CALCIUM CARBIDE

1. Introduction

Chemically pure calcium carbide [75-20-7], is a colorless solid; however, the pure material can be prepared only by very special techniques. China is the world's largest producer of calcium carbide. Commercial calcium carbide is composed of calcium carbide, calcium oxide [1305-78-8], CaO, and other impurities present in the raw materials. The commercial product's calcium carbide content varies and is sold on the basis of the acetylene yield. Industrial-grade carbide contains about 80% as CaC_2, 15% CaO, and 5% other impurities.

Commercial production by the electric furnace method was developed about 1892 by Henri Moissan in France and, independently by T. L. Willson and J. T. Morehead in the United States. The first commercial plant was built ay Spray, North Carolina in 1895. Development of the carbide industry for the generation of acetylene expanded rapidly after that.

Originally acetylene [74-86-2], was used as an illuminant since it burned with a brightness 10–12 times that of coal gas. It later found a use as a fuel gas in oxyacetylene welding and cutting since it developed flame temperatures of 3000°C compared to 1900°C for other gases available at the time. After World War I acetylene became the starting material in the synthesis of a host of organic material such as solvents, plastics, and synthetic rubber. Increased chemical use of acetylene increased demand for calcium carbide (See ACETYLENE-DERIVED CHEMICALS; ACETYLENE). The manufacture of calcium cyanamide from carbide also increased demand. Annual worldwide production of calcium carbide reached a peak of 8000 10^3 t. in the 1960s and has declined steadily since then to about 4700 10^3 t today (at the time of writing). The principal reason for decline was the substitution of acetylene from petrochemical sources (from by-product ethylene production and thermal cracking of hydrocarbons). Other factors include the use of alternative fuel gases replacing acetylene, development of electric welding techniques, and reduced production of calcium cyanamide [156-62-7]. Calcium carbide is, however, used extensively as a desulfurizing reagent in steel and ductile iron production, which allows these manufacturers to use high sulfur coke without the penalty of excessive sulfur in the resultant products. Many countries produce calcium carbide; the largest producer is China.

2. Properties

Table 1 list the more important physical properties of calcium carbide. Additional properties are given in the literature (1). Figure 1 gives the phase diagram calcium carbide–calcium oxide for pure and technical grades.

Table 1. **Physical Properties of Calcium Carbide**

Property	Value
mol wt	64.10
mp, °C	2300
crystal structure	
phase I, 25–447°C	face centered tetragonal
phase II,	triclinic
phase III[a]	monoclinic
phase IV, >450°C	fcc
commercial	grain structure, 7–120 μm
specific gravity, commercial-grade	
at 15°C	2.34
2000°C[b]	1.84
electrical conductivity, technical-grade, $(\text{ohm}-\text{cm})^{-1}$	
at 25°C	3,000–10,000
1000°C	200–1,000
1700°C[b]	0.36–0.47
1900°C[b]	0.075–0.078
viscosity at 1900°C, MPa · s (=CP)	
50% CaC_2	6000
87% CaC_2	1700
specific heat, 0–2000°C, J/mol · K[c]	74.9
heat of formation, H_f,298, kJ/mol[c]	−59 ± 8
latent heat of fusion, ΔH_{fus}, kJ/mol[c]	32

[a] Phase III is metastable.

[b] Material is a liquid.

[c] To convert from J to cal, divide by 4.184.

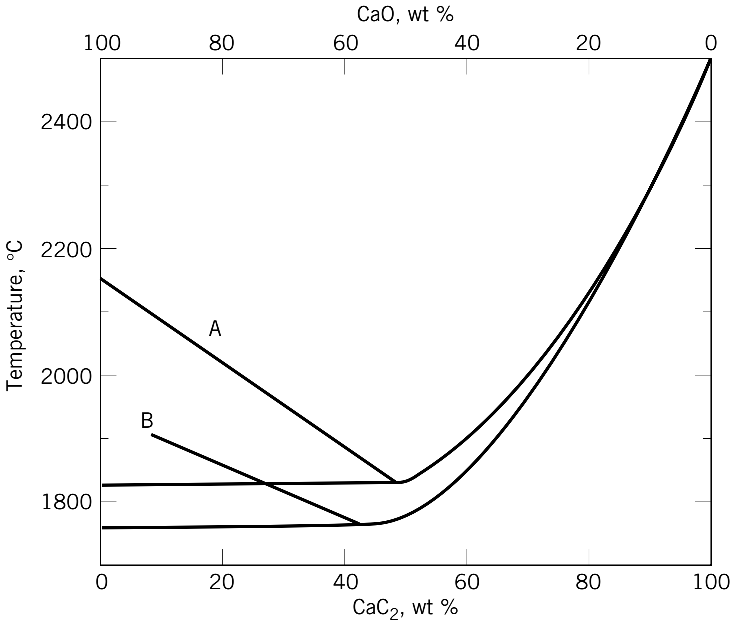

Fig. 1. Calcium carbide–calcium oxide phase diagram using A, pure CaC_2, and B, technical-grade CaC_2.

2.1. Reaction With Water. The following exothermic reaction of calcium carbide and water yielding acetylene forms the basis of the most important industrial use of calcium carbide:

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2 \qquad (H = -130\ \text{kJ/mol}\ ) \tag{1}$$

where H_r = heat produced in the reaction. Wet and dry processes are in use for generating acetylene from calcium carbide. In the wet process, carbide is added to excess water in a generator. Water absorbs the heat of reaction, maintaining a temperature of less than 100°C. A 10% lime sludge slurry is a coproduct. In the dry process, an equal amount of water is added to carbide at a rate such that the heat of reaction evaporates the excess water. The coproduct, $Ca(OH)_2$, containing 2–3% water is a free-flowing powder that can be sold for acid neutralization or soil stabilization. The wet slurry can be used for flue-gas desulfurization at utilities. Both processes yield acetylene of 99.6% purity.

