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(such as grinding and brazing cracks). "Throw-away-tips" can be rotated or inverted in such a way as to utilize several cutting edges on the same tip; when all are blunted the tip is discarded.

The extraordinarily diversified applications of cemented carbides for which wear resistance is important include, among others, drawing dies (for wire and tubes), mining tools (rotary drills, percussion drills, coal cutters, hard-surface deep-drilling tools), projectile cores, as well as wear-resistant parts in machines and instruments, such as stamping and deep-drawing tools, rolls, nozzles, guides, balls for bearings, valves, extrusion dies and press dies, calkins and, lately, spikes for snow tires.

The application of cemented carbides in the chemical industry (corrosion-resistant parts) and for high-temperature applications (hot-pressing dies, balls and points for hot-hardness testers, clamping devices for high-temperature testing machines, valve seats and valve balls, etc) is, by comparison, not yet very extensive. Cemented carbide-lined cylinders for organic high-pressure synthesis and lately also thrust collars and pistons for the production of synthetic diamonds have been found indispensable for such processes.

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CALCIUM CARBIDE

Calcium carbide, CaC_2, when pure, is transparent and colorless, with a specific gravity of 2.22 at 18°C. It may be prepared in the laboratory by the thermal decomposition under vacuum of pure calcium cyanamide (obtained via dicyandiamide; see Cyanamides) in the presence of carbon according to the equation

$$CaCN_2 + C \rightarrow CaC_2 + N_2$$

to produce an absolutely white calcium carbide. Pure CaC_2 is a rarity, and the general properties of calcium carbide have been determined by extrapolation from values obtained on high-purity commercial carbide.

Commercial calcium carbide varies in color from steel-gray to reddish brown, depending on impurities and the method of manufacture. It is made from lime and coke in an electric furnace at temperatures of 2200–2500°C, using large amounts of electric power. Industrial calcium carbide is about 80% pure; the remainder is calcium oxide and 2–5% other impurities. Its outstanding property is that of reacting with water to produce acetylene according to the following equation:

$$CaC_2 + 2\,H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

Commercial calcium carbide is the main source of acetylene, and acetylene is used principally in the synthesis of a series of organic chemicals, resins, and plastics, and in oxyacetylene welding and cutting of metals. Large amounts of carbide are also made for the production of calcium cyanamide by the fixation of atmospheric nitrogen; the cyanamide is, in turn, used as a fertilizer and as the basis for a series of chemicals and resins. Smaller amounts of calcium carbide are used as a dehydrating agent and as a reducing and desulfurizing agent in metallurgical processes.

History. Calcium carbide was made in the laboratory by early workers such as Hare and Wöhler. It also was formed as a side-reaction product in various industrial processes, but it was not isolated or recognized. Production with electric furnaces on a commercial basis was revealed independently about 1892, by Moissan in France and Willson in the United States; industrial development started in 1895, and expansion proceeded rapidly. The anticipated use of acetylene for illumination did not expand, however, and it was only with the development of cyanamide manufacture from 1905 on, and of the oxyacetylene welding and cutting of metals, that the calcium carbide industry assumed a firm footing. During the First World War there developed a synthetic chemical industry based on acetylene generated from calcium carbide. Today the synthetic organic chemicals industry uses by far the largest portion of the carbide manufactured.

Physical Properties

Crystallography. Commercial calcium carbide occurs in four different crystalline modifications—cubic, tetragonal, and two of a lower order of symmetry. The cubic form, designated CaC_2 "IV," is stable above 447°C, the tetragonal form, CaC_2 "I," is stable between 447 and 25°C, and the form CaC_2, "II," below 25°C; the form CaC_2 "III" is known only as a metastable phase. The tetragonal form, CaC_2 "I," is the one most common in commercial carbide.

Melting Point. The most extensive data on technical carbide are those of Aall (1) who used more than eighty samples in which the calcium carbide content ranged from 4 to 94%. The melting point–composition diagram determined by Aall is shown in Figure 1.

By extrapolation of the two ends of the curve, the melting points of calcium carbide and calcium oxide were indicated to be about 2300 and 2500°C; these melting points checked with previous determinations. The maximum in the center of the curve, at 1980°C, corresponds to a composition of 52.6% CaC_2. By recalculating to a pure CaO–CaC_2 system, taking the 2% impurity content into account, this is equal to

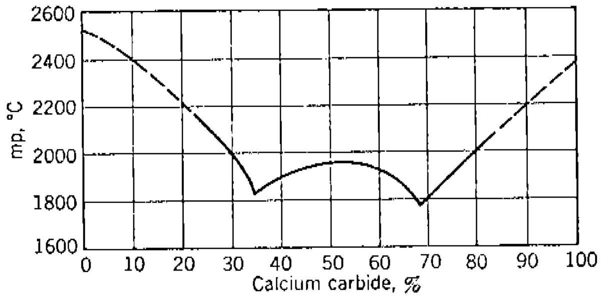

Fig. 1. Calcium carbide–calcium oxide system.

