

THE IRREVERSIBLE EXPANSION OF CARBON  
BODIES DURING GRAPHITIZATION

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The formation of synthetic graphite from amorphous carbon should theoretically be accompanied by a continuous shrinkage of material. However, in many instances an irreversible volume expansion, commonly referred to as puffing, is actually observed to occur at some point in the transformation. The addition of certain metals, particularly iron and calcium or their compounds, is known to inhibit or eliminate this expansion. Although "puffing" has generally been associated with the sulfur content of the petroleum coke, very little information has actually been published concerning this phenomenon. Based largely upon analogies found in the puffing behavior of sulfur-containing petroleum cokes and of carbon-bromine lamellar residue compounds, H. C. Volk<sup>1</sup> advanced the theory that puffing resulted from the decomposition of carbon-sulfur lamellar residue compounds. The formation of a thermally stable carbon-sulfur-metal ternary lamellar compound was proposed as an explanation for the inhibition mechanism. However, the existence of these compounds has not been convincingly established and our results are certainly difficult to reconcile with lamellar compound formation.

EXPERIMENTAL

The carbon bodies were made from a standard mixture of calcined petroleum coke, particle sizes ranging from -35 mesh to -100 mesh, and a coal tar pitch binder by hot pressing in an electrically heated mold at 12,500 psig for thirty seconds at 100°C. The cylindrical plugs were baked to a temperature of 850°C.

The extent of irreversible expansion exhibited by the baked carbon bodies as a function of heat treatment was measured with a graphite dilatometer. The dilatometer holding the carbon plugs was heated in a graphite tube furnace to temperatures as high as 2900°C at a rate of 14°C/min. A nitrogen atmosphere was maintained throughout the heating period.

A 15,000 psi mercury porosimeter was used to obtain micropore volume distribution in the heated carbon plugs. The plugs were crushed to -35/48 mesh and pore volume determinations made on 0.400 g. samples of this material.

X-ray diffraction examinations were made with a recording diffractometer using monochromatic Cu  $k\alpha$  radiation at room temperature.

The sulfur in the carbon samples was determined by igniting the sample in an oxygen atmosphere at 1400°C. The SO<sub>2</sub> formed was titrated continuously by iodometry in the presence of starch indicator. Good agreement was found between this method and the method using the Parr-peroxide bomb combustion technique.

RESULTSCause of the Deformation

The petroleum cokes studied which were subject to deformation could be separated roughly into two broad groups according to their puffing characteristics. Typical dynamic elongation curves of the two groups are compared in Figure 1 and Figure 2. It can be seen that there exists a difference of 300°C between the two groups of carbons with respect to the temperature at which the deformation begins. The cokes which deform at the lower temperature do not respond well to puffing inhibitors and generally have a higher concentration of sulfur, oxygen and nitrogen.

The loss of the volatile constituents of a large number of carbons as a function of heat treatment was determined. In all cases oxygen and nitrogen were lost at temperatures below 1000°C. The sulfurous gases, however, were evolved over precisely the same temperature range as that at which the deformation occurred. The sulfur evolution from the samples was followed by heating the bodies at the same rate, 14°C/min., as was used in the dynamic puffing test to various temperatures before the desired analyses were made. The composition of the samples was compared and correlated with the dynamic puffing characteristics. An example of such a correlation is presented in Figure 3. The rate of sulfur evolution in the carbon samples in which the initial decomposition and corresponding deformation occurred at the lower temperature, 1400°C, was ten to twenty times greater than the rate observed in samples with the more thermally stable sulfur.

The escaping gas from several carbons was carefully trapped and analyzed. The gas was found to be essentially hydrogen sulfide. Unfortunately, all of the carbons studied with a high enough sulfur content to permit meaningful gas analysis puffed in the low temperature range.

If a sample is heated to the temperature at which the sulfur first begins to evolve and is held at that temperature until the desulfurization is essentially complete, deformation of the sample occurs only at this temperature, see Figure 4. There is little doubt that puffing results from internal pressures generated by the sudden expulsion of H<sub>2</sub>S.

