and 4 M zirconium--12 N chloride indicates that zirconyl ions actually promote the desired reaction between peroxide and chloride ion.

Fig. 5. Removal of Chloride from HCl-Zirconium Solutions by the Reaction: $2HCl + H_2O_2 \longrightarrow Cl_2 (g) + 2H_2O$.

The point shown in Fig. 5 for 4 M zirconium--12 N chloride is particularly interesting because this is the desired product solution obtained by sorbing zirconium tetrachloride in boiling water (Sec 2.2.3). That this indicated efficiency is highly reproducible can be seen from the results of a series of similar runs (Table 1). In all cases where analyses were made, about 75% of the initial chloride was removed. The effect of evaporation of water vapor and hydrogen chloride is evident from the increase in zirconium concentration from 4 M to as high as 9 M. Products containing up to 6.6 M zirconium appeared to be permanently stable solutions at room temperature. These product solutions are about 10 times as concentrated in zirconium as the solvent extraction feeds prepared by dissolution of uranium-zirconium alloys in fluoride solutions.^{22,23} The 7 M zirconium solution gelled overnight, and the 9 M solution gelled as soon as it was cooled to 25°C. The gels redissolved upon warming. The raffinate after solvent extraction of uranium (Sec 2.4) might be evaporated to form such a concentrated gel before storage. The addition of uranium in the approximate proportion that it would be introduced by chlorination of a uranium-zirconium alloy¹ did not appear to effect the system in any way (run 7).

Table 1. Removal of Chloride from 4 M Zirconium--12 M Chloride Solutions at 98°C by the Reaction: $2\text{HCl} + \text{H}_2\text{O}_2 \longrightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}$

50% of stoichiometric H_2O_2 used

Run	Final Concentrations (M)			Stability of Product at 25°C
	Zr	Cl ⁻	U	
1	6.1	*	0	Stable at least 1 month
2	6.5	*	0	Stable at least 1 month
3	5.6	4.9	0	Stable at least 1 month
4	4.2	4.0	0	Stable at least 1 month
5	5.6	5.6	0	Stable at least 1 month
6	4.4	3.6	0	Stable at least 1 month
7	6.6	4.3	0.08**	Stable at least 1 year
8	7.0	*	0	Stable 12 hours
9	9.0	*	0	Gelled when cooled to 25°C

* Not determined.

** 0.05 M UCl_4 added before peroxide addition.

The observation that peroxide will cause the evolution of chlorine from chloride solutions disagrees with a previous negative observation,²⁴ but agrees with observations made at Argonne National Laboratory,²⁰ and by Sworski.²⁵ In the latter case, nuclear radiations caused the evolution of chlorine from aqueous chloride solutions, but, since a primary radiolysis product is the hydroxyl radical, the effect is probably similar to that obtained by adding peroxide. The effect of chloride ion on the yield of hydrogen peroxide during radiolysis of water has also been investigated.^{25,26}

2.4 Solvent Extraction of Uranium from Concentrated Solutions of Zirconium and Chloride

Chloride was removed at 98°C from a solution containing 4 M zirconium--0.1 M uranium--12 M chloride in the same manner as described for the solutions listed in Table 1, above. The product was made 0.2 M in nitric acid. This solution was extracted batchwise with three equal volumes of 30% tributyl phosphate (TBP) dissolved in Amsco. Less than 0.001% of the zirconium and 84% of the uranium was removed in the first extraction (Table 2). In further extractions, zirconium was not detectable, and the amount of uranium recovered decreased about sixfold per extraction. It appears from these results that four extractions would have removed over 99.9% of the uranium and that TBP-Amsco is a highly satisfactory solvent for recovering uranium from these solutions.

Table 2. Extraction of Uranium from 4 M Zirconium--0.1 M Uranium--4 M Chloride--0.2 M Nitrate Solution

Volume of each TBP-Amsco extract = volume of aqueous solution		
Fraction	Amount Extracted (% of total)	
	U	Zr
1st TBP extract	84.0	0.0006
2nd TBP extract	13.8	ND ^a
3rd TBP extract	1.94	ND
Aqueous raffinate	0.29	100.00

^a ND = none detectable.

