FUELS AND REFRACTORIES

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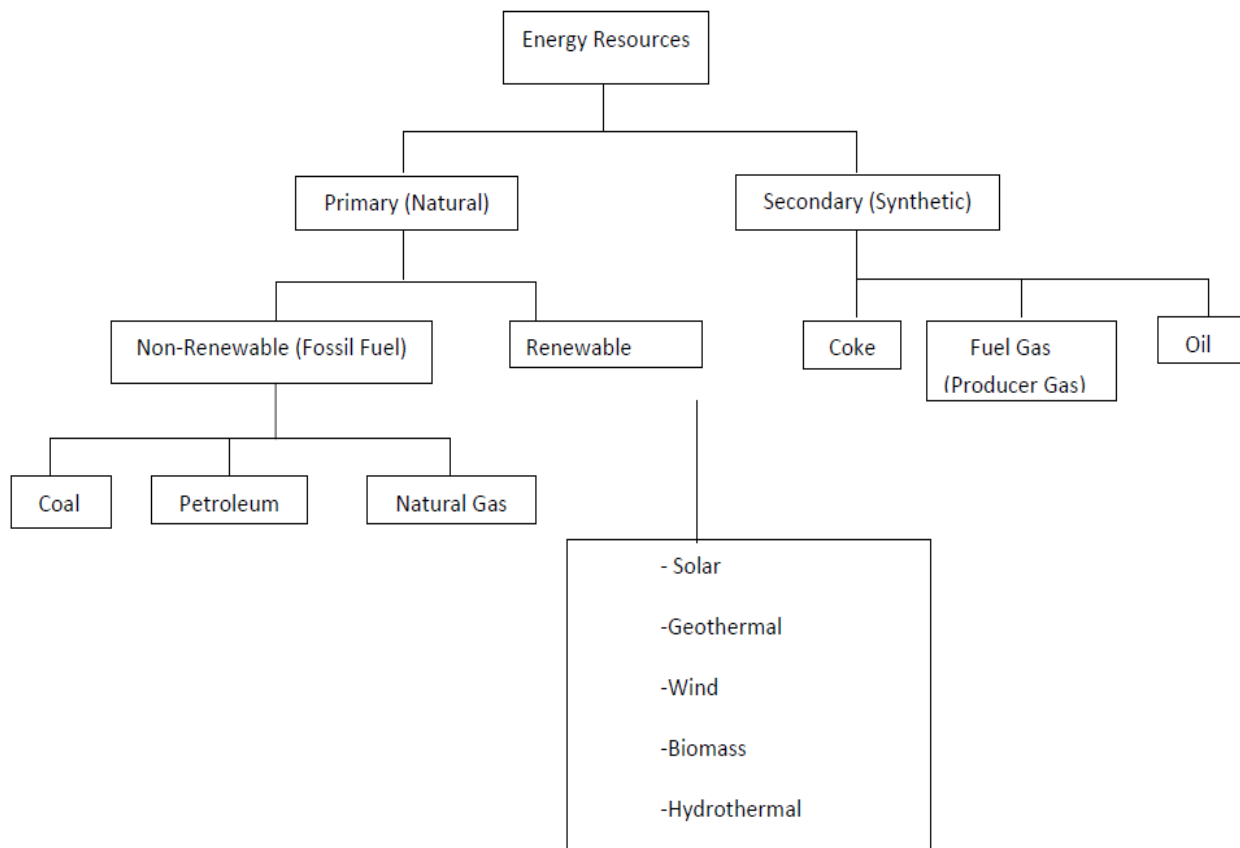
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1.1 FUEL

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.

1.2.FUEL CLASSIFICATION:

TYPE	NATURAL/PRIMARY	SECONDARY
SOLID	WOOD ,COAL	CHARCOAL COKE
LIQUID	PETROLEUM	OIL TAR ALCOHOL
GAS	NATURAL GAS	PRODUCER GAS BLAST FURNACE GAS COKE OVEN GAS

1.3 Use of Fuels by Metallurgical Industries

The metal making process uses different routes to extract metal from its ores.

→The pyro-metallurgical route depends mainly on some solid/gaseous fuels which are used as reductants and heat sources.

→The hydrometallurgical/electrometallurgical methods also need liquid/gaseous fuel to melt and refine the electrodeposited metal from the leached liquor.

Thus, fuels are required for metal extraction from their ores.

→The extracted metals are given shape by processes like casting, rolling, forging, extrusion, etc.
 These processes are conducted at elevated temperature and fuels (liquid/gaseous) are required to raise the temperature of the metal to the required level.

→ In case of electrical heating, the electricity is generated by thermal power plants mainly using coal as a fuel, though liquid and gaseous fuels are used by some plants.

→The suitably-shaped metals are given heat-treatment to generate required micro-structural features in the metal rendering suitable mechanical properties
for use.
This heat-treatment process requires some fuels (liquid/gaseous) to provide suitable temperature and atmosphere.
Thus, we find that fuel is needed at every step in the metallurgical process, and it becomes an essential raw material for any metal industry.

Solid fuels

Merits

(a) Abundance in nature
(b) Ease of availability due to global distribution
(c) Ease of transportation by road, rail and ship
(d) Ease of storage on ground with safety
(e) Ease of use
(f) Low cost

Limitations

(a) Presence of mineral matter yielding ash posing disposal problem
(b) Contamination of product by mineral matter constituents
(c) Environmental issues related with trace elements in mineral matter
(d) Environmental issues related with dust during handling
(e) Handling needs heavy equipment
(f) Needs large floor space for storage which is costly in industrial area

Liquid fuels

Merits

(a) Rich energy source
(b) Ease of combustion with flame and atmosphere control in the furnace
(c) Ease of storage in tank suitable to space, shape and size (over or underground)
(d) Ease of handling through pipes and pumps
(e) Ease of long distant pipe transportation
(f) Free from ash and any major impurity except sulphur content

Limitations

(a) Not evenly distributed on globe
(b) More expensive fuel
(c) Needs extra safety during handling and storage to avoid fire hazard
(d) Needs pre-heating in cold regions to maintain its fluidity
(e) Needs flame temperature control to minimize NOx emission

Gaseous fuels

Merits

(a) Ease of combustion with flame and atmosphere control in the furnace
(b) Free from any impurities
(c) High flame temperature with pre-heating air and/or gas
(d) Ease of handling and use
(e) Ease of transportation by gas pipeline
(f) Surface transportation feasible by road, rail or ship in liquid state, in specially designed cryogenic tanks
 (g) Can be generated by using solid and liquid fuels also

Limitations

(a) Not evenly distributed on globe as natural gas
(b) Needs big storage tanks as the large welded tanks are unsafe under pressure
(c) Needs extra safety during handling and storage to avoid fire hazard

1.4. Energy Scenario under Indian Condition

→India ranks 6th in the world in total energy consumption and needs to accelerate the development of energy sector to meet 8-9% economic growth in the country.

→India though rich in coal and abundantly endowed with renewable energy has very small hydrocarbon reserves (0.4% of the world's reserve).

→India is a net importer of energy, more than 25% of primary energy needs being met through imports in the form of crude oil and natural gas.

→In energy production, coal and oil account for 54% and 34% respectively with natural gas, hydro and nuclear contributing to the rest. Industrial sector in India consumes 52% energy. Consumption of primary energy in India is 530 Kg of oil equivalent/person in 2004 compares to 1240 Kg oil equivalent/person in China and the world average of 1770 Kg of oil equivalent/person.

→Primary energy consumption per person will grow with the growth in economy because energy consumption is an index of country's economic growth and prosperity.
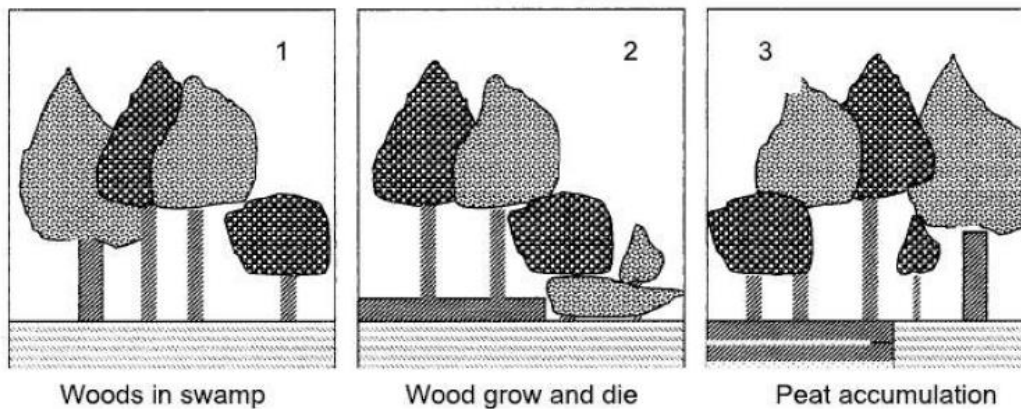
2.1.1 ORIGIN OF COAL :

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.
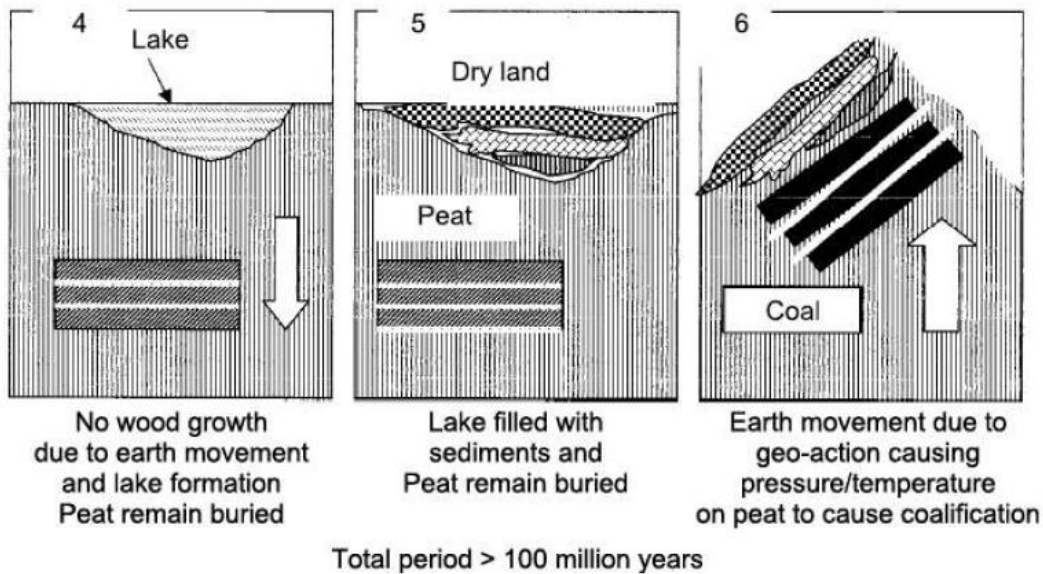
→The 'drift' theory differs in first part of the process of coal formation to deposit peat at other location than its growth, while the second stage process is identical to the *'in-situ'* theory. The 'drift' theory describes the growth of trees in high regions, and these are transported by river water 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.

Peat formation (Biochemical period)

Woods in swamp   Wood grow and die   Peat accumulation

Coalification of peat (Dynamochemical period)

4 — Lake
No wood growth
due to earth movement
and lake formation
Peat remain buried

5 — Dry land — Peat
Lake filled with
sediments and
Peat remain buried

6 — Coal
Earth movement due to
geo-action causing
pressure/temperature
on peat to cause coalification

Total period > 100 million years

2.1.2 COMPOSITION OF COAL

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.

(a) **Vitrinite** 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.

(b) **Exinite** group of macerals are minor component of coal. These are richin volatiles and hydrogen content that render it most reactive.

(c) **Inertinite** 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 uncombustible constituents and remain as ash after coal combustion. These mineral matters are not desired in coal.

COAL:

Coal is formed by the prolonged action of geological forces on the plant and vegetal matter accumulated below the earth crust. The process is called "**COALIFICATION**".

Coalification is both time and force dependent.

Coalification brings following changes to the accumulated plant:

Wood →Peat →Lignite →Bituminous →Anthracite→ Graphite

Increase in time and magnitude of forces →

Both, physical change like colour, strength, density and structure; and chemical change occur.

Chemical changes are important:

→Oxygen decreases from 40% for wood to 305 for peat, 20% for lignite, 5% for bituminous and 2% for anthracite coal.

→Volatile matter decreases from about 70% for wood to 5% or less for anthracite coal.

→Increase in carbon from about 30% for wood and peat to 90-95% for anthracite coal.

Petroleum:

Petroleum is formed in the earth's crust from the accumulated vegetal and animal matter metamorphic processes similar to coalification.

From crude petroleum gasoline, lubricating oil, fuel oils etc. are obtained.

Natural gas:

It is used directly

2.1.3

Fuel characterization concerns with the "analysis" and "energy content of fuel" (also known as calorific value). Fuel analysis comprises of "proximate" and "ultimate".

(A)Proximate analysis:

In the proximate analysis, moisture (M), Ash (A) and volatile matter (VM) are determined. Fixed carbon (FC) is obtained from the following equation:

% Fixed Carbon = 100-(% Volatile Matter + % Ash+ % Moisture)

There are standard tests to determine proximate analysis. Moisture is determined by drying 1gm of sample at 105^0C for 1 hour . Weight loss is expressed in % of initial weight of the sample

%M = (Weight loss/ Weight of the Sample) X 100

Ash is wight of the residue obtained after complete combustion of 1 g of coal at 700-750^{0}C. Ash in % is

%A= (weight of residue / weight of sample) X 100

Volatile matter is the weight loss obtained on heating 1gm sample of coal at 950^0C for 7 minutes in the absence of air .

