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THE COPRECIPITATION OF

THORIUM AND URANIUM PEROXIDES

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THE COPRECIPITATION OF THORIUM AND
URANIUM PEROXIDES - PART II

CONTENTS

THE COPRECIPITATION OF THORIUM AND
URANIUM PEROXIDES - PART II
PILOT PLANT STAGE

ABSTRACT

1. Experiments covering the coprecipitation of Thorium and Uranium peroxides are described on synthetic and actual 1300 cycle machine wash effluents.

2. The more important factors effecting the successful reaction are discussed.

3. Data are presented on the recovery of the initial thorium and its reuse as a precipitant in numerous runs, both in synthetic and 1300 machine wash effluents.

4. A tentative procedure for the coprecipitation of Th_2O_7-UO_4 is outlined.

5. It has been shown in practically every case that the coprecipitation process will reduce Beta machine wash effluents to less than 1 mg uranium per gallon.

6. Almost no uranium is lost in the proposed cycle and the precipitant can be successfully recovered and reused.

7. The reaction becomes more quantitative with increasing pH and wt.Th/wt. U ratio.

8. With the ability to successfully recover uranium concentrations as high as 200 mg/L - if a small quantity of uranium is present as colloidal UO_4 - there are indications that enriched material, other than from machine wash effluents, can be treated also.

I Introduction

Recently this laboratory developed a new process[1], concerned primarily with the removal of uranium from machine wash effluents resulting from the Beta Cold Peroxide treatment, the fundamentals of which are based specifically on the theory of coprecipitation.

At the time of the initial investigation, radioactive tracer work was a major problem of this group and, realizing the significance of carrier methods, it was suggested that the use of another element, forming an insoluble peroxide in an acid solution, might react in similiar fashion to the regular peroxide precipitation and quantitatively coprecipitate with it any uranium in solution.

Since thorium is the only other common element to fulfill the above requirements, it was decided to investigate its behavior in pure solutions. Thorium peroxide formation, resembling aluminum hydroxide, was more evident with increasing thorium concentrations, while dilute thorium solutions precipitated more readily with the presence of increasing amounts of electrolytes.

Addition of small amounts of uranium (10 mg/L) to the thorium system resulted in the formation of a bright yellow-orange solid after H_2O_2 treatment, which appeared of waxy texture upon continued drawing of air through it.

Analysis of this precipitate indicated the presence of the greatest percentage of uranium, while it was practically undetectable in the filtrate.

With the development of an effective fluorescence method of analysis for detection of microgram quantities of uranium in the thorium effluents, it became feasible to vary techniques and conditions of this coprecipi-

tation process more completely. Progress from these variations has been such that at present, numerous successful synthetic runs have been undertaken at the Purdue University Beta Pilot Plant[2] which emulates exact Beta plant conditions, and complete data not only on these runs, but 51 others in our laboratory, of a five gallon capacity, utilizing 1300 cycle material, have been tabulated.

The major portion of material covered by this report includes work accomplished on a laboratory pilot plant scale. With the aid of this plant, it has been possible to develop the basic theory of coprecipitation to the point where a quantitative removal of uranium from the machine wash effluents is now a reality.

II Discussion of Qualitative Aspects of Proposed Process

Parallel with the development of an optimum conditioned precipitation process, has been the development of a method for the separation of uranium from the mass of thorium. This constitutes a simple conversion of the $Th_2O_7-UO_4$, when treated with oxalic acid, to the insoluble $Th(C_2O_4)_2$ and soluble $UO_2C_2O_4$. The separation at present has attained as high as 96% efficiency and with considerably more work contemplated on this phase it is highly probable that a separation approaching quantitativeness will be achieved. However, this apparent 4% loss of uranium in the $Th(C_2O_4)_2$ cake should be of no great concern after the proposed "precipitation-recovery cycle" is understood.

To Calcining & Chlorination   1 Machine Wash ←

Bulk of UO_4 ←— 2 Cold Peroxide Precipitation   5 $UO_2C_2O_4$

3 Effluent & Thorium Coprecipitation —→ 4 Th_2O_7-UO_4 digested with $H_2C_2O_4$

4b $Th(NO_3)_4$ ←——— 4a $Th(C_2O_4)_2$+$KMnO_4$+HNO_3

Thorium Effluent

↓

Discard or storage
(less than 1 mgu/gallon)
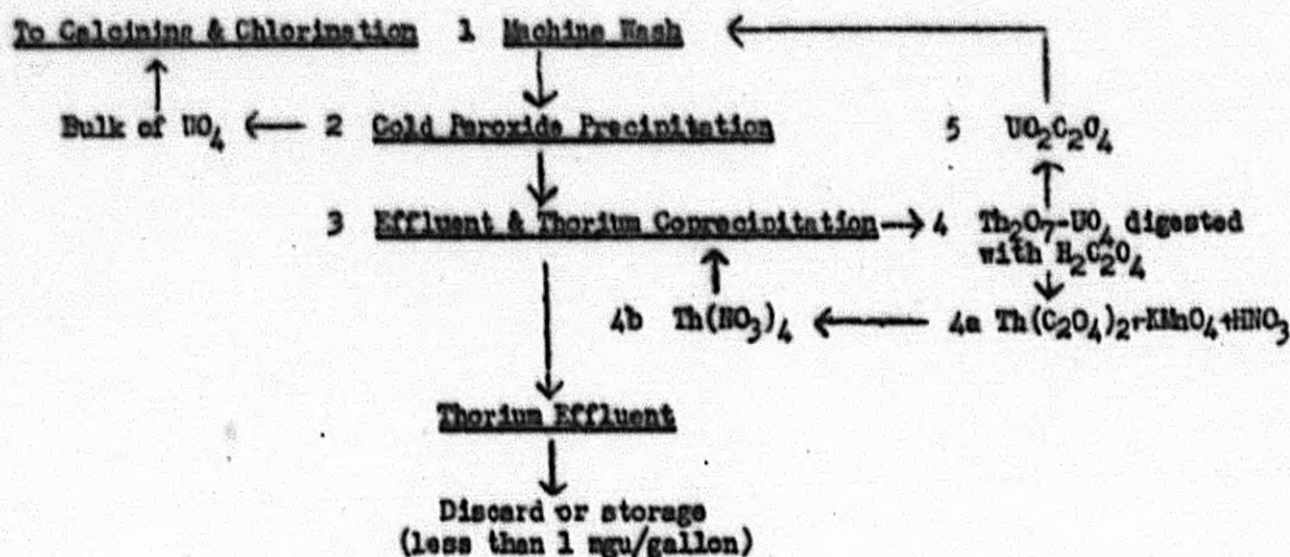
Steps 1 through 5 constitute the primary cycle of the process while 4a and 4b, a recovery of the precipitant, can be regarded as a secondary cycle.

