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CALCIUM CARBIDE  
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# CHEMICAL PROCESS INDUSTRIES

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electrodes are lowered to make contact with opposite ends of the trench. As soon as the alumina begins to fuse, it carries the current, and the starting coke is rapidly consumed. A typical charge to the furnace is calcined bauxite (99%), coke (2%), and scrap iron (9%). The charge is added as fast as it fuses between the arcs, the molten alumina carries the current, and much of the iron and silica is reduced to form a heavy alloy and sinks to the bottom. As the level of fused alumina rises, the electrodes are raised and more charge is added, until finally the furnace is full. Then the current is shut off and the entire mass cooled under controlled conditions to obtain the texture desired. Although this product has the hardness 9 on the Moh scale for corundum, it is dieblubar in structure and not uniform, and therefore bearings cannot be made from it. The cooled ingots are broken up by roll crushers, washed with chemical solutions, and sieved. The product is fabricated into abrasive wheels, papers, and powders or into refractory shapes by sintering.

**ARTIFICIAL CORUNDUM, OR SAPPHIRE** For the hard bearings necessary for watches and modern instruments, *artificial corundum*, or white sapphire, is made by crystallizing through fusion pure alumina in a hydrogen-oxygen upside-down flame at 3500°F by the Verneuil process. The crystal boules are cut and polished as desired. Many gems are also made by this process, such as star and transparent rubies and sapphires of varied color.

**BORON CARBIDES** This is a very hard abrasive. It first made its appearance in 1934 under the name *Norbide*. The reaction for its production is:



The boric oxide is caused to react with coke in a carbon resistance furnace at 2600°C. The product is about 99% B<sub>4</sub>C. It finds specialized use as a powdered abrasive and in molded shapes such as nozzles for sandblasting.

**BORON NITRIDE** *Borazon* is a cubic form of boron nitride formed at 1 million psi and 3000°F to change the ordinary hexagonal boron nitride to this cubic form. Its hardness is comparable with that of diamond, and it has the advantage of resisting oxidation much better. It is made by General Electric Co.

## CALCIUM CARBIDE

**HISTORY** The first production of calcium carbide was an accident. In 1892, T. L. Willson was attempting to prepare metallic calcium from lime and tar in an electric furnace at Spray, N.C. The product obtained, obviously not calcium, was thrown into a nearby stream, and Willson was amazed to note that it liberated great quantities of combustible gas. The first factory for the production of calcium carbide was built at Niagara Falls in 1896.<sup>7</sup>

**USES AND ECONOMICS** Calcium carbide is utilized in two principal procedures: manufacturing cyanamide by combining it with nitrogen, and preparing acetylene by reacting it with water. Cyanamide is made by heating calcium carbide in an atmosphere of nitrogen (Chap. 18). A substantial proportion of the total calcium carbide produced is converted to cyanamide. Calcium carbide was used in large quantities for the manufacture of acetylene, but hydrocarbon-based acetylene has been taking over in the United States. The U.S. production of calcium carbide fell from 625,338 short tons in 1971 to 493,339 short tons in 1972. During the 1960s production was in excess of 1 million short tons/year.

**MANUFACTURE** Calcium Carbide<sup>8</sup> is prepared from quicklime and carbon at 2000 to 2200°C

$$CaO(l) + 3C(\text{anorth}) \longrightarrow CaC_2(l) + CO(g) \quad \Delta H = +103 \text{ kcal}$$

<sup>7</sup>Fluame Grown Gems Stores Enjoy Broadened Use in Optics and Jewelry, *Chem. Eng. (N.Y.)*, 68(26), 26 (1961).

<sup>8</sup>Boron Carbide Process Temperature, *Chem. Eng. News*, Feb. 5, 1968, p. 262.

<sup>9</sup>Carbide and Acetylene, *Chem. Eng. (N.Y.)*, 57(6), 129 (1950); Mandel, *op. cit.*, pp. 491ff. *ECT*, 2nd ed., vol. 4, p. 100.

The source of carbon is usually coke, anthracite, or petroleum coke. Coke is the most widely used. It should be compact and have a low ash content, a low ignition point, and high electrical resistivity, so that the bulk of the furnace charge will be highly resistant to the flow of energy. Thus the energy is concentrated, resulting in a more rapid and complete reaction. Phosphorus should be absent, since it forms a phosphide which is converted to poisonous phosphine (PH<sub>3</sub>) when the carbide is made into acetylene. Quicklime is produced by burning limestone containing at least 97% calcium carbonate. Impurities such as magnesia, silica, and iron hamper production and give a less pure carbide.

The carbide furnace is not a true arc-resistance furnace, but has been developed from the familiar arc furnace. Ingot furnaces, similar to those producing fused aluminum oxide, have been replaced in the carbide industry by continuous or intermittent tapping furnaces producing molten carbide. The furnace consists of a steel shell with the side walls lined with ordinary firebrick and the bottom covered with carbon blocks or anthracite to withstand the extremely hot, alkaline conditions. Most of the larger furnaces use three-phase electric current and have suspended in the shell three vertical electrodes. Improvements include the "closed" furnace, where almost all the carbon monoxide from the reaction is collected and utilized, and Söderberg continuous self-baking electrodes, which permit larger-capacity furnaces than the old prebaked electrodes. The capacity range of the furnaces is generally between 5,000 to 18,000 kWh or higher, and a three-phase tapping furnace of 25,000 kWh produces about 200 tons of commercial product (usually 85% carbide) per day. The approximate consumption of materials per ton of carbide is 1,900 lb lime, 1,300 lb coke, 35 lb electrode paste, and 3,000 kWh energy (Fig. 18.1). The lime and coke are charged continuously with intermittent or continuous tapping of the liquid product directly into cast-iron chills to 220-lb steel drums or up to 5-ton containers for shipping.

## MISCELLANEOUS ELECTROTHERMAL PRODUCTS

**FUSED SILICA** This very useful construction material for the chemical industries is heated to fabrication temperature in an electric furnace.

**SYNTHETIC QUARTZ CRYSTALS** These crystals have been grown successfully by a hydrothermal process at Bell Telephone Laboratories and Western Electric Co. by keeping a supersaturated solution of silica in 1 *N* sodium hydroxide in contact with seed crystal quartz plates at 30,000 psi for 3 weeks at a temperature of about 750°F. They are grown in special autoclaves, with a two-zone electrical heating system having a higher temperature for the dissolving zone, to bring into solution small chips of quartz, and then allowing growth on prepared quartz seed plates at about 109°F lower temperature. A satisfactory product results at less cost than mined quartz. Such quartz crystals are very important, indeed necessary, for use in radar, sonar, radio, and television transmitters and telephone communications. A single telephone wire can carry hundreds of messages at one time, thanks to the unscrambling powers of quartz-crystal filters.

**ARTIFICIAL GRAPHITE AND ELECTRODES** are described in Chap. 8, devoted to carbon, and phosphorus is presented in Chap. 16, on Phosphorus Industries. See also Table 14.1 for a summary of the various products made by electrochemical processes.

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<sup>7</sup>For carbon disulfide, see Chap. 38, and CP 2 for old electrochemical process. Higginson, 30,000 psi for Three Weeks, *Ind. Eng. Chem.*, 54(1), 16 (1962).