Kirk-Othmer Encyclopedia of Chemical Technology.

GRAPHITE, PROCESSING ARTIFICIAL

1. Raw Material Preparation

1.1. Crushing and Sizing

Calcined petroleum coke arrives at the graphite manufacturer's plant in particle sizes ranging typically from dust to 50–80 mm diameter. In the first step of artificial graphite production, the run-of-kiln coke is crushed, sized, and milled to prepare it for the subsequent processing steps. The degree to which the coke is broken down depends on the grade of graphite to be made. If the product is to be a fine-grained variety for use in aerospace, metallurgical, or nuclear applications, the milling and pulverizing operations are used to produce sizes as small as a few micrometers in diameter. If, on the other hand, the product is to be coarse in character for products like graphite electrodes used in the manufacture of steel, a high yield of particles up to 25 mm diameter is necessary.

The wide variety of equipment available for the crushing and sizing operations is well described in the literature (1, 2). Roll crushers are commonly used to reduce the incoming coke to particles that are classified in a screening operation. The crushed coke fraction, smaller than the smallest particle needed, is normally fed to a roll or hammer mill for further size reduction to the very fine (flour) portion of the carbon mix. A common flour sizing used in the graphite industry contains particles ranging from 149 μm (100 mesh) to a few micrometers with about 50% passing through a 74 μm (200 mesh) screen.

For a coarse-grained (particle containing) graphite, the system depicted in Figure 1 is typical. The run-of-kiln coke is brought in on railroad cars and emptied into pits where the coke is conveyed to an elevator. The elevator feeds a second conveyor that empties the coke into any one of a number of storage silos where the coke is kept dry. The manufacturer usually specifies a maximum moisture content in the incoming coke at about 0.1–0.2% to ensure that mix compositions are not altered by fluctuations in moisture content.

In the system shown in Figure 1 the oversized coke particles (heads) are diverted to a roll crusher. Most raw material systems provide the option of further reducing the sizes of particles by passing them through a second crusher directly from the screens and recycling the resulting fractions through the screening system. The undersized coke fractions are transferred to a bin that supplies a mill for production of the flour portion of graphite composition. The mills used in this application may be of impact (hammer) variety or of roller variety. A commonly used mill consists of a rotating roller operating against a stationary steel ring. The coke is crushed to very fine sizes that are air-classified by a cyclone separator. The sizes larger than those desired in the flour are returned to the mill and the acceptable sizes are fed to a charge bin.

The coal-tar pitch binder used in graphite manufacture also arrives in railroad cars. If the pitch is shipped in bulk form, the large pieces must be crushed to ca 30 mm and smaller to facilitate uniform melting in the mixer and control of the weighing operation. Many vendors of binder pitches now form their product either by prilling, extruding, or flaking to ensure ease of handling and storage.

