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THE RECOVERY OF URANIUM
FROM
BYPRODUCT SCRAP MATERIALS

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Written by

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METALLURGY—RAW MATERIALS

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1.

Introductory Section:

In the manufacture of uranium metal and its use, considerable quantities of byproduct materials containing uranium are obtained. It was estimated at the outset of this investigation that there would be available monthly approximately 150 tons of byproduct materials containing 49-50 tons of uranium, and varying quantities of magnesium, calcium, and iron as free elements, their fluorides, their oxides and complex chemical combinations of these materials.

The Manhattan District Project considered it necessary to reclaim uranium values from these byproduct mixtures. It was, therefore, our purpose to investigate the chemical compositions of the scrap materials available from the various uranium metal producers and users; to study methods for the recovery of valuable materials from these mixtures; to develop, preferably, a single process which would quantitatively recover uranium from all types of the byproduct materials, in a form relatively free from undesirable impurities and easily soluble in nitric acid; and to furnish data necessary for the design and operation of a suitable plant for reclaiming uranium by the process or processes developed.

Discussion Section:

A number of the methods described by Meyer and Pietsch⁽¹⁾

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for the processing of uranium, and radium bearing ores involving (a) ignition, roasting, calcining or fluxing of the products under oxidizing conditions, (b) solution of the uranium values in mineral acids, and (c) isolation of the uranium as insoluble uranates, or oxides, were evaluated for the recovery of byproduct materials.

It was found that scrap materials could be put into good physical form for milling or grinding and solubilization with mineral acids, by ignition and roasting under alkaline and oxidizing conditions at 800°C. Fusion at 1000-1600°C. with sodium carbonate and nitrates by methods of Ulrich⁽²⁾ or Curie⁽³⁾ and fusion with sodium chloride (and carbon) as described by Vogt⁽⁴⁾ were not particularly attractive for putting the scraps in workable shape because of the relatively high temperatures needed, and the type of equipment required.

Roasted and ground scrap materials treated with concentrated sulfuric at 175-250°C. by the method of Schlundt⁽⁵⁾ liberated hydrogen fluoride and resulted in a dry powder mixture of sulfates containing water soluble uranyl sulfate. Treatment of powdered scrap materials with dilute sulfuric acid and oxidizing agents preferably air, hydrogen peroxide, or manganese dioxide at 40-95°C. by methods similar to those used on ores by Marckwald⁽⁶⁾, Marckwald and Russel⁽⁷⁾, Fleck, Haldane and White⁽⁸⁾, and Danford, Samuels, and Martersteck⁽⁹⁾ also resulted in the complete solubilization of uranium values. Extraction of powdered scrap materials with aqueous hydrochloric or hydrobromic acids by methods of

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Moore⁽¹⁰⁾ and Parsons, Moore, Lind and Schaefer⁽¹¹⁾ gave no suitable concentration of uranium values. The solution of powdered scrap materials in nitric acid as used by Plum⁽¹²⁾ and Parsons, et al⁽¹¹⁾ was found to be impractical because the mixture of fluorides and nitric acid was excessively corrosive to most construction materials.

Uranyl sulfate solutions obtained as above by action of sulfuric acid were readily freed of excess sulfuric acid, and iron as insoluble iron hydroxide, without loss or precipitation of uranium values, if no phosphates were present, through adjustment to a pH of 3.5 - 3.7 by addition of alkaline agents at 70-90°C.

The recovery of uranium from these sulfate solutions by the formation of water soluble double carbonates of alkali metals or ammonia, and the separation from carbonate insoluble metals by the historic St. Joachimsthal procedure of Petera⁽¹³⁾ when applied to the subject sulfate solutions, gave neither reproducible results nor complete separations from impurities. This seemed to be due to interference from, and co-precipitation of, the relatively large amounts of magnesium ions present in the solutions. The elimination of magnesium sulfate by crystallization or by extraction with aliphatic alcohols was not successful.

Attempts to separate uranium as insoluble uranyl sulfite leaving impurities dissolved as water soluble sulfites by methods of Berthier⁽¹⁴⁾ and Lienau⁽¹⁵⁾ through interaction with sulfurous acid and caustic soda were unsuccessful.

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Separation of uranium as insoluble hydrated dioxide ($\text{UO}_2 \cdot \text{XH}_2\text{O}$) from soluble sulfites and sulfates by reaction of the sulfate solution with sodium hydrosulfite and caustic soda as described by Peligot⁽¹⁶⁾, Zimmerman⁽¹⁷⁾, Rosenheim and Loebel⁽¹⁸⁾ gave a quantitative recovery of a sodium contaminated reduction product.

A quantitative recovery of uranyl nitrate free from sodium, calcium, barium, magnesium or iron nitrates was obtained in laboratory trials by conversion, according to Ordway⁽¹⁹⁾, and de Coninck⁽²⁰⁾, of soluble sulfates to soluble nitrates by the action of nitric acid, calcium carbonate, and barium nitrate; followed by extraction of the concentrated water solution of nitrates with ethyl ether. The great solubility of uranyl nitrate in ether is described by Misciattelli⁽²¹⁾, Lebeau⁽²²⁾ and de Coninck⁽²³⁾. The selective separation of the nitrate from impurities in concentrated solution by this means was used by Pierle^(23a). This procedure for recovery from the byproduct materials was not further developed or considered for plant operation because a better method outlined in more detail below for isolating the peruranic acid $-\text{UO}_4 \cdot 2\text{H}_2\text{O}-$ of Fairley⁽²⁴⁾ was selected for adaptation to large scale production.

Notwithstanding contradictory statements in the literature by Fairley, Alibegoff⁽²⁵⁾ and Mazzucchelli⁽²⁶⁾ that peruranic acid could not be readily or quantitatively precipitated by hydrogen peroxide from solutions containing sulfuric, hydrochloric, or nitric acids, chlorides, fluorides, or sulfates, sodium, potassium, barium or calcium, and statements by Sieverts and Muller⁽²⁷⁾ that

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peruranic acid invariably precipitated in colloidal form and was not readily filtered, it was found that the desired product in good quality with good filtering characteristics could be easily produced by reaction of hydrogen peroxide in excess at 40-45°C. with essentially iron and vanadium free uranyl sulfate solutions of pH 3.5 - 3.7 obtained from ground scrap materials and sulfuric acid; and that a quantitative precipitation could be assured by basing the acid mixture, obtained after the addition of a 20-30% excess of theory hydrogen peroxide, to a pH of 2.8 - 3.5.

Vanadium and iron in solution were observed to interfere with the precipitation by promoting catalytic decomposition of hydrogen peroxide, liberating oxygen.

The fluoride content of the peruranic acid was minimized considerably below corrosive amounts by formation of a soluble AlF_6^- ion which occurred when aluminum sulfate was added to the uranyl sulfate solution prior to precipitation with hydrogen peroxide.

Peruranic acid obtained by the preferred procedures could be used as a wet filter paste and was of quality equal to, or better than black oxide (U_3O_8) used in the preparation of pure orange oxide (UO_3). The wet filter paste was readily soluble in dilute nitric acid at 90-95°C. forming uranyl nitrate and liberating oxygen, as indicated in the following equation:

The studies reviewed in this paper resulted in the development of a general method for the nearly quantitative recovery of high quality peruranic acid from vanadium and

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phosphorus free byproduct scrap materials. This method was successfully translated into large scale production and consists briefly of the following operations:

1. Ignition, and roasting of scrap materials with, present or added if required, calcium oxide and iron oxide bearing materials;
2. grinding and milling of the roasted materials to produce a fine powder;
3. reaction of the powdered materials with sulfuric acid to form water soluble uranyl sulfate, and hydrogen fluoride gas or insoluble magnesium fluoride;
4. adjustment of the pH of the uranyl sulfate solution to 3.5 - 3.7 to remove excess acidity and to precipitate iron hydroxide, and filtration from insoluble products;
5. precipitation of peruranic acid from the filtered sulfate solution containing added aluminum sulfate, by reaction with hydrogen peroxide, and separation from water soluble sulfates and fluorides by filtration or centrifugation procedures.

These operations, their control and their chemistry, are discussed in more detail in the Experimental Section.

Experimental Section:

I - TYPES OF SCRAP MATERIALS STUDIED FOR RECOVERY: SOURCES - CHEMICAL COMPOSITION

The principal types of byproduct materials studied for recovery of uranium were (A) High Uranium-Low Fluoride Scraps, (B) Low Uranium-High Fluoride Scraps, (C) Sludge Materials, and (D) Miscellaneous Wastes and Accumulations

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Containing Uranium. These materials resulted from operations at Iowa State College (a), DuPont Company (d), Electrometallurgical Company (n), Mallinckrodt Chemical Works (m), Westinghouse Lamp and Manufacturing Co. (w), Harshaw Chemical Company (ha), Hooker Chemical Co. (ho), Oak Ridge, Tennessee (t) and Metal Hydrides Co. (mh).

The various types of these available, or anticipated byproduct scrap materials and their approximate chemical compositions are discussed below.

