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Index No. Y-352

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Y-12 Plant

Contract No. W-7405-Eng-26

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DECLASSIFICATION CANCELLED
DATE 12-8-58
For The Atomic Energy Commission

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COMPARISON OF VARIOUS METHODS FOR THE REMOVAL

OF URANIUM FROM CARBON SALVAGE

ABSTRACT

Experiments were conducted in which the removal of uranium by nitric acid leaching of ground carbon salvage was compared with the removal by similar leaching of residues. Those residues were the resultant products of four types of pretreatment of carbon: muffling, burning in continuous carbon burner, heating in an insufficiency of air (coking), and reacting with steam at high temperature. Each sample was subjected to five stages of leaching after pretreatment. Results are presented to show the removal of uranium at each stage of leaching for the various methods of pretreatment and for different acid concentrations. Results are also given to show the portion of uranium from each calutron batch remaining in the final leached residue.

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Oak Ridge, Tennessee
February 11, 1949

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COMPARISON OF VARIOUS METHODS FOR THE REMOVAL
OF URANIUM FROM CARBON SALVAGE

INTRODUCTION

Background

A new salvage process was recently proposed which involved continuous handling of ground graphite from the calutron units. This graphite contained small amounts of uranium which were to be removed as completely and economically as possible. It was desired to devise a process that could be operated in the track buildings and afford sufficient recovery so that 99 percent of the uranium could be retained in the buildings. Certain other salvage items (insulators, leather gloves, floor sweepings, and others) must of necessity be removed from the buildings for salvage. The uranium in these items along with unknown losses is predicted to be 0.8 to 0.9 percent of the uranium in the cycle of the proposed process. Therefore, not more than 0.1 percent of the uranium per cycle could be allowed to remain in the carbon residues for further processing at a central location.

The ground graphite was of nonuniform size with particles ranging from greater than 50 mesh to less than 200 mesh. One-fifth of the carbon (approximately 1000 gm.) from each calutron batch was placed in the machine wash from that batch to act as a filter aid for clarification of the wash. The subsequent filtration removed this carbon as well as other insoluble material in the batch (carbon bowl residue). The filter cake combined with the other four-fifths of the ground carbon was the material which was used for these experiments.

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Purpose

It was desired to make a quantitative comparison of several methods of treatment of the ground carbon for the removal of uranium. It was also the purpose of this work to study the effect of some of the variables involved in the various methods of treatment. It was desired to obtain a qualitative comparison of the ease and cost of operation of the various methods projected to larger scale equipment. Data and observations obtained on these laboratory studies could then be applied to further development work on the proposed continuous salvage process.

EXPERIMENTAL

Methods of Treatment

The removal of uranium from carbon was accomplished by multiple nitric acid leaching of the original carbon mixture as well as the residues from four different pretreatments of that mixture. The four methods of pretreatment were as follows: (1) muffling, (2) burning in a continuous carbon burner, (3) heating in an insufficiency of air (coking), and (4) reacting with steam at high temperatures (water gas reaction). A combination of two treatments was also tested. The carbon was reacted with steam; the residue was leached, ashed in the muffle, and again leached.

In conjunction with the comparison of methods of treatment, a study was made of several variables affecting each of the methods. The residue from each treatment was subjected to a series of leaches at two different nitric acid concentrations (70 percent and 35 percent). The volume of each leach solution per unit weight of residue per stage was also tested

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as a variable. The time of coking was varied from 1/2 to 2-2/3 hours; the temperature of coking was varied from 800°C to 1000°C. Another variable studied was the effect of completeness of the water gas reaction on removal of uranium by subsequent leaching of the residue. A comparison was made of the various methods of treatment with respect to the percentage of the original bulk which remained after leaching.

Apparatus and Procedure

Special apparatus was required for only two of the methods of pre-treatment; the other methods as well as the leaching were readily carried out with standard laboratory procedures and equipment.