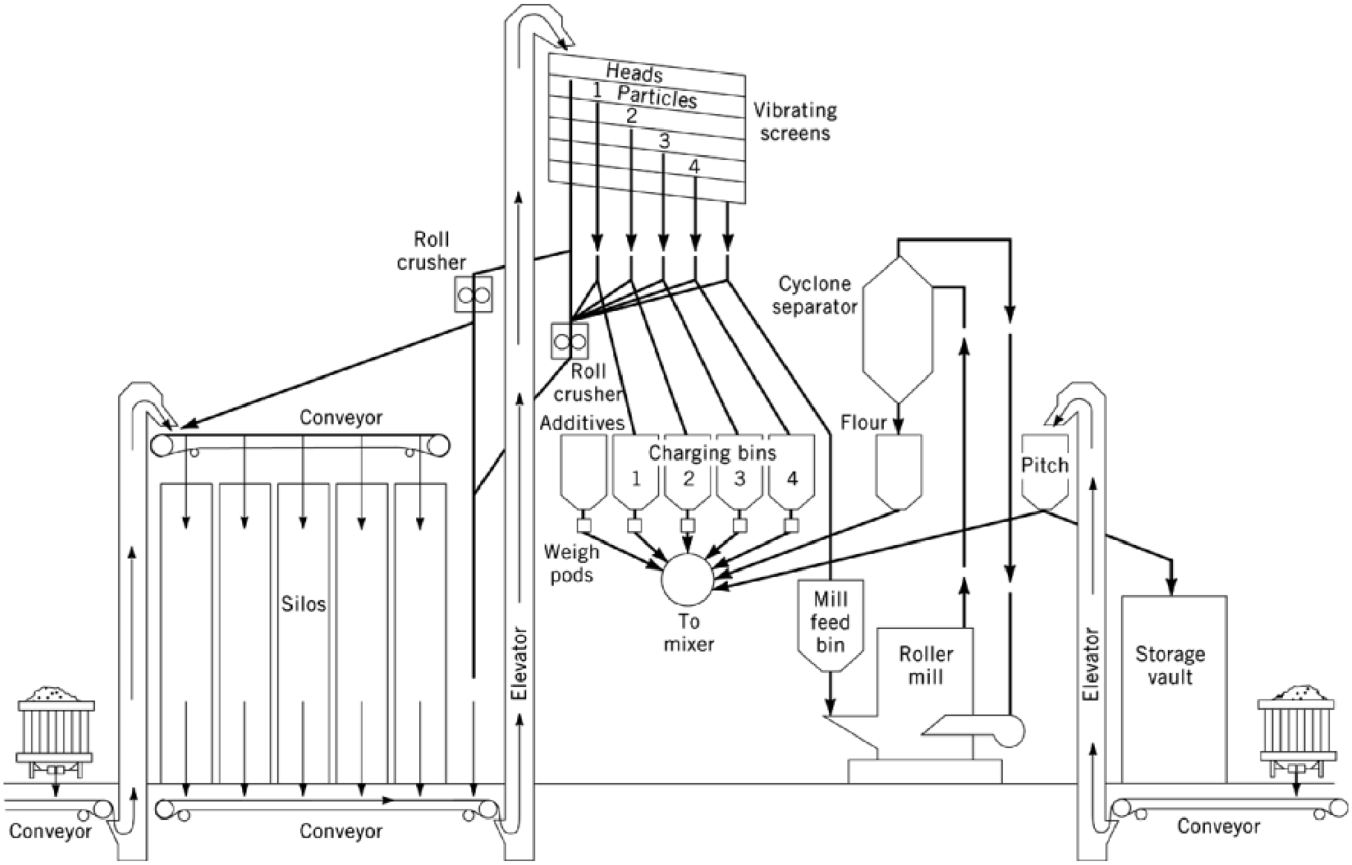

Fig. 1. Raw materials handling system. Courtesy of UCAR Carbon Technology Corp.

The pitch system shown in Figure 1 conveys the incoming pitch through a crusher to an elevator that deposits it into a charging bin. The graphite manufacturer tries to avoid long-term storage of 100°C softening point pitch because of its tendency to congeal at ambient conditions into masses extremely difficult to break up and handle. Thus, whenever possible, cars of pitch are ordered and used as needed at the carbon plant.

In some plants the pitches are received and stored as liquids. Addition to the mixers can be either through a weighing system or positive displacement pumps (3). Except for equipment differences, the results of utilizing liquid pitch are similar to bulk.

1.2. Proportioning

The size of the largest particle is generally set by application requirements. For example, if a smoothly machined surface with a minimum of pits is required, as in the case of graphites used in molds, a fine-grained mix containing particles no larger than 1.6 mm with a high flour content is ordinarily used. If high resistance to thermal shock is necessary, eg, in graphite electrodes used in melting and reducing operations in steel plants, particles up to 25 mm are used to act as stress absorbers in preventing catastrophic failures in the electrode.

Generally, the guiding principle in designing carbon mixes is the selection of the particle sizes, the flour content, and their relative proportions in such a way that the intergranular void space is minimized. If this condition is met, the volume remaining for binder pitch and the volatile matter generated in baking are also minimized. Volatile evolution is often responsible for structural and property deterioration in the graphite product. In practice, most carbon mixes are developed empirically with the aim of minimizing binder demand and making use of all the coke passed through the first step of the system. From an economic standpoint, accumulation of one size component cannot be tolerated in making mixes for commonly used graphite grades since this procedure amounts to a loss of relatively costly petroleum coke. Typically, a coarse-grained mix may contain a large particle, eg, 13 m diameter, two to three intermediate particle sizes, and flour. In this formulation approximately 25 kg of binder pitch would be used for each 100 kg of coke.

Although binder levels increase as particle size is reduced, and they are greatest in all-flour mixes where surface area is very high, the principle of minimum binder level still applies. The application of particle packing theory to achieve minimum binder level in all-flour mixes is somewhat more complex because of the continuous gradation in sizes encountered (4).

For some carbon and graphite grades, particle packing and minimum pitch concepts are not used in arriving at a suitable mix design. For relatively small products, eg, where large dimensional changes can be tolerated during the baking and graphitizing operations, high binder contents are often used. Increased pitch content results in greater shrinkage, which gives rise to high density and strength in the finished products.

1.3. Mixing

Once the raw materials have been crushed, sized, and stored in charging bins and the desired proportions established, the manufacturing process begins with the mixing operation. The purpose of mixing is to blend the coke filler materials and distribute the pitch binder over the surfaces of the filler grains as it melts or is added as a liquid. The intergranular bond ultimately determines the properties and structural integrity of the graphite. Thus the more uniform the binder distribution is throughout the filler components, the greater the likelihood for a structurally sound product.

The degree to which mixing uniformity is accomplished depends on factors such as time, temperature, and batch size. However, a primary consideration in achieving mix uniformity is mix design (see Mixing and blending). A number of mechanically agitated, indirectly heated mixer types are available for this purpose (5, 6). Each mixer type operates with a different mixing action and intensity. Ideally, the mixer best suited for a particular mix composition is one that introduces the most work per unit weight of mix without particle breakdown. In practice, only a few mixer types are used in graphite manufacture.

The cylinder mixer is commonly used for coarse-grained mixes. It is equipped with an axial rotating shaft fitted with several radial arms where paddles are attached. The intensity of this mixer is relatively low to avoid particle breakdown and long mixing times, such as 90 min, are therefore needed to complete the mixing operation. With fine-grained compositions, more intensive mixers may be used with a corresponding reduction in mixing time. Bread or sigma-blade mixers and the high intensity twin-screw mixers of the Werner-Pfleiderer and Banbury variety are examples of the equipment that can be used on fine-grained compositions. For both mixers temperatures at the time of discharge are 160–170°C.

Following the mixing operation, the hot mix must be cooled to a temperature slightly above the softening point of the binder pitch. Thus the mix achieves the proper rheological consistency for the forming operation and the formed article is able to maintain its shape better as it cools to room temperature. At the end of the cooling cycle, which typically requires 15–30 min, the mix is at 100–110°C and is ready to be charged into an extrusion press or mold.