2.2. Reaction With Sulfur. An important use of calcium carbide has developed in the iron and steel industy, where it was found to be a very effective desulfurizing agent for blast-furnace iron. Calcium carbide reacts with sulfur present in the molten metal as follows:

$$CaC_2 + S \longrightarrow CaS + 2\,C \tag{2}$$

Sulfur was controlled in the past in the iron and steel industry by careful selection of raw materials. Since the availability of high-grade raw materials has declined, and in an attempt to maximize production rates, producers have shifted toward external desulfurization using additives such as calcium carbide in a separate step in the reduction process. Desulfurization by using nitrogen gas to inject calcium carbide powders into a ladle or torpedo car is both fast and efficient. Injection using a refractory lance below the metal surface can easily reduce the sulfur content from 0.1% to 0.01%. Other ingredients, such as calcium carbonate or asphaltites, which acts a gas-generating agent; or graphite, which assists in the injection process, are generally added to the desulfurizing reagent. The most modern process employs calcium carbide in combination with magnesium, either as a blend or in a sequential coinjection process. (see SULFUR REMOVAL AND RECOVERY).

2.3. Reaction With Nitrogen.

Calcium cyanamide is produced from calcium carbide

$$\mathrm{CaC_2 + N_2 \longrightarrow CaCN_2 + C} \qquad (H_r = -295\,\mathrm{kJ/mol}) \tag{3}$$

The reaction is carried out in a refractory oven by passing nitrogen gas through finely pulverized carbide at a temperature of 1000–1200°C. To initiate the reaction, the carbide is heated electrically using a graphite electrode located at the center of the charge. Since the reaction is strongly exothermic, it proceeds autogenously. In addition to the batch process, some European and Japanese producers have developed continuous nitrogenation furnaces based on a rotary kiln design. Powdered carbide and nitrogen gas is fed to the kiln and the cyanamide product removed in a granular form.

3. Manufacture and Production

Calcium carbide is produced commercially by reaction of high purity quicklime and a reducing agent such as metallurigical or petroleum coke in an electric furnace at 2000–2200°C.

$$\mathrm{CaO + 3\,C \longrightarrow CaC_2 + CO} \qquad (H_r = 466\ \mathrm{kJ/mol}\ ) \tag{4}$$

Commercial calcium carbide, containing about 80% $\mathrm{CaC_2}$, is formed in the liquid state. Impurities are mainly CaO and impurities present in raw materials. CO is usually collected and used as a fuel in lime production or drying of the coke used in the process. The liquid calcium carbide is tapped from the furnace into cooling molds.

3.1. Raw Materials.

The carbon reducing agent can be metallurgical coke, petroleum coke, anthracite, or charcoal, depending on price and impurities. Metallurgical coke is the most common, because of it's availability. This coke typically contains 85–88% fixed carbon, 9–11% ash, and 2% volatiles. Lime is obtained by calcining limestone in a rotary or shaft kiln. Limestone should contain a minimum of 95–97% $\mathrm{CaCO_3}$. Both furnace raw materials should not contain excessive amounts of dust or fines as this will result in furnace eruptions and unstable operation. In many cases, raw materials are prescreened to remove fines. The collected fines can be reintroduced to the furnace through a hollow electrode feed system.

3.2. Furnace Design. Commercial calcium carbide furnaces have capacities ranging from 25,000 t/y (12 MW) to 130,000 tons/year (50 MW). The majority of furnaces are operated with three-phase current. The electrode arrangement can be either inline, or of a triangular symmetrical configuration. The inline arrangement, due to unsymmetrical arrangement of electrical conductors, causes an inductive effect, which results in a live phase (high power) and a dead phase (low power). The symmetrical arrangement has balanced power to all electrodes.

A cross section of a covered 40-MW furnace is shown in Fig. 2. The shell diameter is 9 m. A taphole to withdraw liquid carbide is located on top of carbon

