Rheology of Coal. III. A Structural Interpretation of Coal Oxidation from the Internal Viscosity Variations

By Katsuya INOUYE

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Introduction

Many results have been reported on the phenomenon that the caking properties of coal are markedly changed by oxidation. R. V. Wheeler and others[1] have shown that even a degree of oxidation insufficient to affect the ultimate analysis reduces the caking properties profoundly. J. D. Davis and his co-workers[2] have reached the same conclusion by their own methods. In other cases, however, it is known that the caking properties can increase by mild oxidation.[3] These experimental facts, apparently contradictory, are readily understood, as H. L. Riley and his collaborators[4] have suggested, when it is accepted that the addition of oxygen to the coal molecules strengthens the intermolecular forces and results in restricting the mobility of the turbostratic system, so that excess of plasticity during carbonization, which may make the weak coke too porous, can be reduced; on the other hand, the appropriate plasticity of the caking coal at the caking temperatures is destroyed by further addition of oxygen atoms.

The author has shown from Young's modulus experiments[5] and the internal viscosity measurements[6] by vibrational methods that the caking properties of coal may be explained by these rheological factors and has proposed a theory on the structure and physical properties of coal. If the proposed theory on the difference between the structures of strongly-caking coal and weakly- or non-caking coal is valid, the corresponding variations in rheological properties should be observed experimentally by oxidation when the strongly-caking coal changes to a less-strongly caking coal. The mechanism of coal oxidation may also be discussed from the rheological standpoint. This report describes the internal viscosity variations during air-oxidation of several typical coals.

Description of Samples and Experimental Method

The coals used in this report are chosen from the same species examined in the preceding experiments, and Table 1 describes some common characteristics of the samples.

The experimental method for measuring the internal viscosity is described in the preceding paper.[6] All specimens were cut parallel to the bedding plane, in rectangular bars with accuracy of 1% in each dimension. The resonance curves between amplitude and frequency were obtained with fixed-free bar specimens at 30.0°C. and at the resonant frequency in the range of 1200~1400 c/sec. and hence the internal viscosity values were calculated according to the relations between vibrational decrement factor and viscosity,

Table 1

Description of Samples

Sample	Origin	Classification	Caking Property	Volatile Matter, Mean Value (dry, ash-free basis) in %
Takashima	Kyushu, Japan	Bituminous	Strongly-caking	38
American	U. S. A.	Bituminous	Strongly-caking	35
Toro	Saghalien, U. S. S. R.	Bituminous	Weakly-caking	46
Yubetsu	Hokkaido, Japan	Producer gas coal	Non-caking	64
Shosaku	China	Anthracite	Non-caking	7.7

(1) R. V. Wheeler and T. G. Woolhouse, *Fuel*, **11**, 44 (1932).
(2) L. D. Schmidt, J. L. Elder and J. D. Davis, *Ind. Eng. Chem.*, **32**, 548 (1940); R. E. Brewer, C. R, Holmes and J. D. Davis, *Ind. Eng. Chem.*, **32**, 930 (1940).
(3) L. D. Schmidt, J. L. Elder and J. D. Davis, *Ind. Eng. Chem.*, **28**, 1346, (1936); T. Iwasaki et al., Annual Meeting, *Chem. Soc. Japan*, 1950.
(4) H. E, Blayden, J. Gibson and H. L. Riley, *Proc. Conf. Ultra-fine Structure of Coals and Cokes, London*, **1944**, 176.
(5) K. Inouye, *J. Colloid Sci.*, **6**, 190 (1951).
(6) K. Inouye, This Bulletin, **26**, 84 (1953).

$$\eta = \frac{2\lambda n \rho l^4}{\kappa^2 m^4}, \quad (1)$$

and

$$\lambda = \frac{\pi \Delta n}{\sqrt{3}\, n}, \quad (2)$$

where, η = internal viscosity, λ = logarithmic decrement, n = resonant frequency, ρ = density of the specimen, l = length of the specimen, κ = radius of gyration of cross section, m = a factor corresponding to the mode of vibration, and Δn = the half value breadth of the resonance curve at the resonant frequency.

The measurement was carried out at first on the original (no oxidation) sample and then it was replaced into an air oven regulated at 120°C. for air-oxidation. The air was introduced from the bottom of the oven and went out of the top through a metal rack on which the specimens were set. After 30 hours' oxidation, the sample was taken out of the oven, cooled to the room temperature and fitted for vibrational measurements. The experiment was repeated after 30 more hours' oxidation (oxidized for 60 hours in total). The cement supporter had sometimes to be renewed after oxidation for the specimen separates from the supporter by heating. The change of dimensions of the specimens was considered sufficiently small, so that the dimensional factors (length and thickness) in Equations 1 and 2 were kept constant even after the oxidation. The change of weight of the specimen remained within 1%.