Total weight loss of a moist coal = Weight loss due to Volatile matter + Moisture

Weight loss due to volatile matter = Total weight loss – moisture

If coal sample is dry then weight loss is due to volatile matter (VM) only .

%VM=(Weight loss due to VM / weight of sample) X 100

Fixed carbon can be obtained from the first equation

Ultimate analysis:

The main chemical elements in coal (apart from associated mineral matter) are C, O, H, N and S. The chemical analysis is very important to calculate material balance accurately and calorific value of coal

For the ultimate analysis C,H,S and N are determined by chemical analysis and expressed on a moisture free basis .Ash is determined as in proximate analysis and is calculated on moisture free basis . Then,

%O = 100 (%C + %H + %N + %S + % ash)

Note on Ash and Volatile Matter

In fact coal contains mineral matter (MM) like $CaCO_3$, $MgCO_3$, SiO_2, Al_2O_3, Na_2CO_3 etc. but not ash. Ash is residue obtained after complete combustion of coal and consists of CaO, MgO,SiO_2 ,Al_2O_3,Na_2CO_3 etc .

In ultimate analysis of coal, the percentage value of all elements are reported including major, minor and trace constituents, depending upon its need. Themajor elements present in coal are carbon, hydrogen and oxygen, while

the minor elements include nitrogen, sulphur and phosphorus. In addition, any known element could be present in trace quantity.

(i) The carbon and hydrogen are determined by burning the coal with oxygen under controlled condition and measuring the product CO_2 and H_2O by suitable absorption tubes.

(ii) Nitrogen in coal could be determined by Kjeldahl method. A small sample of the coal is completely oxidised by boiling with a mixture of concentrated sulphuric acid, potassium sulphate and a little mercury. After precipitating mercury, sodium hydroxide is added in excess and the ammonia formed during the oxidation is distilled off and determined by standard analytical method. The nitrogen in coal varies from 1–2 (wt.%).

(iii) Sulphur in coal is determined by oxidising it to sulphur dioxide and sulphur trioxide. These are absorved by an alkali to form corresponding sulphite or sulphate, which is finally converted to barium sulphate. The weight of clean and dried barium sulphate weight could be used to calculate sulphur in coal sample.

(iv) Phosphorus is present as phosphate and organic phosphoruscompound. The burning of coal yields all phosphorus in ash and can be analysed easily.

(v) Oxygen in coal is obtained by adding all the contents including ash and then subtracting the total from 100, i.e., Oxygen (wt.%) = 100 – (Ash + C+ H + N + S + P) wt.%. This method has a major drawback as all the error in analysis is pushed to oxygen (wt.%).

The impurities like sulphur affect the utility of the coal. Assam coking coal in India is a typical example which cannot be used for coke making due to its high (up to 3%) sulphur content. The sulphur dioxide rich gas emission from cupola furnaces in Agra resulted a total ban on the local foundry units due to its bad impacts on TAJ (a world heritage).

The value of ultimate analysis is useful in estimating the calorific value of coal using **Dulong's formula** : Calorific Value (kJ/kg) = 337C + 1442 [H – (O/8)] + 93 S; where, C, H, O and S are carbon, hydrogen, oxygen and sulphur (in wt.%). The ultimate analysis is also used to estimate the air needed for fuel combustion and flue gas analysis. In view of the need of ultimate analysis on routine basis by many industries, the instruments are available for speedy and reliable analysis.

Ash and mineral matter are not identical

Ash content of coal is important. In high temperature applications where coal is the principle source of chemical and thermal energy, removal of ash is an important issue. In general ash content of coal should be low. In addition, melting point of ash is also important. In furnaces where coal is used to heat the material below its melting point, melting point of ash should preferably be higher than the furnace temperature because of easy disposal

Whereas in applications where coal is carbonized and the carbonized product is used to derive thermal and chemical energy for example in blast furnace iron-making, both amount of ash and its melting point is of considerable importance. In this case ash should be easily fusible and its melting point should be easily fusible and its melting point should be lower than furnace temperature .Larger amount of ash will increase the amount of slag .

Total mineral matter (MM) can be calculated by Parr formula

 MM = 1.08 A + 0.55 % S

While calculating FC on mineral matter basis , Parr subtracts 0.15% S from measured fixed carbon.

It consists of volatile substances formed during heating of coal out of contact of air. Essentially these are gaseous substances like CO, H_2, H_2O, CO_2, CH_4, N_2, O_2 and other hydrocarbons. Volatile matter does not include moisture of coal but includes water formed during reaction between hydrogen and oxygen of coal .

How to report analysis ?

The different ways to report analysis of coal can be illustrated by an example . Consider sub-bituminous coal

(A) Proximate analysis :

	As Received	Dry Basis	Dry-Ash free	Dry Mineral Matter free
%M	6.8	----------------	----------------	-----------
%A	12.3	13.2	----------------	-----------
%VM	36.2	38.84	44.7	44.6
%FC	44.2	47.42	54.7	55.4
%S	0.5	0.54	0.6	-----------
Total	100.0	100.0	100.0	100.0

(A) Ultimate analysis :

Composition(%)	As received		
C			
H			
O			
N			
S			

A			
M			
Total			

2.1.5.Calorific Value

Calorific value (CV) is the amount of heat released on complete combustion of 1 Kg of coal at the reference state of products of combustion (POC hereafter)

For a hydrocarbon fuel containing C,H,S , products of complete combustion are CO_2,H_2O and SO_2

Reference state of POC is

25^0C CO_2(g), SO_2(g) and H_2O liquid= Gross Calorific Value (GCV)

100^0C CO_2(g) ,SO_2(g) and H_2O (v) = Net Calorific Value (NCV)

So GCV> NCV by an amount equal to latent heat of condensation

Dulong's formula (Theoretical calculation)

Dulong's formula for the theoretical calculation of calorific value is

$$\text{GCV (or) HCV} = \frac{1}{100}\left(8080\, C + 34500\, [H - \frac{O}{8}] + 2240\, S\right) \text{kcal/kg}$$

where, C, H, O & S represent the % of the corresponding elements in the fuel.

It is based on the assumption that the calorific values of C, H & S are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely. However, all the oxygen in the fuel is assumed to be present in combination with hydrogen in the ratio H : O as 1 : 8 by weight. So the surplus hydrogen available for combustion is $H - \frac{O}{8}$.

2.1.6 :

The coals when heated in the absence of air behave differently. Certain coal undergo physical change on heating while some coals do not exhibit this behavior . Thus, the coals are grouped as 'caking coal' and 'non-caking coals'.

(i) **Caking coals**: The coals which soften on heating (~ 400 °C) to become plastic in nature and on further heating (~ 600 °C) render them to resolidify as a hard coherent mass are termed as 'caking' coals. These caking coals are used for coke making, but it is not necessary that every caking coal is suitable for coke making. Coke making needs many other properties along with caking property. The caking coals are not suitable for combustion as they fuse on heating and cause difficulty in combustion process.

(ii) **Non-caking coals**: The coals which do not display any change in physical state and give a non coherent mass of char on heating are called 'non-caking' coals.

Caking Index Of Coal :

It is the measure of binding or agglutinating property of coking coal. Numerically , it is the maximum number ratio of sand to coal in a 25 gm mixture of the two(sand + coal) which on heating under standard conditions produces a residue coke capable of supporting a weight of 500gms without producing more than 5% loose grains of coke

The higher the agglutinating propensity of coal (i.e. the caking index), the higher the amount of sand (inert) that can be bound by coal and hence higher the caking index.

The caking index of coal blend charge for coke ovens (for producing metallurgical coke) is about 21 to 22.

Swelling Index (CSN)

The coal undergoes volume change during heating process. The swelling behaviour has been found useful to assess coking coal quality. This test requires 1 g coal sample (–0.212 mm, i.e., –72 mesh size) held in a silica crucible covered with a lid and heated in oven under standard condition. The carbonised

coal button in the crucible is observed and compared with standard samples to assign a **crucible swelling number (CSN)** from 0 to 9 (Figure 2.5). The coals with CSN 4 and above are considered good for coke making.
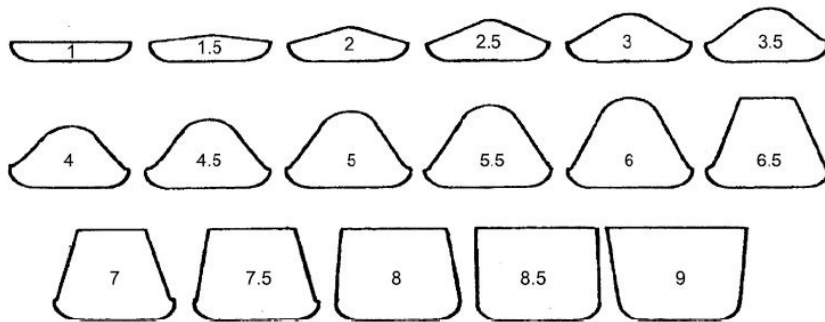

Figure 2.5 Crucible swelling number (CSN) chart.
(Adopted from R.C. Gupta, *Theory and Laboratory Experiments in Ferrous Metallurgy* , PHI Learning, Delhi, 2010.)

2.1.7 Metallurgical coke

The caking coal when heated in the absence of air, at coking temperature, yields a strong and porous carbonaceous mass termed as **coke** . All caking coals do not yield coke and every type of coke is not termed 'metallurgical coke'.

The term **metallurgical coke** is designated to a specific variety of coke useful for iron blast furnace applications, which possesses required low porosity, high strength and low reactivity.
The coke making requires selection of caking coal based on its properties like:

(i) **Caking behaviour:** The coal must be strongly caking in nature.

(ii) **Swelling Behaviour:** The coal must not have swelling behaviour during heating. High swelling nature would cause pressure in coke chamber and may damage it in some cases.

(iii) **Plastic Behaviour:** The coal must not exhibit excess plasticity during heating which may give spongy type of coke with low strength.

(iv) **Ash content:** Ash content in the coal must be in minimum quantity as it adds the demand for fluxing agents during blast furnace iron making and

MODULE 2.2

CARBONIZATION: heating of coal out of contact of air

PHYSICO CHEMICAL CHANGES DURING CARBONIZATION

STAGE 1: 25-700

→primary breakdown of coal at 700 degree centigrade

→products like
H_2O
CO
CO_2
Aromatics
Paraffins
Olefins
Nitrogen compounds etc
Residue : soft coke
Considerable swelling

STAGE 2: 700

→secondary thermal reactions between the liberated products as they pass through the hot coke and coke oven walls

→evolution of hydrogen

→formation of aromatics

→methane at 700 degrees

→ammonia NH_3

Stage 3: 1100

→ progressive removal of hydrogen from residue and hardcoke is produced

During carbonisation coal swells first and then resolidifies

Carobonisation time 16-20 hrs/ 22 tonnes of coke

TECHNOLOGY OF COKE PRODUCTION

(1) Indirect heating of the chamber containing coke is required
(2) Swelling tendency of coal control it

(3)by product recovery(disposed at around 1200 degrees)

→ sensible heat
→ potential energy

(4)sensible heat of product (coke)

TYPES OF COKE OVEN

→ Bee hive coke oven
→ by product coke oven

Rectangular (15 x 0.4 x 5 m) refractory chamber with removable door at both sides

DIMENSIONS OF COKE OVEN
Length: 13 m to 15 m
Height: 4.5m to 5 m (7 m)
Width 400 mm (600 mm)

Fuels used:
→Blast furnace gas (preheated)
→producer gas (preheated)
→coke oven gas (not preheated methane breakdown produces carbon which may choke the passage)
Sillica bricks

By-Product coke-oven

Metallurgical coke (coke used in blast furnace iron making) is produced in by product coke ovens. By-product coke ovens are flexible in treating different types of coal and to control the coke properties.

Coke is charged batch wise into silica lined or refractory lined retorts and these retorts are heated externally by burning gaseous fuels. Note that retorts are heated indirectly and coal is heated through heat transferred from the walls of the retort. Coal near the wall of the retort is heated faster than coal near the centre. As a result, coke near the wall swells much earlier than coal at the centre. Therefore, proper distribution of coal in the retort would be desirable.

The volatile matter from the coal is collected in the by product recovery plant where by product are separated from each other. It takes around 18 hours to convert one batch of coal into coke. Coke is discharged from the other end of the retort by mechanical hopper into a car, where it is wet quenched.

Note that hot coke so produced cannot be used directly into blast furnace hence coke is cooled to room temperature. During wet quenching of coal considerable amount of sensible heat is lost and pollutants are discharged in atmosphere. This aspect of coke making is dealt separately in next lecture with a quantitative illustration.

The quality of coke depends both on temperature and rate of heating. Metallurgical grade coke is produced at temperature higher than 1000 $_o$C.