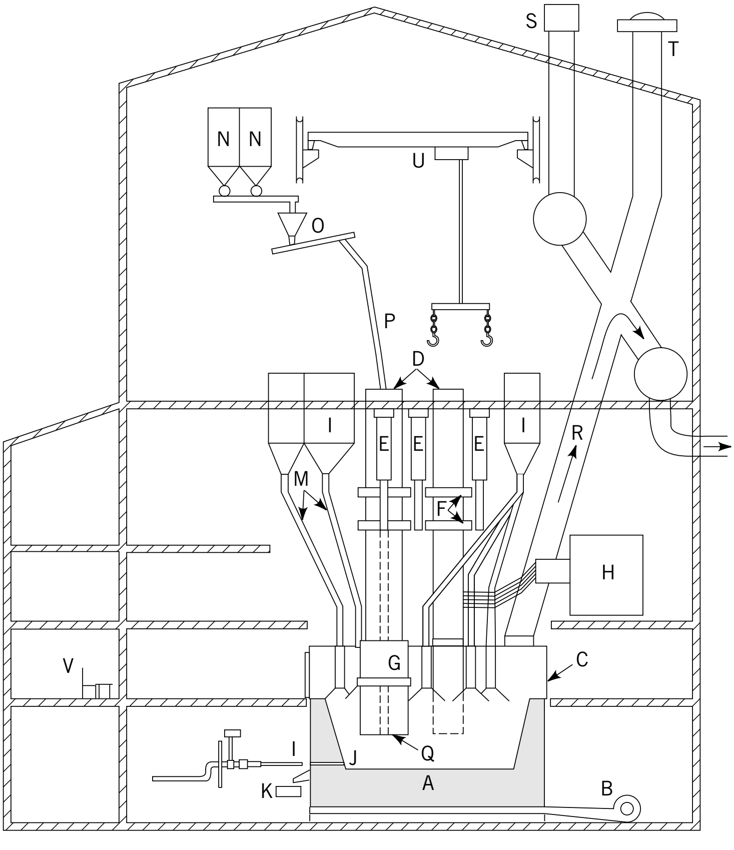

Fig. 2. Calcium carbide furnace. The furnace crucible (a) is constructed of brick sidewalls, a carbon lined bottom; the bottom is cooled by a fan (b). The entire furnace is closed by a cover (c). The Soderberg electrodes (d) are supported and can be moved vertically by hydraulic cylinders (e). They are fitted with a slipping device (f). Contact plates (g) provide power connection to the electrodes from a single-phase transformer (h). A tapping electrode (i) assists the flow of carbide from the taphole (j) to a chill car (k). Raw material is stored in bins (l) and introduced to the furnace through charging chutes (m). Dust raw material is stored in separate bins (n) and fed to the furnace via screw conveyor (o), flexible connector (p), through the hollow electrode (q). Furnace gas is removed through a duct (r). A crane (u) charges fresh electrode paste. An operator monitors operation from a control room (v).

blocks that line the furnace bottom. The furnace cavity is covered with a relatively gastight cover to facilitate CO gas collection. Preweighed raw materials enter the furnace through water-cooled charge tubes. Three electrodes, in a triangular arrangement, enter the furnace through water-cooled sealing devices in the cover. The electrodes are usually of the continuous self-baking Soderberg type with a diameter of 1100–1600 mm. Electric current is bought from transformers by water cooled bus tubes, connecting at the electrode through water-cooled copper contact plates. Each electrode assembly is suspended or supported by hydraulic cylinders, allowing for independent movement and control of electrical current.

Furnaces may be classed as open or closed. Earlier furnaces were open, referring to the fact that the CO gas was allowed to burn open on the surface of the raw-material mix burden. A closed furnace has a sealed cover that allows for 100% collection of the CO gas, which can then be used as a fuel for a lime kiln or drying the carbon reducing agent. Air pollution control requirements are less since only the dust-laden CO gas requires cleaning, compared to the large volume of draft gases from the open furnace. Most modern furnaces incorporate the closed design.

3.3. Electrodes. Furnace electrodes are carbon materials, due to the excellent electrical and thermal conductivity properties of the carbon. Early electrodes were constructed of prebaked carbon pieces fabricated into the electrode shape. Today these have been largely replaced with the Soderberg self-baking electrode (see Fig. 3). This electrode consists of a sheet steel cylinder with vertical ribs filled with Soderberg paste, a formulated mixture of electrically calcined anthracite and coal tar pitch. Heat from the electrical current bakes the green electrode material to form a strong solid baked electrode. As the electrode is consumed in the furnace process, electrode is replaced in a process called "slipping". This is carried out by a pair of hydraulically tightened slipping bands mounted one above the other on the electrode column. The electrode is held by the lower set of bands, allowing the upper set to be raised to a new position. On release of the lower bands, the electrode can be lowered safely using the hydraulic cylinder provided for the upper bands. Normally the electrode is held in the stable position by the action of both bands. New sections of the sheet steel cylinder and electrode paste are added as required.

3.4. Hollow Electrode. Most modern furnaces utilize the hollow electrode feed system. Coke and lime fines, conveyed in a stream of recycle furnace CO gas or nitrogen, can be fed to the furnace through a 10–15-cm pipe channel at the center of each Soderberg electrode. Although the steel pipe melts and disappears in the current carrying zone of the electrode, it remains intact long enough to maintain a continuous opening. Fines delivered to this zone react quickly and provide a valuable tool for adjusting carbide grade and maintaining proper electrical load balance. In addition to the economic gain of utilizing a waste material and eliminating a disposal problem, there is a 30% reduction in usage of electrode carbon. Approximately 15–20% of the total raw material charge can be introduced through the hollow electrodes. It is also possible to recycle calcium carbide dust, which is generated in the carbide crushing process.

3.5. Energy Requirements. Approximately 865 kg of lime and 495 kg of metallurgical coke are required to produce a metric ton of 80% purity calcium

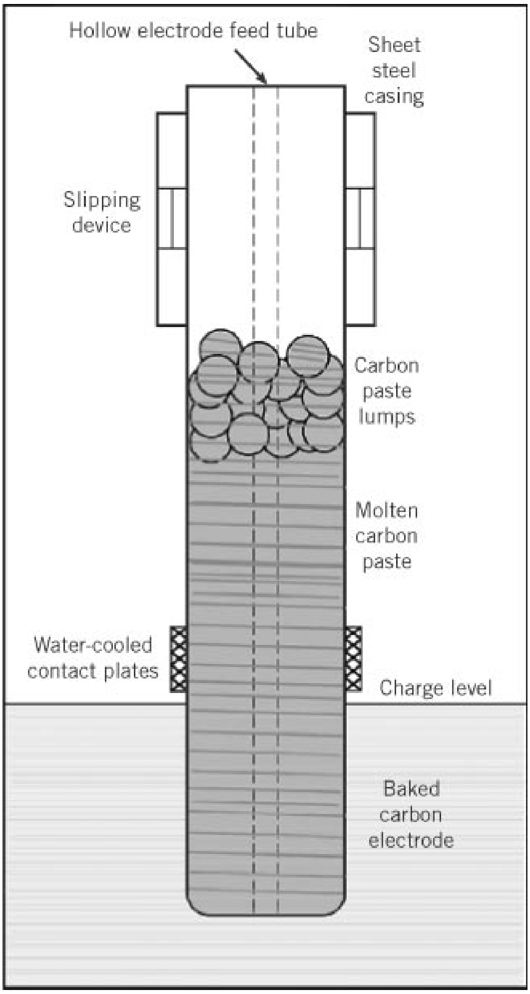

Fig. 3. Soderberg electrode.

carbide. Theoretical energy requirement per metric ton is about 2200 kWh, but because of heat losses, 2900–3300 kWh is required. For every ton of 80% purity carbide produced, about 280 m^3 (15°C) of furnace gas is evolved, which analyzes as 75–85% CO, 5–8% H_2, and the balance as N_2, CO_2, and CH_4. Electrode consumption varies from 10–27 kg/ton of carbide.

