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ABSTRACT

An aqueous solution of uranyl sulfate containing a suspension of subbituminous coal has been heated at 210° C for three days. Examination of the coal at the end of the experiment showed it to contain 31.8 percent uranium recognizable as uraninite by a sharp, strong X-ray diffraction pattern. A similar experiment with degraded spruce wood also led to the formation of uraninite but in lesser quantity and with broader lines in the X-ray diffraction pattern. The ability of coal or wood to reduce the uranyl ion is a critical factor in the correlation of studies of uraniferous coals containing the uranyl ion with studies of uraninite-bearing coalified wood from the Colorado Plateau. Although these results are based on preliminary experiments, they are extremely important geochemically and warrant the development of the series of controlled studies that are proposed.

INTRODUCTION

Studies have shown that low-rank coals are able to absorb relatively large amounts of uranyl ion (UO_2^{++}) from aqueous solution (Moore, 1954; Szalay, 1954). Breger, Deul, and Rubinstein (1955) concluded on the basis of their experimental work with weathered uraniferous coal that the uranium is retained in the coal as a complex of ionic organo-uranium compounds, probably uranyl humates.

On the Colorado Plateau quadrivalent uranium in uraninite or coffinite (Stieff, Stern, and Sherwood, 1955) is frequently found in intimate association with coalified logs and coalified woody debris imbedded in sandstones. There has been uncertainty regarding the valence state of the uranium during its introduction into the region, that is, whether the uranium was introduced as the uranyl ion and subsequently reduced, or whether it was directly introduced in the U^{+4} state. Although it was known that the uranyl ion is avidly absorbed by low-rank coal, there was no information regarding the possible reduction of the ion by coal. Also, nothing has been known regarding the retention of uranous uranium (U^{+4}) by coal. This lack of information has made it difficult to relate the results of studies on low-rank uranium-bearing coals of South Dakota (Breger, Deul, and Rubinstein, 1955) and Wyoming (Breger, Deul, and Meyrowitz, 1955) to studies of coalified uraninite-bearing logs of the Colorado Plateau. Garrels (oral communication) recently reported that, except under extremely acidic conditions, the equilibrium ratio of UO_2^{++} to U^{+4} should be very high even under reducing conditions. This indicates that uranium was introduced into the Colorado Plateau region in the uranyl form and suggests that reduction to U^{+4} must have taken place subsequently. This suggestion has provided the basis for experimental work to determine if the uranyl ion can be reduced by coalified wood.

The results discussed in this report are of considerable interest because they bridge studies of uranium-bearing coals, where the uranyl ion is present, and knowledge regarding the coalified uraninite-bearing wood of the Colorado Plateau. The proposed studies that are discussed are tentative and may be amplified or re-oriented depending upon further experimental and field work carried out by the authors or suggestions made by other investigators.

We wish to thank Joseph Budinsky for the uranium analyses and Evelyn Cisney for the X-ray diffraction patterns. Robert Milkey performed the infrared absorption analyses. This report is part of a study conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

EXPERIMENTAL WORK

Two experiments have been carried out under essentially the same conditions.

Experiment 1.--A sample (1.0368 g) of subbituminous coal from El Paso County, Colorado, was used for this work. The coal sample was provided through the courtesy of B. C. Parks, U. S. Bureau of Mines, Pittsburgh, together with the analytical data given in table 1. The coal, ground to pass a 100-mesh screen, was suspended in 50 ml of distilled water to which 896.5 mg of UO_2SO_4 (508.0 mg U) was added. The entire mixture was placed in a Pyrex test tube that was then inserted in a stainless-steel bomb equipped with a gage to register the pressure within the bomb. The bomb was then placed in a furnace equipped with a controller preset to maintain the temperature at 210° C. This temperature, during which bomb pressure rose to 230-240 psi, was maintained for three days after which the bomb was cooled and opened. The contents of the test tube were filtered to yield a filtrate of pH 1.6. The coal was washed with dilute sulfuric acid (pH 1.5) and dried in a desiccator under vacuum overnight. An X-ray powder pattern of the treated coal showed sharp, strong lines of uraninite. The filtrate and washing from the experiment were diluted to 1000 ml and analyzed for uranium. Data for the experiment are shown in table 2.

Table 1.--Analysis of subbituminous C coal from El Paso County, Colorado.[1]

	Coal (as received)	Coal (moisture free)
Proximate analysis		
Moisture, percent	25.1	
Volatile matter, percent	31.9	42.6
Fixed carbon, percent	37.7	50.4
Ash, percent	5.3	7.0
Ultimate analysis		
Hydrogen, percent	6.1	4.5
Carbon, percent	50.6	67.6
Nitrogen, percent	0.6	0.8
Oxygen, percent	37.1	19.7
Sulfur, percent	0.3	0.4
Ash, percent	5.3	7.0
British thermal units	8650	11540

[1] Analysis by U. S. Bureau of Mines, Lab. No. C-89738, May 18, 1949.

Table 2.--Experimental data.

	Experiment 1 on subbituminous coal	Experiment 2 on degraded wood
Weight of reducing substance, g	1.0368	5.886
Uranyl sulfate added, g (Uranium added, mg)	0.8965 (508.0)	4.868 (2758.)
Ratio of uranium to reducing substance, mg/g	490	469
Uranium in substance-free solution after experiment, mg	6.3	83.4
Uranium precipitated by reducing substance, by difference, mg	501.7	2675.
Theoretical percent uranium in substance	48.4	45.4
Analyzed percent uranium in substance	31.8	6.4

Experiment 2.--This experiment was carried out on a sample of degraded wood in similar fashion to experiment 1. A wedge of ancient buried and degraded spruce wood (Sample SP-1 in Varossieau, 1949; in Varossieau and Breger, 1951) about 1 cm square at its large end, 10 cm long, and weighing 5.886 g was used. A sample of this wood had previously been provided to A. Pommer, U. S. Geological Survey, who found it to be an effective reducing agent for pentavalent vanadium salts (oral communication). As in experiment 1, uranyl sulfate in aqueous solution was added to the sample. In this experiment 4.8678 g of the UO_2SO_4 was used to maintain as nearly as possible the ratio of uranium to sample that had been employed in experiment 1.

