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NYO-1158

PROBLEMS OF REFINING URANIFEROUS RESIDUES

Technology Feed Materials Progress Report
April 1953

By
H. Fleck
J. E. Summers

May 15, 1953

Vitro Manufacturing Company

Technical Information Service, Oak Ridge, Tennessee

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AEC RESEARCH AND DEVELOPMENT REPORT

This document is
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Hugh Kinner
Authorizing Official

Date: 11/24/09

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PROBLEMS OF REFINING URANIFEROUS RESIDUES
TECHNOLOGY - FEED MATERIALS

A. SUMMARY

GENERAL

1. Scope of Program

As of April 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 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.

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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%.

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
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NYO-1155	January	1953 - " " No. 21
NYO-1156	February	1953 - " " No. 22
NYO-1157	March	1953 - " " No. 23

PROJECT STATUS

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

Experiments were initiated on FMPC sump cake using mineral acid digestion to determine if uranium could be extracted from this material, resulting in insoluble discard residues containing less than .05% U308.

In addition, experiments were conducted on the clarified acid filtrates to determine if the precipitation of solublized uranium with ammonium hydroxide would result in an acceptable product containing more than 50% U and less than .5% F.

4. Research Project - Refining of BFC-6

Experiments were continued on BFC-6 using sulfuric acid digest procedures. Additional experiments were completed evaluating the benefits of protracted periods of digest time on the maximum extraction of contained uranium, leading to insoluble discard residues containing less than .05% U3O8.

Experiments were completed on acid insolubles resulting from the sulfuric acid digest treatment to determine if redigestion or recalcination of these residues in sulfuric acid or sodium carbonate would lower insoluble uranium content to less than .05% U3O8.

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

Experiments were conducted on samples of the current Vitro sodium carbonate residues in conjunction with a pilot operation that had been established to determine the effectiveness of the UAP purification process developed for these residues. Samples were taken from production lots and run under laboratory conditions, parallel to pilot experiments, to determine if the procedure was being applied effectively from a mechanical standpoint.

Experiments on pitchblende carbonate residues were initiated to determine if simple procedures could be established which would be effective in extracting uranium from these residues, leading to discard of insoluble residues containing less than .05% U3O8. A series of mineral acid digests and carbonations was tried to determine if this type of a simplified process would be successful.

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

Research Project No: 1

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

6. The Extraction of Uranium From FMPC Sump Cake, Using Mineral Acid Digestion and Ammonium Precipitation

Experiments on FMPC sump cake was initiated during the present report period. The purpose of experimentation was to extract residual uranium from this material using either hydrochloric or sulfuric acid digest techniques, leaving acid insoluble discard residues containing less than .05% U308.

50 gram samples of the raw material assaying 14.7% U308 were pulverized to less than 100 mesh, slurried in 200 ml of water, and digested in hydrochloric acid and sulfuric acid respectively at pH values approximating 0.0 for periods of time up to six hours, using sodium chlorate as an oxidizing agent. Digestion was carried out at 90° to 95° C. After digestion, acid insolubles were removed by filtration and washed with water until colorless. Acid insoluble residues from the hydrochloric acid digestion treatment averaged 32%

of the original volume and were found to contain approximately .07% U308. Acid insolubles resulting from the sulfuric acid digest treatment approximated 75% of the original volume and contained, on the average, .08% U308.

Filtrates from the mineral acid digest treatment were collected, combined with the wash, and neutralized with 2:1 ammonium to approximately pH 7.0. Precipitated hydroxides were removed from the slurry by filtration and washed with water. The end product was dried at 110° C and analyzed for uranium and fluorine content. The end product resulting from the hydrochloric acid digest treatment averaged 62% U308 and .48% F. The end product resulting from the sulfuric acid treatment averaged 60% U308 and .45% F.

The end product obtained by this treatment was calcined at 800° C. This resulted in an increment of uranium content to approximately 75% U308, and a reduction of fluoride values to less than .02% F. It is evident from the data obtained to date that even protracted periods of digest time, using either hydrochloric or sulfuric acid, will not result in acid insoluble residues containing less than .05% U308. Attention will be given in future experimentation to calcination of this material prior to acid digestion to determine if this will result in reduction of insoluble uranium values to the acceptable maximum content of .05% U308. Data may be found in Table I.

