Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

AN OXYHYDROCHLORINATION PROCESS FOR PREPARING URANIUM-MOLYBDENUM REACTOR FUELS FOR SOLVENT EXTRACTION: LABORATORY DEVELOPMENT

T. A. Gens

DATE ISSUED

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION
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.
ABSTRACT

A flowsheet, based on laboratory-scale data, is presented for oxyhydrochlorination of 90% uranium—10% molybdenum alloy (CPPD reactor core) with 15% HCl—air at 400°C in 18 hr. Up to 90% of the molybdenum is volatilized during oxyhydrochlorination and another 3-6% is removed by a 2-hr treatment with pure hydrogen chloride at 400°C. Residual chloride is removed by a 4-hr treatment with moist air at 400°C, and the product uranium oxide is dissolved in 4 M nitric acid to yield a stable solvent extraction feed solution of 1 M uranium, 0.017 M molybdenum, 175 ppm chloride, and 1.7 M nitric acid. The stainless steel cladding of the original fuel would be removed mechanically and the core recanned in aluminum prior to transfer to the core processing facility. The aluminum can would be removed by hydrochlorination prior to core treatment.
CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Introduction</td>
<td>4</td>
</tr>
<tr>
<td>2.0 Flowsheet</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Preparation of Solvent Extraction Feed</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Chemistry of the Process</td>
<td>7</td>
</tr>
<tr>
<td>3.0 Laboratory Studies</td>
<td>8</td>
</tr>
<tr>
<td>3.1 Reactions of Uranium-Molybdenum Alloys with Chlorinating Agents</td>
<td>8</td>
</tr>
<tr>
<td>3.2 Reaction of Various Uranium-Molybdenum Alloys with 15% HCl—Air at 400°C</td>
<td>14</td>
</tr>
<tr>
<td>3.3 Product Purification and Stability</td>
<td>14</td>
</tr>
<tr>
<td>3.4 Reaction of 2S Aluminum with Hydrogen Chloride or Chlorine</td>
<td>17</td>
</tr>
<tr>
<td>3.5 Reaction of 304 Stainless Steel with Chlorine</td>
<td>19</td>
</tr>
<tr>
<td>3.6 Corrosion</td>
<td>20</td>
</tr>
<tr>
<td>4.0 References</td>
<td></td>
</tr>
</tbody>
</table>
1.0 INTRODUCTION

An oxyhydrochlorination process was investigated, on a laboratory scale, for processing of uranium-molybdenum alloy fuels as exemplified by the Power Reactor Development Corporation (PRDC) blanket (uranium-3% molybdenum) and the Consumers Public Power District (CPPD) core (uranium-10% molybdenum). Aqueous processes proposed for uranium-molybdenum alloy fuels include selective dissolution of the uranium in nitric acid followed by separation of solid molybdenum oxide particles (1a, 2, 3) or dissolution of the whole alloy in nitric acid containing ferric (1a, 2, 3) or fluoride (1b) ions. High-temperature hydrochlorination has also been proposed (4, 5). The suggested oxyhydrochlorination method produces smaller high-level radioactive waste volumes than the aqueous processes, does not require an additional solids separation step, and produces a less volatile product, uranium oxide, than does hydrochlorination alone, which produces uranium chloride.

Watson et al. (1c) have proposed mechanical removal of the stainless steel jacket and recanning in aluminum before transfer to the core processing facility. If this procedure is followed the aluminum jacket could be hydrochlorinated and volatilized as the first step in the oxyhydrochlorination procedure.

The laboratory work was performed by E. R. Johns. Analytical work was performed by G. Wilson, M. Murray, and W. Laing of the Analytical Chemistry Division. Corrosion tests were planned by W. E. Clark of the Chemical Technology Division and run by L. Rice and co-workers of the Reactor Experimental Engineering Division.
2.0 FLOWSHEET

The flowsheet involves five operations: can removal, core oxidation, further purification by removal of molybdenum and chloride, and oxide dissolution in nitric acid (Fig. 1). The first four operations are high-temperature gas-solid reactions. The entire process requires 27 hr for CPPD fuel canned in aluminum. It was assumed that stainless steel-clad uranium-molybdenum fuel would be declad mechanically, at which time the sodium bonding material would be destroyed, and the fuel would be recanned in 32-mil aluminum (1c). Zirconium cladding can be removed by techniques developed in the Zircex process (4-6).