(A) High Uranium-Low Fluoride Scraps

<u>Name</u>	<u>Obtained From</u>
Dross	Casting of metal biscuits in remelt operation
Turnings	Machinings of metal
Biscuits	Rejected "off-quality" production from bomb reactions
Billets	Rejected "off-quality" production from remelt operation
Electrode scrapings	Electrolytic Processes

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Analysis of Typical Dross Materials

Metallic "chunks" roasted and ignited in air at
400-500°C. to form powder prior to analysis

<u>Supplier</u>	<u>% U</u>	<u>% Tetra- valent U</u>	<u>% Ca</u>	<u>% Fe</u>	<u>% Mg</u>	<u>% Cl</u>	<u>% F</u>
(a)	79.2	31.9	1.7- 3.0	-	Nil	Nil	1.7- 3.5
(d)	80.7	36.9	Nil	0.03	1.7	Nil	0.27
(w)	80.0	34-40	-	-	Nil	0.8	0.46

(B) Low Uranium-High Fluoride Scraps

<u>Name</u>	<u>Obtained from</u>
Slag	Bomb reaction biscuits

Analysis of Typical Slag Materials

Samples crushed, roasted in air at 800°C., and
ground to 200-300 mesh prior to analysis

<u>Supplier</u>	<u>% U</u>	<u>% Mg</u>	<u>% Ca</u>	<u>% Fe</u>	<u>% F</u>	<u>Alkalinity g. H₂SO₄/g.</u>
(a)	31.2	17.3	10.3	0.20	18.9	0.26
(a)	8.0	30.3	12.0	0.35	20.5	0.61
(a)	5.0	Nil	51.5	0.06	28.6	0.55
(d)	19.4	16.9	24.7	0.53	21.2	0.85
(d)	6.7	30.7	10.6	0.20	26.6	-
(d)	6.6	32.3	10.5	0.50	24.5	0.71
(d)	11.2	25.4	19.4	0.72	22.3	-
(n)	30.7	22.0	5.9	0.21	15.5	0.53
(n)	31.2	21.1	6.7	1.07	13.9	0.55
(m)	9.1	28.0	14.8	0.30	19.0	1.75

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(C) Sludge Materials

<u>Name</u>	<u>Obtained from</u>
Oxide from sludge	Fines from electrolytic cells
Leach tank sludge	Leachings from biscuits in bomb reactions

Analysis of Typical Sludge MaterialsSamples dehydrated at 100-200°C. prior to analysis

<u>Supplier</u>	<u>% U</u>	<u>% Mg</u>	<u>% Ca</u>	<u>% Fe</u>	<u>% F</u>	<u>Alkalinity g. H₂SO₄/g.</u>	<u>% Cl</u>
(w)	45.0	Nil	13.2	0.1	12.6	-	4.5
(d)	52.7	8.7	9.5	0.25	9.2	0.47	Nil

(D) Miscellaneous Wastes and Accumulations
Containing Uranium

<u>Obtained from</u>	<u>Supplier</u>	<u>Analysis</u>				
		<u>% U</u>	<u>% Mg</u>	<u>% Ca</u>	<u>% Fe</u>	<u>% F</u>
Waste lime, or fines - bomb reaction	(m),					
	(d)	1.26	24.6	36.7	0.27	0.86
Burned Paper Liners	(d)	78.5	-	-	-	2.4
Sweepings - UF ₄ operation	(d)	66.3	-	-	-	-
Sweepings - U operation	(d)	23.8	-	-	-	-
Sweepings UO ₂ , UO ₃ operation	(d)	66.3	-	-	-	-
Cyclone sludge - U operation	(d)	55.1	-	-	-	-
Cyclone sludge - UO ₂ , UO ₄ , UO ₃ operation	(d)	28.0	-	-	-	-
Surface Diggings	(a)	2.0	-	-	-	-
" "	(ha)	6.7	-	-	-	-
" "	(mh)	2.4	-	-	-	-
" "	(n)	0.2	-	-	-	-
" "	(ho)	1.0	-	-	-	-
" "	(w)	0.6	-	-	-	-
Wet Iron Cake	(t)	5.0	-	-	-	-
Dry Iron Cake	(t)	20.0	-	-	-	-
Iron Benzoate	(t)	8.0	-	-	-	-
Iron and Ammonium Ppt.	(t)	50.0	-	-	-	-
Carbonate Cake	(t)	2.2	-	-	-	-
Graphite	Various sources	1.0	-	-	-	-

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II. PREPARATION OF MATERIALS FOR
PROCESS STUDY AND ANALYSIS:
ELIMINATION OF CHLORIDES:
CONCENTRATION OF URANIUM

(A) Dross and High Metal Concentrates -
High Uranium-Low Fluoride Scraps

Attempts to grind or pulverize dross or high metal concentrates were found to be impractical and unsuccessful because of fire hazard from "sparking" and the presence or generation of small amounts of acetylene from carbides. Further, the free metal was found to be too ductile for grinding in standard equipment.

Dross or high metal concentrates, however, upon ignition and roasting in air at 300-800°C. in a muffle furnace, became powdered and could be readily milled, without hazard, to 200 mesh particle size.

The probable reaction which occurs on ignition of dross is:

Oxidized dross when mixed with 10-12% of calcium hydroxide or waste lime from bomb liners and roasted in air at 800°C., changed in color from black to orange or yellow, and resulted in material which contained appreciably less tetravalent uranium:

<u>% Tetravalent U</u>	
<u>Oxidized dross</u>	<u>After roasting with lime</u>
31.9	15.0
37.7	18.0

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The probable reaction occurring between oxidized dross and lime on heating is:

Uranium bearing materials with reduced tetravalent content were observed to be more readily soluble in dilute sulfuric acid, and required less oxidation to effect complete solution of metal values⁽³¹⁾. Observed variations in tetravalent content and hydrogen peroxide requirements to effect solution in dilute sulfuric acid are here tabulated:

<u>Type of Material</u>	<u>% Total U</u>	<u>% Tetra-valent U</u>	<u>g. 27.5% H₂O₂ per 100 g. U required for conversion</u>	
			<u>UIV ----</u>	<u>UVI</u>
Oxidized Dross	79-80	31-37	83-84	
Roasted oxidized dross + CaO	75	18	13.0	
Leach tank sludge	53	4.8	0.0	
Westinghouse sludge	55	7.7	4.5	

(B) Slags from Biscuit Manufacture - Low Uranium-High Fluoride Scraps

Attempts to grind slag in a Wiley Mill, after preliminary disintegration to 1-2 in. sizes with a hammer, were not completely successful. Lumps larger than 2 in. could not be ground at all. Elemental metals, such as uranium and magnesium, which were dispersed throughout the slag, "fired" and also stopped the mill.

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However, slags were successfully reduced to uniform powders by the following series of treatment:

- a) "cracking" with a hammer to 1/4 in. size,
- b) roasting in air at 800-900°C. in a muffle furnace, and,
- c) ball milling to 200 mesh particle size.

The probable reactions which occur when slag scrap materials are roasted in air at 800-900°C. are:

(C) Elimination of Chlorides from Scrap Materials

The development of methods for the removal of chlorides from scrap materials obtained from various sources, particularly from the Westinghouse operations, was desirable in order to avoid corrosion of equipment problems.

"Electrode scrapings" containing up to 1.2% Cl, roasted at 800-900°C. with 12.5 g. of waste lime per 100 g. of scrap and 0.75 g. of 325 mesh ferric oxide (Fe_2O_3) per g. of chlorides, resulted in practically complete volatilization of chlorine as ferric chloride⁽³³⁾. A similar reduction in chloride content was obtained with ammonium sulfate.

"Oxide from sludge" containing from 2-5% Cl, as water soluble chlorides, was slurried with ten parts of

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filtered water and 0.01 part of aluminum sulfate (to aid settling of fine colloidal particles) at 50-60°C. for 30 minutes. The pH was then adjusted to 7-8 with 30% caustic soda, and the mixture allowed to settle for 30-60 minutes. The clear liquid was decanted, and discarded.

The remaining sludge was reslurried with water, pH adjusted, and the settling and decanting repeated. The resultant sludge contained but little more chlorides than the filtered water used, and could be dissolved and employed in subsequent operations without corrosion difficulties.

(D) Reduction of Tonnage of Scrap Materials
by Acid Extraction of MgO and CaO.
Concentration of Uranium in Waste Lime
and Low Uranium Scraps

Extraction of waste lime or scraps of low uranium metal content, with dilute hydrochloric acid at pH 5.0-5.2, resulted in solution of magnesium and calcium oxides, and left uranium values and fluorides out of solution. A considerable reduction of tonnage could be effected.

The following illustrates the method employed:

Four hundred g. of waste lime, which had been roasted and ground to 200 mesh size, and which contained 9.28% U, was stirred into 1200 cc of filtered water at room temperature. The pH of the mass was 12.2. 37% HCl was slowly added to the agitated slurry until a pH of 5.0-5.2 was reached. This required 710 cc of HCl. The mass was stirred an additional 60 min. and then filtered. The filter cake was washed with water until essentially free from chlorides and dried, yielding 106 g. of extracted solid containing 36.7% U.

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Extraction of Scrap Materials with Dilute HCl

Analysis

Type of Scrap	<u>Before Extraction</u>				<u>After Extraction</u>				% Ton- age Re- duction
	<u>% U</u>	<u>% F</u>	<u>% Mg</u>	<u>Dry Wt.</u>	<u>% U</u>	<u>% F</u>	<u>% Mg</u>	<u>Dry Wt.</u>	
Waste lime	9.2	6.7	-	165	35.6	19.9	-	52	68.5
	10.0	-	-	400	37.0	-	-	106	73.0
Slag	14.8	17.9	-	200	21.2	26.7	-	136	32.0
	19.5	14.6	24.6	1500	25.4	27.1	15.9	1128	25.0
	11.0	-	-	-	13.0	-	-	-	21.0
Leach tank sludge	51.0	-	-	-	57.0	-	-	-	13.0
Floor sweepings	48.0	-	-	-	53.0	-	-	-	2.0

It was concluded from the experimental results obtained in the laboratory that the bulk of scrap materials in large scale operations, with the incorporation of proper provisions for control of dust losses, could be broken to $1/4 - 1/2$ in. particle size in standard ore crushing equipment; ignited, calcined or roasted in standard commercial type magnesite brick lined roasting ovens and rotary kilns; and pulverized to 200-300 mesh particle size in standard commercial milling and grinding apparatus.

