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UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

EXTRACTION OF URANIUM FROM AQUEOUS SOLUTION
BY COAL AND OTHER MATERIALS*

By

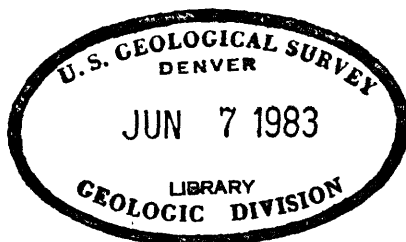
George W. Moore

June 1953

Trace Elements Investigations Report 235

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EXTRACTION OF URANIUM FROM AQUEOUS SOLUTION BY COAL AND OTHER MATERIALS

By George W. Moore

ABSTRACT

Since uranium in nature is commonly associated with carbonaceous material, laboratory studies were conducted to determine the relative ability of various types of carbonaceous material and some other substances to remove uranium from solution. The results of these experiments indicate that the low rank coals are more effective in extracting uranium than any of the other materials used. A chemical determination shows that nearly 100 percent of the available uranium in solution is removed by subbituminous coal. The uranium is apparently retained in the coal by an irreversible process. The notable affinity of uranium for coalified plant remains suggests that some uranium deposits may have been formed over a long period of time by the extraction of uranium from dilute groundwater solutions. A possible application of the results of this work may be the extraction of uranium by coal from natural water or from waste solutions from uranium processing plants.

INTRODUCTION

The association of uranium with carbonaceous material in nature has been recognized for many years. In 1875 Berthoud reported the occurrence of uranium minerals with coal in the Leyden area, Jefferson County, Colo., and in 1905 Boutwell noted the association between uranium and fossil wood on the Colorado Plateau. More recent work has shown that uranium occurs with many types of carbonaceous material including marine black shale



(McKelvey and Nelson, 1950), carbonized plant remains (Fischer and Hilpert, 1952), asphaltite (Davidson and Bowie, 1951), crude oil (Unkovskaya, 1940), and coal (Vine and Moore, 1952).

A detailed study of uranium-bearing lignite in South Dakota led Denson, Bachman, and Zeller (1950) to propose that the uranium in these deposits was introduced by cold groundwater solutions subsequent to coalification. This hypothesis has been summarized by Love (1952). A requirement of this hypothesis is that coalified plant remains and uranium have a strong chemical affinity for each other and that carbonaceous material has capacity for extracting uranium from dilute cold water solutions. Several experiments were conducted in order to establish the relative ability of coal and other materials some of which commonly are found associated with uranium, to remove it from solution under laboratory conditions.

ACKNOWLEDGMENTS

T. S. Lovering participated actively in the early parts of the study and made many suggestions throughout the course of the work. The analytical work was done in the Trace Elements Section Denver Laboratory, U. S. Geological Survey by Wayne Mountjoy, J. P. Schuch, and W. W. Niles, under the direction of L. F. Rader who also suggested methods of procedure and kindly read the manuscript. Samples were obtained from F. C. Bennett of the Colorado Fuel and Iron Corporation, J. B. Goodman of the U. S. Bureau of Mines, and J. W. Adams, J. R. Donnell, Harold Masursky, and H. D. Zeller of the U. S. Geological Survey. This work was done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.



DESCRIPTION OF EXPERIMENTS

A solution of uranyl sulfate containing 1.0000 gram of uranium was prepared by dissolving 1.1793 gram of powdered U_3O_8 ^{1/} in a mixture of concentrated nitric and sulfuric acids. This solution was evaporated to dryness and fumed to remove the nitrate ion, and the residue was then dissolved in 1 liter of 0.01 normal sulfuric acid to provide a pH of 2. The solution of UO_2SO_4 (Latimer and Hildebrand, 1951) thus prepared contained 1000 parts per million uranium. For purposes of the experiments the solution was further diluted with water until it contained about 200 ppm uranium at a pH of 2.45 ^{2/}. The low pH value was selected to prevent the possible formation of insoluble hydrates (Katz and Rabinowitch, 1951).

In an initial experiment, coal from the Centennial mine, Boulder County, Colorado, was ground and screened until it was composed of grains between 40 and 80 mesh (0.42-0.177 mm). This granular coal was placed in an apparatus similar to that described by Garrels and others (1947) which provides a continuous circulation of the solution. A solution (350 ml.) containing 196 ppm of uranium was placed in this apparatus with 28 g. of coal and the solution circulated for 12 days. The results of this experiment are tabulated in table 1.

^{1/} Mallinckrodt standard sample MS-ST, 99.95% U_3O_8 .