Water Gas Reaction. The apparatus for carrying out the water gas reaction is shown in Figure 1. Fifty gram samples of the ground carbon mixture were pelletized using linseed oil as a binder (5 gm. carbon/gm. oil). This batch of pellets was then charged into the vertical vicor tube and heated to about 900°C in a stream of nitrogen. Water was then introduced into the boiler at a dropwise rate, and the nitrogen was shut off. When the steam started entering the reactor, the pilot flame on the exit gas line was lighted and the furnace temperature was raised to the range 1100°C to 1150°C. At this temperature the reaction proceeded quite rapidly according to the equation:

The rate of reaction was readily controlled by the rate of addition of water to the boiler. The exit gases, CO and H₂, were continuously burned while any excess steam passing through the reactor was condensed and

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FIGURE 1
WATER GAS REACTOR

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collected in the trap. A fine mesh screen was placed in the exit line to prevent flash back explosions. As the reaction neared completion the exit gas flame gradually went out, bubbling stopped in the trap, and the amount of steam condensate became larger. Reaction time for fifty grams of carbon was about 1-1/2 hours. The reactor was then cooled with a stream of nitrogen replacing the steam. The residue was removed for leaching.

Carbon Burner. This apparatus is shown in Figure 2. Ground carbon was extruded into sticks which entered the burner and fell onto the grate where they were burned in a stream of air. The grate was shaken periodically to allow the ash to pass into the container below. Steam condensate from the exit gas scrubbing system flowed into the container, was stirred to suspend the ash, and overflowed onto a filter. The ash collected on the filter was then removed for leaching. In actual operation of the burner, the container below the grate could be used as a one stage leacher with nitric acid being continuously added. However, for the purpose of these experiments no acid was used; the leaches were carried out separately, as will be described later. A detailed description of this apparatus and its operating characteristics is given in report number Y-353 . This report is concerned with the design and development work on continuous carbon burning and leaching equipment.

Muffling and Coking. The muffling treatment was carried out by placing samples of ground carbon in a porcelain dish in the muffle furnace and igniting at 1000°C until a constant weight of ash was obtained. The

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FIGURE 2
CONTINUOUS CARBON BURNER

cooking was carried out in a like manner except that the samples were covered so that not enough air was present for complete combustion. These samples were heated for definite time intervals ($1/2$ to $2-2/3$ hours) and at various temperatures in the range from 800°C to 1000°C .

Leaching. Weighed samples of carbon and treated residues were placed in beakers with the desired volume and concentration of nitric acid. (Volumes of leach solution used varied from one to fifty ml per gram of solid for each leaching stage. Acid concentrations of 35 percent and 70 percent were tested.) The samples were then boiled on the hot plate for approximately thirty minutes, cooled, and filtered. The solids were again placed in the beaker, more acid added, and the same procedure carried out until five stages of leaching were completed. The final leached residue as well as the five filtered solutions were then analyzed for uranium to determine the effectiveness of the treatment.

RESULTS

Figure 3 shows graphically the amount of uranium removed from carbon and residues at each stage of leaching with 35 percent nitric acid. Figure 4 gives the same information for 70 percent nitric acid leaching. The concentrated acid gave better removal on all types of material except muffle ash (35 percent and 70 percent acid gave almost identical results on muffle ash leaching). The curves in Figures 3 and 4 are plotted from average results of several runs made on each type of material and acid concentration. Figure 5 compares the various methods of treatment on the basis of the reduction in bulk of material affected by that treatment. Figure 6 shows

PERCENT OF BULK REMAINING AFTER TREATMENT

FIGURE 5

Comparison of Various Methods of Treatment of Ground Carbon with Respect to Reduction in Bulk of Material

FIGURE 6

The Effect of Completeness
of Water Gas Reaction on
Removal of Uranium by Leach-
ing of the Reaction Residue

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the effect of completeness of water gas reaction on removal of uranium from the residue by nitric acid leaching. The point on Figure 6 at 0 percent completeness of reaction is taken as the amount of uranium removed in five leaches of untreated carbon. Table 1 is a tabulation of all data and conditions for the individual experiments performed. Table 2 shows data on the final leached residues from the various treatments. All calculated values are on the basis of one calutron batch; this amounts to approximately 5000 grams of carbon for the salvage cycle. The average uranium content of batches of carbon used for these experiments was 7.3 grams per 5000 grams of carbon.