III - PREPARATION OF URANYL SULFATE (UO_2SO_4)

(A) Studies on the Reaction of Sulfuric Acid with Scrap Materials to Volatilize Hydrogen Fluoride and to Produce Uranyl Sulfate from Fluorides and Oxides⁽³⁴⁾

The procedure developed by the duPont Company for the manufacture of hydrogen fluoride from fluorspar (CaF_2) and concentrated sulfuric acid⁽³⁵⁾ was applied to roasted and ground scrap materials. Batch type experiments were conducted in electrically heated mechanically agitated steel retorts on both fluorspar and uranium bearing slag materials. Hydrogen fluoride evolved was either condensed and collected, or absorbed in caustic soda solution. The sulfated sludges produced from slag materials were studied for isolation of uranium values.

The probable reactions which occur when slags are reacted with concentrated sulfuric acid are:

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A typical batch experiment and results obtained are given below:

Three hundred and forty g. of roasted slag, and 60 g. of roasted dross were charged into an electrically heated steel Werner-Pfleiderer mixer, equipped with a train containing caustic soda solution for absorption of evolved hydrogen fluoride. 710 g. of 98% sulfuric were added over a period of 1-1/2 hrs., while heating gradually to 200-250°C., and the mass was held on temperature until the hydrogen fluoride evolution ceased. This usually took 2-3 hrs. Agitation was continued until the charge was cold enough to discharge (70-90°C.) and resulted in 773 g. of sulfated material, a very hygroscopic pale green powder, with the following analysis.

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Analysis of Sulfated Material

	<u>%</u>
Free sulfuric acid	34.50
Uranium	13.09
Boron	0.00025
Fluorine	0.67
Magnesium	5.41
Calcium	4.01
Iron	0.095

Estimated Composition of Sulfated Sludge

<u>%</u>	
34.5	H ₂ SO ₄
20.2	UO ₂ SO ₄
26.8	MgSO ₄
13.7	CaSO ₄
0.7	Fe ₂ (SO ₄) ₃
<u>4.1</u>	H ₂ O (by difference)
100.0	

The following studies were made for process and design information:

Temperature of Reaction and
Sulfuric Acid Requirements

Temperatures of 175-250°C. gave suitable conversion of metal fluorides to hydrogen fluoride.

The amount of sulfuric acid (110% of stoichiometric requirement) employed for the reaction varied with the composition of the ground and oxidized scrap material to be reacted and was calculated from the analysis of the latter.

Calculation of H₂SO₄ Requirement

$$\% \text{ Mg} \times 2.56 = \text{Mg calculated as MgF}_2 \quad (1)$$

$$\% \text{ F} \times 1.64 = \text{F calculated as MgF}_2 \quad (2)$$

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Condition I

If (1) was greater than (2) excess Mg was present

$$(1) - (2) = \text{Excess Mg calculated as MgF}_2 \quad (3)$$

$$(3) \times 0.647 = \% \text{ MgO}$$

$$(2) = \% \text{ MgF}_2$$

The amount of H₂SO₄ required for Condition (I)

<u>Wt. of scrap multiplied by</u>	<u>g. 100% H₂SO₄ for</u>
% MgO x 2.43 x 1.10 =	MgO
% Mg x 3.15 x 1.10 =	MgF ₂
% Ca x 2.45 x 1.10 =	Ca
% U x 0.41 x 1.46 =	U
	<hr/>
	Total Scrap (4)

Condition II

If (2) was greater than (1) excess fluoride
was present

$$(2) - (1) = \text{Excess fluoride as MgF}_2 \quad (5)$$

$$(5) \times 2.05 = \% \text{ CaF}_2 \text{ in scrap}$$

$$(\% \text{ Ca} \times 1.4) - (\% \text{ CaF}_2 \times 0.72) = \% \text{ CaO in scrap}$$

$$(1) = \% \text{ MgF}_2 \text{ in scrap}$$

The amount of H₂SO₄ required for Condition (II)

<u>Wt. of scrap multiplied by</u>	<u>g. 100% H₂SO₄ for</u>
% MgF ₂ x 3.15 x 1.10	MgF ₂
% CaF ₂ x 1.26 x 1.10	CaF ₂
% CaO x 1.75 x 1.10	CaO
% U x 0.41 x 1.46	U
	<hr/>
	Total Scrap (6)

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Weight ratios of 98% sulfuric acid employed for oxidized slag materials from various suppliers are shown:

<u>Supplier</u>	<u>Wt. Ratio 98% H₂SO₄/slag</u>
(a)	2.04
(a)	1.82
(a)	1.39
(d)	2.20
(d)	2.60
(m)	2.34
(n)	1.83
(n)	1.53

Hydrogen Fluoride Recovery

In batch type experiments, the recovery of hydrogen fluoride from uranium bearing slags gave results which compared favorably with those obtained from fluorspar. 79-80% of theory recoveries of 84.5 - 95% strength hydrogen fluoride containing 0.42 - 1.04% H₂SO₄, and 0.14-0.34% H₂SO₃ were obtained from a slag containing 25.0% F, 30.5% U, 11.0% Ca, 18.0% Mg and an alkalinity equal to 26 g. H₂SO₄/100 g. slag employing 2.16 pts. 98% H₂SO₄/pt. slag.

Slags containing higher proportions of oxides, or alkalinities equal to 50-80 g. H₂SO₄/100 g. slag, gave similar results employing 104-106% H₂SO₄ in place of 98% H₂SO₄.

It was found that weak HF (83-85%) could be mixed with 104-106% H₂SO₄ and employed for reaction with slag to give a 95% of theory recovery of 91-92% strength HF.

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Power Requirements

Power requirements for processing of slag with sulfuric acid at elevated temperatures to recover hydrogen fluoride were observed to be approximately 20% higher than for fluorspar.

Corrosion in Retort

Comparative corrosion tests on slag and fluorspar were made on the following candidate construction materials: Duramet T, 18-8 S. Ch., Inconel, Durco D-10, Alcumite, Hastalloy B, and C, Carpenter 7 Mo, 18-8 S-Mo, Cast Steel, and Monel metals. In the process of reaction with H_2SO_4 , slag was found to be less corrosive than fluorspar on all materials of construction.

The experimental results indicated that roasted and ground slag materials could be pasted, and reacted continuously with concentrated sulfuric acid (98-106% H_2SO_4) at 175-250°C. to produce essentially anhydrous hydrogen fluoride, a small portion of weak HF (70-85%) and a dry powder mixture of sulfates, suitable for further processing to yield concentrated uranium metal values.

Slag materials from various suppliers of scrap materials were processed in the laboratory to check their behavior in proposed plant procedures. All types, alone or in admixture with each other, responded similarly.

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Types of Scrap Materials
 Processed with Conc. H_2SO_4 at 175-250°C.
Analyses of Resultant Sulfated Sludges

<u>Supplier</u>	<u>Type Scrap Material (Roasted and Ground)</u>	<u>Analysis</u>			<u>Ratio</u>
		<u>% H_2SO_4</u>	<u>% U</u>	<u>% F</u>	<u>U/Mg</u>
(a)	Slag (c) + Dross	34.5	13.09	0.67	2.42
(a)	Slag (c)	33.8	11.7	0.64	2.13
		34.3	11.8	0.34	-
(a)	Slag +				
and	UF ₄	25.8	10.6	0.05	-
(c)	Sweeping				
(d)	Slag (c)	26.5	6.6	0.32	1.15
		23.5	6.3	2.05	-
(d)	Slag (c)	32.6	2.3	1.0	0.28
(d)	Slag (Do)	35.3	2.5	0.83	0.43
(d)	Slag + Leach tank sludge	21.1	10.8	1.08	-
(d)	Slag + Dross	25.7	11.5	0.53	-
(d)	Slag + Leach tank sludge	32.0	7.8	0.93	-
(n)	Slag (Do)	32.3	12.1	0.67-	1.33
			0.90		
(n)	Slag (Do)	30.0	13.5	0.95	1.89
(n)	Slag (Do)	32.3	12.1	0.67	-
(m)	Slag (Do)	35.3	2.4	0.75	0.50

Do = Dolomite Liner) in Biscuit manufacture
 c = CaO Liner

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(B) Preparation of Uranyl Sulfate Solutions

Uranyl sulfate (UO_2SO_4) solutions were produced from:

(a) sulfated sludge produced from roasted and ground scrap materials as described under (A), by solution in water,

(b) roasted and ground scrap materials by reaction and solution with oxidizing agents and dilute sulfuric acid at $40\text{--}95^\circ\text{C}$.⁽³⁶⁾

(c) sodium uranate and uranium trioxide by solution in sulfuric acid^{(37),(38)} at $40\text{--}95^\circ\text{C}$. and

(d) by combinations of (a), (b) and (c).

In all cases, whenever necessary, complete oxidation of any tetravalent uranium metal was effected by introduction of oxidizing agents to the solution. Oxidizing agents which were studied and found effective were aqueous hydrogen peroxide, sodium peroxide, air, nitric acid, manganese dioxide, potassium permanganate, sodium dichromate, and mining salt ($\text{NaBrO}_3 \cdot \text{NaBr}$).

The oxidizing agents selected for practical operation were air, hydrogen peroxide, and manganese dioxide. Air being most effective on sulfated sludge solutions (method (a)), and hydrogen peroxide or manganese dioxide being preferred in the aqueous sulfation of roasted and ground scrap materials (method (b)).

Excess of sulfuric acid employed in the preparation of uranyl sulfate solutions was removed by adjustment of pH to 3.5-3.7 by introduction of alkaline materials. Alkaline agents found effective for pH adjustment were: calcium carbonate, sodium uranate, calcium oxide, waste lime

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from bomb reactions in uranium metal productions, caustic soda, sodium carbonate, and ammonium hydroxide. Most suitable from practical considerations were finely powdered (325-mesh) calcium carbonate, sodium carbonate and waste lime, either individually or in combinations.

