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Date: 11/24/09

THE VITRO MANUFACTURING COMPANY

PITTSBURGH, PENNSYLVANIA

**PROBLEMS OF LEACHING
AND DIGESTION OF
URANIFEROUS SLAGS
AND ALLOYS**

Progress Report No. 14

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**NYO-1148
"Technology-Feed Materials"**

Classification cancelled (or changed to **UNCLASSIFIED**)

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THE VITRO MANUFACTURING COMPANY

PROBLEMS OF LEACHING AND DIGESTION OF URANIFEROUS SLAGS AND ALLOYS

Period: July 1952

Contract: AT-(30-1)-1241

* * *

1. Scope of Program

As of July 1, 1952 the research program consisted of the following projects:

Digestion and Refining of C-Slags and Other Residues

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

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

Refining and Processing of Sodium Carbonate Residues

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 Report

Progress Report - June 1952

3. Project Status

Digestion and Refining of C-Oxide and Other Residues

Data accumulated from preliminary experiments designed to establish feasibility of the purification of DC-21 indicates that this material will readily adapt to the present Vitro process as regards purification of C-type materials.

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Digestion and Refining of Sodium Carbonate Residues

A. Pitchblende Carbonate Residues

Tentative results from completed experiments employing the direct sodium carbonate leach and sodium carbonate digestion under low pressures indicate that the Vitro pitchblende carbonate residues will not satisfactorily adapt to this treatment since insoluble residues remain in excess of prospective specifications of .05% U308.

Data collected from experiments using mineral acid digestive procedures indicates that sulphuric acid is not effective in solubilizing contained uranium values from the pitchblende residues. However, a hydrochloric acid treatment is indicated to be effective in solubilizing uranium values from these residues on a quantitative basis.

Experiments involving extraction of solubilized uranium values by means of reprecipitation of the R_2O_3 elements with sodium carbonate have been only partially successful to date. Further treatment of residues resulting from a treatment of this nature may prove successful.

B. Current Carbonate Residues

Preliminary experiments indicate that calcination of residues resulting from current production at temperatures in excess of 1200°F followed by hydrochloric acid digestion will result in the dissolution of uranium contained in these residues on a quantitative basis, leaving an insoluble residue containing less than .05% U308.

Digestion and Refining of BFC-6

Completed pilot level experiments indicate that the elevation of digest pressures to 65 p.s.i.g. will not substantially benefit the extraction of uranium from these residues.

Experiments designed to determine the optimum capacity of the present equipment were initiated. Preliminary results indicate that optimum capacity for the established equipment will be considerably less than expectations.

LABORATORY OPERATIONS

Process Data Concerning the Refining of DC-21

Experiments were conducted of a scoping nature to obtain process data concerning the extraction of uranium values from DC-21. 500 gram charges of the raw material were calcined at 1200° F and carried through the recovery

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process to obtain precipitate volumes, weights, etc. for flow sheet calculations. The process included hydrochloric acid NaClO_3 digestion, ammonia salt precipitation from the filtered digest liquor, dissolution of the ammonia precipitate in sulphuric acid, neutralization of sulphuric acid with excess sodium carbonate, and subsequent recovery of the uranium as sodium diuranate by precipitation with sodium hydroxide. This process parallels the established process for the refining of C-slag materials. Detailed data are as follows:

TABLE I

	Weight	ml-solids 100 ml slurry	Slurry Vol. ml	ml-solids gm. DC-21	Approx. %U308 Content
HCl - NaClO_3	A 5.0	A .25	A 3400	A .017	A .12
Acid Insoluble	B 11.0	B .25	B 3400	B .017	B .10
Ammonium	A 12.0	A 2.2	A 3425	A .15	A 70.0
Uranate	B 12.5	B 2.4	B 3425	B .17	B 72.0
H_2SO_4	A --	A .20	A 250	A .0010	A --
Acid Insoluble	B --	B .25	B 250	B .0012	B --
Sodium Carbonate	A 7.5	A 12.0	A 400	A .09	A .25
Residue	B 8.0	B 10.0	B 400	B .08	B .25
Sodium	A 10.5	A 2.0	A 500	A .020	A 82.0
Diuranate	B 11.0	B 2.2	B 500	B .022	B 82.0