2.5 Corrosivity of Two Process Solutions

Corrosion tests were made in solutions simulating the waste from solvent extraction and the solution in the vessel used to sorb zirconium tetrachloride from the chlorination off-gas (Fig. 2). Results of tests made in hydrogen chloride, chlorine, and carbon tetrachloride vapors at high temperatures are reported elsewhere.^{9,27}

2.5.1 Four Molar Zirconium--Four Molar Chloride

The waste solutions from the solvent extraction procedure described in Sec 2.4 are about 4 M in zirconium and 4 M in chloride. Corrosion tests were made to determine if any suitable container metal exists for use in storing this waste. It was hoped that the relatively small amount of chloride in the solution would be tightly complexed by the zirconium and that this waste solution would be less corrosive than the usual aqueous chloride solutions. The results of tests with several alloys at 25°C and 50°C (Table 3) showed that, of the materials tested, only the Hastelloys, B and C, would serve. Although a small amount of nitric acid (enough to make the solution 0.2 M) was added before solvent extraction tests were made (Sec 2.4), this nitrate would be almost completely removed during extraction; therefore, the corrosion tests were made with nitrate-free solutions. More nitrate could be added, in which case titanium would serve well as a container material.

Table 3. Solution-Phase Corrosion Rates (mils/month) in 4 M Zirconium-4 M Chloride Solutions²⁸

All specimens are welded

Alloy	25°C		50°C	
	96 hr	264 hr	48 hr	96 hr
304L SS	89	Terminated		
309 SCb SS	66	Terminated		
Carpenter 20	1.3	0.6	9.0	8.2
"A" Nickel	1.0	0.4	10.5	10.7
Hastelloy B	<0.1	<0.1	<0.1	0.2
Hastelloy C	<0.1	<0.1	<0.1	<0.1

2.5.2 Three Molar Zirconium--Nine Molar Chloride

By collecting zirconium tetrachloride in boiling water, solutions as concentrated as 4 M zirconium--12 M chloride can be made (Sec 2.2.3). It was assumed for the purpose of making corrosion tests that the collection vessel would be operated continuously, with water added and product removed continuously, and that the composition of the product in the collection vessel would be 3 M zirconium--9 M chloride. Welded specimens of tantalum, crystal bar zirconium and Hastelloy B and Hastelloy C were exposed to the boiling 3 M zirconium--9 M chloride solution (about 110°C) and to the vapor above the solution. An equimolar mixture of hydrogen chloride and hydrogen gas was passed over the boiling solution to simulate process conditions. Hastelloy C underwent rapid intergranular attack during the first 168 hr and was eliminated as a possible container material. In 500-hr tests, zirconium and tantalum showed no measurable weight loss in the vapor or liquid phases, while Hastelloy B corroded at average rates of 0.8 mil/month in the vapor phase and 1.0 mil/month in the liquid phase.²⁸ Further tests are planned with Hastelloy B, because it, in contrast to zirconium and tantalum, is resistant to the hot inlet gas containing hydrogen chloride at about 300°C (Sec 2.2), as well as to the boiling solution containing dissolved zirconium and chloride. Tests under operating conditions will be needed to determine if a rapid, pit-producing type of corrosion, which most nickel-containing alloys undergo in moist chlorinating atmospheres, occurs when Hastelloy B is used for the hot inlet line. This type of corrosion is most severe at lower temperatures²⁹ and probably will not occur to any appreciable extent in the hot inlet line since this line is kept above 300°C.

2.6 Calcination of Raffinate

If the waste aqueous raffinate from the solvent extraction step described in Sec 2.4 is evaporated to dryness and then heated to about 600°C, a white solid is obtained, which is almost pure zirconium oxide. Although zirconium oxide is a stable, water-insoluble salt suitable for long-term storage, this method of calcination involved serious

difficulties because of the nature of the melt during calcination. A heavy film formed on the surface of the melt causing the formation of large bubbles before the melt finally was converted to a glassy solid. The large bubbles caused most of the product to be deposited as a crust on the upper walls of the vessel instead of in the desired form of a salt on the bottom of the vessel.

