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SUBJECT: Recovery of Uranium from Residues Produced in Hydrochlorination Of Nuclear Fuel Alloys

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ABSTRACT

Chlorination at 550-600°C of Zircex residues with carbon tetrachloride resulted in greater than 99.99% recovery of the uranium. Both the hydrochlorination residue and the solids which remain after leaching the hydrochlorination residue with nitric acid were chlorinated with similar results. By this technique, loss of 1-6% of the uranium to the nitric acid insoluble residue, which occurs in simple hydrochlorination and dissolution of STR fuel, is avoided. Other advantages include reduced corrosion and the elimination of possible explosions between U-Zr alloys and nitric acid. A modified flowsheet is proposed.

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1.0 INTRODUCTION

The Zircex Process is based on the use of hydrogen chloride gas at temperatures of 350-800°C to convert various U-Zr alloys to volatile zirconium chloride and relatively non-volatile uranium tri-chloride. After hydrochlorination is complete, the uranium chloride is dissolved in nitric acid. Darex chloride removal and feed adjustment operations are then employed to produce a solvent extraction feed solution which contains little of the original zirconium structural material. Six major problems have prevented the immediate use of the Zircex Process as a means of reprocessing spent nuclear fuel alloys:

1) Removal of the heat generated in the exothermic gas-solid reactions.
2) Uranium loss to the zirconium tetrachloride sublimate.
3) Design of a satisfactory method of removing zirconium tetrachloride from the hydrochlorination off-gas stream.
4) Uranium loss to a nitric acid-insoluble hydrochlorination residue in the case of STX type fuel.
5) Corrosion in the hydrochlorinator caused by cyclic use of hydrogen chloride gas at 350-800°C and boiling nitric acid.
6) The possibility of explosive reactions resulting from the contact of nitric acid with U-Zr alloy, should hydrochlorination be incomplete.

These problems are related and the solution of one problem may increase or decrease the importance of others. The problem of heat removal decreased in importance when it was discovered that uranium chlorides could be easily removed from the off-gas stream. This discovery permitted use of much higher reaction temperatures, and also permitted reduction of the uranium loss to the zirconium tetrachloride sublimate to tolerable levels. In runs in which the inside of the fuel element reached temperatures of 900°C, no damage to the hydrochlorinator was observed. Further engineering work is required to develop a satisfactory desublimer.
No satisfactory method was developed previously to prevent the uranium loss to the nitric-acid insoluble hydrochlorination residue and to handle this residue by remote methods. These losses ranged from 1-6% under practical operating conditions for STR type fuel but were negligible for PWR blanket de-jacketing.\footnote{1}

The losses increased as the maximum reaction temperature increased to about 600°C.\footnote{1} Oxygen, introduced either in the form of water or carbon dioxide, apparently caused the formation of the non-volatile, and nitric acid-insoluble, material.\footnote{3} Analyses have shown that dissolved oxygen is present in the nuclear fuel alloys before hydrochlorination,\footnote{4} so that removal of all oxygen and oxygen-containing compounds from the hydrogen chloride still does not produce an oxygen-free system. A high uranium loss to the nitric acid-insoluble residue has been obtained in one run using carefully purified hydrogen chloride,\footnote{4} suggesting that the presence of oxygen and compounds which contain oxygen may not be the only cause of uranium loss.

The use of carbon tetrachloride as a chlorinating agent has been investigated in this work as a possible method of attacking simultaneously the last three problems listed above. A new flowsheet is proposed on the basis of the experimental results for fuels of the STR and EBWR types. Some advantages of the flowsheet are that all uranium is recovered from the hydrochlorination residue and that no nitric acid is introduced into the hydrochlorinator. Chlorination of zirconium oxide, which is thought to be a major component of the nitric acid-insoluble residue, with carbon tetrachloride gas at 550-600°C was found to be superior to other methods of chlorination in a study at the Y-12 plant.\footnote{4} Oxides of uranium have also been chlorinated successfully with carbon tetrachloride.\footnote{5} The use of carbon-tetrachloride gas at 350°C has been previously recommended as a method of recovering uranium from the nitric acid-insoluble material from the Zircex Process.\footnote{2}

Additional laboratory work is needed to determine the effect of varying the temperature from the 550-600°C used in this work and of varying the amount of carrier gas used. The use of a Darex chloride removal step before solvent extraction, as has been previously proposed,\footnote{2} might require a zirconium-free product, since
zirconyl nitrate solutions can hydrolyze upon boiling. The development of a fractional desublimation technique may be needed to separate the uranium and zirconium chlorides produced by the reaction of carbon tetrachloride with the hydrochlorination residue. The fractional desublimation technique might resemble that now used\(^1\) to recover the uranium chlorides which are present in the hydrochlorination off-gas. Since the conditions under which hydrolysis occurs are not well known, further investigation may uncover alternative solutions to this problem. The hydrochlorination residue, before leaching in nitric acid, will probably contain about ten moles of zirconium per mole of uranium in the case of STR fuel.\(^1\)

The laboratory work described in this report was performed by G. E. Woodall. The spectrographic analyses were performed by C. Feldman and P. Hoffman of the Analytical Chemistry Division.

