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CHEMISTRY

UNITED STATES ATOMIC ENERGY COMMISSION

ZIRCONIUM PURIFICATION PILOT PLANT

By

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Photostat Price \$ 6.30

Microfilm Price \$ 3.00

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

September 12, 1950

Massachusetts Institute of Technology
Engineering Practice School
Oak Ridge, Tennessee

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
ENGINEERING PRACTICE SCHOOL

CARBIDE AND CARBON CHEMICALS DIVISION
Union Carbide and Carbon Corporation

AECD-3743

September 12, 1950

MEMORANDUM

EPS-Y109

TO: T. H. Pigford
FROM: D. C. Lea (leader), A. A. Aykanian, R. F. Abbanat, W. H. Bowman
SUBJECT: Zirconium Purification Pilot Plant

I. INTRODUCTION

To produce zirconium for a construction material in nuclear reactors, the zirconium must be free from the small amounts of hafnium impurity that are naturally present.

The hafnium is removed from a solution of zirconium tetrachloride by a solvent extraction process. In the present method of further treatment the purified solution is treated with salicylic acid, and the resulting precipitate of zirconium salicylate is roasted to convert it to zirconium oxide. No reuse of the salicylic acid is possible since it is all decomposed in the roasting step.

An alternate method for converting the $ZrCl_4$ solution to the oxide was investigated on a laboratory scale. In this method, the zirconium is precipitated as zirconyl phthalate, which is then leached with ammonium hydrox-

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ide to form zirconium hydroxide. The zirconium hydroxide is filtered from the solution containing the recovered phthalate, and the phthalate is recycled to the precipitation unit. By using this method only small amounts of the phthalate are lost.

Laboratory work was conducted by Googin and McLeod, (1), and Sprague, (3), to determine several of the optimum conditions for the zirconyl phthalate and zirconium hydroxide precipitations and for filtration of the two precipitates. Based on their findings, a pilot plant was set up for the complete conversion of zirconium chloride to the hydroxide, using phthalic anhydride and ammonium hydroxide as the processing chemicals. The objective of this investigation was to put the pilot plant into operation and to determine some of the optimum operating conditions. The work was done between August 24 and September 8, 1950.

The chemical reactions involved in this phthalate method are as follows:

This step is defined throughout the report as the precipitation step.

Reaction (3) is defined as the leaching process.

II. RESULTS

The following results illustrate the operation of the pilot plant and the recovery of the zirconium and phthalate:

1.

Table I

Run No.	5	5a	6	6a	8
ZrCl ₄ feed rate, gal/hr	7		7		7
Phthalate feed rate, gal/hr	?		?		?
Leaching hold-up time, min	0		77		30
Product rate, lbs/hr	15.2		6.6		34.6
% Zr in cake, dry	49.46	56.29	57.99	60.15	40.16
% C in cake, dry	33.19	23.96	21.67	18.75	46.00
% Phthalate lost in cake	22.8	2.7	neg.	neg.	52

- The loss of zirconium in the filtrate from No. 1 filter is negligible.
- Overall material balance on Run No. 8. (This was the only run from which enough information was obtained to calculate a complete material balance).

Zirconium In

Feed 4.2 lbs/hr

Total 4.2 lbs/hr

Zirconium Out

Filtrate No. 1 0.009 lbs/hr.

Filtrate No. 2 0.017 lbs/hr

Cake No. 2 4.94 lbs/hr

Total 4.97 lbs/hr

Phthalate In

Feed 8.46 lbs/hr

Total 8.46 lbs/hr

Phthalate Out

Filtrate No. 1 1.83 lbs/hr

Filtrate No. 2 3.98 lbs/hr

Cake No. 2 5.45 lbs/hr

Total 11.26 lbs/hr

Other Components In

ZrCl₄ Feed 54.2 lbs/hr

Phthalate Feed 50.1 lbs/hr

1st Wash 29.2 lbs/hr

Leach 58.4 lbs/hr

2nd Wash 11.7 lbs/hr

Total 203.6 lbs/hr

Other Components Out

Filtrate No. 1 133.5 lbs/hr

Filtrate No. 2 80.3 lbs/hr

Cake No. 2 22.7 lbs/hr

Total 236.5 lbs/hr

4. A conductometric analysis for the phthalate recycle was investigated from the viewpoint of obtaining a rapid and accurate method for the determination of ammonium phthalate in this stream. The conductance of ammonium phthalate solutions of varying pH are presented in Fig. 6.

III. DISCUSSION OF RESULTS

The effect of hold-up time on the amount of phthalate leached from the cake was not definitely established. The scatter of data was so great that several runs should have been made at each hold-up time to determine a mean value for phthalate leached at a given hold-up. One reason for the wide deviation was the analytical method used on the hydroxide cake. The sample was placed in an oven at 250°C to eliminate the H₂O, then in a muffle at 1000°C. The loss in weight at 1000°C is called percent carbon. The rapid decomposition which took place at the latter temperature tended to splatter the sample and cause losses which were reported as "carbon". The residue was assumed to be all of the ZrO₂ and weighed to determine the percent Zr. An alternate method of analysis is suggested in the Appendix.

The proper vacuum to maintain on No. 1 filter was approximately 2 in. of mercury, and on No. 2 filter, it was 7 in. of mercury. A greater vacuum produced a cake which cracked off and left the cloth exposed, with a resultant loss of very finely divided precipitate to the filtrate. A lesser vacuum did not remove sufficient water to permit a firm cake to form. The same results might not be characteristic of the cakes formed under other conditions.

