

Title: MODIFICATION OF PHYSICO-CHEMICAL PROPERTIES OF CARBON PRODUCTS
IN THE PROCESS OF ELECTRICAL GRAPHITIZATION, by B. V. Mintz

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MODIFICATION OF PHYSICO-CHEMICAL PROPERTIES OF
CARBON PRODUCTS IN THE PROCESS OF ELECTRICAL
GRAPHITIZATION.

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As shown by Depre (1), any carbonaceous material is transformed into graphite on being exposed to a high temperature for a long time. However, as has been shown by Ruff (2), a high temperature alone is not sufficient for the graphitization of carbon black (soot): the presence of certain admixtures such as boron, aluminum, and elemental silicon is also necessary.

M. Barthelot (3) pointed out that there are three different types of graphite: natural graphite, the graphite of cast iron, and electrical graphite. LeChatelier and Vologdin (4) showed that these graphites differ from each other by the presence of a different amount of admixtures.

According to Moissan (5), the oxidation of artificial graphite produced in an electric furnace is proportional to the temperature to which the graphite had been heated. The size of graphite flakes obtained by separation from metal solutions diminishes with the increased melting temperature of the metals. Graphites produced in an electric furnace do not swell if the temperature has been merely raised in processing them; while those obtained from molten metal at a high temperature swell easily.

Acheson (6) states that when carbon contains a considerable quantity of inorganic matter, or has been modified by adding to it 2-5% of metal

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oxides, the yield of graphite is considerably increased, and its quality is improved: the graphite exhibits an increased greasiness, lower hardness, and stronger luster. However, Arsem (13) has shown that coke and anthracite are graphitized more readily when their ash content has been reduced by chemical means.

Arndt (7) and Debye (8) demonstrated that in the course of the heating of carbon, graphite crystals are increased in size by a factor of approximately 1000, and that the growth of graphite crystals depends on the properties of the starting material. The increase of electrical conductivity begins together with the evolution of gas, and the point of the greatest increase in conductivity coincides with the maximum evolution of gas. Petroleum and foundry coke are easily graphitized; gas coke with greater difficulty; retort carbon is easily graphitized and swells considerably during the process of graphitization. The anthracite which is geologically oldest, graphitizes best. The process of graphitization has been likened by Rishkevich (9) and Arndt to that of the recrystallization of metals.

As shown in the work by Debye and Scherrer (8), Kohlschuetter (10), and others, amorphous carbon and graphite do not essentially differ from each other: the only difference consists in the different size of crystals which are identical as far as their lattice is concerned. The so-called amorphous carbon is composed of graphite crystals which are so fine that they cannot be obtained from ordinary graphite by using any mechanical method of treatment.

However, the finely crystallized graphites (amorphous carbons) differ from the coarsely crystallized modifications as far as chemical behavior is concerned. For that reason, Ruff suggested that the name amorphous carbons be retained for the first (11).

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Balfour and Riley (12) established that many organic substances which are usually referred to as amorphous are actually conglomerates having a crystalline lattice that is similar to the space lattice of graphite. These substances contain firmly bound hydrogen between the carbon hexagons. The hydrocarbons in question exhibit a considerable stability and begin to decompose only at 600-700°. An additional proof for the existence of a hydrocarbon having this degree of stability is in the authors' opinion the fact that anthracite rather than graphite is the end product of the process of coal formation.

The brief historical account given above illustrates the main trends in the field which is of interest to us. The question of the effect of inorganic admixtures on the process of graphitization can by no means be regarded as solved. This fact induced our present investigation.

1. Physico-Chemical Properties of Carbon Products Graphitized at the Temperatures 1800, 2000, 2200, and 2500°.

We submitted to investigation products prepared according to 8 different prescriptions. The crude material for the first product consisted of petroleum coke, that for the second of mixtures of petroleum coke with anthracite. Then came two grades of anthracite, foundry coke, and a mixture of foundry coke with petroleum coke. The mixtures were prepared on the principle of gradually raising the ash content of the mixture.

All materials had the same particle size composition and the size of the particles was in all cases lower than 0.15 mm. The physico-chemical properties of these materials are listed in Table 1. The temperature of the preliminary heating was the same in all cases and amounted to 1300°. As a binder 25% of soft pitch with a softening temperature of 41-47° were used. Mixtures were made up using equal quantities of the ingredients in the dry

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part, i.e. 50% of anthracite were combined with 50% of petroleum coke, and so forth. After the solid ingredients had been mixed thoroughly with each other and with the molten pitch, the mixture was pressed in an enclosed mold which had been preheated to 60-65°. A momentary rather than sustained pressure of 400 kg/cm² was applied. For each temperature studied, 3 samples having the dimensions 40x40x40 mm were prepared. After being pressed the samples were heat-treated in ordinary Pitthammer ring furnaces and submitted to examination.

Graphitization of the heat-treated material was carried out in special carbon equipment which was inserted into the production furnace and removed from it as soon as the predetermined temperature had been reached. The temperature was measured through a carbon tube by means of a platinum-platinum, rhodium thermocouple or an optical pyrometer. Although we attempted to keep the period of heating at a definite temperature and the conditions under which cooling took place constant, it was nevertheless necessary for technical reasons to carry out heating at higher temperature, for a longer time.

As can be seen from Table 2, a considerable reduction of mechanical strength occurs in graphitization below the temperature of 1800°. This reduction of strength is greatest in the samples made from anthracite having a low ash content. After this, in the order of mechanical strength reduction, follow anthracite — petroleum coke mixtures, anthracite with a high ash content, foundry coke, foundry coke — petroleum coke mixtures, and finally petroleum coke. The factor by which the mechanical strength is reduced comprises 3.0 in the case of anthracite having a low ash content and amounts to 1.5 in the case of petroleum coke. The absolute figures measuring mechanical strength differ to a considerable extent. It is note-

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worthy that even when graphitization is carried out below 1800°, there is a fairly active recrystallization, as can be seen from the resistivity of samples and powders. Graphitization proceeds most actively in materials which have the lowest natural ash content. When graphitization is carried out up to the temperature of 2000° (cf. Table 3), there is further reduction of mechanical strength in all samples with the exception of that made from foundry coke. It is true that this reduction is not as great as in the former series of experiments. The strongest reduction is observed in the case of anthracite having a high ash content (an effect which is 1.4 times greater than that in the graphitization at 1800°), while the strength of products made from foundry coke is even increased by a factor of 1.1.

