

Lecture notes
on
Fuels and Refractories
for
3rd Semester, Metallurgical Engineering

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2022-23

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CHAPTER -1

FUELS

The substances which give energy in the form of heat and light on their combustion with air in a manner which could be utilised efficiently and economically are known as fuel.

These fuels - coal, oil, and natural gas - are often referred to as fossil fuels.

The various types of fuels (like liquid, solid and gaseous fuels) that are available depend on various factors such as costs, availability, storage, handling, pollution and landed boilers, furnaces and other combustion equipment.

The knowledge of the fuel properties helps in selecting the right fuel for the right purpose and for the efficient use of the fuel. Laboratory tests are generally used for assessing the nature and quality of fuels.

Conventional and Non-conventional Source of Energy:**a) Conventional Energy Sources:**

Conventional sources of energy are also called non-renewable sources. These sources of energy are in limited quantity except hydro-electric power.

These are further classified as commercial energy and non-commercial energy:

➤ Commercial Energy Sources:

These are coal, petroleum and electricity. These are called commercial energy because they have a price and consumer has to pay the price to purchase them.

➤ Non-Commercial energy Sources:

These sources include fuel wood, straw and dried dung. These are commonly used in rural India. According to an estimate, the total availability of fuel wood in India was only 50 million tonnes a year. It is less than 50% of the total requirements. Agricultural wastes like straw are used as fuel for cooking purposes. The straw can be used as valuable organic manure for increasing fertility of soil and in turn productivity.

b) Non-Conventional Sources of Energy:

Besides conventional sources of energy there are non-conventional sources of energy. These are also called renewable sources of energy. Examples are Bio energy, solar energy, wind energy and tidal energy.

The various sources are given below:

1. Solar Energy:

Energy produced through the sunlight is called solar energy. Under this programme, solar photovoltaic cells are exposed to sunlight and in the form of electricity is produced.

Photovoltaic cells are those which convert sun light energy into electricity. Solar energy is used for cooking, heating water and distillation of water etc.

2. Wind Energy:

This type of energy can be produced by harnessing wind power. It is used for operating water pumps for irrigation purposes.

3. Tidal Energy:

Energy produced by exploiting the tidal waves of the sea is called tidal energy. Due to the absence of cost effective technology, this source has not yet been tapped.

4. Bio Energy:

This type of energy is obtained from organic matter.

It is of two kinds:

➤ Biogas:

Biogas is obtained from cow dung gas plant by putting cow dung into the plant. Besides producing gas this plant converts cow dung into manure. It can be used for cooking, lighting and generation of electricity.

➤ Biomass:

It is also of a source of producing energy through plants and trees. The purpose of bio mass programme is to encourage afforestation for energy. So that fuel for the generation of energy based on gas technique and fodder for the cattle could be obtained.

5. Energy from Urban Waste:

Urban waste poses a big problem for its disposal and it can be used for generation of power.

Electrical Energy

Electrical energy is not a fuel but is a substitute for fuel and replaces it (or displaces it) in many industrial applications.

Electricity can be generated from several sources of energy.

- By conversion of chemical energy in coal, oil, peat or other conventional fuels into heat by burning, into mechanical energy by steam-raising, and then to electrical energy by using a turbine and dynamo.
- By conversion of the potential energy in water in elevated reservoirs to kinetic energy in raceways and then to mechanical and electrical energy using turbines and dynamos.
- By similar conversion of the kinetic energy in wind.
- By conversion of nuclear energy via heat and steam.
- By the use of electrolytic cells and fuel cells in which chemical energy can be converted directly to electrical energy.

TYPE OF FUELS

The fuels can be commonly classified on the basis of physical state of their occurrence, source, process of production and renewable/non-renewable quality as follows:

- Physical state of fuel, i.e., solid (coal, coke, charcoal, etc.), liquid (petrol, diesel, etc.) and gas (methane, hydrogen, etc.).
- Source of fuel, i.e., primary sources like coal, crude oil, and natural gas which occur in nature or secondary sources like coke, diesel, hydrogen, etc. which are prepared by some industrial processes.
- Process of production, i.e., purposefully manufactured fuel like metallurgical coke or by-product fuel like blast furnace gas.
- Nature of fuel—Non-renewable (fossil) fuels like coal, crude oil, natural gas or renewable fuels like hydrogen, biomass, etc.

PROPERTIES OF FUEL:

The various properties of liquid fuels are given below.

- Chemical composition: Carbon content, water content, ash content, sulphur, nitrogen, hydrogen content etc.
- Density
- Specific gravity
- Viscosity
- Flash point
- Pour point
- Specific heat
- Calorific value

The primary and secondary sources for solid, liquid and gaseous fuels, classified as renewable and non-renewable (fossil) fuel.

Physical State of Fuels	Renewable and Non-renewable (Fossil) Fuels	Primary Sources or Naturally Occurring Fuels	Secondary Sources (Industrial Processes)	
			Manufactured Fuels	Fuels Obtained as By-product
Solid	Renewable fuel	Wood	Wood charcoal	Wood refuse (saw dust, shavings, trimming, etc.), charcoal, sugarcane refuse, waste grains
	Non-renewable (fossil) fuel	Peat, lignite, bituminous coal and anthracite	Semi-coke (LTC), coke, briquettes of lignite char, coal, etc. and pulverised coal	Coke breeze, DRI kiln char and carbonaceous sludge
Liquid	Renewable fuel	Oil seeds and sugarcane	Vegetable oils and alcohol	Paper mill sludge
	Non-renewable (fossil) fuel	Petroleum crude oil	Petrol, solvent spirit, kerosene, diesel, furnace oil, naphtha, coal tar fuels (from oil shale), synthetic oils, etc.	Coal carbonisation by-products during coke making (e.g. tar, pitch, benzol, naphtha, etc.) petroleum refinery residue
Gas	Renewable fuel	Hydrogen in water	Hydrogen	Sewage gas
	Non-renewable (fossil) fuel	Natural fossil gas	Producer gas, water gas, coal gas, oil gas, reformed natural gas, butane, propane, acetylene, hydrogen	Blast furnace gas, coke oven gas, LD steel gas, COREX gas, oil refinery gas

CHAPTER-2

SOLID FUELS

Solid fuel refers to various forms of solid material that can be burnt to release energy, providing heat and light through the process of combustion.

