Rheology of Coal. VI. The Micelle Structure in Relation to Anomalies of Rheological Properties of A Bituminous Coal

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Introduction

The linear relationships between ash concentration in volume percentage and some rheological properties of coals[1,2,3] have made one of the authors (K. I.) propose a theory on the structure of coals, especially for caking coals, in which the coal molecules "solvate" around ash particles as a filler in formation of a micelle-like structure.

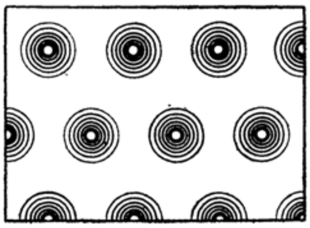

Fig. 1-a. Model of the Structure of Caking Coals.

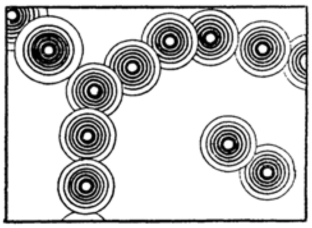

Fig. 1-b. Scaffolding Structure of Micellar Spheres.

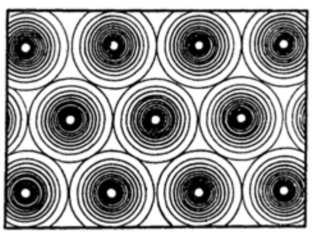

Fig. 1-c. Close-packed state.

The "free" molecules freed from solvation forces act as a plasticizer when the whole system is carbonized. The model would thus appear able to illustrate the cause of caking properties which means and necessitates the mobile condition of the system in caking temperature range, according to the theory, by the "plasticizer effect" of the matrix of micellar system, notwithstanding whether or not the *intra*-micellar changes have to occur. Fig 1-a illustrates the structural model of strongly-caking coal. The concentration of blackening means the strength of intermolecular forces, and the circles represent ash particles as skeletons. High concentration around the circles means strong solvation. For weakly or non-caking coals, the concentration around ash is low and at the same time blackening of the background must be strong; in such conditions thermal mobility of the whole system at higher temperatures cannot be accomplished.

The validity of this model with micelle and matrix may be well demonstrated by using carbon black as rigid micelle spheres and bakelite "A" as more freely combined matrix[4]. This black mixture, preferably with addition of a small amount of alcohol, when "carbonized" up to say 120°C, fuses (cakes) and remarkably swells, resulting in a very porous hard substance which very much resembles coke.

In this paper, the authors make mention of discussing the anomalous behavior of a Japanese bituminous coal, Takashima, in its rheological properties to discuss the model structure by an actual example.

Elasticity, Viscosity and Strength

Takashima bituminous coal, mined in Kyushu, Japan, having the average volatile matter of approximately 38% (d. a. f.), has been distinguished in the authors' experiments by wide distribution of ash concentration between various specimens from 1 to 20 in weight %.

1) Elasticity; Prat I of this study, K. Inouye, *J. Colloid Sci.* 6, 190, (1951).
2) Internal Viscosity; Part II, K, Inouye, This Bulletin, 23, 84, (1953).
3) Breaking Strength; Part V, K. Inouye and H. Tani, This Bulletin, 26, 359, (1953).

4) K. Inouye, Unpublished experiments.

The modulus of elasticity values by resonant frequency method previously reported[1] and further data showed that the variation curve of elastic constant with ash concentration has some ranges of entirely different inclination, as shown in Fig 2. It is noteworthy that a minimum of the elastic moduli exists at $\phi=2$, and also that the elasticity decreases again in the range of $8\sim10\%$ of ϕ. (ϕ is the ash content in volume percentage, dry basis.)

The experiments of internal viscosity from measuring the vibrational decrement at audiofrequencies[2], which suggested that the same relationships as in the Young's modulus experiments exist also in the viscosity data, led to an interesting fact of Fig. 2 that for Takashima coal a minimum at $\phi=2\%$ and second maximum at $\phi=10$ were recognized for the internal viscosity also.

Furthermore, the strength for rupture of the rectangular specimen[3] showed a variation of the strength factors with ϕ in nearly the same form, as illustrated in Fig. 2. The statistical correlation of the breaking strength upon ash concentration[3] has already suggested that the correlation must be considered for every individual range of ash concentration.