3.6. Furnace Operation. In the vicinity of the electrode tip the mix is hot enough to allow the lime to melt. The coke does not melt and the liquid lime percolates downward through the relatively fixed bed of coke forming calcium carbide, which is liquid at this temperature. Both liquids erode coke particles as they flow downward. The weak carbide first formed is converted to richer material by continued contact and reaction with coke particles. The carbon monoxide gas produced in this area must be released by flowing back up through the charge. The process continues down to the taphole level. Material in this area consists solid coke wetted in a pool of liquid calcium carbide at the furnace bottom. The ease with which carbon monoxide can escape from the reaction zone has a bearing on smooth operation of the furnace. The normal furnace charge, consisting of large particles, has a good porosity, allowing a reasonably constant gas flow. Extremely fine material or crusts of condensed impurities impede the escape of gas from the reaction area, allowing pressure to develop and eventually results in "blows" in which hot mix and liquid carbide can be explosively ejected.

Metallurgical coke gives rise to ferrosilicon, which in the liquid phase is more dense than calcium carbide and tends to settle and penetrate the bottom of the furnace. After a lengthy operating period it may extend 30 cm or more below the taphole, eventually reaching the furnace shell, where it causes hot spots requiring repair and replacement of the furnace refractory.

An evenly operating furnace is essential for an efficient process as indicated by steady electrode position, regular descent of mix through all charging chutes, and regular tapping of carbide equivalent to power input to the furnace. These conditions are attained by maintaining standard operating procedures, which include frequent and adequate tapping of carbide constant electrical conditions and hence power input and a constant coke:lime ratio in the mix charge.

3.7. Computer Control. The use of computer control systems to control the operations of submerged arc furnaces, including calcium carbide, has been successfully demonstrated in the United States. Operations directly under control are mix batching, electrode position and slip control, carbide gas yield, power control, and cooling-water systems. Improvements in energy usage, operating time, and product quality are obtained.

3.8. Tapping System. Carbide is tapped from the furnace in a liquid stream at a temperature of 1900–2100°C. Its low thermal conductivity makes it possible to tap directly into cast iron chill molds even though the melting point of the cast iron is lower than that of the carbide. Carbide furnaces can have either a single taphole at one electrode or three tapholes leading to the center of each electrode. With three tapholes, each electrode is tapped in turns at predetermined intervals. Burning through the taphole with a tapping electrode opens the taphole channel. A pneumatic ram bar is also used to poke the taphole at regular intervals and promote the flow of liquid carbide. The liquid carbide is cast into iron chill cars weighing 1–4.5 tons. Following cooling for 24–36 h, the carbide is crushed and screened according to the preestablished sizes that are desired.

4. Grade Specifications

Contracts for acetylene-grade carbide are usually based on size and gas yield specification, with penalties for carbide that fails to meet specified gas yield. In general gas yields range from 280 to 300 L/kg, depending on the screen size of the carbide.

The most important size ranges specified in individual standards are (in millimeters) 0.4–1.7 or 14 ND, 2–4, 4–7, 7–15, 15–25, 25–50, and 50–80. Phosphorus, sulfur, and arsenic levels are determined by analyzing phosphine, hydrogen sulfide, and arsine content of the evolved acetylene according to specified procedures. Gas impurities are typically 0.05% phosphine, 0.15% hydrogen sulfide, and 0.001% arsine.

5. Analytical Methods

Many countries have standards, that specify methods of analysis for gas yield, sieve analysis, and acetylene gas impurities such as phosphine hydrogen sulfide and arsine:

United States	Federal Specification 0-C-101a
Australia	Standards Association of Australia, Publication No. K 49
Europe	Federal Republic of Germany DIN 53922
Great Britain	British Standard 642
India	Indian Standard IS1040
Israel	Israel Standard 267 T (250 × 4) SJ 446
Japan	Japanese Industrial Standard JIS K 1901
Philippines	Philippine standard PNS No. 1991
Mexico	DIN 53922 and Norme Official K 23
South America	Mercosul Standard NM 109:97-Calcium Carbide

Typical analysis of carbide is presented in Table. 2.

6. Shipment and Transportation

Since calcium carbide produces flammable acetylene gas in the presence of water, it is classified as a hazardous material. Each country has developed regulations governing its transport. In the United States these regulations fall under the Department of Transport. In general, calcium carbide is shipped in metal containers, either in bulk bins of up to 4-ton capacity, or in drums ranging in size from 50 to 230 kg. Under certain conditions shipment is allowed in reinforced bulk bags of up to 1-ton capacity. These bags have an advantage of reduced weight of shipping containers. Calcium carbide containers are marked “Flammable solid, dangerous when wet” with the United Nations designation UN 1402.

