~~SECRET~~

~~SECURITY INFORMATION~~

UNCLASSIFIED

This document consists of 17 pages.
No. 47 of 64 copies, Series TA

UNITED STATES ATOMIC ENERGY COMMISSION

NYO-1162

PROBLEMS OF REFINING URANIFEROUS RESIDUES

Technology Feed Materials Progress Report –
June 1953

By
H. Fleck
J. E. Summers

July 15, 1953

Vitro Manufacturing Company

Technical Information Service, Oak Ridge, Tennessee

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

UNCLASSIFIED

~~SECRET~~
~~SECURITY INFORMATION~~

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.

~~CONFIDENTIAL~~

L
UNCLASSIFIED

NYO-1162

NYO-1162

PROBLEMS OF REFINING URANIFEROUS RESIDUES

Vitro Manufacturing Company

H. Fleck and J. E. Summers

July 15, 1953

AEC RESEARCH AND DEVELOPMENT REPORT

~~RESTRICTED DATA~~

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

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

This document is
PUBLICLY RELEASABLE

Hugh Kinser
Authorizing Official

Date: *11/24/09*

Classification cancelled (or changed to) UNCLASSIFIED

by authority of *the Declass. Br. 11/13/56*
by *L. L. Leland*, 11/13/56

~~CONFIDENTIAL~~

UNCLASSIFIED

~~CONFIDENTIAL~~

UNCLASSIFIED

PROBLEMS OF REFINING URANIFEROUS RESIDUES
TECHNOLOGY - FEED MATERIALS

A. SUMMARY

GENERAL

1. Scope of Program

As of June 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 change of equipment.

Refining of BFC-6
(Project No. 4)

Investigate the recovery of uranium from BFC-6 placing emphasis on procedures which will not chemically alter the copper and tin media.

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

~~CONFIDENTIAL~~

UNCLASSIFIED

miscellaneous uranium bearing materials, to reduce the U_3O_8 content of the residues below 0.05%.

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
NYO-1155	January	1953 -	" "	No. 21
NYO-1156	February	1953 -	" "	No. 22
NYO-1157	March	1953 -	" "	No. 23
NYO-1158	April	1953 -	" "	No. 24
NYO-1159	May	1953 -	" "	No. 25

PROJECT STATUS

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

Experiments were conducted on C-Oxide using "Wilson Dam" P_2O_5 contaminated hydrochloric acid to determine if uranium precipitated from a clarified digest filtrate of this acid would constitute an acceptable end product containing less than 0.5% P_2O_5 and more than 50% U_3O_8 .

4. Research Project - Digestion and Refining of BFC-6

Additional experiments were conducted using dilute hydrochloric and nitric acid to determine if these procedures would be effective in satisfactorily extracting uranium from either calcined or uncalcined material. A procedure was sought which would lead to a discard residue containing less than 0.05% U_3O_8 .

Experiments were also conducted using concentrated hydrochloric acid, concentrated nitric acid, and concentrated sulfuric acid respectively as digest media. Digestion of both calcined and uncalcined BFC-6 was investigated using concentrated acid to determine if this would lead to acid insoluble residues containing less than 0.05% U_3O_8 .

Preliminary experiments were initiated on uncalcined and calcined BFC-6 to determine if sodium hydroxide digestion for the removal of metallic tin followed by sulfuric acid digestion of the insoluble residue and removal of solublized copper by neutralization of the digest slurry with ammonium hydroxide would benefit the raw material to such an extent that uranium content would exceed the minimum specification of 50% U_3O_8 for an acceptable end product.

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

Additional experiments were undertaken in the laboratory parallel with pilot level experiments to determine if adjustments in chemical or handling procedures would lead to more efficient extraction of uranium.

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

Research Project No: 1

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

6. Digestion and Refining of C-Oxide using Wilson Dam P_2O_5 Contaminated Hydrochloric Acid

Experiments were initiated on C-Oxide using "Wilson Dam" P_2O_5 contaminated hydrochloric acid as a digest media. Experiments were conducted to determine if this acid would be a satisfactory digest reagent resulting in a clarified hydrochloric acid digest filtrate from which uranium could be precipitated using ammonium hydroxide and standard procedures leading to a satisfactory end product containing less than .5% P_2O_5 and more than 50% U_3O_8 .

