CONFIDENTIAL

UNCLASSIFIED

UNITED STATES ATOMIC ENERGY COMMISSION

NYO-1155

**PROBLEMS OF REFINING URANIFEROUS
RESIDUES TECHNOLOGY FEED MATERIALS**

Progress Report No. 21 – January 1953

**By
H. Fleck
J. E. Summers**

February 14, 1953

Vitro Manufacturing Company

Technical Information Service, Oak Ridge, Tennessee

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

UNCLASSIFIED

NYO-1155

Progress Report No. 21—January 1953

DECLASSIFIED
(Classified) _____
by (author) of Str. Declass. By 11-13-56
by Paul Sellers T.E. date 12-7-56

February 14, 1953

Vitro Manufacturing Company

This document contains ~~restricted data~~ as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

~~This document contains Confidential-Res-~~
~~tricted Data relating to civilian applica-~~
~~tions of atomic energy.~~

Hugh Kinsler
 Authorizing Official
 Date: 11/30/09

~~CONFIDENTIAL~~

UNCLASSIFIED

1
 TYPYST _____ MS PA

NT _____ MU(✓) _____

TECHNOLOGY-FEED MATERIALS

Standard Distribution

NYO-1155
Series TA
Copy No.

American Cyanamid Company (Watertown)	1
Argonne National Laboratory	2- 3
Atomic Energy Commission, Washington	4- 5
Battelle Memorial Institute	6
Carbide and Carbon Chemicals Company (C-31 Plant)	7- 8
Carbide and Carbon Chemicals Company (K-25 Plant)	9
Carbide and Carbon Chemicals Company (ORNL)	10
Carbide and Carbon Chemicals Company (Y-12 Plant)	11
Catalytic Construction Company	12
Chicago Patent Group	13
Cleveland Area Office	14
Division of Raw Materials, Washington	15
Dow Chemical Company, Pittsburg	16
duPont Company	17-19
General Electric Company, Richland	20-21
Iowa State College	22
Mallinckrodt Chemical Works	23-24
National Lead Company of Ohio	25-27
New Brunswick Laboratory	28
New York Operations Office	29-32
Patent Branch, Washington	33
Rohm and Haas Company, Philadelphia	34
Savannah River Operations Office, Augusta	35
Vitro Corporation of America	36-37
Vitro Manufacturing Company	38
Technical Information Service, Oak Ridge	39-44

PHOTOGRAPH

~~CONFIDENTIAL~~ UNCLASSIFIED

NYO-1155

Page: 3

NYO-1155

PROBLEMS OF REFINING URANIFEROUS RESIDUES

TECHNOLOGY - FEED MATERIALS

A. SUMMARY

GENERAL

1. Scope of Program

As of January 1, 1953, the Research Program consisted of the following projects:

Digestion and Refining of C-Slags and Other Residues
(Project No. 1)

Investigate the applicability and refinement of various procedures for the treatment and digestion of C-Slags and other uraniferous residues for recovery of uranium values, placing emphasis on methods adaptable to the Canonsburg Plant with minimum of change of equipment.

Refining and Processing of Sodium Carbonate Residues
(Project No. 5)

Investigate methods of recovery of uranium from various residues, resulting from sodium carbonate digestion of miscellaneous uranium bearing materials, to reduce the U308 content of the residues below 0.05%.

~~CONFIDENTIAL~~

UNCLASSIFIED

586 - 2

2. Previous Reports

NYO-1145	March	1952 - Progress Report No. 11
NYO-1146	April	1952 - " " No. 12
NYO-1147	May	1952 - " " No. 13
NYO-1148	June	1952 - " " No. 14
NYO-1149	July	1952 - " " No. 15
NYO-1150	August	1952 - " " No. 16
NYO-1151	September	1952 - " " No. 17
NYO-1152	October	1952 - " " No. 18
NYO-1153	November	1952 - " " No. 19
NYO-1154	December	1952 - " " No. 20

PROJECT STATUS

3. Research Project - Digestion and Refining of C-Slags and Other Residues

Experiments were completed concerning the continuous precipitation of ammonium di-uranate from hydrochloric acid digest filtrates of C-Oxide. The experiments were conducted on samples taken from a regular production digest. Experimentation was initiated to determine whether or not suspended solids remaining in the pregnant solution after clarification have a detrimental effect on the fluorine content of black oxides formed by calcining continuously precipitated ammonium di-uranate at 800° C.