By carefully measuring the crystallite dimensions during the course of the deformation by means of x-ray diffraction, it becomes apparent that the puffing is an inter-crystalline phenomenon. However, in one experiment in which a sample made from a coke having an unusually high sulfur content was pushed directly into a furnace at 1400°C, an anomalous x-ray pattern was obtained from the sample. The 00 $l$  diffraction peaks were split, one portion of the peak being located at the expected 2 $\theta$  angle and the other occurring at a slightly higher angle, see Figure 5. Upon further heat treatment a coalescence into a single peak occurs, the lower angle portion of the peak overtaking the other. One possible explanation is that the high internal pressure generated within the sample has actually forced part of the sample to a more graphitic state. It is certainly well known that externally applied pressure facilitates graphitization.<sup>2</sup>

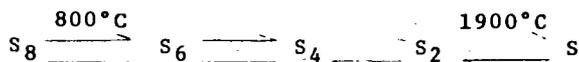
The pore structure of the samples during puffing was evaluated by means of mercury porosimetry. Typical pore size distribution curves are presented in Figure 6. Puffing is characterized by an increase in

pores having diameters in the 0.1-.015  $\mu$  range. The total deformation of the sample can be accounted for by the creation of this additional porosity resulting from the hot expanding gas channeling its way to the sample surface.

The magnitude of the deformation does not depend entirely upon the sulfur content of the coke. The microstructure of the coke is also important. As would be expected, hard carbons characterized by a high degree of cross-linking between crystallites are much more resistant to deformation than the more graphitic "softer" type carbons. For this reason there are several cokes which do not puff although they have a sulfur content comparable to that of a puffing softer type coke and the sulfur is evolved over the same temperature range at the same rate. This microstructural dependence was further illustrated by producing a softer type carbon from a feedstock which ordinarily forms a relatively hard carbon by making certain changes in processing and comparing the puffing characteristics of the two cokes. The sulfur content of the more graphitizable carbon exhibiting a linear CTE of  $5.0 \times 10^{-7}/^{\circ}\text{C}$  was exactly the same as the less graphitizable carbon having a CTE of  $23.0 \times 10^{-7}/^{\circ}\text{C}$ . The softer carbon, however, puffed while the other coke exhibited no measurable deformation.

#### Mechanism of Puffing Inhibition

As illustrated in Figure 7 for the case of iron oxide, certain materials when added to the carbon sample eliminate or at least diminish in magnitude the puffing effect. The temperature required to initiate the volatilization of sulfur is higher and the rate of the subsequent gaseous evolution is lower in the samples containing an inhibitor, see Figure 8. An analysis of the effluent gas reveals that the sulfur is principally in the form of elemental sulfur rather than  $\text{H}_2\text{S}$ . The composition of the sulfur vapor at these temperatures is governed by the following equilibria:



Even above  $1900^{\circ}\text{C}$  the sulfur vapor is 55% associated.<sup>3</sup> An increase in association of the sulfur atoms would, of course, result in a decrease in gas volume. By following the composition of the inhibitor as a function of temperature by means of x-ray diffraction, the mechanism of inhibition becomes apparent. This type of analysis for iron oxide is given in Figure 9. The inhibitor reacts with the sulfur to form a sulfide which subsequently decomposes at a higher temperature liberating sulfur in its elemental form and at a reduced rate. The effectiveness of the metal in preventing puffing is a function of the stability of its sulfide. Sodium, for example, forms a sulfide which is expelled rapidly at a relatively low temperature resulting in distortion of the sample, see Figure 10.

A secondary deformation of reduced magnitude was observed to occur at around  $2500^{\circ}\text{C}$  in the most graphitic or needle type carbons studied upon inhibition with iron oxide, see Figure 11. A gaseous evolution resulting from the decomposition of the iron sulfide is occurring at this temperature, however, the rate of volatilization at  $2500^{\circ}\text{C}$  is not substantially different from that at temperatures immediately below this delayed puffing range. This indicates that structural changes must be occurring in the carbon body which

effectively reduce its resistance to puffing. It is well known that the mechanical strength of graphite increases with temperature to about 2500°C and then decreases sharply with temperature above 2500°C.<sup>4</sup> A substantial amount of creep occurs in graphite at 2500°C and higher. This sudden decrease in strength of the body coupled with the internal pressure generated by the decomposition of the metal sulfide provides a logical explanation for the observed delayed puffing.

