HYDROMETALLURGICAL PROCESSING OF URANIUM-BEARING RESIDUE MATERIALS TO UF4, PRESENTED AT THE SYMPOSIUM ON UNIT PROCESSES IN HYDROMETALLURGY AT THE NATIONAL MEETING OF THE AMERICAN INSTITUTE OF MINING - (USED AS REFERENCE IN 0U1 RI)
HYDROMETALLURGICAL PROCESSING OF URANIUM-BEARING
RESIDUE MATERIALS TO UF₄*

by

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First Issued: November, 1962
Revised: April, 1963

Prepared for presentation at the Symposium on Unit Processes in Hydrometallurgy, held at Dallas, Texas, in February, 1963, at the National Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers

*This work was performed for the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1156
The processes used to recover the uranium values from residues generated during the manufacture of fuel cores at the National Lead Company of Ohio are described.

The various low-grade residues, after suitable feed preparation, are treated in a hydrometallurgical process to recover the uranium values as uranyl ammonium phosphate (UAP). The UAP after calcination to uranium pyrophosphate is returned to the production stream as a uranium concentrate.

High-grade residues, including uranium pyrophosphate, are converted by an aqueous precipitation process to hydrated UF₄, which is dehydrated and used for the production of uranium metal.
INTRODUCTION

At the A.E.C. Feed Materials Production Center, Fernald, Ohio, which is operated by the National Lead Company of Ohio, purified uranium trioxide (UO₃) is converted to uranium tetrafluoride (UF₄), the UF₄ is reduced to massive metal, and the metal is fabricated into fuel cores for the A.E.C.'s plutonium production reactors.

The processes used are shown diagrammatically in Figure 1. The incoming UO₃ is reduced with dissociated ammonia (N₂ + H₂) in fluid bed reactors to uranium dioxide and then converted to UF₄ by reaction with anhydrous hydrogen fluoride in screw reactors. The UF₄ is blended with finely divided magnesium metal and reduced to uranium metal by a thermite reaction. The cleaned massive piece of uranium metal, called a "derby," is remelted with uranium metal recycled from various sources and cast into an ingot. This ingot is rolled into rods, and the rods are converted by a number of machining operations into finished fuel cores.

Uranium-bearing residues are generated in each of the processing steps just described. All of these residues must be processed for uranium recovery either by direct remelting or by hydrometallurgical processing to a usable...
chemical form. In this paper will be described the hydrometallurgical process used to convert the low-grade residues to a uranyl ammonium phosphate (UAP) concentrate. Also described is the aqueous precipitation process used for the conversion of high-grade uranium oxide residues and UAP to uranium tetrafluoride. As an introduction, the preparation required by the various residues will be described.

**FEED PREPARATION**

The preparation and processing of residue materials to UAP and UF₄ are carried out in the Scrap Recovery Plant. These residues may be conveniently considered as high- and low-grade according to the uranium content and subsequent handling. The major categories of material recycled for hydrometallurgical processing are the following:

**High Grade**

1. Ingot end crops and other massive metal pieces not suitable for remelting.
2. Chips, turnings, and sawdust from metal fabrication operations.
3. Black oxide (U₃O₈) from crucible burnout.
Low Grade

1. Magnesium fluoride slag from the UF₄-Mg reduction reaction.
2. Sump cakes from all plants.
3. Dust collector residues and floor sweepings.

High-Grade Residues
Massive metal pieces, such as ingot end cuts, are processed through a hydrochloric acid metal dissolver. The uranous chloride solution from the metal dissolver is oxidized with nitric acid and utilized directly in the manufacture of UF₄ by the aqueous precipitation process which will be described later.

The finely divided metallic residues, such as chips, turnings, and sawdust, are processed in the high-grade feed preparation system shown in Figure 2. This system consists of a series of furnaces in which the metallic particles are burned to U₃O₈. A Rotex screening separates the +8 mesh fraction which contains most of the unoxidized metal. This fraction is recycled for further oxidation. The -8 mesh fraction is drummed as product. A brief
description of the furnaces follows:

1. Oxidation Furnace
   This is a six-hearth rabble-arm type furnace. The charge is fed at the top and proceeds down through the furnace by being rabbled alternately to the outside and to the center of the successive hearths where it drops through openings to the next lower hearth. The furnace is fired by three gas burners on the second and fourth hearths.

