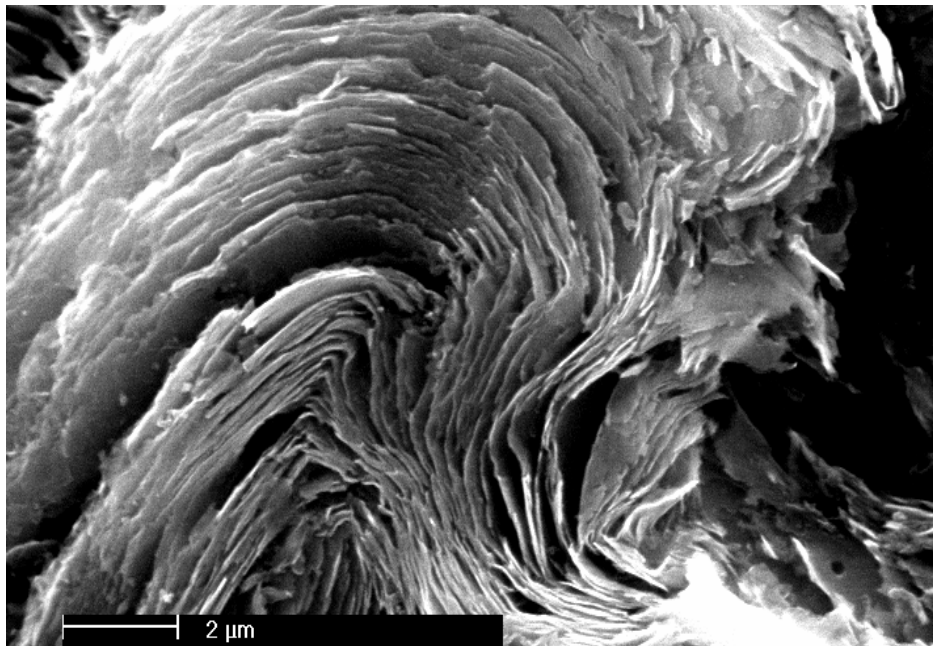


An Introduction to Synthetic Graphite.

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Introduction to Synthetic Graphite

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Part I: Synthetic Graphite Defined

1. Introduction to Synthetic Graphite:

Readers of this section are urged to read the articles in the main heading “A Rigorous Introduction to Graphite” presented on the Asbury Carbons Technical Services page to learn more about the basic structure and properties of graphite materials in general. All of the topics detailed there apply to synthetic graphite.

Synthetic graphite is a man made substance manufactured by the high temperature processing of amorphous carbon materials. The types of amorphous carbon used as precursors to graphite are many, and can be derived from petroleum, coal, or natural and synthetic organic materials. In some cases graphite can even be manufactured by the direct precipitation of graphitic carbon from pyrolysis of a carbonaceous gas such as acetylene (pyrolytic graphite). One important commonality between all graphite precursors is that they must contain carbon. Graphite is carbon, a specific form of carbon, so it can only be derived from other carbon containing substances.

2. A Brief History:

Manufactured or synthetic graphite was discovered by accident during the late 1800's by Edward Goodrich Acheson. While attempting to manufacture silicon carbide (Carborundum) in an electric furnace from a combination of silica and amorphous carbon, Mr. Acheson found that an unintentional reaction product, graphite crystals, was also formed. By refining the process and eliminating silica (SiO_2) from the equation high purity, highly crystalline synthetic graphite could now be manufactured from certain (but not all) solid amorphous carbons. One of the furnace types still used to manufacture graphite, as well as the process method still bears Mr. Acheson's name: the Acheson furnace and the Acheson process.