^{2/} pH values listed in this paper were determined with a glass electrode.



Table 1.--Results of experiment on the precipitation of uranium by subbituminous B coal from the Centennial mine, Boulder County, Colorado

	Before experiment	After experiment
Uranium in the coal (percent)	0.00016	0.21
Uranium in solution (parts per million)	196	0.48
(SO ₄) ⁼ (parts per million)	342	218
pH ⁺	2.45	6.03

From the figures in table 1 it can be shown that the subbituminous coal removed about 100 percent of the uranium in the solution. In order to test whether the reaction between uranium and subbituminous coal is reversible, the material from the experiment was washed with distilled water and decanted 6 times and a sample taken for analysis; then it was washed 6 more times and another sample taken. The analyses showed that with both 6 and 12 washings no uranium had been removed. These results suggest that the uranium is held irreversibly, at least in respect to distilled water, and perhaps in a manner similar to the occurrence of uranium in marine black shale (Tolmechev, 1943). Tolmechev, on the other hand, has shown that uranium is adsorbed by charcoal in accordance with Fruendlich's law and that the quantity of uranium extracted is proportional to the amount of uranium in the solution. He further demonstrated that the uranium could be removed from the uranium-bearing charcoal by flushing with distilled water. Thus it appears that the mechanism whereby uranium is extracted from solution by charcoal is different from that in which it is removed by coal and black shale. A more detailed discussion of the factors influencing extraction is given below.



A second group of similar experiments was conducted using many different materials and employing a more simple apparatus. The samples included all the major ranks of coal and associated carbonaceous materials, as well as clay, phosphate rock, and additional substances considered as potential extracting agents of uranium from solution.

Each sample of material was ground until it would pass through an 80 mesh screen (0.177 mm). Then, 20.0 g. of each sample was placed in a 500 ml. bottle with 250 ml. of uranyl sulfate solution at a pH of 2.45 and a uranium content of 200 parts per million. The contents of each bottle were shaken thoroughly once daily for 19 consecutive days. At the end of this period, all of the solutions were centrifuged at 1450 rpm for 15 minutes. Bentonite and lignite from South Dakota were centrifuged at 2300 rpm as these solutions failed to clear at the lower speed. Even after this treatment the solution containing the bentonite remained cloudy.

Samples of the solid material were analyzed for uranium and the solutions were analyzed for uranium and sulfate ion, and the pH+ ascertained. The results of these analyses are shown in table 2. The results have also been calculated to the percent of uranium removed from solution by each material and these data are presented graphically on figure 1. It is felt that the change of concentration of the uranium in solution represents a more accurate measure of the extracting ability of the material than the final uranium content of the sample, as several materials, particularly the wood, peat, and bentonite, formed spongy or gelatinous masses which held an indeterminate quantity of solution. As a result the values for the uranium content of these samples are probably too high.



Table 2.--Results of experiment in which 16 materials were immersed in a solution of uranyl sulfate for 19 days

Sample	Uranium content of sample (percent)		Composition of solution after experiment		
	Before experiment	After experiment	Uranium (parts per million) $\frac{1}{1}$	pH $\frac{2}{2}$	SO_4 (parts per million) $\frac{3}{3}$
Wood					
White pine	0.0000	0.14	120	2.80	384
Peat					
Chisholm, Minn.	0.0005	0.21	4.0	4.28	268
Lignite					
Sandow mine, Tex.	0.0002	0.17	4.0	6.56	864
Lignite					
Slim Buttes, S. Dak.	0.0003	0.19	2.0	3.97	894
Subbituminous C coal					
Suntrana mine, Alaska	0.0001	0.21	0.24	4.90	321
Bituminous coal (HVC)					
Keblor mine, Colo.	0.0001	0.012	166	7.57	410
Anthracite					
Crested Butte, Colo.	0.0001	0.024	132	5.10	348
Graphite					
Commercial	0.0000	0.044	144	7.74	400
Charcoal					
Commercial	0.0000	0.022	137	7.90	349
Phosphate rock					
Cokeville, Wyo.	0.028	0.11	74	7.28	711
Bentonite					
Upton, Wyo.	0.0030	0.099	145	7.50 $\frac{4}{4}$	---
Oil shale					
Rio Blanca, Colo.	0.0037	0.031	158	7.50	410
Canneloid coal					
Wamsutter, Wyo.	0.0002	0.16	39	1.63	4750
Calcite					
Iceberg mine, N. Mex.	---	0.002	168	7.63	---
Gilsonite					
Middle Park, Colo.	0.0013	0.004	180	2.41	410
Silica flour					
Commercial	0.0000	0.002	200	2.46	350

1/ Uranium in original solution: 200 ppm.