2.1 Preparation of Solvent Extraction Feed

The CPPD fuel, canned in 32-mil aluminum, is treated with 60% HCl—N₂ at 300°C for 2 hr to remove the can as volatile aluminum chloride. The presence of a small amount of ammonium chloride (Sect. 3.4) ensures short initiation periods. Higher rates can be achieved by decreasing the amount of nitrogen used to dilute the hydrogen chloride (Sect. 3.4), but on a large scale this procedure might melt the aluminum with resultant corrosion problems. An ash of nonvolatile aluminum oxide forms as a result of reaction with oxygen-containing impurities in the system, causing nearly 1% of the aluminum to remain with the core.

The off-gas from the decanning and other operations is passed through a caustic scrubber. Can removal produces 125 moles of hydrogen, and a safe hydrogen disposal procedure is required.

Core oxidation proceeds most rapidly under conditions that cause volatilization of molybdenum oxychloride (Sect. 3.1a). Treatment of the CPPD core with 15% HCl—air at 400°C for 18 hr results in complete oxidation and removal of 90% of the molybdenum. The 18-hr reaction time is the result of the large diameter of the CPPD fuel, 1.5 cm. The average reaction rate for the operation is > 12 mg/sq cm.min.

The product of the oxidation step requires additional treatment to remove part of the residual molybdenum (about 9% of the total) and chloride (about 0.3% of the total, based on a uranium trichloride product; Sect 3.3) before a satisfactory solvent extraction feed solution can be prepared by dissolution in nitric acid. Treatment of the product for 2 hr with pure hydrogen chloride at 400°C removes an additional 3% of the total molybdenum and thus ensures stability of the 1.7 M HNO₃—1 M uranium feed solution. Further treatment should remove even more of the molybdenum (Sect. 3.3). This does not appear advantageous to the solvent extraction process but would probably simplify volume reduction in the fission product—bearing waste solution.

A 4-hr treatment with 0.6% H₂O—air at 400°C of the product from the molybdenum cleanup operation removes more than half the remaining chloride. The vessel is allowed
Fig. 1. Oxyhydrochlorination flowsheet for removal of aluminum can and processing of CPPD fuel.
to cool during the last hour of this operation in preparation for the \( \text{U}_3\text{O}_8 \) dissolution. About 0.16% of the chloride, based on a uranium trichloride product, enough to yield 175 ppm of chloride in a 1 M uranium solution, remains in the product after the chloride cleanup. Since this concentration of chloride is as low as is normally achieved by Darex chloride removal, the Darex treatment \((5, 7)\) is avoided.

The \( \text{U}_3\text{O}_8 \) product dissolves readily in 4 M HNO\(_3\) without external heating, to yield a stable solution of 1 M uranium, 0.017 M molybdenum, 0.003 M aluminum, 175 ppm of chloride, and 1.7 M HNO\(_3\).

The caustic waste solution, containing about 0.01% of the uranium, 96-99% of the aluminum, 94% of the molybdenum, unused hydrogen chloride that escaped the reactor, and the oxides of nitrogen produced during the nitric acid dissolution of uranium oxide, has a minimum volume about half that of the solvent extraction feed. The waste solution is not completely stable in that a light, flocculent precipitate, containing molybdenum and aluminum, forms immediately and does not dissolve upon dilution.

2.2 Chemistry of the Process

The reaction involved in can removal is

\[
2\text{Al} + 6\text{HCl} \rightarrow \text{Al}_2\text{Cl}_6 + 3\text{H}_2 \quad (1)
\]

The vapor pressure of aluminum chloride is 1 atm at 183°C. Ammonium chloride initiates the reaction, probably through formation of a low-melting (304°C), volatile (vapor pressure = 1 atm at 420°C) \((4)\) aluminum compound:

\[
\text{NH}_4\text{Cl} + \text{HCl} + \text{Al} \rightarrow \text{NH}_4\text{AlCl}_4 \quad (2)
\]