Calculations based on the analysis of the filtrate from the first filter showed that 16% of the phthalate was lost in this filtrate. Since the zirconium losses in the first filtrate were almost negligible, the use of 10% or more excess phthalate does not seem justified. The same conclusion can also be inferred from the data of McLeod (1).

The percent phthalate loss reported in the Results section does not include the phthalate loss in filtrate No. 1 since this loss is a consequence of the excess phthalate used in the precipitation step and can be reduced by decreasing the excess phthalate. The reduction of phthalate losses in the hydroxide cake, however, is a fundamental problem of the process.

The drift in the flow rates during the two weeks of operation, precluded any rigorous error analysis or material balance. Recalibration of the pumps after the two weeks showed that the flow rates had varied as much as 40%. Consequently a material balance for the overall process served only as a rough indication of the accuracy of the flow rates. A material balance for run No. 8, the only one for which sufficient data were available, is presented. In runs No. 5 and 6 there were sufficient data, but during these runs it was discovered that the phthalate feed pump had been syphoning and that the actual flow rate was almost twice the value indicated by the calibration curve. Since it was not known how long or how constantly this situation had existed, data from these runs were not considered worthy of a material balance. Flow meters in the feed lines should help to eliminate these large errors in the flow rates.

The conductance of ammonium phthalate solutions was found to be nearly independent of the ammonium hydroxide concentration for the range of pH 8.5 to 10. This method would have provided a very rapid means of determining the phthalate concentration in the recycle, and could be adapted to provide a continuous check on the whole purification process. There was however some indication that the conductance of the solution was a function of the method of makeup. This point would have to be cleared up before the analysis could be used.

Operating Difficulties

1. Throughout the runs difficulty was encountered in getting the slurries to flow through the gravity legs between the hold-up tanks and the filters. The precipitate settled too fast in the bottom of the loops and clogged the lines. An overflow system to control the hold-up volume, followed by one downward path to the filter basin would eliminate this problem. The hold-up volume could be varied by the use of a vertical row of outlets on the side of the tanks.
2. When the finger pumps were recalibrated at the end of the investigation period, there was as much as 40% difference from the original values. Because a majority of the operation was at flow rates near the maximum capacity of the pumps, the gum rubber component of the pumps became worn, and the flow rates were affected. Also it was discovered that the pumps did not put out a constant flow rate under varying head conditions.

3. According to McLeod (1) the filters in this pilot plant could handle the quantity of feed solution containing approximately 100 lbs Zr/hr. At the maximum flow rates in the present investigation the Zr rate was only 6 lbs/hr. Therefore, the filters were operating at conditions far below the maximum possible filter rates. Unless a large fraction of the surfaces was masked, no calculations as to maximum capacity could be made.
4. The method used to control the vacuum pressure on the filtrate cycle was the partial blocking of the gauge connection on the distribution plate of the filter drum. To be able to control this vacuum a control valve should be installed at each of the gauge connections.
5. When the temperature in the No. 1 hold-up tank went above 95°C, the slurry foamed. A temperature between 92° and 95°C, the optimum temperature determined by the previous laboratory investigation, was desired. However fluctuations in the steam rate caused the temperature to rise above 95°C. The violent foaming which resulted might be prevented by the use of a suitable anti-foamant.
6. Small amounts of the filter cakes were drawn through the filter cloths and into the filtrate by the vacuum. At high vacuums the holes in the cloth were not plugged. Therefore, the use of a pre-coat should be investigated to prevent the loss of zirconium in the No. 2 filter.
7. In attempting to standardize the zirconium feed solutions, it was decided to adjust the H⁺ concentration to 0.2 moles/liter. However, after the calculated volume of ammonium hydroxide required was added, the pH did not correspond to the expected molality. Because of the presence of large amounts of ammonium thiocyanate in the feed, it was thought that a buffer effect was achieved upon the addition of ammonium hydroxide.
8. The pre-mixer was originally designed with concentric compartment glass housing the agitator rod, and the two feeds were introduced into this inner compartment. The resulting precipitate did not flow down the chamber and up the outside to the outlet as was hoped but rather filled the inner chamber and overflowed. When this shield was removed, the proper flow conditions were achieved.
9. At the maximum flow rate used, (10 gal/hr), the heating coil in the zirconium feed preheater could raise the solution temperature only to about 65°C. For better control of the hold-up temperature the feed temperature should be at least 80°C. A larger coil is needed if these flow rates are desired.

10. There were no drains on the premixer, gravity legs, recycle drum, or the catch basin under No. 1 filter. For a simpler shut-down procedure such drains should be installed.

IV. CONCLUSIONS

1. The use of ammonium phthalate to purify zirconium is practical on a pilot plant level.
2. Loss of phthalate can be reduced to less than 20%.
3. Zirconium losses can be reduced to negligible amounts.
4. Optimum operating conditions determined from the investigations of Googin, McLeod, and Sprague proved satisfactory.

V. RECOMMENDATIONS

1. Further investigation regarding the effects of leaching hold-up time and dilution of leaching slurry on phthalate recovery should be made.
2. The gravity legs on both hold-up tanks should be replaced by an over-flow system consisting of a series of outlets on the sides of the hold-up tanks. The flow should then be downwards to the filter.
3. A portion of the filter surface should be masked so that maximum filtration rates can be determined if desired.
4. A vacuum control valve on the filter distribution plates should be installed.
5. The use of a precoat for the filter cloths should be investigated.
6. Since the premixer outlet has a tendency to become plugged with precipitate, the entire unit should be replaced by a centrifugal pump. The phthalate and zirconium feed solutions should be mixed just before the entrance to the pump chamber.
7. The heating capacity in the preheater for zirconium feed should be increased.
8. A more powerful agitator in hold-up tank No. 2 should be installed, as the present Lightning mixer is not capable of preventing settling of the slurry.