Solid fuels can be contrasted with liquid fuels and gaseous fuels. Common examples of solid fuels include wood, charcoal, peat, coal, Hexamine fuel tablets, wood pellets, corn, wheat and other grains.

Solid fuels are mainly classified into two categories,

- Natural fuel : naturally occurred
Example -wood, coal, etc. and
- Manufactured fuels: manufactured by human being/human made/
Example: charcoal, coke, briquettes, etc.

Different types of solid fuels are

- a. Wood
- b. Biomass
- c. Peat
- d. Coal
- e. Coke
- f. Municipal waste
- g. Fossil fuels

Properties of Solid Fuel:

Specific Heat:

Specific heat is the amount of kCals needed to raise the temperature of 1 kg of oil by 1 degree C.

The unit of specific heat is kcal/kg degree C. It varies from 0.22 to 0.28 depending on the oil specific gravity. The specific heat determines how much steam or electrical energy it takes to heat oil to a desired temperature. Light oils have a low specific heat, whereas heavier oils have a higher specific heat.

Calorific Value:

The calorific value is the measurement of heat or energy produced and is measured either as gross calorific value or net calorific value. The difference is determined by the latent heat

of condensation of the water vapour produced during the combustion process. Gross calorific value (GCV) assumes all vapour produced during the combustion process is fully condensed.

Net calorific value (NCV) assumes the water leaves with the combustion products without fully being condensed. Fuels should be compared based on the net calorific value.

Ash Content:

The ash value is related to the inorganic material or salts in the fuel oil. The ash levels in distillate fuels are negligible. Residual fuels have higher ash levels. These salts may be compounds of sodium, vanadium, calcium, magnesium, silicon, iron, aluminum, nickel, etc.

Carbon Residue:

Carbon residue indicates the tendency of oil to deposit a carbonaceous solid residue on a hot surface, such as a burner or injection nozzle, when its vaporizable constituents evaporate. Residual oil contains carbon residue of 1 percent or more.

Coal:

Coal is a naturally occurring carbonaceous rock. The coal is formed from vegetal matter over a long period on the geological time scale. There are many varieties of coal occurring in nature. The coal suitable for making of coke is designated as coking coal. Every coking coal does not yield coke suitable for metallurgical applications and thus, coals yielding coke for metallurgical applications are termed as metallurgical coal.

Origin and formation of coal:

Coal occurs in nature as sedimentary rock where the carbonaceous matter is present with many other minerals. The structural examination of the coal shows confirmed evidence of its formation from vegetal matter. The fossil imprint of leaf, bark and other tree components on the coal provide evidence of its vegetal origin. The micro-structural examination of the thin section of coal reveals the presence of spores, pollens, resins and other essential components of vegetal matter which help in confirming and identifying the type of tree from which such coal is originated in the nature. It is believed that the large forest vegetation growing long ago got buried in the ground and was fossilised to become coal.

There are two theories for origin of coal: 'In-situ' theory and 'Drift' theory.

- The 'in-situ' theory describes it as natural growth of trees in swamps, their death and accumulation as peat over long period of time followed by its coalification to coal due to some geological action in nature, sustained for long duration of time.

- The 'drift' theory differs in first part of the process of coal formation to deposit peat at other location than its growth, while the second stage process is identical to the 'in-situ' theory. The 'drift' theory describes the growth of trees in high regions, and these are transported by river water after they die and get uprooted down to estuary where they get deposited as peat due to lower velocity of water. This deposited peat gets converted to coal by long geological action of the earth. Such peat formation can be noticed even now in Sunderban area of West Bengal which is the delta region of Ganges river.

Thus, the process of coal formation could be divided in two periods:

- a. Peat formation and
- b. Conversion of peat into coal.

Peat Formation (Biochemical Period)

- The forests grow in tropical climate. The swamps provide ideal place for the thick growth of the vegetation.
- The trees germinate from the fallen seeds on the soil. The tender tree grows fast in tropical climate and dies on maturity. When the tree dies, it falls on the ground and starts decomposing or decaying.
- This decomposition (or rotting) process is the disintegration of plant molecular structure aided by bacteria, moisture and air. When the process of decay of the dead tree is in progress and if another dead tree falls over it then the partially decayed tree gets buried in the soft swamp soil and the decay process is slowed down or arrested depending on the supply of oxygen necessary for the bacterial growth. This partially decayed vegetal matter is termed as peat.
- During the process of peat formation, the various constituents decay at different rate. The protoplasm and oils in the plant matter decay rapidly. The carbohydrates like cellulose, lignin, etc. decay slowly, whereas the spores, pollens, resins and waxes resist decay action.
- Thus, the nature of vegetation, its constituent and extent of decay will decide the peat composition and properties. This process of tree germination, growth, maturity death and partial decay process continues to form peat and its accumulation as layers buried under soft swamp soil.
- The peat layer thickness depends on the period of peat formation which may be hundreds of years. This peat layer awaits some geological action to cause its conversion into coal.