53.6% calcium carbide, a figure very close to 53.3% CaC_2 which would correspond to the compound $CaC_2.CaO$. The flat form of the curve in this part of the melting-point diagram may indicate that the compound is in a partly dissociated condition. The two minima at 1750 and 1800°C with abscissas at 68 and 35% CaC_2, or 69.4 and 36.3% CaC_2 in an impurity-free system, are the two eutectics which $CaC_2.CaO$ forms with CaC_2 and CaO, respectively.

Composition. Microscopic examination of eighteen different samples of the system by Aall showed clearly the three components CaC_2, $CaC_2.CaO$, and CaO in the form of black crystals in a lighter background of the two eutectics. Thus physical, chemical, and optical methods of examination have indicated the presence of the compound $CaC_2.CaO$. This compound is unstable and easily decomposed at temperatures approaching the melting point of the compound. Its heat of formation from CaO and CaC_2 as determined from its heat of solution in dilute hydrochloric acid is 37.4 kcal/g-mole (exothermic).

Specific Gravity. Determination of the specific gravity diagram (by the pycnometer method) on this series of compounds by Aall, confirmed the existence of the compound $CaC_2.CaO$ at about 52% calcium carbide with a sp gr of 2.54. By extrapolation of the specific volume curve, the sp gr of CaC_2 was indicated to be 2.155 within an accuracy of 0.8%. The sp gr of commercial calcium carbide thus depends upon its CaC_2 content, and for the 80% commercial carbide the sp gr of the solid at 15°C is 2.28–2.32, and for the liquid at 2000°C, it is 1.85.

Electrical Conductivity. The electrical conductivity of the system CaO–CaC_2 was determined by Aall at 20°C, and the resulting curve indicates a falling conductivity from calcium carbide to that of lime; the two minima with abscissas at 75 and 38% CaC_2 correspond to the two eutectics formed by $CaC_2.CaO$ with CaC_2 and with CaO, whereas the maximum occurs at about the composition of the compound $CaC_2.CaO$. The electrical conductivity of this compound is indicated to be about 0.3 Ω^{-1} cm^{-1}. Aall also showed that the conductivity of carbide increases with the temperature and that this increase is linear. Thus for the pure compound CaC_2 at any temperature, t°C, the conductivity, K_t, is equal to $1.37(1 + 0.0047t)$. The electrical resistivity of commercial 80% calcium carbide at 25°C is about 6–12 Ω and at 1700 and 1900°C it has been reported to be 0.36–0.47 and 0.075–0.078 Ω, respectively.

Hardness. The hardness curve for the CaC_2–CaO system was determined by the Monotron method, in which the load required to press a diamond indenter a standard depth into the specimen is a measure of its hardness. The hardness curve showed a generally rising hardness from that of calcium carbide to that of lime, with smooth maxima at 70 and 36% CaC_2 (corresponding to the eutectics), and a minimum at about 50% CaC_2. This composition again indicated the presence of the compound $CaC_2.CaO$ which had a hardness of 12.5 kg, and a hardness for CaC_2 of 5.5 kg (one-eighth that of granite) was indicated by extrapolation of the curve. Commercial 80% carbide has a hardness of 30–80 Bhn.

Chemical Properties

Thermal Data. The theoretical heat of formation of calcium carbide, based on the heats of reaction of CaO, CO, and CaC_2, has been calculated as 111.3 kcal/g-mole. For 100% CaC_2 the latent heat of fusion is reported as 120 cal/g and the average specific heat between 0 and 2000°C as 0.28 cal/(g)(°C). For other grades of carbide this data must be corrected with regard to the lime and impurities content. At 25°C the heat content is given as $\Delta H_{298} = -14{,}100$ cal/g-mole and the free energy of formation as $\Delta F_{298} = -14{,}560 \pm 1200$ cal/g-mole.

Reactions. *With Water.* This is one of the most important chemical reactions of calcium carbide; it is highly exothermic and is the source of most of the acetylene used in industry. The reaction equation is given below.

$$CaC_2 + 2\ H_2O \rightarrow C_2H_2 + Ca(OH)_2 + 29.9\ \text{kcal}$$

With a deficiency of water or in the presence of partially slaked carbide, the following reaction occurs:

$$CaC_2 + Ca(OH)_2 \rightarrow C_2H_2 + 2\ CaO$$

This reaction proceeds slowly at ambient temperatures but at about 100–120°C it is stoichiometrically complete in 3–4 days. At still higher temperatures (above about 150°C) the generated acetylene partially decomposes to form acetylene polymers which coat the carbide particles and slow or stop the reaction. This explains the relatively small acetylene loss from hot carbide pigs cooling in humid atmospheres.

With Nitrogen. Another important reaction of calcium carbide is that with nitrogen which produces cyanamide according to the following equation:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C + 70.7\ \text{kcal}$$

The product, which contains about 10% carbon plus the impurities originally present in the carbide, is a gray-black sintered mass known as industrial cyanamide. The reaction is carried out at 1000–1200°C by passing nitrogen through more or less finely crushed carbide heated electrically to initiate the reaction; as the reaction is strongly exothermic it proceeds by itself after the initial ignition.

