

Natubhai V. Patel College of Pure & Applied Sciences

S. Y. B.Sc. (Industrial chemistry)

C-214: Chemical Process Industries

UNIT 3A

SYLLABUS

Electro thermal industries: Introduction, uses and economics of furnaces and their classification, manufacture of silicon carbide, calcium carbide, boron carbide, boron nitride, synthetic graphite, carbon electrode.

ELECTROTHERMAL INDUSTRIES

3.0 INTRODUCTION

A large number of products can only be prepared at very high temperatures. Such type of very high temperature can be attained in an electric furnace which is probably the most general term used for a group of heating apparatus using electrical energy as a source. Fuel fired furnaces have been, used only up to a temperature of about 1700°C, Whereas electric furnaces are capable of producing temperature as high as 4100°C. The high temperature attained in an electric furnace provides two important changes (1) It increases the rate of reaction and (2) New conditions of equilibrium are established as a result of which new compounds not known before the electric furnace have been produced. Silicon and calcium carbides used as abrasives are well known examples of the new products formed by making use of electrical furnaces.

3.1 ADVANTAGES OF ELECTRICAL FURNACES

- It affords more exact control and more concentration of heat with less thermal loss compare to other types of furnaces, such as fuel fired or combustible furnaces.
- It is much cleaner and more convenient to operate than the fuel fired or combustion furnaces.
- It is operated by alternating current of large amperage, whereas the electrolytic furnaces required direct current.
- Temperature as high as 4100°C can be attained in these furnaces, whereas the highest temperature attained in combustion furnace is only 1700°C.

3.2 CLASSIFICATION

There are three types of **electric furnace**, depending upon the manner in which electrical energy is converted into heat. These are:

1. Arc furnace
2. Resistance Furnace
3. Induction Furnace

3.2.1 Arc Furnace

In the arc furnaces heat is generated in the electric arc which can burn only in gaseous atmosphere. In other words, the heat in the arc furnace is generated by an electric arc between two or more electrodes which are usually of graphite or carbon between the electrodes and furnace charge or between two or more electrode. The arc furnaces are therefore **two types**:

- The Direct Arc Furnaces
- The Indirect Arc Furnace

In the **direct heat furnaces**, arc is used to heat a gas in which the arc is burning and the charge forms a part of the electric circuit, while in **indirect heat furnaces**, the arc burns above the charge and the latter does not form a part of the electrical heating circuit. In other words, in **direct arc furnace**, heat is generated directly in the material to be heated and in **indirect arc furnace**, heat is generated in heat source, which is separated from the charge and then heat is transferred to the charge by conduction, convection and/or radiation. The electrodes may or may not consume in the operation. We can thus say that in **direct arc furnaces**, the charge is a part of the electrical circuit, while in **indirect arc furnaces** the charge is not a part of electrical heating circuit.

3.2.2 Resistance furnace

In such type of furnaces, heat is produced by the resistance in the electrical current i.e. heat is generated in a solid or liquid resistor. In some furnaces the material forming the charge acts as the resistance and does self heating while in other furnaces the body of the furnaces is made of a resistance material which causes heating. Hence **resistance furnaces are also of two types**. When the charged material acts as the electric resistance required for the necessary heat, the furnace is called **direct heating resistance furnace** and when high resistance material is added to the charge in order to generate heat, the furnace is known as **indirect heat resistance furnace**.

Arc and resistance furnaces have widely been used in various electrochemical industries. The direct heat furnaces can also be classified into **indirect induction furnace** and **electrode resistance furnaces**.

3.2.3 Induction furnaces

In induction furnaces, the current is transmitted through the charge without physical contact between the charge and electric supply system and such furnaces may be applied only for conducting substances such as metals. In other words, in these furnaces, the electric energy is converted into heat by the induced currents set up in the charge. They can be operated at frequencies as high as 500000cycles/second, but for commercial electro-thermal processes, furnace that operate up to 6000cycles/second are quit sufficient. In the low frequency furnace, the charge is placed around an iron core, while in the high frequency furnace, the iron core is not necessary. The heating effect is caused with lower field strengths as the frequency is increased.

Electrode resistance furnaces are also known in which the charge by means of electrodes. In these furnaces, it is not essential for the electrode to touch the charge when they are operating at high frequency.

Electron beam furnaces have been developed in which heating is carried out by causing a cathode to emit an electron beam which is directed through electric and magnetic fields to impinge on the charge. This is more **recent technique** and may be used in the new fields.