In a more detailed fashion, let us consider the above process.

Actually no material is unaccounted for or wasted in the cycle. The Th_2O_7-UO_4 precipitate, resulting from treatment of the machine wash effluent with a 10% aqueous $Th(NO_3)_4$ solution, is digested with oxalic acid, and the insoluble $Th(C_2O_4)_2$ is filtered and washed free from $UO_2C_2O_4$. It is planned to return the uranium oxalate solution containing approximately 96% of the U from the cold peroxide machine wash effluent directly to the original machine wash solution. Current investigations seem to indicate that the oxalate to be returned as $UO_2C_2O_4$, is of insignificant concentration to effect the cold peroxide precipitation[9].

The initial thorium, now as $Th(C_2O_4)_2$, and containing approximately 4% U unremoved by the oxalate extraction can be treated with an acid $KMnO_4$ solution, to decompose the oxalate and be reused in the original thorium coprecipitation. Thus any uranium occluded with the oxalate cake is eventu-

ally returned to the machine wash after repeated reuse in the primary and secondary cycles.

The effluent from the thorium peroxide, containing less than 1 mg/gal. of uranium, can be discarded or salvaged.

III Factors Effecting Successful Coprecipitation of Th_2O_7-UO_4

Considerable preliminary work involving small scale pure and synthetic systems produced valuable data concerning the effect of other metal ions, pH control, minimum wtTh/wtU ratio, H_2O_2 concentration, limits of U concentration, time of aging and rate of centrifugation, on the coprecipitation of Th_2O_7-UO_4.

A. Effect of pH

Efficient Uranium removal becomes more perceptible with increasing pH over a range of 1.0 to 2.0, and although control of the pH is not critical (± 0.15) at 2.0, incomplete precipitation and an unfilterable product readily results at a range less than 1.8. Precipitation above the range of 2.3, as in any cold peroxide treatment, usually results in the hydrolysis of iron, considerable cake contamination, and subsequent peroxide decomposition.

B. Presence of Other Metal Ions

Other metal ions present in solution, when in the range of Beta process machine wash effluents, seemed to have very little effect on the precipitation. A comparison of the centrifuged cakes and those filtered through fine sintered glass, showed a more compact and cleaner product in the former case. It was evident only with increasing concentrations of metal ions (.3% Fe and .3% Cu) that uranium solubility increased significantly.

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Incomplete data on cake contamination indicates that under optimum conditions, contamination by other metal ions is negligible. Regardless, this should be of no great concern, for the product is eventually returned to the original machine wash solution and reprecipitated with the bulk of uranium as $TO_4 \cdot 2H_2O$.

C. Wt.Th/Wt.U Ratio

A more thorough investigation of the wt.Th/wt. U ratio is necessary before a definite conclusion can be drawn concerning its optimum range. At present a Th/wt. U of 20 to 30 has produced excellent results and the efficiency seems to increase with increasing ratios. Decreasing this ratio tends to delay precipitation and one run, R-18, after aging for one hour showed a marked increase in uranium solubility.

TABLE I

EFFECT OF wt.Th/wt. U VARIATIONS

Run	pH	MgT/L Added	wt.Th/wt. U	MgU/L eff.(fluorescence)
R-15	1.5	50	10	9.2
R-13	1.5	50	20	7.5
R-18	2.0	300	3.33	80
R-17	2.0	100	10	1.0
*R-12	2.0	51	20	0.26
G-1	2.0	30	33	0.09

Conditions: 1 liter solution precipitated; -pH=2.0; temp.= $4^{O}C$; 30 gms. NH_4NO_3; (H_2O_2)=.5M - $\frac{1}{2}$ - 1 hr. aging before centrifugation.

Results of the preceding pure Th-U solutions indicate very strongly that the coprecipitation becomes more quantitative with increasing pH and wt.Th/wt. U ratio.

* .04% Fe added

Further investigation is planned shortly on the effect produced
by varying the Th/wt. U ratio with varying pH's.

D. H_2O_2 Concentration

Numerous runs seem to substantiate evidence that significantly
decreasing H_2O_2 concentration retards the formation of thorium peroxide.
The optimum H_2O_2 concentration appeared to be approximately .5 M and de-
crease in uranium solubility remained negligible with increase of H_2O_2
above this range.

TABLE II

EFFECT OF H_2O_2 CONCENTRATION ON COPRECIPITATION

Run	H_2O_2 M/L	MgU/L	MgTh/L	MgU/L effluent
P-17	.1	30	1000	1.6
P-16	.2	30	1000	0.3
P-10	.5	30	1000	0.2
P-30	1.0	30	1000	0.2

Conditions: pH=2.0; Tem.= 4°C; synthetic machine wash used con-
taining Fe=.05_, Cu=0.3%, Ca=.1%, Cr=Ni=.02% and
$NH_4Cl=NH_4NO_3=1.7\%$. Aged 1 hour and centrifuged.