#### Lamellar Residue Compounds

Lamellar and lamellar residue compounds are known to have a pronounced effect on the resistivity of the carbon. Dilute residue compounds with a composition  $C_{100}X$  ( $X$  = intercalated species) are reported to decrease the resistivity of graphite to between 1/2 to 1/10 of its original value, both for n- and p-type compounds.<sup>1</sup> The resistivity of a sample heated to a temperature at which puffing is initiated should increase with time as the residue compound decomposes. We have not found this to be the case. In some carbons, in fact, the resistivity as illustrated in Figure 12 in which the weight percent sulfur loss and resistivity are plotted against holding time actually bears a direct relationship to sulfur evolution. In these materials a decrease in d-spacing and rapid crystallite growth accompanied the decrease in resistivity, see Figure 13. This is additional evidence that premature graphitization is induced by the high internal pressure of the sulfurous gases.

The presence of sulfur per se does not affect the d-spacing in carbon. Therefore, the proposed carbon sulfur lamellar residue compounds cannot be located between the layer planes since a difference in d-spacing would be observable due to their presence. However, residue compounds located at imperfections in the graphite structure would be unlikely to cause a change in the c axis of the graphite if the imperfections are randomly distributed. The diffraction pattern would either not be changed or else only a slight line broadening would occur due to the enlargement or creation of new random imperfections. The existence of the parent lamellar compounds would be expected to be detectable by means of x-ray diffraction except for the fact that the x-ray pattern of carbon heated only to the low temperatures, below 1200°C, at which they are thought to exist is quite diffuse.

Similarly, the resistivity of an inhibited sample is not adversely affected by the removal of the sulfur and inhibitor by heat treatment. Volk noted that the resistivity of the sample was apparently independent of the inhibitor concentration. For this reason, he postulated that the carbon-sulfur-iron compounds were ternary lamellar compounds in which iron functions as a spacer and is therefore not ionized. However, a lamellar compound such as this should be easily detectable by x-ray diffraction analysis. The x-ray spectra of an inhibited carbon is essentially the same before elimination of inhibitor by means of heat treatment alone or with the aid of a purifying gas as after removal. In addition, the diffraction pattern of an inhibited puffing carbon is not significantly different from that of a non-puffing carbon with the same metal concentration. The existence of a ternary lamellar compound is, therefore, certainly doubtful.

CONCLUSIONS

Puffing of carbon bodies results from internal pressure generated by the sudden formation of sulfurous gases, primarily hydrogen sulfide. This pressure is sufficient, in some cases, to cause premature graphitization. The increased volume of the body is in the form of small micropores 0.1 to .015  $\mu$  in diameter. Various metals act as inhibitors by reacting with sulfur to form sulfides which subsequently decompose at a temperature and with a rate which is dependent upon the stability of the sulfide. The magnitude of the deformation is also a function of the coke structure. The hard, cross-linked carbons are much more resistant to deformation than the softer, more graphitic carbons. No evidence was found for the existence of lamellar or lamellar residue compounds involving sulfur or the inhibitor.

REFERENCES

1. H. C. Volk, "Lamellar Compounds of Non-Graphitized Petroleum Coke", WADD Tech. Report 61-72, Vol. XXV, (August, 1963).
2. T. Noda, "Graphitization of Carbon under High Pressure", Paper presented at Eight Biennial Conference on Carbon, June 19-23, 1967, Buffalo, N. Y.
3. R. C. Brasted (ed.), Comprehensive Inorganic Chemistry, Vol. 8, D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p-29.
4. S. Mrozowski, "Mechanical Strength, Thermal Expansion and Structure of Cokes and Carbon", Proceedings of the First and Second Conferences on Carbon, Univ. of Buffalo (1956) p-31.

Figure 1.