Among the by-products, coke oven gas possesses both sensible heat and potential energy. Coke oven gas is used as a fuel to heat the furnace and also in heating the coke oven. The leakage of atmospheric air into coke oven must be avoided as the air causes oxidation of C and results in decrease in yield.
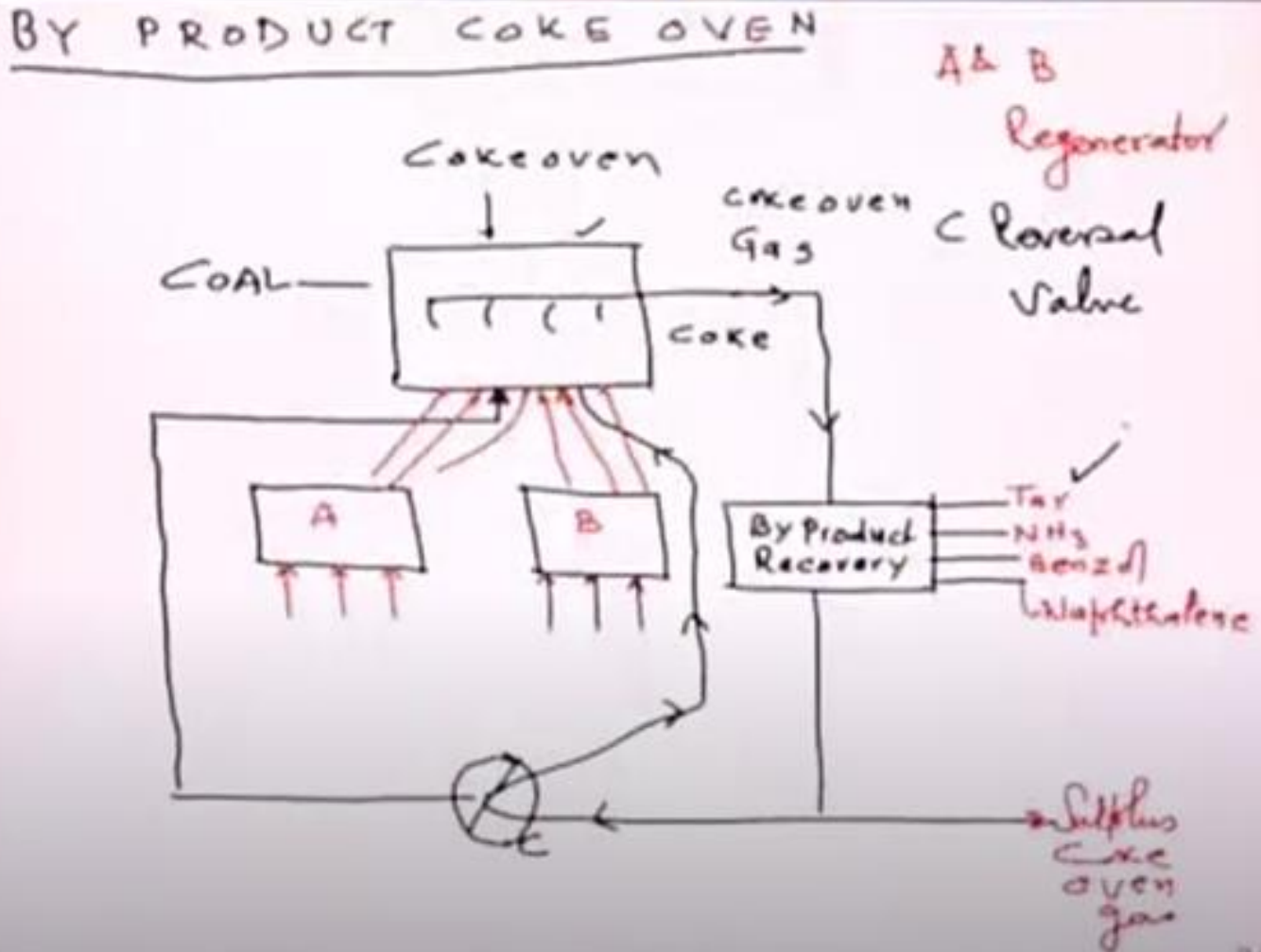
BY PRODUCT RECOVERY

→cooling of gas to recover tar and ammonia gas liquors

→electrostatic separation tar and dust particles

→recovery of ammonia as ammoinum sulphate

→gas is washed to recover napthalene and benzol

→desulphurization of gas with moist ferric oxide

→distribution of fuel gas to the consumer

Hot coke → wet quenching (replaced inert gas quenching)

PHYSICAL AND CHEMICAL PROPERTIES OF COKE

(1)ash and moisture content
.
Higher is the amount of ash higher is the production of slag

Dry quenching for moisture

(2)density and porosity

High density → high strength

Coke is only component of the burden which imparts permeability during the downward movement in the blast furnace

(3)hardness and strength

Resistance of coke to impact breakage
(shatter index)

(4)reactivity of the coke

Porous

(5)phosphorus and sulphur content

Whatever ash is there in coal will remain in the coke

(6)ash
As minimum as possible

In coke-making, it is often required to calculate the amount of coke, coke oven gas and tar produced per ton of coal. This can be done by performing elemental balance. For this purpose ash, C, N, H and O balance can be done to obtain the require information. This is illustrated by the following problem

By product coke ovens are surrounded by air. There may occur leakage of air in the oven. Consider a coke- oven surrounded by moist air, (The air is at 750 mm Hg pressure and 26▢ temperature) . The relative humidity of air is 40%. It carbonizes coal of the composition (Wt%) C76.1, H 4.6, N2.3, S 1.9,O 2.5, H▢O 6.3 and ash 6.3. The following product and by products are produced:

Product: Coke (Wt %) C 85.2, H 1.9, O 2.2, N 0.8, S 1.2 and Ash 8.7

By –product: (a) Coke oven gas (vol % dry basis)

and C_6H_6 1.1,C_2H_4 2.7,CH_4 4.4, CO 1.7, CO_2 1.3, H_2 36.5, N_2 6.9, O_2 2, H_2S 2.1 and NH_3 1.3

(b) Tar (40 kg/ton of coal) analysis (Wt %)

C=89.4, H 4.5, N 1.1. and incombustibles Rest.

Required per ton of Coal

Amount of coke /ton of coal

Amount of coke-oven gas

fraction of S in coke and coke oven gas

Amount of air leakage: The vapor pressure of moisture in air at saturation is 25.21 mmHg

Calorific value in coke and coke oven gas in terms of fraction of calorific value of Coal

Basis of calculation: 1000 kg coal

       i. Amount of coke /ton of coal

Ash balance is used to determine the amount of coke. Let x kg is amount of coke.

ii. Amount of coke oven gas can be calculated by performing C balance

         C from coal= C in tar+ C in coke + C in Cokes oven gas

         Let y kg is the amount of Cokes oven gas

         By solving we get y= 15.357 kg mole

MODULE 2.2.3

Low Temperature Carbonisation (LTC)

→It is carried at 700°C.

→It produces semi-coke which is used as a smokeless domestic fuel. It can sometimes be used in boiler also to avoid smoke.

→Yield of coke oven gas is less in LTC. It is about 150-160 Nm^3 gas/ton dry coal. Less gas yield is due to less devolatalisation of coal and less cracking of hydrocarbons at lower temperature of carbonisation. (d)Yield of tar is high in low temp carbonisation. It is about 10% of dry coal. (e)Ammonia yield is low.

→Calorific value of coke oven gas produced in LTC is more due to higher percentage of methane and unsaturated hydrocarbons in it. C.V. Is about 6000-6500 kcal/$Nm^{3.}$

→The tar produced is aliphatic in nature. It contains less quantity of aromatic ring compounds like benzene, toluene, naphthalene, phenol, anthracene etc. However, tar acid content is higher.

→After carbonisation, discharging of coke is difficult as it swells a lot but does not shrink much finally at the end of coking due to lower temperature of carbonisation.

→Free carbon in tar (which results from the cracking of hydrocarbons) is less. It is about 5-10% of tar.

Since cracking (HC-H+C) is less severe at lower temperature.

→Coke produced is weaker (due to less shrinkage) bigger in size and more reactive (due to higher porosity).

→Volatile matter content in coke is more (5-7%) hence it is easier to ignite it because of lower ignition temperature of high volatile matter containing coke. Ignition temperature of LTC coke is about 425°C. (l)Hydrogen content in coke oven gas is less (35-40%) Hence, difference in gross and net calorific value is less.

→H2 content in coke oven gas is less

→Coke yield is more. It is about 77% of coal.

High Temperature Carbonisation (HTC)

→It is carried at 1000°C.

→IT produces metallurigical coke for use blast furnace and cupolas in foundry etc.

→Yield of coke oven gas is more in HTC due to more cracking of hydrocarbons (maintain methane in coke oven gas) at higher temperature. Yield is about 270-300 Nm^3/to of dry coal. (d)Tar yield is less here. It is 3% of dry coal charged.

→Ammonia yield is more (10-15gm/N coke oven gas).

→C.V. Of coke oven gas produced in H.T.C is less. It is about 4200-4400kcal/Nm only due to lesser percentage of hydrocarbons resulting from its cracking at higher temperature of carbonisation.

→Tar produced has more of aromatic ring compounds (due to crystalisation reaction of straight chain compounds being favoured at higher temperature).

→Discharging of coke is easier as it shrinks finally to a more extent comparatively due to higher temperature of carbonisation.

→Free carbon in tar is more (due to more intense cracking of hydrocarbon at higher temperature. It is about 15-20% of tar. Higher carbon in tar chokes the hydraulic main and other tar flow pipelines). (j)Coke produce is stronger (i.e shalter index micum index, abrasion index are more) smaller in size and less reactive (due to low porosity) due to higher amount of shrinkage of coke at higher temperature

→V.M in coke is less (1-2%) hence the ignition temperature is more. Ignition temperature of high temp coke is about 605°C.

→H2 content in coke oven gas is more (55-60%). It is beneficial for an adjoining nitrogeneous fertiliser plast attached to steel plant (as in the case of Rourkela Steel Plant) which gets hydrogen (for ammonia making) from oven gas by its cryogenic cooling.

→Coke yield is less (about 70% of dry coal).

2.2.5

Micum test : In this method, 50 kg coke sample (−75 to +50 mm size) is tested in a drum (1000 mm diameter and 1000 mm wide) fitted with 4 lifters (100 mm size). The drum is rotated at 25 rpm for 100 revolutions and the product is sized by 60, 40, 20 and 10 mm screens and weighed.

The strength values are represented

Micum 40(M_{40}) Index = (Weight Kg of coke retained on 40 mm screen / 50 Kg (Initial wt.))* 100

Micum 10(M_{10}) Index = (Weight Kg of coke passing 10 mm screen / 50 Kg (Initial wt.))* 100

The higher value of M 40 is indicative of good resistance to impact while higher value of M 10 is indicative of poor resistance to abrasion. A coke with high M 40 and low M 10 value would be appreciated for use in blast furnace.

The Micum 40 (M 40) index represents the tumbler index while the Micum 10 (M 10) index indicates abrasion index. These two indices (M 40 and M 10) are found to change linearly with shatter index as shown in Figure
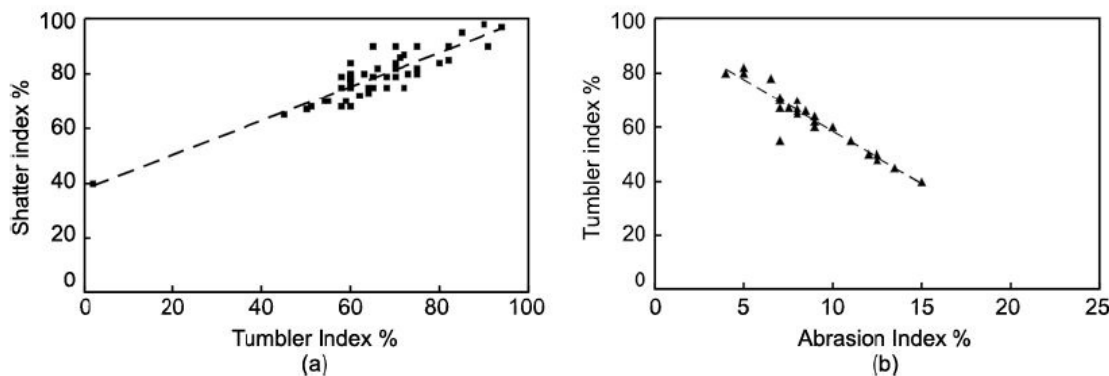

Figure 2.42 (a) Linear relationship between Shatter index vs. Tumbler index and
(b) Tumbler index vs Abrasion index.
(Adopted from R.C. Gupta, *Theory and Laboratory Experiments in Ferrous Metallurgy* ,
PHI Learning. Delhi. 2010.)

Shatter test (impact strength)

(i) Equipment
It consists of a steel box with open top and drop bottom. The base plate is in two half hinged at one end with a locking latch in the middle to be held as 'closed' or 'drop open' position. This box is fitted at a height of 2 meters above the base plate made of thick steel supported on steel frame (Figure 2.39).

(ii) Test procedure

The coke pieces weighing 34 kg bigger than 50 mm is collected as sample to represent the batch. None of the coke piece should pass through a 50 mm screen in any position. Out of this sample, 22.7 kg is selected for the test. The test sample (22.7 kg) is dropped 4 times on steel plate from a height of 2 meters and the surviving material is sized by using 50 mm, 37 mm, 25 mm and 12 mm screens and weighed.