Five-hundred gram samples of C-Oxide were calcined at 1200° F for one hour and were pulverized to less than 100 mesh. Since the Wilson Dam hydrochloric acid contained less than 10% free HCl, experiments were conducted using H_2O to slurry at a ratio of 1:1. Other experiments were completed without the addition of slurry water. Approximately 4000 ml of the low grade hydrochloric acid was added before the pH of digestion was reduced to approximately 0.25. Sodium chlorate was added to oxidize. Digestion was carried out at 90° C for three hours. Acid insolubles were removed from the digest slurry by filtration and washed

with water until color free. Average uranium content of insoluble residues was less than .05% U_3O_8 . The pregnant clarified filtrate obtained by this procedure was neutralized to pH 6.0 by the addition of dilute (6 molar) ammonium hydroxide. The resultant precipitate was separated by filtration and washed until calcium and magnesium free. Average uranium content of precipitates obtained in this manner was 4.5% U_3O_8 . P_2O_5 content exceeded 6.5%. Representative data may be found in Table I.

An additional series of experiments of this nature was conducted to determine the optimum end product that could be obtained from C-Oxide using the low grade phosphate contaminated acid. Two-hundred-fifty gram samples of C-Oxide were calcined at 1200° F for one hour, slurried in 250 ml of water, and digested in approximately 2,150 ml of hydrochloric acid at pH 0.2 - 0.3, in the presence of 0.5% (w/v) sodium chlorate to oxidize, for three hours at 90° C. Acid insolubles were removed by filtration and washed with water until color free. Pregnant liquor obtained by this procedure was precipitated by the addition of dilute (6 molar) ammonium hydroxide over a pH range extending from 1.5 - 3.0. The precipitate was separated from the supernatant liquor by filtration and washed with water until calcium and magnesium free. Optimum precipitation was obtained at pH 1.5 with the resultant end product containing on the average 47.0% U_3O_8 , .85% F and 11.5% P_2O_5 . Specifications for a satisfactory end product are exceeded or not obtained in every instance. It is fairly obvious that it will not be possible to obtain a satisfactory end product using the Wilson Dam hydrochloric acid unless additional purification processes are utilized. Average data may be found in Table II.

C. DIGESTION AND REFINING OF BFC-6

Research Project No.: 4

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

7. Extraction of Uranium from BFC-6 Using Mineral Acid Digestion

Additional experiments using dilute hydrochloric and dilute nitric acid respectively as a digest media for calcined and uncalcined BFC-6 were completed to confirm preliminary data. One-hundred gram samples of BFC-6 were calcined at 1000° F for one hour, slurried in 300 ml of H₂O, and digested in hydrochloric and nitric acid respectively at pH 0.0 for 6 hours at 95 - 100° C in the presence of sodium chlorate as an oxidizing agent. Experiments were also conducted in the same manner using uncalcined material. Acid insolubles were separated from the digest slurry by filtration and washed with water until color free. An investigation of the U content of insoluble residues resulting from this treatment indicated a uranium level averaging .1 - .3% U₃O₈. This is well above the maximum discard specification of .05% U₃O₈ for a discard residue. Representative data may be found in Table III.

Experiments on uncalcined material were conducted using concentrated hydrochloric and sulfuric acids. One-hundred gram samples of uncalcined material were slurried in concentrated sulfuric and hydrochloric acids respectively. Digestion in concentrated hydrochloric was carried out over a three hour period at

90 - 95° C using sodium chlorate to oxidize. Digestion in fuming H_2SO_4 was continued for three hours. An investigation of the uranium level of acid insolubles resulting from procedures using concentrated acids indicated no beneficiation of extraction. Uranium content continued to exceed maximum specifications for a discard residue. Acid insolubles averaged from .1 - .5% U_3O_8 . Data may be found in Table IV.

8. Refining of BFC-6 Using Sodium Hydroxide Digestion

A series of experiments was conducted to determine if the uranium content of BFC-6 could be elevated above the minimum specifications of 50% U_3O_8 for an End-product by digestion of the material in sodium hydroxide to remove metallic tin, digestion of the insoluble digest residue in sulfuric acid followed by removal of solublized copper by the addition of ammonium hydroxide. One-hundred gram samples of both calcined and uncalcined material were slurried in 300 grams of H_2O and digested in 100 grams of sodium hydroxide for three hours at 95 - 100° C. The supernate was removed by a process of decantation and filtration. The insoluble residue from the sodium hydroxide digestion was repulped in 300 grams of H_2O and digested in sulfuric acid at pH 0.0 in the presence of sodium chlorate for three hours at 95 - 100° C. The digest slurry was neutralized to pH 9.0 using 1:1 ammonium hydroxide. Solublized copper was removed by filtration and the resultant residue investigated for uranium content. Average uranium content of the end product obtained by this procedure was 30 - 35% U_3O_8 . Preliminary data may be found in Table V.