3.3 SELECTION OF FURNACE

In selecting the types of electrical furnaces, two important factors are to be taken into consideration.

- The maximum temperature is required
- The electrical conductivity of the charge

In direct heat furnace, including induction and high frequency capacitance heating, dielectric heating, the temperature is limited only by the maximum permissible temperature of the refractory. The temperature of the charge can however be increased, but not more than **4500°C**, Which is the **maximum limit of temperature** that can be attained in **arc furnaces**.

In indirect heat resistance furnaces, the temperature is limited only maximum permissible temperature of the heating resistor. For example, a commonly used resistance material can be used up to 1500°C for the production of silicon carbide, up to 1900°C for metallic resistors and up to 2500°C for graphite.

In direct heat furnaces, the electrical conductors are heated either by induction or by low frequency electrode heating. Now conductors cannot be heated by induction

heating. They can, however be heated conveniently in arc furnace or by high frequency capacitance heating.

Taking economy into consideration, **arc furnaces** are desirable to be used in those processes where high temperature of the arc does not damage the charge or the charge is not to be reduced by thermal barriers. Direct heating of the charge is more rapid and in most cases more uniform than outside or indirect heating but conversion of electrical energy into heat energy in such type of furnaces is less efficient. **Thus gain in thermal performance is balanced by loss in electrical performance.**

3.4 ARTIFICIAL ABRASIVES

Formerly natural products, such as diamonds, garnet, quartz, rouge, kieselguhar, emery and corundum were used as abrasives. In 1891, Acheson produced the **first man made abrasive**, known as **silicon carbide** in a homemade electric arc furnace. Later on various other abrasives, such as fused aluminium oxide, boron carbide, boron nitride and calcium carbide were also prepared commercially in the **electric thermal furnace**.

3.5 SILICON CARBIDE OR CARBORUNDUM

Silicon carbide is one of the most important abrasive and was first discovered by Acheson(1891) while attempting to harden clay in a homemade electric furnace.

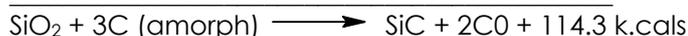
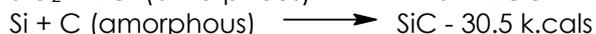
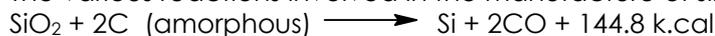
When carbon was dissolved in molten clay it was assumed to be mixture of carbon and fused alumina called **corundum** and hence the name **carborundum**.

3.5.1 Raw Materials

Silicon carbide (SiC) is now manufactured by making use of sand or silica and carbon. The sources of carbon are coke, pitch, petroleum cokes and anthracite. The sand contains pure silica (98 to 99.5%) SiO₂

3.5.2 Reactions

The various reactions involved in the manufacture of silicon carbide are



The temperature is maintained at 2000°C. Higher temperature is prevented as SiC is decomposed into graphite at high temperature.

3.5.3 Manufacture

Special type of open top indirect heating **resistance furnace** is used for manufacture of SiC. The furnace consists of a permanent bed of curved cast iron pieces lined with fire brick on which the charge is placed. The charge is built up in the furnace around a heating core of granular carbon. The 30-50 ft long furnace is provided with about 60 carbon electrodes which are one metre long and 8 cm. in diameter and the central core of iron connects these electrodes. The ends of the furnace are permanent and the sides are built up every time with the charge. Excessive heat loss does not take place because the outside unreacted charge acts as an insulator. The sides are pulled down after the completion of the process to take out the product. The charge which is a mixture of 53.5% SiO₂, 40% coke, 5% saw dust and 1.5% salt is added to furnace until it is full. **Saw dust increase the porosity of the charge to permit the circulation of vapours and the escape of carbon monoxide formed**, CO burns at the top of the furnace. **Salt is added as a flux**. A typical initial current between the electrodes is 6000amps at 250 volts, but its resistance gradually decreases as the reaction proceeds and the final current becomes 20000 amperes at 75 volts. After about 2 hours, the current increases rapidly from 6000 to 20000 amps and remains steady during the whole run of 36 hours. The **temperature at the core is 2200°C** amps and remain steady during the whole run of **36 hour** until the reaction is complete. The product is then cooled for 24hour and crystals of silicon are removed from the furnace. The **yield** is about **6-8 tonnes** per furnace.

The **black crystals** are broken and then treated successively with sulphuric acid and sodium hydroxide solution. It is dried in a kiln and graded through a screening or sieving system into, the powders of various degrees of fitness.