2. Box Furnace
   This furnace consists of a refractory-lined steel fire-box, with a single gas burner which is equipped with a blower for supplying combustion air. The furnace is fed in batches and rabbled manually until the charge is essentially all oxidized. The product is discharged manually into drums.

3. Muffle Furnace
   This is a single rabbled hearth, Manheim-type furnace. The fire-box is a circular refractory-lined steel shell and is fired by a single gas burner. The furnace is fed in batches through an Inconel chute, the charge is rabbled during oxidation by a motor-driven arm. After oxidation is complete the charge is drummed.
Low-Grade Residues

The preparation of low-grade residues for subsequent processing is a more involved process as indicated in Figure 3. Wet materials such as sump cakes are dried in a rotary kiln at about 1200°F then fed to the raw feed hopper. Miscellaneous dry, non-metallic materials are fed directly to the hopper.

A major fraction of the total volume of low-grade residues is the MgF₂ slag from the metal reduction operation. This slag is processed through a series of grinding and classification operations which separate a fraction suitable for recycle as a liner for further metal reductions. The remainder is processed in the Scrap Recovery Plant. By the nature of the grinding and classification operations performed on the slag liner, a portion of the MgF₂ slag contains a high percentage of free Mg and U metal while the remainder contains very little free metal. The high free metal fraction is sent directly to the Scrap Recovery Plant where it is calcined in a rabble-arm furnace at 1500°F to oxidize the free metal to oxides, then ground to 90% -325 mesh in a ring-roll mill and fed to a water slurry tank. The fraction of the slag low in free metal content does not require calcination; it is ground on a spare mill in the Sampling Plant, transported to the Scrap
Recovery Plant, slurried in water in a leach tank, and pumped to the water slurry tank.

Although all material containing free metal is calcined to convert the free metal to oxides, the oxidation is not complete. The free metal contained in the scrap has been found to react slowly with water liberating hydrogen; therefore, it has been found necessary to ventilate the water slurry tank as shown in Figure 3. The air flow rate is measured continuously, and any malfunction in the ventilation system is corrected promptly. The hydrogen concentration of the off-gas stream is monitored continuously, and the feed conveyor is automatically turned off any time the hydrogen concentration in the off-gas exceeds 1.0%, which is 25% of the lower explosive limit for hydrogen.

HYDROMETALLURGICAL PREPARATION OF UAP

The uranium values in the slurry of 60% solids in water resulting from the feed preparation circuit just discussed are recovered as uranyl ammonium phosphate (UAP). The UAP process was originally described(1) in 1957 and has been extensively modified and improved since then.
The present UAP flowsheet is shown schematically in Figure 4. As indicated, the feed slurry is pumped continuously from the water slurry tank to the digester. Hydrochloric acid solution (30% HCl by wt) and MnO₂ are metered continuously to the tank. The acid is added at the rate required to supply the acid consumed by the feed and provide a 1.0N excess HCl in the liquor. At present, the rate of acid addition is controlled by periodic sampling of the digester liquor, titration of the sample for excess acid content, and adjustment of the acid flow accordingly. A continuous titrator is being installed which will control the acid flow automatically to maintain the desired acid excess. The MnO₂ is added at the rate required to maintain the oxidation potential of the liquor above -650 mv. This is also controlled at present by periodic sampling and manual adjustment of the MnO₂ addition. An automatic control system is also being installed for this reagent which will control the MnO₂ rate on the basis of a continuous oxidation potential measurement.
The major chemical reactions taking place in the digestion system may be represented by the following equations:

1. \( \text{U}_3\text{O}_8 + 8\text{HCl} + \text{MnO}_2 \rightarrow 3\text{UO}_2\text{Cl}_2 + \text{MnCl}_2 + 4\text{H}_2\text{O} \)
2. \( \text{U}^0 + 8\text{HCl} + 3\text{MnO}_2 \rightarrow \text{UO}_2\text{Cl}_2 + 3\text{MnCl}_2 + 4\text{H}_2\text{O} \)
3. \( \text{U}^0 + 4\text{HCl} \rightarrow \text{UCI}_4 + 2\text{H}_2 \)
4. \( \text{UCI}_4 + \text{MnO}_2 \rightarrow \text{UO}_2\text{Cl}_2 + \text{MnCl}_2 \)
5. \( \text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} \)
6. \( \text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2 \)
7. \( \text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \)

