Chemistry

This document consists of 21 pages.
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

EXTRACTION OF URANIUM FROM THE RED DESERT COAL OF WYOMING*

By

Irving A. Breger, Robert Meyrowitz, and Jesse J. Warr, Jr.

December 1953

Trace Elements Investigations Report 372

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. <u>It is not for public inspection or quotation</u>.

---

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

CHEMISTRY

Distribution (Series A)	No. of copies
American Cyanamid Company, Winchester	1
Argonne National Laboratory	1
Atomic Energy Commission, Washington	2
Battelle Memorial Institute, Columbus	1
Carbide and Carbon Chemicals Company, Y-12 Area	1
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Butte	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Douglas	1
Division of Raw Materials, Grants	1
Division of Raw Materials, Hot Springs	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, New York	6
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Richfield	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Washington	3
Division of Research, Washington	1
Dow Chemical Company, Pittsburg	1
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
Technical Information Service, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Alaskan Geology Branch, Washington	1
Fuels Branch, Washington	2
Geochemistry and Petrology Branch, Washington	15
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	1
E. H. Bailey, San Francisco	1
K. L. Buck, Denver	1
J. R. Cooper, Denver	1
N. M. Denson, Denver	1
C. E. Dutton, Madison	1
R. P. Fischer, Grand Junction	1
L. S. Gardner, Albuquerque	1
M. R. Klepper, Washington	1
A. H. Koschmann, Denver	1
R. A. Laurence, Knoxville	1
D. M. Lemmon, Washington	1
J. D. Love, Laramie	1
R. G. Petersen, Plant City	1
R. J. Roberts, Salt Lake City	1
Q. D. Singewald, Beltsville	1
J. F. Smith, Jr., Denver	1
R. W. Swanson, Spokane	1
A. E. Weissenborn, Spokane	1
W. P. Williams, Joplin	1
TEPCO, Denver	2
TEPCO, RPS, Washington	3
(Including master)	80

CONTENTS

Page

Abstract 4

Introduction 5

Sample 6

Experimental data 7

Summary and conclusions 13

Literature cited 20

Unpublished reports 21

TABLES

Page

Table 1. Extraction of as-received Red Desert coal by 1N hydrochloric acid 8

2. Extraction of -20 mesh Red Desert coal by 1N hydrochloric acid 9

3. Extraction of as-received Red Desert coal by 6N hydrochloric acid 10

4. Extraction of -20 mesh Red Desert coal by 6N hydrochloric acid 11

5. Extraction of uranium from Red Desert coal 12

6. Semiquantitative spectrographic analyses, in percent, of the ashes from the original -20 mesh Red Desert coal, from the extracts obtained from it by use of 6N hydrochloric acid, and from the extracted coal 14

7. Yield of tar and char from Red Desert coal before and after extraction by 6N hydrochloric acid 15

8. Extraction of uranium from the char obtained when Red Desert coal is retorted 16

EXTRACTION OF URANIUM FROM THE RED DESERT COAL OF WYOMING

By

Irving A. Breger, Robert Meyrowitz, and Jesse J. Warr, Jr.

ABSTRACT

During the course of geochemical studies it has been found that extraction of uranium from the subbituminous coal of the Red Desert, Wyoming, is somewhat more difficult than from the lignite of South Dakota. Batch extraction of the Wyoming coal with 6N hydrochloric acid, however, leads to the solution of almost 90 percent of its uranium. Recovery of uranium is independent of the particle size of the coal between -4 and -20 mesh, and is accompanied by the solution of approximately 70 percent of the inorganic constituents (ash) of the coal. The extract contains a concentration, along with uranium, of several valuable elements such as manganese, cerium, and vanadium which are present in the coal.

Preliminary treatment of the Red Desert coal with 6N acid would necessitate the handling of large volumes of coal. The acid extract from this process would, if burned, produce an ash containing about a tenfold concentration of uranium over that present in the original coal. Yields of char and tar are approximately 15 percent lower with extracted coal than with original coal.