4. Research Project - Digestion and Refining of Sodium Carbonate Residues

Experimental work was continued concerning the precipitation of uranous phosphate from a hydrochloric acid digest filtrate of those pitchblende carbonate residues assaying 0.7% U3O8. Optimum factors concerning quantitative recovery of solubilized uranium were sought.

Experiments with regard to hydrochloric acid digestion of the raw material were continued. It had been observed that pH of acid digestion of the raw material could be correlated to the rate of filtration of the digest slurry. A gel was observed to form at varied digest pH levels which made clarification of the digest slurry exceedingly difficult. The phenomena appeared to be cyclic in nature. Experiments were conducted to determine what pH of digestion would be optimum with regard to filtration rate.

Experiments were conducted to determine the optimum pH of precipitation of uranous phosphate from a clarified hydrochloric acid digest filtrate of pitchblende carbonate residues. Precipitation of solubilized uranium was carried out over pH range 0.5 - 2.5 by reduction of the pregnant solution with sodium hydrosulfite. Accumulated data indicates that the optimum pH of precipitation approximates 2.0.

Experiments were conducted to establish minimum requirements of sodium hydrosulfite which are necessary to obtain quantitative precipitation of uranous phosphate. Accumulated data indicates that it will be necessary to use approximately 300% of the theoretical requirements to obtain satisfactory recovery.

In addition, experiments were completed designed to evaluate the benefits of the addition of excess PO_4 ion on the quantitative precipitation of uranous phosphate using sodium hydrosulfite as the reducing agent. Preliminary results indicate that the P_2O_5 content of the raw material is sufficient to effect maximum recovery without further addition of phosphate compounds.

- ✓ Preliminary experiments were completed designed to determine whether or not uranous phosphate could be precipitated from a pregnant hydrochloric acid digest filtrate of the pitchblende residues by reduction of the clarified filtrate using metallic aluminum or iron. Preliminary results indicate that it may be possible to extract uranium on a quantitative basis in this manner.

B. DIGESTION AND REFINING OF C-OXIDE AND OTHER
RESIDUES

Research Project No: 1

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

5. Continuous Precipitation of Ammonium Di-Uranate From
A Clarified Hydrochloric Acid Digest Filtrate of C-Oxide

Production level experiments had indicated that ordinary means of filtration would not be satisfactory in effecting absolute clarification of hydrochloric acid digest slurries of C-Oxide. Experiments were conducted in the laboratory to determine if micro suspended solids contained in the hydrochloric acid filtrate after filtration would have a detrimental effect upon the fluorine content of black oxides obtained by calcining continuously precipitated ammonium di-uranate at 800° C. Samples were obtained from production filtrates of C-oxide after filtration through plate and frame press and were used for experimentation. Half of the sample was given absolute clarification in the laboratory prior to continuous precipitation. The other portion was continuously precipitated in the laboratory without additional clarification. Precipitation was effected by combining the feed liquor and dilute (3:1) NH₄OH spontaneously at approximately pH 6.0 in the presence of vigorous

(1200 r.p.m.) agitation. The results indicate that absolute clarification of the pregnant filtrates will be necessary to obtain a satisfactory end product containing fluorine in quantities less than 0.5% F. Black oxides obtained from continuously precipitated laboratory clarified pregnant liquor contained less than .1% F. Those samples continuously precipitated without additional clarification contained fluorine in excessive amounts exceeding maximum specification of 0.5%. Representative data may be found in Table I.

