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THE VITRO MANUFACTURING COMPANY

PITTSBURGH, PENNSYLVANIA

AEC RESEARCH AND DEVELOPMENT REPORT

NYO-1156

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

Progress Report No. 22

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PROBLEMS OF REFINING URANIFEROUS RESIDUES
TECHNOLOGY - FIELD MATERIALS

SUMMARY

GENERAL

1. Scope of Program

As of February 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%.

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4. Previous Reports

NYO-1145	March	1952 - Progress Report No. 11	Y
NYO-1146	April	1952 -	No. 12 N
NYO-1147	May	1952 -	No. 13 N
NYO-1148	June	1952 -	No. 14 N
NYO-1149	July	1952 -	No. 15 Y
NYO-1150	August	1952 -	No. 16 N
NYO-1151	September	1952 -	No. 17 N
NYO-1152	October	1952 -	No. 18 N
NYO-1153	November	1952 -	No. 19 N
NYO-1154	December	1952 -	No. 20 N
NYO-1155	January	1953 -	No. 21

PROJECT ST. TUS

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

Experiments were completed to determine if C-Oxide scrubber material could be purified separately rather than by inclusion in the normal C-Oxide purification process. Experimental data indicates that sulfuric acid digestion of the raw material, removal of acid insolubles by filtration, and batch precipitation of ammonium di-uranate from the clarified filtrate with subsequent calcination of the precipitate to black oxide at 800° C will be a satisfactory method for obtaining an end product within purity specifications as regards uranium and fluorine content.

Process data for the sulfuric acid purification of C-Oxide scrubber material with regard to precipitate volumes, weights, slurry densities, etc. were obtained for flow sheet calculations.

Experimental work during the period under report was concentrated on obtaining information and determining optimum factors concerning the wet processing of C-Liner with emphasis on mineral acid digestion. Particular emphasis was placed on digest characteristics, the elimination of abnormal and excessive foaming during acid neutralization of the raw material and other digest factors such as optimum time of digestion and the influence of particle size of the raw material on successful extraction of uranium from the residue.

An extensive series of experiments was conducted to determine the particle size characteristics of wet unpulverized, uncalcined C-Liner. In addition, experiments were completed designed to assay the influence of particle size on successful mineral acid digestion of the raw material resulting in acid insolubles containing less than .05% U3O8.

A series of experiments was completed to determine the optimum time of hydrochloric acid digestion necessary to reduce the insoluble residue to less than .05% U3O8. Based on data accumulated from previous experimentation, and additional data from these experiments, one and one-half hour may be considered to be an adequate time of digestion for satisfactory solubilization of uranium on a laboratory basis.

Preliminary experiments were initiated in order to determine ways and means of reducing the violent foaming characteristics of uncalcined C-Liner to a controllable minimum during mineral acid digestion. Various compounds were tested for their effectiveness in combating the formation of foam. Reagents tested in preliminary experimentation

include Butyl Alcohol, Amyl Alcohol, Aerosol, Heptyl Alcohol, Octyl Alcohol, Napthenic Acid, Capryl Alcohol, G.E. Silicone and Pine Oil.

Pine Oil was indicated to be possibly the most successful and the least expensive anti-foaming agent of those reagents tested. Experiments were conducted to determine the minimum requirements of the additive that would be necessary to reduce foaming to a satisfactory level.

Further experiments were conducted with regard to foam formation during acid addition to the raw material by testing a fifty-fifty mixture of uncalcined C-Oxide and uncalcined C-Liner to determine if this would have a beneficial effect upon foaming to the extent that anti-foaming agents would not be necessary.

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

This project was held in abeyance during the present report period in order to concentrate on obtaining optimum data for the wet processing of uncalcined C-Liner.

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

Research Project No. 1

Research Supervisor J. E. Summers

LABORATORY OPERATIONS

5. Purification of C-Oxide Scrubber Material by Mineral Acid Digestion and Ammonio Precipitation

It had been illustrated by experimentation that micro-suspended solids contained within a clarified hydrochloric acid digest filtrate of C-Oxide have a detrimental effect upon the fluorine content of ammonium di-uranate continuously precipitated from such feed liquor. It was hypothesized that the presence of micro-particles present in C-Oxide filtrates after filtration might be correlated to the inclusion of C-Oxide scrubber material in the normal C-Oxide digest procedure. Experiments were conducted to determine whether or not scrubber material could be processed by mineral acid digestion as a separate feed material thus excluding it from the C-Oxide digest cycle. Experiments were conducted using both calcined and uncalcined scrubber material and both hydrochloric acid and sulfuric acid as digest media. Ammonium di-uranate was precipitated from the pregnant mineral acid filtrate

after removal of acid insolubles by filtration, using dilute ammonia as a precipitant and batchwise techniques of precipitation over a pH range of 7.0-8.0. The resultant precipitate was separated from the supernate by filtration and calcined to a black oxide at 800° C. In every instance the product obtained was within purity specifications as regards 50% uranium content and 0.5% fluorine content.