E. Limits of Uranium Concentration

It was previously reported that 1 gram of Th/liter was incapable
of coprecipitating 100 mg U/L successfully. Since 100 mgU/L is inconsistent
with normal Beta machine wash effluents, it was not considered of a serious
nature. Nevertheless, it seemed to indicate that increasing U concentra-
tion was a critical factor in efficient uranium removal.

More recent work (Table VIII) involving actual enriched Beta
machine wash effluents seemed to discount this theory, for runs with

effluents containing 100 - 200 mg U/L and 1 gr Th/L were reduced upon coprecipitation to more negligible quantities than effluents containing approximately 10 mg U/L.

Closer investigation of actual plant effluents revealed that part of the uranium actually existed as colloidal $UO_4 \cdot 2H_2O$. The postprecipitated UO_4 seemed to act as a seed for the precipitation, and was readily occluded with the formation of Th_2O_7, insuring a more complete U removal.

It can presently be stated that a concentration of approximate 200 mg U/L can be efficiently removed by the coprecipitation process if a significant part of U is present as colloidal $UO_4 \cdot 2H_2O$. It thus appears very possible that additional material with small amounts of U destined for eventual recovery can be blended into machine wash effluents and successfully treated by the thorium coprecipitation process.

Efficiency of the coprecipitation appears to decrease with U concentration less than 5 mg/L. This condition may not be entirely valid, for the few runs observed produced conflicting results due to incomplete centrifugation. Considerably more investigation is contemplated on this phase shortly.

TABLE III

EFFECT OF U CONCENTRATION ON THORIUM COPRECIPITATION

Run	Initial U mg/L	U/mg/L eff.	U Present as
P-14	100	13	$UO_2(NO_3)_2$ - added with Thorium
39	108.8	3.6	$UO_2(NO_3)_2$ - " before "
42	108.8	0.80	3/4 $UO_2(NO_3)_2$ 1/4 TO_4 ADDED BEFORE THORIUM
*B- 8	100	0.03	$UO_2(NO_3)_2$ UO_4
*B-18	120	0.07	" "
*B-34	157	0.08	" "
*B-27	6.9	0.80	"
*B-39	10.0	0.03	'
X- 4	0.5	0.2	"
G-15	2.0	0.06	"

Conditions: Th = 1 gr/L; pH = 2.0; Temp. = 4.0°; H_2O_2 = .5%; aged 15 minutes to 1 hour before centrifugation. Synthetic solution used - Fe = .05%; Cu = .5%; Ca = .1%; Cr = Ni = .025%; NH_4Cl = NH_4NO_3 = 1.7%.

* 1300 Uranium used

F. Rate of Addition and Time of Aging

Rate of precipitant addition and aging of precipitate have always been important factors in the successful development of any process.

Present information shows no evidence that the rate of thorium nitrate addition has any influence on the results of the process. Numerous runs were undertaken in which the precipitant was added rapidly to the solution. Efficient agitation with addition of the thorium nitrate solution seems to insure quantitativeness of the reaction almost immediately, and as presupposed, it is no longer necessary to extend the time of aging of the

precipitate, more than 15 minutes, after addition of the precipitant.

In the runs illustrated in Table IV a close study was made of rate addition of the precipitant, time of aging and corresponding effluent analysis. In practically all cases, it appeared that uranium solubility was at a minimum about 15 minutes after completion of the reaction. This immediate quantitativeness is of prime importance in reducing the time element of the cycle.

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TABLE IV

EFFECT OF RATE OF THORIUM NITRATE ADDITION[1]

AND TIME OF AGING OF PRECIPITATE

Run	MgU/L	Time of Aging Before Centrifugation in min.	Mg U/L of Centrifuged Effluent
44	28.1	5	.03; .03
37	28.1	5	.72; .66
38	28.1	5	.32; .29
49	28.1	10	.18; .11
45	28.1	15	.05; .05
47	28.1	15	.09; .09
48	28.1	15	.22; .16
50	28.1	15	.07; .07
51	28.1	15	.08; .12
43	28.1	30	.20; .20
36	28.1	45	.22; .22
46	28.1	45	.24; .15
*B-44	31	15	.05; .03
*B-45	22	15	.12; .12
*B-46	24	20	.07; .07
*B-47	23	20	.07; .03

Conditions: 20 liter solutions precipitated Th = 1 gr/L; pH = 2.0 @ 4°C; H_2O_2 = .5M. Synthetic solution approximating actual Beta effluent used - Fe = .05%, Cu = .3%, Ca = .1%, Cr = Ni = .02%, NH_4Cl = NH_4NO_3 = 1.7%

* Indicates actual B-cold peroxide effluent used. [1]$Th(NO_3)_4$ Solution in all cases was added rapidly or over a 1 - 2 minute period.

G. Effluent Salt Concentration

Since the plant effluents contain sufficient salt concentration, no further addition is necessary.

Synthetic runs were usually enhanced with approximately a 3% NH_4NO_3 solution to insure the rapid coagulation of the precipitate.

Actual plant and synthetic runs were studied closely with and without the addition of electrolytes. In each case, where synthetic runs were precipitated without the addition of electrolytes, extensive delay was observed in the time of precipitation and rarely was the precipitation quantitative.

In the presence and absence of additional electrolytes to actual plant effluents, the efficiency of recovery remained unaffected.

TABLE V

EFFECT OF ELECTROLYTES ON COPRECIPITATION

Run	Mg's U/L	gm Thorium/L	Electrolyte	mg's U/L effluent
40	30.5	1	----	1.02, .99
41	30.5	1	3% NH_4Cl	.12, .27
*B-40	30.0	1	----	.06, .06
*B-41	24	1	3% NH_4NO_3	.12, .06

Conditions: pH = 2.0 @ 4°C; H_2O_2 = .5M actual and synthetic gunks used to make up precipitating medium.