The compound formed by oxyhydrochlorination of uranium—molybdenum alloys is probably \( \text{MoO}_2\text{Cl}_2 \), since the observed sublimation point of about 100°C agrees well with the reported vapor pressures of \( \text{MoO}_2\text{Cl}_2 \) of 6.57 and 10.99 mm Hg at 95 and 116.5°C, respectively \((8)\). Thus, the reaction would be

\[
\text{Mo} + 1.5\text{O}_2 + 2\text{HCl} \rightarrow \text{MoO}_2\text{Cl}_2 + \text{H}_2\text{O} \quad (3)
\]

The volatile molybdenum oxochloride dislodges the products from the reaction surface, permitting further reaction, and provides a means of separating molybdenum from nonvolatile uranium oxide. Water vapor collects on the cool exit from the reaction tube. The major reaction of the uranium component of uranium—molybdenum alloys is

\[
3\text{U} + 4\text{O}_2 \rightarrow \text{U}_3\text{O}_8 \quad (4)
\]
The small amount of chloride (Sect. 3.3) shows that little uranium chloride is present.

Removal of nonvolatile molybdenum by treatment with hydrogen chloride probably occurs by the reaction (Sect. 3.3)

\[ \text{MoO}_3 + 2\text{HCl} \rightarrow \text{MoO}_3\cdot2\text{HCl} \]  

Either reaction 3 or 5 satisfactorily explains the observed results. Although the same number of molybdenum, oxygen, hydrogen, and chlorine atoms are involved in the two equations, the appearance of water vapor on the cool exit of the reaction tube provides evidence that at least part of the molybdenum volatilization occurs through reaction 3.

3.0 LABORATORY STUDIES

Most of the laboratory studies were made with samples of cast 91.6% uranium—molybdenum alloys from Nuclear Metals, Inc., since this material was readily available. Rate data for 97% uranium—molybdenum alloy were obtained with an extruded alloy from the Sylcor Corporation. The 90% uranium—molybdenum alloy used to simulate CPPD fuel in rate studies and flowsheet runs was a cast alloy from Atomics International Company; it had been heated 24 hr at 900°C and water quenched. The effect of different treatments during alloy preparation was not investigated.

The equipment consisted of a clamshell furnace with a 1-in.-i.d. Pyrex tube in the individual step studies and a 2-in.-i.d. Pyrex tube, in the flowsheet runs (Fig. 2), a gas mixing manifold and flowmeters (not visible in the photograph), and caustic traps to scrub the off-gas. This equipment was highly satisfactory in the individual step studies, but in the flowsheet runs larger equipment designed for the process would probably have given better separation of molybdenum and lower uranium losses to the waste solution.

3.1 Reactions of Uranium—Molybdenum Alloys with Chlorinating Agents

The reaction rates and products of the reaction of 91.6% uranium—molybdenum alloy with hydrogen chloride, hydrogen chloride—air mixtures, chlorine, chlorine—air mixtures, phosgene, phosgene—air mixtures, and phosgene—hydrogen chloride—air mixtures were studied. A 15% HCl—air mixture was chosen as the most attractive reagent from the viewpoint of nearly constant and high reaction rates, separation of molybdenum and chloride from the product, and probably lower corrosion rates.

a. Hydrogen Chloride—Air. The reaction rate of hydrogen chloride—air mixtures with 91.6% uranium—molybdenum alloy in 1-hr runs at 500°C increased
Fig. 2. CPPD fuel and equipment used in flowsheet runs.
from about 3.5 mg/sq cm.min in pure hydrogen chloride to about 8 mg/sq cm.min in 30-70% HCl—air mixtures (Fig. 3a). The amount of molybdenum removed as volatile molybdenum oxychloride exceeded 80% when the air content of the hydrogen chloride—air mixture exceeded 50%. Apparently a temperature of 400°C with 10% HCl—90% air produces a reaction rate and molybdenum removal approximately equal to that achieved at higher temperatures (Fig. 3b).