The mechanical strength of samples made from petroleum coke remains unchanged. There is further reduction of the specific electrical resistance and of the total ash content. In graphitization up to the temperature of 2200°, an interesting phenomenon is observed: the mechanical strength of products increases (cf. Table 4). As distinguished from all other samples, the one made from foundry coke shows a slight reduction of strength here. This may be due to the fact that in the case of foundry coke the change of curvature in the curve expressing mechanical strength begins somewhat earlier.

In graphitization up to 2200° intensive recrystallization takes place in products prepared from foundry coke, anthracites, and mixtures. Furthermore, there is additional reduction of the volume weight and of the ash content, as can be seen from Table 4.

In the graphitization temperature range 2200-2500° (cf. Tables 4 and 5) there is a second abrupt drop of the mechanical strength occurring after the first reduction which takes place below 1800°. The volume weight and the ash content of the material drop sharply. Its specific electrical resistance is also reduced, as can be seen especially clearly from the specific electrical resistance of powders.

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During the whole graphitization period starting with the temperature of "burning" [preliminary heat treatment] which was 1300° and ending with 2500°, the mechanical strength of the product prepared from petroleum coke dropped by a factor of 1.7, that of the product from mixtures of anthracite and petroleum coke on the average by a factor of 3.7, that of the product from mixtures of foundry coke and petroleum coke by a factor of 4.8, in the product resulting from anthracite with a high ash content by a factor of 7.6, and in the product from foundry coke by a factor of 3.8 (cf. Figure 1).

Changes of the specific electrical resistance in the process of graphitization can be best determined on powders, because the data obtained in this manner are the most reliable. The resistance of samples usually depends on a number of fortuitous circumstances such as the presence of cracks, the degree of burning of the surface, etc., while in powders interference due to these causes naturally does not arise.

It is evident from what has been said above that at 1800° the specific electrical resistance drops sharply. Further on, at 2000°, it increases to some extent, but not on the samples made from petroleum coke. This is probably due to the formation of crystalline metal carbides as distinguished from amorphous metal carbides. The latter may form even at temperatures lower than 1400°. When the temperature is raised to 2200°, the resistance of the material begins to drop again and continues to drop until 2500°.

The specific weight of the material does not increase during the whole process of graphitization. After the material has been heated to a certain temperature, the specific weight has a tendency to drop. As can be seen from Tables 2, 3, 4, and 5, the highest specific weight is shown by samples which have been graphitized at 2200°. The ash content drops to an insignificant extent up to 2000°. The reduction of the ash content becomes strongly

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pronounced at 2200° and higher temperatures (cf. Figure 2). If a comparison of the physico-chemical characteristics is carried out, one may arrive at the following conclusions.

A certain increase in the specific electrical resistance of the powdered materials takes place at 2000°, when apparently intensive dissociation and sublimation of carbides have not yet occurred. The latter can be seen from the ash content of the material. This indicates that there is a connection between the specific electrical resistance and the quantity of ash which is present in the material.

The increase of mechanical strength in the range 2000-2200° is accompanied by an increase of the specific weight and followed by a reduction of the latter on subsequent heating. This leads to the conclusion that the mechanical strength is increased due to the formation in the material of a carbide lattice. Then the mechanical strength of the product depends only on the strength of the carbide lattice independently of the absolute quantity of carbide contained in the product. The carbide forming this lattice represents a special modification of the ordinary carbide.

Thus at a definite temperature in the neighborhood of 2200° in the gas phase and at appreciable vapor pressures carbides may form which contribute to an increase of the mechanical strength and of the specific weight of the material.

2. Effect of Added Substances on the Physico-Chemical Properties of Products Graphitized at the Temperatures 1800°, 2200°, and 2500°.

We have shown above that the ash contained in the material has a considerable influence on the physical properties of carbon products, particularly in the 2000-2200° temperature range of graphitization. For that reason it

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is of importance to establish in just what manner individual oxides which compose the ash of carbonaceous materials affect the most important properties of the products, In order to investigate the influence of ash components, it was necessary to select a carbonaceous material having a low ash content and showing only a small reduction of mechanical strength in graphitization. This made it possible to eliminate extraneous factors such as the effects of settling, swelling, formation of layers, etc., which might complicate the matter of drawing a correct conclusion from the experimental results. The most suitable material from this point of view seemed to be petroleum coke. In order to permit a comparison of the new method with the old, as far as the properties of the resulting product are concerned, the process of preparation and preliminary heat treatment of the samples was left unchanged, with the sole exception that 10% of ferric oxide, magnesium oxide, calcium oxide, or silicon^{di} oxide were added to the starting material.

It can be seen from Table 6 that with the exception of products prepared with the addition of ferric oxide, all samples showed an increase in electrical resistance after heating. Upon graphitization at 1800° there was no alteration of physical properties, except that the specific resistance of products to which ferric oxide had been added dropped sharply.

As can be seen from Table 7, heating at a temperature which was higher by 400° resulted in a considerable decrease of the mechanical strength of the products. As compared with products processed at 1800°, the results on samples made from a mixture of petroleum coke and ferric oxide showed a reduction of mechanical strength by a factor of 4.7, on samples with calcium oxide by a factor of 3.9, with magnesium oxide by a factor of 3.5, and with silicon dioxide by a factor of 3.7.

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The electrical conductivity of all samples increased 2.6 times on the average. The volume weight dropped considerably and the ash distilled off [sublimated] almost completely.

If these results are compared with those obtained earlier (experiment No. 1), one notices that the physical properties in this instance differ considerably from those observed earlier.