Conversion of Peat into Coal (Dynamo-chemical Period)

- The earth crust is dynamic in nature, and it undergoes depression or elevation at any given point due to movement of plates in the earth crust. It may be possible that at some time the area having peat deposit underwent depression causing peat layer buried at considerable depth with a formation of large depression of surface on its top.
- This depressed land filled with rain water would destroy all growing vegetation and would look like a huge water lake.
- In every rainy season, the flowing water to the lake would bring soil and get deposited at the bottom of lake. This soil silting process may continue for long time to eventually fill the lake and make it a plain ground over which the vegetation may start growing again with peat formation and accumulation to give another layer of peat deposit.
- It may also happen that another earth movement may push the buried layer of peat upward creating a mountain like elevated topology. In this process of geological action, the peat layer buried in the soil may be subjected to considerable pressure and temperature, rendering chemical and physical changes in peat properties.
- The chemical changes due to application of temperature and pressure would be the loss of moisture and evolution of carbon dioxide and methane.
- The oxygen content of the carbonaceous matter would be decreased with increase in temperature and time. These conversion changes get reflected in physical nature of the deposit.
- The colour, hardness and density keep changing with the advancement of the conversion from peat to anthracite.
- The peat has more than 90 percent of water and can be squeezed by hand. This water content is reduced in lignite which can be felt as wet.
- The bituminous and anthracite coal have very little moisture to be felt by hand. The brown colour of the peat becomes dark brown in lignite which further turns black when it becomes bituminous and anthracite.
- The coal hardness also increases with conversion from lignite to anthracite stage. The lignite is friable in nature, while bituminous is hard, but soils the hand with black carbon. Anthracite is quite hard and does not soil hand on rubbing on its surface.

TYPE, RANK, CLASS AND GRADE OF COAL

The words like type, rank, class and grade of coal are commonly used to differentiate its nature which has specific meaning.

Type of coal

The word type of coal indicates whether it is anthracite, bituminous or lignite coal.

All these three types of coal have distinct properties which render their identification

(i) Lignite:

It is brown/black in colour with considerable amount of moisture to soil the hand. It is fibrous in nature and crumbles easily on pressing. It has high porosity. It contains high volatile constituents with low fixed carbon.

(ii) Bituminous coal:

It has characteristic layers of bright and dull banded matter. It has typical cubic fracture. It is relatively hard (3–4 Mohs scale) in nature. It burns easily with smoky yellow flame. It has many commercial applications. The coking coals falling under this type are used for coke making.

(iii) Anthracite:

It is a hard and compact variety of coal with pitch like appearance. It breaks with irregular fracture and does not soil the finger on rubbing. Anthracite ignites with difficulty, but once ignited, it burns and gives intense local heat with very short and non-luminous flames. Anthracite does not have caking property and is unsuitable for coke making. It has limited industrial use as fuel, but often used to make artefacts.

Rank of coal

The word rank denotes the degree of coalification the peat has undergone to yield coal. The carbon content and calorific value of coal increase with rank, while the volatile matter is found to decrease. The different coals with increasing rank can be shown as:

lignite → bituminous → anthracite.

Class of coal

The term class is retained for its actual use such as coking coal, steam raising coal, gas making coal, etc.

Grade of coal

The grade refers to the degree of purity of the coal. The coals with higher ash and moisture content are referred as lower grade coals, while high grade coal, means coal with low ash and moisture content.

COAL CONSTITUENTS

The coal contains various constituents to render specific properties which cause its selection for various applications. These constituents could be grouped in three categories viz.

- Petrological constituents,
- Elemental constituents and
- Constituents important for its use.

These are discussed in the following sections.

Petrological Constituents in Coal

The coal contains various constituents which can be identified under geological microscope. These petrological constituents are known as macerals. These macerals differ significantly in their properties present in various coals. These macerals are grouped as vitrinite, exinite and inertinite.

➤ Vitrinite:

It is a primary constituent of coal. It usually occurs in bands. It is bright, black and brittle having conchoidal fracture. It is derived from woody tissues of the plant from which it was formed. Chemically, it is rich in polymers, cellulose $(C_6 H_{10} O_5)_n$ and lignin $(C_{30} H_{33} O_{11})$. It burns easily during combustion.

➤ Exinite:

These group of macerals are minor component of coal. These are rich in volatiles and hydrogen content that render it most reactive.

➤ Inertinite

It is oxidised organic material or fossilised charcoal. It is found as tiny flakes, generally forming 1–3 per cent in coal seam. It is least reactive group of macerals. The most common inertinite maceral is fusinite.

The natural minerals of different types are also found to be present in coal. These minerals get incorporated in early stage of peat formation. The intrinsic mineral matter originates from minerals present in the wood, since trees need various minerals as nutrient. These mineral constituents are finely sized and remain distributed in the whole coal body as fine particles. Such fine size mineral matter cannot be separated from coal by washing methods. The extrinsic mineral matters are those which get incorporated with peat during its formation and collection process. The extrinsic mineral matters are present in bulk and could be separated by coal cleaning methods. These mineral matters are un-combustible constituents and remain as ash after coal combustion. These mineral matters are not desired in coal.

Elemental Constituents in Coal

The major elements present in coal are carbon, hydrogen and oxygen. The minor elements include nitrogen, sulphur and phosphorus. In addition, any known element could be present in trace quantity. This elemental analysis is done using different instrumental techniques. The results of the analysis is reported as weight per cent of each element present in coal including major (in bulk percent), minor (in per cent) and trace constituents (in ppm, i.e., parts per million and ppb i.e. parts per billion) depending upon its need. Such elemental analysis of coal is reported as ultimate analysis.