3. Hot Stuff: High Temperature Processing of Amorphous Carbon:

Prior to the second half of the 19th century refractory or high temperature technologies were generally limited to those temperatures that could be achieved by burning fossil fuels. Although flames resulting from the combustion of organic materials are certainly hot, with adiabatic flame temperatures over 2500 °C in many cases, no heat transfer system is capable of the efficient transfer of this thermal energy to a furnace. Therefore the operating temperatures of the furnaces were (and continue to be) drastically lower than the flame used to heat it. For this reason the temperatures required to drive the solid/solid phase transformation of carbon from its amorphous state to its crystalline state (graphite) had not been previously achieved. Man's discovery of methods to generate electrical current and harness its energy in an electric arc or resistance furnace provided a way to generate the ultra high temperatures required to form graphite and a means to manufacture it in bulk.

Natural graphite that forms in the earth's crust forms at temperatures in the neighborhood of 750°C. At 750 °C on the earth's surface virtually nothing will happen to carbon other than oxidation (burning). However, if in addition to heating to 750 °C you apply about

75,000 psi for 10 million years, graphite will form. Although 750 °C is an easily achieved temperature, the pressure and time requirements have obvious drawbacks when it comes to the practical manufacture of graphite.

At ambient pressure the temperature required to create graphite from amorphous graphitizable carbon in a reasonable time period ranges from about 2300-3000 °C. This is a very high temperature, but it is required to provide the mobility needed by carbon atoms to rearrange themselves into a graphite crystal lattice.

4. To Graphitize or Not To Graphitize: Hard and Soft Carbon

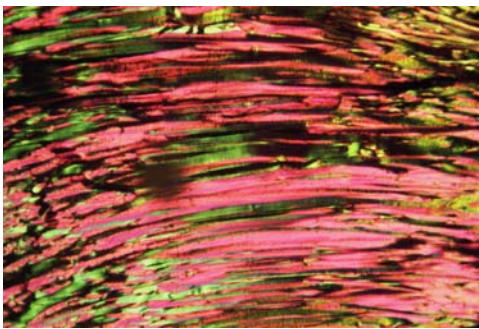
Although all precursor materials used to manufacture graphite must either contain carbon or be some form of pure carbon, not all carbons can be graphitized. The process of *graphitization* involves the limited movement and rearrangement of carbon atoms which must undergo reconstructive transformation during the heat treatment process.

Formation of graphitic carbon from an amorphous carbon precursor requires movement in three dimensions by the pre-graphite matrix. The degree of motion necessary is significant enough to require that the precursor substance pass through a liquid or fluid phase at some point during the material's heat treatment history. By passing through this fluid phase pre-graphitic structures (macromolecules) have mobility and are therefore able to move into semi-ordered positions in a pre-graphite lattice. Once this first organizational step occurs all that remains is the final high temperature heat treatment that results in the "annealing" of carbon into the graphite crystal lattice. This step results in the indexing of graphene layers with respect to each other.

Carbon materials which are able to pass through the temporary fluid phase discussed above are referred to as "soft" carbons. In this context the term soft does not necessarily refer to the carbon's mineralogical hardness. Carbon scientists refer to this intermediate fluid phase as "mesophase". All non-gaseous forms of carbon that ultimately form graphite must pass through this mesophase state. It is in the mesophase that the basic structural units form and align into liquid crystal structures that will ultimately develop into graphite. These liquid crystals actually show a high degree of long range order when compared to most other more "random" liquids.

Mesophase forms as the result of heat driven reactions that occur in the organic substances that make up the precursor carbons suitable for graphite formation, i.e. coal tar pitch, petroleum derived materials, etc. During early stages of heat treatment these substances crack, react, and condense to form regions rich in aromatic sp² carbon structures of limited long range order. These regions are known as *basic structural units* (BSUs). These regions grow at the expense of the mother liquid to form, at first, spherical droplets of liquid mesophase which are themselves composed of regions of *discotic* liquid crystals (disk shaped regions). As the reaction proceeds, these regions polymerize, grow, and coalesce into yet larger domains of mesophase. At a more advanced reaction stage the mesophase "cures" into a non-melting solid which is somewhat organized regarding its pre-graphitic crystalline structure. At this point in the reaction the material can be

classified, although an oversimplification, as *solid carbon with two-dimensional long range order in the “a” crystallographic direction, but still lacking “c” direction orientation or indexing*. Although not all graphitizable carbons follow exactly the process outlined above, the process described is a reasonable generalization of the formation of carbon mesophase as it pertains to pre-graphitic carbon. The figure below is a polarized light micrograph of a graphitizing coke known as needle coke. This material is a solid, non-melting, virtually pure carbon residue. The texture illustrated is indicative of a material that has gone through a state of plastic flow and has solidified into a highly anisotropic solid. Superposition of hexagonal axes onto this micrograph would show that the “a” axes are parallel with the direction of flow. Although the C axis orientation has yet to be developed, this axis would be more or less perpendicular to the apparent flow direction.