Notwithstanding the facts the samples were graphitized in the furnace simultaneously in a limited space, and that the products listed in Tables 7 and 4 respectively were intentionally distributed in different places of this space so as to achieve the same temperature for all samples, the physico-chemical properties of the respective products were entirely different.

Thus, the mechanical strength of samples made from petroleum coke without any addition and heated at 2200° was 228 kg/cm², while the average strength of samples made from petroleum coke with the addition of 10% oxide and heated at the same temperature amounts to only 80 kg/cm², i.e. is lower by a factor of 2.8. It is characteristic that in the second instance there is a greater reduction of the volume weight. If the volume weight of samples from petroleum coke prepared at 2200° and lacking metal oxide is 1.4, the volume weight of samples prepared from the same material and under the same conditions, but with the addition of metal oxide, is on the average only 1.36.

The specific electrical resistance of the samples listed in Table 7 is much higher than that of the samples listed in Table 4. When the temperature was raised still higher (to 2500°), there were further lowering of the mechanical strength of the material, reduction of the ash content, and increase of the electrical conductivity. Notwithstanding the almost complete absence of ash in the material (cf. Table 8), the electrical con-

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ductivity of the samples to which oxides had been added does not in a single case reach the comparatively high value obtained in the case of pure petroleum coke. The mechanical strength is on the average 3.2 times lower.

It can be seen from the above that with temperatures higher than 1800° the mechanical strength of products from pure petroleum coke is higher than that of products obtained after admixing oxide to the same crude material. The same situation obtains with regard to the electrical conductivity.

In order to determine the effect of the quantity of oxide which had been added to the crude material on the mechanical strength of the graphitized products, we have carried out the following investigation. To petroleum coke which had a slightly higher ash content (0.80%) than before, metal oxides were added alternately in sufficient quantity to bring the concentrations up to 1, 2, 5, and 10% respectively.

The technological process of preparing the samples remained the same as before. The temperature of graphitization was 2500°. It turned out that the physical properties of the product made from petroleum coke changed considerably even if only 5% of oxide were added.

The sharpest reduction of mechanical strength (by a factor of 1.8) occurs upon addition of ferric oxide. The reduction is somewhat less pronounced in the case of magnesium oxide (by a factor of 1.3), and is still less with aluminum oxide (by a factor of 1.2). Taking the average reduction of mechanical strength resulting from the addition of 5% of these metal oxides, we get a reduction by a factor of 2.2, and with 10% of metal oxide added, by a factor of 4.6. On the other hand, the mechanical strength of the product from pure petroleum coke is reduced by a factor of only 1.7 upon graphitization at 2500°.

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Even when only 1% of the oxides in question is added, there is some reduction of the mechanical strength of the product. When the content of ferric oxide is increased to 2%, there is some increase in mechanical strength, which is apparently due to an improvement of the mechanical properties of the initial material. As can be seen from Table 9, the specific electrical resistance increases in almost all of the samples roughly in proportion to the quantity of oxide which had been added. This relationship holds independently of the nature of the added oxide and its absolute content in the material. The same relationship is observed as far as the resistivity of the powdered samples is concerned, but some deviations occur there.

The observed increase of specific weight as related to the quantity of oxide added in experiments with ferric oxide and aluminum oxide may be due to the effect of residual ash, although this is not quite probable. As can be seen from Table 10, the specific electrical resistance of powders generally increases upon addition of ferric oxide, aluminum oxide, or magnesium oxide.

Thus a higher ash content than 2% in petroleum coke brings about a sharp reduction in the mechanical strength of the products together with an increase of the specific electrical resistance, if the temperature of graphitization is 2200° or 2500°. Consequently one must prevent contamination of petroleum coke with ash in the process of manufacture of graphitized products.

We have shown that oxides of iron, aluminum, magnesium, calcium, and silicon, even though a small quantity of them may have been added, sharply reduce the mechanical strength of carbon products when the temperature of graphitization is higher than 2500° or in the neighborhood of 2500°.

It appears that the beginning of the sharp drop of mechanical strength depends on the location of the oxides in the material. If they are located

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inside the crystals or are combined chemically with the carbon of the material, then, as shown in the first section of this paper, the beginning of the secondary drop in mechanical strength (taking place above 1300°) will occur at a higher temperature than that which corresponds to the reduction of mechanical strength in the case when the oxides are situated in the pores of the material. The explanation for this is that in the second case the ash may readily sublime [or distill] through the channels of the pores, while in the first case it is prevented from doing so by the thickness of the material.

3. Graphitization of Products in the Vapors of Some Substances.

Under practical conditions graphitization of pressed products is carried out by placing them into a furnace of the Acheson type and interspersing between them finely grained carbonaceous material. This procedure insures a better distribution of the current throughout the cross-section of the furnace and prevents arc discharges which may result in the sublimation of carbon and defective production. Generally very little attention is paid to the presence in the interspersed carbonaceous material of any particular ash constituent.

However, one must assume on the basis of the discussed results that the ash content of the interspersed material may have an effect of the physical properties of the manufactured product, particularly when there is close contact at the temperatures of graphitization. In order to clarify the effect of the composition of the material in the intermediate layers on the physical properties of the product, 9 carbon plates having the dimensions 50 X 180 X 1000 mm were placed into a graphitization furnace used for regular production. The physical properties of the initial material and of the resulting products are listed in Table 11. Five plates were

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graphitized under ordinary conditions with anthracite having a low ash content being used as the interspersed medium, while 4 were graphitized in silicon dioxide vapor. Two packages of plates were prepared for this purpose.

The first package consisted of five plates placed directly on each other without any interspersed material between them. The other package consisting of 4 plates was prepared in a somewhat more complicated manner. Between the plates were placed carbon frames made of the same material and sawn out in such a manner that vacant spaces having the volume of $140 \times 50 \times 900 \text{ mm}^3$ were formed between the plates. The vacant spaces formed by the frames were filled completely with quartz sand. Both sets of plates were graphitized under the same electrothermal conditions. The maximum temperature of graphitization was 2500° and the furnace was heated by the current for 34 hours.