A means of producing a more desirable calcined product was found. By adding to the raffinate at 98°C about 10% more hydrogen peroxide than was used in the chloride-removal experiments (Table 1, Sec 2.3), that is, 55% rather than 50% of the stoichiometric hydrogen peroxide needed according to reaction 4, a moist crystalline product, rather than a liquid was obtained. The composition of the crystals has not been determined as yet. The hydrogen peroxide must be added slowly because the concentrated solution foams vigorously. The product is a porous, moist solid which calcines at 600°C to a fine, free-flowing, white powder of zirconium oxide, with none of the problems described in the paragraph above. A disadvantage of this procedure is that the density of the powder is low; for example, in a demonstration run the density was only 1.2, which is equivalent to about 900 g of zirconium per liter of solid. The density might be increased by variation in heating rate. Other problems in this calcination procedure are: collection and disposal of the chloride-containing off-gas and selection of construction material for the calciner.

2.7 Conversion of Raffinate to Alkaline Waste

The aqueous raffinate from the solvent extraction step described in Sec 2.4 could be stored as a liquid, but these acid chloride solutions are highly corrosive (Sec 2.5), and the waste tanks would have to be made of expensive alloys such as the Hastelloy. The waste solutions might be stored in less expensive tanks if the solutions were made alkaline. If these solutions were made alkaline, zirconium hydroxide would precipitate and, consequently, would produce a less desirable form for storage. On the other hand, if tartaric acid or a tartrate salt is added to the waste solution, a complex hydrated salt forms which can be

dissolved in caustic to form permanently stable solutions. For example, tartaric acid was added to the 6.6 M zirconium solution from run 7, Table 1, and the solution was made alkaline by adding 50% NaOH. However, the zirconium concentration of the product, which has been stable over 1 year, was decreased to 1.7 M. Thus, much of the economic advantage gained from use of cheaper tank material is lost by the need for a larger tank to store a less concentrated product.

Further study is needed to optimize the procedure for producing more concentrated alkaline product solutions. Laboratory work has shown that the minimum number of moles of tartrate required per mole of zirconium lies between 0.125 and 0.25 and that large amounts of sodium or potassium hydroxide are needed to make the solution stable.

Replacement of tartrate lost by radiolytic decomposition during storage of these solutions might be necessary. However the rate of radiolytic decomposition of glycolic acid, which is similar structurally to tartaric acid, was 4.5 molecules per 100 ev of radiant energy absorbed.³⁰ This value is about equal to the radiolytic decomposition rate observed with nitric acid.³¹

2.8 Chlorination of Mixed Uranium Oxide-Zirconium Oxide Fuel

A solid solution of uranium oxide and zirconium oxide is used in place of uranium-zirconium alloy as the fuel in the PWR-Core 2. Samples of this fuel chlorinated in 15% CCl_4 --85% N_2 at rates of about $0.4 \text{ mg cm}^{-2} \text{ min}^{-1}$ at 500 to 550°C and at $3 \text{ mg cm}^{-2} \text{ min}^{-1}$ at 585°C (Fig. 6). At these reaction rates, about 9 hr and 1 hr, respectively, would be required to completely chlorinate the fuel wafers, which are 0.040 in. thick. The rates were not affected by substituting chlorine for the nitrogen in the mixed 15% CCl_4 --85% N_2 reagent. The Zircaloy cladding, which covers the fuel wafers and is only 0.015 in. thick, can be removed by hydrochlorination as in the case of uranium-zirconium alloy fuels. Therefore, with the modification that 15% CCl_4 --85% N_2 is substituted for hydrogen chloride after the cladding is removed, the process outlined in Fig. 1 should serve for the uranium-zirconium oxide fuel, as well as for the uranium-zirconium alloy fuel.

Fig. 6. Rate of Reaction Between 15% CCl_4 -85% N_2 and 34% UO_2 -66% ZrO_2 . Pressure, 1 atm.