Insoluble materials formed, or originally present, such as calcium sulfate, iron hydroxide, calcium and magnesium fluorides, were separated from the solution by filtration. The methods here outlined could not be effectively used for the solubilization of scrap materials containing 0.7 to 1.6% of phosphorus because considerable of the uranium - up to 50% of the total content - remained as insoluble material in the calcium sulfate filter cakes. Typical experiments for preparation of uranyl sulfate solutions are outlined below:

(a) Preparation from Sulfated Sludge
by Solution in Water

Solutions were prepared in a six-liter capacity agitated neoprene coated steel pot. To 3500-3700 cc of filtered water, or wash liquors from a previous run, were added while stirring 1200 g. of sulfated sludge. The mixture was stirred for 1/2 to 1 hr. 38-43 cc of 30% H₂O₂ were then added dropwise until the green color disappeared. The mass was then heated with live steam, or by water bath to 85-90°C., and neutralized over a period of 3-4 hrs. with 400 g. of calcium carbonate until barely alkaline to Congo red test papers (pH 3.5 - 3.7).

The mass was then filtered at 70-80°C. employing a neoprene coated pressure filter, and a canvas (#10 Duck) bag for filtering medium. 2900-3000 cc. of filtrate analyzing as follows was obtained:

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g/100 cc

5.9	U
0.0003	Fe
0.134	Ca
1.94	Mg

The calcium sulfate cake was reslurried with 3500 cc of wash water at 75-80°C. and refiltered. This liquor was used for make-up of a subsequent batch. The reslurry of the calcium sulfate cake was repeated with fresh hot water and the liquors were used as wash liquors for another batch. The calcium sulfate cake when dry weighed 861-900 g. and contained no uranium. This was discarded.

Colorimetric Estimation of Uranium
Content in Uranyl Sulfate Solutions
using the Color of the Cation

A 10 cc pipetted aliquot of filtered uranyl sulfate solution pH 3.5 - 3.7 is diluted to 100 cc with 0.35% H₂SO₄ solution. Twenty-five cc of this 1-10 dilution is read in a standard photo-electric colorimeter vs. a null of distilled water using a blue filter, and the percent uranium in the original uranyl sulfate is in turn read from a calibration curve. The curve is prepared by reading in the above manner a series of known uranyl sulfate solutions containing 0.1 - 2.0 g. of U per 100 cc of solution, all dilutions being made with 0.35% H₂SO₄ solution.

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Method for Determining the Approximate
Mg Content of Uranyl Sulfate
Filtrates by Density Measurements

Density of Pure Uranyl Sulfate Solutions at 25°C.

<u>U g/100 cc.</u>	<u>d^{25°C.}</u>
9.70	1.084
4.85	1.061
2.42	1.029
0.00	1.000

Density of Uranyl Sulfate Solutions
(2.42 g. U/100 cc)
with Variations in Mg Content

<u>g. Mg/100 cc.</u>	<u>d^{25°C.}</u>
0.0	1.029
0.5	1.053
1.0	1.076
1.5	1.099
2.0	1.122
2.5	1.144
3.0	1.166

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Density of Uranyl Sulfate Solutions
(4.85 g. U/100 cc)
With Variations in Mg Content

<u>g. Mg/100 cc</u>	<u>d^{25°}</u>
0.0	1.061
0.5	1.084
1.0	1.107
1.5	1.130
2.0	1.156
2.5	1.175
3.0	1.196

Observed change in density at 25°C. = 0.0046/0.1%
(wt. vol.) Mg conc.

Calculation of % Mg in Uranyl Sulfate Solutions

D' = Density observed

D = Density of pure UO₂SO₄. Solution for U content found

$$\text{g. Mg/100 cc of uranyl sulfate solution} = \frac{D' - D}{0.046}$$

Analysis of Uranyl Sulfate Solutions Prepared from
Various Types of Slags and Mixtures after Reaction
with Concentrated Sulfuric Acid at 200-250°C.

		<u>Analysis: g/100 cc of Solution</u>					<u>Ratio U/Mg</u>
<u>Supplier</u>	<u>Type of Scrap</u>	<u>U</u>	<u>Mg</u>	<u>Ca</u>	<u>F</u>	<u>Fe</u>	
(a)	Slag (c) + Dross	9.32	2.70	0.06	0.05	0.0005	3.45
(a)	Slag (c)	4.10	2.00	0.08	0.08	0.0600	2.05
(d)	Slag (c)	2.50	2.30	0.05	0.01	0.0500	1.08
(d)	Slag (Do) + Leach tank sludge	2.88	1.60	-	-	0.097	1.80
(d)	Slag (Do)	0.51	1.80	0.05	0.06	0.0020	0.28
(n)	Slag (Do)	2.74	2.23	0.04	0.08	0.0033	1.23
(n)	Slag (Do)	3.40	1.80	0.07	0.27	-	1.85
(w)	Sludge	3.26	0.21	-	-	0.0900	15.50

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(b) Preparation from Roasted and Ground
Scrap Materials by Reaction and
Solution with Oxidizing Agents and
Dilute Sulfuric Acid

Into a neoprene lined steel pot were charged 4120 cc of water and 1500 g. of roasted and ground scrap materials equivalent to approximately 270 g. (+20%) of 100% U while stirring with mechanical agitation. 970 g. of 98% sulfuric acid was then added until a permanent pH of 2.8 - 3.2 was reached. After this 255 g. of 98% sulfuric acid were added to a pH of 0.5 - 1.0 and the charge oxidized by dropwise addition of 10-36 cc of hydrogen peroxide and/or air blowing until oxidation to hexavalent uranium was complete at 45-60°C. The amount of hydrogen peroxide required was variable and depended upon the efficiency of the roasting or calcining operation, and upon the efficiency of aeration.

Test for Completeness of Oxidation

Withdraw 10 cc of the solution, and filter through paper into a test tube. Pipette 5 cc of the clear filtrate into another test tube and add 5 cc of water. Boil gently for 5 minutes to decompose excess of hydrogen peroxide and add one drop of a 0.3% potassium permanganate solution. If the permanganate is not decolorized in five seconds the uranium in the solution is considered completely oxidized to the hexavalent state. If it is decolorized, add more hydrogen peroxide to the main solution.

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The charge was then heated to 90-95°C., and held there while blowing with air (1-3 hrs.) until a repeat KMnO_4 test showed oxidation to be still complete; and until no further insoluble uranium materials were present in the suspension. The slurry was then treated with approximately 250 g. of powdered calcium carbonate over a period of 2-3 hrs., to a pH of 3.5 - 3.7 to remove the excess of sulfuric acid and to assure the maximum precipitation of ferric hydroxide. The charge was then held at this temperature and pH for 1-2 hrs. or until the iron content of the solution was less than 10 ppm prior to hot filtration from insoluble hydroxides, fluorides and sulfates. The "gyp" cake was washed by re-slurry with 4 liter portions of water until free of soluble uranium salts, and the wash liquors were recycled in subsequent batches as described under (a).

Colored Spot Test for
Uranium in Wash Liquors

Spot a drop of wash on filter paper.
Place a drop of 10% potassium ferrocyanide solution alongside of the spot so that the two solutions merge. The appearance of a brown color at the junction indicates the presence of uranium.

Sensitivity of Spot Test vs. "In Situ"
Tests with Potassium Ferrocyanide

Studies with pure uranyl acetate comparing spot tests on paper against addition of reagent to uranium solutions ("in situ") showed that the spot sensitivity ended between 0.05% and 0.025% U, whereas the in situ sensitivity extended below 0.005% U.

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Sensitivity Potassium Ferrocyanide
Color Test for Uranium (39)

5-15 sec. for develop-
ment of red-brown color

<u>% U</u>	<u>Color Intensity Observed</u>	
	<u>Spot</u>	<u>In Situ</u>
1.000	Strong	Precipitate
0.100	Mod. strong	Strong
0.005	Definite	Moderate
0.025	None	Definite
0.010	None	Weakly positive
0.005	None	Weakly positive

Tests for Uranium in "Gyp" Cake

(1) Qualitative Color Test

Slurry about 1 g. of the
 filter cake with 10% hydrochloric acid
 and test for uranium by spot with potassium
 ferrocyanide as above. The blue color due
 to iron does not appreciably interfere with
 the brown color developed by uranium.

(2) Colorimetric Quantitative
 Estimation

This method was found to be rapid,
 fairly sensitive, detecting as low as 0.05% U (+10%) in
 "gyp" cakes, and gave readily reproducible analytical re-
 sults.

Suspend a 2 g. sample of dry
 "gyp" or 3 g. wet cake in a mixture of
 75 cc of 5% hydrochloric acid and 10 cc

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of 3% hydrogen peroxide, and boil down to 50 cc volume in 10 min. Add sodium carbonate while shaking to a pH of 10-12. (Red test on Brilliant Yellow paper), then reflux 15 min. Filter into a 100 cc volumetric flask, and wash the insoluble with distilled water. Mix in 5 drops of 3% hydrogen peroxide, and measure the yellow color at room temperature vs. distilled water at 425 mu in a standard photoelectric colorimeter. The result is computed by reference to an established curve of known concentrations of sodium uranyl carbonate made from high quality uranium trioxide.

Colorimetric Estimation of Iron in Uranyl Sulfate Solutions

Preparation of Standards

Materials:

- (1) An iron solution made from analyzed CP ferric sulfate and 3-4 drops of sulfuric acid to contain 0.0000025 g. Fe/cc.
- (2) An iron free 10% uranyl sulfate solution prepared from CP uranium trioxide (UO_3) and CP sulfuric acid.
- (3) A 10% solution of hydroxylamine hydrochloride.
- (4) A 0.1% solution of ortho-phenanthroline.

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A sample of the iron solution is diluted to 25 cc with distilled water and the pH adjusted to 2.5-3 with a drop or two of 10% H_2SO_4 . Add 1 cc of hydroxylamine hydrochloride solution, 10 cc of ortho-phenanthroline solution, and 1 cc of the uranyl sulfate solution and dilute to 50 cc in a Nessler tube. The following standards are then prepared for matching with samples containing known amounts of iron.