As shown in Table 11, the plates graphitized in silicon dioxide vapors have a lowered mechanical strength. On the average the plates graphitized in silicon dioxide vapor have a strength which is 1.7 times lower than that of products graphitized under ordinary conditions. It is

It is noteworthy that the plates graphitized in silicon dioxide vapor had over their whole outer surface a layer of exceptionally soft, easily crumbling graphite penetrating into the depth to the extent of approximately 5-8 mm. The specific electrical resistance of these plates is cited in Table 11, where the lower values represent the resistance of the whole plate, while the higher values represent the resistance of the plate with the layer of soft graphite removed. Naturally, the mechanical strength of the samples was determined with the soft layer removed. The specific electrical resistance of plates graphitized in silicon vapor was found to

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be 1.3 times lower than that of plates graphitized under ordinary conditions (this result applies to plates from which the soft outer layer had been removed). Thus the presence of silicon dioxide in the interspersed material must weaken the products from the point of view of mechanical strength when the graphitization temperature is 2500°, and must also lower their specific electrical resistance. It may occur that the quantity of silicon oxide contained in the interspersed carbonaceous material is just right for the formation of silicon carbide. In this case the situation may change, because sublimation of silicon dioxide below 2100-2200° can hardly be assumed, while at a higher temperature silicon carbide may deposit from the vapor in the pores of the product, or formation of new carbide may take place as a result of the reaction of the carbon of the product with silicon vapor formed by the decomposition of silicon carbide. This may even result in an increased strength of the product. In order to check this possibility, we took 14 similar plates having the dimensions 50 X 180 X 1000 mm and combined them into three packages. The first, or control package consisted of 5 plates and was graphitized under ordinary conditions with the use of anthracite having a low ash content as the interspersion medium. The other two packages were prepared similarly to the one used in the first experiment, except that the frames were filled with a carborundum charge in one case and with siloxicon in the second case. The carborundum charge consisted of 75% SiO₂ and 25% by weight of heat-treated anthracite. An analysis of the carborundum charge showed that the latter consisted of 2.6% C, 70.1% SiO₂, 2.5% Fe₂O₃, and 1.0% Al₂O₃. An analysis of the siloxicon yielded the following values: 12.2% C, 81.3% SiO₂, 1.6% of Fe₂O₃, and 1.4% of Al₂O₃.

Just as in the first experiment, the three packages were placed into the regular production furnace and were exposed to an identical electrothermic

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treatment with a maximum temperature of ~2200°. The results of the latter experiment, which are listed in Table 12, show that on the average all plates graphitized in silicon carbide vapor have a mechanical strength 1.6 times higher than that of the control samples. Somewhat unexpected was the reduction of the specific electrical resistance of the material graphitized under the same conditions, which corresponded to a factor of 1.2 on all plates and to 1.4 on samples sawn out of them.

There is also on the average an increase in the specific weight of these products from 2.13 to 2.22, i.e. by a factor of 1.04, which confirms the correctness of our measurements of the specific electrical resistance of the plates. These experiments have also fully confirmed our prior results cited in Table 4, because they show an increase in mechanical strength at the graphitization temperature of 2200°.

We also conducted a third experiment in order to find out how the physical properties of the products change when the temperature of graphitization is raised to 2500°. As could be expected on the basis of previous experiments (cf. sections 1 and 2), the mechanical strength of plates graphitized in the silicon carbide vapor emitted by the carborundum charge dropped sharply. In order to keep this paper as brief as possible, we are only giving a selection of the data of the third experiment in Table 13. It can be seen from Table 13 that the mechanical strength of plates graphitized at 2500° in the vapor emitted by the carborundum charge has dropped on the average from 164.0 kg/cm² to 97.0 kg/cm² as compared with plates graphitized under the same conditions at 2200° (i.e., by a factor of 1.7) and has been reduced in comparison with the product of graphitization under ordinary conditions by a factor of 1.2 (cf. Table 13).

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The investigation has shown a considerable effect of the ash and of the crude material on the physico-chemical properties of the products of graphitization. Metal oxides and silicon dioxide sharply lower the mechanical strength of graphitized products, particularly at the moment of decomposition and sublimation of carbides above the temperature of 2200°. At lower temperatures the presence of oxides may even bring about an increased mechanical strength.

Furthermore the results of our work have shown that considerable reduction of mechanical strength is brought about already at 1800° in all products submitted to investigation. This is particularly pronounced in the case of products prepared from a mixture of anthracite and an equal quantity of petroleum coke. While in the range 1400-1800° the mechanical strength of samples from petroleum coke dropped 1.5 times, it was reduced on the average 2.9 times in the samples Nos. 2, 3, 4, 5, and 7. The reduction in mechanical strength at 1800° cannot be ascribed exclusively to the presence of ash, because some combustion of the material with formation of carbon monoxide cannot have such a strong effect on the mechanical strength. The phenomenon occurring here must also be due to changes which the material undergoes in the process of graphitization. As our investigation has shown (and this is an observation which is confirmed by practical experience), the principal varieties of anthracite increase considerably in volume during the process of graphitization. This is probably due to their structure as well as to the presence of ash (see Table 14).

It can be seen from Table 14 that on the average 21% of the anthracite grains increase in size by a factor greater than 2 and 70% by a factor somewhat smaller than 2.

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It is quite natural that under these conditions a considerable reduction in the mechanical strength of the material takes place, and that consequently the product has a lowered strength. As distinguished from anthracites, cokes usually do not increase in volume during graphitization; therefore the reduction of mechanical strength in samples made of petroleum or foundry coke and heated at 1800° is not so great as in the case of anthracite, and is apparently due only to crystal growth occurring in the process of graphitization.

It is noteworthy that when the samples are processed at 1800° under conditions of slow heating, crusts of carbidic nature form on the surface, as can be seen from the fact that the resistivity of the material is increased (cf. Table 15). The products are then of very good quality and have a smooth surface which resembles that of metals.