Sulfuric acid was indicated to be a superior digest media with regard to filtration rate of the acid insolubles. Although insoluble residues resulting from the sulfuric acid treatment were voluminous, they were readily removed by filtration and easily washed. Acid insolubles resulting from hydrochloric acid digestion exhibited slime characteristics, were difficult to remove by filtration and were not easily washed free of solubilized uranium. Comprehensive data concerning the purification of this material may be found in Table I.

Additional experiments concerning C-oxide scrubber material were completed in order to determine optimum factors concerning precipitate volumes, weights, slurry densities and other process data for flow sheet calculations. The process outlined consists of sulfuric acid digestion, removal of acid insolubles by filtration, precipitation of ammonium di-uranate from the clarified filtrate, separation of the uranium precipitate by filtration and calcination of the residue to a black oxide at 800° C. Complete data may be found in Table II.

6. Experiments Concerning Raw Material Handling and Mineral
acid Digestion of Uncalcined C-Liner.

Sizing experiments were conducted on wet unpulverized, uncalcined C-Liner to determine the particle characteristics of the raw material prior to material handling or preparation. 100 gram samples of the wet unpulverized material were slurried in water and screened through variable mesh from 10-100 by flushing with additional water. The various fractions were dried and weighed to determine size characteristics. It is apparent from the data obtained that wet unpulverized C-Liner contains about 40% plus 20 mesh material. 98% of the material passing through 20 mesh screen is found to be less than 100 mesh. Representative data for all screen sizes from 10-100 mesh may be found in Table III.

Experiments were conducted on wet uncalcined C-Liner to determine the effect of particle size of the raw material on satisfactory extraction of uranium from the residue using hydrochloric acid digest techniques. 100 gram samples of wet uncalcined, unpulverized C-Liner were pulverized and screened by flushing with water through 10-100 mesh. Digest experiments were also conducted on the raw material without screening. The sized material was slurried in 200ml of water and digested in commercial hydrochloric acid at pH 0.6 for a period of one and one-half hour in the presence of 0.5% (w/v) sodium chlorate, at 90° C. Acid insolubles were removed by filtration, dried and analyzed for uranium content. Preliminary data indicates that screening to 100 mesh will be necessary, to effect satisfactory solubilization of uranium values leaving discard residues containing less than .05% U3O8. Representative data may be found in Table IV.

Preliminary experiments were conducted on pulverized, uncalcined C-Liner to determine the optimum time of digestion necessary to effect satisfactory recovery of uranium contained in the raw material. 100 gram samples of uncalcined C-Liner were pulverized to less than 100 mesh, slurried in 200 ml of water, and digested in commercial hydrochloric acid at pH 0.0-0.25 in the presence of 0.5% (w/v) sodium chlorate at 90° C for periods of time up to four hours. Acid insolubles were removed from the digest slurry by filtration and analyzed for uranium content. On the basis of data accumulated from previous experimentation and experiments just concluded, it is indicated that a digest period of one and one-half hour will be satisfactory in reducing acid insolubles to less than .05% U3O8. Pilot level experiments are planned to determine whether or not build-up of raw material volume will indicate a longer period of digestion to obtain discard residues within uranium specifications. Representative data may be found in Table V.

It has been observed during experimentation on uncalcined C-Liner that excessive amounts of persistent foam are formed during hydrochloric acid addition. Preliminary experiments were conducted in an effort to determine whether or not an anti-foaming agent could be found which upon addition to the digest slurry prior to hydrochloric acid addition would bring about dissipation of the foam to within manageable limits. Reagents tested during preliminary experimentation for their effectiveness as anti-foaming agents include Butyl Alcohol, Amyl Alcohol, Heptyl Alcohol, Octyl Alcohol, Capryl Alcohol, Aerosol, Napthenic Acid, G. E. Silicone and Pine Oil. 500 gram samples of uncalcined, less than 100 mesh, C-Liner were slurried in 1000 ml of water and commercial hydrochloric

acid was added to pH 6.6 in the presence of 1% (w/v) of the various reagents. Foaming characteristics of the slurry in the presence of the anti-foaming agent was observed during addition of hydrochloric acid and comparative remarks on reagent effectiveness were recorded. From preliminary experimentation it is indicated that the most successful and economic reagent, when used in this capacity, was distilled Pine Oil. Additional experiments of this nature are planned when other reagents with foam dissipating ability are procured. The behavior of the various reagents as anti-foaming agents may be summarized briefly as follows:

1. Butyl Alcohol - The behavior may be characterized as "good". Foaming was not eliminated but was held within manageable bounds. The foam that formed dissipated rapidly.
2. Amyl Alcohol - The behavior may be characterized as "fair". Some reduction of foam during acid digestion, but foam still persists in unsatisfactory quantity.
3. Heptyl Alcohol - The behavior may be characterized as "fair to good". Some reduction in foaming was noticed but it still persists in unmanageable amounts.
4. Octyl Alcohol - The behavior may be characterized as "good". Foam still forms but not in unmanageable amounts. Behavior on the same order as Butyl Alcohol.
5. Capryl Alcohol - The behavior may be characterized as "good". Does not exceed Octyl or Butyl Alcohol in effectiveness.

6. Napthenic acid - The behavior may be characterized as fair. Somewhat effective in preventing foaming but foam still forms in excessive quantities without rapid dissipation.
7. Aerosol - The behavior may be characterized as "poor". Foam forms during acid addition in excessive amounts. Some small effect by the addition of this reagent was noticed.
8. G.E. Silicone - The behavior may be characterized as excellent. Small amounts of foam form but dissipate rapidly. However, when used in this proportion it is not economically practical. Additional experiments are planned to determine minimum amounts of this reagent which may be used to obtain satisfactory performance.
9. Pine Oil - The behavior may be characterized as excellent. Very little foam formed when the reagent was used in the indicated proportion, and the foam that did form was rapidly dissipated.

Considering the effectiveness of Pine Oil as an anti-foaming agent when used with C-Liner in the presence of hydrochloric acid, additional experiments were conducted to determine what the minimum requirements would be for the reagent to maintain foam within manageable bounds.

500 gram samples of uncalcined, 100 mesh C-Liner were slurried in 1000 grams of water and commercial hydrochloric acid was added to approximately pH 0.0. Pine Oil was added to the water slurry, prior to the addition of hydrochloric acid, at a ratio ranging from 2% (w/w) - .2% (w/w) of the raw material volume. The effectiveness of the

anti-foaming agent was observed during acid digestion. Comparative observations are recorded. The behavior of Pine Oil as an anti-foaming agent, when used in this manner, may be summarized briefly as follows:

1. 10 ml of Pine Oil - The behavior may be characterized as excellent. Foaming is well within manageable limits and slow steady addition of hydrochloric acid to the C-Liner slurry is possible.
2. 5 ml of Pine Oil - The behavior may be characterized as good. When used in this proportion, the additive is still effective and foaming is within manageable bounds if slow steady addition of hydrochloric acid is carried out.
3. 2.5 ml Pine Oil - The behavior may be characterized as fair to good. Anti-foaming qualities of the additive are somewhat impaired when used in this proportion. Very slow careful addition of hydrochloric acid is necessary in the final stages of neutralization.
4. 1.0 ml Pine Oil - The behavior may be characterized as poor to fair. The effectiveness of the additive is greatly diminished when used in this proportion. Extremely careful addition of acid is required in the final stages of neutralization to maintain foaming within manageable bounds.

In addition to those experiments mentioned above, concerning the problem of combating unmanageable volumes of foam brought about by the addition of hydrochloric acid to uncalcined C-Liner, further experiments were conducted to determine if excessive foaming could be brought within desirable limits

by combining uncalcined C-Liner with uncalcined C-Oxide on a 1:1 basis prior to hydrochloric acid digestion. 250 grams of uncalcined -100 mesh C-Liner were combined with 250 grams of uncalcined -100 mesh C-Oxide and slurried in 1000 ml of water. Commercial hydrochloric acid was added to approximately pH 0.6. By using this technique, foaming was reduced to what may be a manageable limit by slow steady carefully controlled addition of hydrochloric acid. Additional experiments were conducted using this mixture plus the anti-foaming additive of 1 ml of Pine Oil. Careful addition of hydrochloric acid using this mixture, resulted in the elimination of uncontrollable amounts of foam.