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9. Drains should be installed in the recycle drum and catch basin for filter No. 1.
10. A new method for the analysis of hydroxide cake, described in the Appendix, should be attempted.
11. Flow meters should be installed in the zirconium feed, phthalate feed, and leach solution lines as a check on the flow rates.
12. The use of 10% excess ammonium phthalate was not justified and the excess should be reduced.
13. Further investigation of the effect of phthalate recycle make-up upon the conductivity as determined by a conductance meter should be carried out.

VI. PROCEDURE

Variables: To help determine optimum operating conditions for the pilot plant, it was necessary to establish the important variables involved in the zirconium purification process and then to determine for which of these variables optimum values had been established in the laboratory investigation. A list of the important variables and the optimum values for several of them as determined in the laboratory is included in the Appendix. The variables remaining to be optimized either by further laboratory work or by pilot plant operation were:

1. hold-up time for leaching process.
2. dilution of leached slurry.
3. dilution of precipitation slurry.
4. filtration rate for phthalate cake.
5. filtration rate for hydroxide cake.

Operation: A flow sheet of the pilot plant is shown in Fig. 1. Prior to a run, all solutions for the process were prepared in the respective tanks. The procedure for the make-up of the solutions is presented in the Appendix. The zirconium concentration in the feed solution was adjusted to 0.6 lbs/gal. for each run by adding the water required to reach this concentration. The H^+ concentration of the feed solution was standardized at 0.5 molal, the optimum value established in the lab-

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oratory investigation (3). The pH was determined on a Beckman pH meter, and the required ammonium hydroxide was added. The gravity leg from the hold-up tank No. 1 was adjusted to the height required for a hold-up time of thirty minutes, as indicated by the laboratory data to be the optimum for the zirconyl-phthalate precipitation.

To begin a run, steam for heating the phthalate solution tank and the zirconium feed was turned on in order that the optimum temperature of 90-95°C could be reached in hold-up tank No. 1. Then the zirconium feed and phthalate feed pumps were adjusted to give the proper flow rates and started. As the slurry reached hold-up tank No. 1, steam was admitted to the steam jacket to obtain the desired temperature. When the flow reached filter No. 1, the filter vacuum, air blast, drive motor, and wash were turned on. As soon as the cake was removed from the drum, the leach solution pump and agitator were started. The same procedure regarding the filter unit itself was repeated when the leached slurry reached filter No. 2. The wash and filtrate were collected in the recycle drum. Due to the addition of the wash to the filtrate the phthalate recycle was diluted. To offset this dilution, 20% was discarded, and the necessary make-up quantities of ammonium hydroxide and phthalic anhydride were added. In large scale operation, this loss could be avoided by keeping the filtrate and wash separate.

The temperature of the phthalate feed tank, preheater, and hold-up tank No. 1 was checked frequently, and steam adjustments were made until the temperature of the hold-up tank No. 1 was essentially constant between 90 and 95°C. After steady operation was established, samples were taken at various points throughout the pilot plant according to the sampling procedure in the Appendix.

The first four runs were conducted to overcome the operational and mechanical difficulties in the pilot plant in order that continuous operation could be achieved and worthwhile data could be obtained. Runs No. 5, 6, and 7 were conducted to vary the hold-up time for the leaching process. Run No. 8 was conducted to find the optimum vacuum for the two filters. In run No. 9, operation had to be stopped before any data were taken.

Flow rates were set from calibration curves for each pump. Filtrate rates were determined by weighing the total filtrate for a given run and dividing by the elapsed time.

VII. APPENDIX

A-1 Apparatus

A flow sheet of the zirconium purification pilot plant is shown in Fig. 1. The $ZrCl_4$ is fed from two 30-gal glass-lined tanks by a Sigma-motor finger pump through 3/8 in. Saran tubing to the preheater. The pre-heater is a 4 in. i.d. glass chamber heated by an immersed steam coil. The heated $ZrCl_4$ solution overflows from the preheater to the bottom of the premixer, which is a similar glass chamber.

The ammonium phthalate is prepared and stored in a steam-heated 55-gal stainless steel drum, fed into a steam jacketed 15-gal tank for preheating, and then metered by a finger pump to the bottom of the premixer.

The slurry in the premixer is agitated by an air-operated glass stirrer equipped with paddles. It overflows from the premixer through a 2 in. i.d. glass pipe to the No. 1 hold-up tank. This tank is also steam jacketed and has a large agitator driven by a Reeves variable drive. The hold-up volume is regulated by a 1 in. rubber hose gravity leg between the hold-up tank and the No. 1 filter.

The No. 1 filter is an Oliver Rotary filter, 1 ft x 1 ft, with Vinyon as the filter cloth (see Appendix for dressing procedure). The filtrate is pulled into a vacuum tank by a Nash Hytor vacuum pump and discharged to a 55-gal SS drum by means of a centrifugal pump. The speed of the stainless steel filter drum is controlled with a variable speed drive.

The cake is washed at the top of the rotating cycle and is loosened from the cloth by an air blast before being scraped from the drum by an adjustable doctor knife. The cake falls into a trough to which the leaching ammonia is fed, and the entire slurry is agitated by a variable speed paddle.

The leach solution and the wash solutions for both filters are fed from 55-gal stainless steel drums with Sigamotor finger pumps. The slurry from the leach trough overflows into a 10-gal ceramic hold-up tank. A Lightning agitator is used to keep the slurry from settling. The slurry then flows by gravity through a 1 in. rubber tube gravity leg to the No. 2 filter. This filter is similar to the first with the exception that the drum is made of cast iron rather than stainless steel. The filtrate is recycled to the recycle tank by a centrifugal pump.