At temperatures around 2200° decomposition of the carbides on the surface begins and the crust is converted into very soft graphite. This is what is usually observed in production: The surface of the product⁺ very often is of better quality and exhibits a higher^{degree} of graphitisation than the total product.

In view of the increase of mechanical strength in the vicinity of 2200° and the following sharp drop, it is important to know how near to this temperature the materials under investigation have been heated. While the temperatures to which samples a, b, and c in Table 16 had been exposed did not differ by more than $\pm 30^\circ$, the mechanical strength of the resulting products showed considerable differences.

As far as the mechanism of the phenomenon leading to increased mechanical strength in graphitization within the range 2000-2200° is concerned, it can be explained only by formation of a carbide lattice in the material.

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We will show this in greater detail in a subsequent paper. Formation of the carbide lattice evidently takes place in the pores of the material, because otherwise lowering of the electrical conductivity of the products would occur. The formation of carbides is indicated by the facts that the maximum strength of the products corresponds to the maximum specific weight of the material, and that reduction of the mechanical strength follows a drop in the specific weight.

Our investigation has established the following relationships:

1. In the process of graphitization the modification of physical properties of carbon products depends in a complex manner on the temperature.
2. Up to the temperature of 2000° the mechanical strength and the specific electrical resistance of the material drop sharply, while the ash content is reduced somewhat and the specific weight is raised. The greatest drop of mechanical strength occurs in the range 1400-1800°, and there is some increase in the specific resistance of powder made from products which had been processed in the range 1800-2000°.
3. In the temperature range 2000-2200° considerable increases of the mechanical strength, specific weight, and electrical conductivity take place. There is also a sharp reduction in the ash content. The increase of the mechanical strength in the range 2000-2200° may be ascribed to the formation of a carbide lattice within the material.
4. Upon further heating of the material to 2500°, the second sharp drop of the mechanical strength above 1400° takes place. There are also further reductions in the resistivity and the ash content accompanied by some lowering of the specific weight due to decomposition and sublimation of the carbide lattice [carbide skeleton].

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5. It was found that already at 1800° products made from pure anthracite as well as from a mixture of anthracite and an equal quantity of petroleum coke become unsuitable for subsequent use because of their low mechanical strength. For that reason anthracite can be used as a crude material for the production of electrodes only if it has been previously de-ashed and heat-treated at 1700-1800°.

6. The least reduction of mechanical strength is observed in products prepared from petroleum coke by heating the latter through temperatures in the whole range of 1400-2500°. The greatest loss of strength occurs in products prepared from anthracite having a high ash content.

7. Among all the materials investigated, the most suitable for graphitization is petroleum coke. After this comes foundry coke followed by anthracites.

8. One should not add any oxides to material destined for graphitization at a temperature higher than 2200-2300°, because oxides strongly reduce the mechanical strength of the product as well as its electrical conductivity.

9. One must beware of graphitizing carbon products under such conditions that they are exposed to silicon dioxide vapor, because a reduction of mechanical strength results.

10. In graphitization at a temperature which does not exceed 2200°, one must take precautions to insure that a uniform temperature is applied to all individual objects being graphitized with deviations that are no greater than $\pm 20-30^\circ$.

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[2 sheets of figures and 16 tables follow].

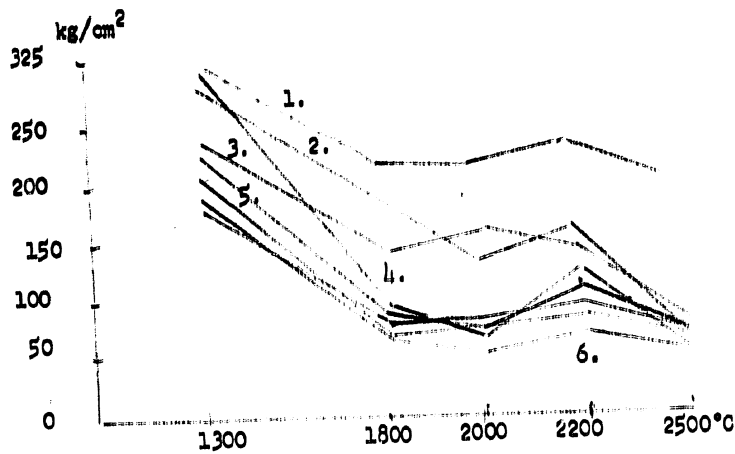


Figure 1. Change in the Compression Strength of Pressed Carbon Products as Affected by the Temperature of Graphitization

1. Petroleum coke.
2. Foundry coke + petroleum coke.
3. Foundry coke.
4. Anthracite having a high ash content.
5. Anthracite having a low ash content.
6. Petroleum coke + anthracites.

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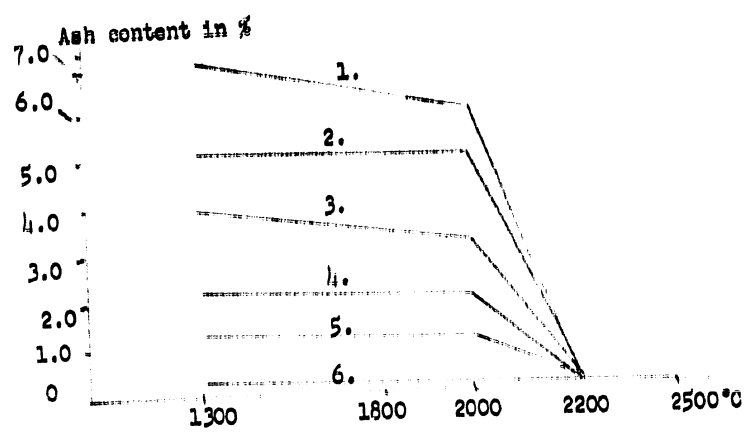