* Actual cold peroxide machine wash effluent.

H. Centrifugation

Great care is necessary in adjusting the rate of centrifugation. If not controlled properly, this simple operation may readily result in the loss of considerable uranium.

In the laboratory pilot plant, one liter per 2-1/2 minutes seemed a reasonable rate for successful centrifugation. Frequent sampling of the effluent may show slow formation of solid material. This, obviously indicates too rapid centrifugation and accordingly, the flow rate should immediately be reduced until the separation is complete.

Pilot plant runs at Purdue University involving 100 gallon synthetic batches, successfully averaged approximately one gallon per minute for centrifugation. It is obvious then, that efficiency of the process increases also with size and type of equipment.

IV Quantitative Data Enveloping the Coprecipitation of Uranium and Thorium Peroxides from Synthetic Solutions

A. Pilot Plant Data

A series of runs, Table VI, utilizing 15 Liter synthetic solutions previously enhanced with sufficient ion concentrations comparable to those found in Beta cold peroxide machine wash effluents, were conducted in the laboratory on a pilot plant scale.

Each run was made under predetermined basic optimum conditions; pH = 2.0, H_2O_2 = .5M, temp. = 4°C, 1 gr Thorium/L. For control purposes the concentration of Uranium was maintained constant, except in a few cases where the effect of its concentration was being investigated.

Considerable emphasis was laid on rate of addition of the precipitant and time of aging before centrifugation. Although 15 minutes seem sufficient for addition and aging time before centrifugation, it is well to note that this time is not a critical factor, for the precipitation is practically quantitative immediately.

In all runs except where extreme variations were exerted, effluent

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analysis were well under 1 mgU/gallon.

The pH 2.38 @ 4°C was taken as corresponding to H ion concentration of 1.0×10^{-2} from Beckman temp. corrections, after the Beckman meter was adjusted to read 4.0 when the electrodes were immersed in standard pH 4.0 buffer at 25°C.

TABLE VI

PILOT PLANT RUNS ON SYNTHETIC BETA MACHINE WASH EFFLUENTS

Run	Volume of Solution	pH*	H_2O_2 M	Initial Thorium mg/L	Initial U mg/L	Mg U/L Effluent	Total Time for Rate of Addition and Aging Before Centrifugation
36	20	2.38	.5	1000	28.6	0.22, 0.22	45 minutes
37	20	2.38	.5	1000	28.6	.72, .66	5 "
38	20	2.38	.5	1000	28.6	.32, .29	10 "
39	20	2.38	.5	1000	108	3.6 , 3.6	1 hour
40	15	2.38	.5	1000	30.5	1.02, .99	no electrolyte added
41	15	2.38	.5	1000	30.5	.12, .27	NH_4Cl added
42	20	2.38	.5	1000	108	.93, .67	1/4 U as UO_4
43	15	2.38	.5	1000	28.1	.20, .20	30 minutes
44	15	2.38	.5	1000	28.1	.03, .03	10 "
45	15	2.38	.5	1000	28.1	.05, .05	15 "
46	15	2.38	.5	1000	28.1	.24, .15	45 "
47	15	2.38	.5	1000	28.1	.09, .09	15 "
48	15	2.38	.5	1000	28.1	.22, .16	15 "
49	15	2.38	.5	1000	28.1	.11, .11	10 "
50	15	2.38	.5	1000	28.1	.07, .07	15 "
51	20	2.38	.5	1000	28.1	.08, .12	15 "

Temperature 4°C. Composition of synthetic gunk: Fe = .05%, Cu = .3%, Ca = .1%, Cr = Ni = .02%, NH_4Cl = NH_4NO_3 = 1.7%.
In every case Mgs. Uranium /L effluent were analyzed in Mr. C. D. Susano's laboratories by Penta-ether extraction-fluorescence analysis.
Thorium added as 10% $Th(NO_3)_4$ solution.

* See page 15, last paragraph for pH convention.

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B. <u>Use of Recycled Thorium in Uranium-Thorium Peroxide</u>
<u>Coprecipitation</u>

Since the wt. thorium / wt. uranium ratio 20 - 30 has proven most satisfactory, it was decided to reclaim and reuse the original charge of thorium as many times as necessary to prove the feasibility of treating the actual plant material in such a manner.

A 15 liter synthetic solution emulating a typical machine wash effluent was precipitated under optimum conditions. The $Th_2O_7-UO_4$ cake was treated with oxalic acid, the resulting insoluble Thorium oxalate decomposed with $KMnO_4$ and dissolved in HNO_3. The oxalate filtrate was analyzed for recovered T.

The solution containing the reclaimed thorium was returned to another original synthetic machine wash effluent for reuse as the precipitant.

This procedure was repeated as many times as indicated under "Recycle #", Table VII.

TABLE VII

EFFECT OF RECYCLED THORIUM ON COPRECIPITATION

Recycle #	Initial Th mgs/L	Initial U and Mgs U/L Total /L		Mgs U/L effluent	U in Ox filtrate mgs.
0	1000	458	30.5	.15, .12	411
1	1000	458	30.5	.28, .24	482
2	1000	458	30.5	.30, .21	461
3	1000	458	30.5	.31, .31	448
4	1000	458	30.5	.60, .48	416
5	1000	no U added		.06, .06	19.7
6	1000	458	30.5	.60, .53	451
7	1000	458	30.5	.21, .15	434
8	--------------$Th_2(C_2O_4)_2$ sol. from R-7				12

A Uranium balance on the recycle indicated that of the total 3206 mgs. involved, 3135 mgs were accounted for in the oxalate filtrate and 35 mg escaped with the Thorium effluent. Results based on volumetric and fluorescence analysis respectively.