While the reaction rates shown in Fig. 3 are moderately high at about 8 mg/sq cm.min, the large diameters of the fuel types under consideration, e.g., 0.415 and 0.59 in. for the PRDC and CPPD, respectively, would lead to processing times of about 20 hr if the rate of 8 mg/sq cm.min could be achieved and maintained. In experiments lasting 2 and 3 hr at 400°C in 10-20% HCl—air rates were equal to those observed in 1-hr studies, within the expected experimental precision, indicating that the rate is independent of the amount of alloy that has reacted (Fig. 4). The flowsheet runs (Table 1) also showed that the initial rate is maintained throughout the reaction, since only 18 hr was required for complete reaction. The amount of molybdenum and chloride removed from the product increased from about 80 to 95% and 99.3 to 99.9%, respectively, based on a uranium trichloride product, as the reaction time increased from 1 to 3 hr. These amounts after 3 hr are slightly higher than in the flowsheet run of 18 hr (run 2).

b. Chlorine. The reaction rate of 91.6% uranium—molybdenum alloy with chlorine was very low at a furnace temperature below 400°C but increased rapidly to 20 mg/sq cm.min as the furnace temperature increased from 425 to 450°C or higher (Fig. 5). The highly exothermic reaction caused the temperature of the alloy to increase rapidly to red heat. A separation of 87-98% of the molybdenum, as volatile molybdenum pentachloride (vapor pressure 1 atm at 268°C), was achieved in the 400-500°C temperature range. These separations exceeded the 80-90% achieved with an HCl—air mixture, probably because some nonvolatile molybdenum oxide was produced by the latter reagent. The reaction of chlorine with uranium—molybdenum alloys was not pursued further because a large amount (not measured) of uranium chloride volatilized and high corrosion rates were anticipated at the required furnace temperature of 425°C or higher.

Attempts to use mixed chlorine—air were not successful. The stronger oxidizing conditions produced by chlorine—air, as contrasted to HCl—air, caused formation of a protective coat of yellow material, possibly uranyl chloride, which inhibited further reaction. For example, the average reaction rate of 91.6% uranium—molybdenum in 1-hr tests at 425°C fell from 3.2 to 0.27 mg/sq cm.min when chlorine was diluted with 25% air.

c. Phosgene. Phosgene, which resembles hydrogen chloride in that the product of its reaction with uranium—molybdenum alloy contains a reducing gas (CO), reacted
Fig. 3. Reaction rate of 91.6% uranium—molybdenum alloy with HCl—air mixtures as a function of (a) percentage of air in the HCl at 500°C, and (b) temperature with 10% HCl—90% air. Reagent flow rate 300 cc/min; 1-in.-i.d. tube.

Fig. 4. Reaction rate of 91.6% uranium—molybdenum alloy with 15% HCl—air at 400°C and molybdenum (bottom curve) and chloride removal as a function of time. Reagent flow rate 300 cc/min; 1-in.-i.d. tube.
Table 1. Oxyhydrochlorination Flowsheet Demonstration with CPPD Fuel Prototype

Temperatures and Reagents: Aluminum hydrochlorination, 300°C, 60% HCl-N₂ (300 cc/min)
Core Oxidation, 400°C, 15% HCl-air (600 cc/min)
Oxide Purification - Molybdenum cleanup, 400°C, HCl (300 cc/min)
Oxide Purification - Chloride cleanup, 400°C, 0.6% H₂O-air (300 cc/min)
Oxide Dissolution, 60-80°C, 4 M HNO₃

Reactor: 2-in. i.d. Pyrex tube
Fuel specimen: 60 g of 90% U-Mo alloy, cylinders 2.00 cm x 1.50 cm dia
0.6 g of 32 mil aluminum 1100-H14 alloy tubing

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Al Sublimate, %</th>
<th>Mo Sublimate, %</th>
<th>Waste, %</th>
<th>U</th>
<th>Al</th>
<th>Mo</th>
<th>HCl</th>
<th>HCl</th>
<th>H₂O</th>
<th>4 M</th>
<th>Feed, M</th>
<th>Feed, Cl, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.006</td>
<td>99.2</td>
<td>1.4</td>
<td>0.01</td>
<td>0.0</td>
<td>48</td>
<td>0.015</td>
<td>99.2</td>
<td>49.4</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.46b</td>
<td>96</td>
<td>85.2</td>
<td>2</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.005</td>
<td>96.9</td>
<td>93.8</td>
<td>18</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Run 1 established the uranium content of the aluminum and molybdenum sublimates. Because pure air was admitted, much nonvolatile MoO₃ formed and prevented preparation of a stable, concentrated feed solution.

This high value resulted from some mixing of the uranium and waste product during removal from the Pyrex tube.
Fig. 5. Reaction rate of 91.6% uranium—molybdenum alloy with chlorine.
Reagent flow rate 300 cc/min; 1-in.-i.d. tube.