Digestion and Refining of Sodium Carbonate Residues

Pitchblende Residues

A sample was collected from the Vitro stockpile assaying 1.69% U308 which may be considered to be representative of all carbonate residues resulting from the refining of pitchblende ores. Leaching experiments of varied nature, using acids and alkalis were initiated to determine if a wet treatment of any nature would be satisfactory in extracting the contained uranium values. Primary experiments on the pitchblende residues were conducted using a hot 5% sodium carbonate leach followed by removal of the insoluble residue by filtration. In most instances recovery was somewhat unsatisfactory varying between 82 and 88%. Residues from the treatment remained well in excess of the proposed specification of .05% U308. Representative data may be found in Table II.

TABLE II

Pitchblende Carbonate Residues - .05% Na₂CO₃

	<u>Experiment No.</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Weight of sample(gm)	250	250	250	250
Weight of H ₂ O (gm)	1000	1000	500	500
Weight of Na ₂ CO ₃ (gm)	50	50	50	50
Digest Time (hr)	4	4	4	4
Digest Temperature (°C)	90	90	90	90
Residue Weight (gm)	212.5	213	212	212
Residue % U308	.26	.22	.34	.332
Recovery %	87	88.5	82	83

Additional experiments were conducted, using a sodium carbonate autoclave digest with elevated temperatures to 290°F at low pressures to 45 p. s. i. g. Little or no improvement in the efficiency of extraction was noted with recovery values averaging 83 to 85%. As may be noted, the residues resulting from this form of sodium carbonate digestion also failed to meet projected purity specifications. Data, as obtained may be found in Table III.

TABLE III

Pitchblende Carbonate Residues - Pressure Digestion

	<u>Experiment No.</u>	
	<u>1</u>	<u>2</u>
Weight of sample (gm)	500	500
Weight of H ₂ O (gm)	1000	1000
Weight of Na ₂ CO ₃ (gm)	100	100
Pressure of Digestion (psig)	45	45
Time of Digestion (hr)	4	4
Residue Weight (gm)	425	425
Residue % U308	.31	.33
Recovery %	85	83

An attempt was made to solubilize the uranium values contained within pitchblende carbonate residues by dissolution in sulphuric acid. Using normal procedures, samples of the residue were pulverized to less than 100 mesh, slurried in water and digested in sulphuric acid. In every instance a large insoluble residue was formed which was almost impossible to filter. The uranium level of the acid insoluble remained well above maximum purity specifications and, in general, this means of extraction may be considered

inapplicable or unsatisfactory insofar as the pitchblende residues are concerned. Detailed data are as follows:

TABLE IV

Pitchblende Carbonate Residue - H_2SO_4 Digestion

	<u>Experiment No.</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of Sample (gm)	100	250	250
Calcination temperature ($^{\circ}\text{C}$)	--	--	1400
Weight of H_2O (gm)	500	500	500
Weight of H_2SO_4	162	234	234
pH of digest	0.0	0.0	0.0
Time of Digest (hr)	4	4	4
Temperature of Digest ($^{\circ}\text{C}$)	90	90	90
Insoluble Residue (gm)	140	355	350
Insoluble Residue % U308	.33	.33	.31
% Extraction	71	73	75

An additional group of experiments was completed using hydrochloric acid digestive procedures. Tentative analyses indicate that this form of extraction of the uranium contained in the pitchblende residues may be considered completely satisfactory. The insoluble level of the carbonate residues, after digestion, was reduced to 6 to 7% of the original bulk and contained only trace amounts of uranium. Data may be found in Table V.