**DYNAMIC ELONGATION OF A  
PETROLEUM COKE (RATE 14°C/min)**

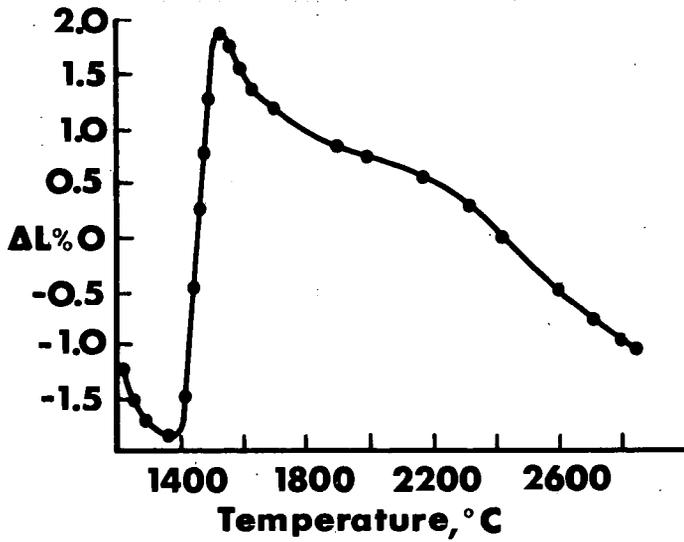


Figure 2.

**DYNAMIC ELONGATION OF A  
PETROLEUM COKE (RATE 14°C/min)**

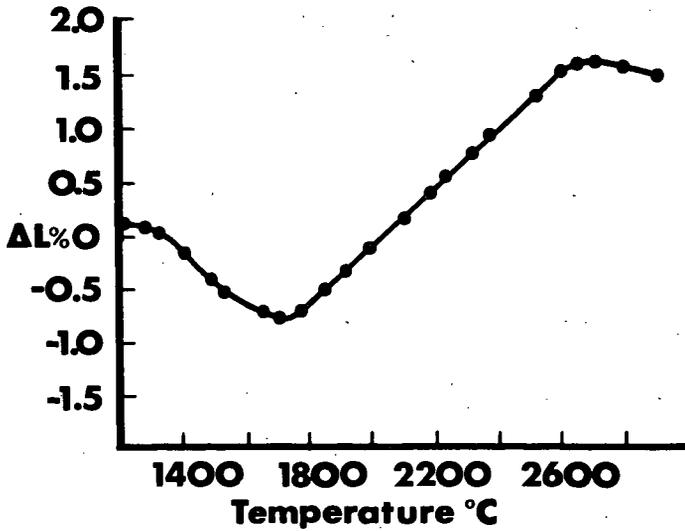


Figure 3.

**EVOLUTION OF SULFUR AND DYNAMIC  
ELONGATION OF PETROLEUM  
COKE VS. TEMPERATURE**

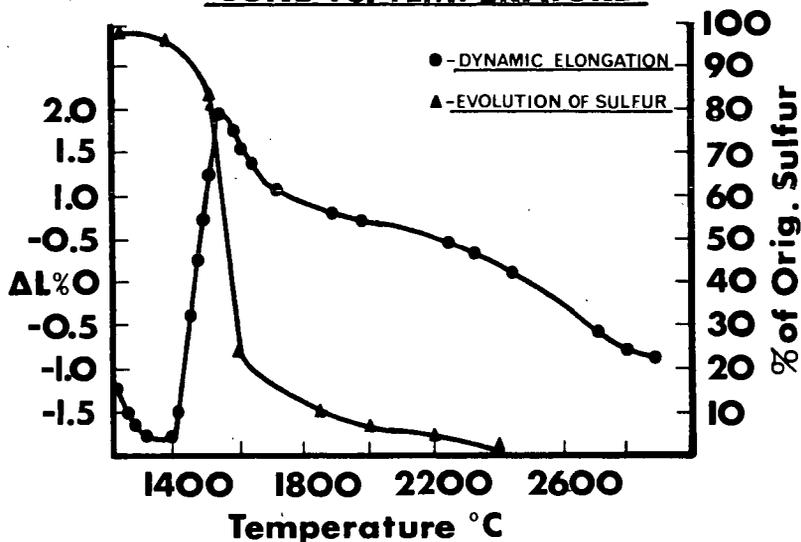


Figure 4.