3. CONCLUSIONS, DISCUSSION, AND RECOMMENDATIONS

The proposal to develop a head-end process for fuels containing zirconium and graphite which feeds a Darex solvent extraction plant is worth pursuing for several reasons: (1) If a titanium solvent extraction column already exists, a special solvent extraction system need not be built for the enriched zirconium-uranium alloy fuel, which by itself represents a relatively small and uncertain fuel load. In this case, the zirconium-containing fuels would make up only a minor portion of the load of spent fuels processed in the plant. (2) The proposed process yields a solvent-extraction feed about 10 times as concentrated as do the aqueous fluoride dissolution processes.^{2,22,23} An aqueous fluoride head-end for zirconium-containing fuels could also be combined with a Darex plant, but the graphite-containing fuels could not be processed in such a combination plant. Attempts to develop multipurpose aqueous dissolution schemes,^{32,33} in which the zirconium-containing fuels are dissolved in the same dissolver used for fuels containing stainless steel and other materials, have not produced very satisfactory results, either because careful control of the dissolvent composition is required or because corrosion rates are excessive. (3) The operations involved in the chlorination head-end, including the collection of the uranium and zirconium chlorides by sorption into boiling water, concentration, chloride removal, and solvent extraction of uranium from the product solution, were investigated on a laboratory scale and appear to be reducible to large-scale practice. (4) The combination of an aqueous and nonaqueous head-end process should provide an efficient and economical method of gaining experience in high-temperature volatility reprocessing methods. Such experience will be increasingly in demand as even more refractory materials are employed to extend the life of reactor fuels and the range of conditions over which they are used.

In the combination process proposed in this work, the first solvent extraction column would have to be constructed of a material resistant to chloride solutions, probably titanium, in which case at least a small amount of nitric acid would have to be present in all feed solutions to keep the titanium corrosion rates low. Chloride contamination would be scrubbed out of the organic phase before this phase left the titanium column,³⁴ and all subsequent processing could be done in stainless steel equipment. Much of the effort in the Darex process has been directed toward removing chloride from the solvent extraction solution before entering the first extraction column.⁷ A major advantage of chloride-removal previous to solvent extraction, in addition to the fact that it increases the uranium extraction coefficient slightly, is that the aqueous raffinate from the first column is free of chloride and therefore less corrosive and easier to store, requiring tanks made of common alloys such as the stainless steels. The continuing development of methods for converting the aqueous raffinate to solids for long-term storage³⁵ suggests that this chloride-removal operation is not as important as it formerly was. However, only a few hundred parts per million of chloride have been present in wastes which have been converted to solids up to the present time, and large amounts of chloride would undoubtedly complicate these processes. Conversion of the acid chloride wastes to alkaline solutions (Sec 2.7) might also simplify the storage problems.

Continued investigation is recommended, on an engineering scale, of the process proposed in this work for handling the uranium-zirconium alloy fuels. Both investigation of the individual operations and demonstrations of the process in which all operations are performed in sequence are needed. The problems involved in handling chloride solutions throughout the process must also be carefully evaluated and weighed against the advantages which the process offers. In this connection, the laboratory corrosion tests should be continued under conditions simulating each operation in the process. The laboratory investigations of the physical properties of solutions of zirconium and chloride should be continued.

4. ACKNOWLEDGMENTS

Analytical work was done by W. R. Laing and co-workers of the Analytical Chemistry Division. Corrosion tests were planned by W. E. Clark of the Chemical Technology Division and run by P. D. Neumann of the Reactor Chemistry Division. Discussions concerning solvent extraction of uranium from aqueous solutions with C. A. Blake of the Chemical Technology Division were most helpful.