C. DIGESTION AND REFINING OF BFC-6

Research Project No: 4

Research Supervisor: J. E. Summers

LABORATORY OPERATIONS

7. Experiments were continued on BFC-6 during the present report period. Optimum conditions necessary to extract uranium from this material using sulfuric acid digest procedures leading to acid in soluble residues containing less than .05% U308 were sought. As indicated in the previous report, ordinary digest periods would not be satisfactory in achieving maximum recovery of uranium from this material. Experiments were conducted to determine if additional time of digestion would be effective in obtaining satisfactory extraction. 100 gram samples of the raw material were water leached to remove soluble barium and then calcined at 900° F for one hour. After slurrying in 300 ml of water, the samples were digested in sulfuric acid at pH 0.0 in the presence of sodium chlorate as an oxidizing agent for periods of time up to eight hours. Acid insolubles were removed from the digest slurry by filtration and washed with water until colorless. Insoluble residues were examined for uranium content and were found to average between .1 - .2% U308. Apparently more protracted periods of digest time will be ineffectual with regard to further extraction of insoluble uranium values. Representative data may be found in Table II.

In order to determine why the sulfuric acid digest technique does not result in acid insoluble residues with discard specifications, 50 gram samples of insoluble sulfuric acid residues from primary digests were slurried in 300 ml of water and redigested in sulfuric acid at pH 0.0 in the presence of sodium chlorate for three hours at 90° C. Acid insolubles were removed by filtration and washed with water until color free. Examination of the residue indicated only a slight reduction in uranium content. Average data may be found in Table III.

It was theorized that the failure of the sulfuric acid digest treatment might be due to incomplete oxidation of metallic uranium. 50 gram samples of acid insolubles from a preliminary sulfuric acid digest treatment were recalcined at 900° F for one hour, slurried in 300 ml of water, and digested with sulfuric acid at pH 0.0 in the presence of sodium chlorate at 90° C for three hours. Acid insolubles were removed by filtration and washed with water until colorless. Analysis of the residues indicated substantial reduction in uranium content. Additional experiments will be performed to determine if longer periods of calcination time will be effectual in reducing acid insoluble residues to less than discard specifications of .05% U308. Sample data may be found in Table IV.

at 90° C. Acid insolubles were removed by filtration and washed with water until color free. The clarified filtrate was combined with the filtrate wash and uranyl ammonium phosphate was precipitated by the addition of 0.5 grams of monobasic ammonium phosphate and elevating the pH to 2.5 by the addition of dilute ammonium. The resultant precipitate was removed by filtration and washed with water until color free. Data accumulated to date indicates that, under optimum conditions with adequate calcination of the raw material, the Vitro sodium carbonate residues may be successfully treated by this process. Data may be found in Table VI.

EXHIBITS

TABLE I

EXTRACTION OF URANIUM USING MINERAL ACID DIGESTION

Material: "FMPC" Sump Cake

Assay: 14.7% U308

	<u>EXPERIMENT NUMBER</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Weight of sample (gm.)	50	50	50	50
Weight of H ₂ O (gm.)	200	200	200	200
Acid used for digestion	HCl	HCl	H ₂ SO ₄	H ₂ SO ₄
Acid (gm.)	110	110	65	65
Digest Time (hr.)	3	6	3	6
Digest pH	0.0	0.0	0.0	0.0
Digest Temperature (°C)	95	95	95	95
Acid Insolubles (gm.)	16	15	37.0	37.75
Acid Insolubles (% U308)	.07	.07	.08	.07
pH of Precipitation	7.0	7.0	7.0	7.0
Ammonia Salts (gm)	13	12	11.0	11.5
Ammonia Salts (% U308)	52.60	52.08	60.84	59.98
Ammonia Salts (% F)	.45	.48	.47	.46
Temperature of Calcination (°F)	1500	1500	1500	1500
Black Oxide (% U308)	62.36	61.88	71.20	70.84
Black Oxide (% F)	.019	.02	traces	.001

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TABLE II

DETERMINATION OF OPTIMUM TIME OF SULFURIC ACID DIGESTION

Material: BFC-6 (Water Leached)

Assay: 19.6% U308

	<u>EXPERIMENT NUMBER</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of sample (gm)	100	100	100
Calcination Time (hr.)	1.0	1.0	1.0
Calcination Temperature (°F)	800	900	1000
Weight of H ₂ O (gm)	300	300	300
Weight of H ₂ SO ₄ (gm)	71.76	66.24	64.40
Weight of NaClO ₃ (gm)	8.8	7.7	7.0
pH of Digestion	0.0	0.1	0.0
Temperature of Digestion (°C)	95-100	95-100	95-100
Time of Digestion (hr.)	8	8	8
Acid Insolubles (gm)	60.9	61.8	61.5
Acid Insolubles (% U308)	.21	.23	.28