Figure 2. Reduction of the Ash Content of Pressed Carbon Products as Influenced by the Temperature of Graphitization . 1 - foundry coke; 2- anthracite with a high ash content; 3 - foundry coke + petroleum coke; 4- anthracite with a low ash content ; 5 - anthracite + petroleum coke; 6 - petroleum coke

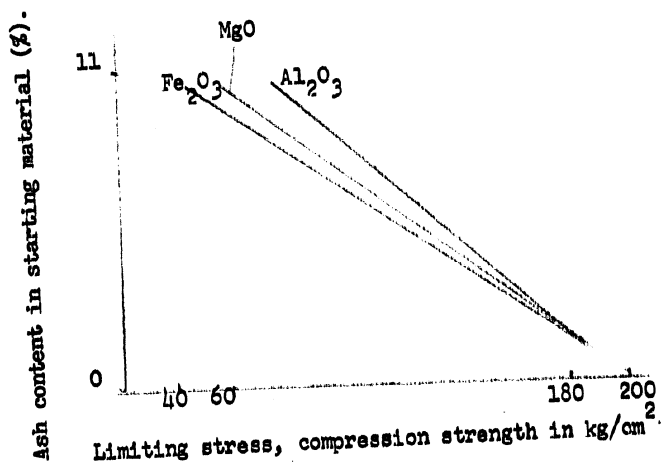


Figure 3. Effect of Ash Constituents on the Mechanical Strength of Graphitized Products.

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Table No. 1. Properties of Crude Materials.

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No.	Kind of Material.	Ash content in %	Composition of ash in %				Content of volatile substances in %	Specific weight	Specific resistance of powder according to Arndt.
			SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO			
1.	Petroleum coke	0.36	0.17	0.14	0.02	0.02	0.28	1.86	300
2.	Anthracite with low ash content	2.48	0.55	1.35	0.33	0.14	0.31	1.78	5700
3.	Anthracite with high ash content	5.34	0.45	4.56	0.30	0.03	0.12	1.80	—
4.	Foundry coke	8.13	2.80	1.75	3.02	0.50	1.38	—	1100

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Table 2. Results of Graphitization at 1800°.

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No.	Kind of material.	Properties of starting material after preliminary heat treatment of sample				Properties of graphitized samples						
		Ash in %	Limiting stress* strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴ of powder of samples*	Ash in %	Specific weight	Volume weight	
1.	Petroleum coke	0.35	315.0	75/80	1.96	1.14	215.0	17/21	35.0	0.53	2.0	1.44
2.	50% of anthracite A + 50% of petroleum coke	1.32	230.0	67/78	1.85	1.36	85.0	20/25	—	1.24	—	1.34
3.	50% of anthracite B + 50% of petroleum coke	1.52	190.0	71/80	1.86	1.37	80.0	21/26	—	1.36	1.96	1.36
4.	50% of anthracite C + 50% of petroleum coke	1.96	196.0	73/82	1.89	1.39	66.0	28/34	—	1.36	2.04	1.38
5.	Anthracite with low ash content	2.39	222.0	78/82	1.83	1.36	70.0	29/31	52.0	2.17	2.01	1.36
6.	50% of foundry coke + 50% of petroleum coke	4.05	290.0	71/83	2.03	1.39	175.0	26/27	48.0	3.95	2.14	1.37
7.	Anthracite with high ash content	5.66	322.0	64/81	1.84	1.43	91.0	30/35	61.0	5.65	—	1.43
8.	Foundry coke	7.20	243.0	69/71	2.05	1.36	140.0	32/37	63.0	6.82	2.13	1.35

* The specific electrical resistance was measured in two different directions perpendicular to each other.

Table 3. Results of Graphitization at 2000°.

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No.	Kind of material	Properties of starting material after preliminary heat treatment of samples					Properties of graphitized samples					
		Ash in %	Limiting stress = resistance in compression in strength in ohm-cm 10 ⁻⁴ kg/cm ²	Specific electrical weight	Specific weight	Volume weight	Limiting stress = strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴ of powder	Ash in %	Specific weight	Volume weight	
1.	Petroleum coke	0.35	315.0	68/70	1.96	1.47	210.0	14/15	30.0	0.26	2.15	—
2.	50% of anthracite A + 50% of petroleum coke	1.32	230.0	80/88	1.85	—	68.0	20/25	32.0	0.62	1.98	—
3.	50% of anthracite B + 50% of petroleum coke	1.52	190.0	71/84	1.86	1.36	70.0	20/24	35.0	1.16	2.08	1.35
4.	50% of anthracite C + 50% of petroleum coke	1.96	196.0	70/74	1.89	1.39	51.0	27/33	—	1.98	2.11	1.36
5.	Anthracite with a low ash content.	2.39	212.0	69/72	1.83	1.38	67.0	21/23	—	2.24	2.17	1.34
6.	50% of foundry coke + 50% of petroleum coke	4.05	290.0	70/74	2.03	1.38	127.0	25/28	52.0	3.63	2.12	1.38
7.	Anthracite with a high ash content	5.66	322.0	70/76	1.84	1.43	65.0	32/42	79.0	5.62	—	1.40
8.	Foundry coke	7.20	243.0	68/69	2.05	1.37	158.0	30/38	72.0	6.12	2.17	1.34

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Table 4. Results of Graphitization at 2200°.

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No.	Kind of material	Properties of starting material after preliminary heat treatment of samples					Properties of graphitized samples.					
		Ash in %	stress = compression strength in kg/cm ²	electrical resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Ash in %	Specific weight	Volume weight	
1.	Petroleum coke	0.35	315.0	51/58	1.96	1.47	228.0	—	26.0	0.23	2.15	1.40
2.	50% of anthracite A + 50% of petroleum coke	1.32	230.0	60/80	1.85	1.34	—	15/20	31.0	0.17	2.19	1.30
3.	50% of anthracite B + 50% of petroleum coke	1.52	190.0	55/64	1.83	1.36	89.0	13/16	28.0	0.15	2.20	1.34
4.	Anthracite with a low ash content	2.39	212.0	72/100	1.83	1.37	85.0	—	40.0	traces	2.21	1.32
5.	Anthracite with a high ash content	5.66	322.0	80/81	—	1.44	116.0	14/20	34.0	0.15	2.20	1.37
6.	Foundry coke	7.20	243.0	82/85	2.05	1.38	140.0	18/24	51.0	traces	2.23	1.33

Table 5. Results of Graphitization at 2500°.