Plant experience has shown that a significant quantity of hydrogen is released; therefore, control of the concentration of hydrogen in the off-gas is necessary to prevent build-up of explosive concentrations. This control is accomplished by air ventilation. A wet scrubber system pulls a minimum of 1000 cfm of air through the digestion tank at all times. This air flow is monitored continuously, and any drop below 1000 cfm is corrected promptly. The hydrogen concentration in the off-gas stream is monitored continuously. The monitoring instrument turns off the feed slurry pump any time the hydrogen concentration exceeds 1.0%. (This value is 25% of the lower explosive limit for hydrogen-air mixtures.)
The material flow rates to the digestion system are set so the average hold time in the digester is approximately 6.0 hours. The temperature is maintained at 130°F to 190°F. Under these conditions digestion efficiency is greater than 99%.

The digested slurry is pumped continuously from the bottom of the digestion tank by a diaphragm pump to a filter feed tank. The digested slurry is fed from this tank to a rotary vacuum precoat drum filter. The insoluble tailings are separated from the uranium-bearing liquor and washed on this filter. The uranium content of the tailings normally averages about 0.07% (specification limit: 0.1%) giving an overall recovery efficiency for digestion and filtration of about 99%.

The filtrate containing approximately 30 g/l uranium is discharged into a surge tank from which it is withdrawn to a continuous UAP precipitator. In the precipitator, sufficient phosphoric acid is added to maintain a PO₄:U ratio of 0.6:1 by weight; and the pH is brought up to 1.5 with aqueous ammonia. The PO₄:U ratio is maintained automatically by a control system consisting of a continuous uranium analyzer and a flowmeter on the uranium...
feed stream and a flowmeter and an automatic control valve on the phosphoric acid feed stream. The mass uranium flow is determined from the feed liquor flow and uranium analysis; and the phosphoric flow is set to deliver 0.6 of the uranium flow in phosphate. The aqueous ammonia flow is automatically set to maintain the pH at 1.5.

Precipitation of the uranium at the relatively low pH of 1.5 results in separation of most of the impurities from the uranium. A typical analysis of the digest liquor feed to UAP precipitation is as follows:

- \( U \) - 24 g/l
- \( H^+ \) - 0.91 N
- \( \text{Cl} \) - 125 g/l
- \( F \) - 4.6 g/l
- \( \text{Fe} \) - 1.3 g/l
- \( \text{Mg} \) - 18 g/l
- \( \text{Mn} \) - 4.1 g/l
- \( \text{Ca} \) - 12 g/l

The concentration of the major contaminants given above may vary over a considerable range, and minor quantities of almost all elements may be present. From this type of feed a UAP product assaying 55% to 60% uranium, and about 25% phosphate is produced. The stoichiometric composition of uranyl ammonium phosphate is 62.2% uranium and 24.8% phosphate. Therefore, it can be seen that the UAP product contains 89% to 97% \( \text{UO}_2\text{NH}_4\text{PO}_4 \), with the remaining 3% to 10%...
of the material being made up of co-precipitated metal phosphates and filter aid. Analysis of a typical UAP product is as follows:

<table>
<thead>
<tr>
<th>Wet Chemical (%)</th>
<th>Spectrochemical (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U - 57.5</td>
<td>Al - 400</td>
</tr>
<tr>
<td>PO₄ - 24.8</td>
<td>Bi - &lt;20</td>
</tr>
<tr>
<td>F - 0.5</td>
<td>Ca - 160</td>
</tr>
<tr>
<td></td>
<td>Cd - &lt;200</td>
</tr>
<tr>
<td></td>
<td>Cr - &lt;100</td>
</tr>
<tr>
<td></td>
<td>Cu - 300</td>
</tr>
<tr>
<td></td>
<td>Fe - 3000</td>
</tr>
<tr>
<td></td>
<td>Mg - 1600</td>
</tr>
</tbody>
</table>