<u>cc of</u> <u>Fe soln.</u>	<u>g. of Fe</u> <u>in the Std.</u>	<u>ppm Fe</u>
1	0.0000025	2.5
2	0.0000050	5.0
3	0.0000075	7.5
4	0.0000100	10.0
5	0.0000125	12.5
6	0.0000150	15.0

Preparation of Sample

A sample of the uranyl sulfate extraction slurry is filtered by gravity through paper. One cc of the filtrate is diluted to approximately 25 cc with distilled water, treated with H_2SO_4 , hydroxylamine hydrochloride solution, ortho-phenanthroline solution and diluted to 50 cc as with standards.

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The unknown is compared with the set of standards by visual inspection. If the unknown color is too dark, it is reduced by dilution until it is within the range of the standards. The dilution is accomplished by discarding 25 cc of the Nessler tube contents and adding 25 cc of distilled water. The value of the standard in ppm is progressively multiplied by two for each such dilution as follows:

No. of dilutions	1	2	3	4	5
Multiply Std. by	2	4	8	16	32

The probable reactions, not shown in stoichiometric proportions or by mechanism, which occur in the solution of scrap materials with dilute sulfuric acid, can be graphically indicated as follows:

Action of Dilute H₂SO₄

Oxidation of Tetravalent Uranium

Precipitation of Calcium Sulfate and Iron Hydroxide at pH 3.5 - 3.7

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Characteristics of Uranyl
Sulfate Solutions Obtained from Scrap Materials
Processed with dilute H₂SO₄ and Oxidizing Agents

Roasted and Ground Dross
(High Uranium-Low Fluoride Scrap)

<u>Supplier</u>	<u>Analysis: g/100 cc of solution</u>				
	<u>U</u>	<u>Mg</u>	<u>Ca</u>	<u>F</u>	<u>Ratio U/Mg.</u>
(a)	5.3	Nil	-	0.08	∞
(a)	4.4	Nil	-	0.08	∞
(a)	4.5	Nil	-	0.09	∞
(a)	3.6	Nil	-	0.08	∞
(a)	4.9	-	-	0.11	-
(a)	6.5	Nil	-	0.12	-
(a)	6.12	Nil	0.05	0.10	∞
(a)	6.5	-	-	0.25	-
(d)	4.6	-	-	0.14	-
(d)	4.9	-	-	0.03	-
(d)	7.4	0.14	0.07	0.13	53.0
(d)	6.1	0.60	-	0.13	10.0
(d)	6.9	-	-	0.13	-
(d)	6.6	0.07	0.08	0.11	94.0
(d)	6.7	0.9	0.60	0.11	7.4
(d)	4.2	0.08	0.06	0.07	52.0
(d)	5.8	-	-	0.13	-

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Mixtures of Roasted and Ground
Slag (Low Uranium-High Fluoride
Scrap) and Dross

Analysis: g/100 cc of solution

<u>Supplier</u>	<u>U</u>	<u>Mg</u>	<u>Ca</u>	<u>F</u>	<u>Ratio U/Mg</u>
(a)	4.7	-	-	0.38	-
	3.5	-	-	0.35	-
	4.2	-	-	0.37	-
	4.35	-	-	0.29	-
	4.36	-	-	0.32	-
	4.7	-	-	0.36	-
	4.7	-	-	0.31	-
	4.0	0.71	0.05	0.23	5.7
	4.0	0.68	0.00	0.28	5.9
	6.69	0.81	0.07	0.52	8.3
	0.63	-	-	0.06	-
	4.0	-	-	0.23	-
	3.8	-	-	0.22	-
	3.2	-	-	0.19	-
	4.7	-	-	0.38	-
	9.4	-	-	0.66	-
	3.7	-	-	0.21	-
	1.4	-	-	0.12	-
(d)	2.3	-	-	0.29	-
	2.5	2.19	-	0.09	1.2
	3.0	5.60	-	0.14	0.5
(n)	3.3	-	-	0.21	-
	3.5	-	-	0.20	-
	4.6	-	-	0.29	-
	3.3	-	-	0.20	-

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Sludge Materials, and MixturesAnalysis: g/100 cc of Soln.

<u>Supplier</u>	<u>Type or Mixture</u>	<u>U</u>	<u>Mg</u>	<u>Ca</u>	<u>F</u>	<u>Ratio U/Mg</u>
(d)	Leach Tank Sludge	5.7	0.25	-	0.17	13.2
		5.7	0.45	0.09	0.63	12.7
		6.0	-	-	0.25	-
	Dross + Leach tank Sludge	6.8	0.10	0.10	0.26	68.0
		6.8	0.26	0.08	0.23	26.0
(w)	Fines from electrolytic cells	5.3	0.03	0.07	0.17	177.0
		6.2	-	-	0.36	-
		5.7	-	-	0.42	-

Sulfated Sludge (See A)
and Mixtures of Roasted
and Ground Slag and Dross

<u>% U From</u>			<u>Analysis of Solution Gm./100 cc</u>				<u>Ratio U/Mg</u>
<u>Sulfated Sludge</u>	<u>Dross</u>	<u>Slag</u>	<u>U</u>	<u>Mg</u>	<u>F</u>	<u>Fe</u>	
20.0	80.0	0.0	6.40	1.57	-	0.0002	4.1
100.0	0.0	0.0	1.30	2.40	0.04	0.0005	0.5
100.0	0.0	0.0	2.2	2.20	0.03	-	1.0
47.5	52.5	0.0	2.75	2.30	0.07	0.0005	1.2
27.5	72.5	0.0	4.70	2.30	0.08	0.0005	2.0
12.7	87.3	0.0	10.20	2.40	0.14	0.0005	4.2
20.0	77.0	3.0	7.85	-	0.28	0.0036	-
42.3	0.0	58.7	5.2	3.9	0.19	-	1.3

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Factors Influencing the Precipitation
of Iron Hydroxide from Uranyl Sulfate Solution

Studies on the precipitation of iron hydroxide from pure uranyl sulfate solutions containing controlled amounts of iron and magnesium sulfates, and from solutions produced from scrap materials, resulted in the following conclusions:

- (1) maximum precipitation occurred at a pH of 3.7
- (2) temperatures as low as 70-75°C. gave satisfactory results
- (3) incomplete oxidation of the extraction slurry prior to treatment with neutralizing agents interfered
- (4) an extremely high Mg content interfered. A ratio of U/Mg above 0.8 allowed satisfactory iron precipitation. A ratio of 0.2 definitely kept iron in solution.

Effect of pH on Precipitation of Iron in
Uranyl Sulfate Solutions Containing 4.85% U,
0.108% Fe, and 2.4% Mg at 90-95°C.

Ratio U/Mg = 2

ppm Fe in solution after pH adjustment

<u>pH</u>	<u>hr:</u>	<u>Elapsed Time, Hr.</u>		
		<u>0</u>	<u>1</u>	<u>2</u>
2.5		160	192	128
3.0		40	44	32
3.5		36	28	18

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Effect of Temperature on the Precipitation
of Iron in Uranyl Sulfate Solution at a pH of 3.7

4.84% U 0.108% Fe 2.4% Mg

ppm Fe in solution after
adjustment of pH to 3.7

<u>Temp. °C.</u>	<u>hr:</u>	<u>Elapsed Time, Hr.</u>		
		<u>0</u>	<u>1</u>	<u>2</u>
70-75		20	14	12
80-85		20	12	12
90-95		18	12	10

Effect of Incomplete Oxidation of Uranyl
Sulfate Solution on Precipitation of Iron

The extraction slurry was oxidized with
H₂O₂ after one hour on temperature

ppm Fe in solution

<u>pH</u>	<u>Temp. °C.</u>	<u>hrs:</u>	<u>Elapsed Time, Hr.</u>		
			<u>0</u>	<u>1</u>	<u>2</u>
3.0	90-95		256	40	40
3.0	70-75		288	40	32
3.7	70-75		224	2	0

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Effect of Variations in U/Mg Ratio
at Different U Concentrations
on the Precipitation of Fe

pH 3.7 Temp. 90-95°C.

Concentration 1.21% U 0.108% Fe

ppm Fe in Solution after
pH adjustment to 3.7

<u>% Mg</u>	<u>Ratio U/Mg</u>	<u>Elapsed Time</u>			
		<u>hr:</u>	<u>0</u>	<u>1</u>	<u>2</u>
0.25	4.84		48	24-30	24-32
0.50	2.42		30	8	12
0.75	1.61		10	6	6
1.00	1.21		20	12	12
1.25	0.97		22	10	14
1.50	0.81		10	8	12

Concentration 2.42% U 0.108% Fe

0.75	3.22		16	18	8
1.50	1.61		21	16	14

Concentration 4.84% U 0.108% Fe

0.097	50.0		24	12	8
0.242	20.0		22	12	12
0.484	10.0		22	12	10
0.969	5.0		20	10	12
2.42	2.0		18	10	10
24.2	0.2		224	128	64

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(c) Preparation from Sodium Uranate
or Uranium Trioxide by Solution
in Sulfuric Acid

Four hundred cc of water, 16 cc of 96% sulfuric acid, and 64 g. of sodium uranate (70.7% U, 3.23% Na from Carnotite) were heated and stirred for one hour at 70-75°C. Five g. of calcium carbonate were then added in small portions until neutral to Congo red paper and still acid to Bromocresol green paper, (pH 3.0-3.5). The mass was further heated at 70-75°C. for one hr. Insoluble calcium sulfate, and precipitated iron hydroxide were removed by suction filtration through cloth on a Buchner funnel. The precipitate was washed with 100 cc of hot water. When dry, the insoluble matter weighed 7 g. The combined filtrate volume was 555 cc and contained 45.3 g. of uranium.

The probable reactions which occur in the above procedure are:

Uranyl sulfate solutions were readily obtained from uranium trioxide by the same procedure, or by employing stoichiometric quantities of diluted CP sulfuric acid and the oxide suspended in water.