2/ pH of original solution: 2.45.

3/ Concentration of SO_4 in original solution: 342 ppm.

4/ Determination probably inaccurate as sample contained colloidal bentonite which could not be separated without changing the pH.



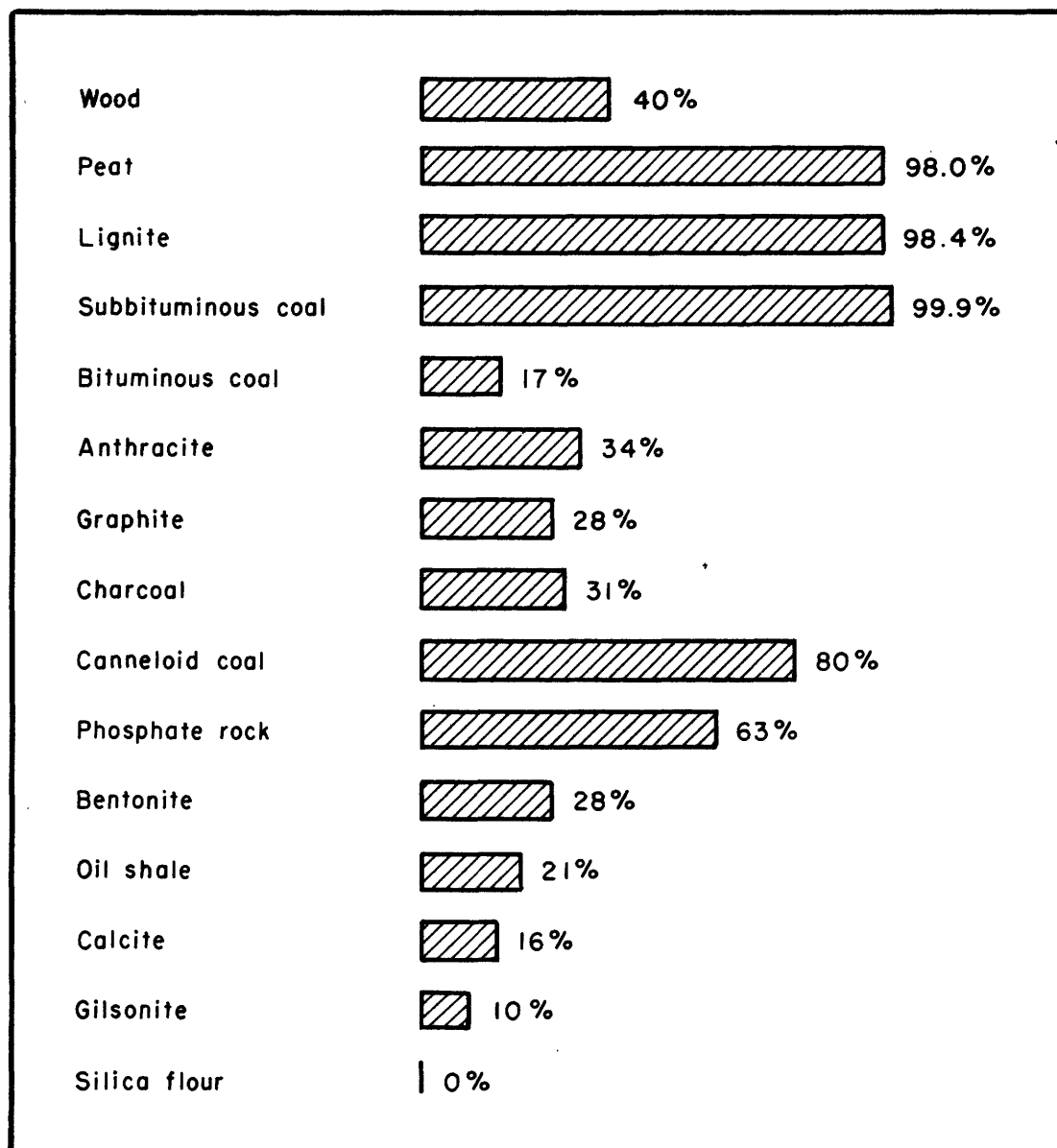


Figure 1.--Percent uranium extracted by coal and other materials from uranyl sulfate solutions containing about 200 parts per million uranium.



DISCUSSION

The first and most obvious fact shown by these experiments is that the lower rank coals were more effective in extracting uranium than any of the other materials used. A maximum of 99.9 percent uranium was removed from solution by subbituminous coal; phosphate rock follows subbituminous coal, lignite, and peat as an extracting agent, for it removed 63 percent of the uranium from solution. These results are in harmony with the association of uranium in nature with coal, coalified logs, and carbonaceous shale and with phosphate rock and fossil bones.