An alternate scheme for recovery of uranium from the Red Desert coal might involve carbonization and the production of tar as an industrial raw material. If this approach is followed the char will contain nearly a twofold concentration of uranium over that in the

original coal. Use of the char as a fuel will allow recovery of uranium from its ash. If the char is to be extracted before use, however, recovery of uranium will be only approximately 55 percent. It is possible that some of the uranium in the coal may be reduced during retorting to UO_2, which is quite insoluble in 6N hydrochloric acid.

Ultimate choice of process for the recovery of uranium from the Red Desert coal will depend upon economic factors. It is clear, however, that uranium can be recovered from low rank coal or from retort char in high yield.

INTRODUCTION

As an integral part of geochemical studies of uraniferous coals undertaken by the U. S. Geological Survey on behalf of the U. S. Atomic Energy Commission, it has been necessary to determine the manner in which the uranium can be isolated from the coals. In previous investigations with the uraniferous lignite from Harding County, S. Dak., it was found that continuous treatment of the coal with 1N or 6N hydrochloric acid resulted in extraction of the uranium (Breger and Deul, 1952). Recently studies have been carried out with the subbituminous coal obtained from the Red Desert, Sweetwater County, Wyo. The geology, distribution, and reserves of the Red Desert coal have been described by Masursky and Pipiringos (1953), and Masursky, Pipiringos, and Gower (1953). The subbituminous coal from the Red Desert is of higher rank than the lignite and probably differs in porosity and permeability from the lignite. Detailed chemical studies to compare the subbituminous coal and lignite have yielded data on the subbituminous coal that have implications for the utilization of the coal and the recovery of its uranium. For this reason, the results of these studies are being presented in this report.

In view of the possible interest in the recovery of uranium as a byproduct of the utilization of this coal, preliminary assays were made by the Fischer retort method to compare the yields of char and tar both before and after extraction with 6N hydrochloric acid. Moreover, experiments were undertaken to determine the extractability of the uranium from the char produced when the coal is retorted.

While it is possible, as has been suggested by others, to recover uranium from the ash of coals which have been utilized as fuels, these studies show that it is also possible to recover the uranium in high yield from the coal prior to its combustion or from its retort char. Although the ultimate process for the recovery of uranium from the Red Desert coal will depend upon economic factors, it is clear that a technique which would utilize the coal as both a source of chemical raw materials and as a fuel, and which would also lead to the production of uranium as a byproduct merits additional study.

SAMPLE

The coal used for these studies was collected in October 1952 from an outcrop of the Luman No. 1 bed near the center of sec. 28, T. 24 N., R. 95 W., in the Red Desert. The coal was collected in 5-gallon carbide cans which were shipped to the Geological Survey's laboratory in Washington. Upon receipt the sample, approximately -4 mesh, was thoroughly mixed and quartered, following which a split was crushed until it completely passed a 20-mesh screen. A sieve analysis of the -20 mesh coal, obtained by shaking 100 g of the material mechanically for 30 minutes, showed the following size distribution:

Sieve size	Percent
-20+50	51.6
-50+100	21.1
-100+140	7.1
-140+200	5.0
-200+230	2.9
-230+325	1.9
-325	10.4

EXPERIMENTAL DATA

Batch extraction of the coal, both unground (approximately -4 mesh) and -20 mesh, was carried out on 50-g samples. Each sample of coal was refluxed for two hours with 500 ml of either 1N or 6N hydrochloric acid. After cooling, the suspension was filtered twice through a fritted glass funnel of medium porosity and the filtrate was then evaporated to approximately 250 ml and diluted exactly to that volume with appropriate acid. The coal was recovered from the funnel and returned to the flask where it was extracted a second time with 500 ml of acid. The coal was again separated from the solvent which was diluted to 250 ml as before. After the second treatment with acid, the residue was washed with fresh acid of the proper normality and then oven dried at 105 C.

Samples of the original and extracted coal were analyzed for percent ash and percent uranium in the ash, analyses being calculated on the dry basis. The two extracts were also analyzed to obtain data for material balance calculations. The data for the experiments are shown in tables 1 through 4 and are summarized in table 5. Semiquantitative spectrographic

Table 1.--Extraction of as-received Red Desert coal by 1N hydrochloric acid

	Weight (g)	Water 1/ (percent)	Dry sample (g)	Ash in dry sample 2/ (percent)	(g)	U in dry ash (percent)	(mg)
Original coal (31 A)	50.0	30.3	34.9	12.4	4.33	0.017	0.74
First extract	--	--	5.6	53.0	2.96	--	0.18
Second extract	--	--	0.6	62.1	0.37	--	0.06
Extracted coal	35.3	16.7	29.4	6.0	1.77	0.027	0.48

1/ Two hours at 105 C.