1.4. Forming

One purpose of the forming operation is to compress the mix into a dense mass so that pitch-coated filler particles and flour are in intimate contact. For most applications, a primary goal in the production of graphite is to maximize density; this goal begins by minimizing void volume in the formed, green, product. Another purpose of the forming step is to produce a shape and size as near that of the finished product as possible. This reduces raw material usage and cost of processing graphite that cannot be sold to the customer and must be removed by machining prior to shipment. Two important methods of forming are extrusion and molding.

1.4.1. Extrusion

This process is used to form most carbon and graphite products. In essence, extrusion presses comprise a removable die attached by means of an adapter to a hollow cylinder called a mud chamber. The cylinder is charged with mix that is extruded in a number of ways depending on the press design. For one type of press, the cooled mix is introduced into the mud chamber in the form of plugs that are molded in a separate operation. A second type of extruder called a tilting press makes use of a moveable mud chamber-die assembly to eliminate the need for precompacting the cooled mix. Loading occurs directly from coolers with the assembly in the vertical position; the mixture is extruded with the assembly in the horizontal position. A third type of extrusion press makes use of an auger to force mix through the die. This press is used principally with fine-grained mixes because of its tendency to break down large particles.

The basic steps in the extrusion operation when a tilting press is used are depicted in Figure 2. The cooled mix is usually fed to the press on a conveyor belt where it is discharged into the mud chamber in the vertical position. A ram descends on the filled chamber, tamping the mix to compact the charge. A closing plate located in the pit beneath the press is often used to seal off the die opening, thereby preventing the mix from extruding during the application of high tamping pressures. In addition, a vacuum can be applied to the mud chamber during tamping to remove entrapped air. The filling and tamping procedures are repeated until the mud chamber is filled with tamped mix and then rotated back to the horizontal position. The extrusion ram then enters the mud cylinder forcing the mix through the die at 3–15 MPa (30–148 atm). A guillotinelike knife located near the die outlet cuts the extruded stock to the desired length. Round products are rolled into a tank of water where the outer portions are quickly cooled to prevent distortion of the plastic mass. Products having large rectangular cross-sections may be transferred from the press to the cooling tank by means of an overhead crane. Water temperatures are regulated to avoid cracking as a result of too rapid cooling. Products with smaller cross-sections, such as $32 \times 152 \times 810$ mm plates used as anodes, may be cooled in air on steel tables. Bulk densities of green products range typically from 1.75–1.80 g/cm^3.

The anisotropy, usually observed in graphite products, is established in the forming operation. In extruded products, the anisotropic coke particles orient with their long dimensions parallel to the extrusion direction. The layer planes of the graphite crystals are predominantly parallel to the long dimension of the coke particle. Accordingly, the highly anisotropic properties of the single crystal are translated, to a greater or lesser degree depending on several factors, to the graphite product. The most important of these factors are coke type, particle size, and the ratio of die-to-mud chamber diameters. The more needlelike the coke particle, the greater the difference is between properties with-grain (parallel to the extrusion direction) and cross-grain. The use of smaller particles in the mix design also increases this property difference; the presence of large particles interferes with the alignment process. As the ratio of mud cylinder-to-die diameter increases, the with-grain to cross-grain ratios of strength and conductivity increase, whereas the with-grain to cross-grain ratios of resistivity and expansion coefficient decrease. Thus anisotropy is increased for the same coke type and mix design when going from a 600 mm diameter die to a 400 mm diameter die on the same extrusion press. As a result of particle orientation in extruded graphitized products, strength, Young's modulus, and thermal conductivity values are greater; whereas, electrical resistivity and coefficient of thermal expansion are smaller in the with-grain direction than in the two cross-grain directions.