D. REFINING AND PROCESSING OF SODIUM CARBONATE RESIDUES

Research Project No: 5

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

9. The Extraction of Uranium from Pitchblende Carbonate Residues by a Process of Sodium Carbonate and Hydrochloric Acid Digestion

Experiments were conducted on Pitchblende carbonate residues in parallel with a pilot operation to determine if adjustments in procedure could possibly lead to more efficient extraction of uranium from this material with minimum handling. One hundred gram samples of Pitchblende carbonate residues assaying 1.6% U_3O_8 and .69% U_3O_8 respectively were slurried in 200 ml of water and digested in 5% (w/v) sodium carbonate for three hours at 90° C. The digest slurry was filtered and the insoluble residue washed with hot 5% sodium carbonate solution until colorless. This procedure was successful in removing 50 - 55% of the contained uranium. The resultant residues were slurried in 200 ml of water and digested in hydrochloric acid at pH .25 for one hour at 90° C. The acid slurry was neutralized with sodium carbonate and digested for three hours at 90° C. After filtration the insoluble residue was washed until color free with hot 5% sodium carbonate solution. Insoluble residues resulting from this treatment averaged .1 - .3% U_3O_8 . The residues were repulped in 200 ml of water and redigested in 5% (w/v) sodium

carbonate for three hours at 90° C. The supernate was removed by filtration and the residue washed until color free using hot 5% sodium carbonate solution. Insoluble sodium carbonate residues obtained by this procedure averaged between .03 - .06% U_3O_8 . Representative data may be found in Table VI.

EXHIBITS

TABLE I

PURIFICATION OF C-OXIDE USING P_2O_5 CONTAMINATED HCl

Reagent: "Wilson Dam" Hydrochloric Acid

Assay: 0.5% P_2O_5 ; 9.0% HCl

	<u>EXPERIMENT NUMBER</u>	
	<u>1</u>	<u>2</u>
Weight of Sample (gm)	500	500
Weight of H_2O (gm.)	500	-
Weight of Hcl (gm.)	4,200	4,200
Digest Time (hr.)	3	3
Digest pH	0.25	0.25
Digest Temperature (°C)	95	95
Acid Insoluble (gm.)	273	274
Acid Insolubles (% U_3O_8)	.05	.05
pH of Precipitation	6.0	6.0
Residue (gm.)	152	153
Residue (% U_3O_8)	4.57	4.65
Residue (% P_2O_5)	6.84	6.82
Residue (% F)	1.12	1.04

12

TABLE II

PURIFICATION OF C-OXIDE USING P_2O_5 CONTAMINATED HCl

Reagent: "Wilson Dam" Hydrochloric Acid
 Assay: 0.5% P_2O_5 ; 9.0% HCl

	<u>EXPERIMENT NUMBER</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Weight of Sample (gm.)	250	250	250	250
Weight of H_2O (gm.)	250	250	250	250
Weight of Hcl (gm.)	2,220	2,220	2,220	2,220
Digest Time (hr.)	3	3	3	3
Digest pH	0.25	0.25	0.25	0.25
Digest Temperature ($^{\circ}C$)	95	95	95	95
pH of Precipitation	1.5	2.0	2.5	3.0
Discard Effluent (% U_3O_8)	.001	.0006	.0007	.0002
Residue (% U_3O_8)	47.04	44.44	44.30	42.28
Residue (% P_2O_5)	10.90	11.43	11.68	11.43
Residue (% F)	.86	1.30	1.41	1.70

TABLE III
EXTRACTION OF URANIUM USING DILUTE HYDROCHLORIC
AND NITRIC ACIDS

Material:	BFC-6			
Assay:	19.66% U_3O_8			
	<u>EXPERIMENT NUMBER</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Weight of Sample (gm.)	100	100	100	100
Calcination Temperature ($^{\circ}F$)	1,000	1,000	-	-
Calcination Time (hr.)	1.0	1.0	-	-
Weight of H_2O (gm.)	300	300	300	300
Reagent	Hcl	HNO_3	Hcl	HNO_3
Weight of Acid (gm.)	136.8	110	142	115
Digest pH	0.1	0.1	0.0	0.1
Digest Temperature ($^{\circ}C$)	95	95	95	95
Digest Time (hr.)	6.0	6.0	6.0	6.0
Acid Insolubles (gm.)	47.2	63.0	45.0	61.5
Acid Insolubles (% U_3O_8)	.17	.21	.23	.28
Recovery (%)	99.60	99.30	99.46	99.15

