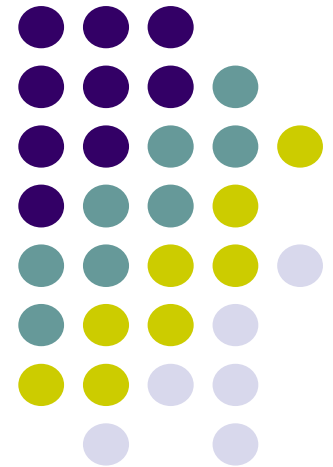# ME 216 – Engineering Materials II

Chapter 6

Production of Iron and Steel
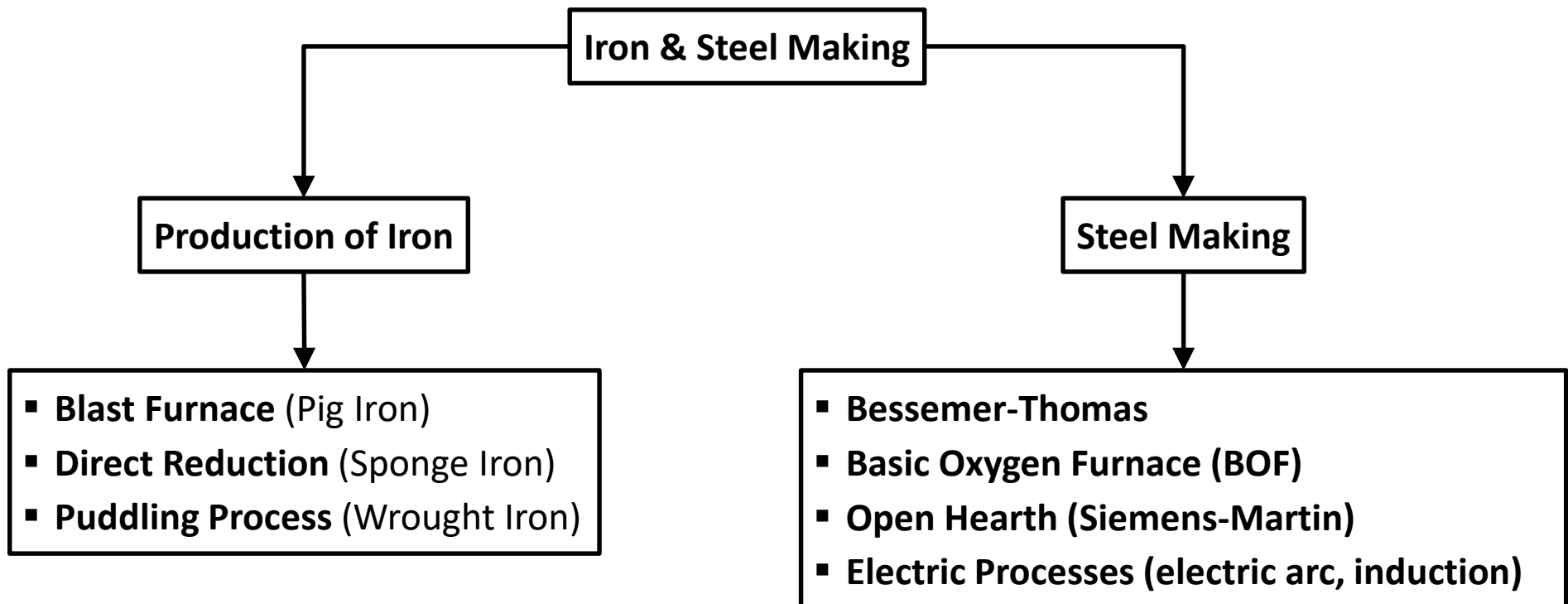
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➤ **Ferrous metals (steels and cast irons)** are the most widely used engineering materials.

➤ A variety of structures and properties can be obtained from steels (to some extent from cast irons) by changing carbon content, adding alloying elements, heat treatments, or processing.

➤ In this chapter, the objective is to understand making of iron & steel and to familiarize with the constituents of ferrous metals in order to facilitate the study of their physical metallurgy.

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                          ┌──────────────────────┐
                          │  Iron & Steel Making │
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Production of Iron

- **Blast Furnace** (Pig Iron)
- **Direct Reduction** (Sponge Iron)
- **Puddling Process** (Wrought Iron)

Steel Making

- **Bessemer-Thomas**
- **Basic Oxygen Furnace (BOF)**
- **Open Hearth (Siemens-Martin)**
- **Electric Processes (electric arc, induction)**

➢ Iron is **the fourth most plentiful element** in earth's crust.

➢ Iron ores are almost never found in their native or metallic state. Instead, they are found all over the world in the form of various compounds **(mainly oxides)**.