Changes of Caking Properties by Oxidation

The grains having diameter of approximately 0.5 cm. of each sample were prepared and oxidized in the same oven at 120°C. This diameter preferred was the mean thickness, i. e., the minimum dimension which may determine the oxidation velocity, of the specimen. Table 2 shows the changes of oxygen contents for four coals after 60 hours' oxidation. The moisture and ash contents listed are based on 76% humidity, the ultimate analysis on dry basis. The oxygen increases rather remarkably by the oxidation.

Table 3 shows the changes of the amount of extractable portion by pyridine on the existence of which the strong caking properties of the coals depend, and of the Lessing index. The pyridine extraction was carried out by the Soxlet method and the content was calculated in dry-ash-free bases, from the weight of α portion (steam distilled and dried). The Lessing caking index is a ratio of the height of carbonized sample after heating for 7 minutes at 900°C. in a silica retort to the height of 1 g. of the original coal of minus 100 Tyler mesh.

These changes seem to show that the oxidation method in this experiment can add oxygen to the coals and make the caking properties decrease. A recovery of the extraction data after 60 hours' oxidation may suggest, as explaind later, the decomposition in the coal samples.

Internal Viscosity Changes by Oxidation

As already reported in the preceding articles,[5][6] Young's modulus, E, and internal viscosity, η, of coal are respectively linear functions of ash volume concentration, ϕ,

$$\eta = \eta_0(1 + K'\phi) \quad (3)$$

Table 2

Changes of Oxygen Contents

Sample	Moisture	Ash	H	C	N	O and etc.	O and etc. (dry-ash-free)
Original Coals:							
Takashima	2.42	7.25	5.36	77.30	1.38	15.96	17.24
American	1.79	10.65	5.36	76.83	1.67	16.14	16.28
Yubetsu	4.98	11.83	5.36	67.94	1.17	25.53	29.16
Shosaku	4.50	9.29	2.31	82.27	0.91	14.51	16.07
After 60 Hours' Oxidation:							
Takashima	2.65	4.44	5.38	76.63	1.44	16.55	18.38
American	1.71	14.66	4.67	70.83	1.75	22.75	26.74
Yubetsu	3.64	17.29	5.15	63.83	1.17	29.85	36.11
Shosaku	3.79	11.05	2.33	81.18	1.08	15.41	17.41

Table 3

Changes of Properties

	Takashima			American		
	0 hour	30 hours	60 hours	0 hour	30 hours	60 hours
Extracted Portion, %, Dry-ash-free Bases	11.5	0.03	1.8	8.6	0.005	0.14
Lessing Index	3.14	1.18	1	4.99	3·84	—

and

$$E = E_0(1 + K\phi) \qquad (2)$$

where, E_0 and η_0 show the rheological values of "pure" coal molecules and K and K' represent the solvation factors of coal molecules with ash. Small E_0 and η_0 as well as large solvation factors distinguish the strongly-caking coals. The internal viscosity and ϕ relationship of the original coals is shown in Fig. 1, which also contains several data published in the preceding paper.[6] The detailed description of the curves especially minima and maxima which appeared for the caking coals will be given in the following article.* Figs. 2 and 3 show the internal viscosity values after 30 and 60 hours' oxidation. The values of η_0 and K' of the coals both before and after 30 hours' oxidation are given in Table 4.

The variations of the internal viscosity by oxidation are as follows: (1) the inclination of the linear relationship becomes flat, (2) the internal viscosity

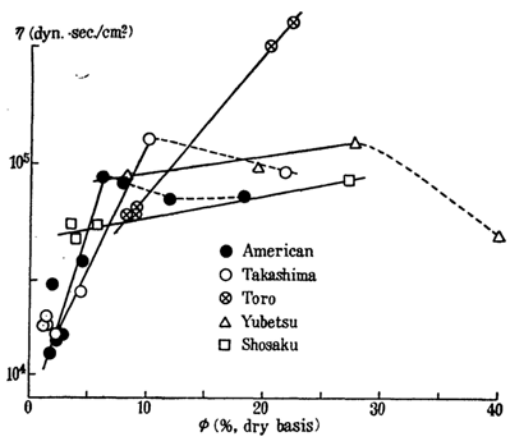

Fig. 1.—Internal Viscosity and Ash Content. Original Coals.