**DYNAMIC ELONGATION OF PETROLEUM  
COKE AT CONSTANT TEMP.**

(Held at 1400°C 3.5 hrs, then to 2900°C @ 14%/m)

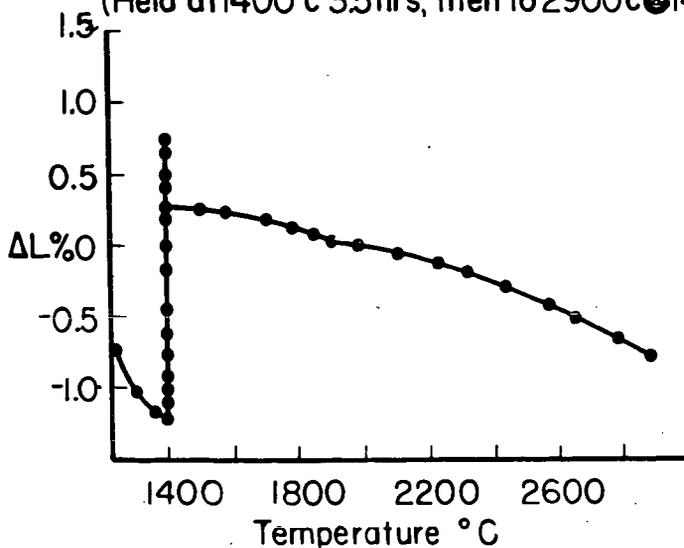


Figure 5. .002 X-RAY DIFFRACTION PEAK

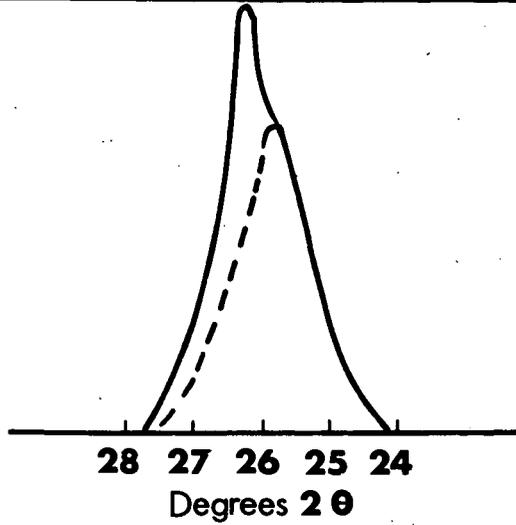


Figure 6. PORE SIZE DISTRIBUTION IN PETROLEUM COKE HEATED TO VARIOUS TEMPERATURE

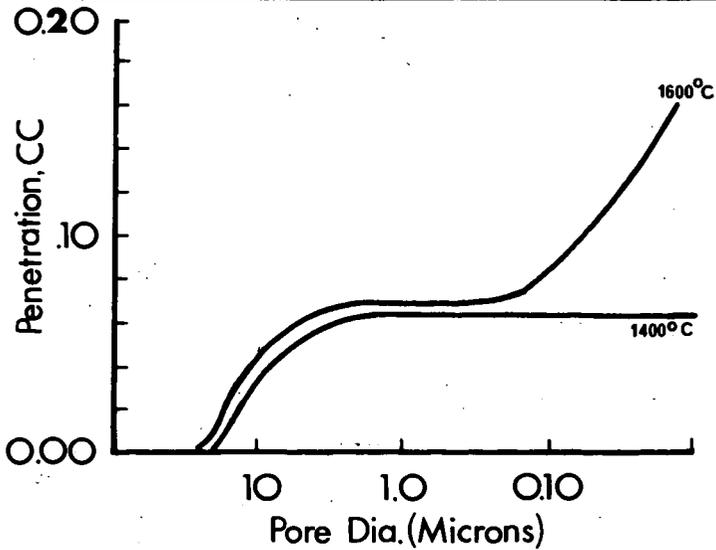


Figure 7. DYNAMIC ELONGATION OF A PETROLEUM COKE CONTAINING  $\text{Fe}_2\text{O}_3$

