This document contains 12 pages.

UNCLASSIFIED BY: 60420.1. DATE: 1

AEC-D-4181

**CLINTON ENGINE WORKS
TENNESSEE EASTMAN CORPORATION**

Contract No. W-7401-eng-23

**CHEMICAL DEVELOPMENT DIVISION
Dr. C. E. Larson - Director**

Photostat Price \$ 2.30
Microfilm Price \$ 2.40
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

**THE SEPARATION OF URANIUM FROM THORIUM
THE OXALIC ACID LEACH**

This report was prepared as a scientific account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights. The Commission assumes no liability with respect to the use of, or from damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

**E. W. Christopherson
H. R. Grady
R. W. Woodard
C. E. Larson**

**Oak Ridge, Tennessee
July 3, 1946**

1791

ABSTRACT

The use of the oxalic acid method for the separation of uranium from mixed thorium-uranium peroxides has been investigated, and appears to be the most satisfactory of the obvious methods of separation. One oxalic acid leach removes nearly all of the uranium from the thorium with approximately one mg Th/L remaining in the uranium solution phase. An excess of 10% oxalic acid, and a nitric acid concentration of 0.1M., or less, is recommended. The use of thoron as a colorimetric reagent for the detection of small quantities of thorium has been employed quite satisfactorily. A solubility product constant of 7.0×10^{-20} is reported for thorium oxalate.

THE SEPARATION OF URANIUM FROM THORIUM

THE OXALIC ACID LEACH

Introduction

In another report⁽¹⁾, the use of thorium peroxide as a carrier in the recovery of uranium from Beta cold peroxide process effluents has been described. That report dealt exclusively with the efficiency of the carrier process. Assuming that the carrier step is completely satisfactory, the usefulness of the thorium peroxide method is dependent upon the ease with which a small quantity of uranium may be recovered from a large quantity of thorium. The thorium concentration under the conditions employed amounts to approximately fifty times the concentration of uranium. Fortunately, the separation need not be sharp; any method which will remove 90% of the uranium from the thorium is satisfactory for the purposes of the cyclical recovery process outlined in another section of this report. However, it is necessary that the uranium thus extracted contain no thorium.

Although several methods suggest themselves for the isolation of uranium from thorium, this report deals primarily with the oxalic acid leach method. Considerable work has already been done by other workers with respect to this separation by employing ion exchange resins and organic solvents. Both give promise of successful separation under the conditions specific to the thorium peroxide carrier process, and deserve detailed investigation.

In addition, thorium forms sparingly soluble compounds in alkaline peroxide, fluoride, and sodium hydroxide-sodium carbonate systems. When thorium peroxide containing a small amount of uranium is treated with alkaline peroxide or $\text{NaOH-Na}_2\text{CO}_3$ solutions, thorium precipitates are formed

which retain the greater portion of uranium. Although no quantitative results are presented here, many attempts were made to exploit either of these agents because in both cases the thorium precipitate is readily soluble in nitric acid. No work was done with hydrofluoric acid because of the difficulty anticipated in converting thorium fluoride to the nitrate, whereby the thorium could be used repeatedly.

Oxalic acid attacks thorium peroxide quickly, yielding a readily filterable precipitate. Unexpected difficulty was met in converting thorium oxalate into a usable form, however. When ignited to the oxide, a refractory form of thorium dioxide is obtained which is extremely slow to dissolve in hydrochloric acid, nitric acid, and mixtures of these acids. Thorium oxalate itself shows the same behaviour. Sulfuric acid converts both the oxide and oxalate to an acid sulfate, which is but slightly soluble. Hydrogen peroxide has no action on thorium oxalate.

When thorium oxalate is suspended in perchloric acid or nitric acid, potassium permanganate destroys the oxalate radical quickly, and the thorium passes readily into solution.

For analytical work, thorium and oxalate can be separated in the following way: sodium hydroxide added to thorium oxalate causes thorium hydroxide to precipitate, while the oxalate passes into solution quantitatively.

Despite the difficulty of destroying oxalate, this agent appears to be the best of the precipitants.

The Oxalate Extraction Method

When thorium peroxide is precipitated in the presence of uranium, the precipitate is consequently deep yellow in color. Subsequent treatment

with oxalic acid causes the mass to be decolorized immediately, and a dense, insoluble, granular, white substance is formed, presumably thorium oxalate. The experiments listed below in Table I illustrate the effectiveness of this procedure in separating uranium from the thorium peroxide cake.

A single extraction seems to be optimum, since the second extraction, in the few cases tried, removed very little of the residual uranium. With 100 ml. of oxalic acid solution per gram of thorium, variation in the oxalic acid concentration over the range 0.1N. to 1.0N. produced no appreciable change in the efficiency of the uranium extraction.

If the thorium peroxide is precipitated from a machine wash type solution, various metals besides uranium are carried with it. After the oxalate treatment the disposition of these metals should be as follows: copper and calcium largely in the cake, iron largely in solution. The presence of copper oxalate in the cake imparts a faint blue tinge to it; the presence of iron oxalate complex in solution colors this phase apple green. In this regard it is interesting to note that if the thorium peroxide is first dissolved in nitric acid, and then precipitated with oxalic acid by adjusting the pH to 1.0 (that is approximately the pH of 1.0N. $\text{H}_2\text{C}_2\text{O}_4$) most of the copper present passes into solution along with the iron.