Miscellaneous. Other reactions of practical importance are those which use the reducing properties of calcium carbide. Examples are the manufacture of calcium silicide, the Murex process for the reduction of magnesium oxide, the reduction under high vacuum of zinc oxide, and the deoxidation and desulfurization of iron, cobalt, manganese, etc. Another interesting reaction is that producing calcium hydride from calcium carbide previously ground under an argon atmosphere and then heated to 500–800°C in a stream of hydrogen. Methane and ethane are also produced in this reaction, whereas at lower temperatures and pressures and high hydrogen flow, acetylene is the only gas formed.

Manufacture

In principle the manufacture of calcium carbide is simple and has changed little since it was first developed in 1892. A mixture of lime and carbon heated in the intense heat of the electric arc reacts according to the following equation:

$$CaO + 3\ C \rightarrow CaC_2 + CO - 111.3\ \text{kcal}$$

The carbide formed is in the liquid state and contains an excess of lime and a large part of the impurities which were present in the raw materials. The carbon monoxide escapes through the furnace charge.

RAW MATERIALS

The basic raw materials used in the manufacture of calcium carbide are limestone and coal or coke. Since there is little elimination of impurities in the smelting process, the use of high-grade raw materials is essential. Most manufacturers calcine their own limestone so that the lime reaches the furnace with a minimum of slaking or formation of fines because of handling. The lime may be burned in rotary kilns or in vertical shaft kilns. A limestone of high quality should be used, with a minimum of 95–97% $CaCO_3$, a maximum of 1% MgO, 1–1.5% SiO_2, 1% Fe_2O_3 plus Al_2O_3, 0.006% phosphorus, and 0.1% sulfur. The structure of the stone also is important so that a lime sufficiently strong for handling with a resulting minimum of fines may be produced. Lime to be used in closed carbide furnaces is generally screened to eliminate undersize materials which might interfere with the evolution of carbon monoxide during the smelting process. In the case of shaft-kilned calcined limestone it may be necessary to crush the lime to obtain the 1.5–2 in. size best suited for the carbide furnace.

Various materials may be used as a source of carbon, such as metallurgical coke, petroleum coke, and anthracite; the former being the most common and petroleum coke being desirable due to its low ash content and high resistivity. The choice of a particular carbon depends upon its price and impurity content. In North America metallurgical coke is the major source of carbon; in Europe anthracite may comprise up to 20–30% of the carbon requirement, whereas in the U.S.S.R. up to 75% anthracite is said to be used. This latter is a "soft" anthracite having a low ash and volatile matter content and a sp gr no greater than 1.45. If the moisture content of the carbon is more than about 2–5% it should be dried before mixing with the lime to prevent slaking and the formation of fines. The screen size of coal and coke is usually somewhat smaller than that of lime.

Effects of Impurities. Of the impurities present in the charge to the carbide furnace, silica usually is present in the greatest amount. Part of the silica may be volatilized as silicon and later reoxidized in the cooler parts of the furnace; some is reduced and combines with the iron present to form a ferrosilicon alloy or with carbon to form silicon carbide. A large proportion combines with lime to form a low fusion point calcium silicate. Iron and aluminum oxides behave alike in being reduced to the ferrosilicon phase, although the greater proportion of iron oxide and relatively little alumina are so reduced; the remainder of the alumina forms a soluble calcium aluminate. Magnesia, on the other hand, is 80–90% reduced to metallic magnesium and is flushed from the smelting zone by the evolved carbon monoxide; later it is reoxidized in the cooler parts of the furnace. Sulfur and phosphorus in the charge largely remain with the carbide as calcium sulfide and calcium phosphide.

The carbide impurities consume power in the smelting process and tend to distill off, being reoxidized and forming crusts near the top of the charge or around the cooler parts of the reaction crucibles. These crusts can cause trouble in furnace operation. Large amounts of dissolved calcium silicate, and aluminate, may form a viscous melt and cause difficulties in tapping the carbide. The ferrosilicon settles out below the molten carbide and, though part of it is removed when the carbide is tapped, the accumulation of a large pool in the furnace can result in attack on the furnace refractory or on tapping pots or chills when the carbide is tapped. Attempts to remove ferrosilicon through a separate taphole have not been successful. It is commonly removed from the crushed and screened carbide by electromagnets, but these may be inefficient if the ferrosilicon has low magnetic permeability. Thus, of the impurities present, calcium silicate and aluminate reduce the CaC_2 content of the carbide; ferrosilicon later may cause trouble by blocking the screens of wet acetylene generators, whereas calcium phosphide and sulfide may be of concern as they can form phosphine and hydrogen sulfide when acetylene is generated.