2/ Ash at 800 C to constant weight.

Table 2.--Extraction of -20 mesh Red Desert coal by 1N hydrochloric acid

	Weight (g)	Water (percent)	Dry sample (g)	Ash in dry sample		U in dry ash	
				(percent)	(g)	(percent)	(mg)
Original coal (33A)	50.0	13.0	43.5	15.5	6.71	0.0175	1.18
First extract	--	--	6.8	45.6	3.08	--	0.16
Second extract	--	--	1.2	38.6	0.45	--	0.13
Extracted coal	37.3	0.2	37.2	4.3	1.60	0.0230	0.37

Table 3.--Extraction of as-received Red Desert coal by 6N hydrochloric acid

	Weight (g)	Water (percent)	Dry sample (g)	Ash in dry sample		U in dry ash	
				(percent)	(g)	(percent)	(mg)
Original coal (32A)	50.0	14.8	42.6	14.0	5.95	0.0140	0.83
First extract	--	--	7.0	41.0	2.86	--	0.42
Second extract	--	--	1.5	38.4	0.56	--	0.10
Extracted coal	36.1	0.6	35.8	4.8	1.73	0.0076	0.13

Table 4.--Extraction of -20 mesh Red Desert coal by 6N hydrochloric acid

	Weight (g)	Water (percent)	Dry sample (g)	Ash in dry sample		U in dry ash	
				(percent)	(g)	(percent)	(mg)
Original coal (36A) 1/	50.0	10.7	44.6	12.0	5.37	0.0164	0.88
(37A)	50.0	10.2	44.8	11.7	5.26	0.0167	0.88
First extract (36A)	--	--	8.1	38.8	3.14	--	0.51
(37A)	--	--	8.2	39.7	3.24	--	0.51
Second extract (36A)	--	--	1.3	30.3	0.38	--	0.13
(37A)	--	--	1.0	31.3	0.36	--	0.11
Extracted coal (36A)	38.7	0.7	38.4	4.4	1.68	0.0053	0.09
(37A)	39.1	0.6	38.8	4.3	1.66	0.0061	0.10

1/ Experiments 36A and 37A are duplicates.

Table 5.--Extraction of uranium from Red Desert coal 1/

Coal	Uranium extracted by hydrochloric acid	
	1N (percent)	6N (percent)
As received	35.1	84.4
-20 mesh	68.6	89.9, 88.7

1/ Percent of uranium extracted $= \dfrac{\text{Mg of uranium in original coal} - \text{mg of uranium in extracted coal}}{\text{Mg of uranium in original coal}} \times 100$

analyses of the ashes from the original coal, from the extracted coal, and from the extracts are shown in table 6.

Fischer assays to determine yields of tar and char were carried out with the original coal and with the coal following two batch extractions by 6N hydrochloric acid using the retort procedure recommended by Stanfield and Frost (1949). The established Fischer assay technique was followed in order to obtain yields for comparison with those from other coals (Parry et al., 1953). Data from this work are shown in table 7.

The extractability of the uranium from the char obtained from the Fischer assay of the original Red Desert coal was determined by extraction with 6N hydrochloric acid using the procedure described above. The availability of only 40 g of sample for this work dictated the use of 400 ml of acid to maintain the acid-sample ratio of 10 ml/g which had been used in previous experiments. Data from this work are shown in table 8.

SUMMARY AND CONCLUSIONS

Material balances for ash and uranium, using the data of tables 1 through 4, are not consistently good. Sampling difficulties caused by the tendency of sediment to separate from the extracts on standing led to poor duplicate analyses. As the most reliable analyses are those of the original and of the extracted coal, these have been used for calculation of the data shown in table 5.