Reuse of 15 grams of Thorium as a precipitant on eight successive runs, thus resulted in a 98% recovery of Uranium and an average effluent loss of well under 1 mg/gallon. The unaccounted 2% can be attributed to the present inefficient laboratory pilot plant centrifugation system.

It is safe to assume that with the increased efficiency of centrifugation and general procedures resulting from actual large scale plant equipment, no material will remain unaccounted for. Some data is presently available on the loss of thorium from the original charge (see page   ).

According to Alpha counting experiments[*], and Th_2O_7 solubility determinations[*] equilibrium constants for Th and U show:-

$$\frac{(Th)(H_2O_2)^{3/2}}{(H)^4} = K = 1.5 \times 10^{-3}$$

$$\frac{(UO_2)(H_2O_2)}{(H)^2} = K = 1.3 \times 10^{-3}$$

Since thorium solubility is relatively similar to that of uranium, then on a plant scale, one pound of thorium can be successfully reused many times without fear of significantly reducing the optimum Th/wt. U ratio.

V   Quantitative Data Enveloping Coprecipitation of Th_2O_7-UO_4 from 1300 Cycle Machine Wash Effluents.

   A.   Pilot Plant Data

[*] Work done by H. Cragg and H. Grady respectively. A more complete discussion of these phases will be presented in separate reports in the near future.

A series of 51 runs were carried out on actual machine wash efflu-
ents obtained from the Beta plant after cold peroxide treatment of machine
wash solutions.

Two batches each day were received from the process group. These
batches, usually 18-20 liters, were maintained at $4^{\circ}C$ until precipitation.

Prior to precipitation, samples of each corresponding batch re-
ceived were analyzed by C. D. Susano's group for total uranium. As the
initial uranium concentration varied considerably day by day, it was decided
to obtain a rapid polarographic analysis. This method noticeably decreases
in efficiency with increasing uranium concentration and so, too much empha-
sis cannot be placed on the results, if a uranium balance is being sought.
The analysis was desired primarily for a rough determination of the total
uranium present and thus an estimate of the efficiency of the thorium car-
rier method.

Effluents from the thorium coprecipitation were analyzed by the
more accurate and reliable fluorescence method.

Upon receipt of the effluent, a permanganimetric determination for
H_2O_2 was performed. The pH, if necessary, was adjusted to 2.38 at $4^{\circ}C$ be-
fore addition of sufficient H_2O_2 to make the effluent .5M.

A 10% aqueous solution of the $Th(NO_3)_4$, based on one gram of
Thorium/liter of effluent, was added to the solution and the pH readjusted
in cases where necessary. Quite often the pH of the plant machine wash
effluent recieved in the laboratory ranged from 2.6-2.8 @ $4^{\circ}C$, and in this
case no adjustment was necessary, for upon addition of the thorium, the pH
usually dropped to 2.3 @ $4^{\circ}C$ or the true pH = 2.0 @ $25^{\circ}C$.

Centrifugation was usually in progress 15 minutes after precipi-

tation and two effluent samples in each case were taken for analysis. Table VIII.

The purpose of using actual plant effluents was towfold. First to measure realistically the efficiency by which small quantities of uranium could be recovered with aid of the thorium coprecipitation process, and second, the separation of uranium from thorium and reclamation of thorium for reuse as a precipitant.

As can be established from Table VIII under column labeled "Cycle #", the initial charge of 20 grams of thorium - based on the average volume and 1 gram Th/liter - was recovered and reused a total of seven times.

The method of recycle consisted of combining six separate charges of thorium as $Th(C_2O_4)_2$ into one large batch, from which the total thorium was recovered as $Th(NO_3)_4$. The recovered thorium was divided into 6 equal volumes and reused as previously. This process was repeated on 7 occasions.

After the fifth recycle, it was found that 90% of the initial thorium charge was still present. The final two recycles showed no decrease in the thorium carrier efficiency.

The thorium loss was of no great consequence for it's initial ratio of 20-30, wt. Th/wt. U, was considerably in excess. Nevertheless it may be valuable practice to check the strength of thorium in the recycle at various intervals at the start of the process. Since $Th(C_2O_4)_2$ is very insoluble, theoretically the only thorium capable of escaping is that through poor centrifugation.

As previously stated, the polargraphic analysis offers no great accuracy with increasing uranium concentrations, results, often varying by 10%. Thus no desire to maintain an accurate uranium balance was intended.

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TABLE VIII

STUDY OF THORIUM CARRIER PROCESS UTILIZING 1300 URANIUM

Run	Effluent Volume in Liters	Initial Uranium Mgs	PH Start	Finish	H_2O_2 M	Cycle #	Aging hrs.	Centrifuged hrs.	Uranium Effluent-mgs	Remarks		
B-7	20	76	2.7	2.4	.5	0	1/2	1	.03, .14	350gmNH$_4$NO$_3$; 350NH$_4$Cl, 400ccH$_2$O$_2$ added		
B-6	20	72	2.6	2.38	.5	0	"	"	.16, .16	"	"	"
B-8	20	100	----	2.38	.5	0	"	"	.03, .03	"	"	"
B-9	20	96	----	"	.5	0	"	"	.03, .03	"	"	"
B-10	15	81	2.6	"	.5	0	"	"	.04, .07	250	250	300
B-11	20	84	2.6	"	.5	1	"	"	.44, .68	350	350	350
B-12	20	44	2.8	"	.5	0	"	"	.03, .03	"	"	"
B-13	20	44	2.8	"	.5	0	"	"	.03, .03	"	"	"
B-14	20	15	2.8	"	.5	2	"	"	.09, .13	"	"	"
B-15	20	12	2.8	"	.5	0	"	"	.09, .13	"	"	"
B-16	20	21	2.75	"	.5	1	"	"	.22, .29	"	"	"
B-17	20	24	2.75	"	.5	2	"	"	.22, .22	"	"	"
B-18	20	120	2.3	"	.44	2	"	"	.06, .09	"	----	H$_2$O$_2$ titrated with KMnO$_4$
B-19	20	----	2.3	"	.45	2	"	"	.06, .09	"	----	"
B-20	20	48	2.8	"	.45	2	"	"	.03, .03	"	----	"
B-21	20	63	2.8	"	.43	2	"	"	.06, .06	"	----	"
B-22	19	----	----	"	.34	3	"	"	.09, .15	"	----	.16M H$_2$O$_2$ added
B-23	20	----	----	"	.33	3	"	"	.12, .15	"	----	.17M