Calcium carbide for desulfurization is usually sold on the basis of a specified minimum CaC_2 content, together with minimum levels of various additives, and a specified particle size distribution. This can vary considerably according to the

Table 2. **Typical Analysis**

	Calcium carbide
CaC_2	79.0
CaO	13.2
C	0.7
CaS	0.9
mineral impurities (Al_2O_3, SiO_2, MgO, FeSi)	6.2

reagent formulation. Domestic shipments are either in steel tote bins of 2–4-ton capacity, bulk railcars, or trucks with pneumatic unloading capabilities. Containers are usually pressurized slightly with an inert gas such as dry nitrogen to avoid reagent contact with atmospheric moisture and generation of acetylene.

6.1. Environmental Concerns. The major environmental problem in carbide production is the prevention of particulate dust emission. Normally cloth filtration equipment is used in handling of raw materials, at furnace tapping, and product crushing and screening. The carbide furnace CO gas steam can be treated by high temperature cloth filtration, ceramic filters, or wet scrubbers. The dust collected by either wet or dry methods may contain trace cyanide that must be treated before disposal.

The hollow electrode system allows for the use of small coke and lime particles, which could not otherwise be used in the furnace in the main furnace charge. A covered furnace collects all the CO gas generated during carbide manufacture. This fuel gas can provide energy for a lime kiln operation or drying carbon raw materials.

Acetylene generators produce a calcium hydroxide coproduct during acetylene manufacture. In the dry process the powder can be used for acid neutralization or soil stabilization. In the wet process the slurry can be used for flue-gas desulfurization at utilities. If the wet process is used the hydrate is collected in settling lagoons for disposal. The dry process produces a powder hydrate that can be used for flue gas desulfurization or soil stabilization.

7. Health and Safety Factors

The usual precautions must be observed around high-tension electrical equipment supplying power. The carbon monoxide formed, if collected in closed furnaces, is usually handled through blowers, and scrubbers, and thence to a pipe transmission system. As calcium carbide exposed to water readily generates acetylene, the numerous cooling sections required must be constantly monitored for leaks. When acetylene is generated, proper precautions must be taken because of the potential explosiveness of air–acetylene mixtures over a wide range of concentrations (from 2.5%–82% acetylene by volume).

Although acetylene is considered to be a material with a very low toxicity, a threshold value (TLV) of 2500 ppm has been established by NIOSH. In the presence of small amounts of water, calcium carbide may become incandescent and ignite the evolved air–acetylene mixture. Non sparking tools should be used when working in the area of acetylene-generating equipment.

Calcium carbide dust, in the presence of hydrated, lime is a skin irritant. Full garment protection (long sleeves, gloves, long underwear, etc) is usually practiced.

8. Economic Aspects

Generally worldwide production of calcium carbide and calcium cyanamide have declined steadily since reaching peaks in the 1960s. Calcium carbide has fallen

Table 3. **Historical Trends of Calcium Carbide Production, 10^3**

Region	1936	1962	1972	1982	1997[a]
USA, Mexico	145	982	447	350	270
Canada	209	318	73	100	
Europe	1335	4740	4710	3260	1320
Asia	477	1800	2000	2420	2962
Africa	15	60	80	250	90
South America		100	190	220	70
Total	*2181*	*8000*	*7500*	*6600*	*4712*

[a] Estimated

from about 8000 to 4700 10^3 mt/y in 1997 (Table 3). The major reason for decline was due to the substitution of acetylene from petrochemical sources (from by-product ethylene production and thermal cracking of hydrocarbons). This substitution occurred in the late 1960s and early 1970s. Other factors include the use of alternative fuel gases replacing acetylene, development of electric welding techniques, and reduced production of calcium cyanamide. (Prices listed in Table 4).

8.1. North America. There are currently three producers of calcium carbide in North America: The Carbide Graphite Group Inc., Elkem-American Carbide Company in the United States, and Metaloides SA de CV in Mexico (Table 5). There is no production in Canada following the shutdown of Shawbec in Shawinigan, Quebec in 1988 and Cyanamid Canada's carbide plant in Niagara Falls, Ontario in 1992.

Elkem-American and Carbide Graphite supply the domestic U.S. market and exported 33,479 t. in 1995, (3) mainly to Canada. Imports to the United States are relatively low, at 1479 t. in 1995. Metaloides SA de CV supplies the market in Mexico as well as exporting carbide to Central America, South America, and the Caribbean.

8.2. Western Europe. Calcium carbide production has declined from about 2200×10^3 t/yr in the 1970s to about 450×10^3 t/yr today (at the time of writing) (Table 6). The uses are split between calcium cyanamide manufacture, acetylene, and desulfurization reagent.

Table 4. **Estimated Price of Calcium Carbide (FOB plant)[a]**

Country	Price (local currency) per ton	Exchange rate Local Currency per U.S. $	U.S. $ per ton
United States	$500		500
Germany	850 DM	1.80	472
Japan	93,800 yen	125	750
South America			460
South Africa			550
India	21,000 rupees	40	525
Asia	57,500 yen	125	460

[a] Estimated.