TABLE V

Pitchblende Carbonate Residue - HCl digest

	<u>Experiment No.</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of sample (gm)	100	100	100
Weight of H_2O (gm)	500	500	500
Weight of HCl (gm)	161	165	168
pH of digest	0.0	0.0	0.0
Temperature of Digest ($^{\circ}\text{C}$)	90	90	90
Time of Digest (hr.)	3	3	3
Insoluble Residue (gm)	7.0	11.0	9.0
Insoluble Residue % U308	traces	.085	.10
Recovery %	100	99.6	99.5

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Preliminary experiments were conducted on the pregnant filtrates resulting from the hydrochloric acid digestive procedures to determine the most satisfactory form of recovering uranium values. Reprecipitation of the R_2O_3 group by neutralization with sodium carbonate was the first means considered. The results of preliminary experiments tentatively indicate that the use of this method of extraction results in additional occlusion of uranium by the precipitate bulk leaving a residue considerably in excess of discard values. Additional experiments are planned pursuing this line of investigation to determine if a satisfactory procedure may be established. Data as obtained to date is presented in detail below:

TABLE VI

Pitchblende Carbonate Residue - Purification

	<u>Experiment No.</u>	
	<u>1</u>	<u>2</u>
Filtrate Volume (ml)	750	750
Na_2CO_3 - added (gm)	133	135
Digest Time (hr)	4	4
Digest Temperature ($^{\circ}C$)	60-70	60-70
Carbonate Residue - gm	86	85
Carbonate Residue % U_3O_8	.70	.61
Recovery %	62	68

It was believed that recovery of uranium by a reprecipitation of the R_2O_3 group by neutralization with sodium carbonate may have been satisfactory due to the presence of large quantities of barium which may have formed insoluble complexes of uranium in the presence of the carbonate ion. Consequently, experiments were conducted to determine if the removal of barium as a soluble hydroxide, prior to the precipitation of the R_2O_3 group with sodium carbonate, would beneficiate extraction. An ammonia salt was precipitated from a hydrochloric acid digest filtrate of the pitchblende residues, redissolved in sulphuric acid, followed by precipitation of the R_2O_3 group by neutralization with sodium carbonate. The carbonate residue was reduced in bulk with a consequent improvement in recovery values although uranium levels remained well in excess of maximum specifications. It is proposed and probable that a repulp wash of the carbonate residue produced by this means of purification will result in the recovery of additional values. Detailed data to date are presented in Table VII.

TABLE VII

	<u>Experiment No.</u>	
	<u>1</u>	<u>2</u>
Filtrate Volume (ml)	750	750
NH ₄ OH added - gm	81	80
pH of precipitation	6.5	6.5
Weight of H ₂ SO ₄ (gm)	90	90
Weight of H ₂ O (gm)	500	500
Digest pH	0.0	0.0
Digest Time (hr.)	1	1
Digest Temperature (°C)	90	90
Na ₂ CO ₃ (gm)	140	140
Digest Time (hr.)	4	4
Digest Temperature (°C)	60-70	60-70
Carbonate Residue - gm	66	65
Carbonate Residue % U ₃ O ₈	.71	.60
Recovery %	71	78

Current Carbonate Residues

As previously reported, extraction of uranium values from current carbonate residues, using a hot 5% sodium carbonate leach, has proved to be completely unsatisfactory. A series of experiments was conducted to determine if digestion in the presence of sodium carbonate at elevated temperatures under low pressures would be a more satisfactory means of purification. The results as obtained indicate that while this is a superior means of purification as compared to digestion at atmospheric pressure the sodium carbonate leach continues to be unsatisfactory. Therefore, this line of experimentation has been discarded as regards residues resulting from current production. Representative data are as follows:

TABLE VIII

Carbonate Residue - Pressure Digestion

	<u>Experiment No.</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Weight of sample	1000	1000	800
Weight of H ₂ O	1000	1000	1000
Weight of Na ₂ CO ₃	100	100	100
Pressure of Digest	45	45	45
Time of Digest	4	4	4
Residue - gm	825	830	660
Residue % U ₃ O ₈	.14	.12	.18
Recovery %	58	62	56