TABLE VIII

(Continued from the preceding page)

STUDY OF THORIUM CARRIER PROCESS UTILIZING 1300 URANIUM

Run	Effluent Volume in Liters	Initial Uranium Lgs	PH Start	PH Finish	H_2O_2 u	Cycle #	Aging mins.	Centrifuged hrs.	Uranium Effluent-mgs	NH_4NO_3 g	Remarks H_2O_2 added
B-24	19	42	——	2.38	.61	3	30	1	.15, .21	300	.00M
B-25	18.5	42	——	"	.62	3	"	"	.15, .15	"	"
B-26	20	7.8	——	"	.45	3	"	"	.64, .48	350	"
B-27	20	6.9	——	"	.45	3	"	"	.71, .97	"	"
B-28	20	60	——	"	.18	4	"	"	6.0, 6.9	"	.00
B-29	20	54	——	"	.19	4	"	"	1.5, 1.3	"	.00
B-30	20	10.8	——	"	.22	4	"	"	.09, .15	——	.25
B-31	20	15.6	——	"	.23	4	"	"	.18, .06	350	.25
B-32	20	26	——	"	.15	4	"	"	.15, .24	"	.34
B-33	20	26	——	"	.15	4	"	"	.15, .18	"	.34
B-34	20	157	——	"	.42	5	"	"	.03, .12	00	00
B-35	20	126	——	"	.42	5	"	"	.09, .54	350	00
B-36	19	13	——	"	.38	5	35	"	.46, .47	——	——
B-37	20	14	——	"	.38	5	40	"	.47, .50	350	.12
B-38	21	9.7	——	"	.28	5	57	"	.20, .35	——	"
B-39	19	10	——	"	.28	5	46	"	.03, .03	350	.22
B-40	20	30	——	"	.41	6	35	"	.06, .06	——	"

(Concluded on next page)

TABLE VIII

(Continued from preceding page)

STUDY OF THORIUM CARRIER PROCESS UTILIZING 1300 URANIUM

Run	Effluent Volume in Liters	Initial Uranium mgs	PH Start	Finish	H_2O_2 M	Cycle #	Aging mins.	Centrifuged hrs.	Uranium Effluent-mgs	NH_4NO_3 g Remarks	H_2O_2 added
B-41	20	24	—	2.38	.41	6	40	1	.12, .06	350	.10 M
B-42	20	25	—	"	.38	6	105	1-1/2	.16, .19	—	.11
B-43	20	26	—	"	.38	6	25	"	.61, .10	350	.12
B-44	20	31	—	"	.37	6	15	"	.12, .05	—	"
B-45	20	22	—	"	.37	6	15	"	.05, .03	350	.13
B-46	19	24	—	"	.26	7	20	"	.07, .07	—	"
B-47	19	23	—	"	.26	7	20	"	.07, .03	350	.24
B-48	18	32	—	"	.62	7	15	"	.22, .07	—	"
B-49	18	40	—	"	.62	7	15	"	.00, .00	—	—
B-50	19	25	—	"	.25	7	15	"	.15, .22	—	.25
B-51	18	41	—	"	.25	7	15	"	.26, .32	350	"

Conditions: Thorium = 1 gr/L; H_2O_2 = .5 M ; PH = 2.0 at 25°C or 2.38 @ 4°C; effluent from actual cold H_2O_2 precipitation used as precipitating medium.

720 024

The prime purpose was to prove the efficiency of the carrier process on actual plant material and of 225 gallons treated the effluent loss averaged well below 1 mg/gal.

B. Effect of Temperature on Coprecipitation

Recently a desire was expressed to investigate the possibility of carrying the reaction out at higher temperatures.

It does not seem very feasible to carry the reaction out at room temperature 25°C, in the presence of H_2O_2 decomposing ions. Although their concentrations are not great, the resulting catalytic action on the decomposition at 25°C may be sufficient to retard, and cause incomplete precipitation along with considerable contamination of the precipitate.

Since it is not reasonable to expect that the temperature of a cold peroxide machine wash effluent, upon prolonged standing and continued water cooling, should rise above 15°C, this temperature was selected as the basis for further investigations.

TABLE IX

ACTION OF COPRECIPITATION AT 15°C

1 liter solutions precipitated	Run 1	Run 2
Settling of precipitate	normal	normal
H_2O_2 decompose	"	"
Mgs U/L effluent	.22	.24

Conditions: Th = 1 gr/L. U = 22.9 mg/L, H_2O_2 = .5M, pH = 2.0, Temp. = 15°C.

Actual thorium centrifuge effluent from original Beta machine wash effluent used for precipitating medium. Both solutions filtered 10-15 minutes after

precipitation.

Both precipitates settled at a normal rate and H_2O_2 decomposition, although normal, was noticeably more rapid than runs at $4^{o}C$.

Effluent analysis indicate that both runs are below 1 mg U/gallon.

Further investigation on the action of higher temperatures is contemplated shortly on numerous pilot plant batches.