The substances referred to above as “precursor carbons suitable for graphite formation” are able to flow because at the onset of the mesophase forming reaction they are relatively low in heteroatoms, contain only limited cross-linked structures, and are low enough in molecular weight to melt at reasonable process temperatures.

Carbons that do not pass through the mesophase state during their thermal history will not readily graphitize. This is due in part to the fact that these types of carbon are usually heavily cross linked or otherwise composed of “pinned” structures that cannot move or flow, asphaltenes for example. The lack of internal mobility inherent to these materials results in the inability for carbon atoms to align themselves in the pre-graphitic “lattice” structure required to be present prior to the final graphitization heat treatment. In other words, these carbon materials do not form significant mesophase, or form only mesophase that has “short range order” since discotic liquid crystal structures do not readily form. Carbon materials such as those described here are known as “hard” carbons. Hard carbons will not readily graphitize, or will graphitize only slightly. In the context used the word “hard” does not refer to mineralogical hardness.

The important concept to remember is that soft carbons can be readily graphitized and hard carbons cannot be readily graphitized.

Part II Manufacturing Synthetic Graphite:

1. Basic feed stocks: Although synthetic graphite can be manufactured from any number of precursor materials the primary material used to manufacture it in the United States is petroleum coke. As noted above only certain types of carbonaceous feeds are suitable for graphite production. Therefore the petroleum coke used for the synthetic graphite industry must be carefully specified to assure it is of the type that will ultimately result in high quality graphitic carbon.

2. Petroleum Coke and Calcined Petroleum Coke: Petroleum coke, or *pet* coke, is the solid carbon residue remaining after the *coking process* is performed on some petroleum residue. The process of *coking* is performed on petroleum residue that has been generated from some refinery process designed to crack, fractionate, or otherwise remove low boiling, high value components from crude oil or other crude oil-based refinery fluid.

The process of coking oil or other refinery by-product is performed to remove the last remaining fraction of low boiling, valuable component from refinery residues. These residues are typically very high molecular weight, high in impurities, difficult if not impossible to refine further by other methods, and are of low value. During the coking process any remaining useful component is cooked out of the residue and fed back to standard refinery process streams. The residue remaining behind is a solid, non melting carbon known as petroleum coke. It is this carbon residue that is used as the primary material for the production of synthetic graphite in the United States.

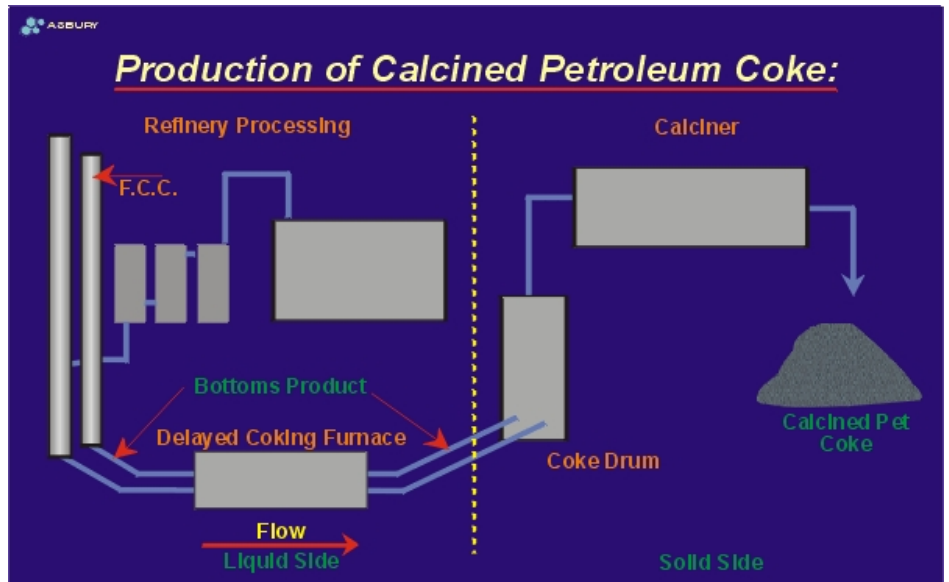
Petroleum coke, as removed from the coking process, contains approximately 10-20% volatile component in the form of water and volatile organic matter. Before it is suitable for the manufacture of synthetic graphite, as well as other uses, this volatile component must be removed. The removal or reduction of this volatile fraction is performed by the *calcining process*. Calcining involves heating the coke to a high enough temperature to volatilize, vaporize, or burn off any volatile components still remaining in the coke. Once the calcining process is completed the coke is known as *calcined petroleum coke*.

