~~CONFIDENTIAL~~

This Copy NYO-1147

~~SECRET~~ UNCLASSIFIED

~~SECURITY INFORMATION~~

THE VITRO MANUFACTURING COMPANY

PITTSBURGH, PENNSYLVANIA

PROBLEMS OF LEACHING AND DIGESTION OF URANIFEROUS SLAGS AND ALLOYS

Progress Report No. 13

NYO-1147
"Technology-Feed Materials"

DISCLAIMER

THE VITRO MANUFACTURING COMPANY

PROBLEMS OF LEACHING AND DIGESTION OF URANIFEROUS SLAGS AND ALLOYS

Period: May 1952

Contract: AT-(30-1)-1241

* * *

1. Scope of Program

As of May 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 - April 1952

3. Project Status

Digestion and Refining of C-Oxide and Other Residues

Data accumulated from a series of experiments conducted to establish optimum efficiency of the continuous precipitation techniques by adjusting certain variables such as agitator blade size, blade pitch and speed of agitation,

were completed. The results indicate an increment in efficiency by increasing speed of agitation and the size of the propeller blade, resulting in a more superior product as regards both uranium and fluorine content of the precipitate.

Tentative results establish that a product conforming to purity specifications may be precipitated(using ordinary batch techniques) from the acid digest filtrates of C-oxide with pyridine.

Continuous filtration of continuously precipitated ammonium diuranate from the acid digest filtrates of C-oxide has not given desirable results to date. The failure of ammonia salts to filter on a continuous basis may in all probability be attributed to the use of the plate and frame press. It may be that filtration could be accomplished through the use of up to date equipment such as the pre-coated drum filter or specialized equipment such as the leaf-type filter designed for slime forming precipitates. The lack of such equipment has proven detrimental in definitely establishing the complete process in its most desirable form.

Digestion and Refining of Sodium Carbonate Residues

Preliminary experiments conducted on additional samples of the carbonate residues resulting from Vitro's current product indicate that ordinary means of purification will not effect satisfactory recovery. Neither the direct sodium carbonate leach or acid digestion have proven satisfactory when used on the raw material without additional refinements.

Process Data on the Refining of BFC-6

Evaluation of the data collected on the pilot level concerning the recovery of contained uranium values from BFC-6 indicates that the efficiency of this process could be considerably improved if the equipment were available to establish a carefully controlled calcination cycle with the human element eliminated through the use of a modern rotary furnace and electronic control of calcining temperatures.

Continuous Precipitation of Ammonia Salts From the Acid Digest Liquors of C-oxide

Consideration of the theory of continuous precipitation demonstrates that a spontaneous mixing of the digest filtrates of C-oxide and ammonia at a specific pH below neutrality, (usually pH 6.0), should obtain an ammonia salt which when converted to black oxide will contain in excess of 90% U_3O_8 (plus whatever iron or aluminum should be present)since on a theoretical basis calcium and magnesium do not precipitate below pH 7.0. As may be noted

from data previously reported, ammonia salts obtained in the laboratory and on the pilot level contain various amounts of alkaline earths usually correlated with fluoride content which we may assume precipitated due to momentary formation of localized areas of high alkalinity during the mixing process. Under optimum conditions of mixing we would presume that this would not occur.

Although, in general, the uranium levels were below 80% a satisfactory product in excess of purity specifications has been obtained on a pilot level when experiments were conducted by skilled, professional employees. When the operation, on a production basis, is placed in the hands of non-technical personnel it is felt that some margin of safety should be established, if economically feasible, due to the possibility of error.