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No.	Kind of material	Properties of starting material after preliminary heat treatment of samples					Properties of graphitized samples					
		Ash in %	Limiting stress = compression strength in kg/cm^2	Specific electrical resistance in $\text{ohm-cm } 10^{-4}$	Specific weight	Specific Volume weight	Limiting stress = compression strength in kg/cm^2	Specific electrical resistance in $\text{ohm-cm } 10^{-4}$ of samples of powder	Ash in %	Specific weight	Volume weight	
1.	Petroleum coke	0.80	270.0	53/73	—	—	187.0	12/16	23.0	0.01	2.10	—
2.	50% of anthracite A + 50% of petroleum coke	1.32	230.0	68/76	1.85	1.35	53.0	Samples were deformed.	228.0	0.05	2.19	1.28
3.	50% of anthracite B + 50% of petroleum coke	1.52	190.0	70/71	1.85	1.36	58.0		—	0.10	2.19	1.30
4.	50% of anthracite C + 50% of petroleum coke	1.96	196.0	82/91	—	1.39	55.0		28.0	0.06	2.18	1.27
5.	50% of foundry coke + 50% of petroleum coke	4.05	290.0	70/74	2.03	1.38	60.0		28.0	0.12	—	1.29
6.	Anthracite with a high ash content.	5.66	322.0	69/71	—	1.43	42.0		25.0	0.13	2.11	1.25
7.	Foundry coke	7.20	243.0	70/76	2.05	1.37	64.0		24.0	Traces	2.18	1.25

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Table 6. Properties of Products Graphitized at 1800° as Affected by the Addition of Various Ash Constituents.

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No.	Kind of material	Properties of starting material after preliminary heat treatment of samples					Properties of graphitized samples.					
		Ash in %	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Ash in %	Specific weight	Volume weight	of samples of powders acc. to Arndt
4.	Petroleum coke + 1% Fe ₂ O ₃	10.55	460.0	54/55	2.09	1.65	460.0	37/45	—	9.98	2.03	1.60
5.	" " + 10% Al ₂ O ₃	10.55	—	69/73	2.03	—	243.0	64/77	2690.0	14.01	2.10	1.53
6.	" " + 10% CaO	10.55	—	64/69	—	1.45	254.0	74/81	—	11.00	—	1.44
7.	" " + 10% MgO	10.55	86/107	86/107	—	—	290.0	70/76	1620.0	10.83	2.09	1.57
8.	" " + 5% SiO ₂	5.50	—	74/96	—	—	285.0	69/76	1205.0	5.88	2.01	1.46
9.	" " without any additions	—	270.0	53/73	—	—	—	—	—	—	—	—

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Table 7. Properties of Products Graphitized at 2200° as Affected by the Addition of Various Ash Constituents.

No.	Kind of material	Properties of starting material after preliminary heat treatment of samples				Properties of graphitized samples						
		Ash in %	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Ash in %	Specific weight	Volume weight	
3.	Petroleum coke + 10% SiO ₂	10.55	—	100/130	—	—	77.0	30/31	345.0	—	—	1.41
4.	" " + 10% Fe ₂ O ₃	10.55	460.0	43/49	2.09	1.46	97.0	20/33	246.0	0.23	2.15	1.38
5.	" " + 10% Al ₂ O ₃	10.55	—	84/124	2.03	1.40	—	25/29	362.0	traces	2.16	1.31
6.	" " + 10% CaO	10.55	—	72/77	—	1.44	65.0	20/35	267.0	0.25	2.15	1.37
7.	" " + 10% MgO	10.55	—	69/71	—	1.45	82.0	28/32	324.0	0.03	2.14	1.34

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Table 8. Properties of Products Graphitized at 2500° as Affected by the Addition of Various Ash Constituents.

No.	Kind of material	Properties of starting material after preliminary heat treatment of samples				Properties of graphitized samples						
		Ash in %	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴	Ash in %	Specific weight	Volume weight	
1a.	Petroleum coke without any additions	0.8	270.0	53/73	—	—	187.0	12/16	—	0.01	2.10	—
2a.	Petroleum coke + 10% Fe ₂ O ₃	10.8	185.0	97/112	—	1.49	41.0	17/18	126.0	0.03	2.16	—
3a.	" " + 10% Al ₂ O ₃	10.8	315.0	58/118	—	1.37	80.0	21/28	144.0	0.06	2.18	—
4a.	" " + 10% MgO	10.8	330.0	91/94	—	1.48	56.0	—	140.0	Traces	2.13	—

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Table 9. Effect of the Content of Metal Oxide on the Physical Properties of the Product.

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No.	Oxide added	Percent of oxide added	Limiting stress = compression strength in kg/cm ²	Specific resistance of samples in ohm-cm 10 ⁻⁴	Ash in %	Specific weight
1	-	0.0	187.0	12/16	0.01	2.10
2	Al ₂ O ₃	1.0	159.0	15/19	Traces	2.17
3	"	2.0	170.0	12/18	0.01	2.18
4	"	5.0	143.0	14/15	-	-
5	"	10.0	80.0	21/29	0.06	2.18
6	Fe ₂ O ₃	1.0	182.0	11/19	Traces	2.13
7	"	2.0	240.0	12/16	.	2.15
8	"	5.0	107.0	16/19	-	-
9	"	10.0	41.0	17/18	0.03	2.16
10	MgO	1.0	180.0	13/18	Traces	2.14
11	"	2.0	175.0	15/18	Traces	2.14
12	"	5.0	128.0	21/29	0.10	2.14
13	"	10.0	56.0	40/41	Traces	2.13

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Table 10. ~~Modification of the Mechanical Strength~~ and Resistivity of Products Made From Petroleum Coke/Graphitized at 2500° and the ~~the~~ Which Take Place as a Result of the Addition of Varying Quantities of Metal Oxide That Had Been Added.