5. REFERENCES

1. The Shippingport Pressurized Water Reactor, Addison-Wesley, Reading, Massachusetts, 1958, p. 586.
2. P. Burn, An Evaluation of Four Processes for Recovering Uranium from Zirconium Fuels at the Idaho Chemical Processing Plant, IDO-14564 (April 1962).
3. AEC to Revise Charges for Enriched and Depleted Uranium, AEC Press Release E-176 (May 29, 1962).
4. J. J. Perona, J. B. Adams, J. E. Savolainen, and T. A. Gens, Status of the Development of the Zircex Process, ORNL-2631 (March 1959).
5. T. A. Gens, "New Developments in Uranium-Zirconium Alloy Fuel Re-processing," Nucl. Sci. and Eng., 9, 488-494 (1961).
6. T. A. Gens and R. L. Jolley, New Laboratory Developments in the Zircex Process, ORNL-2992 (April 1961). T. A. Gens, U.S. Patent 3,043,653 (July 10, 1962).
7. W. E. Clark, J. R. Flanary, and F. G. Kitts, The Darex Process: the Treatment of Stainless Steel Reactor Fuels with Dilute Aqua Regia, ORNL-2712 (May 1962).
8. W. E. Clark, L. Rice, D. N. Hess, and E. S. Snavely, Supplemental Studies of the Corrosion of Materials of Construction for the Darex Process, ORNL-TM-417 (November 1962).
9. T. A. Gens, Laboratory Development of Chloride Volatility Processes for the Recovery of Uranium Directly from Spent Rover Fuel or From Its Combustion Ash, ORNL-3376 (May 1963) (Confidential).
10. T. A. Gens and L. M. Ferris, Chloride Volatility Processes for Nuclear Reactor Fuels--Present Status and Outline of Future Work, ORNL-CF-61-1-33 (January 1963).
11. T. A. Gens, Laboratory Development of a Process for Chlorinating the Combustion Ash from UC_2 - ThC_2 -Graphite Fuels and Solvent Extracting Uranium from a Solution of the Chlorination Products (in preparation).
12. J. E. Savolainen and R. E. Blanco, "Preparation of Power Reactor Fuels for Aqueous Processing," Chem. Eng. Progr. 53, 78-81 (1957).
13. V. R. Thayer and T. J. Colven, Some Comments on the Economies of Fuel Processing, Preprint Paper No. 83, 1962 Nuclear Congress, New York, June 4-7, 1962. Reactor Fuel Processing, 5, No. 4 (October 1962), p. 2.

14. W. H. Farrow, Jr., Radiochemical Separations Plant Study, Part II. Design and Cost Estimates, DP-566 (March 1961).
15. F. L. Culler, General Economics of Chemical Reprocessing for Solvent Extraction Processing, from Symposium on the Reprocessing of Irradiated Fuels held at Brussels, Belgium, May 20-25, 1957, TID-7534, p. 1108.
16. L. J. King, Oak Ridge National Laboratory, private communication to T. A. Gens, July 19, 1963.
17. W. B. Blumenthal, The Chemical Behavior of Zirconium, D. Van Nostrand Co., Princeton, New Jersey, 1958, p. 107.
18. W. A. DuPraw, Problems in the Processing of Zirconium and its Compounds, from First Conference, Analytical Chemistry in Nuclear Reactor Technology, November 4-6, 1957, TID-7555 (August 1958) p. 138.
19. Argonne National Laboratory Reactor Development Program Progress Report, September 1962, ANL-6619 (October 1962).
20. R. Larsen, M. Beederman, G. Kesser, and H. M. Feder, Argonne National Laboratory Summary Report April, May, and June 1954, ANL-5290 (August 1954) (Secret), p. 18.
21. R. E. Connick, "The Interaction of Hydrogen Peroxide and Hypochlorous Acid in Acid Solutions Containing Chloride Ion," J. Am. Chem. Soc. 69, 1509 (1947).
22. D. G. Reid, C. E. Stevenson, R. B. Lemon, and F. K. Wrigley, "Zirconium Alloy Fuel Reprocessing," Proc. 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva 17, 145 (1958).
23. F. G. Kitts, Evaluation of an Engineering Demonstration of the Modified Zirflex and Neuflex Processes for the Preparation of Solvent Extraction Feeds from Unirradiated Zirconium-Base Reactor Fuels, ORNL-3465 (in press).
24. E. R. Johnson, L. M. Levy, R. L. Maddox, and J. Blum, Oxidation of Chlorides in Raffinate Materials, FMPC-207 (April 1953).
25. T. J. Sworski, "Yields of Hydrogen Peroxide in the Decomposition of Water by Cobalt γ -Radiation: II. Effect of Chloride Ion," Rad. res. 2, 26 (1955).
26. M. Burton and K. C. Kurien, "Effects of Solute Concentration in Radiolysis of Water," J. Phys. Chem. 63, 899 (1959).