2.0 FLOWSHEET

The use of carbon tetrachloride to convert all residues left after hydrochlorination to volatile chlorides from which all uranium is recoverable introduces some changes in the Zircex flowsheet\(^2\),\(^3\) (Fig. 1). The first operation is hydrochlorination at 350-800°C as before. Hydrochlorination removes about 98% of the zirconium from the reactor in the case of STR fuel. Essentially all of the uranium remains in the reactor or in a filter chamber at the exit from the dissolver. The zirconium tetrachloride is removed from the off-gas stream and discarded as waste. After hydrochlorination, a stream of nitrogen, which is saturated with carbon tetrachloride by bubbling through liquid carbon tetrachloride at room temperature, is passed into the reactor which is held at temperatures between 550 and 600°C. All of the hydrochlorination residue is converted to volatile chlorides which are removed from the nitrogen gas stream by desublimation. The desublimation can be performed at room temperature. No nitric acid or water is introduced into the reactor, thereby simplifying the corrosion problem and eliminating all possibility of explosive reactions between U-Zr alloys and nitric acid. The uranium-containing chlorides
Fig. 1. Modified Zircex Process: Gas-Phase Hydrochlorination Followed by Chlorination with Carbon Tetrachloride
dissolve readily in nitric acid to yield a HNO₃-HCl solution from which the uranium might be recovered by the same techniques used in the Darex Process.²

3.0 EXPERIMENTAL RESULTS

The chlorinations were performed in a quartz tube 1" in diameter placed in a horizontal 8" clam-shell furnace. A sample of the residue from a Zircex hydrochlorination was placed in a platinum boat near the center of the furnace. In runs 1 through 4, only, the sample had been previously leached with nitric acid and oven dried at 120°C (Table 1). A thermocouple-actuated Simplytrol was used to maintain the furnace at the desired temperature of 550 or 600°C. For chlorination, a carrier gas was saturated with carbon tetrachloride by passage through a liquid carbon tetrachloride bubbler at room temperature.

In all chlorinations, nearly 100% of the starting material was converted to volatile chlorides. These chlorides, which collected on the cool exit of the quartz tube, dissolved completely and rapidly in warm 7 M HNO₃. The residue in the platinum boat from run ZR1 was analyzed spectrographically. No uranium was found and the major component appeared to be silicon. The volatilization of uranium chlorides was expected, since carbon tetrachloride has been observed to convert uranium oxides to the higher chlorides of uranium.⁵ In all chlorinations, except runs ZR5 and ZR8, a deposit of carbon was observed collecting on the reaction surface. This carbon, which seemed to inhibit the reaction slightly, burned off immediately when oxygen was passed into the quartz tube. No appreciable differences were observed in behavior between the residues from three Zircex runs (HC76, HC79γ, and HC82) during chlorination with carbon tetrachloride. Very little reaction occurred when no carbon tetrachloride was added to the hydrogen chloride gas (run ZR2) or when air was used as a carrier gas (run ZR3). Pure carbon tetrachloride has not been used as yet.
Table 1. Recovery of Uranium from Zircex Residues by Chlorination with Carbon Tetrachloride