Comparison of contaminant concentrations in the feed and UAP product shows the process provides a good separation from most contaminants. The only impurity which may be present in appreciable quantities in the feed that does not have a satisfactory decontamination factor is ferric iron. It is co-precipitated essentially quantitatively with the uranium. However, if the iron is reduced to the ferrous state by adjusting the oxidation potential to -300 mv with a reducing agent such as sodium thiosulfate, iron co-precipitation is minimized. This reduction step is necessary to provide UAP suitably pure for later processing and also, when processing materials containing high concentrations of iron, to prevent formation of a slimy, gelatinous UAP that is difficult to
filter, wash, and calcine. The reducing agent is now added manually to maintain the -300 mv potential, but an automatic system is being installed to meter a solution into the filtrate surge tank in response to a signal from an oxidation potential meter installed in the tank.

After precipitation, the UAP slurry is collected and fed to a rotary vacuum precoat filter. The UAP is separated from the waste liquor and washed with water on this filter. The UAP ordinarily forms a dry-appearing cake that can be easily filtered. Filtration rates are usually in the range of 25 to 30 gallons per hour per square foot. The uranium content of the waste filtrate is less than 0.05 g/l, which represents a loss of approximately 0.2% of the uranium fed to the process.

The UAP cake from the filter is packaged into drums and transported to the calcination furnace where it is roasted at 1200°F to 1400°F for a period of 2 to 3 hours. This roasting drives off the ammonia from the UAP and converts it mainly to a uranyl pyrophosphate, \((UO_2)_2P_2O_7\). (A small percentage of the uranium is reduced by the \(NH_3\) in the furnace atmosphere to a uranous form.) The calcination is carried out in a 6-hearth rabble-arm type furnace.
The furnace is equipped with burners which may be either gas or oil fired. An automatic temperature control system is available.

The calcination also serves to reduce volatile contaminant levels in the material. The fluoride content is reduced from about 0.5% to about 0.1%. An operational problem that has arisen periodically is conversion of excessive quantities of uranium to an acid insoluble form. This can occur if the furnace temperature becomes too high; but it also can occur at normal operating temperatures if the iron content of the UAP cake is high. This problem is one of the reasons for the iron reduction step described above.

**PRODUCTION OF UF₄ BY AQUEOUS PRECIPITATION**

During the summer of 1962, a new facility began operation for the production of UF₄ hydrate by an aqueous precipitation technique known as the Winlo process. The Winlo process was developed at the A.E.C. Raw Materials Development Laboratory, Winchester, Massachusetts, operated by the National Lead Company(2,3,4). The process was refined and reduced to practice at the National Lead Company of Ohio(5,6).
The Winlo flowsheet is shown schematically in Figure 5. As indicated, the feed to the system may consist of any combination of the following three sources: the black oxide produced in the high-grade feed preparation system, the UAP produced in the UAP system and uranous chloride liquor produced in the metal dissolver. The proportion of the different components making up the feed depends on whether normal or slightly enriched uranium is being processed.

The Winlo digestion of solid feed is conducted in batches. First, the estimated requirement of hydrochloric acid and nitric acid (as oxidant) is pumped into the digester. Then, the solid feed is added by a screw feeder at the maximum rate consistent with low foaming in the digester and maintenance of a hydrogen concentration of 1.0% or less in the off-gas stream. The hydrogen concentration is monitored continuously, and the feeder is automatically turned off any time the concentration exceeds 1.0%. A leach time of 3.0 hours is allowed at a temperature of approximately 160°F. The batch is sampled during the leach cycle and checked for acid concentration and oxidation potential. If these analyses indicate the desired acid excess of 1.2N and oxidation potential of -650 mv has not been
attained, adjustment is made by adding hydrochloric or nitric acid as required. The proportion of feed and acid to the Winlo digestion is adjusted to produce a digest liquor assaying about 225 g/l uranium.