The final cake from the No. 2 filter is caught in a stainless steel tray, weighed on a platform scale, and then stored in a 55-gal stainless steel drum.

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A-2 Summary of Previous Laboratory Work

Prior to the construction of a pilot plant for the purification of Zr by the phthalate method, a laboratory investigation was conducted to study the precipitation characteristics involved in the phthalate method, (1) and (2). This section is devoted to a summary of the work as derived from data books, No. Y-NB-1091 and No. Y-NB-1201.

The investigation was divided into three parts. Part one was a study of variables affecting the precipitation of Zirconyl phthalate from zirconium chloride feed solution using ammonium phthalate. Part two was a study of variables affecting the leaching process, whereby the precipitated zirconyl phthalate was converted to zirconium hydroxide by the use of an ammonium hydroxide leach solution. Part three was an investigation regarding the filtration of zirconyl phthalate and zirconium hydroxide cakes.

Precipitation of Zirconyl Phthalate

Investigated by Sprague. (Equal volumes of $ZrCl_4$ solution and ammonium phthalate solutions were mixed.)

Effect of Temperature on Zr Recovery

Temp	% excess $C_6H_4(CO_2NH_4)_2$	% original Zr lost in filtrate	Type of filtrate
53-57°C	5 %	1.700	heavy post precipitation
72-75°C	5 %	0.130	slight post precipitation
92-97°C	5 %	0.023	very slight post precipitation and foaming

Effect of Acid Concentration on Zr Recovery at 72-75°C

Final acidity (HCl molality)	% excess $C_6H_4(CO_2NH_4)_2$	% Zr in filtrate	Type of filtrate
* 0.19	5 %	0.027	clean filtrate
* 0.39	5 %	0.066	very slight post precipitation
0.44	5 %	0.130	slight post precipitation
0.51	5 %	0.290	post precipitation
* 0.69	5 %	0.700	" "
* 0.94	5 %	2.500	" "

* See next page.

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*Final acid concentrations reported here are calculated without regard for any buffer affect, but since the solution was later found to be buffered, they do not represent the actual H^+ concentration. The actual H^+ concentration for the most favorable "final acidity" of 0.190 was later determined by a pH meter to be 0.5M.

Effect of Excess Ammonium Phthalate on Zr Recovery

% excess $C_6H_4(CO_2NH_4)_2$	% Zr in filtrate	Type of filtrate
2.5	0.270	post precipitation
5.0	0.130	slight post precipitation
10.0	0.078	slight post precipitation

Investigations by Googin and McLeod.

Effect of Acid Concentration on Zr Recovery

After NH_4OH was added to the feed solution, which has a Zr conc. of 0.635 lb/gal, the mixture was then added to the phthalic anhydride.

Estimated acid	% loss of Zr to filtrate
0.25 m	2.03
0.36 m	2.76
0.46 m	7.80
0.40 m	9.40

Effect of Dilution on Completeness of Zr Removal

				% Original Zr lost in filtrate	
				Run I	Run II
1.	50 ml feed sol.	+ 50 ml $C_6H_4(CO_2NH_4)_2$		3.46	1.02
2.	" " " " " "	"	+ 50 ml H_2O	1.12	0.84
3.	" " " " " "	"	+ 100 ml H_2O	3.4	4.00
4.	" " " " " "	"	+ 150 ml H_2O	2.5	3.20

Effect of Hold-Up Time on Zr Recovery

<u>Hold-up time</u>	<u>% Zr lost to filtrate</u>
10 min	1.5
20 "	0.55
30 "	0.41
45 "	0.47

The solubility of zirconyl phthalate in a standard wash solution, in HCl (pH=1), or in water was negligible for all three washes. It was found that better zirconyl phthalate crystal size was obtained when the anhydride was dissolved in dilution water prior to addition to the feed solution. With the better crystal size, a filtration rate which was comparable to that obtained with salicylate cakes was possible.

Precipitation of Zirconium Hydroxide (Leaching)

Investigated by Googin and McLeod.

The Comparison between salicylic acid precipitation and phthalic anhydride precipitation after calcination.

<u>ZrO₂(phthalic)</u>	<u>ZrO₂(salicylic)</u>
98.7 % Zr recovered	94.4 % Zr recovered

The solubility of $Zr(OH)_4$ in leach solution was found to be negligible.

Effect of Temperature on Leaching Process

<u>Run</u>	<u>Temp.</u>	<u>% Zr in Cake</u>
I	25°C	54.5
II	25°C	56.2
I	50°C	54.2
II	50°C	56.1
I	first cold-then 75°C	54.1
II	75°C	56.1
I	95°C	52.1

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Effect of Leaching Time on Leaching Process

(1) liter of feed solution + 640 ml of 3.276 N NH_4OH + 360 ml of H_2O)

Leaching time	% Zr in cake	% zirconium phthalate leached to ammonium phthalate	<u>Confirmatory Tests</u>	
			% Zr in cake	
	Run I	Run I	Run II	Run III
5	63.4 *	91.5	60.4	63.0
10	62.1	93.5	57.8	63.8
15			59.2	63.2
20	62.7	86.6	63.1	64.4
30	59.6	85.8		
60	60.2	86.8		

* The stoichiometric percent of Zr in pure $\text{Zr}(\text{OH})_4$ is only 57.5 %. In this table and several following, higher percentages are reported. These data were taken directly from the data books of the investigators, where no explanation of this discrepancy was found.