FURNACE DESIGN

Although little change has occurred in the principles that underlie carbide manufacture, important progress has been made in the electric furnaces and auxiliary equipment used in its production. These improvements include the general adoption of three-phase current and an improved design of the secondary bus, thus reducing the reactance losses (the bus connects the transformers to the electrode clamps). The process is now continuous; the molten carbide is tapped from the furnace either intermittently or continuously. Carbon or graphite prebaked electrodes have been replaced largely by Soderberg, continuous, self-baking electrodes. Submerged electrode clamps (below the furnace cover) have permitted more efficient electrode contact and have minimized electrode breakage caused by thermal shock. Most open furnaces from which the evolved carbon monoxide was burned above the charge have been superceded by "closed" furnaces from which most of the carbon monoxide furnace gas is collected, cleaned, and used. Rotating or oscillating hearth furnaces have been introduced and these are said to maintain steadier electrode penetration and a more uniform charge crucible around the electrodes. Multiple-taphole furnaces from which the carbide is removed from a particular taphole on a regular cycle are becoming common and these help maintain more uniform furnace conditions and electrode positions in the charge. These and other improvements have made possible a steady increase in furnace capacity from the early ingot-type series furnace of 200–300 kW to the present-day, three-phase tapping furnace of 50,000 kW, capable of producing up to 400 tons of carbide a day.

Although the early carbide furnaces were true arc furnaces, they have evolved into submerged-arc furnaces in which the ends of the electrodes are from 2 to 4 ft below the surface of the charge. A large part of the heating is thus caused by the resistance of the unsmelted charge. This charge cover acts as a preheating zone, serves as a thermal insulator for the submerged arc, and contributes to the present-day, relatively high efficiencies of the larger furnaces. Comparatively low voltages of from 75 to 250 V with currents of 50,000–125,000 A at 0.80–0.95 power factor are characteristic of modern carbide furnaces.

The furnace itself is usually of simple construction, consisting of reinforced steel sidewalls and bottom. The sidewalls are lined with several layers of ordinary refractory brick and are usually slightly tapered toward the bottom. The bottom is covered with a hearth made of carbon blocks or rammed anthracite paste above refractory brick; the tapholes are placed just above the level of this hearth. The shape of the furnace shell varies with the type of furnace—ie, rectangular to circular depending on the electrode arrangement. The large furnaces use three-phase current and have three vertical electrodes suspended within the furnace shell. In older furnaces the electrodes were in line, whereas in present-day practice they are in the form of a triangle. The former arrangement dictated a rectangular furnace shell; the latter permits a circular or a triangular shell with rounded angles. Since most of the smelting takes place in cruciblelike zones around and below the electrodes, the remainder of the lime–coke charge outside these zones acts as the main refractory and insulator for the furnace. Thus the dimensions of the furnace shell are determined by the electrical energy input and the thickness of the charge insulation necessary to maintain a reasonable thermal efficiency. A large modern carbide furnace is shown in Figure 2 (2).

Types of Furnaces. There are two basic types of carbide furnaces: (*1*) the open furnace, in which the carbon monoxide burns to carbon dioxide when it comes in contact