The completed digest batch is pumped to a rotary vacuum precoat filter where the insoluble solids are separated from the digest liquor and washed with a volume of water equal to 12% to 15% of the liquor volume. The small volume of residue is recycled to the UAP system for further processing to recover the remaining uranium. The filtrate, diluted to about 200 g/l uranium and 1.0N HCl by the filter wash, is pumped to a surge tank to await transfer to UF₄ precipitation.

The UF₄ precipitation operation is carried out in either of two identical precipitation tanks (one is shown in Figure 5). These tanks are cylindrical with a truncated-cone bottom. They are constructed of steel and lined with rubber. The precipitation tanks are provided with agitators, also covered by rubber, and Karbate heat exchangers. Sulfur dioxide is introduced through a sparge line which extends down near the bottom of the tank. The off-gas is vented to a caustic scrubber.
The precipitation cycle is initiated by adding acid filtrate from the surge tank to a specified level. The concentration of uranium in the liquor is determined by analyzing a sample on a gamma absorptometer instrument. From this concentration and volume and the concentration of aqueous HF available, the required volume of aqueous HF is determined that will supply the stoichiometric requirements plus at least a 12 to 15 g/l excess of HF. (When processing UAP, the excess is raised to 40 g/l HF to minimize phosphate contamination of the product.) This quantity of HF is pumped to the precipitator. Sufficient CuSO₄·5H₂O is added to the batch to produce a cupric ion concentration of about 5 g/l. The batch is heated by steam in the Karbate heat exchangers to about 190°F. The agitator is turned on, and SO₂ is sparged into the batch at a rate calculated to provide the stoichiometric requirement for reaction plus a 50% excess over a 4-hour period. Completion of the reaction is determined by withdrawing a sample near the end of the 4-hour period and checking the uranium concentration by a "spot" test. This is a simple color comparison test performed in the plant by the operator. Uranium concentration of the liquor is reduced to 0.2 g/l at the end of the reaction, which is the solubility of UF₄ in the liquor under the conditions in the precipitator.
The uranium is precipitated from the hot solution as $\text{UF}_4 \cdot \frac{3}{4}\text{H}_2\text{O}$. The $\text{SO}_2$ will not reduce the uranium (VI) to uranium (IV) directly but does reduce the cupric ion to cuprous. The cuprous ion then reduces the uranium from the hexavalent to the tetravalent form, and is, in turn, oxidized back to the cupric state. The uranium precipitates as $\text{UF}_4$ as rapidly as it is reduced to the tetravalent state, since an excess of fluoride is always present in the solution. The rate of formation of $\text{UF}_4$ is controlled by the solubility of $\text{SO}_2$ in the hot solution. Since this solubility value is low, the rate of the reaction forming $\text{UF}_4$ is slow; and a dense, crystalline, easily filterable $\text{UF}_4$ is formed, compared with the fluffy gelatinous product usually associated with aqueous precipitation of $\text{UF}_4$.

The following equations represent the pertinent reactions in the precipitation process.

$$2\text{CuCl}_4^{2-} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CuCl}_2^- + \text{SO}_4^{2-} + 4\text{H}^+ + 4\text{Cl}^-$$
$$2\text{CuCl}_2^- + 4\text{HF} + \text{UO}_2^{++} + 4\text{Cl}^- \rightarrow \text{UF}_4^\downarrow + 2\text{CuCl}_4^{2-} + 2\text{H}_2\text{O}$$

After the precipitation reaction is complete, the $\text{UF}_4$ slurry is filtered on a rotary horizontal vacuum filter, located directly under the precipitators. The slurry is fed by gravity from the precipitators to the filter, the
liquor is separated, the UF₄ cake is washed in water and discharged from the rotating filter pan to the dryers by a scroll-type unloader. The filter is hooded and vented to prevent escape of obnoxious fumes and is covered by rubber on all parts in contact with process liquor. Filtration rate of the UF₄ slurry averages 100 to 150 gallons per hour per square foot. The filtrate is pumped to a continuous neutralizer where the pH is raised to 9.0 by addition of lime slurry. The neutralized waste is pumped to a settling pit. The wet UF₄·3/4H₂O cake from the filter discharges by gravity to a dryer for removal of free moisture. The dryer is composed of two sections in series of Holoflite conveyors. Steam is supplied both to the screws and to jackets on the casings. A sweep of air is pulled through the dryers by a water scrubber countercurrent to the flow of UF₄. Essentially all the free moisture is removed in the dryer, and the dried product is discharged to an inclined screw conveyor which carries it to a surge hopper. From the surge hopper it is packaged into mobile hoppers for transfer to the Green Salt Plant for dehydration.