DISCUSSION OF RESULTS

From Figure 3 it is apparent that the greatest removal of uranium by 35 percent HNO_3 leaching is achieved after a muffling treatment of the carbon (98.5 percent removed). One leach removes practically all the uranium that can be leached out. Water gas residue can be efficiently stripped in two leaching stages, coked carbon in three stages, and burner ash in four stages. Appreciable amounts of uranium are removed from untreated carbon in each of five 35 percent HNO_3 leaches. When 70 percent acid is used (Figure 4), water gas residue, coked carbon, and muffle ash give almost identical results with removal effective only in the first two stages. Removal by all three methods is better than 98 percent of the uranium in the original carbon. Less effective recovery (88 to 90 percent) is obtained by 70 percent HNO_3 leaching of burner ash and original carbon, and at least five stages are required.

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Tabl 1

Removal of Uranium from Ground Carbon Salvage

Experiment Number	Type of Treatment Before Leaching	1st Leach		2nd Leach		3rd Leach		4th Leach		5th Leach		Ml. Leach Sol'n. per Gm. Solid per Stage	% of Bulk Remaining
		Conc. of HNO ₃ Leach Sol'n. (%)	% of U Removed (cumulative)	Conc. of HNO ₃ Leach Sol'n. (%)	% of U Removed (cumulative)	Conc. of HNO ₃ Leach Sol'n. (%)	% of U Removed (cumulative)	Conc. of HNO ₃ Leach Sol'n. (%)	% of U Removed (cumulative)	Conc. of HNO ₃ Leach Sol'n. (%)	% of U Removed (cumulative)		
1	None	70	38.1	70	57.7	70	76.7	70	85.9	70	90.9	1.0	-
2	None	70	84.6	70	86.9	70	87.6	70	88.3	70	89.0	3.3	93.6
3	None	35	24.8	35	36.0	35	40.4	35	44.8	35	47.5	3.3	-
4	None	35	25.8	35	53.2	35	37.6	35	41.0	35	42.4	10.0	91.8
5	None	35	24.4	35	34.4	35	39.1	35	42.0	35	44.9	1.7	-
6	Coked 1 hour at 800°C.	70	92.9	70	98.8	70	98.9	-	-	-	-	3.0	87.2
7	Coked 1 hour at 900°C.	70	98.0	70	98.8	70	99.0	-	-	-	-	3.0	89.4
8	Coked 1/2 hour at 1000°C.	70	96.6	70	98.4	70	98.6	-	-	-	-	3.0	88.0
9	Coked 1 hour at 1000°C.	70	96.2	70	97.4	70	97.5	-	-	-	-	3.0	81.4
10	Coked 1 hour at 1000°C.	70	96.2	70	96.5	70	96.8	70	97.1	70	97.4	10.0	93.5
11	Coked 2-2/3 hours at 1000°C.	70	98.3	70	98.7	70	98.8	-	-	-	-	3.0	79.8
12	Coked 1 hour at 1000°C.	35	71.2	35	78.0	35	82.3	35	82.7	35	83.1	3.3	-
13	Ashed in Burner	70	49.8	70	53.4	70	67.1	70	74.4	70	78.3	1.7	-
14	Ashed in Burner	70	86.7	70	95.9	70	97.6	70	97.8	70	97.9	3.3	4.3
15	Ashed in Burner	35	62.2	35	72.7	35	78.4	35	78.6	35	78.8	1.7	-
16	Ashed in Burner	35	46.7	35	56.8	35	62.3	35	65.1	35	67.1	3.3	-
17	Ashed in Burner	35	78.6	35	95.9	35	96.5	35	96.8	35	96.9	10.0	4.0
18	Ashed in Muffle	70	97.6	70	97.8	70	98.0	70	98.1	70	98.2	10.0	1.2
19	Ashed in Muffle	35	96.6	35	96.9	35	97.1	35	97.2	35	97.2	20.0	1.1
20	Ashed in Muffle	35	97.7	35	99.6	35	99.7	35	99.8	35	99.8	17.0	1.5
21	Water Gas Reaction	70	97.4	70	98.5	70	98.7	70	98.9	70	99.0	25.0	8.4
22	Water Gas Reaction	35	85.8	35	91.0	35	92.5	35	92.8	35	92.8	10.0	56.0
23	Water Gas Reaction	35	92.0	35	96.5	35	97.3	35	97.6	35	97.8	13.0	15.6
24	Water Gas Reaction	35	91.5	35	94.9	35	95.4	35	95.8	35	96.1	50.0	1.1
25	Double Treatment (Water Gas, Muffle)	70	98.6	70	99.6	70	99.8	70	99.8	-	-	25.0	0.8