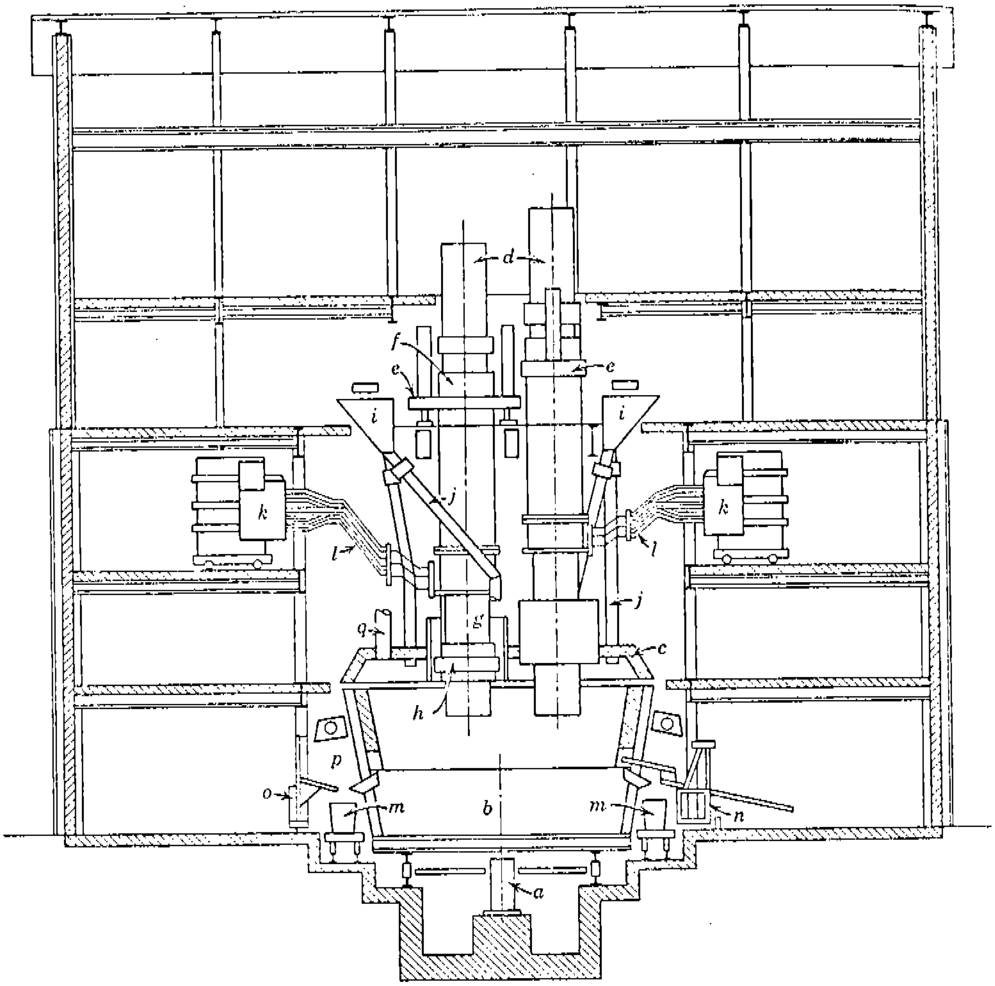

Fig. 2. A 250 ton/day carbide furnace. The furnace rests on the furnace rotating mechanism *a*; the crucible *b* is built of brickwork and is closed with the furnace cover *c*. The Soderberg electrodes *d* can be moved with a hydraulic lifting device *e*. They are fitted with an electrode slipping device *f*. The contact shoes *g* provide the power connection to the electrodes. They are, contrary to conventional design (contact shoes outside of the cover), designed as low-position shoes; this affords some electrical advantages. The Soderberg electrodes are supported by a clamp ring *h*. The raw materials from the feed bunker *i* are conveyed to the furnace by feed chutes *j*. The single-phase transformers *k* may be in delta arrangement thereby giving a more favorable cos ϕ. The secondary leads *l* are connected to the electrodes. In place of the tapping receivers *m*, tapping channels or cooling drums may be used. During tapping with the tapping device *n* the working crew is protected by the tapping screens *o*. Fumes are removed by the hood *p*, and gases from the furnace are taken out through the tubes *q*; it is not necessary to erect a stack. Courtesy *Chemie-Ingenieur-Technik*.

with freely accessible air above the charge; and (*2*) the closed furnace, from which air is excluded and the gas is collected from the furnace. In the open type of furnace a hood, connected to a stack, is usually provided above the furnace to remove the hot gases and dust. In the closed furnace, brick-lined sidewalls may or may not be extended up above the charge level to a water-cooled cover which contains electrode ports and charge hoppers. The electrode ports are sealed and insulated with refractory to prevent current transfer to the cover, and the charge hoppers are kept filled with mix to prevent access of air. Gas pressure under the furnace cover is regulated by means of blowers and pressure regulators; special precautions must be observed in the gas collecting and scrubbing to ensure that no explosive mixture with air is formed.

Electrodes. Prebaked, square or rectangular, amorphous-carbon electrodes were first used in the industry and are still used to some extent. Their use results in a short stub or butt as the electrode is consumed, and thus only a fraction of the electrode can be used. These were replaced with round graphite electrodes which may be joined by threaded connecting nipples. As the electrode is consumed it is slipped in its holder and new lengths of electrode are threaded on at the top. Thus no butts remain to be discarded.

Today most furnaces of large capacity use Soderberg, continuous, self-baking electrodes. Their use involves pouring a hot premixed paste of coal tar and calcined anthracite into a sheet-metal electrode casing which forms an upper extension of the actual electrode in the furnace. As the electrode is consumed in the furnace and the casing and the green paste approach the electrode contact clamps, the paste is heated by the electric current. The volatile matter in the coal tar is decomposed and, as the contact area is reached, the paste is baked into a hard, monolithic, amorphous-carbon mass.

The manufacture of Soderberg paste, though essentially a simple process, requires close control of the aggregate and binder to obtain optimum mechanical and electrical properties in the baked electrode. Paste aggregate consists of good grade anthracite coal which first is calcined in an electric furnace to increase its electrical conductivity. The screened, calcined anthracite, varying in size from $\frac{1}{2}$ in. to -200 mesh, is added to a coal tar–pitch binder having specified chemical and physical properties, contained in a steam-jacketed mixer. After thorough mixing the hot green paste is either transferred directly to the electrode casing or poured into block molds to solidify. These blocks, without preheating, may later be positioned in the electrode casing, in which case preheated air is directed down the electrode dust shield to soften the paste. The casing consists of 4–6.5 ft high annular sections of 12–20 gage steel sheet; inside there are radial fins of the same gage running the length of the section. As the electrodes are consumed in the furnace the electrode and casing must be slipped in the clamps to maintain a proper electrode penetration of the charge. This brings a section of the electrode containing the green paste closer to the clamp, preheats it and at the same time completes the baking of the lower sections of electrode opposite and somewhat below the clamp. As the electrode continues to be consumed and lowered, additional sections of casing are welded on at the top, and additional amounts of green paste are added. Thus a continuous, self-baking electrode is formed.

The electrodes are slipped in their holders about every four hours, or automatically at much shorter intervals, to ensure uniform heating and baking of the paste. Two Wisdom ribbons are sometimes used to support the electrodes partially during the slipping operation. The ribbons are coils of light-gage steel, which are welded progressively to the electrode casing as it is lowered; as these coils are unwound the electrode slips through the electrode clamps. To maintain clean contact between the clamps and electrode casing, a "dust shield" or concentric shell delivers clean air around the electrode for a few feet above the clamps. The electrode and contact clamp assembly may be suspended from several cables connected to motor-operated winches. These are used to adjust the electrode position in the furnace charge; they may be controlled either manually by push-button or automatically to maintain a constant current load on each electrode. Upper and lower limit switches restrict excessive electrode movement which might damage equipment or aggravate furnace upsets.