The ultimate analysis of coal is useful in estimating air requirements for its combustion, flue gas analysis along with estimation of its calorific value. The presence of minor constituent like sulphur (wt.%) helps in deciding pollution abatement methods caused by its emission. The trace elements in coal would be discharged along with ash and flue gases. The presence and quantity of trace elements in coal help in providing adequate management systems to avoid hazards caused by toxic elements like Hg, As, Cd, Pb, Cr and radioactive elements.

Constituents Important for Coal Use

The coal contains moisture, incombustible inorganic matter and volatile constituents in addition to carbon. These constituents affect the use of coal. The proximate analysis of coal deals with the determination of following constituents by weight per cent:

- Moisture
- Volatile matter
- Ash, and
- Fixed carbon

The knowledge of these constituents is useful in the selection of coal for a given purpose.

Moisture

The moisture is present in every type of coal in varying amount (0.5 wt.% to 20 wt.%). In peat, the moisture content could be 90 per cent. It is an undesired constituent in solid fuels. The moisture present in the solid fuel is removed during use at the expense of its heating value. The moisture could be present in free (surface), adsorbed (inherent) or combined (chemical compound) state.

➤ Free or surface moisture

As the name suggests, this kind of moisture is loosely present on the surface or in the pores of coal. This moisture is derived from rain during storage, transportation and washing of coal. When water saturated coal is left in air for sometime, the excess free water evaporates and the moisture content in the coal attains equilibrium with the atmospheric humidity. The

per cent weight loss of free water by air drying at room temperature is termed as free or surface moisture.

➤ **Inherent moisture**

The water molecules adsorbed on the external surface and internal open pore surface is termed as inherent moisture. Its value would depend on porosity and atmospheric humidity. As the lower rank coals possess high porosity, therefore, the inherent moisture content would also be more in lower rank coals compared to higher rank coals.

The coal sample when heated to 110 ± 5 °C temperature for sometime, then the adsorbed (inherent) moisture molecules are detached and get removed. However, if the coal sample is left again in open atmosphere for longer time, then it may regain its inherent moisture content. This regaining tendency for inherent moisture will be more for high rank coals, while this readsorption will be less in lower rank coals, since their cell walls may breakdown during drying stage due to weak structure. This reduces the number of pores available for readsorption of moisture, causing lower inherent moisture in coal sample which has been heated and cooled.

This inherent moisture content in coal cannot be avoided. However, a lower value would be appreciated.

➤ **Combined moisture**

Coal contains mineral matter which, sometimes, contains water molecules that are chemically attached. Such chemically bonded water molecules do not evolve when the coal is heated at 100°C. This kind of moisture can be removed only when the coal is heated at higher temperature. Such combined moisture forms the part of volatile matter, and it is not determined separately. However, the presence of combined water in coal is not appreciated as it consumes some heat for its own dissociation, rendering lower net calorific value of coal for use.

Volatile matter

It is the part of coal which is evolved as volatile (gaseous) product when the coal is heated in the absence of air. As the quantity of volatile product is dependent on temperature, time, surface area, etc., therefore, a specified procedure is adopted to make the result reproducible and comparable.

The quantity of volatile matter in coal may range from 2 wt.% to 40 wt.%, while it is below 2 wt.% in coke and wood char. The volatile matter content plays an important role during its selection for a given application. Its higher content could be useful in gas making coals, but may not be appreciated in coking coal. The knowledge of volatile matter content helps in designing combustion system to provide appropriate primary and secondary air.

Mineral matter and ash

Coal contains various minerals which are uncombustible part of coal, called ash. It is common to state that coal contains ash, but technically coal contains mineral matter and yields ash on combustion. Chemically, mineral matter is different from ash. The coal may have following minerals in varying quantities in addition to oxides of sodium and potassium:

- Shale or silt (Hydrated silicates of aluminium)
- Pyrite (FeS_2)
- Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
- Lime stone (CaCO_3)
- Siderite (FeCO_3)
- Magnesite (MgCO_3)
- Apatite ($\text{Ca}_5(\text{PO}_4)_3 (\text{F}, \text{Cl}, \text{OH})$)

Some of these minerals originate from the vegetal mass from which the coal was formed. These minerals are required by the tree for its growth. Such mineral matter is known as intrinsic mineral matter and is present in very fine form in the matrix of coal which cannot be liberated or separated by coal cleaning methods. The bulk of the mineral matter present in coal is incorporated during peat formation stage and termed as extrinsic mineral matter. These could be present in coarser form which could be removed by coal cleaning methods.

When the coal is heated or burned, the minerals undergo changes depending upon temperature to yield ash. The ash content in a given coal is determined by observing the weight of uncombusted matter left after exposing the coal sample to oxidising condition at 800°C . In Indian coals, which contain low 'sulphur' and 'carbonate' minerals, the mineral matter (M % wt.) is given by:

$$M = 1.1 A$$

where, A is the ash (wt.%) determined by proximate analysis of coal sample assuming the sulphur and carbonate are very low.

Fixed carbon

Fixed carbon content in the coal is considered to be useful for a given application, e.g. combustion, reduction, etc. There is no direct method for its determination.

It is estimated as:

$$\text{Fixed carbon} = 100 - [M + VM + A]$$

where, M, VM and A are moisture, volatile matter and ash content in coal determined experimentally.

This fixed carbon value is not the total carbon in coal. A higher fixed carbon content in coal increases its commercial value.