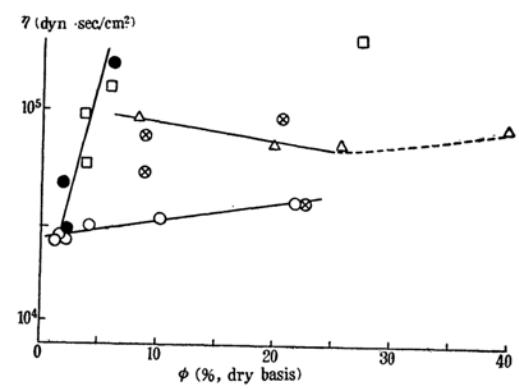

Fig. 2.—Internal Viscosity and Ash Content. Oxidized Coals for 30 hours.

* Rheology of Coal. VI. Unpublished work by K. Inouye and H. Tani.

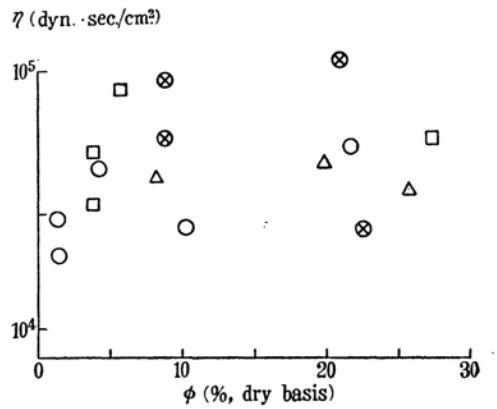

Fig. 3.—Internal Viscosity and Ash Content. Oxidized Coals for 60 hours.

Table 4

Changes of η_0 and K' by Oxidation

Sample	Duration of Oxidation: 0 hour η_0, c.g.s.	0 hour K'	30 hours η_0, c.g.s.	30 hours K'
American	1×10^{3}	16	2×10^{4}	0.95
Takashima	3×10^{3}	3.5	4.5×10^{4}	1.8×10^{-2}
Toro	2.3×10^{4}	2.7×10^{-1}	—	—
Yubetsu	8.4×10^{4}	1.0×10^{-2}	1.0×10^{5}	-6.1×10^{-3}
Shosaku	6.8×10^{4}	1.3×10^{-2}	—	—

value at $\phi = 0$ increases, and (3) further oxidation (see Fig. 3) appears to destroy the definite relationship between molecules and inorganic ash. The experimental facts suggest that the rheological conditions in strongly-caking coals change to those in weakly- or non-caking coals, i. e., the free molecules which act as a plasticizer when the coal is carbonized, obtain stronger intermolecular forces by adding the oxygen atoms, so that the micelle structure by solvation becomes indefinite.

It may be interesting to note that the changes of viscosity for Takashima coal, which showed rapid decrease of the Lessing index by oxidation, were more remarkable than in the case of American coal, although the values for the latter sample after oxidation are not many for the brittle nature of the specimens.

When the oxidized coal, originally strongly-caking, is carbonized in the coke oven, the coal cannot fuse and swell at the caking temperatures of the original coal, say at 400~500°C., because of the too strong intermolecular interactions of the matrix (bitumen) molecules of the micelle system.

Discussions

These facts may give the interpretation of the mechanism of coal oxidation, as suggested by H. L. Riley et al., that the addition of oxygen to the coal molecules causes an increase of forces between molecules and hence a decrease of the

caking properties. The experiments may also support the author's proposed theory on the mechanism of caking properties and coal structure.

Some possible causes of the experimental errors are considered.

(1) Dependence of η on the frequency. The η values are influenced by the frequency measured. The author, however, cannot state the dependence, although some results have been given in the preceding report.[7] The causes of experimental difficulty for adjusting the frequency were in the fact that the correction of the dimensions of the oxidized specimens by re-shaping was very difficult for weak mechanical property, and that there is doubt that the oxidized layers of the specimen may be removed by re-shaping. The measurements, therefore, had to be carried out at the frequency range of 1200~1400 c/sec., notwithstanding the fact that the resonance frequency of an oxidized specimen decreases in most cases.

(2) Homogeneity of oxidation. It is known that the oxidation does not proceed homogeneously when the blocks are oxidized, but the oxidized layer may be formed to prevent further oxidation. In this experiment this point is not considered and the oxidation was presumed to be homogeneous.

(3) Decomposition of coal. The decomposition of coal during oxidation was mentioned above, and the influence of decomposition upon the changes of weight, density and ash concentration of the specimen is considerable. These factors, however, were maintained constant in calculation as the weight decrease after even 60 hours' oxidation was within 1%. The most important influence of the decomposition is in the fact that the decomposition may make internal flaws by which occurence the internal viscosity values increase. The consideration of internal flaws on the rheological properties will be reported in future articles concerning the rheological studies of coke.

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Shigen-gijyutsu-shikenjo
(Resources Research Institute),
Saitama-Kawaguchi

(7) Reference 6 and the Report of the Fuel Research Institute, No. 66.