Shatter Index % =

(Weight of the coke surviving bigger than 50 mm / 22.7 kg of coke of + 50 mm size) * 100

However, the better practice would be to report material weight (%) on all
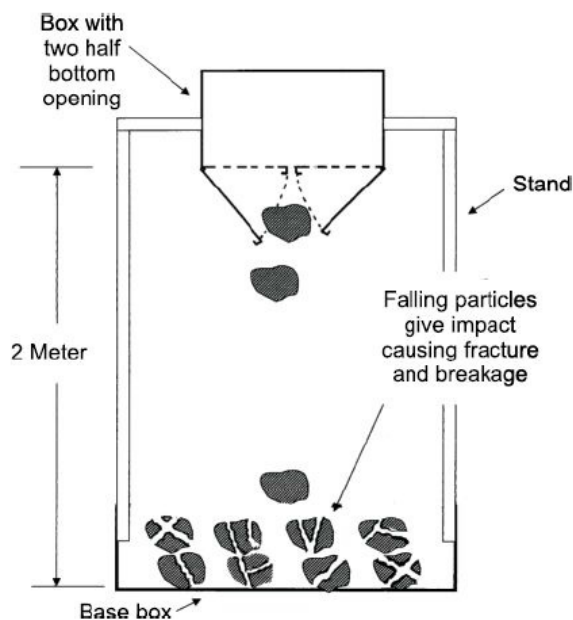

Figure 2.39 Shatter test (schematic).
(Adopted from R.C. Gupta, *Theory and Laboratory Experiments in Ferrous Metallurgy* ,
PHI Learning, Delhi, 2010.)

3.1.2

Specific Gravity

The specific gravity is an important property of an oil. It gives an indication for mass per unit volume. This is important for designing oil storage tanks and oil carriers It also gives calculated gross calorific values of petroleum products (by using US Bureau of Mines Formula) as: Calorific value (Gross) = $12400 - 2100\rho^2$ kilo-calorie/kg

where ρ is the specific gravity of oil at 15.5 °C.
The specific gravity of oil (ρ) can be determined by various methods as given below:

a. **Hydrometer:** The hydrometers are common for measuring specific gravity of oils which are available in different ranges giving upto 10–3 value.

b. **Specific gravity bottles:** Standard specific gravity bottles are available for different volumes (10–50 ml). These bottles could be used for oils which are fluid at room temperature.

c. **Specific gravity for viscous oils:** The viscous oil like tar is made fluid by mixing with equal volume of kerosene to yield a mixture which is fluid enough to be tested by specific gravity bottle.
The specific gravity of tar is then calculated as:

(Specific gravity)Tar (ρ_T)= (ρ_M) – (ρ_K) where,

ρ_M is specific gravity of tar and kerosene mix and

ρ_K is specific gravity of kerosene.

d. **API gravity:** It is the ratio of the density of a substance to that of water at 15 °C. It can be determined with specific gravity bottle or hydrometers.

Flash point

It is the lowest temperature at which oil gives sufficient vapour which offers a momentary flash on exposure to a standard flame in air.

At the flash point, oil may ignite briefly but vapour might not be produced at a rate to sustain the fire. It is, thus, a measure of fire risk of oil stored or transported in oil tanks.

Fire point

It is the temperature at which oil will continue to burn for at least 5 seconds after ignition by an open flame.
The fire point temperature is little higher than flash point temperature.

Most tables of oil properties will only list flash points, but in general the fire points can be assumed to be about 10°C higher than the flash points. However, for critical applications the fire point must be tested

methods of testing

The following two equipment are commonly used:

a. Abel apparatus (Figure 3.4) for flash point below 50 °C
b. Pensky Marten apparatus for flash point above 50 °C.

Both these apparatus work on same principle, but differ in design and method of heating the oil held in the cup. The cup is fitted with spring loaded window which can be opened by pressing a latch for a second. The cup is also fitted with a stirrer for homogenisation of oil bath temperature and a thermometer to indicate its temperature. A tiny flame is kept burning close to the window to ignite the oil vapour emitted through it on opening. The test procedure involves filling the cup with test oil up to the given mark and then heating at a prescribed rate (5 °C per min). The oil is kept stirred continuously and slowly (1 rpm). The window is opened after every 5 °C rise in temperature. The lowest temperature at which a momentary flash is observed is taken as an approximate flash point. The test is terminated and used oil is discarded. The test is repeated with fresh oil sample. Now, since approximate flash point is known, the window is opened 5 °C before the approximate value. In case no flash is noted, it is closed and opened after every 1 °C rise in temperature to reach the exact flash point temperature. The used oil is never tested again as some volatiles are lost and its value will change.
.

Cloud Point

When oil is cooled at specified rate, it becomes hazy or cloudy at some
temperature to be termed as 'cloud point'. This haziness is due to separation of wax crystals rendering increase in its viscosity at low temperature. This property is tested for those petroleum products which are transparent to 40 mm thick layer and have cloud point less than 50 °C. This is important for oils since it may clog filters.

methods of testing
The cloud point is tested by taking oil in a flat bottom glass test tube (30 mm diameter and 120 mm long). This test tube is encased in a air jacket which is placed in the ice box containing freezing mixture (ice and common salt). The flat bottom glass test tube is filled half by oil to be tested and a thermometer is placed inside to indicate its temperature. Once the oil filled glass test tube is placed in air jacket surrounded by freezing mixture, the oil temperature starts dropping. This tube is withdrawn for 2–3 seconds after every

1°C drop in temperature to note the oil transparency till a haze is noted in the oil which is taken as 'cloud temperature'.

Pour Point

The pour point of a liquid is the lowest temperature at which it becomes semi solid and loses its flow characteristics. The oils flow is retarded due to increase in viscosity at low temperature due to the formation of wax crystals. The pour point is a temperature 3 °C higher than temperature at which oil ceases to flow when poured in a prescribed manner.

methods of testing
This can be tested by manual or using standard automatic device.

Manual method
The oil sample held in a wide test tube is cooled inside a cooling bath to allow the formation of paraffin wax crystals. At about 9 °C above the expected pour point and for every subsequent 3 °C, the test tube is taken out and tilted to check for its surface movement. When the oil does not flow, the test tube is held horizontally for 5 sec. If it does not flow, then the pour point is taken as 3 °C
higher than the oil temperature.

Automatic device
The standard test method for pour point of petroleum products (automatic pressure pulsing method) is based on ASTM standard. Under This automatic equipment, for testing oil sample, has arrangement to heat and then cool oil by a Peltier device at a rate of 1.5 + 0.1 °C/min. The pressurised pulse of compressed gas is imparted onto the surface of the sample at an intervals of 3 °C. The detectors (multiple optical devices) continuously monitor the sample for its surface movement.. The lowest temperature, at which movement is detected on the sample surface is determined to be the pour point

Octane number

Octane number expresses the knocking characteristics of petrol. n - heptane (a constituent of petrol) knocks very badly, so its anti-knock value has been given zero. On the other hand, iso-octane (also a constituent of petrol) gives very little knocking, so its anti-knock value has been given 100.

Percentage of iso-octane present in iso octane & n-heptane mixture, which matches the same knocking characteristics of gasoline mixture test sample.

If a petrol sample behaves like a mixture of 60% iso-octane and 40% n-heptane, its octane number is taken as 60.

Cetane number (or) Cetane Rating

Cetane number expresses the knocking characteristics of diesel. Cetane ($C_{16}H_{34}$) has a very short ignition delay and hence its cetane number is taken as 100. On the other hand, alpha - methyl napthalene has very large ignition delay and hence its cetane number is taken as zero

Cetane number is defined as "the percentage of cetane present in a mixture of alpha–methyl naphthalene and cetane".

MODULE 4

GASIFICATION:

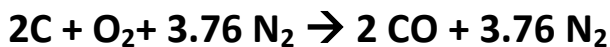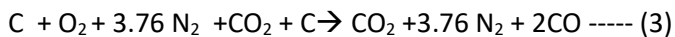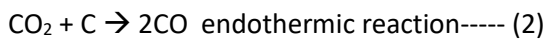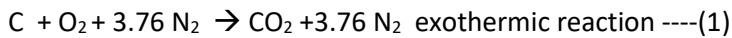Conversion of solid fuels into gaseous fuels

→producer gas

→water gas

→fuel gas

How is it made?

Producer gas: coal or coke with mixture of air and water in a high temperature reactor

$C + O_2 + 3.76 N_2 \rightarrow CO_2 + 3.76 N_2$ exothermic reaction ----(1)

$CO_2 + C \rightarrow 2CO$ endothermic reaction----- (2)

$C + O_2 + 3.76 N_2 + CO_2 + C \rightarrow CO_2 + 3.76 N_2 + 2CO$ ----- (3)

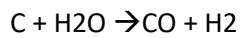# $2C + O_2 + 3.76 N_2 \rightarrow 2 CO + 3.76 N_2$

CO: 34.6 %

N_2 : 65.4 %

Producer gas consists of CO plus N_2

Volume of producer gas = (2.88 X 22.4)/ 12 = 5.38 m^3/Kg of carbon (273 K and 1 atm)

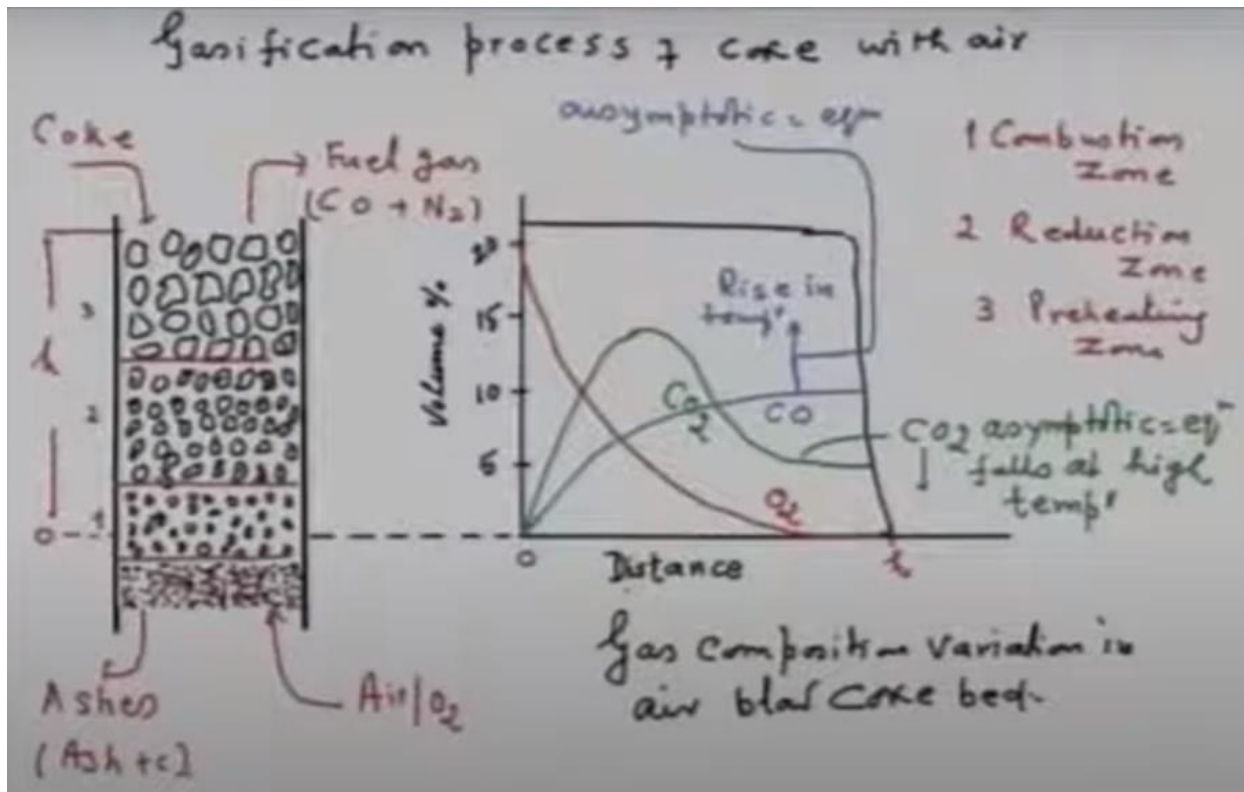Steam is used to gasify carbon

$$C + H_2O \rightarrow CO + H_2$$

ADVANTAGES:

→producer gas which is formed enriched in calorific value (h2 additional cv)

→Excess heat is utilized

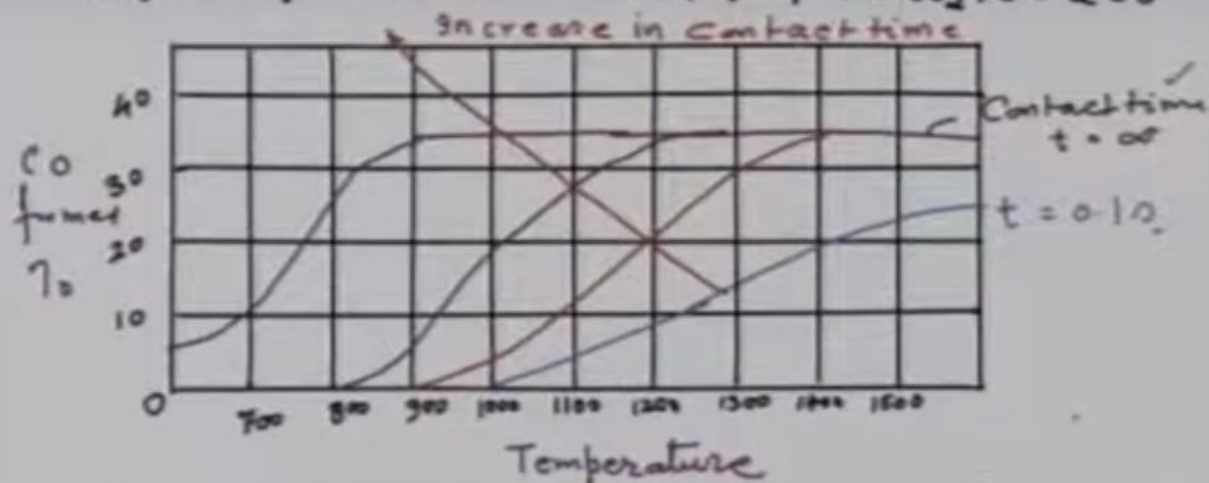→Fuel gas contains H2

→Gas is enriched on per unit volume basis

Amount of steam fed = required to absorb excess heat

Note: not all steam decomposes to hydrogen

Not all CO2 converted to CO

Gasification process 7 coke with air

Effect of contact time & temp' on $CO_2 + C = 2CO$

increase in contact time

Contact time
$t = \infty$

$t = 0.10$

CO
formed
η_o

Temperature

From design point 7 view

$CO_2 + C = 2CO$

Residence time between CO_2 & C

$C + H_2O \longrightarrow CO + H_2$

$C + 2H_2O \longrightarrow CO_2 + 2H_2$

$CO_2 + C \longrightarrow \ ?$

Decomposition of steam in coke bed.