C. REFINING AND PROCESSING OF SODIUM CARBONATE
RESIDUES

Research Project No. 5

Research Supervisor: J. L. Summers

LABORATORY OPERATIONS

7. Development of Processes for The Extraction of Uranium
From Sodium Carbonate Residues Resulting From A By-
Product of Pitchblende Purification

Developmental work on Pitchblende Carbonate Residues was held in abeyance during the period under report in order to concentrate on prospective processes for the purification of C-Liner.

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E X H I B I T S

TABLE I

PURIFICATION OF C-OXIDE SCRUBBER MATERIAL

55 Y: 4.76% 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 (gr.)	500	500	500	500	500	500	500	500
Weight of H_2O (gm.)	1000	1000	1000	1000	1000	1000	1000	1000
Calcination Temperature of Raw Material ($^{\circ}F$)	---	1200	---	1200	---	1200	---	1200
Digest Acid	HCl	HCl	HCl	HCl	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
Weight of Acid (gm.)	1265	1380	1265	1380	708	715	708	715
pH of Digestion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Time of Digestion (hr.)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Temperature of Digestion ($^{\circ}C$)	90	90	90	90	90	90	90	90
Acid Insolubles (gm.)	87.5	89.0	86.5	88.5	220	220	216	218.5
Acid Insolubles (% U_3O_8)	.055	.035	.075	.050	.050	.035	.075	.055
pH of Precipitation of Ammonium Di-Uranate	7.0	7.0	8.0	8.0	7.0	7.0	8.0	8.0
Calcination Temperature of Precipitate ($^{\circ}C$)	800	800	800	800	800	800	800	800
Black Oxide (% U_3O_8)	78.60	80.12	75.00	74.32	80.26	81.30	78.60	77.66
Black Oxide (% F)	.05	.12	.23	.11	.01	.05	.10	.09

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TABLE II

PROCESS D T ON C-OXIDE SCRUBBER MATERIAL

S MPLE WEIGHT: 500 gm.

SS Y: 1.50% U_3O_8

	<u>Wet Weight (gm.)</u>	<u>ml Solids 100 ml Slurry</u>	<u>Slurry Volume ml</u>	<u>ml Solids per gm. Scrubber</u>	<u>Approx. % U3O8 Content</u>
H_2SO_4 - NH_4NO_3	. 44.0	. 30	. 1775	. 1.13	. .05
acid Insolubles	B. 44.0	-B. 30	B. 1900	B. 1.14	B. .05
Ammonium	. 83.0	. 7.5	. 1900	. .28	. 80.0
Di-Uranate	B. 81.5	B. 7.0	B. 1975	B. .27	B. 80.0

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TABLE III
PARTICLE SIZE CHARACTERISTICS OF WET, UNCALCINED C-LINER

SS Y: 1.50% 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
Sieve Mesh Used For Screening	10	20	40	60	80	100
Oversize Fraction (%)	17.5	32.0	29.5	32.5	29.5	32.5
Oversize Fraction (% U_3O_8)	2.17	1.77	1.70	1.62	1.72	---
Screened Fraction (% 100 Mesh)	78	98	98	99	99.5	100

TABLE IV

EFFECT OF PARTICLE SIZE ON HYDROCHLORIC DIGESTION OF C-LINER

S. Y: 1.50% 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>
Weight of Sample (gm.)	100	100	100	100	100	100	100
Mesh Size of Particle	10	10	20	40	60	80	100
Weight of HCl (gm.)	250	250	250	250	250	250	250
pH of Digestion	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Temperature of Digestion ($^{\circ}C$)	90	90	90	90	90	90	90
Time of Digestion (hr.)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
acid Insolubles (gm.)	19.0	18.0	18.5	17.5	17.5	18.0	18.5
acid Insolubles (% U_3O_8)	.78	.68	.63	.65	.61	.666	.635

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TABLE V

EFFECT OF TIME ON HYDROCHLORIC DIGESTION OF C-LINER

SS Y. 1.50% U_3O_8

MESH: -100

	<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 (gr.)	100	100	100	100	100	100	100	100
Weight of H_2O (gr.)	200	200	200	200	200	200	200	200
Weight of HCl (gm.)	250	250	250	250	50	250	250	250
pH of Digestion	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Temperature of Digestion ($^{\circ}C$)	90	90	90	90	90	90	90	90
Time of Digestion (hr.)	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Acid Insolubles (% U_3O_8)	.1.	.055	.035	.035	.025	.035	.05	.035

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FROM A. M. Johnson

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