VI Tentative Recommended Plant Operating Procedure

It is intended by the proposed operating procedure to develop a basic plan for plant use which will include specific optimum conditions that have already proven successful in numerous laboratory pilot plant experiments.

As stated this is merely a basic plan, and undoubtedly considerable cirticism and improvements can be offered.

1. Adjust the pH of the peroxide effluent from the machine wash to 2.7-2.8 @ $4^{o}C$ * approximately 2.35 at $25^{o}C$ with the appropriate neutralising agent.

2. Titrate permanganimetrically, an aliquot sample of the effluent for available H_2O_2 and add sufficient 30%·H_2O_2 to make the solution .5$\underline{M}$.

3. Add to the effluent, over a few minute period, a 10% aqueous Thorium nitrate solution 1 g-Thorium/liter effluent .

4. Upon complete addition of the thorium solution, the pH @ $4^{o}C$ should drop to 2.3-2.4. If below or above this range, readjust with appropriate acid or base.

5. Agitate solution for 5 minutes after precipitation, and begin

* See page 15, last paragraph, for pH convention

centrifugation about 15 minutes after reaction is complete. Slow agitation is necessary throughout the centrifugation to prevent the precipitate from clogging or seeping through the centrifuge bowl in one mass.

6. Considerable care should be taken to observe the passage of any solid material through the centrifuge. If this condition is evident, immediate reduction in the flow rate is necessary for a more complete centrifugation.

7. Upon completion of the centrifugation the Th_2O_7-UO_4 cake is quantitatively removed from the centrifuge bowl and digested for one hour on a steam bath with the theoretical, plus 10% excess, oxalic acid added in solid form.

8. The insoluble Thorium oxalate is filtered from the solution, treated potentiometrically with an acid $KMnO_4$ solution to decompose the oxalate and the solution reused per second as the precipitant in the next cold peroxide effluent.

9. The filtrate containing the bulk of uranium, from the machine wash effluent, as $UO_2C_2O_4$, is returned as is to an original machine wash solution for blending and precipitation by the cold peroxide treatment.

VII Analytical Methods

A. Fluorescent Analysis for Minute Amounts of Uranium With Thorium Present

To date the fluorescence method of analysis for minute amounts of uranium in solutions with comparable thorium concentrations has proven to be the most feasible[3].

Thorium in concentrations of 10-15 mg/L exhibits a quenching effect on the analysis, but due to the fact that the thorium concentration in the reported analyzed solutions is comparable to the U concentration, the results can be considered approximating the true values.

To substantiate this statement, samples submitted for the regular pentather extraction and fluorescence analysis were also analyzed by the recently developed diethyldithiocarbamate-fluorescence method.

This method is an extension of the pentaether fluorescence and although more tedious, claims a higher degree of accuracy in the presence of thorium.

The method[4] developed in the analytical research section of this division, takes advantage of the preliminary pentaether extraction. By pH adjustment of the solution from the etherate to 6.7 ± 0.1, and the addition of a 2% diethyldithiocarbamate solution, a U complex, easily extractable with $CHCl_3$, is formed. Subsequent fluorescence analysis can then be carried out on the thorium-free $CHCl_3$ layer.

A comparison of the pentaether fluorescence and diethyldithio-carbamate methods follow in table X. As indicated, both methods agree fairly well and differences at the most average no more than a factor of 2-3.

TABLE X

COMPARISON OF PENTA ETHER AND

CARBAMATE FLUORESCENCE ANALYSIS URANIUM, mg/L

Run	Penta Ether	Carbamate
P-24	0.2	0.18, 0.17
P-28	0.2	0.6, 0.6
P-33	0.2	0.29, 0.45
*B-44b	0.12	0.22
*B-45b	0.03	0.09
*B-45c	0.05	0.10

Above runs under optimum conditions.
* Indicates 1300 material used in run.

Further evidence supporting the accuracy of fluorescence methods was obtained from a series of runs in which solutions of known uranium concentrations were submitted for analysis.

In each case, results corresponded very closely with the material added.

TABLE XI

PENTA-ETHER-FLUORESCENCE ANALYSIS OF SOLUTIONS WITH

KNOWN URANIUM ADDED

	Added Mgs U	Flourescence-Mgs U found
NATA-3	1.1	.96
NATB-3	.06	.15
NATE-1	.00	.12
NATE-2	.55	.52
NATD-1	.00	.00
*NATF-2	6.3	5.7

All above solutions from synthetic thorium effluents, precipi-
tated under optimum conditions, before uranium added.

* Run NATF-2 - 10cc of effluent containing 2.5 mg uranium by previous
fluorescence analysis and sufficient uranium to total 6.3 mg added.

B. Analysis of Th_2O_7 - UO_4 Cakes for Uranium

In each case where a material balance or a check on the efficiency
of the thorium and uranium separation was desired, the cake was quantita-
tively removed from the centrifuge bowl, digested on a steam bath for one
hour with the theoretical plus 10% excess oxalic acid solution and $.1\underline{M}$ HNO_3,
and the $Th(C_2O_4)_2$ filtered off. The filtrate was fumed with H_2SO_4, insolu-
ble SO_4s filtered off, and the solution electrolyzed to remove Fe and other
reducible ions. Upon completion of the electrolysis, the solution was passed
through a Jones reductor and titrated with $K_2Cr_2O_7$ for uranium.

The $Th(C_2O_4)_2$ cake was treated with theoretical $KMnO_4$ to decompose
the oxalate, the solution treated with $HClO_4$, electrolyzed, and prepared for
analysis as above.

C. <u>Analysis of Th_2O_7 - UO_4 Solutions for Increasing Thorium Concentration</u>

On a few occassions where recycled thorium was used, it was desired to check and compare it with its initial concentration. A rapid determination was performed by precipitating an aliquot of the Thorium nitrate solution with $H_2C_2O_4$, filtering the $Th(C_2O_4)_2$, drying and igniting it at $1000°$ to the oxide and calculating per cent Th.