A more recent type of slipping device uses four hydraulic lifts surrounding the electrode; they are located above the dust shield with their axes vertical and spaced 90° to one another. These lifts work in opposite pairs and support the electrode by means of a removable, reinforced, sectional channel ring attached to the top section of the electrode casing. By means of each pair of lifts the electrode may be partly supported and slipped in its contact clamps, or the lifts may be used to raise the electrode relative to the clamps and thus decrease the electrode penetration in the charge. The lifts are located on a heavy-section platform, which in turn is elevated or lowered hydraulically. The method thus exerts positive control of electrode position and is very versatile.

Electrical Connections. The electrical current is carried from the transformers to the furnace by means of solid copper or water-cooled tubular bus bars, interlaced to minimize reactance losses. This compensation is continued from the fixed bus to the electrode contacts by arrangement of the flexible leads which, together with the contact clamps and clamp supporting ring, are water-cooled. This design has helped reduce total reactance losses in the circuit to about 700–1200 $\mu\Omega$ for 25,000-kW furnaces.

FURNACE OPERATION

The lime and coke are proportioned from stock bins by automatic weighing scales or weighing belts. This charge generally receives sufficient mixing in the weighing and subsequent handling to the mix bins above the furnace so that no special mixing equipment is necessary. The theoretical carbide equation calls stoichiometrically for 56 parts calcium oxide and 36 parts carbon but, because of the impurity content of the raw materials and because there is usually from 15 to 20% excess CaO in the carbide, the actual proportion of lime used is somewhat greater. The ratio of lime to coke charged to the furnace is adjusted according to the purity of the raw materials, the operating characteristics of the furnace, and the grade of carbide desired.

The level of the charge in the furnace is controlled by adding fresh mix every few minutes to open furnaces, or continuously to the closed furnaces. In the open furnaces the fresh charge must be rabbled around the electrodes to replace the charge descending to the reaction zones; for the closed furnaces the charge is delivered by feed pipes located above and around the electrodes. At the surface of the charge the coke and lime are heated only by the escaping gases. As the charge descends it becomes progressively hotter and from 10 to 12 in. below the surface it is hot enough to carry an appreciable part of the current from electrode to electrode. About 36–40 in. below the surface the charge reaches the electrode tips where, at a temperature of 1600–2000°C, it is conductive but not hot enough to melt the lime. Below the level of the electrode tips the mix is still solid and granular for a further depth of 10–20 in.; a shallow cavity in the form of an inverted cone exists under each electrode. About 10–20 in. below the electrode tips the temperature is hot enough to melt the lime (2200–2500°C); the coke does not melt but does react with the liquid lime to form liquid calcium carbide and carbon monoxide gas. The liquid calcium carbide dissolves in more liquid lime to form a dilute carbide which drips through the coke toward the furnace hearth. As the dilute carbide percolates downward the lime diluent reacts with the coke to form a richer carbide. This reaction continues to the level of the taphole, and this zone is filled with solid coke and liquid CaC_2–CaO—the closer the taphole level is approached the higher the CaC_2 content in the mixture. In intermittently tapped furnaces this liquid carbide will completely fill the spaces between the coke particles to a depth of 10–15 in. Here the reaction between the lime of the carbide and carbon of the coke continues, with the evolved carbon monoxide bubbling up through the liquid carbide. The ease with which the furnace gas escapes has an important bearing on the smooth operation of the furnace. Easy access by the gas through open and numerous alternative paths results in low gas velocity and little chance of entraining liquid lime and carbide. On the other hand, if the escape of gas is difficult, such as may be caused by the use of fine raw materials or by crusts of condensed impurities, the escaping gas velocity will be high and the danger of liquid entrainment will be increased. This entrainment causes further reduction of the escape paths for the gas, further increase in gas velocity and pressure and if it continues to build up may result in a "blow" in which either liquid or dry mix is ejected from the furnace. Below the taphole level the spaces between the coke particles are filled mostly with ferrosilicon; the ferrosilicon may extend a foot or more below the taphole, depending upon the extent to which the bottom of the furnace has been eroded by the lime.

An evenly operating furnace is essential for the efficient production of carbide. Smooth operation is indicated by (*1*) steady electrode penetration of the charge as indicated by the distance of electrode tip above the taphole, (*2*) regular descent of the mix through all charging chutes, and (*3*) regular tapping of a tonnage of carbide equivalent to the power input to the furnace. These steady conditions are attained by maintaining standard operating procedures which include (a) frequent and adequate tapping of carbide, (b) constant electrical conditions, such as constant and equal electrode currents, voltages, and hence power input, and (c) a constant coke to lime ratio in the mix charge to the furnace.