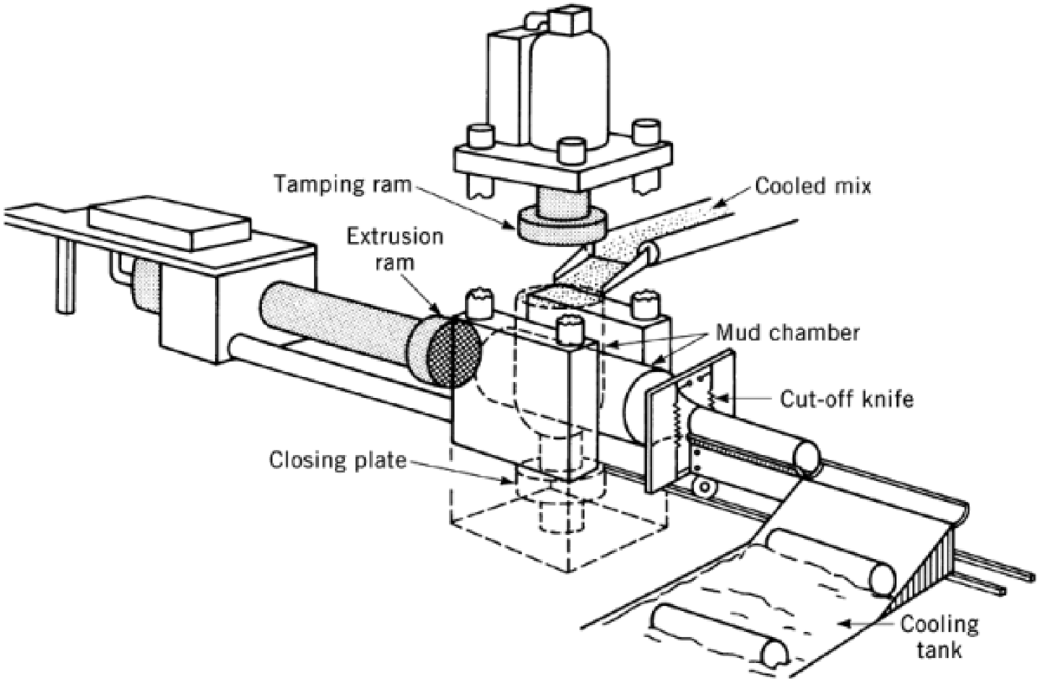

Fig. 2. Tilting extrusion press. Courtesy of UCAR Carbon Technology Corp.

1.4.2. Molding

Molding is the older of the two forming methods and is used to form products ranging in size from brushes for motors and generators to billets as large as 1.75 m diameter by 1.9 m in length for use in specialty applications.

Several press types are used in molding carbon products. The presses may be single-acting or double-acting, depending on whether one or both platens move to apply pressure to the mix through punched holes in either end of the mold. The use of single-acting presses is reserved for products whose thicknesses are small compared with their cross-sections. As thickness increases, the acting pressure on the mix diminishes with distance from the punch because of frictional losses along the mold wall. Acceptable thicknesses of molded products can be increased by using double-acting presses that apply pressures equally at the top and bottom of the product.

Jar molding is another method used to increase the length of the molded piece and keep nonuniformity within acceptable limits. By this technique, the heated mold is vibrated as the hot mix is introduced, thus compacting the mix during the charging operation. Pieces as large as 2.5 m in diameter and 1.8 m in length have been molded in this way; the green densities are comparable with those obtained in extruded materials.

Smaller products, such as brushes and seal rings, are often molded at room temperature from mix that is milled after cooling. When binder levels exceed approximately 30% of the mix, the compacted milled mix has sufficient green strength to facilitate handling in preparation for the baking operation.

In a typical hot molding operation to form a 1.7 m diameter billet 1.3 m long, approximately 7200 kg of mix at 160°C is introduced into a steam heated mold without cooling. The platens of the press compact the mix at ca 5 MPa (49 atm), holding this pressure for 15–30 min. The cooling step for pieces of this size is the most critical part of the forming operation. Owing to the low thermal conductivity of pitch, 0.13 W/(m·K)

(7), and its relatively high expansion coefficient at 25–200°C ($4.5 \times 10^{-4}/^{\circ}\mathrm{C}$) (8), stresses build rapidly as the outer portions of the piece solidify. If cooling is too rapid, internal cracks are formed that are not removed in subsequent processing steps. As a result, a cooling schedule is established for each product size and is carefully followed by circulating water of various temperatures through the mold for specified time periods. When the outside of the piece has cooled sufficiently, it is stripped from the mold and the cooling operation continued by direct water spray for several hours. If cooling is stopped too soon, heat from the center of the piece warms the pitch binder to a plastic state, resulting in slumping and distortion. The cooled piece is usually stored indoors prior to baking in order to avoid extreme temperature changes that may result in temperature gradients and damage to the structure. Bulk density of the green billet is usually 1.65–1.70 g/cm^3.

As with extruded products, molded pieces have a preferred grain orientation. The coke particles are aligned with their long dimensions normal to the molding direction. Thus the molded product has two with-grain directions and one cross-grain direction which coincides with the molding direction. Strength, modulus, and conductivity of molded graphites are higher in both with-grain directions and expansion coefficient is higher in the cross-grain direction. Isostatic molding is a forming technique used to orient the coke filler particles randomly; thereby imparting isotropic properties to the finished graphite. One approach to isostatic molding involves placing the mix or blend into a rubber container capable of withstanding relatively high molding temperatures. The container is evacuated then sealed and placed in an autoclave that is closed and filled with heated oil. The oil is then pressurized to compact the mass, which may then be processed in the usually way to obtain isotropic graphite. Cold isostatic molding is also used. In this process, room temperature water fills the autoclave and is pressurized to compact the mass.

1.5. Baking

In the next stage, the baking operation, the product is fired to 800–1000°C. One function of this step is to convert the thermoplastic pitch binder to solid coke. Another function of baking is to remove most of the shrinkage in the product associated with pyrolysis of the pitch binder at a slow heating rate. This procedure avoids cracking during subsequent graphitization where very fast firing rates are used. The conversion of pitch to coke is accompanied by marked physical and chemical changes in the binder phase, which if conducted too rapidly, can lead to serious quality deficiencies in the finished product. For this reason, baking is generally regarded as the most critical operation in the production of carbon and graphite.