It should be noted that the temperature of the core should not exceed 2200°C. **Higher temperature** leads to the **decomposition of silicon carbide into graphite** with the volatilization of silicon. The graphite formed in this manner is called **artificial graphite**. The outer unreacted part of the charge is combined with the next charge for the furnace and next to the core some graphite formed as a result of decomposition of SiC is obtained. After complete run, which takes about 36+24=60 hours, the graphite can be separated as a byproduct from silicon carbide and converted to desired shapes. A part of the core used in the furnace can be made of coke suitable for graphite manufacture.

A **good yield** of carborundum can be obtained by taking the following points into consideration.

- Silica or sand used should be of about 98% purity.
- The carbon used may be petroleum coke, metallurgical coke, anthracite etc. having low ash and sulphur contents.
- Fe₂O₃ and Al₂O₃ in silica should be as low as possible as they catalyse the decomposition of SiC. The carbide undergoes decomposition at 2830°C.
- The temperature of formation of silicon carbide is about 1840°C ± 30°C
- 100 parts by weight of finest grade sand, 60 parts by weight of coke and 19 parts by weight of saw dust is the charge composition for a good yield of SiC. Saw dust increases the porosity of the charge or escape of CO and other volatile matter during SiC formation.

3.5.4 Properties

Silicon carbide has **high thermal conductivity** due to which it is resistant to shock because of temperature fluctuations. Its **conductivity** lies between those of metals and non-metals or insulators and so it **acts as semiconductor**. Its **radiation resistance** is much higher than pure silicon. It is exceptionally stable to most chemicals at low temperatures but reacts at high temperatures.

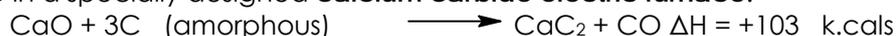
3.5.5 Uses

The most notable property of silicon carbide is its hardness. It is almost **as hard as diamond** and is used for making grinding machines, grinding stones, crushers, for giving edge to cutting tools (razors, knives, swords etc.). On account of its **refractory nature** and **higher heat conductivity**, it is also used for making crucibles. It has also been used as a refractory material, both in the form of bricks and as loose material. Silicon carbide has also been used as an abrasive for making the modern grinding tools, which are used as in fabricating the metal parts of modern automobiles, tanks, engines, rifles, aeroplanes and other machines. It is also used for carbon rods in resistance heaters.

3.6 CALCIUM CARBIDE

3.6.1 Raw Materials

Calcium carbide is commercially manufactured from **carbon and quick lime** at 2000-2200°C in a specially designed **calcium carbide electric furnace**.



The **carbon** is obtained from **coke**, anthracite or petroleum coke. Coke has, however, widely been used. The coke must be compact and have low ash content, low ignition point and high electrical resistivity (or low electrical conductivity) so that the bulk of the furnace charge may be highly resistant to the flow of energy. As a result, the energy becomes concentrated in the charge rapidly producing high temperature required for the reaction to take place and to go for completion. The **coke** should also be **free from phosphorus**, because it forms a phosphide, which is converted to poisonous phosphine (PH₃), when acetylene is formed by the action of water on carbide. The presence of phosphine may even causes serious explosion. The coke must contain **low ash contents** (about 3% or less) otherwise the carbide formed will be viscous and therefore, will create difficulty during tapping from the furnace.

The **quicklime** is obtained by burning limestone containing about 97 percent CaCO_3 .



Magnesia, silica and iron oxides present in the form of impurities **hamper production** and give **less pure carbide**. These impurities should, therefore, be properly controlled before the charge is fed to the furnace.

Basis: 1 tone of Calcium carbide

Lime: 1900lbs.

Coke: 1300lbs

Electrode paste: 35lbs

Energy: 3000kw/hr

3.6.2 Manufacture

A typical three phase furnace of 25000 kilowatts-hr produces about 200 tonnes of 85% carbide per day is as shown in figure.