Tapping. Carbide furnaces are operated continuously with more or less continuous addition of the charge, but they may be tapped either continuously or intermittently. There may be one taphole per furnace, but many modern furnaces have a taphole opposite each electrode; some have as many as nine tapholes. It has become more or less standard custom to tap from each of the three tapholes in turn, usually at 20–40 min intervals, thereby maintaining an even temperature profile and uniform charge crucibles about the electrodes. The taphole is usually opened with a tapping electrode connected by separate bus to one of the furnace transformers, or to a separate tapping transformer. The tapping electrode is a 3–4 in.-diameter graphite electrode in a clamp; it is manipulated up to and about the taphole with a long wooden handle. When the tip of the electrode is applied to the hot solidified carbide in the taphole, a circuit is completed with the electrodes in the furnace, and sufficient heat develops in one to two minutes to melt the carbide and establish the flow from the furnace. Intermittently tapped furnaces should be drained to a uniform level which usually takes from five to ten minutes. If tapping difficulties occur, a pneumatically operated two-inch metal ram may be driven through the taphole to establish a drainage channel for the carbide from the back parts of the furnace, or the solid carbide in the taphole may be burned out with an oxygen lance. To plug the taphole a shovelful of cold, crushed carbide may be thrown in the taphole and rammed with a metal plugger, or a water-cooled conical plugger may be used.

Material and Energy Requirements. Material requirements per ton of carbide vary within moderate limits. On the basis of 95% available CaO in the lime and 88% fixed carbon in the coke, the coke-to-lime ratio required to produce 80% carbide (4.80 ft³ acetylene/lb) is about 0.57, or about 2100 lb of lime and 1200 lb of coke/ton of carbide. Electrode consumption varies from 35 to 65 lb/ton carbide. Theoretical power requirements per ton of calcium carbide are calculated to be about 2200 kWh, but in actual practice, due to various heat losses, about 2800–3100 kWh is required. Power requirements for a 25,000-kW furnace have been analyzed as follows (3):

formation of calcium carbide	49.9%
reduction of oxides	4.1%
heat of fusion and sensible heat of the tapped carbide	24.6%
sensible heat of furnace gases	1.4%
electrical losses	10.1%
gas off-takes and piping losses	3.6%
furnace radiation losses	6.3%

For every ton of 80% carbide produced, about 10,000 ft³ (at 15°C) of furnace gas is evolved; the gas analyzes 75–85% carbon monoxide, 5–12% hydrogen, and the remainder N_2, O_2, CO_2, and CH_4.

PRODUCT HANDLING

The carbide is tapped from the furnace in a fluid stream at a temperature of 1900–2100°C but, due to its very low thermal conductivity, it can be tapped directly into cast-iron chills, even though the melting point of cast iron is lower (1200–1400°C). Methods of handling the fluid carbide vary: (a) It may be cast into chills capable of containing one complete tap, which yields a pig weighing up to 5 tons. (b) It may be cast into smaller chills positioned on a tapping wheel, thus producing pigs weighing about 200 lb. (c) It may be tapped into self-discharging tapping conveyors. (d) The carbide may be continuously tapped into a slightly inclined water-cooled rotating cylinder. In methods c and d the carbide is ready for crushing upon discharge from the conveyor or cylinder; in methods a and b the pigs must be cooled up to several hours before removal from the chills, and then cooled an additional 24–30 hr before being crushed. All methods are used, but the continuously tapped, water-cooled equipment seems to find favor in the newer installations.

Crushing and Screening. The carbide, if cast in large pigs, is first processed on a breaking table and then in a large-jaw or gyratory crusher in which it is reduced to pieces about 3 in. or less, in size. It then is passed to a crushing and screening plant where a series of finer crushers and screens successively reduce the size and screen out the carbide according to definite screen-size designations. Magnetic pulleys or cross-belt magnetic separators remove the bulk of ferrosilicon metal formed in the carbide reaction, and the carbide is packed immediately in drums or cans. The cans are usually made in the carbide plant from thin-gage steel sheet, and they have a screw top and dummy cover to ensure waterproofness. The drums have gasketed, clamp-bolted covers.

Table 2. World Production of Calcium Carbide and Manufacturing Capacity, short tons[a]

Continent and country	Production 1936	Production 1959	Capacity 1936	Capacity 1959
North America				
Canada	230	350[b]	375	550
United States	160	1,020	175	1,200
Total[c]	*420*	*1,400*	*575*	*1,875*
Europe				
Czechoslovakia	28	77	44	110
France	138	383	385	440
Germany	785	2,080	1,000	2,200
Great Britain		192		250
Italy	172	354	385	440
Norway	64	68	175	182
Poland	46	280	210	310
Rumania	4	155	33	165
Spain	17	89	44	132
Sweden	39	87	44	127
Switzerland	22	83	110	110
U.S.S.R.[c]	120	550	88	660
Yugoslavia	36	73	100	100
Total[c]	*1,490*	*4,470*	*2,750*	*5,500*
Asia				
China[c]		232[b]		265
Formosa		100[b]		100
Japan	360	1,100[b]	800	2,040
Korea		165[b]		187
Total[c]	*360*	*1,650*[b]	*800*	*2,700*
Africa				
Total[c]	*17*	*88*	*28*	*110*
Australia				
Total[c]	*8*	*11*	*11*	*17*

[a] Thousands of tons. [b] Figures are for 1958. [c] Estimated.

acetylene generated from the carbide may make this carbide process economic as a raw materials source for chemical synthesis.