Table 5. **Calcium Carbide Producers and Capacity, 1997**[a]

Region	Producers	Estimated annual capacity 10^3 mt	
North America	The Carbide Graphite Group Inc.		
	Calvert City, KY, USA	80	
	Louisville, KY, USA	110	
	Elkem American Carbide Co.		
	Ashtabula, Ohio, USA	110	
	Pryor, OK, USA	35	
	Metaloides SA, Puebla, Mexico	40	
Western Europe	Donau Chemie, Landeck, Austria	40	
	Pechiney Electrometallurgie, Bellegarde, France	60	
	SKW, Hart, Germany	320	
	Odda Smelteverk, Odda, Norway	130	
	Carburos del Cinca, Monzon, Spain	40	
	CEDIE SA , Orense, Spain	30	
	Casco Nobel AB, Sundsvall, Sweden	50	
Eastern Europe	Zakledy Azotowa, Chorzow, Poland	140	
	Bicapa, Tirnaveni, Romania	220	
	Novacke Chemicke, Preividza, Slovak Republic	110	
	Jugorom, Tetovo, Yugoslavia (former)	34	
	Etibank Antalya, Antalya, Turkey	20	
	Russia (several locations)	600	
South Africa	Karbochem, Newcastle	120	
South America	Carbometal SA, Mendoza, Argentina	56	Closed
	Electrometalurgica Andina, San Juan, Argentina	50	
	Companhia Brasileria Carbureto de Calcio, Brazil	60	Closed
	SA White Martins, Iguatama, Brazil	65	
	Columbiana de Carburo y Derivados, Cajica, Columbia		Closed
	Hornos Electros de Venezuela CA	5	
India	Birla Jute \amp Industries Ltd, Calcutta	16	
	Panyam Cements \amp Mineral Industries, Hagari	15	Closed
	Shriram Alkali \amp Chemicals, Jhagadiya	55	
	Tecil Chemicals \amp Hydro Power Ltd.	40	
	Industrial Chemicals \amp Monomers Ltd., Madrass	10	
	Small scale units in other places in India	20	
	Bhutan Carbide \amp Chemical	25	
Asia — Japan	Denki Kagaku Kogyo		
	Omi, Niigate	300	
	Omata, Fukuoka	110	
	Toyo Denka Kogyo, Kochi	60	
Asia—China	Many producersbSee Table 5 for individual producers.	3450	

Table 5 (*Continued*)

Region	Producers	Estimated annual capacity 10^3 mt
Asia—other countries	Emdeki Utama PT, Gresik, East Java	25
	Tae Kyung Industrial Co., Chongson, Korea	60
	MCCI, Iligan City, Philippines	30
	Formosa Plastics, Ilan, Tiawan	70
	MCB Industries, Perak, Malaysia	25
	M Thai Industrial, Samut Sakorn Thailand	30

[a] Estimated.

Calcium carbide-derived acetylene has declined considerably, much for the same reasons as in North America: oxyacetylene welding techniques replaced by electric welding and plasma techniques and less expensive acetylene obtained from ethylene. This decline is expected to continue at about 5% annually.

Calcium carbide–based desulfurization reagents declined in the early 1990s as magnesium-based reagents gained increased use. In the late 1990s years this market stabilized as users realized the benefits of using carbide–magnesium combined processes. Calcium carbide use in this application is expected to continue at the current level.

Exports of calcium carbide are in the order of 10–15,000[2] t/yr, mainly to North Africa, with some going to Australia.

8.3. Eastern Europe. All countries except Hungary produce calcium carbide. Overall, production has fallen from about 2500×10^3 t. annually in the 1970s to about 870×10^3 t today (Table 6). The reasons for decline are similar to those of Western Europe and North America.

Carbide is used primarily for acetylene generation for industrial applications in oxyacetylene welding and cutting. Acetylene is also used to produce

Table 6. **Calcium Carbide Production by Region, 1997, 10^3 t**

		Calcium Carbide Consumption[a]			
		Acetylene			
Region	Total production	Chemical	Industrial	Desulfurization	Calcium cyanamide
North America	270	68	135	68	
South America	70		60	10	
Western Europe	450		140	130	150
Eastern Europe	870	675	180	15	
South Africa	90	15	32	23	20
India	100	22	68	10	
Japan	250b	107	45	15	83
China	2512				
East Asia, others	100	25	71	4	
Total	*4712*	*912*	*731*	*275*	*253*

[a] Ref. 2, other values are estimated.

chemicals such as vinyl chloride monomer for PVC. The steel industries are just starting to use calcium carbide for desulfurization of hot metal. It is expected that the use of calcium carbide for chemical manufacture will decline, but its use as a desulfurizing reagent is expected to expand quite rapidly from a low base.

8.4. Japan. There are only two producers of calcium carbide:Denki Kagaku, which also produces calcium cyanamide, and Toyo Denka. As in other regions of the world, production has declined.

Chemical uses of acetylene (eg, PVC, chloroprenes, and acetylene black) account for about 42% of carbide consumption. However, the increased use of olefins such as ethylene and propylene instead of acetylene for various derivatives has weakened the demand for carbide. Industrial uses in cutting and welding have also declined because of changing welding techniques.

Calcium carbide desulfurizing reagent accounts for about 6% of carbide consumption, and use of these reagents has declined gradually with replacement by other less expensive reagents.

8.5. China. China is the worlds largest producer of calcium carbide, with a volume of 2512×10^3 t in 1995 (Table 6) or about 53% of the world's production. Unlike Western countries, where carbide production has declined, China's has increased from a level of $2200^3 \times 10^3$ t in 1990 (estimated). Carbide is used to produce acetylene for industrial and chemical applications (PVC, acetylene black), calcium cyanamide, and dicyandiamide; the majority is probably used in industrial and chemical applications. In the current 9th Five Year Plan energy conservation is a main goal for the Ministry of Chemical Industry (4). For the calcium carbide industry a reduction of electrical energy consumption from 3550 to 3360 kWh/tonne carbide is targeted. To achieve this, new furnace installations must be rated greater than 45,000 t/yr. Also, energy-saving features should be used in new and expanded units. These include technologies such as closed furnace design, hollow electrode system, furnace dry gas cleaning, and furnace gas-fired lime kilns. The major calcium carbide producers in China are listed in Table 7.