CHAPTER-3

LIQUID FUELS

Liquid fuels are mainly oils, tars and pitches and are derived from the following sources:

- Petroleum
- Oil Shales
- Coal, by carbonization
- Coal, by hydrogenation

At present petroleum provides the majority of our liquid fuel requirements. The reserves of oil shales are immense, however, and these will probably increase in importance in the future. The liquid and tarry products of carbonization are used by industry near coalfields and carbonizing centres and, as a result, the steel industry employs these in fairly large quantities.

Refining of Petroleum:

Refining is the fractionation of the petroleum into its components and the first stage is a simple fractional distillation as follows:

- Natural gas—Boiling range below 30°C. This is usually removed under reduced pressure at the oilfield, initially to permit safe handling of the crude oil.
- Gasoline—Boiling range 30-200°C. This is "petrol" and may be further divided into aviation spirit (30-150°C), motor spirit(40-180°C), and vaporizing oil (110-200°C) for tractors, etc.
- Naphtha—Boiling range 120-200°C. There is usually a surplus at the top end of the gasoline range which is used for further processing. This is the fraction which is reformed to high octane gasoline and supplied to petrochemical plants as feedstock. It was also used for making into town's gas during the 1960s.
- Solvent spirit—Boiling range 120-250°C. This is white spirit or turpentine substitute and is used as a solvent, a cleansing agent and in paint manufacture.
- Kerosene—Boiling range 140-290°C. This fraction includes domestic paraffin oil (140-250°C) and heavier slow-burning fractions used as illuminants in railways (signal oil) and in lighthouses.
- Gas oil—Boiling range from 180°C and leaving a residue of carbon at 350°C. This is used as a carburetting oil in the gas industry and also in diesel engines.
- Fuel oils—Boiling above 200°C. Beyond this point vacuum distillation is necessary to avoid cracking of these heavy oils with the formation of lighter oil and carbon residue.

- Light fuel oil—Boiling above 200°C.
- Heavy fuel oil—Boiling above 250°C These are fractions of interest to furnace operators—for use in ships, land boilers, metallurgical furnaces, etc.
- The residue from these stages is becoming very thick and yields on further treatment, if paraffinic, wax (paraffin wax), mineral jelly ("Vaseline"), and lubricating oils and greases or, if asphaltic, bitumens and lubricants.

Tests for liquid fuel:

Two main tests done for liquid fuel are:

- Flash point: It is the minimum temperature at which the oil will catch fire if exposed to a naked flame
- Viscosity: It is also determined in standard equipment as a check on specification as regular behaviour in pipelines and burners is desirable. Viscosity varies logarithmically with temperature and would best be determined over a range of temperature.
- Pour Point: The pour point of a fuel is the lowest temperature at which it will pour or flow when cooled under prescribed conditions. It is a very rough indication of the lowest temperature at which fuel oil is ready to be pumped.

Uses:

The uses of oils are as varied as those of gas and include domestic heating and lighting, steelmaking, all kinds of engines, the generation of electricity, and the production of gas.

- Oil is also used as a raw material in the chemical industries. It can be almost as clean as gas in use but spillage and leaks of thick oil and tar are unpleasant features of many plants.
- The need for steam for warming the storage tanks and pipelines and for injection through the burners involves the use of space and money and the delivery of oil in quite small and very frequent batches by road tanker necessitates some careful organization and numerous checks on quality.
- Liquid fuels like furnace oil and LSHS (low sulphur heavy stock) are predominantly used in industrial applications.

CHAPTER-4

GASEOUS FUELS

Gas fuels are the most convenient because they require the least amount of handling and are used in the simplest and most maintenance-free burner systems. Gas is delivered "on tap" via a distribution network and so is suited for areas with a high population or industrial density. However, large individual consumers do have gas holders, and some produce their own gas.

Types of gaseous fuel

The following is a list of the types of gaseous fuel:

- Fuels naturally found in nature:
 - Natural gas
 - Methane from coal mines
- Fuel gases made from solid fuel
 - Gases derived from coal
 - Gases derived from waste and biomass
 - From other industrial processes (blast furnace gas)
- Gases made from petroleum
 - Liquefied Petroleum gas (LPG)
 - Refinery gases
 - Gases from oil gasification
- Gases from some fermentation process

Gaseous fuels in common use are liquefied petroleum gases (LPG), Natural gas, producer gas, blast furnace gas, coke oven gas etc. The calorific value of gaseous fuel is expressed in Kilocalories per normal cubic meter (kCal/Nm³) i.e. at normal temperature (20 degree C) and pressure (760 mm Hg).

Properties of gaseous fuels:

Since most gas combustion appliances cannot utilize the heat content of the water vapour, gross calorific value is of little interest. Fuel should be compared based on the net calorific value. This is especially true for natural gas since increased hydrogen content results in high.

Fuel Gas	Relative Density	Higher Heating Value kcal/Nm³	Air/Fuel ratio- m³ of air to m³ of Fuel	Flame Temp. °C	Flame Speed m/s
Natural Gas	0.6	9350	10	1954	0.290
Propane	1.52	22200	25	1967	0.460
Butane	1.96	28500	32	1973	0.870

CHAPTER-5

REFRACTORIES

The refractory is an essential requirement for any furnace to sustain high temperature. These refractory materials must possess sufficiently high fusion temperature to retain their shape at working temperature. Further, such materials must have required porosity, strength at high temperature, thermal conductivity, resistance against corrosion and erosion with many other properties at affordable cost. The production of quality refractory with low cost has always posed challenge to ceramic industries. The larger high temperature metallurgical units (e.g. blast furnaces producing more than 4000 ton hot metal per day) constructed these days for economic reasons, demand very stringent quality of refractory materials.