Most of the other materials extracted some uranium but probably none can be considered as effective extracting agents as the coal. Gilsonite, an asphalt-like substance, extracted only 10 percent of the uranium from solution. The adsorptive properties of bentonite for uranium have been attributed by Frederickson (1948) to the high base-exchange capacity of the montmorillonite clays that constitute most of this rock. It is of interest to note that the bentonite used in these studies extracted only 28 percent of the uranium available in solution.

Concerning wood, peat, and the various ranks of coal, the results of these experiments (fig. 1) indicate that these materials are not equally effective agents for removing uranium from solution. Wood, for example, extracted 40 percent of the uranium and peat extracted 98 percent. Passing to the low ranks of coal there is a slight increase in the efficiency of extraction until a peak is reached at subbituminous coal where almost 100 percent of the uranium was extracted. Bituminous coal, on the other hand, extracted only 17 percent, while anthracite and graphite removed only 30 and 28 percent respectively.



These results are of a preliminary nature, based in most cases on a single sample for each rank of coal, so additional studies may alter the pattern which seems indicated. If these results are accepted as approximating those which would be obtained regardless of the number of samples used, the chief factors influencing the extraction of uranium by coal may be considered. These are: Surface adsorption, ion exchange, chemical reduction, change in pH, and the formation of metalo-organic compounds.

The fact that the uranium is held irreversibly by the coal suggests that surface adsorption phenomena are not important in determining the affinity for uranium. Also, Breger and Deul (1952) have shown by base-exchange studies that the uranium in coal is not held to any appreciable extent by ion exchange.

Coal is generally regarded as a good reducing agent, but these experiments are inconclusive as to the role chemical reduction may play in the extraction of uranium. Bituminous coal, anthracite, and charcoal are relatively poor extracting agents for uranium, but there is no chemical reason known to the writer for regarding these as less effective reducing agents in general than the low ranks of coal. Until further studies are made it is suggested that chemical reduction is not an important factor in the precipitation of uranium under the conditions of these experiments.

There also appears to be little relation between the ability of materials to extract uranium and the final pH of the solution as indicated in Table 2. Precipitation as an insoluble hydrate in a neutral solution does not seem to have been an important factor since anthracite, a poor extracting agent, had a more nearly neutral final solution than, for example, subbituminous coal, a good extracting agent. Similarly the concentration of sulfate ion in the final solution seems to have little relation to the amount



of uranium extracted.

Since the uranium is apparently held irreversibly in the coal, it is possible that the uranium is precipitated as a metalo-organic compound as suggested by Breger and Deul (1952). If this is the mechanism, the organic compound which combines with the uranium may reach its maximum development in subbituminous coal. Further metamorphism of subbituminous coal to bituminous coal could destroy the organic compound important in extracting uranium. Breger and Whitehead (1951, fig. 7) have shown by thermographic studies that a relatively strong exothermic peak occurs at about 650° C with subbituminous A and high volatile C bituminous coals. This peak is not present in subbituminous C coal or in lignite. It is possible that the same conditions which give rise to these thermographic characteristics may also reflect changes which make the higher ranks of coal less effective extracting agents for uranium.

The anthracite and graphite used are somewhat better extracting agents than the bituminous coal. It is possible that further metamorphism of the bituminous coal to anthracite and graphite could create the ability for removal of the uranium in a different manner--perhaps by ionic adsorption between the graphitic layers. This would be similar to the mechanism whereby charcoal is thought to adsorb uranium and if it is true, the uranium would not be fixed, as the reaction is reversible for charcoal. The possibility of the uranium being held in this manner by anthracite and graphite was not tested.



CONCLUSIONS

Of the several materials studied, the peat, lignite, and subbituminous coal are the most effective agents for the removal of uranium from solution. Phosphate rock may be considered as a fair extracting agent under the conditions of these experiments. It is suggested that the common association between uranium and carbonaceous material in nature may result from the ability of these substances to remove uranium from natural solutions by the formation of metalo-organic compounds. Breger and Deul (1952) have also suggested that uranium is retained in this manner on the basis of experimental work on natural uranium-bearing lignite.

A possible application of the results of this work may be the commercial extraction of uranium from solution by coal and other carbonaceous materials. Subbituminous coal, lignite, or peat might be employed to concentrate uranium either from natural water containing small quantities of uranium, or from waste solutions from uranium processing plants.

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