8.6. South Africa. The calcium carbide business in South Africa has undergone some restructuring, with Karbochem in Newcastle the only remaining producer in Africa. The AECI carbide plant at Sasolburg was purchased by Samancor in 1993. This plant is currently mothballed and may be converted to ferroalloy production in the future. Another AECI carbide plant at Bellengeich was taken over by Karbochem. The Bellengeich furnaces have been sold to Siltech, who use them for producing ferrosilicon. Carbide from Sasolburg was used extensively to produce acetylene-based chemicals (PVC); however, these are now produced from ethylene sources. Acetylene black for dry batteries continues to be produced from carbide. South Africa exports an estimated 20×10^3 t annually to neighboring countries.

8.7. South America. Only three carbide producers remain active in South America (Table 6) with Carbometal SA, Mendoza, Argentina, Companhia Brasileria Carbureto de Calcio, Brazil, and Columbiana de Carburo y Derivados, Cajica, now closed. White Martins and Andina are the only suppliers. The present level of carbide demand is expected to continue in both desulfurization and acetylene uses.

Table 7. **Calcium Carbide Producers, China**

Producer	City	Province	Capacity[a]
Yunnan Chemical Engineering Factory	Kumming	Anning	20
Wuhu Chemical Plant	Wuhu	Anhui	
Beijing Chemical Industry Group	Beijing	Beijing	
Fujian Sanming Chemical Industry Complex[b]	Sanming	Fujian	
Gansu Calcium Carbide Plant	Yongdeng	Gansu	106
Hebei Tangshan Dongkuang Chemical Factory	Dongkuang	Hebei	
Ganchan Fuyang Chemical Group Corp.	Ganchan	Hebei	
Hebei Jiheng Chemical Factory	Hengsui	Hebei	
Hebei Luquan Tianyuan Dianhua Factory[b]	Luquan	Hebei	
Wuhan Gehua Industrial Group	Wuhan	Hebei	
Zhangjiakou Xiahuayuan Calcium Carbide Plant	Zhangjiakou	Hebei	105
Harbin Petrochemical Industry Corp.	Harbin	Heilongjiang	
Mudonjiang Petroleum Chemical Co.	Mudonjiang	Heilongjiang	80
Huangshi Calcium Carbide Factory	Huangshi	Hubei	
Hubei Dayan Chemical Fertilizer Plant	Huangshi	Hubei	
Hubei Jinmen Calcium Carbide Works	Jinmen	Hubei	
Hubei Zhongtian Group Company Xinhuo Chemical Corp.	Jinmen	Hubei	
Xitujiazhu Chemical Plant	Sien	Hubei	
Hubei Changyi Resin Plant No.7	Yichang	Hubei	
Hubei Changyli Chemical Plant	Zijiang	Hubei	
Zhuzhou City Xiangdong Chemical Plant	Zhuzhou	Hunan	
Nanjing Lanye Group Corp.	Jiangnin	Jiangsu	
Shanhai Railway Industry Co.	Nanjing	Jiangsu	
Jiangxi Gannan Chemical Factory[b]	Ganzhou	Jiangxi	
Nanton Roudon Chemical Plant	Ludon	Jiansu	
Jilin Chemical Industry Group	Jilin	Jilin	60
Sinochem Siping Chemical Complex	Siping	Jilin	

Table 7 (*Continued*)

Producer	City	Province	Capacity[a]
Fushun Organic Chemical Factory	Fushun	Liaonin	
Jinzhou Organic Chemical Plant	Jinzhou	Liaoning	
Baotou No. 2 Chemical Factory	Baotou	Nei Mongol	80
Huhehote Chemical Factory	Hohhot	Nei Mongol	
Huanghe Chemical Factory	Wuhai	Nei Mongol	
Wuda Calcium Carbide Factory[b]	Wuhai	Nei Mongol	
Wuhai Calcium Carbide Factory	Wuhai	Nei Mongol	
Ningxia Darong Dicyandiamide Co[b]	Shizuishan	Ningxia Hui	
Ningxia Shizuishan National Chemical Co[b]	Shizuishan	Ningxia Hui	
Qingdao Honqui Chemical Works	Qingdao	Shandong	
Zibo Organic Chemical Factory	Zibo	Shandong	
Shanghai Wusong Chemical Factory	Baosan	Shanghai	
Calcium Carbide Chemical Group of Changzhi City	Changzhi	Shanxi	
Yang Quan Chemical Material Plant	Yang Quan	Shanxi	10
Shanxi Chemical Industry Factory	Datong	Shanxi	
Niang Zhi Guan Asia Pacific Calcium Carbide Co.[b]	Ping Ding	Shanxi	11
Taiyuan Chemical Industry Group	Taiyuan	Shanxi	
Tianjin Bohai Chemical Group Co.	Tianjin	Tianjin	
JianDe Genglou Chemical Plant	Hangzhou	Zhejiang	
Huzhou Chemical Factory[b]	Huzhou	Zhejiang	
Juhua Group Corp.[b]	Quozhou	Zhejiang	
Quzhou Chemical Group Corp.[b]	Quzhou	Zhejiang	
Hangzhou Electrochemical Co.[b]	Xiaoshan	Zhejiang	

[a] Probable capacity less than 100×10^3 t per plant.

[b] Also produces calcium cyanamide.

8.8. Asia. In other regions of Asia, such as Korea, the Philippines, Indonesia, and Thailand, carbide is used mainly for industrial uses as a fuel gas, with a small amount for chemicals (acetylene black).

9. Uses

Calcium carbide has three primary applications today. It is used to produce acetylene gas for heating, oxyacetylene welding, metal cutting, acetylene black, and acetylene-derived chemicals such as vinyl ethers and acetylenic chemicals and alcohols. It is also used as a desulfurizing reagent for iron and steel, and as an intermediate for calcium cyanamide manufacture.

