PUFFING OF ELECTRODE STOCK AS INFLUENCED BY SULFUR CONTENT AND HEATING RATE

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The relationships among acicular petroleum coke sulfur level, upheat rate during graphitization and puffing test characteristics of typical electrode type mixes have been evaluated in detail. Also, other physical properties have been measured on the 1"øx1" long puffing plugs after graphitization to determine whether these properties can be correlated to puffing behavior. Baked electrode type stock (all with the same coke-sizing, the largest coke particle size 6.7mm) from four different cokes were evaluated for puffing behavior through the temperature range 1200°C to 2900°C at 3°C/min., 5°C/min., 10°C/min., and 14°C/min. upheat rates.

Cokes with the following S contents were evaluated:

Coke A %S = 0.5, non puffer
Coke B %S = 0.8, low to moderate puffer
Coke C %S = 1.15, high puffer
Coke D %S = 1.25, very high puffer

Whittaker and Grindstaff[1] have shown that the changes in microporosity which accompany this irreversible expansion during graphitization occurs because of the sudden formation and rapid evolution of hydrogen sulfide gas. Letizia[2] studied the puffing of several cokes with and without puffing inhibitor and found that puffing of non-inhibited cokes was proportional to the sulfur content.

The special puffing test used in this evaluation consists of heating 1"øx1" long cylinders, cut from 4" diameter moldings, at a controlled uniform upheat rate. Changes in sample length perpendicular to the axis of molding are measured by means of a calibrated graphite dilatometer. The accuracy of this test is such that total puffing is measured to $\pm 0.25\%$. Figure I illustrates puffing curves of two types. Curve A is typical of an inhibited formulation of coke C while curve B represents that of uninhibited coke C stock. Total puffing values, defined as $\%\Delta L$ from minimum length to maximum length are designated as $\%\Delta L_1$ and $\%\Delta L_0$ for inhibited (curve A type) and uninhibited (curve B type) stock, respectively. As shown in Figure I, the two values $\%\Delta L_1$ and $\%\Delta L_0$ are defined differently. Only primary puffing, which usually occurs in the 1500-2300°C region, is included in $\%\Delta L_1$. Total puffing occurring between 1200-2900°C is the $\%\Delta L_0$ value.

Puffing was almost nil regardless of upheat rate among the four rates studied on baked electrode stock made with low-sulfur coke A, and containing 1 pph Fe_2O_3 inhibitor (Fig. II & III). Even in baked coke A electrode stock with no puffing inhibitor, puffing is nil at the two slower upheat rates and low to moderate at the faster upheat rates (Fig. II). In contrast, puffing is pronounced in baked electrode stock fabricated with coke D, a high sulfur coke. With coke D, puffing increases appreciably with increasing upheat rate. At the fastest upheat rates, 1 pph Fe_2O_3 does little to inhibit high sulfur coke D as puffing severity of the inhibited stock is almost equivalent to that of uninhibited stock.

Coke B baked electrode stock exhibits puffing characteristics similar to coke A stock but total puffing levels of the former are about 3-5 times that of the latter depending upon upheat rate. This is true for both inhibited and uninhibited stock. Puffing characteristics of coke C stock are similar in trend to those of coke D stock discussed above, but total puffing is about 25-50% lower at a given upheat rate for the former.

Figures IV and V graphically illustrate the relationships of coke-sulfur level and puffing behavior for the electrode stock during graphitization. Similarities of cokes A and B on one hand and cokes C and D on the other hand are clearly depicted in the figures. Total puffing levels of the two highest puffing, high-sulfur cokes rise sharply with increasing upheat rates while upheat rate has much less impact on the low-sulfur cokes.

Coefficient of linear thermal expansion (CTE) and apparent density were measured on the 1"øx1" long graphitized plugs after the puffing experiments. A good correlation exists between coke-sulfur content and apparent density of the graphitized plug at fast heating rates (Fig. VI). Correlations are poorer at slow heating rates. Also, moderate to good correlation exists between CTE and heating rate among the puffing cokes. Figure VII illustrates this relationship.

In summary, magnitudes of both $\%\Delta L_0$ and $\%\Delta L_1$ of electrode stock are related to the sulfur level of the coke from which it was prepared. Low sulfur coke is easily inhibited to almost zero puffing with low to moderate levels of Fe_2O_3 inhibitor. Graphitization rates have a significant effect on total puffing ($\%\Delta L_0$ or $\%\Delta L_1$) of electrode stock. This effect is greatest in stock formulated with high-sulfur cokes.

A good correlation exists between coke-sulfur level and density of graphitized plugs at fast heating rates. Also, a moderate to good correlation exists between CTE of graphitized plugs and heating rate for puffing (high-sulfur) coke stock.

References

1. M.P. Whittaker and L.I. Grindstaff, Carbon, 7, pp. 615-21 (1969)
2. I.Letizia, Abstracts of the Tenth Biennial Conference on Carbon, July, 1971.