Effect of Concentration of NH_4OH Leach on Leaching Process

Leaching time	% Zr in cake for 2.18 N NH_4OH	% Zr in cake for 2.08 N NH_4OH
5	54.4	63.4
10	56.4	62.1
20	65.4	62.7
30	56.2	59.6
60	55.0	60.2

Effect of Two-Stage Leaching

	% Zr in cake	% C in cake	<u>Confirmation Tests</u>	
			% Zr in cake	
1st leach (1 hr)	44.6	21.2	1st leach (10 min)	53.6
2nd leach (10 min)	60.7	6.88	2nd leach (6 min)	63.6
one stage leaching (1 hr)	60.2	8.00		

Effect of Temperature on Leaching Process for Various Leaching Times

<u>Time</u>	<u>% Zr in cake at 98-100°C</u>	<u>% Zr in cake at room temp.</u>
5	62.0	63.4
10	54.1	62.1
20	61.1	62.7

Effect of Agitation on Leaching Process

<u>Time</u>	<u>% Zr in cake with agitation</u>	<u>% Zr in cake without agitation</u>
5	55.1	63.4
10	56.6	62.1
15	56.5	
20	56.3	62.7

During present investigation some agitation was found necessary to prevent precipitate from settling out of solution.

Effect of Dilution on Leaching Process

<u>Time</u>	<u>% Zr in cake (diluted to 1000 ml total sol.)</u>	<u>% Zr in cake (diluted to 1500 ml total sol.)</u>
5	63.4	54.9
10	62.1	54.8
15		55.0
20	62.7	55.5

Effect of Excess NH_4OH on Leaching Process

<u>Time</u>	<u>% Zr in cake with 10% excess NH_4OH</u>	<u>% Zr in cake with no excess NH_4OH</u>
5	62.2	63.4
10	64.4	62.1
15	64.4	
20	60.7	62.7

Filtration Results

Investigations by Googin and McLeod.

Zirconyl Phthalate Precipitate (based on 1 ft diameter Oliver filter)

1. Density of phthalate cake was 121.1 lb/cu ft.
2. Void space of the phthalate cake was about 70 % of the total volume.
3. Data and plots for filtration and wash rates for phthalate cake (conducted on a laboratory scale) are shown on pages 80, 81, and 82 of data book No. Y-NB-1091).
4. Calculation results for 7/16 in. cake and displacement washing (enough wash water to occupy cake void space).

- a. Cake forming cycle at aspirator vacuum = 35 sec
- b. 1st drain cycle = about 7 sec
- c. Wash cycle (1b) = 7.5 sec
- d. 2nd drain cycle = about 12 sec

e. Total cycle:	<u>Time</u>	<u>% of Circumference</u>
Cake forming	35 sec	50
1st drain	7	10
wash	7.5	10.7
2nd drain	12	17.1

total = 61.5 sec
                                 other 12.2
                                 total = 100

Note - Assume 17 sections in Oliver filter. Use one section for cake removal and one section for flow back, therefore

15 sections would require 61.5 sec, and
 17 sections would require $17/15 \times 61.5 = 69.8$ sec.

Rotational speed = $\frac{60}{70} = 0.857$ rpm

Zirconium Hydroxide Precipitate (Leach Precipitate)

1. Density of leach cake (dried) was 3.125 g/ml.
2. Moisture content of leached cake was about 78 %.
3. Calculation results - for 1/4 in. cake and displacement washing:
  - a. Cake forming cycle = 40 sec/.26 lb Zr/sq ft
  - b. 1st drain = about 10 sec
  - c. Wash (0.15 gal/sq ft/.26 lb Zr) = 6.5 sec
  - d. 2nd drain cycle = about 12 sec
  - e. Total cycle:

	<u>Time</u>	<u>% of circumference</u>
cake forming	40 sec	51.5
1st drain	10	12.9
wash	6.5	8.4
2nd drain	<u>12.0</u>	15.5
	other	<u>11.7</u>
total =	68.5 sec	100

Note - Assume 17 sections in Oliver filter. Use one section for cake removal and one section for blow back.

15 sections would require 68.5 sec.

17 sections would require $17/15 (68.5) = 77.6$ sec.

Rotational speed = $60/77.6 = 0.773$ rpm

A-3 Detailed Operating Procedure

The feed, leach, and wash solutions are prepared as outlined in the section on preparation of solutions. The five finger pumps are set to meter the desired amount of solution, using the calibration charts prepared for each pump.

The zirconium chloride and ammonium phthalate solutions must be heated before the plant is put in operation. The main steam inlet valve is first opened and the pressure regulator adjusted to 10 psig. The valve for the ammonium phthalate tank steam coil is opened. (This valve setting will have to be changed as the ammonium phthalate is consumed, since this is

a batch process and the temperature of the feed will tend to increase as the liquid level drops). The steam to the preheater for the zirconium chloride is also turned on and left open during the run.

As soon as the desired temperatures are reached in both feed solutions, the respective pumps are started. The air valve for the agitator in the premix is then opened.

As the slurry from the premixer flows into No. 1 hold-up tank, the agitator is started and steam to the jacket is turned on and adjusted for the desired temperature. Also, the gravity leg must be adjusted to maintain the desired hold-up volume in the No. 1 hold-up tank.

When the slurry flows through the gravity leg into the No. 1 filter, the filter is started as follows; the drum motor is turned on and set for the desired speed, the water valve on the Nash Hytor vacuum pump is opened, and then the motor on the vacuum pump is started. As soon as the cake begins to form on the drum, the wash pump is started. Once the cake reaches the doctor knife, the air blast is opened, the leach pump is turned on, and the leach tank agitator is started.

The No. 2 hold-up tank and No. 2 filter are adjusted by the procedure just outlined. The filter cake off No. 2 filter is caught in a tray, weighted on a platform scale, and dumped into a storage drum.