A series of experiments were completed which were designed to indicate the influence of propeller size, blade pitch and the speed of agitation on the quality of the precipitate. It is presumed that should optimum conditions be established by the influence of one or several of these factors conversion could be made on the production scale at minimum expense. Experiments were conducted on samples from the same digests with fixed speed of propeller agitation to 4000 r.p.m. and with variation of propellor size and blade pitch. It was found that by using these techniques the product was improved as a result of more intense mixing of the acid filtrate and the precipitant. Although the precipitate seldom contained more than 3 to 5% alkaline earths we were unable to obtain a product absolutely free of calcium and magnesium. As a result of the reduction of alkaline earth content fluoride levels were reduced to less than .05%. Presumably, various factors of mixing could be incorporated on a production level which would be beneficial to both fluoride and uranium levels. Consideration will be given to incorporation of superior features of agitation into the pilot phase. Data as obtained in the laboratory is presented below:

Experiment	1	2	3	4	5	6	7	8	9
pH of precipitation	5.7	6.05	6.3	6.6	5.9	6.0	7.2	5.8	6.45
Discard Effluent (%U308)	.0005	.0001	.0001	.0001	.0001	.0005	.0004	.0006	.0003
Speed of agitation(r.p.m.)	5000	5000	5000	5000	5000	5000	5000	5000	5000
Radius of blade	1/2"	1/2"	1/2"	3/4"	3/4"	3/4"	1"	1"	1"
Pitch of blade	45°	45°	45°	45°	45°	45°	45°	45°	45°
Calcination temperature(°C)	800	800	800	800	800	800	800	800	800
% U308	85.2	85.5	84.5	85.12	86.24	85.5	76.19	84.5	82.8
% F	.017	.011	.02	.0004	.01	.01	.066	.007	.03
% CaO, MgO	4.2	5.4	6.2	5.2	2.9	4.8	15.9	3.4	2.9

[redacted]

Precipitation of Uranium From the Acid Digest Filtrates of C-Oxide With Pyridine

Emphasis being placed upon obtaining a satisfactory product from the acid digest filtrates of C-oxide without further purification has led to a search for precipitating agents, other than ammonia, which may be effective. Since pyridine forms soluble complexes with calcium and magnesium it was decided that it may be of some value in the precipitation of uranium from the acid digest filtrates of C-oxide, for, in general, fluoride levels and uranium levels may be directly correlated with alkaline earth content of the precipitate. Since pyridine is of a basic nature it may be successfully used as a uranium precipitant at pH 5.5 to 6.0. In this range uranium is quantitatively precipitated. Pyridine may not be used above this range due to the buffering characteristics of the compound in excess of pH 6.0. Samples of laboratory hydrochloric acid digests of C-oxide were partially neutralized with dilute ammonia to pH 2.0, adjusted to pH 5.5 to 6.0 with pyridine, filtered and washed until calcium and magnesium free, and calcined at 800°C. The resultant data established this as a satisfactory means of obtaining an acceptable product. The economics of precipitation on this basis are as yet undeveloped. No additional experiments are considered. Complete data is presented in Table II. It may be noted that it is possible that this may be a satisfactory form of recovering uranium from C-liner. No experiments are contemplated to prove the validity of this hypothesis.

Experiment	1	2	3	4
pH of precipitation	5.5 plus	5.5 plus	5.5 plus	5.5 plus
Pyridine used (% w/u)	10	1	1	1
Discard effluent(%U308)	.0001	traces	.0003	.0005
Calcination temperature (°C)	800	800	800	800
% U308	86.24	80.64	85.96	86.24
% F.	.004	.093	.038	.019
% CaO, MgO	traces	5.04	traces	traces

Digestion and Refining of Carbonate Residues Resulting From Current Production

Additional samples were prepared from the Vitro stockpile of carbonate residues and were found to average .295% U308. These samples were prepared from an extensive sampling of the entire Vitro stockpile and may be said to be representative of all residues resulting from the purification process as established and continued over a large period of years. Methods employing the direct sodium carbonate leach were applied to these samples and were found to be ineffective as compared to the same treatment applied to the original sample. Recovery did not exceed 60%. The same samples were pulverized to 100, 200 and 325 mesh to see if this would facilitate recovery. No further improvement, except of a minor nature, was noted.