The process and process parameters used to manufacture petroleum coke and calcined petroleum coke will be described in more detail below.

3. The Coking Process Schematic:

The figure titled *Production of Calcined Petroleum Coke* presents a schematic of the coking and calcining process. The left side of the figure is the *liquid side* of the process and the right side of the figure is the *solid side* of the process.

The liquid side of the coking process refers to those processes in which petroleum fluids are fractionated, rectified, cracked or otherwise processed to remove low boiling substances. In general these



processes result in a concentrated material such as *bottoms* or other process residue suitable for coking. The coke feed and product steams flow from the left hand side of the schematic toward the right hand side.

The right side of the figure represents the solid side of the process. It is in this part of the unit operation that solid coke forms, is matured, and finally calcined yielding calcined petroleum coke.

4. Coking Liquid Side Details: It is not the goal of this article to describe in detail the process or unit operations that result in the production of *bottoms product* or other high molecular weight refinery feed that ultimately may undergo coking. Suffice it to say that some refinery process designed to refine oil into low molecular weight components produces a by-product which is a high molecular weight residue that, for reasons of economy, must ultimately be coked.

The unit operation highlighted in the figure is the column structure on the extreme left labeled *FCC*. In this case FCC stands for *fluidized catalytic cracker*, but the unit could be any unit that produces fluid materials suitable for coking. To the direct right/center of the FCC are a number of structures that simply represent some post cracking process where high value fluids produced by the FCC are utilized or collected. These process units have no further bearing on the coke process proper; however these units may receive high value fluids which are outputs of the coking process.

At the bottom of the FCCs are product lines labeled *Bottoms Product*. The bottoms product is removed from the bottom of the FCC (or other process) and directed to the device known as the delayed coking furnace. In the delayed coking furnace bottoms are heated to approximately 450 °C. Subsequent to heating in the furnace the hot fluid is directed to the solid side of the process where coking ensues.

Liquid Side Review: Crude oil or other refinery stream enters a unit operation where distillation, cracking, rectification or other process results in a high boiling, high molecular weight, and low value residue. This residue is pumped through a delayed coking furnace where it is heated in order to start the coking process, which is completed on the solid side of the coking operation.

5. Coking Solid Side Details:

The solid side of the process has two primary units, the coke drum and the calciner. The coke drum is the device that accepts pre-heated, liquid bottoms product and where coke formation occurs. The calciner is a kiln where coke is heated to remove residual volatile components.

6. Coking:

The coke drum is a batch process and most coking operations consist of multiple coke drums where the process is in various stages of progress, i.e. one drum is filling while another is being emptied.