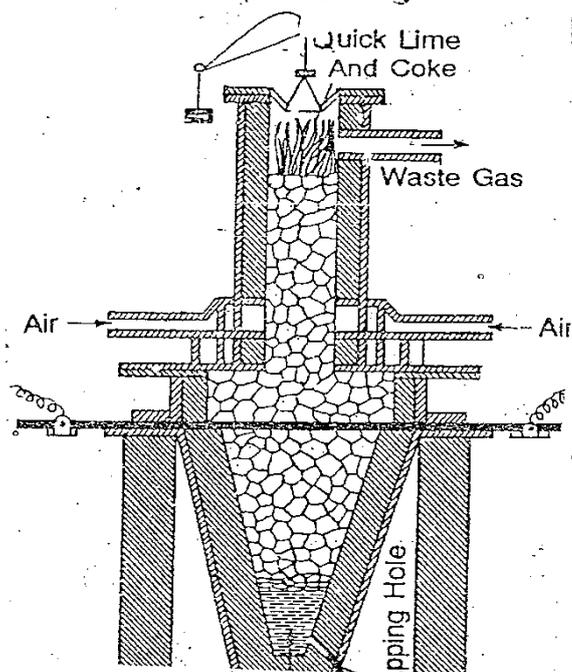


Figure: Manufacture of CaC_2

Carbide furnaces fall in the class of combined resistance and direct arc heating, since some of the heat is due to the resistance of the raw material, but most part of it is due to sparking across the charge. The furnaces consist of a steel shell 10 X 3 meter in area or more with the side walls lined with refractory material and the bottom covered with carbon block, or anthracite to withstand extremely hot alkaline conditions. Most of the **recent large furnaces** have closed top (where almost all the CO evolved during the reaction is collected and utilized) and three phase electric current i.e. they have three vertical electrodes suspended in the shell and each is connected to one of the low tension bars. The electrodes are made up of graphite, fitted and bound. They may be as long as 10 X 2ft and may be round or oval in the cross section. They are also provided with arrangement for lowering because they are consumed.

Recently Soderberg Continuous Self Baking Electrodes have been used in place of prebaked electrodes, since the former permit large capacity furnaces. The electrodes are dipped in the charge which almost fills the furnace. The layer of carbon or anthracite in the bottom acts as the bottom electrode. The charge consisting of 60% calcium oxide and 40% coke is fed from the top. Before it reaches the region of high temperature (2000°C) provided by the furnace, it gets heated by the burning of carbon monoxide (liberated in the reaction) in air. The latter is pumped through side tubes in the middle of the furnace. Calcium carbide is formed at the bottom as a result of reaction of calcium oxide and coke. The molten calcium carbide is periodically tapped out of the furnace and fresh charges added into cast iron chilled pots of about 5 tones capacity each. The carbide is cooled, crushed and sized.

Commercial calcium carbide thus obtained is generally black, reddish black or reddish brown, depending upon the presence of iron or other constituents.

3.6.3 A good yield of calcium carbide is obtained when

- Lime is prepared from lime stone of about 96-97% purity.
- MgO content of lime should not exceed 1%. Higher amount may cause reduction of fluidity of molten CaC₂ creating difficulty in tapping.
- Al₂O₃ should be as small as possible, because it also creates the same problem as created by MgO.
- SiO₂ should not exceed 1.25%
- Fe₂O₃ + Al₂O₃ should not exceed 0.5%, because Fe₂O₃, if present reacts with SiO₂ and produce ferrosilicon. The latter settles down below CaC₂ and attacks the refractory material of the furnace.
- Impurities of phosphorus and sulphur in lime should not be more than 0.1% because they would produce Ca₃P₂ and CaS which in their turn produce PH₃ and H₂S during water treatment of the carbide.
- Metallurgical coke, petroleum coke and soft coke with low ash content and volatile matter should be used. Petroleum coke is most commonly used because of its low ash content and high resistivity.
- The moisture content of coke used should not exceed 2%.
- 60 parts of CaO and 40 parts by weight of coke are used.
- The electrodes may be prebaked, square or rectangular made from amorphous carbon, graphite or continuous self backing type made from calcined anthracite and coal and pitch as binder.

3.6.4 Uses

Today calcium carbide is used as an abrasive and for the manufacture of acetylene which is used in oxyacetylene blow pipes acetylene lamps and as starting material for the preparation of many compounds, such as CH₃CHO, CH₃COCH₃, CH₃COOH, CH₃COOC₂H₅. It is also used in the manufacture of calcium. A small amount of the calcium carbide is used as reducing agent in some metallurgical processes and as a drying agent.

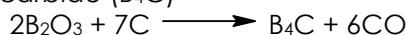
In India calcium carbide is manufactured at various places. Imports have already been stopped in 1961.

Some **leading manufactures** are

- Birla Jute Manufacturing CO. Ltd. Birlapur (W.Bengal)
- Calico Mills Trombay, Bombay.
- Industrial Chemicals Ltd. Talaiyuthu, Tamil Nadu (Madras)

3.7 BORON CARBIDE

It is another very hard abrasive also known as **norbide**. It is manufactured by heating boric oxide with coke in a carbon resistance furnace at 2600°C. The product is about 99% boron carbide (B₄C)



It is used in the nozzles for sand blasting.