Other minor uses for carbide continue to be developed.

Uses

By far the largest use for carbide is in the production of acetylene (qv). A small part of this acetylene (currently about 20%) is used for oxyacetylene cutting and welding; the carbide used for this purpose comprises most of the carbide packed in drums. Companies producing compressed gas, the largest users of the packed carbide, are strategically located near the acetylene users to minimize freight costs on the gas cylinders. Other carbide customers use the generated acetylene in their own plants for welding, or for illumination in the case of some remote plants and in mines. By far the greater part of the acetylene generated is produced in the plant of the carbide manufacturer. The carbide goes directly from the crushing and screening plant to the gas generation plant, and thence, after purification, to the synthesis of organic chemicals such as acetaldehyde, acetic acid, acetic anhydride, vinyl acetate, polyvinyl compounds, butanol, and chlorinated derivatives.

Another important use of calcium carbide is in the production of cyanamide, where it serves as a nitrogen fixative. Cyanamide, $CaCN_2$, is used as a fertilizer and as a raw material for the production of a series of nitrogenous compounds of which dicyandiamide, guanidine, and melamine are the most important.

Carbide is used in metallurgy as a desulfurizing and deoxidizing agent, as a nodulizing agent in the production of nodular graphite in iron, and as a finishing-slag component in ferrous and nonferrous refining. It is also used in certain industrial processes as a reducing and dehydrating agent.

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SILICON CARBIDE

Silicon carbide, SiC, formula weight 40.07, is a crystalline material varying in color from nearly clear, through pale yellow or green, to black, depending upon the amount of impurities. Green hexagonal plates of silicon carbide have been reported occurring naturally in the meteoric iron of Cañon Diablo, Arizona, and given the mineral name Moissanite after Henri Moissan, but, apart from this, it is a synthetic substance. The commercial product, made in electric furnaces, is usually obtained as aggregates of iridescent crystals. The iridescence is due to a thin layer of silica produced by superficial oxidation of the silicon carbide. This layer can be removed by washing with hydrofluoric acid. The loose grain of commerce is prepared from the manufactured product by crushing and grading for size; it is black or green in appearance.

The abrasive and refractory industries are the largest users of silicon carbide. It is also used for heating elements in electric furnaces, in electronic devices, and in applications where its resistance to damage by nuclear radiation is advantageous.

In 1891 Acheson produced a small amount of silicon carbide while conducting experiments with the aim of obtaining a hard material from the reaction of clay and carbon (1). He passed a strong electric current from a carbon electrode through a mixture of clay and coke contained in an iron bowl, which served as the second electrode. Acheson recognized the abrasive value of the crystals obtained, had them analyzed, found the formula to be SiC, incorporated The Carborundum Company in September 1891, and filed application for a patent (2) on May 10, 1892.

Reference is sometimes made to earlier work on compounds of carbon and silicon, particularly that of Colson and Schutzenberg, who were working on oxycompounds (3). They reported tetratomic radicals of silicon ($Si_2C_2O_2$, Si_2C_2N) in 1881, and Colson, in 1882, reported carrying one reduction to completion, obtaining SiC_2. Ten years later, Ref. [illegible]. The Louisville Air Pollution Study. USDHEW, Public Health Service. Cincinnati, Ohio. 1961.

FEB '73
Ch 8 Sec 8.4
Ref. 3

Calcium Carbide +

Calcium Carbide Calculations

1. 420 Tons/day Calcium Carbide.
2. 9x10⁶ cu ft/day Acetylene.

#/ton

Pollutant	~~Main stack~~ Coke Drier (cyclone + spray Chamber)	Electric Furnace ~~Hood~~ NO control	Furnace ~~room vent~~ Room Vents No control	Main Stacks Impingement Towers
Acetylene	—	—	1.8	—
H_2S	—	—	—	—
SO_2	0.1	~~t~~ —	—	1.9
SO_3	0.2	—	—	0.8
Particulate	0.2	1.7	2.6	2.0

Acetylene #/10⁶ cu. ft. of Acetylene

POLLUTANT	~~Hopper~~ Charging	Slurry pit and Tails Pond
Acetylene	174	330
H_2S	0.06	27

Data from Ref. 306

COKE DRYER following cyclone & spray wet collectors

Part = $\frac{(147)(2000)}{(365)(420)}$ 1.9

SO_3 = $\frac{(155)(2000)}{(365)(420)}$ = 2.02

$SO_2 = 1/2\ SO_3$

Elec. furnace hoods

Part = $\frac{(1340)(2000)}{(365)(420)}$ = 17.5

Furnace vent

Acet $\frac{(1370)(2000)}{(365)(420)}$ = 17.9

Part $\frac{(2000)(2000)}{(365)(420)}$ = 26.1

Main Stack following wet imp. scrubber

SO_3 = $\frac{(60)(2000)}{(365)(420)}$ = 0.78 $SO_2 = 2\ SO_3$

Part $\frac{(1520)(2000)}{(365)(420)}$ = 19.8