Since the heart of the Winlo process is the precipitation step, the major variables of this step will now be briefly discussed. It has been found in both laboratory testing
and plant operation that the major variables affecting the character of the product formed are the operating temperature in the precipitator and the concentration of certain impurities. A temperature of 190°F to 195°F has been selected as the optimum. As the temperature is decreased from this value, the UF₄ hydrate progressively retains more water until a UF₄·2.5H₂O product is formed at ambient temperature. Also, the product becomes progressively less dense, forms a slimy cake upon filtration, and has generally less desirable characteristics for both the Winlo process and later dehydration and metal reduction. Therefore, it is desirable to keep the temperature high. However, when the temperature increases appreciably above the 190°F to 195°F range, the solubility of SO₂ drops so drastically that a practical reaction rate is not maintained, and SO₂ consumption is greatly increased. Therefore, the control of the operating temperature very close to the optimum is essential for satisfactory operation.

The other major factor besides low precipitation temperature which adversely affects the physical properties of the product is the presence of any appreciable concentration of alkali or alkaline earth metals in the precipitator feed solution. These metal ions form insoluble double fluoride salts with
the uranium and cause the formation of a very fine precipitate which is difficult to filter and wash and which yields a UF₄ product of significantly lower density after drying and dehydration.

Decontamination of metal impurities other than alkali and alkaline earths during precipitation has been found to be good, so a reasonable concentration of these metals can be tolerated in the precipitator feed stream without exceeding the specifications for metal grade UF₄ in the product.

It has been found in plant practice that agitation in the precipitator is very important. Proper dispersion of the gaseous SO₂ by the agitator is essential for efficient use of SO₂. The UF₄ precipitate is very dense and difficult to keep in suspension; hence, good agitation is necessary to maintain the homogeneous slurry required for good filtration operation.

A copper concentration of about 5.0 g/l is essential to maintain the maximum rate of reaction. Higher copper concentration does not increase the rate; therefore, it is probable that the concentration of 5.0 g/l is sufficient to accommodate all the SO₂ soluble in the liquor under the reaction conditions. High concentrations of free acid, sulfate, and phosphate reduce the reaction rate, probably because of an adverse effect on SO₂ solubility.
CONCLUSION

The combined UAP-Winlo process has demonstrated its ability to make metal-grade UF₄ from the combination of low and high-grade residue materials generated during the processing of uranium oxide to finished uranium metal cores.
REFERENCES


FIGURE 3 Feed Preparation from Low Grade Scrap

FIGURE 4 UAP System
FIGURE 1  Preparation of Fuel Cores

FIGURE 2  High Grade Feed Preparation
FIGURE 5  Winlo System
NATIONAL LEAD CO.
OF OHIO

W. O. I. 45 RH 1863

CHEMICAL PLANTS
SUPERINTENDENT
AMERICAN AIR FILTER COLLECTOR
RATED CAPACITY - 1,800 cfm
8 BAGS 9" x 9'
NATIONAL LEAD COMPANY OF OHIO
FERNALD, OHIO
DEPARTMENT: INDUSTRIAL HYGIENE

AMERICAN AIR FILTER COLLECTOR
RATED CAPACITY 1600 cfm
6 BAGS 9" x 9'
35" DIA. AXIAL FLOWER

SCALE
NONE

DATE
11-3-61

CHARGE
PLANT 8

DRAWN BY
R.L.P

APPROVED BY

SK. NO.

10" DIA.

STACK SAMPLER

6024
MUFFLE
FURNACE
DUST
COLLECTOR

12" DIA.

SECOND FLOOR

4½" DIA.

10" DIA.

MUFFLE FURNACE

DUST COLLECTOR
DRUMMING STATION

MUFFLE FURNACE
DRUMMING STATION

Product
Schematic Drawing of Oxidation Furnace off gas Scrubber