The experiments in Table II show the efficiency of the oxalate method under the conditions which might be expected to obtain in plant operation. Approximately fifteen liters of synthetic machine wash solution, containing a known quantity of uranium was treated by the thorium peroxide process. The slurry was passed through a Sharples Laboratory Model centrifuge. The effluent was analyzed for uranium by the fluorescent method. The cake was carefully removed from the bowl by scraping and washing, oxalic acid and

TABLE I

OXALATE EXTRACTION RESULTS PURE SYSTEM

Thorium peroxide cake formed in usual way at pH 2.0 with 500 mg. thorium. Volume of system was one liter. In every case the peroxide cake was treated with 100 ml. of $H_2C_2O_4$ solution, mixture heated on steam bath for 30-60 minutes, and filtered immediately.

Peroxide Cake Formation			Peroxide Cake Extraction					
Expt.	mg U/L Initial Soln.	mg U/L- Th_2O_7 Filtrate	First Extraction		Second Extraction		Oxalate Filtrate mg U	Oxalate Filtrate mg U
			$H_2C_2O_4$ Conc. M	Oxalate Cake mg U	$H_2C_2O_4$ Conc. M	Oxalate Cake mg U		
C-1	46.0	4.0	1.0	---	1.0	---	0.9	---
C-2	9.5	0.05	1.0	---	1.0	0.8	0.2	---
C-3	47.4	3.3	1.0	---	1.0	0.8	0.2	---
C-4	94.8	20.2	1.0	---	1.0	0.9	0.3	---
C-5	47.4	0.2	0.1	1.6	---	---	---	---
C-6	47.4	0.4	0.2	1.5	---	---	---	---
C-7	47.4	0.4	0.4	2.2	---	---	---	---
C-8	47.4	0.3	0.6	1.4	---	---	---	---
C-9	47.4	0.2	0.8	1.5	---	---	---	---

179

TABLE II

OXALATE EXTRACTION RESULTS GUNK SYSTEM

Expt.	Initial Solution Approximate Concentration mg U/L	mg Th/L Added	H ₂ O ₂ Conc.	Peroxide Effluent mg U/L (average of two or more determinations)	Total mg. U Peroxide Effluent Calculated 1	mg. U Oxalate Cake 2	mg. U Oxalate Filtrate 3	Total mg. U Recovered Sum (1)(2)(3)	Total mg. U Added
P-34	45	1000	0.5	0.05	0.75	4.7	660	666.5	687
P-33	30	1000	0.5	0.35	5.3	34.6	436	475.9	458
P-21	10	500	0.5	0.39	5.9	3.3	148	157.2	160
P-18	30	1000	0.4	0.79	11.9	8.0	421	441	458
P-9	30	1000	0.5	0.50	7.5	23.7	415	446.2	458
P-12	30	1000	0.5	0.4	6.0	26.5	427	459.5	458
P-13	30	1000	0.5	0.5	7.5	12.4	417	436.9	458
P-15	30	1000	0.5	0.4	6.0	19.2	438	463.2	458

1797

water were added so that finally the thorium peroxide was in contact with 25 ml. of 1.0 M. $\text{H}_2\text{C}_2\text{O}_4$ per gram of thorium. Thus, after complete conversion of the peroxide to the oxalate, the solution should have been about 0.8 M. with respect to oxalic acid. This mixture was heated on the steam bath for one and one half hours, filtered, and the liquid and solid phases were analysed for uranium in the following ways:

The solution phase was taken to fumes with sulfuric acid, so that decomposition of oxalate was complete. After electrolysis of this solution to remove iron, copper, etc., the uranium was determined in the usual way by reduction, and titration with potassium dichromate.

The solid phase was suspended in 1.0M. excess perchloric acid, and solution was effected by addition of concentrated potassium permanganate solution. Since no iron was found in this solution, uranium was determined directly by reduction, and titration with potassium dichromate. Results of several experiments appear in Table II.

Thorium was determined in several oxalate filtrates from pilot plant runs similar to those in Table II. The data appears in Table III.

TABLE III

<u>Run</u>	<u>Added $[\text{HNO}_3]$</u>	<u>Thorium in Oxalate Filtrate</u>
15-1	---	2.1 p.p.m.
15-2	---	1.0
17-2	---	1.6
20-1	---	0.7
20-2	0.1	0.3

1798

The presence of uranium in the thorium oxalate cake is not a serious disadvantage. As previously reported⁽¹⁾, the thorium cake when dissolved can be used repeatedly for subsequent precipitations of uranium. Hence, the uranium in the cake is continuously returned to the system.

Necessarily the concentration of manganese will be high in the recycle thorium solution. It has been observed however, that peroxide decomposition was not increased appreciably. Quantitative information⁽²⁾ has shown this observation to be correct.