Fig. 6. Reaction rate of 91.6% uranium—molybdenum alloy with phosgene-HCl-air mixture at 400°C. Reagent flow rate 300 cc/min; 1-in.-i.d. tube.
with 91.6% uranium—molybdenum at 500°C at rates double those of HCl—air when the phosgene was mixed with 50% air but left 39% of the molybdenum and 45% of the chloride (based on uranium trichloride) in the product. Pure phosgene produced very little reaction. Addition of phosgene to 10 and 30% HCl—air decreased the reaction rate (Fig. 6). The reaction of phosgene with uranium—molybdenum alloys was not pursued further because of the unfavorable reaction rates.

3.2 Reaction of Various Uranium-Molybdenum Alloys with 15% HCl—Air at 400°C

In 1-hr runs the average reaction rate of uranium alloys with 15% HCl—air at 400°C increased from 6.3 mg/sq cm.min with pure uranium to nearly 13 mg/sq cm.min with a uranium alloy containing 10% molybdenum (Fig. 7). Pure molybdenum reacted at a rate of 0.5 mg/sq cm.min. No uranium alloys were readily available for investigating the range between 10 and 100% molybdenum. The 3 and 10% molybdenum alloys both reacted at higher rates than the approximately 8 mg/sq cm.min observed with 8.6% molybdenum alloy (Sect. 3.1), probably because the 8.6% alloy contained small amounts of iron. These results indicate that the oxyhydrochlorination process is applicable at 400°C to uranium-molybdenum alloys containing up to perhaps 50% molybdenum.

3.3 Product Purification and Stability

Short laboratory studies indicated that the objective of the oxyhydrochlorination process (a nitric acid solvent extraction feed solution containing less than 250 ppm chloride and a small enough quantity of molybdenum that the solution is stable) might be met with a simple treatment of oxyhydrochlorination product with air to remove chloride. The flowsheet runs (Table 1), however, indicated a need for a molybdenum cleanup operation, and a method of removing more molybdenum from the product with pure hydrogen chloride was also worked out. Further removal of molybdenum not only permits preparation of a stable concentrated uranium solution but simplifies decreasing the volume of waste solution after solvent extraction of uranium.

The product of the reaction of 91.6% uranium—molybdenum alloy with 10% HCl—air at temperatures above 400°C appeared to be mostly uranium oxide. Assuming that the product of hydrochlorination would be uranium trichloride, over 99% of the chloride was removed in 1-hr runs at reaction temperatures of 400°C or higher (Fig. 8). At 400°C, the amount of chloride remaining in the product of a 1-hr run corresponded to 700 ppm chloride in a 1 M uranium solution. The amount of chloride removed from the product increased to 99.7% (420 ppm in a 1 M uranium solution) when the reaction time was increased to 3 hr (Fig. 4). A 4-hr treatment at 400°C of the product from this 3-hr run with 0.6% water—air decreased the chloride content from 420 to 60 ppm (Fig. 9a). Dry air and air containing 3% moisture was less satisfactory, and further treatment with air—20% HCl only increased the chloride content.
Fig. 7. Reaction rate of uranium-molybdenum alloys with 15% HCl—air at 400°C. Reagent flow rate 300 cc/min; 1-in.-i.d. tube.

Fig. 8. Volatilization of chloride from the 91.6% uranium-molybdenum oxyhydrochlorination product during preparation. Reagent flow rate 300 cc/min; 1-in.-i.d. tube; 1-hr studies.
Fig. 9. Volatilization of (a) chloride and (b) molybdenum from the 91.6% uranium--molybdenum oxyhydrochlorination product. Reagent flow rate 300 cc/min; 1-in.-i.d. tube.
In contrast, the treatment with air—20% HCl at 400°C was the most effective in removing molybdenum from the oxyhydrochlorination product (Fig. 9b). The molybdenum remaining in the product was decreased from 13.5 to 9% of the molybdenum originally present within 0.5 hr, and further treatment had no effect. In the case of CPPD fuel, this amount of molybdenum in the product leads to a stable 1 M uranium solution containing 0.025 M molybdenum. As expected, air containing 3% water vapor caused hydrolysis of the volatile molybdenum oxychloride to form nonvolatile oxide. Dry air or air containing 0.6% water vapor decreased the molybdenum to less than 12% of the molybdenum originally present in the alloy within 0.5 hr. Therefore, air—0.6% water vapor was chosen for the chloride cleanup operation since it not only volatilizes chloride but also molybdenum.