The coke-drum itself is a large cylindrical vessel with inside dimensions of approximately 20ft diameter and 80 ft in height. Preheated bottoms product enters the bottom of the coke drum (fill is bottom to top). Once the fluid enters the drum it begins to *polymerize*. The polymerization process is quite complex and involves condensation and other complex organic reactions that produce lower molecular weight compounds that form a vapor fraction and are removed at the top of the drum, as well as a solid residue. The residue of this reaction is the petroleum coke. It is during the coke formation that the petroleum based carbon passes through the mesophase or liquid crystal state described above. Once the solid coke forms it is non-melting and has the pre-graphitic microstructure which makes it suitable for graphite production.

Upon completion of the batch coking process the coke drum is filled with a mass of porous but tough solid phase carbon. This mass of carbon is very difficult to remove from the drum and must be cut into smaller pieces to permit removal. Coke is typically removed from the drum by cutting it out with a high pressure water jet. Coke drums are typically built with tall stanchions above that hold water/steam jet cutters. These high pressure cutters are manipulated downward into the coke drum to drill into and cut up the solid coke facilitating its removal from the drum. Coke removed from the coke drum, but not yet calcined is referred to as *green coke*. A sample of green coke is pictured in the accompanying figure, notice that the coke illustrated is very dark in color with low reflectance. This dark, almost sooty appearance is the result of residual hydrocarbons. These hydrocarbon residues are removed during the calcining process.

7. Calcining: Coke removed from the coke drum may or may not require calcining. The decision to put more energy into what is already a very low value product depends ultimately on the end use of the coke. Petroleum coke destined for graphitization is typically calcined.

Calcining is a process where a material is heated to remove constituents that are, for one reason or another, thermally unstable at the calcining temperature. In the case of petroleum coke the substances removed during calcination are hydrocarbons and water.

Calcining of petroleum coke is performed in a rotary kiln very similar in appearance and function to the type of kiln used to manufacture Portland cement. Green coke is added cold at one end of the horizontally mounted rotating kiln and heated as it moves through the kiln. Kilns are usually direct fired. The time a given plug of material spends in the kiln may be from 30-60 minutes. A typical calcining temperature is 1250-1350 °C.



Once removed from the kiln the coke is cooled and routed to whatever application it is destined for. The accompanying photo is of a sample of calcined petroleum coke. Notice that this material has a much higher reflectance than the green coke pictured. Calcined



petroleum coke is virtually free of the hydrocarbons which result in lower reflectance. Calcined petroleum coke similar to the material pictured here is the type of coke used as feedstock to make synthetic graphite.

Solid Side Review: Preheated bottoms product is fed into the bottom of the coke drum. Upon

entering the coke drum the fluid begins to react, forming low molecular weight overhead product and solid coke residue. After this batch coking process is completed the feed coming from the delayed coking furnace is diverted to an empty coke drum where the drum filling and coking process is repeated. The coke drum containing coke is opened and the coke removed by cutting it out with a high pressure water/steam cutter.

Green coke extracted from the coke drum is finally fed into a rotary kiln and calcined to approximately 1300 °C, where volatile residues are removed. The final product is calcined petroleum coke which, in addition to graphite manufacture, may be used in any number of applications.

8. Not All Petroleum Coke is Created Equal: Refinery processes represent highly complex unit operations which accept any number of different chemical feed stocks. Oil is not a homogeneous substance and therefore most bottoms products, vacuum residues, and other coking refinery streams are also very non-homogeneous. The type and nature of coke produced can be as varied as the different process streams that are diverted to the coker. Although, for example, ten different low value refinery streams may all produce coke, it is likely that the coke produced from each stream will be unique.

Coke produced from the by-products of one crude oil may be completely different from the coke produced from another crude oil stream. In most cases the petroleum coke manufactured is not suitable for the production of graphite, which requires the highest quality, most “crystalline” coke available. Such cokes are manufactured only from the highest grade crude oil and feedstock that must be high in aromatic organics. By-product streams diverted for coking must be carefully chosen and controlled if high quality graphite is to be manufactured from it.

9. Synthetic Graphite Production: The exact process used to manufacture synthetic graphite is varied and can be quite complex. It is beyond the scope of this article to discuss this process in great detail. The following is provided only as a basic outline to give the reader an introduction to the manufacturing of this material.