C. REFINING AND PROCESSING OF SODIUM CARBONATE
RESIDUES

Research Project No: 5

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

6. Mineral Acid Digestion of Sodium Carbonate Residues
Assaying 0.7% U308 As A By Product of Pitchblende
Purification

Experiments were conducted to correlate pH of hydrochloric acid digestion with filtering characteristics of the digest slurry. It had been observed during previous acid digest experimentation that a gel formed at various pH levels which made clarification of the digest slurry very difficult. Experiments were carried out over a pH range of less than 0.0 - 2.5. 500 gram samples of the raw material were slurried in 1500 grams of water and digested in hydrochloric acid in the presence of 0.5% (w/v) sodium chlorate at variable acidity for one-half hour at 90° C. The phenomena appears to be cyclic in nature. Optimum filtration rate of the digest slurry was found within the pH range of 0.0 - 0.5, with maximum filtration at approximately 0.25. At variable acidity both above and below this range a digest gel makes filtration of the slurry practically impossible. Data may be found in Table II.

7. Precipitation of Uranous Phosphate From a Clarified Hydrochloric Acid Filtrate of Pitchblende Carbonate Residues Containing 0.7% U308

Extensive experiments were conducted to determine the optimum pH of precipitation of uranous phosphate from a pregnant hydrochloric acid filtrate of pitchblende carbonate residues by reduction with sodium hydrosulfite. 100 gram samples of the raw material were slurried in 400 ml of water and digested in hydrochloric acid at approximately pH 0.25 in the presence of 0.5% (w/v) sodium chlorate for one-half hour at 90° C. Acid insolubles were removed by filtration and the clarified filtrate was used for experimentation. Uranous phosphate was precipitated from the pregnant filtrate over a pH range extending from 0.5 - 2.5 by reduction of the solution with excess amounts of sodium hydrosulfite. The resultant precipitates were removed by filtration and the discard effluents analyzed for uranium content. The data accumulated to date indicates that maximum extraction of uranium will be effected within a pH range from 1.5 - 2.0. At this acidity solubilized uranium may be quantitatively precipitated with effluents averaging .003% U308 establishing a total yield of approximately 97%. Representative data of precipitation at variable acidity may be found in Table III.

Additional experiments were conducted on pitchblende residues using the tentatively established optimum pH of precipitation to determine the minimum chemical requirements of sodium hydrosulfite which would be necessary to effect complete reduction of solubilized uranium leading to precipitation of uranous phosphate. 100 gram samples of pitchblende carbonate residues assaying 0.7% U308 were slurried in 400 ml of water and digested in commercial hydrochloric acid at approximately pH 0.25 for one-half hour at

90° C in the presence of 0.5% (w/v) sodium chlorate. The digest slurry was clarified by filtration and the filtrate, after removal of acid insolubles, was used for experimentation. Uranium was precipitated at pH 1.75 as uranous phosphate by reduction of the pregnant liquors using variable quantities of sodium hydrosulfite ranging from 100% to 1000% of the theoretical requirements. The resultant precipitates were removed by filtration and the discard effluents examined for uranium content. Preliminary data indicates that approximately 300% of the theoretical requirements for quantitative precipitation will be necessary to effect satisfactory recovery. Further experimentation of this type is planned to determine if sodium hydrosulfite requirements may be lowered by further adjustment of pH of precipitation. Representative data may be found in Table IV.

A series of experiments was completed designed to evaluate the influence of excess quantities of PO_4 ion on the precipitation of uranous phosphate from hydrochloric acid digest filtrates of pitchblende carbonate residues assaying 0.7% U308 by reducing the pregnant liquor with sodium hydrosulfite. 100 gram samples of the raw material were slurried in 400 ml of water and digested in hydrochloric acid at approximately pH 0.25 for one-half hour at 90° C in the presence of 0.5% (w/v) sodium chlorate. Acid insolubles were removed by filtration and the clarified filtrates used for experimentation. Prior to precipitation phosphate ion was added to the clarified filtrates as sodium phosphate. Uranous phosphate was then precipitated at pH 1.75 by the addition of the theoretical requirements of sodium hydrosulfite. After removal of the precipitate by filtration the discard effluent was examined for solubilized uranium. It is apparent from the preliminary data that the further addition of phosphate ion has no appreciable influence on uranous phosphate precipitation. The raw material apparently

contains sufficient P_2O_5 to effect satisfactory recovery without further additions. Complete data may be found in Table V.