The refractory materials are required to possess many properties. Refractory materials should have the ability to:

- a. withstand high temperature
- b. withstand corrosive action of molten slag and hot gasses
- c. withstand abrasion and erosion by moving solid charge, flowing liquids and blowing gases
- d. withstand working load during service
- e. retain dimensional stability at working temperatures
- f. sustain repeated thermal cycling
- g. sustain thermal shock (sudden change in temperature)
- h. conduct/resist heat flow as needed during use
- i. store heat in the system

In addition to the above properties, the availability of refractory at suitable cost would be a desirable factor for its use.

Properties and testing methods of Refractories

➤ High Temperature Behaviour:

The refractory materials are required to serve at high temperature, and hence they must have sufficient strength at working temperature to retain their shape and size. This high temperature strength becomes more important when the size of the furnace is large and load on the hot refractory structure becomes high. It must be noted that strength measured at room temperature is not the indication for its fitness to use the refractory at high temperature. As we know that any solid material when heated starts becoming soft at some

temperature due to fusion/melting at grain boundaries, and eventually it becomes liquid at its melting point. This requires the knowledge of maximum temperature for safer use of the refractory. This high temperature behaviour of the refractory is tested by measuring the following properties:

- a. PCE (Pyrometric Cone Equivalent) value
- b. RUL (Refractoriness Under Load) value
- c. Creep at high temperature
- d. High Temperature Modulus of Rupture (HMOR)
- e. Thermal shock resistance
 - Spalling test
 - Loss in MOR strength
- f. Reversible thermal expansion
- g. PLC (Permanent Linear Change) test

a. PCE (Pyrometric Cone Equivalent) value

It is the measure of refractory's ability to sustain high temperature without fusion or deformation. This is measured by heating a standard size cone made of the material to be tested in a furnace along with another standard cone having refractoriness very close to the test material (determined by a pre-test), and noting the furnace temperature at bending (9' or 3' o'clock positions viewed upside down) of the cone inclined at one end due to its own weight.

b. RUL (Refractoriness Under Load) value

It is the capability of a brick to sustain itself without breaking at high temperature under pressure of overlying load. This working load could be due to burden, liquid metal or its own structural weight. In simple words, RUL is the crushing strength of a brick at elevated temperature. The crushing strength of the refractory brick is lowered at elevated temperature due to fusion/melting of grain boundaries.

c. Creep at high temperature

Creep is a property which indicates deformation of the refractory at high temperature which is subjected to stress for longer period.

d. High Temperature Modulus of Rupture (HMOR)

It is the maximum stress that a rectangular test piece of defined size can withstand when it is bent in a three point bending device. It is expressed as N/mm² or MPa.

e. Thermal shock resistance

Thermal shock resistance is a measure of refractory property when it is exposed to alternate heating and cooling. This thermal shock leads to breaking of refractory particles which is termed as 'spalling' and loss of strength due to micro-cracks and is noted as MOR value after thermal treatment.

f. Thermal expansion

The increase in volume of the material due to heating is called thermal expansion. This expansion process is reversible in nature, and material regains its size on cooling, hence, it is also called reversible thermal expansion. It is the inherent property of all the materials. This property is measured as linear expansion with heating due to practical reasons. Figure 7.8 shows the thermal expansion of some refractory items.

g. PLC (Permanent Linear Change) test

The materials expand on heating, but they regain original shape on cooling (reversible thermal expansion). The permanent linear/volume change refers to non-reversible expansion in the refractory materials due to heating process.

This permanent linear/volume changes could be due to the following reasons:

- a. Phase changes in the refractory due to allotropic forms having different specific gravity.
- b. Chemical reactions causing formation of new compound having different specific gravity. This could be due to chemical attack by gas or slag in the system leading the formation of different compounds with changed properties.
- c. Sintering of the material causing densification and shrinkage.
- d. Melting of some phase causing densification and shrinkage.

➤ Corrosion Resistance

It is the wear and tear of refractories caused by static chemical attack of slag. The eating away of refractory material due to chemical reaction between refractory and molten fluid (slag) at high temperature is termed as 'refractory corrosion'.

➤ Erosion Resistance

The ability of a refractory to sustain the mechanical erosive action of sliding burden, moving products (liquid melt and slag), flowing gases (e.g. hot flue gases laden with solid particles) is termed as 'erosion resistance'.

➤ **Thermal Conductivity**

Thermal conductivity is defined as the quantity of heat that will flow through a unit area in a direction normal to the surface area in a given time with a known temperature gradient under steady state thermal conditions. It is indicative of heat flow characteristics of the refractory and depends upon the nature of mineralogical constituents as well as the physical properties of the refractories.

➤ **Porosity**

Porosity is a measure of the vacant space as pores and voids/cavities in the refractory material. The pores and cavities could be differentiated on their length to diameter ratio. The pores have longer length and their length to diameter ratio is more than the cavity. The pores present in refractory are of three types: open pores, inter-connected pores and sealed pores. These are explained in the following sections:

a. Open pores

These have one of their ends on the outer surface of the particle. This open end allows the movement of fluids (gas/liquid) to the interior location of the particle permitting chemical reaction and adsorption/absorption processes. The liquid metal may penetrate under pressure and get solidified to cause refractory failure. The refractory with large sized open pores are undesirable for places facing liquid metal or slag.

b. Interconnected pores

These have both of their ends opening to the outer surface of the refractory. This allows a free movement of fluids (gas/liquid) and offers site for chemical reactions and adsorption/absorption of fluids. Such pores are useful in manufacturing ceramic filters, but are not desirable in refractory brick used in furnaces which may cause leakage of gases in the furnace.

c. Sealed pores

There are deep seated and do not open up to the surface of the particle. These sealed pores do not offer any site for chemical reaction nor allow adsorption/absorption of fluids. However, these sealed pores act as a good thermal barrier and increase the heat insulating power of the material. Such sealed pores are useful while making heat insulating materials.