9.1. Acetylene. Acetylene production accounts for about 75% of calcium carbide consumption (Table 6). There are two main areas of use: industrial applications, which include heating, welding, and cutting; and chemical uses, which include calcium carbide–derived acetylene for various chemicals.

Acetylene is generated by the chemical reaction between calcium carbide [75-20-7] and water. Most carbide acetylene processes are wet processes from which hydrated lime, $Ca(OH)_2$, is a by-product. The hydrated lime slurry is allowed to settle in a pond or tank after which the supernatant lime-water can be decanted and reused in the generator. Federal, state, and local legislation restrict the methods of storage and disposal of carbide lime hydrate and it has become increasingly important to find consumers for the by-product. The thickened hydrated lime is marketed for industrial wastewater treatment, neutralization of spent pickling acids, as a soil conditioner in road construction, and in the production of sand-lime bricks.

The purity of carbide acetylene depends largely on the quality of carbide employed and, to a much lesser degree, on the type of generator and its operation. Carbide quality in turn is affected by the impurities in the raw materials used in carbide production, specifically, the purity of the metallurgical coke and the limestone from which the lime is produced.

All North American suppliers produce carbide for industrial applications. Carbide is sold to companies such as BOC Gases, Air Liquide America Corp., Air Products and Chemicals Inc., and Liquid Carbonic Industries, which produce acetylene for use as an industrial gas. The use of acetylene for welding and cutting has declined in recent years because of replacement with alternative fuel gases, such as propane and propylene based gas mixtures, and the use of electric welding machines. This tend may continue at an average rate of 2–5% per year. The Carbide Graphite Group is the only company producing calcium carbide derived acetylene for chemical use. It is shipped via pipeline to International Specialty Products Inc. and Air Products and Chemicals Inc. (to produce vinyl esters, acetylenic chemicals and alcohols) and to Du pont for vinyl fluoride.

Since calcium carbide-derived acetylene competes with less expensive acetylene derived from the oxidation of natural gas and acetylene produced as a by-product from the manufacture of ethylene, it is not used on large scale for chemical production.

9.2. Calcium Cyanamide. Calcium cyanamide can be manufactured by either the Frank–Caro batch oven process or a continuous processes such as a rotary furnace developed in Trotsberg, Germany. In both processes the carbide is first ground to a powder in a ball or rod mill. The charge is further prepared by the addition of 1–2% fluorspar and recycled calcium cyanamide. The cyanamide dilutes the carbide, thereby preventing a temperature rise that would tend to decompose cyanamide.

The most important use of calcium cyanamide is as fertilizer, but it is also effective as a herbicide and defoliant. It was used as a starting material for ammonia until it was displaced by the Haber process. Several derivatives of calcium cyanamide have also been developed: hydrogen cyanamide (intermediate for insecticides, pharmaceuticals, soil sterilants), dicyandiamide (intermediate for flame and fire retardants, viscosity reducers for glues and adhesives, nitrification inhibitors in fertilizers), melamine (thermoset plastic), and calcium cyanide (gold extraction and fumigant). Calcium cyanamide production has fallen from a 1960s peak of 1300 to about 320×10^3 t/y today (excluding China). The use of cheaper ammonia-based fertilizers is the main reason for decline, as well as melamine, which is now being produced from urea sources instead of from cyanamide. Producing countries include Norway, Germany, China, and Japan.

Generally worldwide production of *calcium cyanamide* has declined since reaching peaks in the 1960s. The major producers of Calcium cyanamide worldwide are listed in Table 8.

Calcium cyanamide production has fallen from a 1960s peak of 1300 to about 320×10^3 t/yr at the time of writing. Cheaper ammonia based fertilizers is the main reason for decline, as well as melamine (trimer of cyanamide) now being produced from urea sources instead of from cyanamide.

9.3. Desulfurizing Reagent. Calcium carbide for metallurgical applications accounts for about 25% of its use (Table 6). Carbide for desulfurization in steel mills began in the 1970s and has allowed steel mills to use to use high-sulfur coke in the blast furnace without the penalty of excessive sulfur in the resultant steel. The reagent generally consists of commercial carbide that has

Table 8. **Calcium Cyanamide Producers**[a]

	Cyanamide products produced			
Producer	Cyanamide fertilizer	Dicyandiamide	Cyanamide solutions	Calcium cyanide
SKW, Trotsberg, Germany	Yes	Yes	Yes	
Odda smeltverk AS, Odda, Norway	Yes	Yes		
Polifin, Witbank, South Africa				Yes
Shin-Etsu Kasei, Japan	Yes			
Denki Kagaku Kogyo, Japan	Yes			
Nippon Carbide, Japan	Yes	Yes	Yes	
China	Yes	Yes		

[a] Author's estimate.

been ground to a powder, or the pulverized carbide mixed with other ingredients such as lime, limestone, graphite, coal, solid hydrocarbons, and silicone. The powdered regent is injected into molten iron using an inert-gas carrier. Calcium carbide competes with magnesium based desulfurizing reagents, and switching costs between these reagents are low. Calcium carbide has the advantage of being less expensive; however, magnesium has a higher affinity for sulfur.

Calcium carbide and magnesium are also used as simple blends or in coinjection processes. With coinjection, the two reagents can be injected simultaneously or sequentially. The less expensive carbide removes 90% of the sulfur, and then the remaining sulfur is removed by magnesium injection.

For the foreseeable future it is expected that both reagents will be used in steel mills and demand will change in line with steel production. Carbide Graphite, Elkem-American, and Metaloides all produce powdered carbide for desulfurization. All producers market carbide of a granular size for desulfurizing ductile iron in foundries. This market is expected to be stable.

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WILLIAM L. CAMERON
William Cameron Consulting