

SOME CHEMICAL CHANGES IN COAL SAMPLES DURING STORAGE

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The oxidation of coal has received considerable study, especially in the commercial aspects of the problem. In addition some work has been done on the relation of oxidation to analysis.^{1, 2, 3, 4} Ease of oxidation increases, in general, with decrease of rank of the coal; for example, the high volatile bituminous coals such as are found in Illinois oxidize rather easily on exposure to air. An understanding of the oxidation or weathering characteristics is therefore desirable in the use and study of these coals.

Knowledge of the effects of different kinds of storage of laboratory samples of coal is of the greatest importance to the coal analyst. Oxidation of coal samples may influence the analytical results markedly, so that it is important that analysis take place before such changes have occurred.

Some of the factors which influence the oxidation and deterioration of coal are rank and type of coal, volatile matter content, sulfur content, size, amount of handling, presence of moisture, accessibility of oxygen, temperature, and kind of storage. Recently we had the opportunity of determining the effect of cold storage on calorific and sulfate sulfur values. A description of the methods of sampling, storage, and analysis follows.

Sampling and Storage.—Special column samples about 10 by 12 inches in cross section, and representing the entire thickness of the coal seam were cut in several different mines, and brought to the laboratory. Approximately one-fourth of each column was cut for study and the remaining samples were placed in long wood boxes which were carefully covered with paraffin and stored in the store room of a local ice plant. The temperature of this store room was controlled thermostatically at 30 to 32° F. The samples were allowed to remain in storage for about one year when they were removed and portions about 4 inches in cross section by the length of the coal seam were cut out and the rest of the coal discarded. These newly cut column samples were returned to the storage boxes, two or three

being placed in each box to conserve space, the boxes were again paraffined, and returned to the storage room of the ice plant. After having been stored about 3½ years they were removed, crushed and analyzed.

At the time the column samples were cut in the mine, channel samples taken adjacent to the column samples were obtained for analysis. Owing to the fact that the analytical laboratories of the Geological Survey were in the process of building and organization at that time, analyses of these samples were delayed for some time. While the calorific values obtained by these analyses may be somewhat lower and the sulfate sulfur values somewhat higher than the original values for the coal as taken from the mine, they serve very well for comparison with the values obtained for the samples after long storage.

Analysis.—Analyses of all samples were made according to the standard procedures of the American Society for Testing Materials, A. S. T. M. Designation D-271-33° with the exception that sulfate sulfur determinations were made according to the procedure of Powell and Parr.⁶

Results.—The results of analyses for 13 coal samples, both before and after storage for 4½ years, are given in table 1. B.t.u. values are given for the moisture and ash-free basis for better comparison while the sulfate sulfur values shown are moisture free values. Reference to this table will show definite losses in heating values and increases in sulfate sulfur values.

An attempt was made to correlate the loss in B.t.u. of the various samples with certain items of their proximate analysis. It was found that a rough correlation might be made between the ratio of fixed carbon to volatile matter and the per cent loss in B.t.u. taking place during storage. This correlation is shown in table 2. Reference to this table will show a tendency for the loss in heat value to decrease as the ratio of fixed carbon to volatile matter increases. The

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TABLE 1—ANALYSES OF COALS BEFORE AND AFTER STORAGE

Sample	B. t. u.—moisture and ash free				Sulfate sulfur—moisture free			
	Before Storage	After Storage	Loss B. t. u.	Loss %	Before Storage	After Storage	Gain %	Gain % of original
A	14,186	13,703	483	3.40	0.09	0.44	0.35	390
B	14,205	13,751	454	3.20	0.09	0.51	0.42	470
C	14,140	13,766	374	2.64	0.12	0.46	0.34	280
D	14,073	13,824	249	1.77	0.10	0.45	0.35	350
E	13,981	13,849	132	0.94	0.19	0.36	0.17	89
F	14,295	13,923	372	2.60	0.14	0.35	0.21	150
G	14,102	13,585	517	3.67	0.04	0.40	0.36	900
H	13,872	13,446	426	3.07	0.06	0.55	0.49	820
I	14,001	13,568	433	3.09	0.06	0.33	0.27	450
J	13,862	13,707	155	1.12	0.10	0.24	0.14	140
K	14,395	14,303	92	0.64	0.02	0.05	0.03	150
L	14,463	14,263	200	1.38	0.05	0.15	0.10	200
M	14,561	14,223	338	2.32	0.03	0.08	0.05	170
Av.	14,164	13,839	325	2.29	0.08	0.34	0.26	330

TABLE 2—COMPARISON OF RATIO OF FIXED CARBON TO VOLATILE MATTER TO LOSS IN CALORIFIC VALUE ^a

Sample	Volatile Matter	Fixed Carbon	Loss Per cent ^b	Fixed carbon
				Volatile matter
A	46.95	53.05	3.40	1.13
B	46.53	53.47	3.20	1.15
C	47.90	52.10	2.64	1.09
D	48.22	51.78	1.77	1.07
E	45.40	54.60	0.94	1.20
F	45.63	54.37	2.60	1.19
G	47.08	52.92	3.67	1.12
H	46.98	53.02	3.07	1.13
I	46.00	54.00	3.09	1.17
J	45.93	54.07	1.12	1.18
K	40.40	59.60	0.64	1.48
L	40.93	59.07	1.38	1.44
M	39.10	60.90	2.32	1.56

^a All values moisture and ash free basis.^b Loss heat value in per cent.

fact that exceptions to this general tendency appear indicates that other factors are involved in the oxidation of the coal.

The increase in sulfate sulfur is due to the oxidation of other forms of sulfur in the coal. However, attempts to correlate these increases with other analytically determined constituents proved unsuccessful. It is unfortunate that pyritic and organic sulfur values for the coal after storage are not available for comparison with those determined before storage. Such a comparison might show the relative tendencies of these two forms of sulfur to oxidize to sulfate sulfur under the conditions of storage studied.

It would be interesting to compare the rate and amount of oxidation taking

place in these samples as stored with the rate and amount of oxidation taking place in similar samples stored at higher temperatures. However, it has been shown that appreciable oxidation did take place as evidenced by resulting lower heat values and higher sulfate sulfur values.

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