The ammonium phthalate recycle is collected in the recycle drum until the drum is full. To prepare the recycle for re-use, the volume is measured, and 20% is discarded because of the dilution. It is then transferred to the make-up drum where the necessary make-up quantities are added.

A-4 Procedure for Preparation of Solutions

Zirconium Chloride ($ZrCl_4$) Feed

Zirconium chloride feed is transported from the tank-truck at the loading dock to the pilot plant by means of a 50-gal Hastelloy tank dolly. The contents of the dolly are discharged by air pressure into two porcelain-lined 30-gal feed storage tanks. Another 50-gal of feed is stored in the dolly.

The zirconium content of the feed solution in each tank-truck is recorded on the feed batch make-up chart. Using the calibration on the feed storage tanks and a suitable concentration graph, Fig. 2, the feed is diluted with water to 0.6 lb/gal Zr and the concentration recorded. A dilution of one part $ZrCl_4$ solution to ninety-nine parts distilled water, is used in determining the pH of the feed. The pH found is then recorded and adjusted to 0.3 by the addition of NH_4OH .

Ammonium Phthalate $[C_6H_4(CO_2NH_4)_2]$ Feed

The ammonium phthalate feed is made for start-up as follows: 33.47 liters of H_2O , 4.38 liters of 28.3% NH_3 , and 10.70 lb of phthalic anhydride per 10 gal batch are mixed in the make-up tank for at least 15 min before using. This corresponds to 10% excess ammonium phthalate. The pH of this ammonium phthalate should be adjusted to neutrality.

Once the pilot plant is operating, the filtrate from the No. 2 filter is recycled as ammonium phthalate feed. The recycle has been diluted due to the addition of the wash; therefore, based on the phthalate concentration determined by a conductance test and the volume of recycle in the tank, pre-determined amounts of phthalic anhydride and ammonium hydroxide are added. These amounts are based upon a graph prepared for this purpose. The pH is checked, and the solution is made neutral. After the batch is made-up, a sample is sent to the laboratory and the volume of recycle make-up recorded.

Wash for No. 1 Filter (H_2O)

Tap water is used as wash for No. 1 filter. This water is fed from a 55-gal stainless steel drum.

Leach Solution for No. 1 Filter (NH_4OH)

The leaching solution for No. 1 filter is made by adding 20.15 liters of 28.3% NH_3 to 133 liters of water, making a 40.5 gal batch. This solution is fed from a 55-gal stainless steel drum.

Wash for No. 2 Filter (2% NH_4OH)

The wash for No. 2 filter is made by adding 4.03 liters of 28.3% NH_3 to 133.6 liters of water and is fed from a 55-gal stainless steel drum.

A-5 Dressing Procedure for Oliver Filter

The filter cloth used in this process is Vinyon, a corrosion-resistant plastic fabric. A strip 1/2 in. wider than the drum is cut, and the edges are fused by heating to prevent ravelling. The cloth is then placed around the drum and secured in place by twelve 16 gauge (B. and S.) wire rods pressed into horizontal slots in the drum surface. These rods are held in place temporarily by twine, while a 21 gauge (B. and S.) wire is wound around the cloth for a permanent binding. Two turns are made next to either drum edge and are connected by a spiral of about a 3 in. pitch. A tension is put on the wire during winding. Some information on dressing procedures can be obtained in the instruction booklet (2).

Table 2

A-6 Sample Designation, Analysis, and Units

<u>Symbol</u>	<u>Material</u>	<u>When Taken</u>	<u>Analysis</u>	<u>Units</u>	<u>Sample Size</u>	<u>Where sample was Taken</u>
Z-( )*	ZrCl ₄ Feed	Every Batch	Zr pH**	lb/gal	25 cc	Composite Sample from both feed tanks
A-( )	Ammonium Phthalate Solution	Each batch before and after make-up	Phthalate pH**	lb/gal	25 cc	From make-up drum
P-( )	Phthalate Filter Cake	2 spot checks each smooth run	Zr*** C*** HOH***	g/g g/g g/g	25 to 50 g	From scraper blade
H-( )	Hydroxide Filter Cake	2 spot checks each smooth run	Zr C HOH	g/g g/g g/g	25 to 50 g	From scraper blade
F-( )	Filtrate from No. 1 Oliver	1 spot check and 1 sample from residue in each smooth run	phthalate pH** Zr	lb/gal	500 cc	From barrel (which is to be emptied after each run)

* Designate the sample by making a dash and adding a sub number for consecutive samples. For instance, the first ZrCl₄ sample on run 10 would be Z-10-1.

** Taken by operator and not requested from laboratory.

*** Taken for plant personnel but not used in calculations.

Z-240-22

A-7 Analysis of Ammonium Phthalate Recycle

A rapid and easily performed method of analyzing the filtrate from the second filter for phthalate and zirconium is required if a continuous check is to be kept on the process. Rapid methods of analysis usually involve testing the physical properties of a solution such as its density, absorption of light, refractive index, or conductivity. Analysis can also be made, chemically, by a specific color or precipitation test.

Density of the filtrate was tested and found to be too close to that of water to produce acceptable results. In addition, the density was found to be a rather sensitive function of the pH of the solution.

Specific color or precipitation tests for the phthalate ions suffer from the long time required to carry them out. (This can be shortened to a minimum of two and one half hours.) Tests for refractive index or absorption of light in the ultraviolet range were not tried but might prove quite satisfactory. Their precision may be increased by extraction of the filtrate with ether to eliminate any solids or ions and to concentrate the solution.

