Chemistry

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EFFECTS OF DESTRUCTIVE DISTILLATION ON THE URANIUM ASSOCIATED WITH SELECTED NATURALLY OCCURRING CARBONACEOUS SUBSTANCES*

By

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EFFECTS OF DESTRUCTIVE DISTILLATION ON THE URANIUM ASSOCIATED WITH SELECTED NATURALLY OCCURRING CARBONACEOUS SUBSTANCES

By Irving A. Breger, Robert Meyrowitz, and Maurice Deul

ABSTRACT

During the course of geochemical investigations on uraniferous coals and shales it became necessary to determine if dry distillation of these substances would result in the formation of volatile uranium compounds. Several selected substances have been retorted and material balances based on the uranium contents of the original substances and of the retort chars obtained from them indicate that, within the limits of accuracy of the analytical procedures employed, volatile uranium compounds are not formed.

INTRODUCTION

Little is known regarding the organo-uranium compounds or complexes which may exist in uraniferous coals, shales, or other naturally occurring carbonaceous substances.

During the course of geochemical studies on uraniferous coals (Breger, Deul, Meyrowitz, and Rubenstein, 1953), yields of oil, water, and char were determined by a standard Fischer assay method (Stanfield and Frost, 1949). Because of the nature of this technique it was difficult to establish with certainty if volatile uranium compounds had been formed during the course of the retort assay. In order to investigate this possibility, a number of naturally occurring carbonaceous substances have been subjected to dry distillation in small-scale glass apparatus. Experimental results were evaluated on the basis of material balances using

accurate techniques for determining the uranium content of the original substances and of the chars obtained from them. A preliminary search of literature has revealed no publications regarding the volatilization of uranium from such substances during dry distillation.

Although these studies are primarily of a geochemical nature, the results may be of interest in the development of techniques for the processing of uraniferous shales and similar substances.

This work is part of a program undertaken by the Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission.

SAMPLES

The following samples were chosen to provide a variety of carbonaceous substances; the uranium contents ranged from approximately 0.002 to 0.3 percent.

Chattanooga shale.--Top black interval, 0.94 to 2.44 feet below top of black at station R-C2, Cannon County, Tenn. (Conant and Swanson, 1952). This material was collected from the same stratigraphic interval at the same locality where a 5-ton sample was collected for Battelle Memorial Institute in 1949 (Conant, Brown, and Hass, 1950).

Subbituminous coal.--Sample collected from the upper foot of the Luman No. 1 bed, Red Desert area, Sweetwater County, Wyo. (Masursky and Pipiringos, 1953, Field Station RW-513). Geochemical and mineralogic reports on this coal have been issued (Breger et al., 1953).

Organic seam from the Chattanooga shale.--Black, lustrous, brittle organic material collected in 1953 by L. C. Conant and T. Kehn, U. S. Geological Survey, from an outcrop approximately 15 miles north

of Nashville, Tenn. Beds of similar material having a maximum thickness of 0.04 foot are sparsely scattered in the shale averaging 3 to 5 seams per 30-foot core.

Swedish kolm.--Lenticular specimens of kolm were colllected at Kvantorp, Sweden, in 1951, by one of the authors (I. A. B.).

EXPERIMENTAL METHODS

The following techniques were used to obtain the data shown in table 1 for the original samples and in table 2 for the chars obtained from them:

Dry distillation.--Small samples (approximately 1 g) were retorted using a modification of the procedure suggested by Cuttitta (1953). In this procedure the material to be retorted was weighed in an 18 x 250 mm glass-stoppered Pyrex test tube. The lightly stoppered tube was then placed, sloping slightly down toward the stopper, in the tubular electric furnace where distillation was carried out for 11 minutes at 500 C. After cooling the tube in a horizontal position to prevent contamination of the char by the oil and water distillates, the tube was scored and broken at a point immediately above the char. The char was weighed and analyzed to determine its uranium content.

Determination of moisture.--Weighed samples (approximately 0.5 g) of original material or char were dried in an oven for two hours at 105 ± 5 C. Loss of weight was recorded as moisture.

Determination of ash.--Dry samples (approximately 0.5 g) were ignited to constant weight in an electric furnace at 800 C. Residual material was calculated as the ash content of the original dry sample.

Table 1.--Analyses of substances prior to retorting.

Sample	Moisture (percent)	Ash 1/ (percent)	Uranium 1/ In ash (percent)	Uranium 1/ In original substance (percent)
Chattanooga shale	-- 2/	75.5	0.011	0.0083
Subbituminous coal	11.8	11.6	0.012	0.0014
Organic seam from Chattanooga shale	2.3	1.27	2.58	0.033
Swedish kolm	0.87	20.8	1.83	0.38

1/ Dry basis

2/ Analysis on predried sample

Table 2.--Analyses of chars

Sample	Moisture (percent)	Ash 1/ (percent)	Uranium 1/ In ash (percent)	Uranium 1/ In original char (percent)
Chattanooga shale	<0.1	81.9	0.010	0.0082
Subbituminous coal 2/	2.4	19.0	0.016	0.0030
	2.0	18.8	0.016	0.0030
Organic seam from Chattanooga shale 2/	0.3	2.2	2.10	0.046
	0.4	2.4	1.93	0.046
Swedish kolm 2/	<0.1	26.1	1.96	0.51
	<0.1	26.1	1.96	0.51

1/ Dry basis

2/ Duplicate analyses

Determination of uranium.--Using the dry ash the extraction-fluorimetric procedure described by Grimaldi, May, and Fletcher (1952) was employed without modification.

SUMMARY AND CONCLUSIONS

Uranium balances based on the original samples and on the chars obtained from them are shown in table 3; uranium contents have been calculated from the data of tables 1 and 2.

The final column of table 3 shows recoveries of uranium in the char ranging from 91.4 to 111.9 percent. These recoveries are based on a minimum of one ash, two moisture, and two uranium analyses. As the accuracy of the uranium determination alone is at best ± 4 percent (Grimaldi, May, and Fletcher, 1952), these analyses are all within the limits of analytical error. It seems from the data, therefore, that distillation of these naturally occurring uranium-bearing carbonaceous substances results in no appreciable loss of uranium in the distillate.

Table 3.--Uranium balances

Sample	Sample for distillation (g)	Uranium in sample (γ) 1/	Char (g)	Uranium in char (γ) 1/	$\frac{\text{Uranium in char}}{\text{Uranium in sample}} \times 100$ (percent)
Chattanooga shale	0.9897	82.0	0.9150	75.0	91.4
Subbituminous coal 2/	0.9978	16.0	0.6034	17.9	111.9
	0.9858	15.8	0.5928	17.5	111.1
Organic seam from Chattanooga shale 2/	1.0019	320	0.6796	310	97.0
	0.9522	305	0.6349	305	100.0
Swedish kolm 2/	0.9784	3720	0.7811	3960	106.2
	1.0149	3860	0.8097	4130	107.0

1/ Micrograms

2/ Duplicate analyses

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