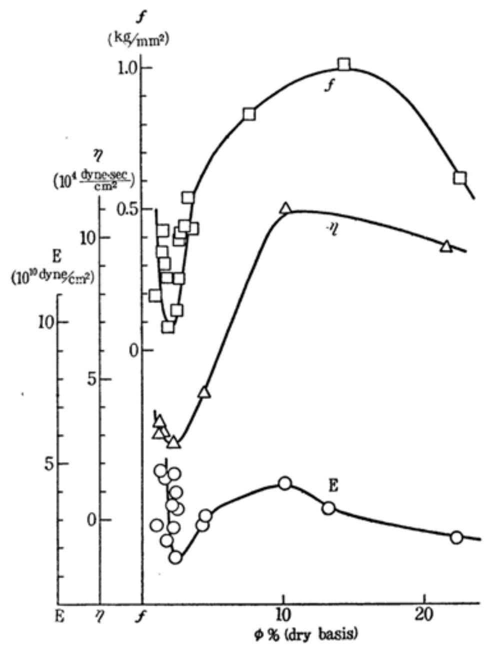

Fig. 2. Varication of Rheological Properties with Ash Concentration.
E: Young'g Modulus
: Internal Viscosity
f: Breaking Strength

An Interpretation of Variations in Rheological Properties

It is recognized in the rubber science that the loading with carbon black to improve mechanical properties of rubber causes perturbation of the stresses and strains set up in the body, and hence this leads to an increase in the elastic and viscosity constants, i, e., a stiffening of the solid, in linear relationships with carbon content.[5,6] Tensile strength, for instance, increases by the loading. However, the changes of strength are considered to be not in linear relationship with loading but in varying manner according to the ranges of loading. E. Guth[6] suggested that the decrease of the tensile strength of rubber-carbon black system for small loadings is caused by the stress concentrations occurring around the carbon particles when the stress is applied, and the increase of the strength for greater loadings by the tendency of the carbon black particles (perhaps of the "solvated" micellar spheres) to form chains and finally some type of network. This increase with loading continues up to the point where the suspension becomes a dilution of carbon by rubber. He made mention of carbon content for the first range as up to 10% by volume, for the second 10 to 30%.

Such descriptions are apparently very suggestive for the present case of coal, by the close similarity of the fundamental characteristics, in spite of the numerical differences. The minimum of Young's modulus, internal viscosity coefficient and breaking strength at 2% of ash content by volume appears to correspond to the state where the micelle spheres, in which the ash particles as nuclei solvate coal molecules, first contact each other to form a scaffolding structure, as schematically illustrated in Fig 1-b. In other words, the modellic picture as Fig. 1-a, homogenious in distribution of the micelles, may not represent the actual structure, because if all micellar spheres could touch each other even at the ash concentration of 2% by volume, the dimension of a micellar sphere must be very large.

If the maximum of the rheological properties at approximately 8 to 10% by volume of ash means the point where the micellar spheres exist in a closed-packing state, as Fig. 1-c, the total internal surface of the micellar system is calculated as,

$$S=\frac{m(\text{area of a sphere})}{m(\text{volume of a sphere})d}$$
$$=m4\pi R^2/m(4/3)\pi R^3 d$$
$$=3/Rd,$$

where S is the total specific surface area per one gramme of the coal, m the number of micellar spheres per gramme, R the radius of the sphere and d is the true density. Hence the radius of the micelle can be obtained if the specific internal surface area of the sample with 10% of ash content by volume is known. A specimen with 10.13% of ϕ was examined at first for Young's modulus (4.19×10^{10} dyne/cm²) and internal viscosity coefficient (1.1×10^5 dyne. sec/cm²) to ascertain

5) H. M. Smallwood, *J. Appl. Phys.*, **15**, 758, (1944).
6) E. Guth, *J. Appl. Phys.*, **16**, 20, (1945).

to assume as the appropriate sample for this purpose, and then powdered. The range of particle size of 30 to 60 Tyler mesh was chosen to measure the specific surface area by the iodine adsorption method at 25.0°C[7]. Using the obtained value of specific area, 9.51×10^4 cm²/g (dry basis), and the density measured in methanol at 25.0°C, 1.24, R was calculated as 2,540Å. As the value of ϕ of this sample is 10.13%, the radius of the ash particle is estimated as 1,160 Å; the value of the radius of "filler" particle in coal is in the same order, but slightly larger, as those of some kinds of carbon blacks[8]. The value of the micellar radius may mean, on the other hand, that solvation forces or internal pertubation caused by ash particles reach in the space of radius of approximately 2,500 Å. However, it may not be true that the dimension of ash particles is always constant overall the ranges of ash concentration, but varying dimensions according to the ash content and therefore to the variation of micellar structure itself are more probable.

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(7) K. Inouye, *J. Fuel Soc. Japan*, **29**, 112, (1950).

(8) J. Sameshima, H. Akamatsu, K. Inouye, S. Kawamura, R. Matsuura, H. Hamada and K. Tamaru, *Rev. Modern Colloid Sci. Japan*, Vol. **1**, 250, (1948). R. B. Anderson and P. H. Emmett, *J. Appl. Phys.*, **19**, 367, (1948)