Table 2

Average Data on Final Treated, Leached Residues

(Based on one calutron batch: 5000 gm. carbon containing an average of 7.3 gm. U)

Type of Material	Conc. of HNO ₃ Leach Solution (%)	Weight of Residue per 5000 gm. Carbon (Gm.)	Weight U Remaining in Residue from 5000 gm. of Carbon (Gm.)	% of U from Original Calutron Charge Remaining in Final Residue	Conc. of U in Final Residue (Composited %)
Original Carbon	35	4750	3.30	0.23	0.07
Original Carbon	70	4680	0.73	0.05	0.02
Coked Carbon	35	4500	1.23	0.09	0.03
Coked Carbon	70	4350	0.11	0.01	0.002
Water Gas Reaction Residue	35	850	0.32	0.02	0.04
Water Gas Reaction Residue	70	420	0.07	0.01	0.02
Burner Ash	35	200	1.39	0.10	0.69
Burner Ash	70	215	0.87	0.06	0.40
Muffle Ash	35	50	0.11	0.01	0.22
Muffle Ash	70	55	0.12	0.01	0.22
Residue (Water Gas Reaction, Leach, Muffle, Leach)	70	42	0.39	0.004	0.12

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Experience in the past has indicated that in the treatment of residues, a reducing atmosphere converts the uranium to a more soluble form for removal by leaching. The effect is verified in these experiments to some extent. Coked carbon (presumably producing a CO atmosphere) is more effectively stripped of uranium than untreated carbon. Water gas reaction residue (subjected to a CO and H₂ atmosphere) is more effectively stripped than carbon burner ash (subjected to air and CO₂). However, the effect is reversed in the case of muffle ash; removal of uranium is very efficient even though the material has been subjected to oxidizing conditions. A possible explanation to this might be that the muffle ash is the only material from which carbon has been completely removed. The leaching is performed on a smaller bulk of material containing only metallic oxides which probably adsorb uranium to a lesser extent than does the carbon.

In Figure 5 a comparison is made between the various methods of treatment with respect to the reduction in weight of material. This is quite important since in actual operation any residue would probably have to be further processed in order to recover the last traces of uranium. The graph shows that muffling most effectively reduces the bulk; burning and water gas treatment do quite well, while coking and no pretreatment leave the majority of the material still to be handled.

Figure 6 shows the effect of completeness of the water gas reaction on removal of uranium from the residue. The reason for this study was that it was quite difficult to approach completion of reaction without prolonging the time of treatment considerably. At temperatures between

1100°C and 1150°C the reaction would go quite readily to 85 or 90 percent completion. The graph shows that little advantage is gained by carrying the reaction beyond 60 percent complete except for the previously mentioned advantage of reducing the weight of material. Below 60 percent completion the efficiency of uranium removal decreases rapidly.