Several studies discuss the kinetics of pitch pyrolysis and indicate, in detail weight loss and volatile evolution as functions of temperature (9, 10). Weight losses of 30–40% occur, indicating that for every 500 kg of green product containing 20% pitch, 30–40 kg of gas must escape. In terms of gas volume, approximately 150 cm^3 of volatiles at standard conditions must be evolved per gram of pitch binder during the baking operation. The product in the green state is virtually impermeable, and the development of a venting porosity early in the bake must be gradual to avoid a grossly porous or cracked structure. The generation of uniform structure during the bake is made more difficult by the poor thermal conductivity of pitch. Long firing times are usually needed to drive the heat into the center of the product, which is necessary for pitch pyrolysis and shrinkage. If the heating rates exceed a value which is critical for the size and composition of the product, differential shrinkage leads to splitting. Shrinkage during baking is of the order of 5% and increases with increasing pitch content. Added to these difficulties is the complete loss of mechanical strength experienced by the product in the 200–400°C range where the pitch binder is in a liquid state. To prevent slumping and distortion during this period, the stock must be packed in carefully sized coke or sand, which provides the necessary support and is sufficiently permeable to vent the pitch volatiles.

A variety of baking furnaces are in use to provide the flexibility needed to bake a wide range of product sizes and to generate the best possible temperature control. One common baking facility is the pit furnace, so named because it is positioned totally or partially below ground level to facilitate improved insulation. In essence, the pit furnace is a box with ceramic brick walls containing ports of flues through which hot gases are

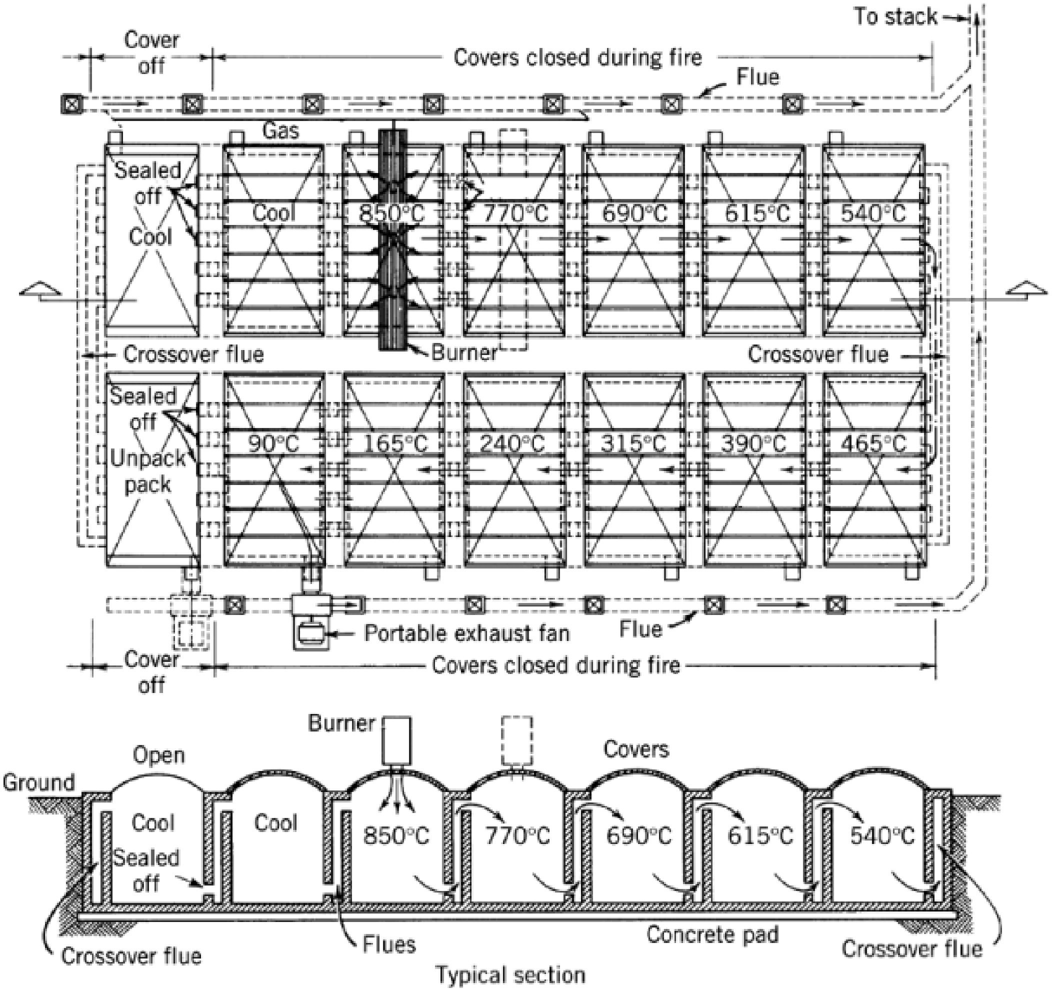

Fig. 3. Ring furnace system.Courtesy of UCAR Carbon Technology Corp.

circulated. Traditionally, natural gas has been the fuel used to fire pit furnaces; however, pit furnaces can also be converted to use fuel oil (see Furnaces, fuel-fired).

Another common baking facility is the so-called ring furnace; one form of this is depicted in Figure 3. Two equal rows of pit furnaces are arranged in a rectangular ring. Ports in the furnace walls permit the heated gases from one furnace to pass to the next until the cooled gases are exhausted by a movable fan to a flue leading to a stack. A movable burner, in this case located above one furnace, fires it to a predetermined off-fire temperature. The firing time per furnace is 18–24 h. When the desired temperature has been reached, the burner is moved to the adjacent furnace which has been heated by gases from the most recently fired pit. At the same time, the fan is moved to a furnace that has just been packed. This process continues, with packing, unloading, and cooling stages separating the fan and the burner. Cycle times in this furnace are three to four weeks. Thermally, the ring furnace is highly efficient but it has the disadvantage that very little control can be exercised over heating rates.