$Mol\ H_2$
CO
CO_2
formed
her
original
$mol\ H_2O$

$\%\ of\ H_2O$
decomposed.
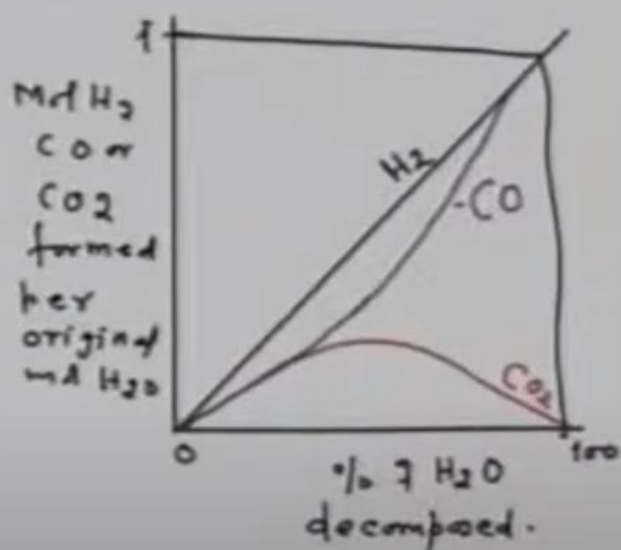
Air & steam are
blown simultaneously
& continuously through
the fuel bed.

Principle reactions and reaction zone when a mixture of air + steam is passed up a bed fed with raw Coal

COAL

GAS show

ASH zone
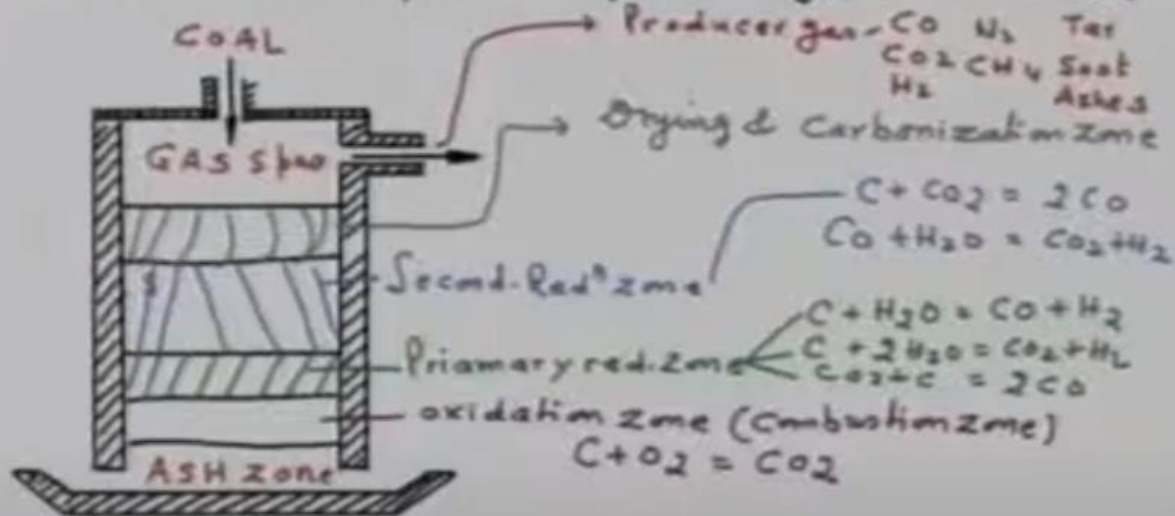
→ Producer gas - CO N_2 Tar
   CO_2 CH_4 Soot
   H_2 Ashes

→ Drying & Carbonization zone

$C + CO_2 = 2CO$
$CO + H_2O = CO_2 + H_2$

Second. Red^n zone

Primary red. zone

$C + H_2O = CO + H_2$
$C + 2H_2O = CO_2 + H_2$
$CO_2 + C = 2CO$

oxidation zone (combustion zone)
$C + O_2 = CO_2$

Coke or anthracite is better than coal

TECHNOLOGY FOR GASIFICATION

→feeding of coal

→disposal of ash during the process

→air plus steam supplied

→discharge of producer gas / fuel gas

→maximization of residence time

COAL

COAL Bunker

Screw feeder →

Steam →

Air / O_2

Secnd air/O_2

Product gas

Air + Steam (O_2 + Steam)

Ash removal

Ash

Winkler gasifier.

Fluidized bed gasifier
at atmospheric pressure

Lignite & subbituminous
Coal are used.

Co = 44.4%.
H_2 = 36%.
Co_2 = 15.7%.
N_2 = 2.3%.
CH_4 = 1.5%.

GCV 2 looked/h3
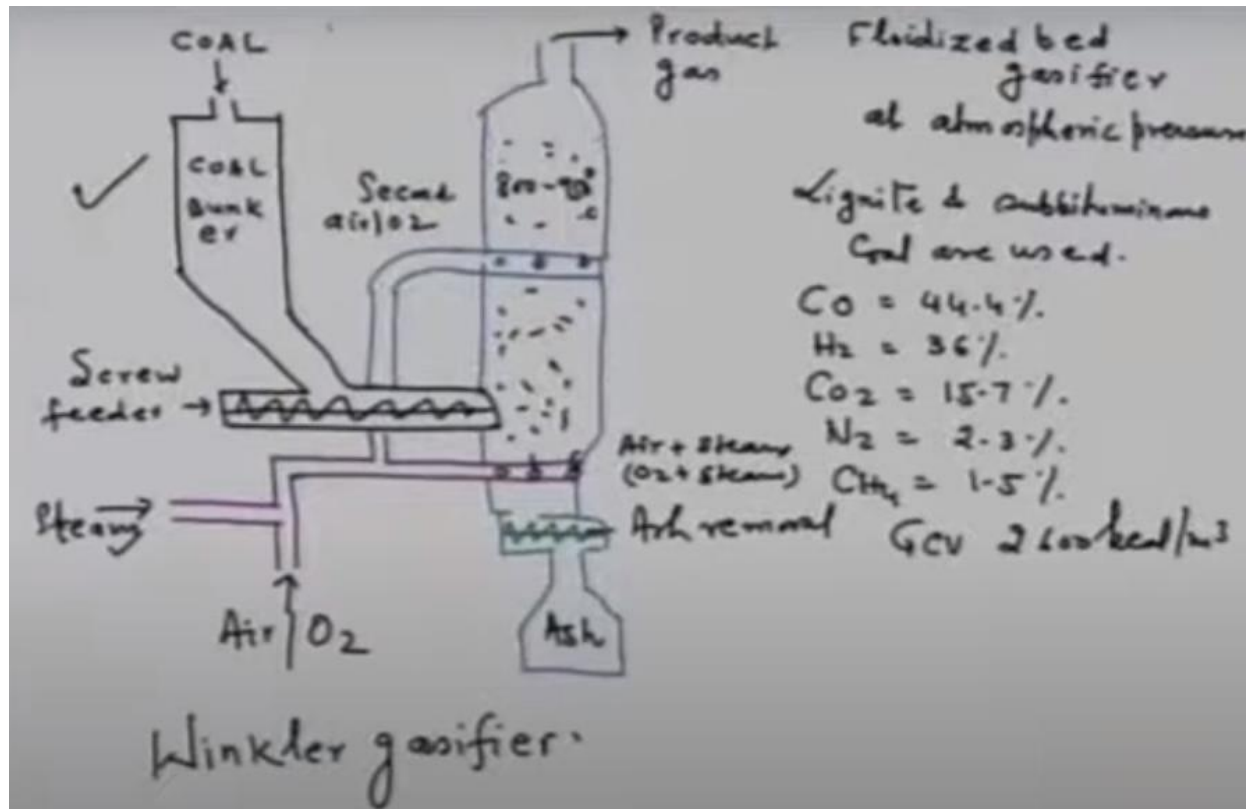
Kobber Totzek process.

Pulverized Coal is gasified.
    gasification temp ~ 1600°c.

Product gas   low - 1300°c

CO 53-3 %. H_2 31-1 %.

$CO_2 + H_2S = 12-2$%.

$GCV = 2670$ kcal/m³

Lurgi pressure gasifier

$$C + 2H_2 = CH_4$$

H_2 50 %. CO 35 %. CH_4 ~ 15%.

1 N m³ gas   0-85 kg Coal, 1·4 kg steam &

0- 21 N m³ O_2.

$G CV = 3900$ kcal/N m³ dry

4.0 NATURAL GAS

Natural gas is found in nature, buried under the rocks. The origin of natural gas is related with fossil fuel formation. The hydrocarbons released by the decaying vegetal and marine matter buried under the earth remains entrapped between rocks. The pressure and temperature of the overlying earth exerted on the vegetal and marine matter help in release of gaseous constituents. This natural gas is explored and taken out by drilling bore up to the deep pockets of gas in earth.

Petroleum is also another resource found in proximity to and with natural gas.Natural gas is a hydrocarbon gas-mixture consisting primarily of methane, but commonly includes varying amounts of other higher alkanes or paraffins (saturated hydrocarbons) and even a lesser percentage of carbon dioxide,nitrogen and hydrogen sulphide. Natural gas is an energy source often used for heating, domestic cooking and electricity generation. It is also used as a reductant for producing DRI (sponge iron) in processes like MIDREX.The natural gas recovered from wells is treated to remove solid particulates. The natural gas containing less recoverable condensate (< 15 g/m3) is termed as

'dry natural gas'. When the recoverable condensate is more than 15 g/m3 , it is called 'wet natural gas'. The hydrogen sulphide (H2 S) present in the gas is removed as elemental sulphur and the sulphur free natural gas is known as'sweet natural gas'. Thus, the processing ofraw natural gas yields products like LNG (liquefied natural gas), CNG (compressed natural gas), ethane, propane, butane, pentane and elemental sulphur. Figure 4.1 shows a typical natural gas processing plant. In such plant, various unit processes are used to convert raw natural gas into saleable gas for the end user and various other products.
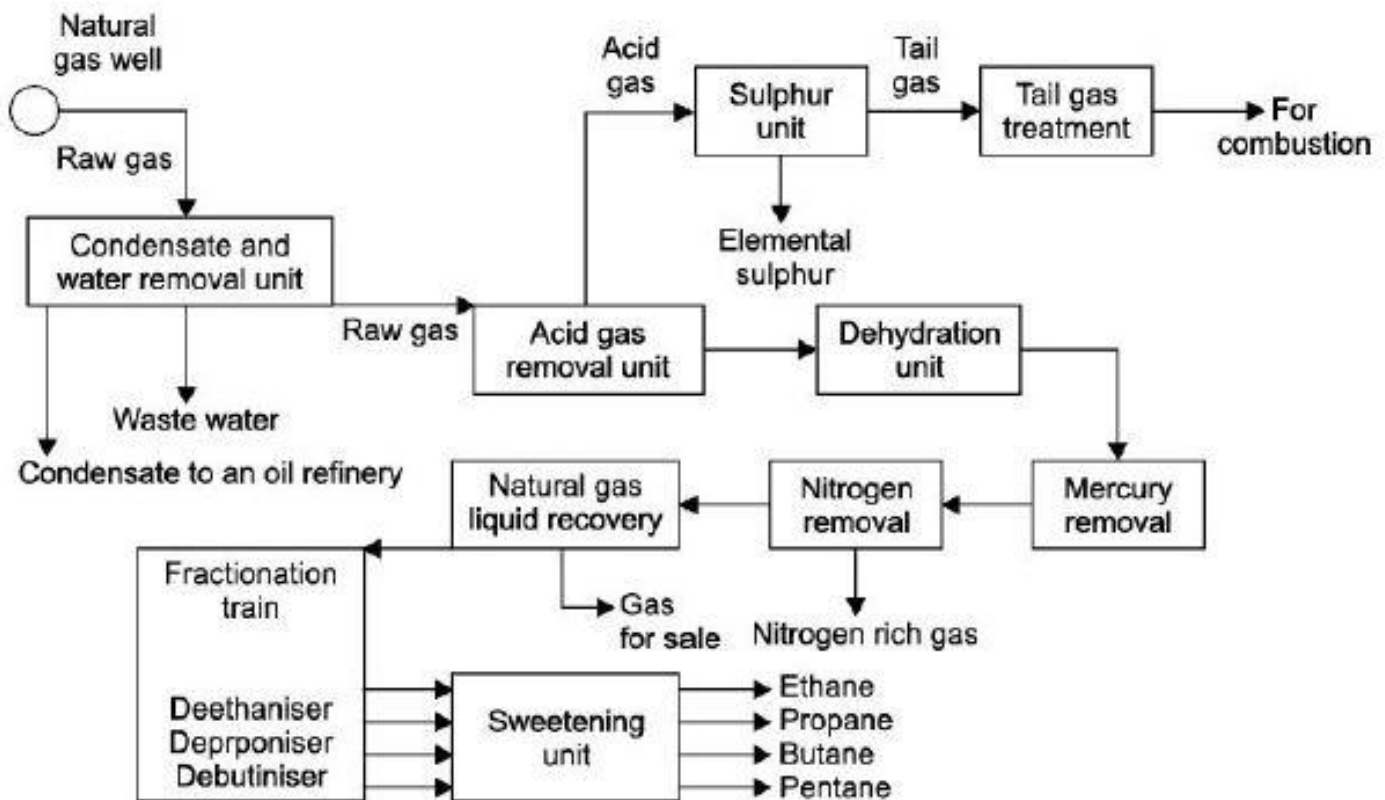

Figure 4.1 Natural gas processing plant flow-sheet.