Maximum amount of uranium not recovered by chlorination is $10^{-3}$% of that in the residue sample.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$T, ^\circ C$</th>
<th>Residue Sample</th>
<th>Carrier Gas</th>
<th>Sample Leached in 7 M HNO$_3$ Before Chlorination</th>
<th>Total Time</th>
<th>Sample Remaining in Boat, %</th>
<th>No. of Times Carbon Burned Off During Run</th>
<th>Quantity of CCL$_4$, Multiple of Stoichiometric</th>
<th>Source of * Hydrochlorination Residue, Zircex Run No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZR1</td>
<td>550</td>
<td>2.9422 (13.4% U)</td>
<td>HCl</td>
<td>Yes</td>
<td>3.0</td>
<td>1.1</td>
<td>2</td>
<td>HC76</td>
<td></td>
</tr>
<tr>
<td>ZR2</td>
<td>550</td>
<td>2.9422 (13.4% U)</td>
<td>HCl</td>
<td>Yes</td>
<td>0.2</td>
<td>100</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ZR3</td>
<td>550</td>
<td>2.9422 (13.4% U)</td>
<td>Air</td>
<td>Yes</td>
<td>0.2</td>
<td>100</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ZR4</td>
<td>550</td>
<td>1.0067 (13.4% U)</td>
<td>N$_2$</td>
<td>Yes</td>
<td>4.0</td>
<td>0.3</td>
<td>1</td>
<td>49</td>
<td>HC76</td>
</tr>
<tr>
<td>ZR5</td>
<td>600</td>
<td>1.0948 (13.4% U)</td>
<td>N$_2$</td>
<td>No</td>
<td>0.8</td>
<td>0.03</td>
<td>0</td>
<td>29</td>
<td>HC76</td>
</tr>
<tr>
<td>ZR6</td>
<td>600</td>
<td>1.9446 (13.4% U)</td>
<td>HCl</td>
<td>No</td>
<td>1.0</td>
<td>0.02</td>
<td>1</td>
<td>11</td>
<td>HC76</td>
</tr>
<tr>
<td>ZR7</td>
<td>600</td>
<td>1.2904 (2.77% U)</td>
<td>N$_2$</td>
<td>No</td>
<td>1.0</td>
<td>0.2</td>
<td>1</td>
<td>48</td>
<td>HC79</td>
</tr>
<tr>
<td>ZR8</td>
<td>600</td>
<td>4.1583 (57.0% U)</td>
<td>N$_2$</td>
<td>No</td>
<td>1.1</td>
<td>0.0</td>
<td>0</td>
<td>7.4</td>
<td>HC82</td>
</tr>
</tbody>
</table>

* STR fuel (1% U, 97% Zr, 2% Sn) was used in Zircex runs HC76 and HC79. Before treatment with CCl$_4$, 7.5% and 19.5%, respectively, of the uranium in the residue samples was insoluble in nitric acid. EBWR fuel (93.5% U, 5% Zr, 1.5% Nb) was used in Zircex run HC82. Before treatment with CCl$_4$, 0.02% of the uranium in the residue sample was insoluble in nitric acid. All uranium was soluble in all runs after treatment with CCl$_4$. 
By assuming all solids present in the hydrochlorination residue to be ZrO₂ in the STR case, an approximate calculation was made of the excess carbon tetrachloride that was used above that required by the reaction:

\[ \text{ZrO}_2 + \text{CCl}_4 \rightarrow \text{ZrCl}_4 + \text{CO}_2 \]  \hspace{1cm} (1)

In the EBWR case (run ZR8), a similar calculation was made by assuming that the minimum amount of carbon tetrachloride required was one mole per mole of uranium in the residue. The amount of carbon tetrachloride used was measured by the reduction in volume of the liquid carbon tetrachloride in the bubbler during the chlorination experiment. The smallest amount of carbon tetrachloride used in the STR case was eleven times the stoichiometric quantity required for equation 1. Considering the vapor pressure of carbon tetrachloride to be 116 mm at 25°C,³ the volume of gas (STP) which was required to carry the 0.18 moles of carbon tetrachloride used in run ZR6 to chlorinate about 2 g of Zircex residue was about 25 liters. If a single charge to the hydrochlorinator is assumed to produce about 4 kg of residue, the volume of carrier gas (STP) required under the conditions of run ZR6 would be 5000 liters. This amount can probably be reduced by proper design of the chlorinator and by control of the flow rate and temperature.

Many of the chlorides of the fission products are less volatile than the uranium and zirconium chlorides and would remain behind in the reactor. Preliminary calculations indicate that most of the ruthenium and cesium chlorides would volatilize from the reactor during a single chlorination with carbon-tetrachloride, while all but a small percentage of Sr, Y, Ce, Ba, and the rare earths would remain behind. Thus, a fission product buildup would probably take place in the reactor at the rate of 100-200 g per charge. Some method of periodically removing these fission products will be needed.

Chlorinations were performed three times as rapidly if the salts taken from the hydrochlorinator were not leached in nitric acid before chlorination. The time required for complete chlorination was only 1 hr. Since there is no apparent reason why the reaction surface per unit mass of hydrochlorination residue should be smaller on full scale runs, the time required for complete chlorination in full scale runs should not vary greatly from those listed in Table 1.
4.0 REFERENCES