A more recent development is the carbottom furnace, which is an above ground rectangular kiln; the bottom is mounted on wheels and set on tracks so it is movable. The carbottom is isolated from the heating chamber by a water seal. These furnaces provide improved temperature and pressure control and better uniformity.

In addition, the development of stainless steel cans, saggers, into which green stock is loaded and then surrounded by packing media, has improved furnace heating effectiveness by reducing the ratio of packing media to green electrode. The can diameter is slightly larger than the stock diameter to accommodate this process. Beside reducing total energy requirements as much as 60–70%, the sagger allows the use of automated equipment in loading, unloading, and handling of the electrodes (11).

The firing schedules used in the baking operation vary with furnace type, product size, and binder content. A bulk furnace packed with $610 \times 810 \times 4600$ mm pieces of specialty graphite may require six weeks to fire and an additional three to four weeks to cool. In contrast, very small products, such as seal rings, may be baked in tunnel kilns in a few hours. A sagger furnace containing electrodes may require 12–14 days to reach final temperature with an additional 3–5 days to cool. Firing rates early in the baking schedule are reduced to permit pitch volatiles to escape slowly, minimizing damage to the structure. For most carbon products, temperatures must be well below 400°C prior to unpacking to avoid cracking because of thermal shock. The product is scraped or sanded to remove adhering packing materials and is then weighed, measured, and inspected prior to being stored for subsequent processing. Some products that are sold in the baked state are machined at this stage. Baked products include submerged arc-furnace electrodes, cathode blocks for the electrolytic production of aluminum, and blast furnace lining blocks.

1.6. Impregnation

In some applications, the baked product is taken directly to the graphitizing facility for heat treatment to 3000°C. However, for many high performance applications of graphite, the properties of stock processed in this way are inadequate. The method used to improve those properties is impregnation with coal-tar or petroleum pitches. The function of the impregnation step is to deposit additional pitch coke in the open pores of the baked stock, thereby improving properties of the graphite product. Table 1 shows the graphite properties of unimpregnated and impregnated stock 150–300 mm diameter and containing 1.5 mm particles as the largest particle.

Further property improvements result from additional impregnation steps separated by rebaking operations. However, the gains realized diminish quickly, for the quantity of pitch picked up in each succeeding impregnation is approximately half of that in the preceding treatment. Many nuclear and aerospace graphites are multiple pitch-treated to achieve the greatest possible assurance of high performance.

During the baking operation, binder pitch exuding the product surface creates a dense impermeable skin. In addition, the exuding pitch causes packing material to adhere to the baked stock. The skin and the packing material must be removed by sanding, scraping, or machining before the stock can be impregnated on a reasonable time cycle. Unless this operation is properly performed, the impregnant may not reach the center of the product and a so-called dry core results. When this condition exists, the product usually splits during graphitization as a consequence of the greater concentration of pitch and greater shrinkage in the outer portions of the stock. The likelihood of a dry core increases with the quinoline-insoluble solids content of the impregnant. During the impregnation process, the insolubles form a filter cake of low permeability on the stock surface, reducing the penetrability of the impregnant. Quinoline insolubles significantly greater than 5% reduce the penetration rate and increase the incidence of dry cores.

A schematic diagram of the pitch impregnation process is shown in Figure 4. Before it is placed in an autoclave, the skinned baked stock is preheated to 250–300°C to thoroughly dry it and to facilitate free flow of the molten impregnant into the open pores. The first step in the impregnation process is to evacuate the stock to pressures below 3.5 kPa (26 mm Hg) for a period of one hour or more depending on the size and permeability

Table 1. Effect of One Pitch Impregnation on Graphite Properties

	Unimpregnated[a]		Impregnated[b]	
Property	wg[c]	ag[d]	wg[c]	ag[d]
Young's modulus, GPa[e]	7.4	4.4	11.0	6.3
flexural strength, MPa[f]	10.	7.1	17	13
tensile strength, MPa[f]	5	4.4	8.1	7.3
compressive strength, MPa[f]	21	21	34	33
permeability, μm^2[g]	0.39	0.35	0.19	0.16
coefficient of thermal thermal expansion, $10^{-6}/°C$	1.3	2.7	1.5	3.1
specific resistance, $\mu\Omega \cdot m$	8.8	13.0	7.6	11.0

[a] Bulk density = 1.6 g/mL.

[b] Bulk density = 1.7 g/mL.

[c] With the grain, ie, samples cut parallel to the molding plane or extrusion axis.

[d] Across the grain, ie, samples cut perpendicular to the molding or extrusion force.

[e] To convert GPa to psi, multiply by 145,000.

[f] To convert MPa to psi, multiply by 145.

[g] To convert μm^2 to darcys, divide by 0.9869.