The results of the conductance tests are shown in Fig 6. The method is insensitive to the pH of the solution and minor temperature variations can be automatically accounted for by the use of the compensator on a Leeds and Northrup type 4866 Conductivity Bridge. The test solution should be kept within 20° to 30°C. The reproducibility of readings for a given solution is within 2%. An error in measuring the solution temperature results in a deviation of about 5%/°C. Additional work needs to be carried out to determine whether or not the method of solution make-up affects the conductivity, since some experimental evidence indicates that the method of solution make-up may cause significant changes in conductivity.

A-8 Table III

Summary of Operating Conditions

Run No.	1	2	3	4	5	6	7	8	9
ZrCl ₄ rate, gal/hr	10	10	10	9.9	7	7	7	7	7
Zr ⁺⁴ conc., lb/gal	0.685	0.685	0.6	0.6	0.6	0.6	0.6	0.6	0.6
ZrCl ₄ sol. pH (final)					0.3	0.3	0.3	0.3	0.3
Phthalate feed rate, gal/hr	10	10	10	10	1	1	7	7	7
C ₆ H ₄ (CO) ₂ O conc., lb/gal	1.22	1.22	1.22	1.22	1.07	1.07	1.07	1.07	1.07
Phthalate feed pH (final)					8.5	8.5		6.0	6.0
Phthalate feed Temp. °C			80	80	70	50		88	88
Preheater Temp. °C			65	81	80	65		70	70
Volume No.1 Hold-up Tank, gal					8	8	8	7	7
No. 1 Hold-up Temp. °C			70	87	88	85		90	90
No. 1 Filter rate, rpm			0.5	0.5	0.7	0.7		0.31	0.31
Vacuum No. 1 in. of Hg								1.5	1.5
Wash No. 1 rate, gal/hr	2	2	2	2	4	4	3.5	3.5	3.5
Filtrate No. 1 rate, gal/hr								13.1	
% Zr ⁺⁴ in Filtrate No. 1								0.008	
% Phthalate in Filtrate No.1								1.66	
Leach rate, gal/hr	10	10	8.6	10	7	7	7	7	7
% NH ₄ OH in Leach	-----7.78-----								
Volume No. 2 Hold-up Tank, gal					0	10		4	
No.2 Hold-up Temp. °C			34	36	30	30		30	30
No.2 Filter rate, rpm			0.5	0.5	0.6	0.6		0.74	0.74
Vacuum No.2, in. of Hg								7	7
Wash No. 2 rate, gal/hr	2	2	2	2	1.6	1.6	1.4	1.4	1.4
% NH ₄ OH in Wash No. 2	-----2.00-----								
Product Weight, lb			40.75	53.1	35.5	20.75		23.2	
Filtrate No. 2 rate, gal/hr								10.1	
% Zr ⁺⁴ in Filtrate No. 2								0.02	
% Phthalate in Filtrate No. 2								4.69	
Time of run, min			35	75	140	198		40.2	

Z-240-2

Table IV

A-9 Important Variables for the Pilot Plant

	<u>Variable</u>
1. Zirconium chloride feed solution	pH
2. Ammonium phthalate solution	excess ammonium phthalate dilution
3. Hold-up tank No. 1	hold-up time, temperature
4. Filter No. 1	filtration rate
5. Ammonium-hydroxide leaching agent	concentration, excess
6. Hold-up tank, No. 2	hold-up time, temperature.
7. Filter No. 2	filtration rate

Optimum values for some variables determined by laboratory investigation
(1), (2)

	<u>Variable</u>	<u>Optimum Value</u>
Zirconium Chloride Feed	pH	0.3
Ammonium phthalate solution	excess ammonium phthalate	5 %
Hold-up tank, No. 1	hold-up time	30 min
Hold-up tank, No. 1	temperature	92-95°C
Ammonium hydroxide leaching agent	NH ₄ OH	no excess
Hold-up tank No. 2	temperature	no effect

A-10 Alternate Method for Analysis

In the analysis of hydroxide cakes, the water content should be determined by the loss in weight on heating at 250°C for one hour. The residue should be agitated in 1-2N HCl until the Zr(OH)₄ has dissolved. After the solution is filtered, the solid is washed, dried, and weighed to determine the percent zirconium phthalate. The zirconium hydroxide can be determined by difference or by reprecipitating and weighing the zirconium hydroxide.

Z-240-25

A-11 Sample Calculations

Make-Up of Ammonium Phthalate (Initial Batch)

$$\text{Zr in feed} = 0.6 \text{ lbs/gal}$$

$$\text{Zr in feed} = \frac{(0.6)(454)}{91.22} = 2.98 \text{ g-moles/gal}$$

To prepare 10% excess ammonium phthalate solution

$$\text{NH}_4\text{OH needed} = \frac{(110)(2.98)(2 \text{ moles NH}_4\text{OH})}{100 \text{ mole Zr}} = 6.56 \text{ g-moles/gal of ZrCl}_4 \text{ feed}$$

$$\text{C}_6\text{H}_4(\text{CO})_2\text{O needed} = \frac{(110)(2.98)}{100} = 3.28 \text{ g-moles/gal of ZrCl}_4 \text{ feed}$$

The available NH_4OH concentration = 15 moles/liter

$$\frac{6.56}{15.0} = 0.438 \text{ liters NH}_4\text{OH/gal ZrCl}_4 \text{ feed}$$

Molecular weight of $\text{C}_6\text{H}_4(\text{CO})_2\text{O} = 148.1 \text{ g/g-mole}$

$$\frac{(3.28)(148.1)}{(454)} = 1.07 \text{ lbs C}_6\text{H}_4(\text{CO})_2\text{O/gal ZrCl}_4 \text{ feed}$$

$$\text{Water needed} = 3.785 \text{ liters/gal} - 0.438 \text{ liters/gal} = 3.347 \text{ liters/gal ZrCl}_4 \text{ feed}$$