As is to be expected for safety and control measures, a fairly rapid method for the determination of minute amounts of thorium in solution is desirable. Many methods have been proposed[5] but all seem impracticable because of serious limitations imposed by the presence of increasing amounts of uranium or failure to detect minute amounts of thorium.

A search of the literature has produced one method[6] which seems promising. It is capable of determining thorium in the range of 5 to 85 micrograms, with uranium in quantities less than 1000 micrograms causing no interference.

The method makes use of a recently reported complex organic reagent[7], 2-hydroxy-3, 6-disulfonapthalenazobenzene-2-arsonic acid, which forms a precipitate with
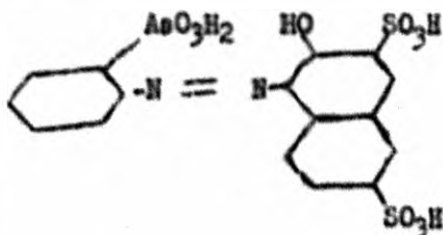
thorium, the color of which differs from that of the reagent. Determination of the thorium present is accomplished merely by ph adjustment, addition of the organic reagent, dilution to required volume and spectrophotometric

measurement against a reference solution of the reagent.

Considerable work is contemplated shortly with this reagent, to develop a rapid analytical procedure or spot test for obvious plant control purposes.

Due to the difficulty of obtaining the reagent, it has recently been synthesised.*

D. Determination of H_2O_2 in Plant Ounks

Since it is advantageous to maintian a H_2O_2 concentration of 0.5% excess during the reaction, it was found feasible to measure the H_2O_2 concentration present in machine wash effluents, prior to the thorium treatment, by a simple permanganimetric titration.

E. Alpha Counting Experiments

From the results of earlier work on the development of a control method for the detection of minute amounts of uranium in the thorium plant effluent, α - counting does not appear very possible due to the incomplete precipitation by H_2O_2 of certain highly radio active substances in the thorium salts. It was found that the residue from a single H_2O_2 precipitation filtrate contained material which often gave counts up to 8000/min/mg.

It is obvious that a count of this magnitude would render it impossible to detect even milligram quantities of uranium in the presence of Th^{232} disintegration products $U =$ approximately 790 c/m/mg and any further attempt to develop an α - counting method for plant control was discontinued on these grounds.

However, a counting method to substantiate the quantitativeness of the thorium coprecipitation was developed, utilising previously purified

* Synthesis being carried on by H. Cragg, according to Kuznetsov's[7] method.

thorium. This method proved to be very tedious, for it necessitated numerous successive precipitations of the initial thorium.

Increasing the number of precipitations and reducing the time interval between precipitations produced favorable results, and it was shown that by the use of highly purified thorium, results comparable to the fluorescence method could be obtained.

An effort to reduce this tedious process of purification led to the use of methyl isobutyl ketone "Hexone" [8].

An aqueous solution of $Th(NO_3)_4$ was extracted with hexone, the hexone layer backwashed with water, reprecipitated with H_2O_2 and the precipitate redissolved in HNO_3.

A single extraction seemed to remove practically all the Th^{232} disintegration products or at least reduce the impurities to a count comparable to approximately 6 successive H_2O_2 precipitations. The residue counts in this case ranged from approximately 100-150 c/m and so it was evident that with the addition of some purified 1300 cycle uranium any appreciable filtrate count could then be attributed to uranium.

Approximately one gram of 1300 uranium was purified by ether extraction after electrolysis and counts were taken on increasing concentrations of this material.

TABLE XII

α-COUNTS/mg 1300 URANIUM

α - counts/min	Wt. of U(1300)
1102	.05 mg
2088	.10 "
3768	.20 "
5328	.30 "
6128	.40 "
6744	.50 "
8224	.60 "
8296	.70 "
9632	.90 "
10,120	1.0 "

Although counts/minute decreased by one-half with concentrations of 1300 uranium ranging above .4 mg, intensity of the radioactivity of 1 mg of 1300 material is still approximately twelve times greater than 1 mg of U^{238}. With this in mind it was fairly simple to count minute quantities of uranium in the presence of daughter free Thorium.

C.P. $Th(NO_3)_4$ was extracted with hexone and half of an aliquot was precipitated by H_2O_2; to the other half was added 10 mg of (1300) uranium and the solution was precipitated by H_2O_2 in a similar fashion. Both solutions were filtered and equal portions of the filtrates evaporated to dryness and counted.

TABLE XXII

DETERMINATION OF MINUTE QUANTITIES OF U BY α COUNTING

Run	Thorium Only	Counts/s Thorium and Uranium (1300)	U in Filtrate mg/l
A	156	124	- 1.4x10^{-3}
B	90	89.5	- 2.0x10^{-5}
C	158	183	1.1x10^{-3}
D	103	106	1.4x10^{-4}
E	80	98	6.8x10^{-4}

In each of the above cases it is apparent that the coprecipitation of thorium and uranium is very quantitative. Assuming by difference in run C, above, that 25 counts are due to the 1300 U, then we find 25/10,120 or approximately .001 mg uranium in the filtrate.

REFERENCES
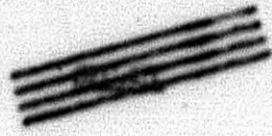
(1). C-0.380.4.

(2). B-2214.

(3). C-3.360.9.

(4). C-4.10025, 26 and 27.

(5). CC-3336, CC-2937, CC-2962, BB.369, CC-2670, P.1..

(6). P. Thomason, M. Perry and W. Byerly, Non C-6).

(7). Razmetaev, V. I., : Gen Chem (U.S.S.R.) 14, 914-19 (1944).

(8). CC-3246.

(9). C-2.361.9.

10/4b

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