[redacted]

Samples were then digested in sulphuric acid at pH 0.0 and oxidized with sodium nitrate. Investigation of the acid insoluble residue revealed it to be 63% of the original weight containing an average .21% U308. In this instance also recovery did not exceed approximately 60%. We conclude that uranium must be present in insoluble form, possibly in conjunction with silicates. The presence of some vanadium was observed in the samples.

Experiments are planned using either the sodium carbonate leach or acid digest in which the residues will be calcined at various temperatures to determine if this facilitates recovery. Experiments have been initiated to determine if the elevation of digest temperatures through the use of low pressures will aid in extracting the contained uranium values. Representative data is as follows:

TABLE I

	Experiment			
	1	2	3	4
Weight of sample (gm)	100	100	100	100
Mesh of sample	60	100	200	325
Weight of H_2O(gm)	500	500	500	500
Weight of Na_2CO_3(gm)	30	30	30	30
Time of digest(hr)	4	4	4	4
Temperature of digest (°C)	80	80	80	80
Residue (%U308)	.22	.12	.11	.14
% Recovery	25	60	63	53

TABLE II

	Experiment				
	1	2	3	4	5
Weight of sample(gm)	100	100	100	100	100
Mesh of sample	100	100	200	200	325
Weight of H_2SO_4(gm)	110	110	110	110	110
pH of digestion	0.0	0.1	0.0	0.15	0.1
Time of digestion(hr)	2	4	2	4	2
Temperature of digestion (°C)	90	90	90	90	90
Weight of residue(gm)	63.0	64.5	63.0	64.0	62.0
Residue (%U308)	.23	.18	.21	.23	.24
% Extracted	53	62	57	53	53

PILOT OPERATIONS

Pilot scale production and recovery of uranium values from BFC-6 was continued through the month of May on an active basis and data collected and evaluated.

Calcination of the Water Leached Material

Calcination of the raw material was continued as previously reported, and the efficiency of the manual type operation as previously established was accepted as maximum. Recovery during this period was normal as compared to recovery during previous months. Since this type of a manual calcination phase is obviously not as efficient as desired, it is planned during the following period to establish an automatic calcination operation using a rotary hearth furnace and automatic temperature control and stirring. This should give recovery values as desired. Portions of Lot #52 were also carried through the calcination operation and subsequent digestion in order to establish whether or not additional lots were amenable to the same treatment. In addition, sizing experiments were conducted on the raw material prior to calcination to establish whether or not further reduction of mesh size would benefit oxidation. All oxidation was carried out at 800°F for six hours.

On the laboratory level, additional experiments are planned concerning the oxidation of the raw material. A laboratory model of a rotary kiln is being constructed and when finished will be placed in operation to determine whether or not this would be a more efficient means of calcination than the methods of calcination now in use or planned.

Autoclave Digestion

The efficiency of the operation as correlated with the calcination operation was normal as compared with previous figures of total recovery. Recovery varied slightly from charge to charge. This is presumed to be due to variations in the calcination phase brought about by the human factor as a result of manual stirring. During the next period build-up will begin to establish the maximum capacity of the equipment now available for the production phase. Representative processing data for the entire period is as follows:

	Charge Number												
	24**	25	26**	27	28	29	30	31	32	33	34	35	36
BFC-6 (lb.)*	189	184	193	194	196	198	197	189	196	189	205	205	198
Mesh of BFC-6	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-100
Lot No.	20	52	20	52	20	52	20	20	20	20	20	20	20
H_2O (lb.)	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
Na_2CO_3 (lb.)	300	300	300	300	300	300	300	300	300	300	300	300	300
Digest Time (hr)	6	6	6	6	6	6	6	6	6	6	6	6	6
Digest Pressure (p.s.i.g.)	45	45	45	45	45	45	45	45	45	45	45	45	45
Insoluble Residue (%U308)	7.91	2.75	6.8	2.85	3.00	2.66	2.50	2.50	2.52	2.42	2.60	2.58	2.46
Recovery (%)	67.3	91.5	71.7	91.0	87.7	92.8	89.7	89.7	89.6	90.1	89.3	89.3	90.0

All charges with the exception of 24 and 26 were recycled through the digestion process to establish optimum recovery.