Preliminary experiments were conducted to determine whether or not uranous phosphate could be precipitated from a hydrochloric acid digest filtrate of pitchblende carbonate residues assaying 0.7% U308 by reduction of the pregnant liquor using either metallic aluminum or metallic iron. 100 gram samples of the raw material were slurried in 400 ml of water and digested in hydrochloric acid at approximately pH 0.25 in the presence of 0.5% (w/v) sodium chlorate for one-half hour at 90° C. Acid insolubles were removed by filtration and the pregnant liquor used for experimentation. Metallic aluminum was added to the pregnant filtrate and allowed to react until pH 2.0 was obtained. Preliminary experimentation indicates that precipitation of uranous phosphate in this manner may not be entirely satisfactory due to the addition of considerable quantities of solubilized aluminum to the filtrate. This type of precipitation seems to be greatly effected by soluble aluminum content.

In the same manner, pregnant filtrates were neutralized to approximately pH 2.0 by the addition of metallic iron. From preliminary data it appears that this may be a possible means of uranium reduction resulting in satisfactory precipitation of uranous phosphate. The results obtained to date are only preliminary and further experimentation is planned to confirm results obtained to date. Preliminary data may be found in Table VI.

NYO-1155

Page: 13

EXHIBITS

14

TABLE I

CONTINUOUS PRECIPITATION OF AMMONIUM DI-URANATE

MATERIAL: C-OXIDE

	<u>EXPERIMENT NUMBER</u>	
	<u>A</u>	<u>B</u>
Feed Liquor (% U308)	0.2716	0.2716
Feed Liquor (pH)	0.25	0.25
Feed Liquor (%F)	0.275	0.275
Feed Liquor (% Ca-Mg)	6.72	6.72
Extent of Filtration	Laboratory	Production
	Clarified	Clarified
pH of Precipitation	5.82	5.90
Precipitate Calcination Temp. (°C)	800	800
Black Oxide (%F)	0.08	0.76
Black Oxide (% U308)	86.24	80.08

 586
 13

15

TABLE II

ACID DIGESTION OF RAW MATERIAL

MATERIAL: PITCHBLEND CARBONATE RESIDUES

ASSAY: 0.7% U_3O_8

	<u>EXPERIMENT NUMBER</u>							
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Weight of Sample (gm)	100	100	100	100	100	100	100	100
Weight of H ₂ O (gm.)	400	400	400	400	400	400	400	400
Weight of HCl (gm.)	245	231	220	213	200	192	175	165
pH of Digestion	-0.0	0.0	0.25	0.5	1.0	1.5	2.0	2.5
Time of Digest (hr.)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Temp. of Digestion (°C)	90	90	90	90	90	90	90	90
Acid Insolubles (gm.)	--	4.5	4.0	10.5	--	--	9.5	24.0
Acid Insolubles (%U308)	--	.055	.035	.075	--	--	0.116	0.14
Filtration Time (min.)	Non Filterable	4.5	0.75	3.0	Non Filterable	Non Filter.	10.0	0.75