3.8 BORON NITRIDE

Its hardness is comparable with that of diamond with the advantage of resisting oxidation much better. It is also known as **borazon** and is prepared by converting hexagonal boron nitride into cubic form at 3000 F temperature and 1 million psi pressure in an electric furnace.

3.9 SYNTHETIC GRAPHITE

Graphite mixed with impurities is found in nature and is known as **natural graphite**. Natural graphite is found in Siberia, Sri Lanka, USA, Canada and Czechoslovakia. In India it occurs in small amounts at Visakhapatnam, Travancore, Rajasthan and Orissa. The **artificial graphite** was first prepared by **A. G. Acheson** by heating amorphous carbon with certain catalysts, such as SiO₂ or Al₂O₃ in an electric furnace at a temperature of about 3000°C. It is

known that the industrial process converts amorphous carbon directly to artificial or synthetic graphite in an electric furnace.

3.9.1 Raw Materials

The raw material for the manufacture of artificial graphite is petroleum coke or anthracite or pitch coke. All these contain small amount of ash (SiO_2) which acts as a catalyst. The reaction for the allotropic change is



3.9.2 Manufacture

The furnace used for the manufacture of artificial graphite is an **open top resistance furnace** and consists of a core of the coke being graphitised. The front, back and the floor of the furnace are made **mainly of concrete**, with **cooling coils** in the ends in order to reduce the temperature of electrodes in contact with air to prevent them from burning. The side walls of the furnace are built of loose **refractory blocks and plates** which are torn down during unloading. Several **graphite or carbon rods** are inserted through the front and back walls. The core of **coke** to be graphitized is also surrounded by a layer of **sand, coke and raw dust**. The **raw dust acts as insulation**. The resistance of the charge increases the temperature of the furnace to **3000°C**, at which amorphous carbon is converted into graphite and voltage decreases from **200 to 40 volts**, because of lowered resistance. Some heat is generated due to exothermic reaction but bulk of the heat is generated by the resistance provided by the charge to the flow of electricity. At a temperature of 3000°C, any silicon carbide that may be present also decomposes into graphite and silicon. The latter volatilizes off at this temperature leaving graphite in the furnace. After cooling the furnace is torn down and graphitized carbon taken out. The insulating sand, coke and silicon carbide mixture is again fed to the furnace to be utilized again. Power rating is 6000-10000 Kw-hr per tonne of finished graphite. The **complete cycle** of the furnace consist of: loading: 1 day; heating-5-6 days; cooling 15 days and unloading 2 days. Hence about **23 days are required** from charge to charge.

3.9.3 Properties

Graphite has a two dimensional structure and series of layer. In graphite only 3 valance electrons of each carbon atom are involved. Thus each carbon atom makes use of sp^2 hybrid orbital forming three covalent bonds and three other carbon atoms in the same plane. The fourth valence electron remains unpaired or free. This makes graphite a good conductor of electricity. The C-C covalent distance is 1.42°A and the distance between two successive layers is 3.34°A . The sheets or layers are held together by weak Vander Waal's forces. Lead of lead pencils contain graphite and variable quantities of clay depending upon the hardness required.

Some of the **unusual characteristics of graphite** are.

- Extremely high fusion point under pressure
- Low density
- High resistance to chemical and mechanical corrosion
- Strong resistance to mechanical shocks
- Strong resistance to temperature fluctuations
- Good electrical conductivity
- High sublimation temperature (3600°C)
- High arc plasma temperature ($>5000^\circ\text{C}$)
- High degree of insolubility in molten salt

3.9.4 Uses

Natural graphite has widely been used in the manufacture of clay-graphite crucibles, lead pencils and as a lubricant. It is, however, not suitable for the manufacture of graphite electrodes which are extensively used in the manufacture of large number of electrochemical and electro-thermal products (such as aluminium, magnesium, caustic soda, chlorine etc). This is probably due to the impurities associated with natural graphite.

Artificial graphite can be substituted for any of the use of the natural product **except** in the production of **clay-graphite crucibles**, although several crucibles and trays have also been manufactured from artificial graphite. For **lubricating purposes**, it is suspended in water or oil

and placed in contact with moving parts. In **electrical industries**, graphite is used for electrodes, brushes, contacts and electronic tube rectifier elements.