	Charge No.										
	25	27	28	29	30	31	32	33	34	35	36
BFC-6 (lb.)	140	150	151	153	152	144	152	145	158	159	151
H_2O (lb.)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Na_2CO_3	100	100	100	100	100	100	100	100	100	100	100
Digest Time (hr.)	4	4	4	4	4	4	4	4	4	4	4
Digest Pressure (p.s.i.g.)	45	45	45	45	45	45	45	45	45	45	45
Insoluble Residue (% U308)	2.21	2.18	2.31	2.10	2.10	2.16	2.06	2.00	2.20	2.21	2.04
Total Recovery (% U308)	94.2	94.1	91.7	94.4	91.6	91.4	91.8	91.8	91.4	91.1	92.2

*Weights represent the concentrated residue resulting from the water leach treatment assaying 18.66% U308 for Lot No. 20 and 24.4% U308 for Lot No. 52.

**Failure to recover the expected values from these charges may be attributed to faulty calcination resulting from material handling error. A recalcination is planned.

Continuous Precipitation of Ammonia Salts From the Acid Digest Filtrates of C-Oxide

Ammonia salts were precipitated from the acid digest filtrate of C-oxide on a pilot level over a twenty-four hour period with direct filtration of the resultant residue immediately following precipitation, in order to establish the feasibility of the use of these techniques on a continuous production basis. Precipitation was considered normal in every respect but filtration of the precipitate was exceptionally slow. A 24 inch iron plate and frame press was used with cotton filter cloths. The prolonged periods of time necessary for filtration have resulted in a change in the thinking as regards filtration of ammonia salts. It is now presumed that the precipitate will be allowed to settle and the supernate decanted prior to filtration. This is possible since we have established that under proper conditions prolonged periods of hold-up in the collection tank do not influence uranium or fluoride content of the product. The use of settling agents was considered as a means of expediting settling and subsequent filtration but no satisfactory agent could be found. The most efficient agent found was Gum Tragacanth but it left much to be desired. Filtration aids were also considered but although several satisfactory aids are available unfortunately the economics will not permit their use.

The study of continuous precipitate techniques as regards the precipitation of ammonium diuranate from the acid digest filtrates of C-oxide is expected to enter an intensive stage of investigation on the pilot level during the next period which should satisfactorily resolve any problems brought about by build up to the production phase. A comprehensive report concerning the development of the process will be compiled and included in the monthly progress report.

* * *

NYO-1147
"Technology-Feed Materials"

UNCLASSIFIED

~~SECRET~~

~~CONFIDENTIAL~~

28460

THE VITRO MANUFACTURING COMPANY

PITTSBURGH 4, PENNSYLVANIA

SEC~~URITY INFOR~~MATION

COVER & ROUTING SHEET

THIS COPY TO BE ROUTED TO:

1. USAEC, Cleveland Area Office
2. USAEC, New York Operations Office
3. USAEC, New York Operations Office
4. USAEC, New York Operations Office
5. The Vitro Mfg. Co., Pittsburgh, Pa.
6. The Vitro Mfg. Co., Canonsburg, Pa.
7.
8.
9.
10. Job Files

COPY NO 2/6A

DATE June 20, 1952

SUBJECT Problems of Leaching and Digestion of Uraniferous Slags and Alloys. Progress Report No. 13

TO NYO-1147 "Technology-Feed Materials"

FROM A. J. Strod
A. J. Strod

CLASSIFICATION SECRET

BEFORE READING OR HANDLING THIS DOCUMENT, SIGN AND DATE BELOW:

SIGNATURE	DATE	SIGNATURE	DATE

DO NOT PHOTOSTAT

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~~