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Tests on Materials of Construction for Plant Design.
Preparation of Uranyl Sulfate Solutions

The bulk of the experimentation on the preparation of uranyl sulfate solutions was conducted in neoprene coated steel pots. These gave good service and showed no visible wear on the neoprene coating.

Other materials of construction which were tested and found suitably resistant were Karbate, Carbon AGR, Carbon C-13, lead, Buna S and cypress wood. The use of lead indicated a probable pick up of 4-200 ppm of Pb.

Chlorides were found to be detrimental and corrosive on test lead pieces in the preparation of uranyl sulfate solutions.

Stainless steels 18-8, C.B.S., Mo-4 were not suitable, showing excessive corrosion, etching, pitting and intergranular attack from fluorides present in the solution.

Corrosion of Uranyl Sulfate Solutions on Stainless Steels

Uranyl sulfate solutions of pH 3.5 - 3.7 obtained after the "gypping" operation showed no measurable corrosion at 90-95°C. on stainless steels types 304 and 347. Chlorides at 0.01% Cl^- in solution gave similar results. About 1% concentration chlorides showed a tendency towards pitting.

Materials for Valve and Pump Construction

Lapp Porcelain, Olivit (A) and (B), Haveg 41 and 43 were tested as candidate materials of construction for valves and pumps. They were observed to be suitably resistant and free from contaminating influences.

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IV - PREPARATION OF PERURANIC ACID
(UO₄.2H₂O) FROM URANYL SULFATE
SOLUTIONS

Peruranic acid (UO₄.2H₂O) of good quality was obtained from uranyl sulfate solutions by reaction with hydrogen peroxide. Complete and almost quantitative precipitation was assured by adjustment to a pH of 2.8-3.5 and by maintenance of a 20-30% excess over theory of hydrogen peroxide. The product was isolated by filtration procedures and water soluble sulfates were removed by washing with distilled water. Yields in the order of 99.6-100% of theory were obtained. The probable reactions involved in the above process are:

A typical experiment for precipitation and isolation of peruranic acid from sulfate solutions follows:

Two and one-half liters of uranyl sulfate solution pH 3.5-3.7 containing 6.68 g. U/100 cc, were heated to 40°C., 110 cc of 27.5% hydrogen peroxide were added dropwise over a period of 30-45 min., while stirring. Upon agitating 3/4 - 1 hr. longer, the pH of the mass gradually changed to 1.45-1.5. 32% by wt. caustic soda solution were then dropped in slowly over 1-1/2 - 2-1/2 hrs., while stirring rapidly to avoid local basification and excessive co-precipitation of magnesium, until a pH of 2.8 - 3.5 was reached. This usually required 110-120 cc of caustic soda solution. The reaction temperature was held at 40-45°C. for 3/4 - 1 hr. longer until the precipitation was complete as shown by test on the liquors with potassium ferrocyanide.

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Ring Test for Uranium in
Peruranic Acid Effluent Liquors

This method was developed in order to extend the sensitivity and reliability of the customary spot test for uranium with potassium ferrocyanide, especially with respect to interference of iron which causes a masking of the red brown uranium color by Prussian blue. It was found useful as a corroborating test after the spot test showed the effluent liquors to be uranium-free.

A 10 cc portion of the filtered effluent liquors is acidified with sulfuric acid to a pH of 1 to 2 and boiled for 5 min. The solution is diluted to 10 cc vol., cooled to 25-30°C. and placed in a test tube.

Two cc of 10% potassium ferrocyanide solution is now added carefully by means of a tube bearing a capillary tip so that the solution forms a layer on top of the effluent. The tube is now allowed to stand without any mechanical mixing or jarring.

The presence of UO_2^{++} in the effluent is indicated by the appearance of a red brown color in the upper layer. If there is appreciable UO_2^{++} , this coloration occurs in a few seconds and may be quite dark. When there is less UO_2^{++} , the color formation requires a longer time, and usually appears as a brown ring forming as a layer near the interface of the two portions of the solution.

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Gravimetric check analyses on samples of effluent thus tested indicate that if the formation of the brown ring requires more than five minutes, the concentration of UO_2^{++} is low enough to consider the precipitation completed for all practical purposes.

The amount of iron in the effluent is also indicated by the depth of green to blue color in the lower layer.

Tests for excess of hydrogen peroxide were made with potassium iodide starch papers. A strong blue coloration was obtained when hydrogen peroxide was present in the sufficient excess required for complete precipitation of uranium values.

The pH was then finally adjusted, if required, by addition of either dilute sulfuric acid or caustic soda. The peruranic acid precipitated as a creamy yellow colored body, and was isolated either by centrifuge or filtration procedures. The wet paste (690 g.) was washed free from water soluble sulfates with 6-9 l. of distilled water. The product dried 24 hours at $75-80^\circ\text{C}$. in air weighed 241 g.

	<u>% U</u>	
	<u>Calc.</u>	<u>Found</u>
$\text{UO}_4 \cdot 2\text{H}_2\text{O}$	70.4	69.4
M.W. = 338		

The absolute density of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ prepared as above was found to be 4.832.

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Quality of Peruranic Acid ProducedAnalysis by U. S. Bureau of Standards

%

Rare Earths	Not detected on 100 g. of sample
Chlorides	Less than 0.001
Heavy Metals	0.002
Boron	Not detected
S	0.057
Nitric Insoluble	0.009
Si	0.001
Fe	0.002
F	0.18 - 0.30

Spectrographic Analysis: ppm

-- = Not detected
 VW = Very Weak
 L = Less than

Ag	VW	Cd	--	Li	--
As	--	Co	L10	Mg	W
Au	--	Cr	--	Mn	--
B	--	C	L10	Mo	--
Bi	--	Ge	--	N	L50
Be	--	Fe	VW	Na	W
Ca	2.5	In	--	Pb	L50
Sb	--	Si	L100	Tl	--
		Zn	--		

The above quality was better than the required D-1 Specification on uranium oxide (U₃O₈) (Black Oxide) which is shown below:

	<u>ppm</u>
Insoluble	3000
Heavy Metals	800
Boron	2.5
Rare Earths	40.0
Chlorides	30.0

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Particle Size Control of Peruranic Acid
Effect of Variations in Temperature of
Precipitation on Crystal Size and Settling Rate

The effect of temperature upon crystal size of peruranic acid obtained from uranyl sulfate solutions containing calcium, magnesium, iron, and fluorine, as impurities are shown in the following microphotographs, Figs. 1, 2, 3 and 4. These show crystal structure for precipitations at 5-10°C., 20-25°C., 30-35°C., and 40-45°C. Crystal size improved with ascending temperatures from 5°C. to 45°C. Variations in concentration from 3-10 g. U/100 cc. precipitated at 40-45°C. showed no appreciable differences in peruranic acid crystal formations.

All types of precipitate produced at different temperatures, could be filtered on a Buchner funnel in the laboratory. The type shown in Fig. 1 showed a very poor settling rate, filtered very slow and required return of filtrates because of excessive turbidity. The types shown in Figs. 2, 3 and 4 showed very rapid settling rates in centrifuging tests, and filtered rapidly.

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Addition of magnesium sulfate, sodium sulfate, or ammonium sulfate to uranyl sulfate solutions prior to precipitation increased the density of the peruronic acid precipitate, gave improved settling rates, and formed large agglomerated particle sizes. Ammonium sulfate gave good results employing 75-100 parts of ammonium sulfate per 100 pts. of U in solution.

Effect of $(\text{NH}_4)_2\text{SO}_4$ Addition on
Density of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Formed and Settling Rate

<u>Fig. No.</u> <u>Photo-</u> <u>graph</u>	<u>Solution</u> <u>from</u> <u>Type</u> <u>Sulfation</u>	<u>Ratio</u> <u>$(\text{NH}_4)_2\text{SO}_4/\text{U}$</u>	<u>Definite</u> <u>Layer</u> <u>of</u> <u>Solid</u>	<u>Clear</u> <u>Super-</u> <u>natent</u> <u>Liquid</u>	<u>% Solids</u> <u>in Press</u> <u>cake</u>
5	Aqueous (b)	0.00	Several days	Several days	42
6	" "	0.50	13 min.	11 min.	80
7	" "	1.25	5 min.	20 min.	81
8	Retort (a)	0.00	Several hours	Several hours	47
9	" "	0.75	130 min.	" "	58
10	" "	1.00	100 min.	" "	57
11	" "	1.25	45 min.	90 min.	69

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Effect of Iron and Magnesium Sulfates
on Hydrogen Peroxide Requirements for
the Precipitation of Peruranic Acid (41)

Variations were observed in the quantity of hydrogen peroxide required for complete precipitation of peruranic acid from uranyl sulfate solutions produced from (a) retort sulfations, and (b) wet sulfation. These variations were traceable to differences in the magnesium content of the solutions obtained by the two methods, and to variations in iron content caused by improper conditions for the precipitation of iron hydroxide in the preparation of the solutions.

Test precipitations of peruranic acid with hydrogen peroxide at 40-45°C. under process conditions, were made on solutions prepared from pure uranium trioxide and dilute sulfuric acid using controlled amounts of CP magnesium sulfate, $MgSO_4 \cdot 7H_2O$ and CP ferric sulfate, $Fe_2(SO_4)_3 \cdot 9H_2O$ in order to establish limits on tolerance towards iron with various concentrations of magnesium and uranium.

In the absence of iron sulfate, peruranic acid was completely precipitated from solutions containing uranium in concentrations from 2.5 - 10 g./100 cc, and containing magnesium from 0.2 g/100 cc, employing 123% of theory hydrogen peroxide.