As previously determined, extraction of uranium from these residues by dissolution in mineral acids was only partially satisfactory. Consequently, portions of the current residues were calcined at temperatures approximating 1200° F prior to digestion in sulphuric and hydrochloric acid to determine if this would aid in the recovery of uranium from these residues. While somewhat improved as compared to digestion of uncalcined material, sulphuric acid was not satisfactory in reducing the residues below proposed recovery specifications. However, hydrochloric acid digestion is tentatively indicated to be a notable success with insoluble residues reduced below .05% U3O8. The line of investigation will be pursued to determine if consistent results may be obtained. Preliminary data is presented below:

TABLE IX

Carbonate Residues - Calcined, HCl and H₂SO₄ Digestion

	<u>Experiment No.</u>	
	<u>1</u>	<u>2</u>
Weight of Sample (gm)	500	500
Calcination Temperature (°C)	1400	1400
Acid Used for Digestion	H ₂ SO ₄	HCl
pH of Digest	0.0	0.0
Time of Digest (hr.)	3	3
Temperature of Digest (°C)	90	90
Insoluble Residue (gm)	220	210
Insoluble Residue % U3O8	.187	.035
Recovery %	95	99.5

PILOT OPERATIONS

Digestion and Refining of BFC-6

Pilot level experiments were continued, data collected and evaluated. Experiments designed to establish optimum capacity of the present equipment were initiated and completed. Charge weights of the water leached material were increased to 400 lbs. and digested for six hours at 45 p. s. i. g. under optimum conditions as previously established. In general, recovery was not considered satisfactory and it is presumed, therefore, that maximum capacity for the Vitro autoclave is considerably less than anticipated. Additional experiments will be conducted to determine whether or not any increase of the present 200 lb. charge weight will be feasible.

In addition, experiments were conducted to establish whether or not increasing autoclave pressures to 65 p. s. i. g. with a corresponding increment in digest temperatures would benefit extraction. No apparent value, except of a minor nature, was derived by the increase in pressure.

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Experiment No.

	<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>	<u>10</u>	<u>11</u>
BFC-6 (lb.)*	403	404	385	397	404	386	383	397	397	133	184
H ₂ O (lb.)	5940	5940	5940	5000	5000	5000	5000	5000	5000	2000	3045
Na ₂ CO ₃	600	600	600	500	500	500	500	500	500	200	300
Digest Time	6	6	6	6	6	6	6	6	6	6	6
Digest Pressure	45	45	45	45	45	45	45	45	45	65	65
Insoluble Residue(%U308)	10.5	6.97	5.11	7.7	8.8	5.9	5.8	4.70	5.67	2.80	3.20
Recovery %	52.3	71.2	76.4	66.4	57.0	74.1	75.2	79.1	77.3	89.2	87.6

All charges were re-cycled through the digest process to establish optimum recovery.

BFC-6 Charge No.

H ₂ O (lb.)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
Na ₂ CO ₃	300	200	200	200	200	200	200	200	200	200	200
Digest Time (hr.)	4	4	4	4	4	4	4	4	4	4	4
Digest Pressure (psig)	45	45	45	45	45	45	45	45	45	65	65
Insoluble Residue(%U308)	7.4	5.2	4.3	5.1	5.4	4.2	4.1	3.6	4.1	2.00	2.10
Total Recovery %	68.6	77.2	80.8	75.9	76.1	81.3	82.6	86.1	83.1	92.1	91.8

*Charge weights represent the water leached material assaying approximately 18.6%U308

Inadequate recovery may generally be attributed to charge weights in excess of optimum capacity and while uranium contained within the residues may be assumed to be in a recoverable form, it will be necessary to return those residues to the digest cycle to obtain recovery values comparable to those previously established.

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Progress Report No. 14
NYO-1148

TO "Technology-Feed Materials"

FROM Arden M. Johnson

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