➤ **Density**

The refractory is a porous material, and therefore its density is seriously affected by pore volume. Following three terms are used to differentiate various types of density values:

True density

This refers to the ratio of mass to volume of solid particle without any pores or cavities.

Apparent density

It refers to the ratio of mass to volume of a single solid particle including closed pores (i.e., volume of solid material + volume of closed pores within the particle).

Bulk density

It refers to the ratio of bulk mass to total bulk volume (solid volume + pore volume + void volume) of the refractory brick.

➤ **Cold Crushing Strength (CCS)**

The cold crushing strength (CCS) represents the ability of a refractory to resist failure under compressive load at room temperature. The compressive load is applied on the refractory block till its fracture. The CCS is then calculated as total load applied divided by the surface area.

Types of Refractories:

➤ **Classification of Refractory based on Chemical Nature**

The furnaces use several types of refractory bricks made from refractory materials. The refractory materials are generally classified on the basis of their chemical behaviour, i.e., their reaction to the type of slag. Accordingly, refractories can be classified as: acid, basic and neutral.

Acid refractories

Acid refractories are those which are attacked by basic slag. These are not affected by acid slag, and hence it can be used in furnaces having acidic work environment. The following types of refractories fall in this group:

- (a) Silica (most acidic)
- (b) Semi silica
- (c) Alumino-silicate refractories (e.g. high alumina (as exception since it reacts with slag), Fireclay group refractory (e.g. LHD-Low Heat Duty, HHD-High Heat Duty, SD-Super Duty and Grog), Kyanite, Sillimanite and Andalusite.

Basic refractories

Basic refractories are those which are attacked by acid slag. These refractories are of considerable importance for furnace linings where the environment is basic, for example, basic steel making and furnaces for non-ferrous metallurgical operations. The following refractories fall in this category:

- (a) Magnesite
- (b) Magnesite-Chrome
- (c) Chrome-Magnesite
- (d) Dolomite
- (e) Forsterite

Neutral refractories

These refractories are attacked neither by acid nor by basic slag. The following refractories are known for their inertness:

- (a) Graphite (most inert)
- (b) Chromites
- (c) Synthetic refractories (e.g. zirconium carbide and silicon carbide)

➤ **Classification of Refractory based on Other Considerations**

The refractory materials find high temperature applications in many forms and shape. These refractory materials could be classified as: Special refractories, Insulating refractories and Cermets.

Special refractories

These refractory materials are specially manufactured using synthetic (fused/sintered) grains free from impurities under highly controlled production parameters for special applications. They are used for purposes like fabrication of crucible, some parts of furnaces and research and developments. These applications of the refractory do not consider cost as a factor for selection. The refractories included in this group are:

- (a) Alumina,
- (b) Pure sialons (Si-Al-O-N),
- (c) Thoria (ThO_2),
- (d) Beryllia (BeO),
- (e) Zirconia,
- (f) Boron nitride,
- (g) Spinel, etc.

Insulating refractories

These are high porosity refractories having low thermal conductivity used for reducing the rate of heat flow (heat losses) to maximize heat conservation within the furnace. The development and application of a wide variety of insulating refractory materials are gaining importance with increasing energy costs in present days. The production of brick shape refractories utilises China clay, asbestos (kieselguhr), glass wool, mica (vermiculite), bubble alumina, carbon, paper wool, ceramic fibers, saw dust, etc. as raw materials.

Cermets

The refractories produced from the mixtures of high purity refractory oxides, carbides, borides, and metals or alloys fall under this category. Depending on the composition and quality, they are used as abrasives (cutting, grinding, boring tools), in parts of spacecrafts, missiles, atomic power plants, etc.

RAW MATERIALS FOR REFRACTORY MANUFACTURE

The refractory preparation exploits natural resources together with synthetic materials. These refractory raw materials can be broadly divided into two categories: clay based and non-clay based.

Clay based Refractory Raw Materials

The naturally occurring clays having high percentage of refractory constituents find use in refractory industry. These include fireclay and high alumina clays.

Fireclay

It is generally defined as a “mineral aggregate composed of hydrous silicates of aluminium ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) with or without free silica”. It is also known as kaolinite. It is generally found as white in colour, but sometimes red, blue or brown tints come from impurities.

High alumina clay

It is composed of bauxite riched or other raw materials that contain 50 to 87.5% alumina. High alumina refractories are generally multipurpose, offering resistance to chipping and higher volume stability. High alumina refractories are used to produce brick and insulating refractories.

Non-clay based Refractory Raw Materials

These refractory materials are prepared from naturally occurring minerals and synthetically processed materials.

Magnesite

It is a mineral with the chemical formula MgCO_3 (magnesium carbonate). It is found as colourless, white, pale yellow, pale brown, faintly pink, lilac-rose mineral having conchoidal fracture, possessing hardness of 3.5–4.5 on Mohs scale.

Extra-high alumina

It is prepared predominately from bauxite or alumina (Al_2O_3). The extra-high alumina refractories contain 87.5% to 100% alumina and offer good volume stability. They are typically poured into special shapes using a fused casting process.

Mullite

Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) is made from kyanite, sillimanite, and andalusite, bauxite or mixtures of alumina silicate materials. The mullite refractories contain ~ 70% alumina. It possesses specific gravity of 3.11–3.26 and hardness 6–7 on Mohs scale. They maintain a low level of impurities and high resistance to loading in high temperatures.