TABLE IV
EXTRACTION OF URANIUM USING CONCENTRATED
Hcl, HNO_3 AND H_2SO_4

Material:	BFC-6 (Uncalcined)		
Assay:	19.66% U_3O_8		
	<u>EXPERIMENT NUMBER</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of Sample (gm.)	100	100	100
Reagent	Hcl	HNO_3	H_2SO_4
Weight of Reagent (gm.)	295	280	184
Digest Time (hr.)	6.0	6.0	3.0
Digest Temperature ($^{\circ}C$)	95	95	120
Acid Residue (gm.)	36.5	54	37.2
Acid Residue (% U_3O_8)	.19	.23	.19
Recovery (%)	99.65	99.36	99.60

TABLE V

REFINING OF BFC-6 USING NaOH DIGESTION,
H₂SO₄ DIGESTION AND NH₄OH PRECIPITATION

Material:	BFC-6	
Assay:	19.6% U ₃ O ₈	
	<u>EXPERIMENT NUMBER</u>	
	<u>1</u>	<u>2</u>
Weight of Sample (gm.)	100	100
Calcination Temperature (°F)	1,000	-
Weight of H ₂ O (gm.)	300	300
Weight of NaOH (gm.)	100	100
Digest Time (hr.)	3	3
Digest Temperature (°C)	95	95
Residue (gm.)	96.9	92.3
Residue (% U ₃ O ₈)	20.3	21.7
Weight of H ₂ O to Slurry (gm.)	300	300
Weight of H ₂ SO ₄ (gm.)	68.1	64.4
Weight of NaClO ₃ (gm.)	6.9	10.0
Digest pH	0.0	0.0
Digest Temperature (°C)	95	95
Digest Time (hr.)	3.0	3.0
pH of Precipitation	9.0	9.0
Precipitant	NH ₄ OH	NH ₄ OH
Residue (gm.)	63.0	58.2
Residue (% U ₃ O ₈)	30.9	34.8

~~CONFIDENTIAL~~

UNCLASSIFIED

NYO-1162

15-16

15

TABLE VI

EXTRACTION OF URANIUM FROM SODIUM
CARBONATE RESIDUES

Material: Pitchblende Carbonate Residues

Assay: .79 - 1.6% U_3O_8

EXPERIMENT NUMBER

	<u>1</u>	<u>2</u>
Assay of Sample (% U_3O_8)	1.6	.79
Weight of Sample (gm.)	100	100
Weight of H_2O (gm.)	400	400
Weight of Na_2CO_3 (gm.)	20	20
Digest Time (hr.)	3.0	3.0
Digest Temperature ($^{\circ}C$)	90	90
Residue (% U_3O_8)	.59	.43
Weight of H_2O to Slurry (gm.)	200	200
Weight of Hcl (gm.)	155	205
pH of Digestion	.25	.25
Digest Time (hr.)	1.0	1.0
Digest Temperature ($^{\circ}C$)	90	90
Weight of Na_2CO_3 Added (gm.)	125	120
Digest Time (hr.)	3.0	3.0
Digest Temperature ($^{\circ}C$)	90	90
Residue (% U_3O_8)	.25	.11
Weight of H_2O to Slurry (gm.)	200	200
Weight of Na_2CO_3 (gm.)	10	10
Digest Time (hr.)	3.0	3.0
Digest Temperature ($^{\circ}C$)	90	90
Residue (% U_3O_8)	.06	.035

~~CONFIDENTIAL~~

UNCLASSIFIED

1-15

~~SECRET~~

NYO-1162

17

TECHNOLOGY-FEED MATERIALS

Standard Distribution

NYO-1162
Series TA
Copy No.

American Cyanamid Company	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)	9-10
Carbide and Carbon Chemicals Company (ORNL)	11-14
Carbide and Carbon Chemicals Company (Y-12 Plant)	15-17
Catalytic Construction Company	18
Chicago Patent Group	19
Cleveland Area Office	20
Division of Raw Materials, Washington	21
Dow Chemical Company, Pittsburg	22
duPont Company, Augusta	23-25
General Electric Company, Richland	26-27
Goodyear Atomic Corporation	28-29
Iowa State College	30
Mallinckrodt Chemical Works	31-32
National Lead Company of Ohio	33-35
New Brunswick Laboratory	36
New York Operations Office	37-40
Patent Branch, Washington	41
Rohm and Haas Company	42
Savannah River Operations Office, Augusta	43
Vitro Corporation of America	44-45
Vitro Manufacturing Company	46
Technical Information Service, Oak Ridge	47-64

~~SECRET~~