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Effect of Magnesium Conc. on H₂O₂ Consumption

<u>gm. Mg/ 100 cc</u>	<u>Ratio U/Mg</u>	<u>H₂O₂ Consumed % of Theory</u>
<u>10 g. U/100 cc</u>		
2.0	5.0	123
1.0	10.0	123
0.6	16.7	123
0.2	50.0	123
0.0	∞	123
<u>5 g. U/100 cc</u>		
2.0	2.5	123
1.0	5.0	123
0.5	10.0	123
<u>2.5 g. U/100 cc</u>		
2.0	1.25	123
1.0	2.50	123
0.5	5.0	123

In solutions containing uranium in concentration of 5 g/100 cc and magnesium in concentration of 5 g/100 cc, Ratio U/Mg = 1, iron sulfate in excess of 100 ppm iron in solution, increased the hydrogen peroxide consumption to approximately 140% of theory. When, however, the uranium to magnesium ratio was high - as in the wet sulfation - iron sulfate up to 1000 ppm of iron did not cause any appreciable variation in hydrogen peroxide usage.

In solutions containing dissolved magnesium, the hydrogen peroxide requirements increased directly in proportion to the iron sulfate content, and became more marked with increasing amounts of magnesium.

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Effect of Iron Sulfate on
H₂O₂ Consumption in Various
Magnesium Concentrations

<u>Ratio U/Mg</u>	<u>Fe ppm</u>	<u>H₂O₂ Consumed % of Theory</u>
<u>6.68 g. U/100 cc</u>		
8.25	10	137
	100	137
	500	137
	1000	137
<u>5.0 g. U/100 cc</u>		
1.0	5	123
	50	123
	100	138.5
2.0	5	123
	50	123
	100	123
3.0	5	123
	50	123
	100	163
<u>2.5 g. U/100 cc</u>		
1.0	5	146
	50	320
	100	320
	500	Not complete with 320
2.0	5	130
	50	177
	100	192
	500	Not complete with 200

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Tolerable Impurities

Precipitation of peruranic acid was successfully effected on sulfate solutions containing the following ions in solution:

Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Gallium
Iron
Lanthanum
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Samarium
Silicon
Sodium
Vanadium

Chlorine
Fluorine
Nitrate

The extent to which a number of these impurities could be eliminated in the filtrates when precipitating peruranic acid, are shown in the following tabulation:

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Impurities Eliminated in
Peruranic Acid Filtrate

<u>Impurity</u>	<u>Parts Impurity</u> <u>per 100 parts Uranium</u>	
	<u>Initially</u> <u>present</u>	<u>In UO₄.2H₂O</u> <u>Isolated</u>
Boron	4.000	0.00004
Cadmium	2.000	0.0010
Chlorine	1.000	L 0.0001
Chromium	0.0500	L 0.0001
Cobalt	0.0500	Not detected
Copper	0.0500	0.0005
Gallium	1.0000	0.0065 - 0.0070
Lanthanum	2.0000	0.3070
Lithium	2.0000	0.0040
Manganese	0.0500	L 0.0005
Mercury	2.0000	0.0200
Molybdenum	0.0500	0.0045
Nickel	0.0500	Not detected
Samarium	1.0000	0.2000
Sodium	39.4	1.0 - 2.0

Effect of Vanadium on Precipitation of Peruranic Acid

Vanadium in excess of one part per 100 parts of uranium was observed to interfere with the precipitation and formation of peruranic acid due probably to an accelerated and catalytic decomposition of hydrogen peroxide. These results are reflected in the following tabulation:

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Effect of Vanadium on
Precipitation of Peruranic
Acid. Vanadium Added as
 $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$

	A	B	C	D	E
Conc. g. U/100 cc	6.68	6.68	6.68	6.68	6.68
g. V/100 cc.	0.134	0.067	0.0335	0.0167	0.000
ppm V	20,000	10,000	5,000	2,500	0.000
Ratio V/100 pt. U	2.0	1.0	0.5	0.25	0.00
% of Theory H_2O_2 consumed	214	158	135	135	135
Time for complete ppt. hr.	Not complete in 4	2	1/2	1/2	1/2
% of Theory yield $\text{UO}_4 \cdot 2\text{H}_2\text{O}$	83	100	100	100	100
V in $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ ppm	-	58-80	-	-	0.0

Fluorine Content of Peruranic Acid

Uranium solutions containing both magnesium and fluorine ions with sulfates present, resulted in peruranic precipitations containing variable amounts of fluorine in probable combination with magnesium.

In the absence of magnesium with fluorides present, peruranic acid was precipitated relatively free of fluorine contamination. With low concentrations of fluorine in solution and large amounts of magnesium present, peruranic acid relatively free of both impurities was obtained.

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Effect of Mg and F in U Solution
on Ppt. $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Quality

Type or Source of Uranium Solution	Analysis, %					
	Uranium Solution				Ppt. Per- uranic acid	
	Ratio					
	U	Mg	F	Mg/F	Mg	F
Sulfate sludge, retort sulfation of slag & dross	4.0	2.0	0.08	25.0	-	0.15
Aqueous sulfation of dross (low fluoride)	6.7	0.9	0.11	8.2	-	0.46
Aqueous sulfation of slag (high fluoride)	6.69	0.81	0.52	1.5	-	4.40
Uranyl fluoride UO ₂ F ₂	5.0	0.0	0.80	0.0	0.0	0.53
Uranyl fluoride and magnesium sulfate	5.0	1.3	0.80	1.6	5.4	8.40

Solution of F from MgF_2 in H_2SO_4 ,
and UO_2SO_4 Solutions at pH 3.0-3.5

g. F/100 cc After 90-95°C. di- gestion with MgF_2	g. U/100 cc.
0.01	0.0
0.48	5.0

The solution of fluorine from magnesium fluoride in uranyl sulfate solutions is probably explained by the formation of water soluble salts of magnesium sulfate and uranyl fluoride as follows:

The above reaction was found to be reversible.

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Uranyl fluoride, UO_2F_2 , was prepared from uranium trioxide by reaction with anhydrous hydrogen fluoride. 32.5 g. of the powder was dissolved in 500 cc of water and resulted in a solution with a pH of 3.2 which gave no precipitate upon introduction and solution of magnesium sulfate. This indicated that XO_2F_2 is probably not readily dissociated into free F^- ions. Prolonged boiling for 5-6 hours, of XO_2F_2 solutions with 35 and 70 g. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, gave insoluble MgF_2 in yields of 22.8 and 45.6% of theory; indicating that the reaction could be reversed by the mass action of an excess of magnesium sulfate.

The probable reaction which occurs when uranyl solutions which contain dissolved fluorides, magnesium, and sulfates are precipitated with hydrogen peroxide may be presented as follows:

Elimination of Fluorine Content of Peruranic Acid

In subsequent operations for the preparation of purified uranyl nitrate, it was proposed to dissolve peruranic acid, or oxides of uranium produced therefrom⁽¹⁴⁾ in nitric acid, employing stainless steel equipment. To minimize corrosion of apparatus from excessive amounts of fluorides it was desirable to produce high quality feed materials with a low fluorine content. The studies described below indicated that this could be accomplished to a considerable extent by a variety of procedures.

(a) Formation of Water Soluble Complex Fluorides in Preparation of Peruranic Acid

Significant reductions of the fluoride content in the

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finished peroxide precipitation were obtained by the addition of ammonium⁽⁴²⁾, borate⁽⁴³⁾ or aluminum ions to the uranyl sulfate solutions prior to precipitation. The effectiveness of the ammonium ion was not permanent and required immediate filtration after precipitation, because the fluoride content of the peroxide precipitate increased with the lapse of time. The aluminum method forming a stable water soluble $AlF \equiv$ ion, established from studies made at the Sterling Chemistry Laboratory, Yale University, gave the best results and was adopted for large scale operations. Peruranic acid containing less than 0.1% F was readily obtained by this means from uranyl sulfate solutions produced by wet sulfation of all types of scrap materials. Three to six times the stoichiometric requirement of aluminum ion as $Al_2(SO_4)_3 \cdot 15H_2O$ based on the fluoride content of the uranium solution added prior to precipitation with hydrogen peroxide gave maximum eliminations.

Fluorine Elimination by Ammonium
Ion in $UO_4 \cdot 2H_2O$ Precipitation

NH_4^+ was introduced either as NH_4OH in neutralization of excess sulfuric acid employed for sulfation, or as ammonium sulfate prior to reaction with H_2O_2 , or for final pH adjustment in peruranic precipitation. Filtrations were made 30 min. after precipitation, unless otherwise indicated.

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<u>g. per 100 cc of uranium soln.</u>		<u>Molal Ratio</u>	<u>% F in</u>
<u>(NH₄)₂SO₄ added</u>	<u>F</u>	<u>NH₄⁺⁺/F⁻</u>	<u>UO₄·2H₂O</u>
16.0	0.17	25.7	0.27
16.0	0.17	25.7	1.13 ^(a)
9.5	0.17	15.3	0.70
8.4	0.21	11.5	0.45
6.6	0.25	7.7	1.31
2.9	0.21	4.0	1.60
0.0	0.25	0.0	2.16
0.0	0.52	0.0	4.40

(a) Filtration 3 hrs. after precipitation

Fluorine Elimination by Borate Ion
in UO₄·2H₂O Precipitation

<u>g. per 100 cc of uranium soln.</u>		<u>Molal Ratio</u>	<u>% F in</u>
<u>H₃BO₃ added</u>	<u>F</u>	<u>BO₃⁼/F⁻</u>	<u>UO₄·2H₂O</u>
0.00	0.38	0.00	3.40
1.33	0.38	1.07	1.20
2.00	0.38	1.66	1.20
2.66	0.38	2.05	0.96

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Fluorine Elimination by Aluminum
Ion in $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Precipitation
(Yale University)

g. per 100 cc
of uranium soln.