Silica

The quartz mainly containing silica is used for this purpose. The silica refractories are characterised by a high coefficient of thermal expansion between room temperature and 500 °C. Silica bricks are prepared in three grades: super-duty (low alumina and alkali), regular, and coke oven quality. Silica compositions can be used for hot patching, shrouds, and bricks.

REFRACTORY MANUFACTURING PROCESS:

Refractory manufacturing process basically consists of four steps:

(i) Raw material processing

This step involves crushing and grinding of raw materials obtained from various sources followed by their classification according to particle size by screening and sieving. These raw materials also sometimes need washing, calcinations and drying operations to meet the chemical specifications. The dry refractory powder of one size is mixed with other size to meet specific grain size distribution along with other chemical constituents desired for specific need. The dry refractory powder is packed and marketed as such for various applications. This dry refractory powder mass with specific size mix serves as feed for making refractory bricks and other components.

(ii) Shaping

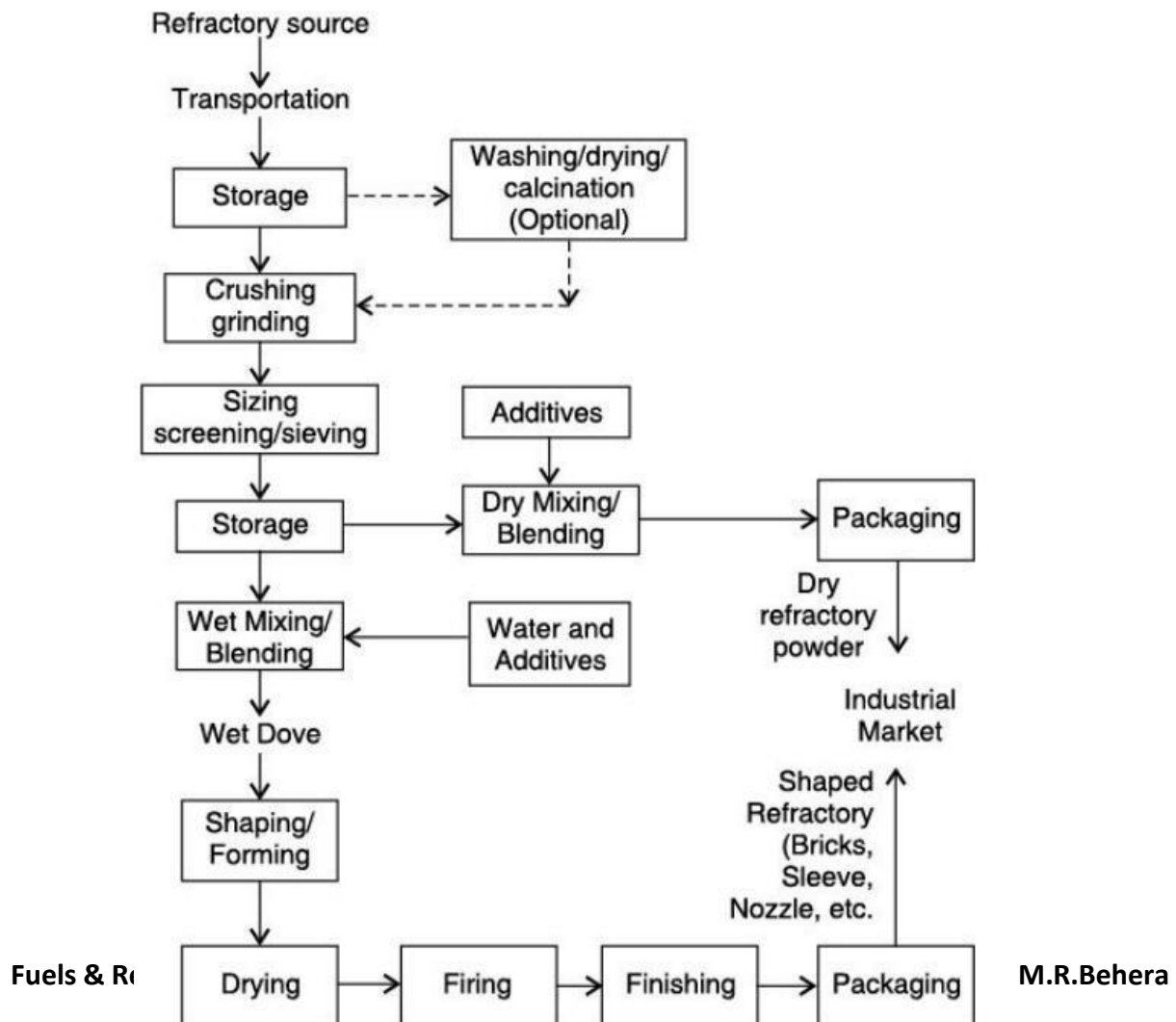
The dry powder is mixed with water and other additives to prepare wet dove for giving shape to the refractory using different types of machines and technique. The shaped refractory is air dried before firing.

(iii) Firing

The shaped refractory is subjected to firing to cause heat hardening by ceramic bonds and bring desired phase changes to have a stabilised refractory. This firing is done in kilns having high temperature caused by combustion of fuels mostly gaseous in nature for better quality product.

(iv) Final processing

The final processing step includes milling, grinding, and sand blasting of the final product to give finished and desired surface quality. The certain products may also need impregnation with tar/pitch or armouring by some other material like steel sheet. Finally the products are packaged for safe transportation.



References:

1. Elements of Fuels, Furnaces and Refractories by O.P. Gupta, Khanna Publisher