TABLE III

DETERMINATION OF pH OF PRECIPITATION OF URANOUS PHOSPHATE

MATERIAL: PITCHBLEND CARBONATE RESIDUES

ASSAY: 0.7% U_3O_8

	<u>EXPERIMENT NUMBER</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Weight of Sample (gm.)	100	100	100	100	100	100
Weight of H_2O (gm.)	400	400	400	400	400	400
Weight of HCl (gm.)	220	220	220	220	220	220
pH of Digestion	0.25	0.25	0.25	0.25	0.25	0.25
Time of Digest (hr.)	0.5	0.5	0.5	0.5	0.5	0.5
Temperature of Digest ($^{\circ}C$)	90	90	90	90	90	90
Acid Insolubles (gm.)	4.0	4.0	4.0	4.0	4.0	4.0
Acid Insolubles (% U_3O_8)	.05	.05	.05	.05	.05	.05
$Na_2S_2O_4$ added to Filtrate (gm.)	2.0	2.0	2.0	2.0	2.0	2.0
pH of Precipitation	0.5	1.0	1.5	1.7	2.0	2.5
Discard Effluent (% U_3O_8)	.035	.014	.004	.0018	.003	.003
Total Recovery (%)	65	86	96	08.2	97	97

 5
 8
 15

TABLE IV

DETERMINATION OF $\text{Na}_2\text{S}_2\text{O}_4$ REQUIREMENTS FOR URANOUS PHOSPHATE PRECIPITATION

MATERIAL: PITCHBLEND CARBONATE RESIDUES

ASSAY: 0.7% U_3O_8

	<u>EXPERIMENT NUMBER</u>								
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>
Weight of Sample (gm.)	100	100	100	100	100	100	100	100	100
Weight of H_2O (gm.)	400	400	400	400	400	400	400	400	400
Weight of HCl (gm.)	220	220	220	220	220	220	220	220	220
pH of Digestion	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Time of Digest (hr.)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Temperature of Digest ($^{\circ}\text{C}$)	90	90	90	90	90	90	90	90	90
$\text{Na}_2\text{S}_2\text{O}_4$ added to Filtrate (gm.)	0.5	1.0	1.5	1.75	2.0	2.5	3.0	3.5	4.0
pH of Precipitation	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Residue (gm.)	2.5	3.0	4.5	4.5	4.5	6.0	6.0	6.0	6.0
Discard Effluent (% U_3O_8)	.098	.078	.014	.004	.002	.003	.004	.0012	.003
Recovery (%)	2	22	86	96	98	97	96	98.8	97

18

TABLE V

DETERMINATION OF PO_4 REQUIREMENTS FOR URANOUS PHOSPHATE PRECIPITATION

MATERIAL: PITCHBLEND CARBONATE RESIDUES

ASSAY: 0.7% U_3O_8

	<u>EXPERIMENT NUMBER</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of Sample (gm.)	100	100	100
Weight of H_2O (gm.)	400	400	400
Weight of HCl (gm.)	220	220	220
pH of Digestion	0.25	0.25	0.25
Time of Digestion (hr.)	0.5	0.5	0.5
Temperature of Digestion ($^{\circ}\text{C}$)	90	90	90
pH of Precipitation	1.75	1.75	1.75
Na_3PO_4 added to Filtrate (gm.)	0.5	1.0	1.5
$\text{Na}_2\text{S}_2\text{O}_4$ added to Filtrate (gm.)	0.75	1.0	1.0
Discard Effluent (% U_3O_8)	0.98	.067	.078
Recovery (%)	?	33	22

582

17

19

TABLE VI

URANOUS PHOSPHATE PRECIPITATION USING METALLIC IRON AND ALUMINUM

MATERIAL: PITCHBLEND CARBONATE RESIDUES

ASSAY: 0.7% U308

	<u>EXPERIMENT NUMBER</u>	
	<u>A</u>	<u>B</u>
Weight of Sample (gm.)	100	100
Weight of H ₂ O (gm.)	400	400
Weight of HCl (gm.)	220	220
pH of Digestion	0.25	0.25
Time of Digestion (hr.)	0.5	0.5
Temperature of Digestion (°C)	90	90
pH of Precipitation	2.0	2.0
Reducing Agent	Metallic Fe	Metallic Al
Discard Effluent (% U308)	.010	.046
Recovery (%)	90	54

~~CONFIDENTIAL~~

UNCLASSIFIED

~~CONFIDENTIAL~~

UNCLASSIFIED