Table 4.1 Properties of Natural Gas		
Properties	Natural Gas	
Composition, % Vol.	Dry and sweet	Wet and sweet
CH_4	96.9	77.2
C_2H_6	1.3	11.2
C_3H_8	0.2	5.8
C_4H_{10}	0.05	2.3
C_5H_{12}	0.02	1.2
CO_2	0.8	0.8
N_2	0.7	1.4

Calorific value: MJ/m^3 $kcal/m^3$	37.68 9000	46.89 11200
Specific gravity	0.57	0.74
(Air specific gravity = 1)		

PRODUCER GAS

Producer gas, rich in CO and H2 is manufactured by using solid fuel like coal or coke. The manufacture of this gas combines the merits of easily available solid fuel as primary source and clean rich gaseous fuel as final product for use. The producer gas is manufactured by blowing air with or without steam through a thick bed of hot solid fuel (coal/coke). The air blown causes carbon in coal/coke to get converted into CO and CO2 gas. The introduction of steam gives hydrogen as a result of reaction with carbon. The volatile matter present in the upper layer of coal/coke bed evolves due to heat and joins the out going gases.

Table 4.7 Properties of Producer Gas						
Gas Analysis, % Vol.	CO	H_2	CH_4	CO_2	N_2	
	20–30	1–15	0–3	1–6	45–75	
Calorific value, kcal/m^3 MJ/m^3	1000–1400 4.0–6.0					
Specific gravity	0.85–0.90					

BLAST FURNACE GAS

It is a by-product gas generated by conventional blast furnace iron making process. The exit gas laden with dust (10–25 g/m3 with size 5 mm to 0.1 μm)emerges out at 200–380°C temperature and 1.03–1.14 atmospheric pressure. Theexit gas contains considerable amount of carbon monoxide gas which is needed to maintain reducing atmosphere inside the blast furnace. This CO is generated by the gasification of coke fed from top and coal fines injected through tuyeres. The blast furnace yields nearly 2.5–3 tons off gas for every ton hot metal (thm)produced when coke rate is 550–700 kg/thm. This amounts to 1800–2000 m3 gas per thm or 3000–3200 m3 gas per ton coke charged in the blast furnace.

In view of this large quantity of CO rich gas generated during iron making, it is utllised as fuel gas. The off gases are passed through dust catcher which removes nearly 60–70% dust to bring down dust level from 10–25 g/m3 to 4–6g/m3 . This dust is further removed in a wet scrubber to a level of 5 mg/m3 . However, this old wet method of dust cleaning causes moisture saturation in the gas, which is passed through chilled chamber to remove moisture to a level of 5g/m3 . This cooled and cleaned blast furnace gas is stored in gas holders for use in the plant.

In the modern plants, this wet gas cleaning is replaced by bag filters and electrostatic precipitators to get the dust level below 5 mg/m3 for use. This dry method of gas cleaning has several advantages like producing hot blast furnace clean gas which is good for use in blast furnace stoves. This dry method generates dry dust for reuse in the plant. The avoidance of water lowers the water need/thm and does not pose any waste water disposal issue.

The blast furnace gas is colourless, odourless and tasteless. It is highly **poisonous** due to its high CO content. The presence of the blast furnace gas in the working area is detected by various devices for safety of working people.The devices include old technique of keeping bird in a cage, pocket pen size indicator filled with chemical (palladium sulphide) and electronic devices (hand held indicator or wall mounted alarm system). The exposure of CO gas beyond acceptable limits causes bird to faint, change of colour of chemical from green to blue or beep from electronic systems as a warning sign to move out and takeremedial measures.

The blast furnace gas and air form a explosive mixture when gas is present between 37–71% in gas–air mix. The gas pipe is, therefore, always kept with positive pressure to avoid air infiltrating into gas pipe line and form explosive mix.

The blast furnace gas is used for various applications in the steel plant including:
a. Blast furnace stove heating,
b. Coke oven heating,
c. O perating gas engines for blowing air or power generation,
d. Heating applications in plant, e.g. soaking pits, reheating furnaces, etc.
e. Heat treatment furnaces and
f. Foundry and melt shop for ladle drying, mould drying, etc.

Table 4.4 Properties of Blast Furnace Gas	
Properties	Blast Furnace Gas
Composition	CO 21–23%
	CO_2 18–20%
	H_2 4–5%
	N_2 53–55%
	O_2 0.2–0.5%
Calorific value, kcal/m^3 MJ/m^3	800–850 3.3–3.5
Specific gravity (air as 1.0) Density kg/m^3 (air as 1.28 kg/m^3)	1.01–1.09 1.3–1.4
Maximum flame temperature, °C	1450

COKE OVEN GAS

The coal carbonisation in by-product coke oven yields metallurgical coke as main product and coke oven gas as by-product. When the coking coal is heated in the coke ovens the volatile matter present in it is evolved as gas which is collected for the preparation of various liquid fuels (coal tar fuels–CTFs) and gaseous fuel termed as 'coke oven gas'. Nearly 280–350 m3 gas is generated for every ton coke

production, however, the amount of gas and its composition depend on operating parameters like coke oven temperature and volatile matter present in coal.

The quantity and composition of coke oven gas are affected as follows:

Factors affecting the quantity of coke oven gas

a. The gas yield increases with higher carbonisation temperature due to cracking of hydrocarbons, e.g. tar.

b. The gas yield increases with higher volatile matter content in the coal which is carbonised.

Factors affecting the composition of coke oven gas

a. The hydrogen content of the gas increases with higher carbonization temperature due to cracking of hydrocarbons.

b. Methane and other hydrocarbon constituents decrease with higher carbonisation temperature due to their cracking into hydrogen.

c. The higher volatile matter in coal gives a gas rich in hydrocarbons.

d. The calorific value of gas decreases with higher carbonization temperature due to reduction in hydrocarbons which is not compensated by increase in hydrogen content.

The composition and properties of coke oven gas are given in Table 4.5. The coke coven gas is used as fuel in various sections of the steel plant which include the following:
a. Coke oven heating
b. Blast furnace stoves
c. Blast furnace cast area for drying runners
d. Power plant
e. Furnaces like soaking pits, reheating furnaces, heat-treatment furnaces, etc.
f. Foundry shop for baking and drying
g. Forge shop for reheating billets
h. SMS for ladle drying

Density, kg/m^3	0.43–0.45
Specific gravity	0.33–0.36
Calorific value, kcal/m^3 MJ/m^3	4200 17.58
Explosion limit, percentage of gas in gas–air mix	5–32
Theoretical flame temperature, °C	>2000

WATER GAS (OR BLUE GAS)

The water gas or blue gas is manufactured to obtain rich fuel gas containing H2 and CO. This gas burns with non-luminous intense flame. This gas is produced when steam is passed though hot bed of carbon (coke) giving H2 and CO according to the following endothermic reaction:
C + H2 O → CO + H2 The endothermic reaction between carbon and steam lowers the coke bed temperature after certain period and this reaction cannot be sustained further. Therefore, gas generation has to be carried out for short period, called 'run period' followed by flow of air to burn carbon (coke) to regain the coke bed temperature which is called 'blow period'. Thus, the water gas plant follows 'blow' and 'run' period in cyclic manner to generate the gas. The gas generated during 'run' period is collected while gas generated in 'blow period' is bled out as it contains waste gases like carbon dioxide, nitrogen and oxygen

Applications of Water Gas
It is used for burning at places which require non-luminous (blue) flame or need reducing atmosphere containing CO and H2 . The water gas also forms a source of hydrogen for chemical plants. The applications include:

a. Heating furnace
b. Chemical plants
c. Synthesis of liquid fuel (Methanol) [CO + 2H2 → CH3OH liquid (Methanol)]
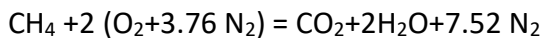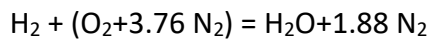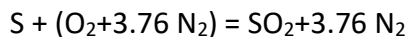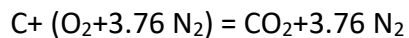
CARBURETTED WATER GAS
The carburetted water gas is a mixture of water gas and oil gas. The oil is heated to give various hydrocarbons which when mixed with water gas renders it higher calorific value and flame luminosity which is needed for some applications

Table 4.10 Carburetted Water Gas Properties						
Gas Analysis, % Vol.	CO	H_2	CH_4	$C_m H_m$	CO_2	N_2
	30.5	37	14	7	5	5.5
Calorific value, kcal/m^3 MJ/m^3	4700 19.67					
Specific gravity	0.63					

5.0 COMBUSTION

5.1. Principles of combustion

Combustion is a fast chemical reaction between combustible component(s) and an oxidizing agent. Mostly air is used for combustion

$C + (O_2 + 3.76\ N_2) = CO_2 + 3.76\ N_2$

$S + (O_2 + 3.76\ N_2) = SO_2 + 3.76\ N_2$

$H_2 + (O_2 + 3.76\ N_2) = H_2O + 1.88\ N_2$

$CH_4 + 2\ (O_2 + 3.76\ N_2) = CO_2 + 2H_2O + 7.52\ N_2$

Objective of combustion

All fuels whether naturally occurring or synthetically prepared contain potential energy. Potential energy of the fuel, on combustion with air is released in products of combustion (POC) at the temperature which is termed flame temperature. POC transfer their heat to sink (sink could be furnace chamber, charge materials etc) and then exit the system.

Potential energy of the fuel →sensible heat of POC→ heat transfer between POC and the →furnace →POCs exits the furnace

Temperature of the POC is at least equals to the temperature of the furnace

POC COULD BE SOLID LIQUID or GAS

POC s are the carrier of potential energy of the fuel

Complete combustion: $CO_2, H_2O, N_2, SO_2, O_2$
Incomplete combustion: $CO, CO_2, H_2O, N_2, SO_2, O_2$, unburnt fuel, Soot

Release of potential energy : maximum can be obtained on complete combustion
Lower than that of complete

Objective: To attain complete combustion with a given amount of air/O_2

From combustion point of view oxygen is important

N_2 of air is inert and consumes potential energy of the fuel

For any given type of fuel, some amount of CO is always observed in POC even at stoichiometric amount of air in all practical combustion systems. Presence of CO in POC denotes incomplete combustion and combustion efficiency will be low. So,excess air has to be used to increase combustion efficiency. Increase in excess air decreases drastically CO in POC but at the same time increases amount of POC due to increase in nitrogen and oxygen (at stoichiometric air no oxygen is present in POC). The additional nitrogen and oxygen in POC due to excess air will carry heat of combustion with them. Thus, control of excess air is important. The following plot illustrates the relationship between excess O_2, CO and heat losses.
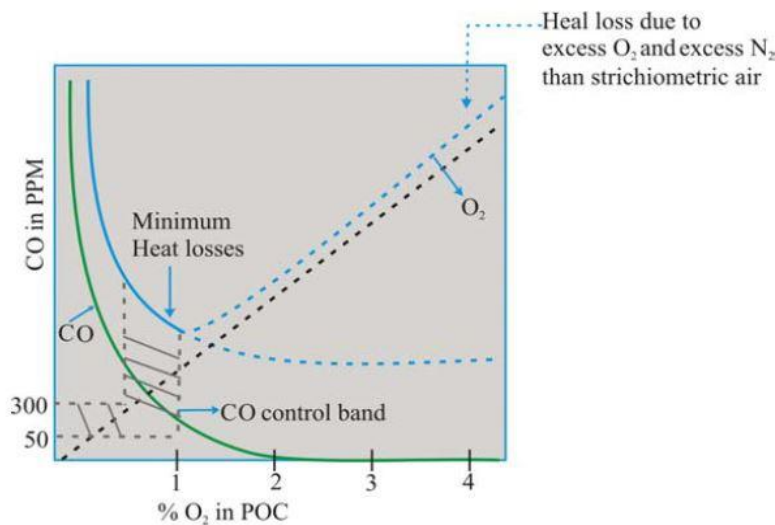

Figure: Plot of variation of CO and heat losses with excess oxygen in POC. Note zero value of oxygen in POC denotes stoichiometric oxygen used for combustion

X- axis on the figure is % O_2 in POC. Theoretically percent oxygen in POC is zero at theoretically amount of air. Increase in excess air increases percent oxygen in POC (see black line in the figure). It can be seen in the figure that amount of CO (see green line) decreases drastically by using slight amount of excess air. Beyond around 1 to 2 % O_2 CO in POC disappears completely. But increase in excess air at the same time increases O_2 in POC as shown by (blue line).