Although hydrochloric acid has been used in past work (Breger and Deul, 1952) and in these studies of the Red Desert coal, it is possible that any highly ionized acid will serve as an effective extracting

Table 6.--Semiquantitative spectrographic analyses, in percent, of the ashes from the original -20 mesh Red Desert coal, from the extracts obtained from it by use of 6<u>N</u> hydrochloric acid, and from the extracted coal 1/

	Over 10	1-10	0.1-1.0	0.01-0.1	0.001-0.01	0.0001-0.001
Original coal	Al Si	Mg Ca	Fe Na B	Mn Pb Sr Ti Ni Ce Co Ba Nd Cu Mo Cr La	Ga Zn V Y Yb Sc Be	Ag
First extract	Al Mg	Ca Fe	Si Ce Na B Mn Sr	Ni Ti Nd La Co Y Ba Cr V Cu	Zn Mo Pb Be Sc Ga Yb	Ag
Second extract	Al	Mg Fe Si Ca	Na Ba Ti B	Pb Sr Mn Cr Cu Ce Mo Ni Nd Zn Co La	Y V Sn Ga Sc	Yb Be Ag
Extracted coal	Si Al	K 2/	Fe Ca Mg Na B	Ti Ga Ba Ni Cr	Sr Pb Cu Mo Mn V Ag Y	Yb Be

1/ Analysts: Charles Annell and Mona Frank, U. S. Geological Survey.
2/ The lower limit for the detection of potassium by the analytical procedure used is 1 percent.

Table 7.--Yield of tar and char from Red Desert coal before and after extraction by 6N hydrochloric acid.

	Original coal		Extracted coal	
	As received	m.a.f. 1/	As received	m.a.f. 1/
Tar (percent)	5.3	6.8	5.7	6.0
(gals/ton)	13.0	16.2	14.4	15.2
Char (percent)	43.8	57.1	46.0	48.6
(lbs/ton)	876	1142	920	972

1/ Moisture and ash free

Table 8.--Extraction of uranium from the char obtained when Red Desert coal is retorted

	Weight (g)	Water (percent)	Dry sample (g)	Ash in dry sample (percent)	Ash in dry sample (g)	U in dry ash (percent)	U in dry ash (mg)
Original char	40.0	0.5	38.8	18.5	7.40	0.0165	1.22
Extracted char	35.7	5.4	33.8	8.2	2.77	0.0206	0.57

agent. Hydrochloric acid was chosen because it can be handled easily in laboratory operations and especially because it forms an azeotrope of convenient composition.

The experiments which are summarized in the accompanying tables show the following effects of acid concentration and of particle size on the extractability of uranium from the Red Desert coal:

(1) Treatment of the as-received coal with 1N hydrochloric acid resulted in the extraction of only 35 percent of the uranium. When as-received lignite from South Dakota was similarly treated, 75 percent of its uranium was extracted.

(2) Treatment of the Red Desert -20-mesh coal with 1N hydrochloric acid led to the extraction of 70 percent of the uranium. Use of 6N acid resulted in the recovery of 84 percent of the uranium. As the treatment of the coal with 6N acid did not cause the formation of a gel, as was the case with the lignite from South Dakota, it is apparent from table 5 that when 6N acid is used the extraction of uranium is not only very high, but also nearly independent of particle size within the range tested.

Extraction of uranium a subbituminous coal is, therefore, somewhat more difficult than from a lignite. If 6N rather than 1N acid is used with the coal of higher rank, however, complete extraction of the uranium can still be expected. Among the factors that have been considered in attempting to explain the need for 6N acid is the fact that increase in rank of coal from lignite to subbituminous may result in partial polymerization or condensation of organic substances responsible for the retention of the uranium in the coal (Breger and Deul, 1952). If the increased molecular weight of the organo-uranium compound is an important factor, then 6N acid may be required to dissolve the compound.

Recovery of the uranium by the batch extraction technique using 6N acid, is accompanied by the solution and removal of approximately 70 percent of the inorganic components of the coal. Recovery of uranium, therefore, is effected simultaneously with an upgrading of the coal. If the extraction were to be carried out in a continuous process, the recovery of uranium would probably approach 100 percent and the ash content of the residual coal would undoubtedly be further reduced.

The solid extract recovered on evaporation of the hydrochloric acid contains uranium in a concentration of approximately three times that in the original coal; the ash from the acid extract contains a tenfold increase in the concentration of uranium.