27. C. L. Peterson, P. D. Miller, E. L. White, and W. E. Clark,
"Materials of Construction for Head-End Processes, Aqueous Re-
processing Nuclear Fuels," Ind. and Eng. Chem. 51, 32 (1959).
C. L. Peterson, P. D. Miller, J. D. Jackson, and F. W. Fink,
Construction Materials for Various Head-End Processes for the
Aqueous Reprocessing of Spent Fuel Elements, BMI-1375 (August 1959).
28. P. D. Neuman, Oak Ridge National Laboratory to W. E. Clark, Oak
Ridge National Laboratory, private communication, April 10, 1963.
29. M. H. Brown, W. B. DeLong and J. R. Auld, "Corrosion by Chlorine
and by Hydrogen Chloride at High Temperature," Ind. and Eng.
Chem. 39, 839 (1947).
30. A. J. Swallow, "Radiation Chemistry of Organic Compounds, from
International Series of Monographs on Radiation Effects in
Materials," p.108, general ed., A. Charlesby, Pergamon Press,
New York, 1960.
31. H. E. Gilliland and D. M. Jenkins, Radiolysis of Concentrated
Nitrate Solutions, KT-537 (October 1960).
32. W. E. Clark, Corrosion of Materials of Construction for Multi-
purpose Head-End Equipment in Proposed Fuel Processing Schemes,
ORNL-TM-60 (November 1961).
33. T. A. Gens, Continuous Dissolution of Zirconium Reactor Fuels in
Titanium Equipment: Laboratory Demonstration, ORNL-TM-395
(January 1963).
34. Chemical Technology Division Monthly Progress Report for February 1957,
ORNL-2270 (June 1957) (Confidential), p.57.
35. W. E. Clark and H. W. Godbee, "Fixation of Simulated Highly Radio-
active Wastes in Glassy Solids," Proceedings of the Symposium on
the Treatment and Storage of High Level Radioactive Wastes,
Vienna, October 8-13, 1962, SM-31/12.

DISTRIBUTION

1. R. E. Blanco	31. L. P. Hatch, BNL
2. J. C. Bresee	32. B. R. Hayward, Atomics Int'l.
3. L. Carter	33. O. F. Hill, Hanford
4. W. E. Clark	34. K. K. Kennedy, ICPP
5. F. L. Culler	35. S. Lawroski, ANL
6. L. M. Ferris	36. J. A. McBride, ICPP
7. D. E. Ferguson	37. B. Manowitz, BNL
8-9. T. A. Gens	38. A. R. Matheson, General Atomics
10. H. E. Goeller	39. Paul Miller, BMI
11. F. E. Harrington	40. J. W. Morris, du Pont, SRL
12. R. W. Horton	41. J. Nehls, ORO
13. L. J. King	42. H. Pearlman, Atomics Int'l.
14. F. G. Kitts	43. W. H. Reas, Hanford
15. R. P. Milford	44. K. L. Rohde, ICPP
16. E. L. Nicholson	45. C. A. Rohrman, Hanford
17. A. M. Rom	46. O. T. Roth, AEC, Wash.
18. M. J. Skinner	47. Harry Schneider, AEC, Wash.
19. S. H. Smiley	48. C. M. Slansky, ICPP
20. E. G. Struxness	49. C. E. Stevenson, ANL, Idaho
21. P. D. Neumann	50. K. G. Steyer, General Atomics
22. M. E. Whatley	51. V. R. Thayer, du Pont, Wilm.
23. E. L. Anderson, AEC, Wash.	52. R. E. Tomlinson, Hanford
24. W. G. Belter, AEC, Wash.	53. F. M. Warzel, ICPP
25. R. F. Benenati, General Atomics	54. W. E. Winsche, BNL
26. S. Bernstein, Paducah	55. Document Reference Section
27. J. A. Buckham, ICPP	56-57. Central Research Library
28. J. T. Christy, AEC, Hanford	58. ORNL-RC
29. F. R. Dowling, AEC, Wash.	59-62. Laboratory Records
30. M. K. Harmon	63-77. DTIE
	78. Research and Dev. Div., ORO