While heating at 210° C for 3 days the pressure within the bomb rose to 350 psi; after cooling to room temperature, the pressure within the bomb was still 100 psi indicating that a gas, later identified as hydrogen sulfide, had been produced during the experiment.

The wood was blackened and had powdery surfaces. The filtrate from the experiment had a phenolic odor; extraction with carbon disulfide led to recovery of 10.0 mg of an oily substance. Infrared absorption analysis indicated that this material has bonded hydroxyl (-OH) groups, aliphatic saturated or unsaturated -C-H groups, and a very small carbonyl (-C=O) content. Ionic sulfonate or sulfonic acid structure is also indicated by the spectrum.

An X-ray powder pattern obtained from the treated wood, after drying under vacuum overnight, showed a strong pattern for uraninite. Line broadening was indicative of small crystal size.

The filtrate and washings from the experiment were diluted to 500 ml and analyzed for uranium. Data for the experiment are shown in table 2.

Blank.--A solution of 0.9589 g of uranyl sulfate in 50 ml of distilled water was heated at 210° C for three days. Removal of the solution from the bomb showed the presence of a small quantity of a black crystalline precipitate that was identified by X-ray diffraction as U_3O_8.

DISCUSSION

The experiments reported are preliminary, but two important conclusions can be drawn:

1) At 210° C, both degraded wood and subbituminous coal are effective agents for the reduction of the uranyl ion to quadrivalent uranium.

2) Low-rank coal is a surprisingly effective reducing agent for uranium.

The knowledge that low-rank coals are avid absorbing agents for uranyl ion and the new experimental finding that after absorption the ion can be reduced effectively ties together information on the origin of uraniferous coals with data on occurrences of coalified wood containing uraninite.

In these preliminary experiments moisture in the samples was not carefully controlled and has undoubtedly resulted in some errors. Uranium analyses were also conducted fluorimetrically, a procedure that is not recommended where large percentages of the element are present. In future work complete and more accurate analyses of samples will be carried out.

The uranium balance for the subbituminous coal is fair in view of expected analytical error. For the degraded wood the balance is poor showing that uranium, as uraninite, is lost by washing of the powdery material from the sample surfaces prior to analysis. This point has been confirmed by collecting a small amount of the powder and identifying it as uraninite by X-ray diffraction. It is thought that formation of hydrogen sulfide during experimentation with the wood resulted in a side reduction of the uranyl ion. Kerr and others (1954) have shown this reaction to take place readily even at low temperatures. Under the conditions of experiment 2, the uranyl sulfate solution would be depleted, but uranium would not necessarily be directly associated with the wood. Washing the sample after heating removed loosely held UO_2 and led to analysis only for that uranium actually retained by the wood.

A sample of the treated coal has been examined by J. M. Schopf, U. S. Geological Survey, to determine the association of the uraninite with the coal particles. Schopf (written communication) reports that the individual coal grains are coated by opaque cubic crystals that are 4 or 5 µ in diameter. These crystals are undoubtedly uraninite. The uraninite is present as a surface incrustation on the particles and is not present within the cell walls of the coalified wood as is the case with samples from the Colorado Plateau.

Although analytical data upon which to base a conclusion have not as yet been obtained, it is possible that the coal and the degraded wood are equally effective reducing agents for the uranyl ion. This is indicated by the quantity of uranium remaining in solution following each experiment. Gruner (oral communication, 1954) reported the reduction of the uranyl ion by extracts from peat. Inasmuch as extracts from peat contain many partly degraded plant constituents with high reducing capacity, it is particularly interesting to note the high reducing capacity of the subbituminous coal.

PROPOSED WORK

Future experiments will be carried out with unmineralized, coalified wood from the Colorado Plateau. A coalified log, collected by Breger and

Deul in 1953 in the Virgin mine, Montrose County, Colorado, is being hand-cleaned to remove extraneous mineral matter. The washed coal, with the exception of several chips for petrographic study, will be subjected to complete coal, spectrographic, and chemical analysis after which it will be used as a primary standard for the work outlined below. Samples of the coal will also be made available for studies with vanadium salts that are being carried out by A. Pommer.

This coal will be treated with a uranyl salt, preferably uranyl chloride, as in the experimental work summarized in this report. The relative ease of decomposition of uranyl sulfate to U_3O_8 at 200° C recommends against further use of the salt. The formation of uraninite in the coal will be studied quantitatively by X-ray diffraction techniques, using known quantities of halite or quartz as an internal standard, under three sets of conditions. In the first series of experiments only time will be a variable; in the second, temperature will be varied; and in the third, time and temperature will be maintained constant while the ratio of uranium to coal is varied.

Relationships derived from the percent uraninite-temperature curve, the percent uraninite-time curve, and the percent uraninite-uranium/coal curve will provide data regarding the conditions under which uraninite can be produced by the reduction of the uranyl ion by coal. Experimentation over a range of geologically significant pressures may lead to the formation of uraninite within the cell walls, thus duplicating the product from the Colorado Plateau. As indicated above, this program is tentative and subject to amplification.

As a corollary to the experiments with uraninite, a mixture of the coal, a uranyl salt, and silicic acid is being prepared in an effort to synthesize coffinite.

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