The second flowsheet run (Table 1) indicated that decrease of the molybdenum content of the oxyhydrochlorination product with air—0.6% water vapor to 9% of that originally present in the alloy was not possible with specimens as large in diameter (1.5 cm) as the CPPD fuel, probably because the large mass of product inhibited the volatilization of molybdenum oxychloride. Since 9% of the molybdenum originally present in the product in the experiments described above with air—0.6% water vapor was apparently in the form of nonvolatile molybdenum oxide, a method was sought to convert molybdenum oxide to a more volatile compound. It was found that molybdenum oxide could be volatilized by treatment with hydrogen chloride gas and that the rate of volatilization increased 10-fold as the temperature increased from 200 to 400°C (Fig. 10). Dilution of the hydrogen chloride with air reduced the rate of molybdenum volatilization. A 2-hr treatment at 400°C of the CPPD oxyhydrochlorination product with hydrogen chloride decreased the molybdenum concentration in the solvent extraction feed solution from 0.0375 to 0.017 M (runs 2 and 3, Table 1). The lower chloride concentration in the product from run 3 indicates that much of the residual chloride is associated with molybdenum, and the molybdenum cleanup operation is needed to reduce residual chloride as well as molybdenum.

The product solution from run 3 (Table 1) was refluxed several hours with no evidence of instability. However, molybdenum oxide precipitated after 48 hr refluxing. Precipitation also started upon evaporation over several days at room temperature to between 50 and 60% of the original volume. Solubility studies (2) indicate that a product solution containing up to 0.06 M Mo should be stable.

3.4 Reaction of 2S Aluminum with Hydrogen Chloride or Chlorine

Rate studies made with samples of 2S aluminum indicated that the aluminum can in which the fuel will be received can be removed by reaction with either hydrogen chloride or chlorine at furnace temperatures as low as 300°C (Fig. 11) to form volatile aluminum chloride (vapor pressure = 1 atm at 183°C). Neither hydrogen chloride nor chlorine reacts rapidly with the 91.6% uranium—molybdenum
Fig. 10. Volatilization of molybdenum oxide with hydrogen chloride as a function of (a) temperature with pure HCl and (b) percentage of air in the HCl at 400°C. Reagent flow rate 300 cc/min; geometric reaction surface 6 sq cm; bed depth 1 cm; 1-in.-i.d. tube.

Fig. 11. Reaction rate of 2S aluminum with HCl or Cl₂ - N₂ mixtures at 300°C. Reaction initiated with ammonium chloride; reagent flow rate 300 cc/min; 1-in.-i.d. tube.
alloy at 300°C (Figs. 3b and 5). In 5- to 15-min studies of both gases with aluminum, the reaction rate decreased approximately linearly from 11.4 mg/sq cm.min as they were diluted with nitrogen. The rate decrease with dilution is probably caused by a decrease in both the reagent concentration and the temperature of the aluminum. When reacting with pure hydrogen chloride or chlorine, the aluminum soon reached red heat and began to flow but did not melt (melting point of pure aluminum = 660°C).

Initiation periods for the reaction at 300°C between hydrogen chloride or chlorine and aluminum were between 3 and 9 min when a small amount of ammonium chloride was added, except in the case of chlorine diluted with 85% nitrogen where the initiation period was 28 min (Fig. 11). Apparently some unknown variable, perhaps a small amount of air or moisture in the reagents, caused the aluminum samples to be passive for periods which varied between runs. For example, in one run at 300°C in pure chlorine without any ammonium chloride, no reaction occurred in 1 hr; in a duplicate run, reaction started within 30 min. In all cases in which some ammonium chloride was added and the reagent gas was not diluted more than 50% with nitrogen, reaction started in less than 10 min at 300°C.