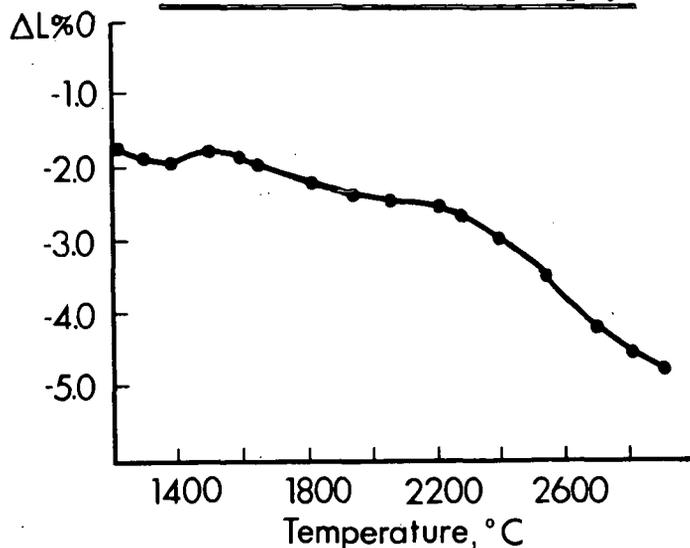


Figure 8. EFFECT OF ADDED  $\text{Fe}_2\text{O}_3$  ON THE THERMAL STABILITY OF SULFUR IN PETROLEUM COKE

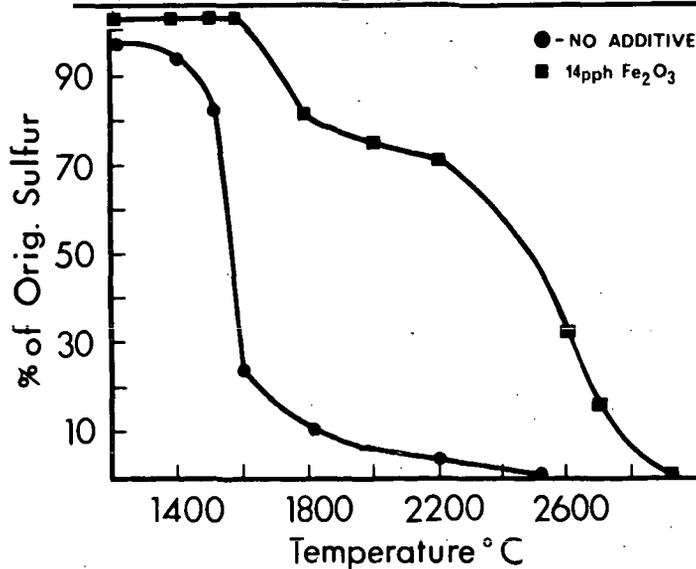


Figure 9.

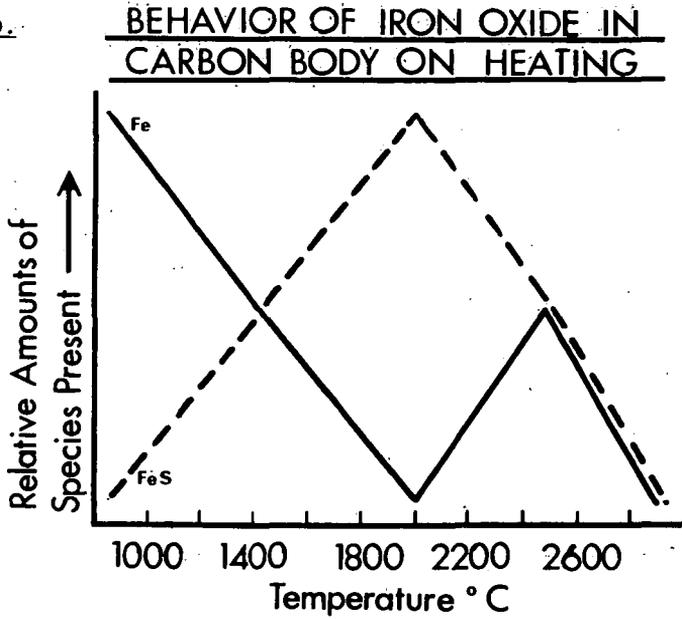


Figure 10. DYNAMIC ELONGATION OF A PETROLEUM  
COKE CONTAINING  $\text{Na}_2\text{CO}_3$