Although it is difficult to draw any conclusions on the basis of the semiquantitative data of table 6, extraction of the coal may have led to the concentration of manganese, cerium, and vanadium along with the uranium. Extraction has not resulted in the solution of silicon, molybdenum, lead, or several other elements.

The yields of tar and char shown in table 7 are based on a standard technique. These data can be compared with recently published information for the yields of char and tar from other low rank coals (Parry et al., 1953). The data indicate a drop of 11.8 percent in the yield of tar (moisture and ash free basis) as a result of extraction; for the most part this yield is probably a reflection of the amount of organic material of lower molecular weight which has been removed. The decrease in yield of char (moisture and ash free basis) is of the same order of magnitude (14.9 percent).

While extraction of -20 mesh Red Desert coal by 6N hydrochloric acid leads to the removal of nearly 90 percent of the uranium, similar treatment of the char from this coal (table 8) results in the solution of only 53 percent of the uranium. When the coal is retorted, therefore, the uranium becomes less soluble in 6N hydrochloric acid. In view of the possibility that uranium is probably carried into the coal in ground water, and in view of the fact that uraniferous coal is commonly weathered and partly oxidized, it has been considered likely that the uranium is present in the coal in the form of the uranyl (UO_2^{++}) ion. A possible explanation for the relatively low solubility of the uranium in the char is that the uranyl ion might be partly reduced during retorting to uranium dioxide which is insoluble in 6N hydrochloric acid.

Although the geochemical investigations described in this report were not specificially concerned with the development of industrial techniques for the recovery of uranium from low rank coals, the data obtained indicate that the following procedures may be worthy of consideration:

(1) Direct continuous extraction of as-mined coal with highly ionized acid, perhaps constant-boiling hydrochloric acid (approximately 6N). This approach will require the handling of large volumes of coal containing high percentages of water (10 to 40 percent) and will lead to very high recovery of uranium. Products will consist of a concentrate containing uranium and other minor and trace elements of value, de-ashed and dry coal, water, and acid recovered in high yield. Should it be desirable to retort the extracted coal, the yields of tar and char will be about 15 percent

lower than those obtained with the untreated coal.

(2) The coal can be retorted to produce gas, tar for chemical purposes, and char. The char, containing a twofold increase in content of uranium and ash, can then be either extracted or used as a fuel. If the char is extracted, then it may be necessary to use an oxidizing acid such as nitric acid to recover uranium greater than that afforded by hydrochloric acid, assuming part of the uranium in the char to be in the form of UO_2. The acid from this process could be recovered in high yield. If the char is burned as a fuel under controlled conditions, then the uranium can be further concentrated into the ash for eventual recovery.

Choice of procedure to be used in recovery of uranium will depend upon economic factors and the evaluation of a process on pilot plant scale. These studies should be carried out by organizations concerned with the development of extractive procedures. Proper engineering will probably eliminate problems associated with the use of 6N hydrochloric acid, should that acid be chosen for large scale operation. It is clear, however, that uranium can be recovered directly from low rank coal or from retort char in high yield.

LITERATURE CITED

Parry, V. F., Landers, W. S., Wagner, E. O., Goodman, J. B., and Lammers, G. C., 1953, Drying and carbonizing fine coal in entrained and fluidized state: U. S. Bur. Mines Rept. Inv. 4954.

Stanfield, K. E., and Frost, I. C., 1949, Method of assaying oil shale by a modified Fischer retort: U. S. Bur. Mines Rept. Inv. 4477.

UNPUBLISHED REPORTS

Breger, I. A., and Deul, M., 1952, Status of investigations on the geochemistry and mineralogy of uraniferous lignites: U. S. Geol. Survey Trace Elements Inv. Rept. 284.

Masursky, H., and Pipiringos, G. N., 1953, Uranium-bearing coal in the Red Desert, Great Divide Basin, Sweetwater County, Wyoming: U. S. Geol. Survey Trace Elements Memo. Rept. 601.

Masursky, H., Pipiringos, G. N., and Gower, H. D., 1953, Results of exploratory core drilling for uranium-bearing coal in the northern part of the Red Desert area, Sweetwater County, Wyoming: U. S. Geol. Survey Trace Elements Inv. Rept. 332.