Synthetic graphite can be manufactured in any number of forms including solid articles of varied shape and size, granular materials, and powders. The intention of this article is to describe in very general terms the process where calcined petroleum coke is converted into synthetic graphite. The reader must keep in mind that many variations in the process and ingredients are possible.

Our example will be the manufacturing of a conductive graphite electrode, the type used to melt or refine iron in an electric furnace. Electrodes of this type are typically made using only the highest quality petroleum coke filler particles.

Graphite electrodes are used in metallurgical applications as a source of energy for melting scrap iron in an electric furnace, refining certain types of ceramic materials, manufacturing chemicals (i.e. calcium carbide), and other applications requiring a high temperature, clean energy source. These electrodes must be highly conductive and free of contamination. High conductivity and high purity are attributes of synthetic graphite.

The graphite electrodes described above are typically two or three component systems. The primary component is the carbon filler which will be converted to graphite. This filler is calcined petroleum coke (described above). Since during the graphitization step no melting, sintering of the carbon filler occurs a matrix is required to hold the filler together. As with the petroleum coke fraction the matrix must be composed of a material that will form graphite upon heat treatment. Since the final electrode must have excellent electrical continuity the filler and matrix must have similar electrical properties. This is only possible if both components are graphitic.

Electrode production begins by mixing calcined petroleum coke(CPC) filler particles with coal tar pitch. This process is performed at elevated temperatures so the pitch component is soft or liquid, and mixes and coats the CPC particles forming flexible and moldable dough. The mixture is roughly 80% CPC and 20% pitch. This doughy mixture is then extruded into a solid cylinder that is roughly the same length and diameter as the nominal size of the particular electrode being manufactured.

After extrusion to nominal size the green electrode blank is cooled and becomes rigid (the coal tar pitch freezes). At this point in the process the electrode blank is composed of calcined petroleum coke filler particles held together in a solidified coal tar pitch matrix.

Green electrode blanks are now baked. Baking consists of slowly heating the formed electrode blanks in an oven to approximately 1000 °C. The heating rate must be carefully controlled to prevent excessive degassing, melt flow, or other process that would result in deformation from occurring. During the baking process air is excluded from the electrode blank to prevent or reduce oxidation losses.

As the baking process proceeds many changes occur to the coal tar pitch fraction. As the pitch thermally matures it passes through the mesophase state (described above), polymerizes, and cures to a non melting coal tar pitch-coke. No changes occur to the

calcined petroleum coke filler. Upon completion of the baking process the electrode blank consists of calcined petroleum coke particles held together by a non-melting calcined coal tar pitch (or coal tar coke) matrix.

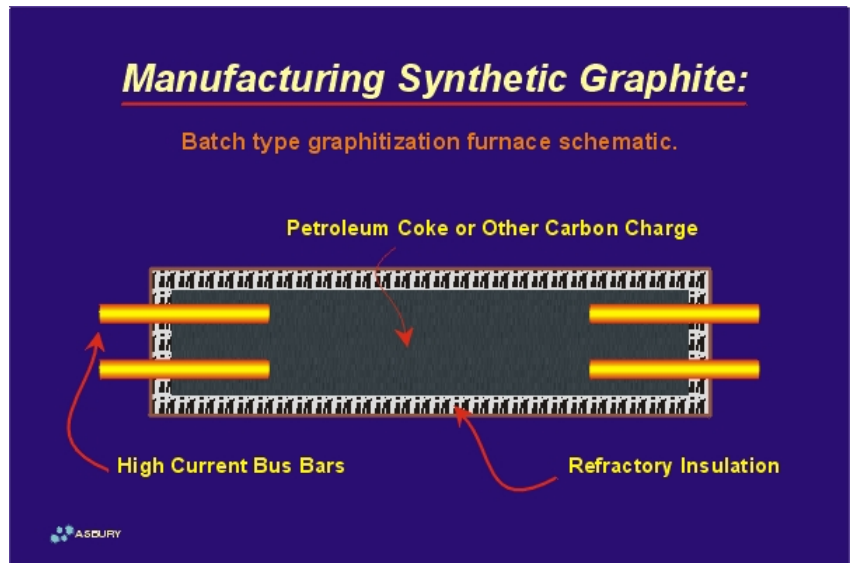
The act of baking a green electrode results in a certain amount of degassing as the pitch changes chemically. This results in the introduction of pores that reduce the density of the carbon article. At this point in the process the electrode blank may be impregnated with pitch and re-baked to reduce its porosity. Impregnation is typically performed using a pitch lower in viscosity than the original binder pitch. Low viscosity is required in order to affect more complete void filling. Petroleum pitch is normally utilized for this function.