<u>$\text{Al}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ added</u>	<u>F</u>	<u>Molal Ratio $\text{Al}^{+++}/\text{F}^-$</u>	<u>% F in $\text{UO}_4 \cdot 2\text{H}_2\text{O}$</u>
0.0	0.11	0.000	0.98
0.3	0.11	0.166	0.60
0.6	0.11	0.333	0.23
0.9	0.11	0.500	0.08
1.8	0.11	1.000	0.06
0.0	0.29	0.000	1.41
4.8	0.29	1.000	0.05

(b) Purification of Peruranic Acid

Solution in Sulfuric Acid and Reprecipitation:

The fluorine content of peruranic acid filter cakes could be appreciably reduced by solution in dilute sulfuric acid at 80-90°C. and reprecipitation with hydrogen peroxide.

Purification of Peruranic Acid
by Solution in H_2SO_4 and Reprecipitation

<u>Starting Material</u>	<u>% F in $\text{UO}_4 \cdot 2\text{H}_2\text{O}$</u>	<u>Reprecipitated</u>
4.80		1.50
3.80		0.70
1.44		0.51
1.15		0.39

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Solution in Alkali Carbonates
and Reprecipitation⁽⁴⁴⁾

Peruranic acid containing 2-6% fluoride ion could be readily dissolved (max. 5 g. U/100 cc solution) in 4 mol. equivalents of sodium bicarbonate, or a mixture of one mole equivalent of sodium carbonate and two mole equivalents of sodium bicarbonate in aqueous solutions at $70 \pm 5^\circ\text{C}$. without change in the oxidation state of the uranium. The solution, filtered from insoluble impurities, including fluorides and ferric compounds, reprecipitates peruranic acid containing less than 0.1% fluorides upon acidification.

The solubilization of peruranic acid by bicarbonate or carbonate is believed due to the following reactions:

where UO_2 radical may be $\text{U} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array}$ and/or $\text{U} \begin{array}{c} \text{O} \\ \diagup \diagdown \\ \text{O} \end{array}$

When less than three -O-COONa groups are involved, the $\text{UO}_2(\text{OCOONa})_x (\text{ONa})_y$ molecule does not appear to be soluble, judged by the failure of $2\text{Na}_2\text{CO}_3$, or a mixture of Na_2CO_3 and

NaHCO_3 to dissolve the peroxide compound. With 3 mole equivalents of Na_2CO_3 solution of the peruronic acid occurs rapidly but a precipitate soon develops. This was found to contain carbonate, but possessed physical properties similar to sodium uranate. This phenomenon is believed due to the high alkalinity of the solution pH 10.8 causing more than one-COONa group to be replaced by -ONa, thus insolubilizing the molecule. In the presence of excess CO_2 , a solution (max. 7 g. U/100 cc) can be obtained by the use of one mole equivalent of Na_2CO_3 . With any combination of carbonates it was found necessary to maintain a sufficient excess of carbonate during the solution stage to avoid separation of insoluble intermediate forms.

The following illustrates a typical experiment: One hundred sixteen g. of peruronic acid paste 60.3% solids, analyzing on a dry basis 66.2% U, 2.5% F, 0.94% SO_4 , 582 ppm heavy metals, 51 ppm Fe, was added to a solution of 70 g. of sodium bicarbonate in 1000 g. of water agitated at 70°C. After 45 min. the peruronic acid had dissolved and no further decrease in turbidity occurred. The pH was 8.6 measured at 70°C. Ten grams of filtercel was added, and the slurry filtered at 70°C. The filtrate analyzing 0.03 g. F/100 cc was acidified by adding it portionwise to 100 cc of water with intermittent additions of 48% sulfuric acid to hold the pH to Congo acidity. This was carried out at 50°C. and required 82.5 - 83 cc of acid to finish with a pH of 2. Ten cc of 30% hydrogen peroxide

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was now added which lowered the pH to 1.6. 32 cc of 30% caustic soda was then added to finish the precipitation at a pH 2.7 - 3.0. The peruranic acid isolated by filtration and washed free from sulfates with distilled water analyzed 0.06% F on a dry basis.

Extraction with Dilute Nitric Acid⁽⁴⁵⁾

Peruranic acid slurried with dilute nitric acid for 10-12 hrs. at a pH of 0.7 - 0.9 in the presence of an excess of hydrogen peroxide, was found to considerably reduce the fluoride content of the suspended product. Material with 1.5 - 3.0% F content could be purified to contain about 0.25 - 0.35% F. Ten to 20% of the peruranic acid was dissolved in the nitric acid liquors and required recovery by other means, such as precipitation by raising the pH to 3.5, or by conversion to insoluble sodium or calcium uranate.

(c) Volatilization of Fluorides from Peruranic Acid by Ignition⁽⁴⁶⁾

Peruranic acid ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$) heated to 150-300°C. yields uranium trioxide (orange oxide, UO_3). When ignited above 500°C. it yields black oxide (U_3O_8) (47).

Fluoride containing peruranic acid converted to orange oxide showed no appreciable reduction in fluorine content; ignition at 800°C. to black oxide, however, resulted in the elimination of fluorine when the initial content did not appreciably exceed 1.5%, and ignition to temperatures above 900°C. resulted in black oxide with fluoride content well below 0.1%.

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Effect of Temperature on Peruranic
Acid and F Content of Resultant Oxides

Before Heating -----> After Heating
 $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ UO_3

% F

Temperature 150-165°C. 2 hours

0.15	0.17
0.18	0.17
0.25	0.29
0.45	0.68

Temperature 160-185°C. 2 hours

0.18	0.23
0.25	0.40
0.10	1.54
1.40	2.10
1.75	2.80
2.10	1.80

Temperature 300-320°C. 2 hours

0.19	0.22
------	------

Before Heating -----> After Heating
 $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ U_3O_8

% F

Temperature 800-850°C. 2 hours

0.45	0.08
1.1	Nil
1.1	0.04
1.5	Nil
4.0	1.52

Temperature 900-950°C. 2 hours

1.52	0.03
1.65	0.03
1.90	0.06
2.05	0.02
2.36	0.03

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Tests on Materials of Construction
for Plant Design for Precipitation
of Peruranic Acid

Uranyl sulfate solutions from all sources of scrap materials were successfully precipitated by hydrogen peroxide, in many laboratory experiments, employing either stainless steel or neoprene coated vessels. No visible wear was noted, although a tendency toward hardening of the neoprene was noted. 18-8 stainless steel did not catalytically decompose hydrogen peroxide under the conditions required for precipitation. Lead was found to decompose hydrogen peroxide with deposition of lead sulfate.

V. ISOLATION OF PURE URANYL NITRATE
FROM SCRAP MATERIALS BY CONVERSION
OF SULFATE SLUDGE TO NITRATES AND
CONTINUOUS EXTRACTION WITH ETHER

The method outlined below was not developed beyond the laboratory scale. Roasted and ground scrap materials, after reaction with concentrated sulfuric acid to volatilize hydrogen fluoride were dissolved in water and reacted with nitric acid, calcium carbonate and barium nitrate. This converted the soluble sulfate products into soluble nitrates and eliminated sulfate ion by precipitation as insoluble sulfates. The mixed nitrates with or without concentration were extracted with ether at room temperature by counter-current flow methods. Magnesium, calcium, barium and iron nitrates remained in water solution, insoluble in ether. The recovery of uranyl nitrate was

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practically quantitative, and could be readily extracted from the ether solution with distilled water.

Equally good results were obtained with sodium uranate dissolved in nitric acid, eliminating sodium ion, as sodium nitrate.

The following illustrates, in principle, the method employed in several laboratory experiments on sodium uranate, and on mixtures from scrap materials which contained magnesium nitrate, barium nitrate, calcium nitrate and iron nitrate as impurities.

To 300 g. of water and 250 g. of 70% nitric acid at 80°C. were added while stirring 478 g. of sodium uranate (73% U). The 600 cc of solution of pH 2.66 was then concentrated to a b.p. of 117.5°C., 360 cc volume or 780 g. weight. The mass was cooled to 80°C. and added carefully to an extractor containing ether at 20-22°C. The extractor was equipped with an agitator and an overflow pipe at the top of the extractor which allowed the clear ether extract layer to drop into a boiler containing distilled water at 32-40°C. Ether vapor distilling from the boiler was condensed and piped into the agitated water-nitrate layer at the bottom of the extractor.

Complete extraction of uranium nitrate was accomplished in 8-12 hours. The water solution obtained weighed 1497 g. in 760 cc volume, and contained 347 g. uranium (Theory = 348 g.) as uranyl nitrate. No sodium or iron could be detected in the solution. The residual sodium nitrate layer in the extractor analyzed nil for uranium.

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Summary

Processes, process controls and design data were developed for the almost quantitative (98.5 - 99%) recovery as peruranic acid ($\text{UO}_4 \cdot 2\text{H}_2\text{O}$) of the uranium values of byproduct scrap materials such as dross, slag, sodium uranate, uranium contaminated carbon, and scrap metal turnings such as turnings, offgrade biscuits and billets, sweepings, etc.

The chemistry of the process and its controls were especially directed to the production of peruranic acid of high purity suitable for direct conversion to uranium nitrate and reprocessing to metal.

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Effect of Precipitation Temperature on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Particle Size. Scale = 1 Mic./Small Div.
Mag. = 725X.

Figure 1

Figure 2

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Effect of Precipitation Temperature on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Particle Size. Scale = 1 Mic./Small Div.
Mag. = 725X.

Figure 3

Figure 4

Effect of $(\text{NH}_4)_2\text{SO}_4$ on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Particle Size. Scale = 1 Mic./Small Div. Mag = 725X.

Figure 5

Figure 6

Effect of $(\text{NH}_4)_2\text{SO}_4$ on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Particle Size. Scale = 1 Mic./Small Div. Mag = 725X.

Figure 7

Figure 8

Effect of $(\text{NH}_4)_2\text{SO}_4$ on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Particle Size. Scale = 1 Mic./Small Div. Mag = 725X.

Figure 9

Figure 10

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Figure 11

Effect of $(\text{NH}_4)_2\text{SO}_4$ on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ Particle Size.
Scale = 1 Mic./Small Div. Mag. = 725X.

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