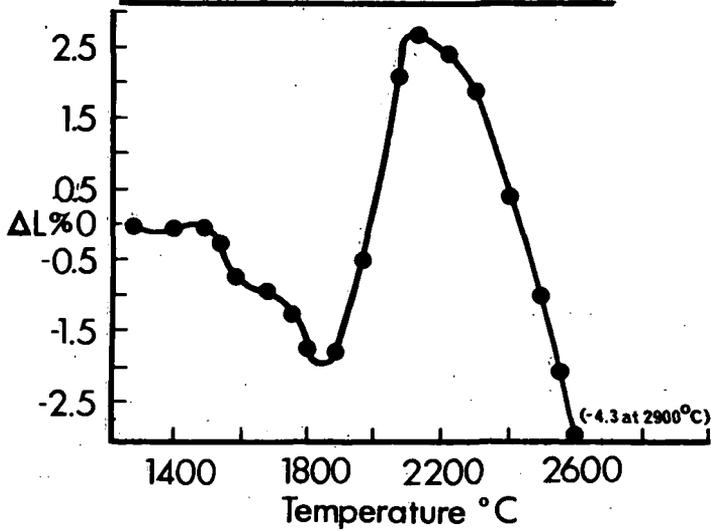


Figure 11. DYNAMIC ELONGATION OF A PETROLEUM COKE CONTAINING  $Fe_2O_3$

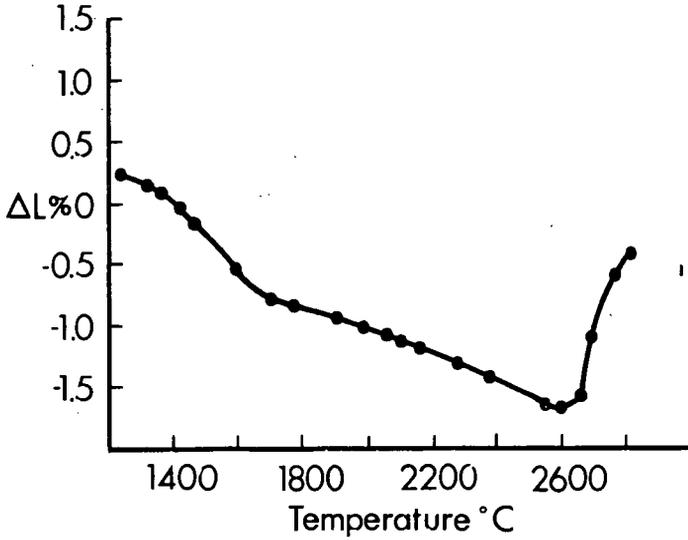


Figure 12. EFFECTS OF HEATING A PETROLEUM COKE AT 1400°C

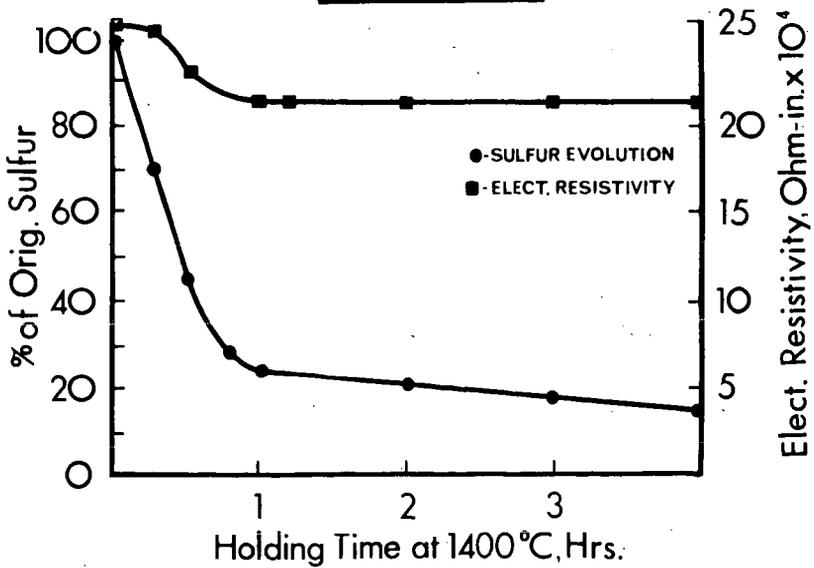


Figure 13.

### D-SPACING AND CRYSTALLITE GROWTH IN COKE HEATED AT 1400°C