When the manufacturer determines the properties of the baked electrode blank are adequate the blank is graphitized. Electrode blanks, or carbon articles in general can be heated to the graphitization temperature any number of ways including the Acheson process, longitudinal heating, or magnetic induction. This discussion will describe the Acheson process as the method of graphitization.

The Acheson process is performed in an Acheson-type furnace. This furnace consists of a central chamber surrounded by external walls made of some refractory material such as firebrick. The chamber is roughly rectangular in outline. The top is open. The Acheson furnace is nothing more than a room without a ceiling, designed to keep in the heat generated by electrical resistance heating of the carbon charge.

The end walls of the Acheson furnace are fitted with graphite buss bars. These buss bars extend to the outside wall of the furnace where they are coupled to large caliber copper buss bars that may or may not be water cooled. Copper or other metallic materials are not permitted within the inter confines of the furnace since they would vaporize at the high process temperatures. The accompanying figure presents a schematic image of an Acheson type furnace.

Loading of the empty furnace proceeds by placing the baked carbon electrode blanks in some pre-determined configuration. Carbon articles may be loaded parallel or perpendicular to the power supply buss bars located on the furnace end walls.



Since graphitization process temperatures are expected to reach 2800 °C or more it is of

paramount importance that oxygen be excluded from the furnace. This is accomplished by covering the carbon articles with some oxygen scavenging material. Petroleum coke, metallurgical coke, or other carbon containing oxygen getter is typically used for this function. This “packing” as it is called must also be somewhat conductive to electricity since it will form part of the electrical pathway through the furnace.

In addition to restricting oxygen from the articles being graphitized the coke or other packing material used to protect the electrode blanks also serves as a thermal insulator. It is important to keep the heat in the furnace so that the extreme process temperature required for graphitization to occur can be reached.

Once the articles to be graphitized are placed in the Acheson furnace and covered with the appropriate packing material a DC current of low voltage and very high amperage is applied to the furnace charge. The furnace load heats up due to its own electrical resistance. As the heating progresses the furnace resistance goes down due to the increase in conductivity that results from the formation of graphitic carbon at the expense of amorphous carbon.

Furnace conditions are constantly monitored, this includes the power consumed. At the point where the operator determines that the proper furnace temperature has been achieved, or that the charge is fully graphitized, power to the furnace is cut. The furnace is allowed to cool and the graphitized articles, electrodes in this example, are removed.

The total process time for graphitization using the Acheson method can be as long as 2-3 weeks. The heating cycle is typically rapid, with the graphitization temperature being reached in a few days. However, cool down time is slow and it can take up to two weeks until the furnace is cool enough to unload.

The electrodes, which started out as calcined petroleum coke particles and molten coal tar pitch are now fully graphitized articles. At this final process stage they are composed of graphitized calcined petroleum coke particles held together in a graphitized coal tar pitch matrix, which may contain graphitized petroleum pitch if the electrode blanks received secondary impregnation.

The form of the carbon in the heat treated electrode is completely different from the starting carbon. The electrode started out as an amorphous carbon with limited long range crystalline order defined by the mesophase from which it was composed. In contrast the heat treated article is composed of carbon atoms arranged in a true crystal lattice structure. What began as relatively low end petroleum by-product has been transformed into a high value versatile form of carbon that has literally hundreds of industrial applications.



The accompanying photograph shows coarse synthetic graphite particles. Visit the Asbury Materials Gallery on this Web page for more pictures of synthetic graphite.