Table 1 includes results and conditions for all of the individual experiments. Three of the variables studied could not be correlated in the number of experiments performed. Neither time of coking (between 1/2 hour and 2-2/3 hours) nor temperature of coking (between 800°C and 1000°C) resulted in an appreciable difference in removal of uranium by subsequent leaching. The variation of volume of leach solution did not lead to any results which could be correlated. Differences occurred in the amount of uranium removed, but no general trend was observed. It might only be possible to obtain such a correlation in a statistical manner involving a very large number of experiments.

In Table 2 a tabulation is made of average data and calculated values relating to the final leached residues produced by the various treatments. These values are based on one calutron batch (approximately 5000 grams carbon to salvage). The uranium content in the carbon batches used in this work averaged 7.3 grams uranium per 5000 grams carbon. The chart shows that any of the methods of treatment (except 35 percent HNO₃ leaching of original carbon) would be satisfactory with respect to removal of enough uranium to allow 99 percent to remain in the track buildings. The selection of the best method of treatment depends upon the degree of enhancement of the uranium involved and thereby the maximum concentration

that could be discarded. If none of the treatments yield a residue of low enough uranium content to eliminate further treatment, then the least expensive method would be best. However, if one of the methods does yield a residue low enough in uranium to be discarded, then that would be the best treatment. The treatment resulting in the lowest concentration is 70 percent HNO_3 leaching of coked carbon (U in residue, 20 ppm). However, the bulk of the carbon still remains. Muffling results in the greatest reduction in bulk, and subsequent leaching gives very good recovery of uranium. Water gas reaction residue leached in 70 percent HNO_3 gives the smallest amount of uranium remaining (0.07 grams per 5000 gram batch of carbon). Also, this method gives second lowest concentration of uranium in the final residue and 92 percent reduction in bulk of material. All of the above refer to single step pretreatments. The two step pretreatment (water gas reaction followed by muffling with leaching of residues after each treatment) gives only slightly better removal of uranium than any of the single step methods. This double treatment would only be justified if the resultant residue were low enough in uranium to discard.

A qualitative comparison of methods of treatment can be made with respect to ease and cost of operation projected to full scale.

Ease of Operation. Direct leaching of carbon would be the easiest operation since it eliminates any pretreatment. Residues from all other methods have to be leached anyway. Coking and muffling would be the next simplest operations to carry out. They would involve placing the carbon

in containers which would pass through a long muffle furnace. In the case of coking, the containers would be covered and the material would be in the furnace only a small fraction of the time required for complete muffling. The carbon burner and water gas reactor would be somewhat more difficult to operate in that gas flow rates would have to be controlled and feed mechanisms would be more complicated. The water gas reaction would also involve the possibility of an explosion of CO and H₂ gases.

Cost of Operation. This is probably the most important item in picking a process if none of the methods remove uranium well enough to eliminate further treatment. The carbon burner should be by far the least expensive pretreatment to operate. All of the other methods require an external source of heat to varying degrees. The only expense involved in burning would be power for compressed air and linseed oil for binder. Muffling would be most expensive since large amounts of electrical power would be required; coking would be less expensive since a shorter time of heating would be required. The water gas reactor would be somewhat cheaper to operate than coking but more expensive than the burner. Again external heat would be required, but there is a possibility of utilizing the CO and H₂ to supply part of that heat.

Summary. Muffling can be eliminated as a possible treatment because of excessive cost and time of operation. Leaching of the original carbon can be eliminated in favor of leaching coked carbon; a much more efficient removal of uranium is obtained by this method. Therefore, on the basis of this study, the following order of steps is proposed for the carbon salvage process:

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(1) Coke at 800°C for 1/2 hour, (2) leach in 70 percent HNO_3 (2 stages), (3) subject to water gas reaction or carbon burner, and (4) leach residue in 70 percent HNO_3 (2 stages for water gas residue, 5 stages for burner ash). The carbon burner should be used if further processing of the residue is to be required; the water gas reactor should be used if the enhancement level is such that the leached residue is low enough in uranium to be discarded.

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