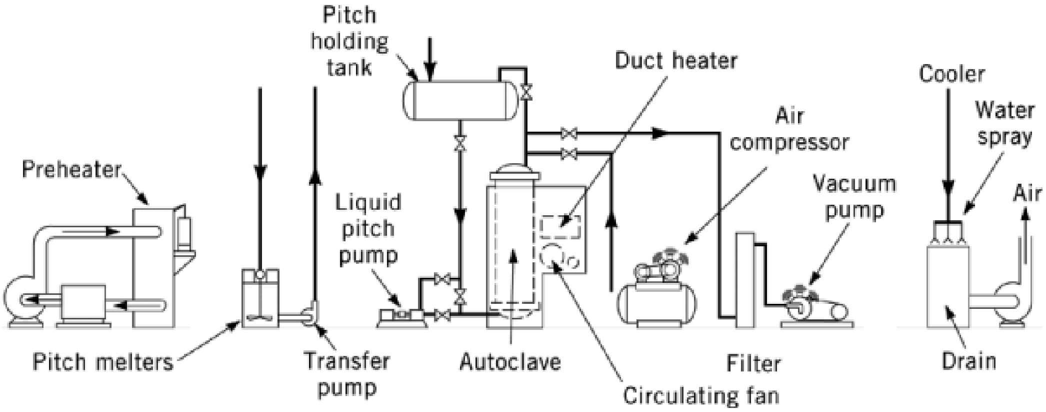

Fig. 4. Pitch impregnation system. Courtesy of UCAR Carbon Technology Corp.

of the stock. Unless the stock is adequately evacuated, the remaining air prevents thorough penetration of the impregnant to the center of the product. Heated pitch is then introduced by gravity flow into the autoclave from a holding tank until the charge is completely immersed. The system is then subjected to pressures of 700–1500 kPa ($\sim 7-15$ atm) for several hours to shorten the time for pitch penetration. When the pressure cycle has been completed, the pitch is blown back to the holding tank by means of compressed air. The autoclave is then opened, and the stock is transferred to a cooler where water and/or circulating air accelerate the cooling process. After cooling, the stock is weighed to determine the quantity of pitch picked up. If the pickup is below a specified limit, the stock is scrapped. Depending on the density of the baked stock, the pickup is 12–16% on the first impregnation and 6–8% on the second impregnation.

If the stock is to receive a second impregnation, it must be rebaked. In the past, stock containing raw impregnating pitch could be graphitized directly. However, the air polluting effect caused by this practice has made rebaking a necessary preliminary step to graphitization in order to achieve effective environmental control.

1.7. Graphitization

Graphitization is an electrical heat treatment of the product to ca 3000°C. The purpose of this step is to cause the carbon atoms in the petroleum coke filler and pitch coke binder to orient into the graphite lattice configuration. This ordering process produces graphite with intermetallic properties that make it useful in many applications.

Very early in the carbonization of coker feeds and pitch, the carbon atoms are present in distorted layers of condensed benzene ring systems formed by the polymerization of the aromatic hydrocarbons in these materials. X-ray studies of raw coke, for example, show two-dimensional order at that early stage of graphite development (12). As the temperature of coke increases, the stack height of the layer plane increases. The layers are skewed about an axis normal to them, however, and it is not until a temperature of ca 2200°C is reached that three-dimensional order is developed. As the graphitizing temperature is increased to 3000°C, the turbostratic arrangement of the layer planes is effectively eliminated, and the arrangement of the carbon atoms approaches that of the perfect graphite crystal. Depending on the size and orientation of these crystals, the properties of manufactured graphites can be varied controllably to suit a number of critical applications.

The furnace that made the graphite industry possible was invented in 1895 by Acheson (13) and is still in use today with only minor modifications. It is an electrically fired furnace capable of heating tons of charge to temperatures approaching 3000°C. The basic elements of the Acheson furnace are shown in Figure 5. The furnace bed is made up of refractory tiles supported by concrete piers. The furnace ends are U-shaped concrete heads through which several graphite electrodes project into the pack. These electrodes, which are water-cooled during operation, are connected by copper bus work to the secondary of a transformer. The product is placed on a layer of metallurgical coke with its long axis transverse to current flow. Although a cylindrical product is shown in Figure 5, any product shape can be graphitized in the Acheson furnace so long as the product pieces are carefully spaced. This feature of the Acheson furnace makes it extremely versatile. The spacing between pieces may vary from less than a centimeter to several centimeters, depending on the shape and size of the product. With the product in place, a coarsely sized metallurgical coke, called resistor pack, is used to fill the interstices between pieces; most of the heat needed to reach graphitizing temperatures is generated in the resistor material. Once the charge and resistor material are loaded, the furnace is covered with a finer blend of metallurgical coke, sand, and silicon carbide to provide thermal and electrical insulation. Concrete side blocks, usually 0.5–1 m from the charge ends, are used to retain the insulation. The procedure for loading a furnace usually requires one day.

Acheson furnace sizes may vary, depending on the product size and the production rate desired. Typically, the furnace may be 12–15 m by 3–3.5 m. Loads ranging from 35–55 metric tons of product are charged to these furnaces. The transformers used are rated 4000–6000 kW and are capable of delivering up to 60,000 A to the charge. Heating rates are usually 40–60°C/h; the total firing time is approximately three days. At the end of this time, the product temperatures are 2800–3000°C. Total power input varies, depending on the product and load size; for graphite electrodes, total power (energy) inputs average 4.5 kW·h/kg, and total power inputs in excess of 9 kW·h/kg may be used in the thermal purification of nuclear graphites. Following the heating cycle, 8–10 days are needed to cool and unload the furnace. The total cycle time on an Acheson furnace is ca two weeks. The cooling procedure is hastened by the gradual removal of pack with care to leave sufficient cover to prevent oxidation of the product. The insulation and resistor materials are screened to specified sizes and proportions for reuse; new materials are added as necessary. The product is cleaned and inspected prior to being measured and weighed for bulk density and resistivity determinations. If the properties are within specified limits, the product is stored and is ready for machining.