Heat losses are shown by the blue line. Heat losses decrease drastically with the excess air and become minimal at around 1% O_2 which is due to decrease in CO. Beyond 1% O_2 heat losses increases further because now nitrogen and oxygen in POC increases.

Hess's law of constant heat summation, also known as **Hess's law** (or Hess' law), is a relationship in physical chemistry named after Germain Hess, a Swiss-born Russian chemist and physician who published it in 1840. The law states that the total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps.

Hess's law derives directly from the law of conservation of energy, as well as its expression in the first law of thermodynamics. Since enthalpy is a state function, the change in enthalpy between products and reactants in a chemical system is independent of the pathway taken from the initial to the final state of the system.

Hess's law can be used to determine the overall energy required for a chemical reaction, especially when the reaction can be divided into several intermediate steps that are individually easier to characterize
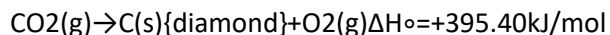
Calculating Standard Enthalpies of Reaction Using Hess's Law

$C(s)\{graphite\} \rightarrow C(s)\{diamond\} \Delta H_{rxn} = ?$
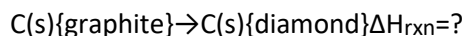
Turning graphite into diamond requires extremely high temperatures and pressures, and therefore is impractical in a laboratory setting. The change in enthalpy for this reaction cannot be determined experimentally. However, because we know the standard enthalpy change for the oxidation for these two substances, it is possible to calculate the enthalpy change for this reaction using Hess's law. Our intermediate steps are as follows:

$C(s)\{graphite\} + O_2(g) \rightarrow CO_2(g) \Delta H\circ = -393.41 kJ/mol$

$C(s)\{diamond\} + O_2(g) \rightarrow CO_2(g) \Delta H\circ = -395.40 kJ/mol$

In order to get these intermediate reactions to add to our net overall reaction, we need to reverse the second step. Keep in mind that when reversing reactions using Hess's law, the sign of ΔH will change. Sometimes, you will need to multiply a given reaction intermediate through by an integer. In such cases, you need always multiply your ΔH value by that same integer. Restating the first equation and flipping the second equation, we have:

$C(s)\{graphite\} + O_2(g) \rightarrow CO_2(g) \Delta H\circ = -393.41 kJ/mol$

$CO_2(g) \rightarrow C(s)\{diamond\} + O_2(g) \Delta H\circ = +395.40 kJ/mol$

Adding these equations together, carbon dioxides and oxygens cancel, leaving us only with our net equation. By Hess's law, we can sum the ΔH values for these intermediate reactions to get our final value, ΔHrxn∘.

$C(s)\{graphite\} \rightarrow C(s)\{diamond\} \Delta H_{rxn}\circ = 1.89 kJ/mol$

<u>Summary of Hess's Law</u>

• A reaction and its reverse have equal magnitude, opposite sign ΔH values

If A → B has ΔH = 100 kJ, then B → A has ΔH = −100 kJ

• If you multiply a reaction by a factor, then you multiply the ΔH by the same factor

If A → B has ΔH = 100 kJ, then 2A → 2B has ΔH = 200 kJ

• When you add two reactions, you add the ΔH values

If A → B has ΔH = 100 kJ, and C → D has ΔH = 50 kJ,

then A + C → B + D has ΔH = 100 + 50 kJ = 150 kJ

Hess's law of constant heat summation

1. Calculate ΔH for the reaction

$$2\,C\,(s) + H_2\,(g) \rightarrow C_2H_2\,(g)$$
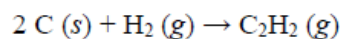
given the following chemical equations and their respective enthalpy changes.

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \rightarrow 2\,CO_2\,(g) + H_2O\,(l) \quad \Delta H = -1299.6\,kJ$$

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad\qquad\qquad \Delta H = -393.5\,kJ$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(l) \qquad\qquad\quad \Delta H = -285.8\,kJ$$

In summary:

$$2\,CO_2\,(g) + H_2O\,(l) \rightarrow C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \quad \Delta H = +1299.6\,kJ$$

$$2\,C\,(s) + 2\,O_2\,(g) \rightarrow 2\,CO_2\,(g) \qquad\qquad\qquad \Delta H = -787.0\,kJ$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(l) \qquad\qquad\qquad \Delta H = -285.8\,kJ$$

2. Calculate ΔH for the reaction

$$NO\ (g) + O\ (g) \rightarrow NO_2\ (g)$$
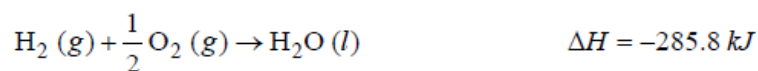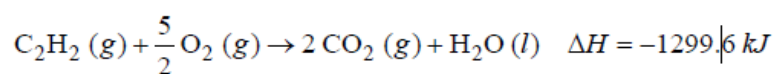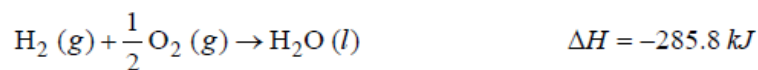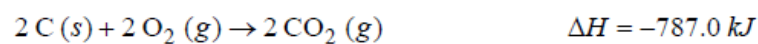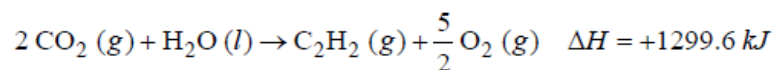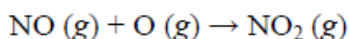
given the following information

$$NO\ (g) + O_3\ (g) \rightarrow NO_2\ (g) + O_2\ (g) \quad \Delta H = -198.9\ kJ$$

$$O_3\ (g) \rightarrow \frac{3}{2} O_2\ (g) \qquad\qquad\qquad \Delta H = -142.3\ kJ$$

$$O_2\ (g) \rightarrow 2\ O\ (g) \qquad\qquad\qquad \Delta H = +495.0\ kJ$$
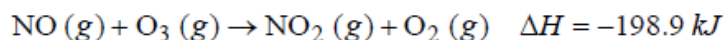
Answer: -304.1 KJ

Kirchhoff's Law

Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature.

$$Cp = \Delta H / \Delta T$$

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities. The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants. A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

$$H_{T_f} = H_{T_i} + \int_{T_i}^{T_f} c_p dT$$

If the heat capacity is temperature independent over the temperature range, then Equation 1 can be approximated as

$$H_{T_f} = H_{T_i} + c_p(T_f - T_i)$$

with

- c_p is the (assumed constant) heat capacity and
- H_{T_i} and H_{T_f} are the enthalpy at the respective temperatures.

Equation 3 can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

Example Problem:
The standard enthalpy of formation of gaseous H_2O at 298 K is -241.82 kJ mol^{-1}. Estimate the value at 100°C given the following values of molar heat capacities at constant pressure: $H_2O(g)$: 33.58 kJ K^{-1} mol^{-1}; H_2 (g) : 28.84 kJ K^{-1} mol^{-1}; O_2 (g) : 29.37 kJ K^{-1} mol^{-1}. Assume heat capacities are independent of T.

Answer: -242.6 KJ/mol

SUPPLIMENTARY

FLAME TEMPERATURE:

Flame is a mixture of Product of Combustion(POC) which are obtained by combustion of fuel (solid,liquid and gaseous) with air or O2

Assumptions:

(1)Combustion is adiabatic
(2)Complete combustion
(3)No dissociation of product of combustion

THEORITICAL ADIABATIC FLAME TEMPERATURE:
Temperature basing on these assumptions is called
However at higher temperature the product of combustion dissociates

CO2--→ CO+ O2
H2O --→H2 +O2
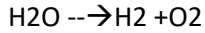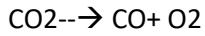
ADIABATIC FLAME TEMPERATURE: considers the dissociation of product of combustion

THEORITICAL ADIABATIC FLAME TEMPERATURE > ADIABATIC FLAME TEMPERATURE

THEORITICAL ADIABATIC FLAME TEMPERATURE & THEORITICAL ADIABATIC FLAME TEMPERATURE both depend on

(1) Type of fuel
(2) Proportion of air and oxygen (theoretical or more than theoretical amount of air)
(3) Sensible heat of reactants

Actual flame temperature

(1) Heat losses
(2) Imperfect combustion

ACTUAL FLAME TEMPERATURE< ADIABATIC FLAME TEMPERATURE <THEORITICAL ADIABATIC FLAME TEMPERATURE

Importance of adiabatic flame temperature calculations :

Characterization of Quality of fuel (higher or less flame temperature)

Suitability of fuel for an application (not only heat but also temperature)

Extent of substitution of a lower quality fuel to conserve high quality fossil fuel reserve

Calculation of theoretical adiabatic flame temperature(no dissociation of POC)

$\sum(H_T-H_{298})$ for fuel and air + $\sum(\Delta H$ for all combustion reaction)= $\sum\sum(H_T-H_{298})$ for all combustion products
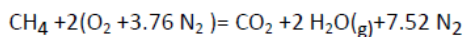

Reference temperature : 25^0C

$(H_T-H_{298})=$ integeration (298 to T) $C_p dT$ = integeration (298 to T) $a+ 2bT+ (-c/T^2)$

$$C_p\,(CO_2) = 10.55 + 2\times1.08\times10^{-3}\,T - \frac{2.04\times10^5}{T^2} \quad \frac{cal}{m\,A\,°C}$$

$$C_p\,(CO) = 6.79 + 2\times0.49\times10^{-3}\,T - \frac{0.11\times10^5}{T^2} \quad ''$$

$$C_p\,(H_2O)_v = 7.17 + 2\times1.28\times10^{-3}\,T + \frac{0.08\times10^5}{T^2} \quad ''$$

$$C_p\,(N_2) = 6.66 + 2\times0.51\times10^{-3}\,T \quad ''$$

$$C_p\,(O_2) = 7.16 + 2\times0.5\times10^{-3}\,T - \frac{0.4\times10^5}{T^2} \quad ''$$

$$C_p\,(H_2) = 6.52 + 2\times0.39\times10^{-3}\,T + \frac{0.12\times10^5}{T^2} \quad ''$$

Exercise- 1Flame temperature with theoretical air

Calculate theoretical maximum adiabatic flame temperature of fuel gas of composition 96 % CH_4, 0.8 % CO_2 and 3.2 % N_2 when burnt with theoretical air. Assume fuel and air are mixed at $25^{\circ}C$

Consider 1 mole of fuel gas

$CH_4 +2(O_2 +3.76\ N_2)= CO_2 +2\ H_2O_{(g)}+7.52\ N_2$

POC	Amount (kg mole)
CO_2	0.968
H_2O	1.920
N_2	7.52

Heat balance: Reference Temperature $25^{\circ}C$ Or 298 k.

Sensible heat in air & fuel +Heat of combustion = Heat in products of combustion 1)

Sensible heat of reactants = 0 since they are Supplied $25^{\circ}C$.

$-\Delta\,H^{Comb.}_{298} = 0.968\,(94.05 \times\,10^3) + 1.920\,(57.80) \times -10^3\,[\,0.96 \times 17.89] \times 10^3 = 184 \times 10^3$ kcal.   -------------- (2)

This heat of combustion raises the temperature of POC to the flame temperature.

The heat capacity of POC i. e. Cp'

$$Cp' = n\,CO_2\,C_P\,CO_2 + n\,H_2\,OC_P\,H_2O + n\,N_2\,C_P\,N_2$$

Where nCO_2, nN_2 and nH_2O are moles of CO_2 N_2 H_2O respectively.

$$C_p^1 = 0.968\,(10.55 + 2.16 \times 10^{-3}\,T - \frac{2.04\times10^5}{T2}) + 1.92(7.17 + 2.56 \times 10^{-3}T + \frac{0.08\times10^5}{T^2}) +$$

$$7.25\,(6.66 + 1.02 \times 10 - 3T) = 72.27 + 14.41 \times 10 - 3\,T - \frac{2.11\times10^5}{T^2}\,\frac{kcal}{kg\,mole^{o}k.} \quad - \quad (3)$$

By 1 and 3

$$184 \times 10^3 = \int_{298}^{T_f} c^1\,P^{dT} \text{-----------------------} \quad (4)$$

By 3 and 4

$$184 \times 10^3 = \int_{298}^{T_f}(72.27 + 14.41 \times 10^{-3}T - \frac{2.11\times10^5}{T^2})dT$$

Solution gives T_f =2300K.