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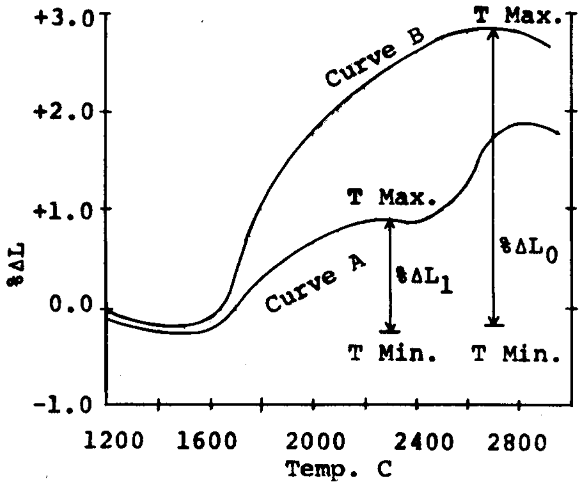

Fig. I. Puffing Curves for Coke C stock with (A) and without (B) Inhibitor

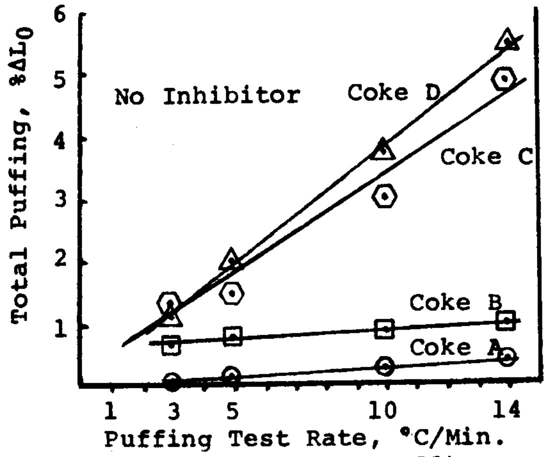

Fig. II. Upheat Rate Vs. Puffing

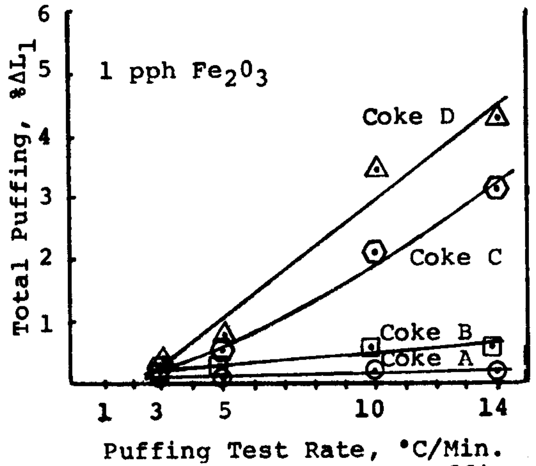

Fig. III. Upheat Rate Vs. Puffing

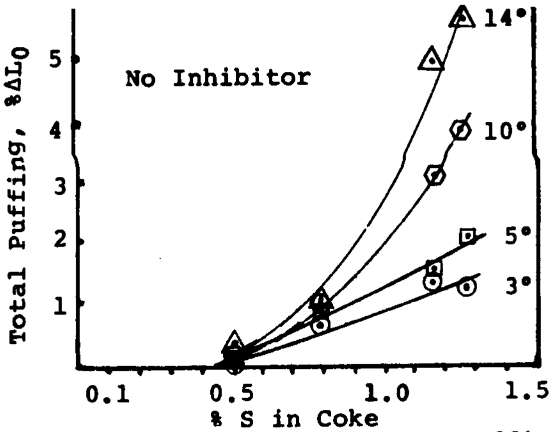

Fig. IV. Coke Sulfur Vs. Total Puffing

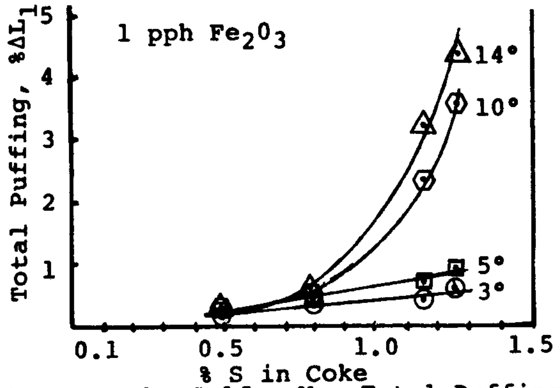

Fig. V. Coke Sulfur Vs. Total Puffing

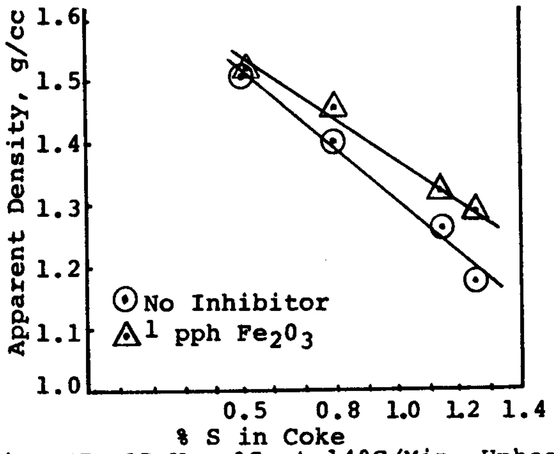

Fig. VI. AD Vs. %S at 14°C/Min. Upheat

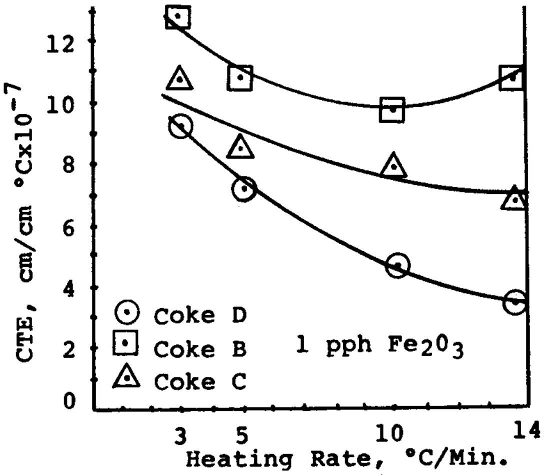

Fig. VII. CTE Vs. Heating Rate