Furnaces other than the Acheson furnace are used commercially but on a much smaller scale and usually for smaller products. For example, electrographitic brushes are graphitized in tube furnaces, wherein a current-carrying graphite tube is the heating element. These furnaces are particularly useful in the laboratory because of the ease with which they can be loaded and unloaded without the need for handling large quantities of

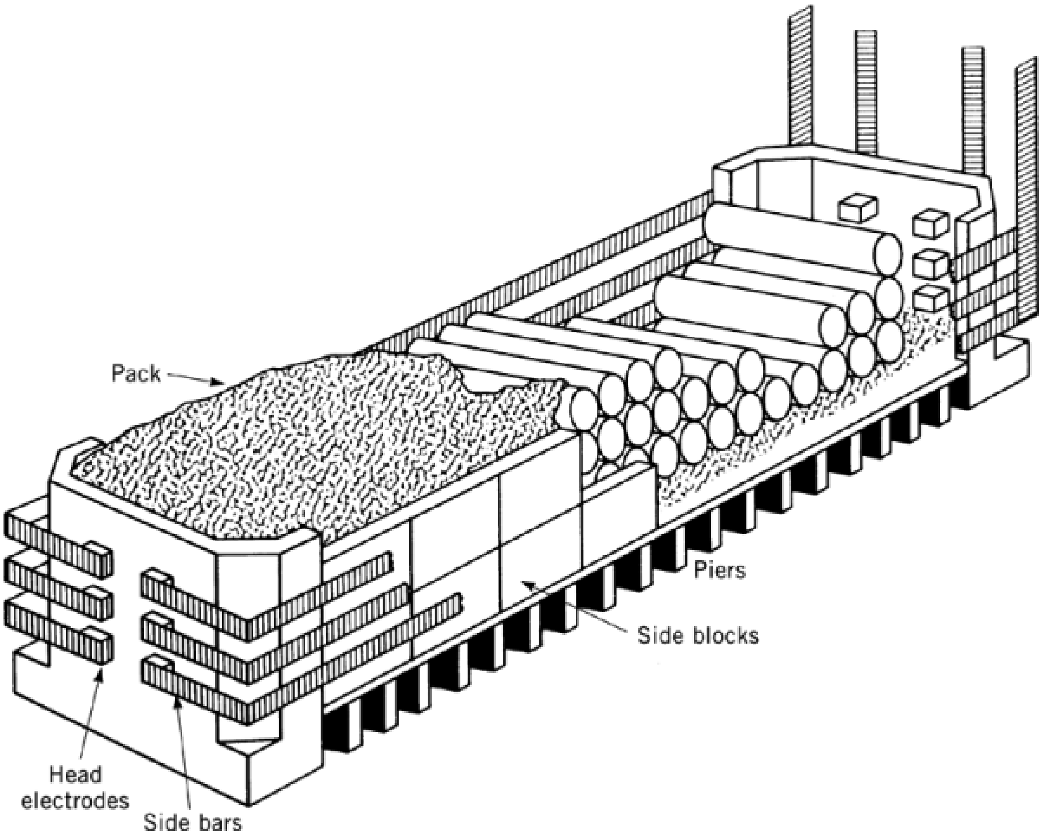

Fig. 5. The Acheson furnace. Courtesy of UCAR Carbon Technology Corp.

packing material. Inductively-heated furnaces are also used commercially to graphitize a limited number of products, such as some aerospace grades and carbon fibers. These furnaces, also popular in the laboratory, consist basically of a cylindrical graphite shell susceptor positioned inside a water-cooled copper coil. High frequency power supplied to the coil induces current to flow in the susceptor, heating it and causing it to radiate heat to the contained charge (see Furnaces, electric).

Several patents (14–18) have been issued describing a process for graphitization where the carbon charge to be heated is placed in a longitudinal array and covered with insulation to prevent heat losses and oxidation of the charge. An electric current is passed directly through the carbon array, generating within the carbon the heat required to raise the carbon to the graphitization temperatures. These furnaces, because of the direct heating of the carbon charge, utilize less than 4.4 kW·h/kg and can be cycled from load-to-reload in less than a week (11).

1.8. Puffing

In the temperature range of 1500–2000°C, most petroleum cokes and coal-tar pitch cokes undergo an irreversible volume increase known as puffing. This effect in petroleum cokes has been associated with thermal removal of sulfur and increases with increasing sulfur content. Some mechanisms other than sulfur removal may be more dominant in coal-tar pitch cokes. Because of the recent emphasis on the use of low sulfur fuels, many of the sweet crudes that had been used to produce coker feedstocks are now being processed as fuels. Desulfurization of sour crudes or coker feeds is possible but expensive. The result is an upward trend in the sulfur content of many petroleum cokes, leading to greater criticality in heating rate in the puffing temperature range during graphitization.

Many studies of the puffing phenomenon and of means for reducing or eliminating it have been made (19–22). As a general rule, puffing increases as particle size increases and is greater across the product grain. Depending on particle size and on the product size, heating rates must be adjusted in the puffing range to avoid splitting the product. Fortunately, the use of puffing inhibitors has eased the problem and has permitted the use of graphitization rates greater than would otherwise be possible.

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Related Articles

Graphite, artificial; Furnaces, fuel-fired; Carbon, Structure, Terminology, and History; Graphite, Artificial; Graphite, Properties of Artificial; Graphite, Applications of Artificial; Graphite, Specialty