3.5 Reaction of 304 Stainless Steel with Chlorine

If high-temperature chlorination or hydrochlorination could be used to remove the stainless steel cladding from the original PRDC fuels, the mechanical decladding operation might be avoided. Such a process offers the potential advantage that the sodium bonding material may be destroyed in a gas-solid reaction with the same reagent used for cladding removal. Studies of the reaction rate of 304 stainless steel with chlorine showed that a temperature of at least 600°C is required to achieve rates of over 0.5 mg/sq cm.min (Fig. 12). A small amount of water vapor, not exceeding 6%, increased the rate slightly. Although a light-yellow surface coat developed during chlorination, average reaction rates with pure chlorine at 600°C were the same in a 0.5-hr run as in a 2-hr run. The x-ray pattern of nickel chloride was observed from the material in the surface coat. The chief chlorination product is thought to be ferric chloride (vapor pressure = 1 atm at 315°C). Chromium may be forming either the volatile chromic chloride hydrate (vapor pressure = 1 atm at 83°C) or chromyl chloride (vapor pressure = 1 atm at 118°C). The fuels under consideration have 10-mil stainless steel cladding, which would require 6 hr for complete reaction at a rate of 0.55 mg/sq cm.min. At 600°C, the chlorine would also react extensively with the core and cause volatilization of some uranium (Sect. 3.1). The chloride salts of sodium and nickel might have to be dissolved in water and removed prior to processing of the core unless chloride is removed by techniques used in the Darex process (6, 7) if stainless steel solvent extraction equipment is to be used. Chlorine at 600°C would probably produce severe corrosion in most metallic materials of construction. Reaction rates of hydrogen chloride with 304 stainless steel were about an order of magnitude lower than those of chlorine.
3.6 Corrosion

The objective of the first corrosion tests was to find a material that would be resistant to a mixture of 15% HCl–air at 400°C. Materials that were resistant to the Zircex cycle (4, 6) were suggested, since it would be desirable to construct a single vessel for both this process and Zircex. All of four materials tested appeared very resistant to attack by this gaseous mixture:

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosion Rate, mils/month</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hr</td>
</tr>
<tr>
<td>Haynes 25</td>
<td>(+)</td>
</tr>
<tr>
<td>Pyroceram</td>
<td>(+)</td>
</tr>
<tr>
<td>INOR-8</td>
<td>0.02, 0.03</td>
</tr>
<tr>
<td>Nichrome V</td>
<td>(+), 0.03</td>
</tr>
</tbody>
</table>

where a (+) indicates a weight gain.

Fig. 12. Reaction rates of 304 stainless steel with chlorine-water vapor.
4.0 REFERENCES


INTERNAL DISTRIBUTION

1. Biology Library
2. Health Physics Library
3-4. Central Research Library
5. Reactor Division Library
6. ORNL - Y-12 Technical Library, Document Reference Section
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. E. D. Arnold
29. R. E. Blanco
30. G. E. Boyd
31. J. C. Bresee
32. K. B. Brown
33. F. R. Bruce
34. C. E. Center
35. R. A. Charpie
36. R. S. Cockreham
37. Esther Cohn
38-39. F. L. Culler
40. W. K. Eister
41. D. E. Ferguson
42. J. H. Frye, Jr.
43. T. A. Gens
44. H. E. Goeller
45. A. T. Gresky
46. C. E. Guthrie
47. C. W. Hancher
48. C. S. Harrill
49. A. Hollaender
50. A. S. Householder
51. R. G. Jordan (Y-12)
52. W. H. Jordan
53. C. P. Keim
54. M. T. Kelley
55. J. A. Lane
56. T. A. Lincoln
57. S. C. Lind
58. R. S. Livingston
59. K. Z. Morgan
60. J. P. Murray (K-25)
61. M. L. Nelson
62. D. Phillips
63. P. M. Reyling
64. H. E. Seagren
65. E. D. Shipley
66. M. J. Skinner
67. A. H. Snell
68. J. A. Swartout
69. E. H. Taylor
70. J. W. Ullmann
71. W. E. Unger
72. A. M. Weinberg
73. M. E. Whatley
74. C. E. Winters
75. R. G. Wymer
76. J. W. Youngblood
77. D. L. Katz (consultant)
78. C. E. Larson (consultant)
79. I. Perlman (consultant)
80. J. H. Rushton (consultant)
81. Hood Worthington (consultant)
82. T. H. Pigford (consultant)

EXTERNAL DISTRIBUTION

83. Division of Research and Development, AEC, ORO
84-585. Given distribution as shown in TID-4500 (16th ed.) under Chemistry category (75 copies - OTS)