QUANTITATIVE CONSIDERATIONS ON THE SOLUBILITY OF THORIUM OXALATE

In the early work done in this laboratory on the separation of uranium from thorium, employing oxalic acid, a qualitative knowledge of the relative insolubility of thorium oxalate was all that was required. A more quantitative estimate of solubility values later became necessary. The synthesis of a colorimetric reagent for thorium, thoron, by Mr. H. Cragg facilitated this program considerably.

According to work done by Kusnetsov⁽³⁾ a very accurate estimate of microgram quantities of thorium may be obtained colorimetrically by the use of thoron as a complexing agent. Use of thoron, of course, necessitates the removal of other colored ions, and radicals that precipitate or complex thorium. This meant that in our work on pure thorium oxalate-water systems, the oxalate radical must be destroyed. This was accomplished by the fuming to dryness of the sample in the presence of perchloric acid, the latter reagent being added to prevent the formation of the difficultly soluble thorium dioxide. The soluble thorium perchlorate residue was then dissolved in a small amount of water, which together with washings, was transferred to a 10 ml. volumetric flask. To this was added 1 ml. of 0.1% thoron solution, five drops of conc. HCl, and water sufficient to bring the final volume to exactly 10 ml. A portion of this solution was then placed in a 1 cm. cell of a Beckman spectrophotometer, and compared at a wavelength of 545 m with a duplicate solution of thoron containing no thorium.

Using known concentrations of thorium in the above procedure, verification of Beers' Law was obtained in a plot of percent transmission versus thorium concentration. This curve was used in the calculation of thorium concentrations in unknown solutions.

17910

The effect of excess oxalic acid was first investigated. This was accomplished by precipitating a definite concentration of thorium nitrate with oxalic acid, filtering on a grade F sintered glass funnel, and analysis of the filtrate by the above method. These runs, listed in Table IV were performed at room temperature.

TABLE IV

<u>Run No.</u>	<u>Th Conc. Moles/L</u>	<u>H₂C₂O₄ Conc. Moles/L</u>	<u>Th in Filtrate M/L</u>
4	2.15×10^{-2}	6.3×10^{-2}	0.5
3	2.15×10^{-2}	1.3×10^{-1}	0.6
2	2.15×10^{-2}	2.5×10^{-1}	1.1
1	2.15×10^{-2}	5.0×10^{-1}	2.0

The effect of nitric acid was determined on samples of constant thorium and oxalic acid concentrations. These are listed in Table V below.

TABLE V

<u>Run</u>	<u>Th Conc. Moles/L</u>	<u>H₂C₂O₄ Conc. Moles/L</u>	<u>HNO₃ Conc. Moles/L</u>	<u>Th in Filtrate M/L</u>
8	2.15×10^{-2}	5×10^{-1}	1.6×10^{-2}	0.9
7	2.15×10^{-2}	5×10^{-1}	4.0×10^{-2}	1.9
6	2.15×10^{-2}	5×10^{-1}	1.6×10^{-1}	2.0
5	2.15×10^{-2}	5×10^{-1}	4.0×10^{-1}	12.2

Under the conditions suggested for plant operation, that is approximately 0.1 M. HNO₃, the increasing of the oxalic acid concentration over a small range reduces slightly the solubility of thorium oxalate for pure thorium systems. Table VI includes this data.

TABLE VI

Run	Initial Th Conc. Moles/L.	Oxalic Acid Added			HNO ₃ Conc. Moles/L.	Th in Filtrate mg./L.
		Theoretical Moles/L.	Excess Percent	Excess Moles/L.		
9	0.022	0.044	10	0.0044	0.1	1.1
10	0.022	0.044	15	0.0066	0.1	1.0
11	0.022	0.044	25	0.011	0.1	1.0
12	0.022	0.044	35	0.015	0.1	1.0
13	0.022	0.044	50	0.022	0.1	0.8
14	0.022	0.044	100	0.044	0.1	0.6

To offer an explanation for the increased solubility of thorium oxalate as the concentration of oxalic acid is increased over ranges several times greater than the theoretical amount required the existence of somewhat soluble thorium oxalate-oxalic acid complex is postulated. It is known that with an excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ a soluble oxalate base complex of the general type $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot \text{X}(\text{NH}_4)_2\text{C}_2\text{O}_4$ is formed, with X probably equal to two. There is a possibility that a less soluble complex of the type $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot \text{X} \text{H}_2\text{C}_2\text{O}_4$ exists in acid solution. If such is the case, the addition of nitric acid HNO_3 up to a concentration of approximately 0.1 M. tends to hinder formation of the complex.

The solubility of thorium oxalate in water (no excess oxalic acid) is 0.06 Mg Th/L. Thus:

$$[\text{Th}^{+4}][\text{C}_2\text{O}_4^{2-}]^2 = -K_{s.p.} = 7.0 \times 10^{-20}$$

REFERENCES

- (1). C-0.380.4
- (2). C-2.381.9
- (3). Kusnetsov, V. I., J. Gen. Chem. (U. S. S. R.) 14, 914-19 (1944)

SECRET

12.

E. W. Christopherson
E. W. Christopherson

H. R. Grady
H. R. Grady

R. W. Woodard
R. W. Woodard

C. E. Larson
C. E. Larson

END

177 14