Recycle Ammonium Phthalate Make-up (cf. Fig. 3)

NH_4OH from leach = 2 g-moles/mole Zr

$$\frac{(110)(2.98)(2)}{100} = 6.56 \text{ g-moles NH}_4\text{OH/gal ZrCl}_4 \text{ feed}$$

NH_4OH added in Wash No. 2 (0.2 gal/gal ZrCl_4 feed)

$$\frac{(9.7 \text{ g NH}_3/\text{liter of wash})(0.2)(3.785)}{\frac{17 \text{ g NH}_3}{\text{g-mole}}} = 0.431 \text{ g-mole/gal ZrCl}_4 \text{ feed}$$

Total NH_4OH in 1.2 gal phthalate recycle = $6.56 - 0.431 = 6.99$ g-moles

$$\frac{6.99}{1.2} = 5.82 \text{ g-moles/gal phthalate recycle}$$

Let x = liters 15.0 molal NH_4OH to be added per gal recycle.

$$(15x + 5.82) \text{ g-moles} = \frac{\text{desired } \text{NH}_4\text{OH conc.}}{\text{gal}} \left(1 + \frac{x}{3.785} \text{ gal}\right)$$

$$x = 0.0559 \text{ liters}$$

let y = lb phthalate / gal of recycle as analyzed

$$\frac{(y)(454)}{164 \text{ g phthalate}} = 2.76 y \text{ g-moles of phthalate/gal of recycle}$$

desired phthalate conc.	recycle phthalate conc. after NH_4OH addition	added
$\frac{3.28 \text{ g-moles}}{\text{gal}}$	$\frac{2.76 y \text{ g-moles}}{(1 + \frac{0.0559}{3.785}) \text{ gal}}$	$\frac{3.28 - 2.72 y \text{ g-moles } \text{C}_6\text{H}_4(\text{CO})_2\text{O}}{\text{gal recycle}}$

Dilution of ZrCl_4 feed to standard 0.6 lbs Zr/gal

For undiluted feed conc. of 0.75 lb/gal, a 25 gal batch of feed with conc. of 0.6 lb/gal is desired.

Let x = gal of H_2O to add

$$(25-x) \text{ gal undiluted feed } (0.75) \text{ lb/gal} = (25 \text{ gal})(0.6 \text{ lb/gal})$$

$$x = 5 \text{ gal } \text{H}_2\text{O}$$

Add 5 gal H_2O to 20 gal undiluted feed.

Note. Volume of NH_4OH added to adjust pH was neglected.

Calculation of percent phthalate lost in hydroxide cake:

Basis: 100 grams hydroxide cake.

x = grams of zirconyl phthalate (molecular weight = 272g)
 y = grams of zirconium hydroxide (molecular weight = 160g)
 x+y= 100

$$\frac{148x}{272} + \frac{36}{160} y = \text{g C}, \quad \frac{\text{gC}}{100\text{g cake}} \times 100 = \% \text{ C}^*$$

$$\begin{aligned} 0.545x + 0.225y &= \% \text{C} \\ 0.225x + 0.225y &= 22.5 \\ \hline 0.320x &= \% \text{C} - 22.5 \end{aligned}$$

$$x = \frac{\% \text{C} - 22.5}{0.320}$$

$$\frac{\% \text{Zr}}{92/272} = \text{grams } \text{ZrOC}_6\text{H}_4(\text{CO}_2)_2 / 100 \text{ grams leached cake}$$

$$\% \text{ phthalate lost} = \frac{100x}{\frac{\% \text{Zr}}{92/272}} = \frac{100(\% \text{C} - 22.5)(92)}{(0.320)(272)(\% \text{Zr})}$$

$$\% \text{ phthalate lost} = \frac{105.5(\% \text{C} - 22.5)}{\% \text{Zr}}$$

* The sample is heated at 1000°C. The loss in weight at this temperature is all called "carbon". This value includes the C₁H₁ and O present in the sample, exclusive of the oxygen in ZrO₂ (See description of sampling procedure in Discussion of Results).

The following figures are included to aid future investigations of the process utilizing the same equipment.

Fig. 2 indicates the amount of water that should be added to the ZrCl₄ feed solution to obtain the desired concentration of 0.6 lbs Zr/gal.

Fig. 3 indicates the amount of NH₄OH and C₆H₄(CO)₂O which should be added to the recycle to prepare it for re-use.

Figs. 4 and 5 are calibrations of the filter drum rates based on the dial settings of the drive motors.

Fig 6 indicates the change in conductivity of ammonium phthalate with change in concentration if the conductivity method of analysis is used for phthalate determination. This graph provides a rapid conversion from conductivity to concentration. Within the range indicated, the pH of the solution has a negligible effect.

Z-240-28

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REQUIRED FEED DILUTION			
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8/12/50	W.H.B.	EPS 4100	2

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RECYCLE MAKE-UP QUANTITIES

DATE 9/12/80	DESIGN BY A.A.A.	FILE NO. EPS Y-109	FIG. 3

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CALIBRATION CURVE			
ZIRCONYL PHTHALATE FILTER			
DATE	DRAWN BY	FILE NO.	FIG.
5/12/50	A.A.A.	EPS Y-109	4

Z-240-31

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UNITED STATES GOVERNMENT			
CALIBRATION CURVE			
ZIRCONIUM HYDROXIDE FILTER			
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Z-240-32

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AMMONIUM PHTHALATE			
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2-12-50	809	EPB 7-100	6

Z-240-33

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A-12 Literature Citations

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- (2) Oliver United Filters Inc., "Instruction Booklet", New York, (1943).
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Z-240-34