Consider the use of expression C_p =a +b T and recalculating flame temperature Calculating C_p^1 and making heat balance gives

$$0.0072 \, T_f^2 + 72.27 \, Tf - 206 \, 157 = 0.$$

This is a quadratic equation whose solution gives

$$T_f = 2319 \text{ K.}$$

Let us calculate flame temperature by using average C_P values of POC. Average C_P values of POC are given in lecture 12.

$$184000 = 0.96 \times 12.5 \, (T_f - 25) + 1.92 \times 7.73(T_f - 25) + 7.12 \times 7.25(T_f - 25)$$

Solution gives T = 2643K.

We note that the accuracy of calculation depends on C_P values. For accurate calculations $C_P = a + b \, T + c/T^2$ must be used. However using $C_P = a + bT$, though simplifies calculation but flame temperature is slightly greater (a difference of 20 K in this example). Use of average C_P values though simplifies the flame temperature calculation but calculated flame temperature is greater than earlier ones

MODULE : 6

Refractories

Unit processes →
(a)below the melting point of the material

1.reduction of oxide (800-1000C)(sponge iron)
Solid phase
Gaseous phase CO,H2,H2O,N2

2.Roasting
Temperature (900 c)
Soild and gaseous CO,CO2,SO2,N2

3.calcination

4.Cement(1200-1250)
CaO ,CO2(solid,gaseous)

5.Drying alumina(anhydrous alumina(1300C)

6.Deformation processing(1200-1250)(bloom,billet)

(Solid,gaseous)

7.Heat treatment
(900-950)
Annealing
(solid and agseoues(if reducing atmosphere CO
                        IF OXIDIZING ATMOSPHERE CO_2
                  N_2 if inert atmosphere is required)
8.Sintering(1200-1300C)
Solid& gaseous

→(b)above the melting point of the materials

Smelting**(i) matte smelting**(Cu)(liquid matte (Cu_2S FeS)and slag(1400c)

(ii) reduction smelting(B/F (Hot metal(1300C),slag(1300-1400),gas(CO,CO_2,H_2,H_2Onad N_2)
Slag and metal separation

Imperial Smelting Process(Zn vapour,CO,CO_2,Pb,Slag)

Converting

Matte(1300C-1400c),SO_2,N_2

Refining
Steel (Liquid steel,liquid slag and gases)(1600-1700C)
LD,EAF

Melting
Al,
Cu

Phases:
SLAG(MIXTURE OF OXIDES)
MOLTEN METAL(Fe,C,N etc) (CONTINUOUS MOTION)
GASEOUS CO_2,SO_2,SO_3,N_2,CO (SPEED OF MOVEMENT IS IMPORTANT)
SOLID PHASES

Refining of liquid metals

Smelting

Retorting

Distillation

Heating

Tempertature,time,torbulence,nature,phses

Autogenous(steel)(Roasting)

(1)To minimize heat losses(CONSERVATION OF ENERGY)
(2)to allow themal energy dependent conversion of reactants into product

Can we use metals?

What is available to us

Refractory materials
Anything which can sustain a high temeperature

Cost,thermal conductivity(metals are out of question)

6.1 REFRACTORIES

Oxidic
Slag is a mixture of SiO2,MgO,CaO

Acidic (SiO2) main component(cant be used in basic environment)
(Fire ClayAl2O3(30-40%) and SiO2) ,Quartz,Ganister

Basic: Magnesite, Dolomite, Mgo-C(cant be used in acidic environment)

Neutral: Chromite, Carbon

Special material: **SiC (carbon content greter than 85%**)
High thermal conductivity
High refrectoriness
Decomposes at 2200C and doesn't melt
Light weight
Excellent mechanical properties
High thermal spalling resistance

Very very expensive

Cermets(ceramic and metals)
Combination of a metal or an alloy and non metal
e.g.metal plus oxide carbide nitride and boride

Properties
Low thermal shock resistance
And high strength at high temperature
Produced by processing of powders of ceramic plus metal→powder metallurgy

SiAlON
Solid solution of alumina in silicon nitride

Powder metallurgy route

Good resistance to oxidation also resistance to action of molten metal like akluminium copper iron steel and zinc

Very very expensive

Production route is very complicated
Cant be used for large application
Not affected by H2SO4 Hcl
Borax

Fireclay(not natural)

Mixture of SiO_2(50%-80%) and Al_2O_3 (25%-45%)

Properties

Porosity: 8-24% (depending on firing temperature)
At high tememperature fire clay refractory combine with alkali such as soda and potash
Cant be used where basic environment

Depending on alumina content medium duty(30-32)
High duty (38-40)
Super duty (40-45)(special applications)

Uses:
Furnaces ,regenerators,ovens and kilns(below the melting point application)

High Alumina refractory
Sillimanite(61% alumina)
Mullite(70-80%)
Pure alumina

High refractoriness
Better resistance to slag and higher load bearing capacity

Fusion point 1850 C
Blast furance stoves
Cement and rotary kilns
EAF roof

Chromite Magnesite refractory
Chorome ore is greater than magnesite
Upto 1700 degree centigrade
Resistant to thermal shock
And they are basic in nature

Inner lining of BOF and side walls of soaking pits

Magnesite chrome refractory(MgO content is greater)

High refractorines
And thermal conductivity
Great resistance to basic slag
And they are cant be used in acidic environment

Choice of refractory:

The furnace design
(ii)Condition of heating(cupola) (coke oven)
(iii) loading
(iii) degree of insulation

Operation

(i)Chemistry of phases
 (ii)Whats the temperature
(iii)What is the fliuidity of the phases
(iv)Abrasion due to movement

6.2 PROPERTIES OF REFRACTORIES

(I)REFRACTORINESS OR FUSION POINT

--Temperature at which refractory will deform under its own load(just begin to fuse)
--Pyrometric cone equivalent(PCE)

--Refractoriness under load :temperature at which the refractory begins to fuse under a specified load

--The refractory at the bottom takes up all the load of the refractory coloumn

 (II) POROSITY AND SLAG PERMEABILITY

--Chemical reaction may collapse

--Chemical attack of phases e.g.molten slag metal matte and gases

--High Porosity low thermal conductivity but strength is less

(iii) strength :
hearth roof or side wall
--Resistance of refrcatory to compressive loads tension and shear stress
-- in Taller furnace : heavy load

(iv) specific gravity :
Low to produce to more number of bricks
(v) spalling:
--Fracture of refractrory may occur due to the following reason
Temperature gradient(may be caused by sudden heating or cooling)
Thermal stress
--compression in a structure due to expansion
--variation of coefficiemnt of thermal expansion between the surface layer and the body of the brick
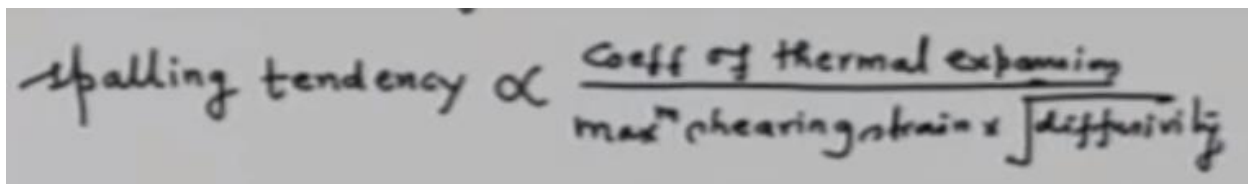
$$\text{spalling tendency} \propto \frac{\text{Coeff of thermal expansion}}{\text{max}^m\text{ shearing strain} \times \sqrt{\text{diffusivity}}}$$

(vi)Thermal conductivity

(**vii) chemical composition**

(viii) permanent linear changes(PLC)
Volume stability
Expansion
Shrinkage at high temperature
Due to changes in allotropic form/due to chemical reaction/liquid phase formation
Sintering reaction
Gap if we know brick will expand

$$PLC \% : \frac{\text{Increase} / \text{decrease in length}}{\text{original length}} \times 100$$

$$PLC \% \ volume : \frac{\text{Increase} / \text{decrease volume}}{\text{orignal volume}} \times 100$$

(ix)Thermal expansion
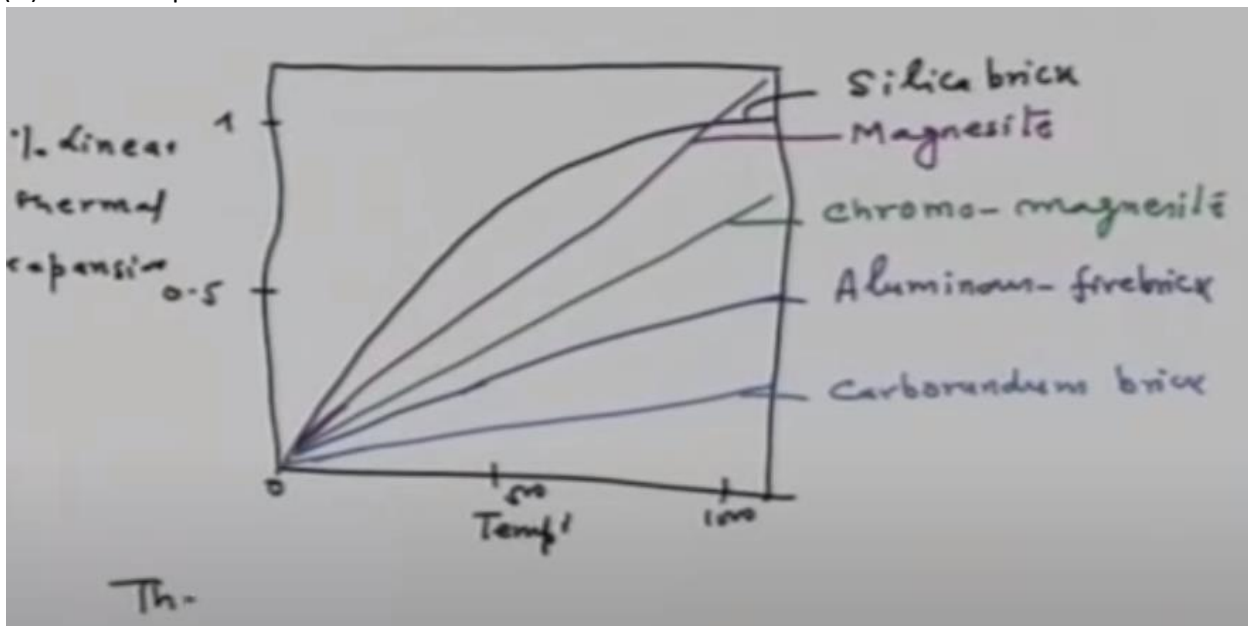
6.3 MANUFACTURURING OF REFRACTORIES

Refractory material are not naturally occuring but they are made from naturally coccuring refractories

```
┌──────────────────────┐
│    Mined Material     │
└──────────┬───────────┘
           ↓
┌──────────────────────┐
│    Ground Material    │
└──────────┬───────────┘
           ↓
┌──────────────────────┐           ─── To allow phase transformations
│  Pretreatment at high │
│  temperature to       │           ─── To allow allotropic transformations
│  calcine the material │
│                       │           ─── To remove water of hydration
└──────────┬───────────┘
           │                        ─── To remove CO₂ from MgCO₃ or MgCO₃+CaCO₃
```

Pretreatment at high temperature to calcine the material
- To allow phase transformations
- To allow allotropic transformations
- To remove water of hydration
- To remove CO_2 from $MgCO_3$ or $MgCO_3$+$CaCO_3$
- To promote formation of some high temperature phase e.g mullite formation

Binding Material →

Mixing

Could be dry or wet

↓

Moulding

↓

Drying
- Atmospheric
- Mechanical

↓

Firing
- Batch
- Continuos

↓

Cooling & Sorting

Recirculate for mixing

— Reject

Useful refractory

Manufacture of refractory

Mined material
↓
Grinding (size reduction unit operation)
↓

To heat & Calcination
↓
Binding material
↓
dry / semi plastic / wet mixing
↓
Moulding
↓
✗

To allow Phase Trans.

To allow allotropic transformation
e.g. quartz is unstable at high temperature.
Tridymite. Cristoballite
Quartz – Tridymite up.vd.
($870 - 1470°C$)
$T > 1470$ Tridymite —
Cristoballite,

To remove water of hydration

To dead burn magnesite

In fireclay - mullite formation

x **Moulding**

```
        ┌──────────────┬──────────────┐
   slip casting       Hand         Machine
        └──────────────┼──────────────┘
                       ↓
                   Drying  <  Atmospheric
                             Mechanical
                       ↓
                   firing  <  Batch
                             Continuous
                       ↓
                   Curing
                       ↓
                   Reject ──→
                       ↓
```

Objective of Pre treatment :

 allow phase transformation
allow allotropic transformation
to remove the water of hydration
dead burn magnesite,dolomite so as to remove CO_2
to form mullite in fireclay

e,g quartz is unstable at high temperature
two phases form at high temperature
quartz to Tridymitee: increase in 16%V volume change (870-1470)
tridimite to crystballite: greater than 1470 contraction of volume

Monolithic refractories: (unshaped refractories products)powder form→ suspension→harden

Types:
Castables: mixture of coarse plus fine refractory grains granis
Gelled by a binder system
 Installatiion: free fow castables(low water
                     Gunning technique
Coating refractories: useed to cat the lining
Refractory mortars: finely ground refractory material mixed t o form a paste(bricklaying)
Insulating castables: cold phase application(light weight aggregates) low density low thermal conductivity
Hearth making and crack sealing