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No.	Oxide added.	Specific resistance of powder in ohm-cm 10 ⁻⁴ after addition of the quantity of oxide given below.							
		1%	2%	5%	10%	1%	2%	5%	10%
1.	Ferric oxide	182.0	240.0	107.0	41.0	115.0	—	113.0	126.0
2.	Aluminum oxide	159.0	170.0	143.0	80.0	142.0	141.0	—	144.0
3.	Magnesium oxide	180.0	175.0	128.0	56.0	135.0	—	—	140.0

Note: The compression strength of the product from pure petroleum coke which had been graphitized without any additions is 187 kg/cm²

Table 11. Graphitization in Silicon Dioxide Vapor and Graphitization Under Ordinary Conditions at 2500°.

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No.	Kind of material and conditions of graphitization.	Properties of starting material				Properties of graphitized products.						
		Ash in %	Limiting stress = compression strength in kg/cm ²	Specific resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Limiting stress = compression strength in kg/cm ²	Specific electrical resistance in ohm-cm 10 ⁻⁴ of samples of complete plates	Ash in %	Specific weight	Volume weight	
1.	180 X 50 X 1000 mm carbon plates graphitized in SiO ₂ vapor	3.98	250.0	54.0	1.96	1.61	49.0	14/22	15/17	0.23	2.14	1.49
2.	Ditto	3.80	228.0	55.0	1.95	1.60	68.0	10/13	13/14	0.33	2.21	1.49
3.	"	4.01	347.0	52.0	1.97	1.65	65.0	16/22	15.0	0.30	2.15	1.52
4.	"	4.41	283.0	53.0	1.93	1.62	40.0	12/16	—	0.29	2.16	1.54
10.	180 X 50 X 1000 mm carbon plates graphitized under ordinary conditions	—	—	—	—	—	78.0	11/13	17.0	0.17	2.12	1.57
11.	Ditto	—	—	—	—	—	91.0	20/25	18.0	0.75	2.15	1.54
On the average.												
12.	"	4.05	276.0	53.0	1.95	1.62	106.0	11/23	18.0	0.19	2.14	1.55
13.	"	—	—	—	—	—	91.0	18/24	16.0	0.78	2.16	1.56
14.	"	—	—	—	—	—	85.0	14/22	—	0.41	2.11	1.58

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Table 12. Graphitization at 2200° in Vapor Emitted by a Silicon Carbide Charge and Under Ordinary Conditions.

No.	Kind of material and conditions of graphitization.	Ash in %	Limiting stress = compression strength in kg/cm ²	Specific resistance in ohm-cm 10 ⁻⁴	Specific weight	Volume weight	Porosity	Temperature at which oxidation begins.	
1.	180 X 50 X 1000 mm carbon plates graphitized in SiC vapor	1.37	138.0	—	—	2.23	1.55	30.1	495.0
2.	Ditto	0.60	244.0	10/19	14.1	2.20	1.66	24.5	493.0
3.	"	1.32	141.0	18/19	13.3	2.23	1.59	28.5	493.0
4.	"	2.86	150.0	—	14.0	2.24	1.55	30.6	519.0
5.	"	0.18	106.0	18/19	14.6	—	—	—	515.0
6.	"	—	205.0	15/18	15.3	—	—	—	—
10.	180 X 50 X 1000 mm carbon plates graphitized under ordinary conditions with interspersed anthracite	0.37	109.0	17/24	15.4	2.12	1.62	28.5	490.0
11.	Ditto	0.78	—	24/27	16.4	2.08	1.69	28.2	521.0
12.	"	1.03	102.0	20/25	16.8	2.12	1.61	23.7	486.0
13.	"	—	102.0	22/23	17.6	2.21	1.54	30.3	515.0
14.	"	0.94	97.0	22/29	17.5	2.24	1.60	25.2	518.0

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Table 13. Graphitization at 2500° μ in Vapor Emitted by a Silicon Carbide Charge and Under Ordinary Conditions.

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No.	Kind of material and conditions of graphitization.	Properties of starting material		Properties of graphitized products	
		Limiting stress = compression strength in kg/cm ²	Ash in %	Limiting stress = compression strength in kg/cm ²	Specific ρ resistance of plates in $\frac{1}{4}$ ohm-cm 10 ⁻⁴
1.	50 X 180 X 1000 mm plates graphitized in SiC vapor	250.0	1.1	96.0	16.0
2.	Ditto	197.0	1.6	90.0	16.0
3.	"	419.0	4.4	106.0	18.0
4.	50 X 180 X 1000 mm plates graphitized under ordinary conditions	203.0	1.7	104.0	14.0
5.	Ditto	237.0	—	102.0	14.0
6.	"	314.0	2.5	150.0	16.0

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Table 14. Growth of Anthracite Grains at the Graphitization Temperature of 2100°.

No. of experiment	Weight of material in kgs.	Percent of grains of the size 2-5 mm in the anthracite.	Percentage of grains of the dimensions given below in the graphite prepared from the anthracite			
			+ 10 mm	+ 5 mm	+ 2 mm	- 2 mm
1	0.72	100.0	11.0	77.0	7.0	5.0
2	0.73	100.0	24.0	65.0	4.0	7.0
3	0.82	100.0	28.0	64.0	5.0	3.0

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Table 15. Formation of Carbide Crusts on the Surface of the Material.

No.	Kind of material.	Specific resistance of samples in $\text{ohm-cm} \cdot 10^{-4}$		
		With carbide crust removed		With carbide crust intact
1.	Petroleum coke	19/21	16/21	38/40
2.	50% of anthracite A + 50% of petroleum coke	23/26	16/25	32/38
3.	50% of anthracite B + 50% of petroleum coke	20/25	22/27	48/49

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