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TABLE III

RE-DIGESTION OF ACID INSOLUBLES IN SULFURIC ACID

Material: BFC-6 Acid Insolubles

Assay: .34% U308

	<u>EXPERIMENT NUMBER</u>	
	<u>1</u>	<u>2</u>
Weight of Sample (gm)	50	50
Weight of H ₂ O (gm)	.00	300
Weight of H ₂ SO ₄ (gm)	36.80	37.0
Weight of NaClO ₃ (gm)	0.3	0.5
Time of Digestion (hr.)	3	3
pH of Digestion	0.0	0.0
Temperature of Digestion (°C)	90	90
Acid Insolubles (gm)	45.9	50.0
Acid Insolubles (% U308)	.21	.22

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TABLE IV

DETERMINATION OF THE BENEFITS OF RE-CALCINATION OF ACID INSOLUBLES

Material: BFC-6 Acid Insolubles

Assay: .36% U308

	<u>EXPERIMENT NUMBER</u>	
	<u>1</u>	<u>2</u>
Weight of Sample (gm)	50	50
Calcination Temperature (°C)	900	900
Calcination Time (hr.)	1.0	1.0
Weight of H ₂ O (gm)	300	300
Weight of H ₂ SO ₄	33.12	33.00
Weight of NaClO ₃	1.4	1.5
Digest Time (hr.)	3	3
Digest pH	0.0	0.0
Digest Temperature (°C)	90	90
Acid Insolubles (gm)	44.4	45.0
Acid Insolubles (% U308)	.12	.11

TABLE V

EXTRACTION OF URANIUM BY HYDROCHLORIC
ACID AND RECARBONATION

Material: Pitchblende Carbonate Residue

	<u>EXPERIMENT NUMBER</u>	
	<u>1</u>	<u>2</u>
Assay (% U308)	1.6	0.7
Weight of Sample (gm)	100	100
Weight of H ₂ O (gm)	400	200
Weight of HCl (gm)	165	220
Weight of NaClO ₃ (gm)	0.25	0.25
pH of Digestion	0.0	0.0
Time of Digestion (hr.)	1.0	1.0
Temperature of Digestion (°C)	90	90
Acid Insolubles (gm)	8.0	6.5
Acid Insolubles (% U308)	.050	.035
Filtrate Volume (ml)	650	500
Filtrate (% U308)	0.17	0.14
Na ₂ CO ₃ added (gm)	135	120
Time of Digestion (hr.)	3.0	3.0
Temperature of Digestion (°C)	60	60
Residue (gm)	85	86
Residue (% U308)	.65	.22
H ₂ O added to Re-slurry Residue (ml)	200	100
Na ₂ CO ₃ added to Slurry (gm)	10	5
Time of Digestion (hr.)	3.0	3.0
Temperature of Digestion (°C)	90	90
Residue (gm)	83.0	84.0
Residue (% U308)	.15	.10
H ₂ O used to Re-slurry Residue (gm)	100	100
Na ₂ CO ₃ added (gm)	10	10
Time of Digestion (hr.)	3.0	3.0
Temperature of Digestion (°C)	90	90
Residue (gm)	82.5	83.0
Residue (% U308)	.046	.035
Combined Filtrate Volume (ml)	1100	850
Combined Filtrate (% U308)	.12	.08
NaOH added to Filtrate (gm)	22.0	17.0
Residue (gm)	2.0	0.80
Residue (% U308)	78.2	80.02
Recovery (%)	97.0	93.5

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TABLE VI

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PRECIPITATION OF URANYL AMMONIUM PHOSPHATE FROM AN HCl FILTRATE

Material: Vitro Carbonate Residue

Assay: .26% U308

	Experimental Lot #1		Charge #1		Charge #3	
Weight of Sample (gm)	100	100	100	100	100	100
Laboratory Calcination Temperature (°F)	--	1300	--	1300	--	1300
Weight of H ₂ O (gm)	200	200	200	200	200	200
Weight of HCl (gm)	50	50	50	50	50	50
Acid Insoluble (gm)	86.0	86.0	85.5	84.5	85.0	85.0
Acid Insolubles (% U308)	.056	.017	.087	.028	.03	.01
Digest pH	0.9	0.95	0.9	0.85	0.8	0.8
Digest Time (hr.)	0.5	0.5	0.5	0.5	0.5	0.5
Digest Temperature (°C)	90	90	90	90	90	90
NH ₄ H ₂ PO ₄ added (gm)	0.5	0.5	0.5	0.5	0.5	0.5
Filtrate Volume (ml)	325	330	325	325	320	330
pH of Precipitation	2.5	2.5	2.5	2.5	2.5	2.5
Discard Effluent (% U308)	.023	.008	.02	.005	.013	.001
Recovery - Total (5)	44.0	84.8	47.4	84.7	74.0	94.25

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