➢ Depending on the type, **iron content** of the ore ranges **from 25% up to 70%**. Until recently, ores containing less than 30% iron were not considered viable. However, a shortage in iron supply has changed the scenario, and taconite is now readily mined for iron.
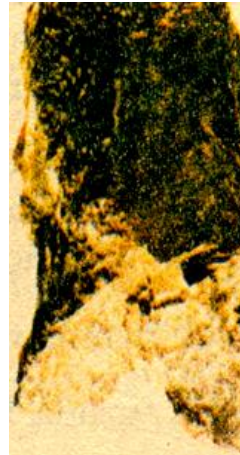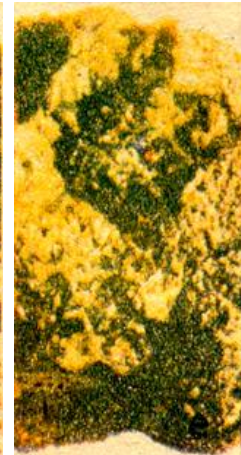

magnetite   **hematite**   **limonite**   **siderite**   **pirite**

Iron Ore	Compound	Content (%)
Magnetite	Fe_3O_4	72.4
Hematite	Fe_2O_3	70.0
Goethite	$Fe_2O_3.H_2O$	62.9
Limonite	$2Fe_2O_3.3H_2O$	59.8
Siderite	$FeCO_3$	48.2
Taconite	Fe_3O_3	25-35
Pirite	FeS_2	46.6

➢ Ores are removed by open-pit mining (instead of costly and hazardous underground mining). Then, they are separated from the worthless material (gangue) and refined to produce iron.

➢ The procedure is: **mining ► concentration ► purification ► reduction ► refining**

2

➤ Pig iron is produced in **the blast furnace** (a refractory lined chamber of 11 m wide and 40 m high).

➤ Three raw materials (iron ore, coke, limestone) are put into furnace, and **molten iron with slag** is produced.

Raw Materials (7 tons)
- **iron ore** (2 tons)
- **coke** (1 ton)
- **limestone** (0.5 tons)
- **various gases** (3.5 tons)
  - carbon monoxide (CO)
  - hydrogen (H_2)
  - carbon dioxide (CO_2)
  - water (H_2O)
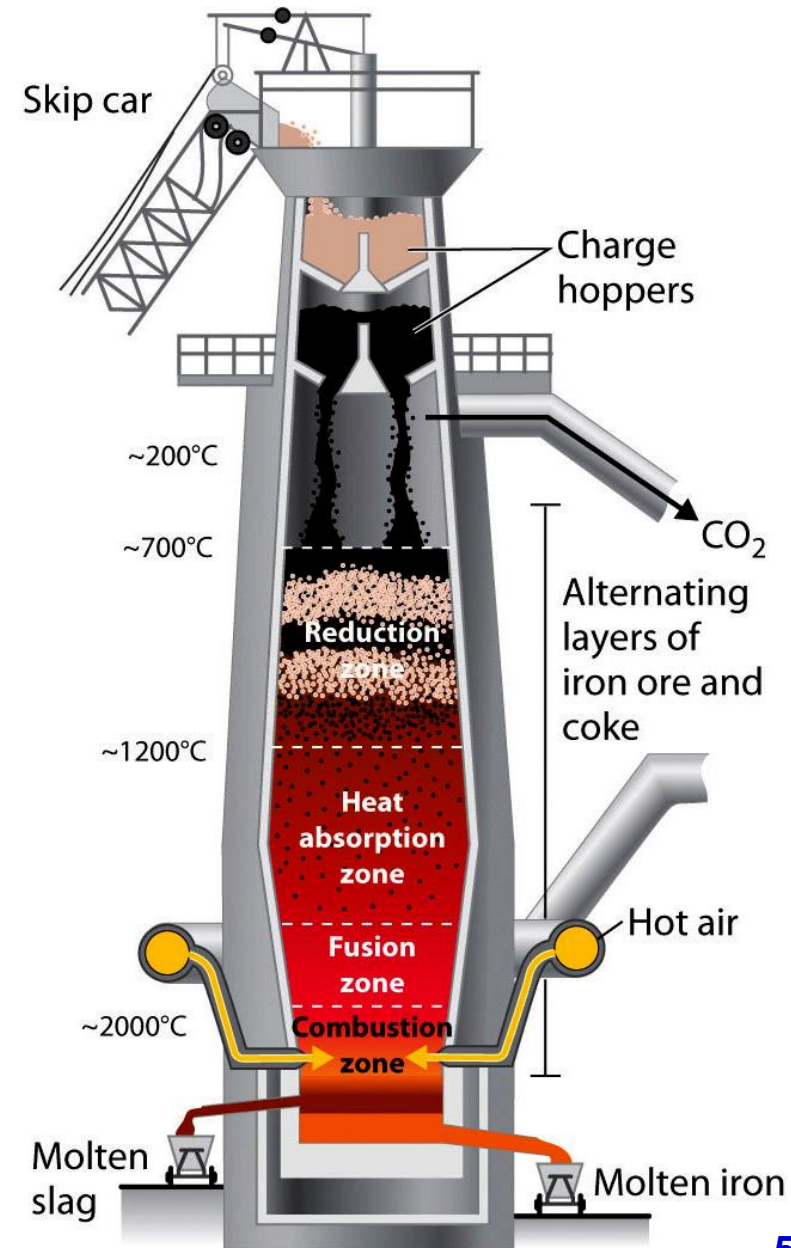 - nitrogen (N_2)
  - oxygen (O_2)

⬇

Pig Iron (1 ton)
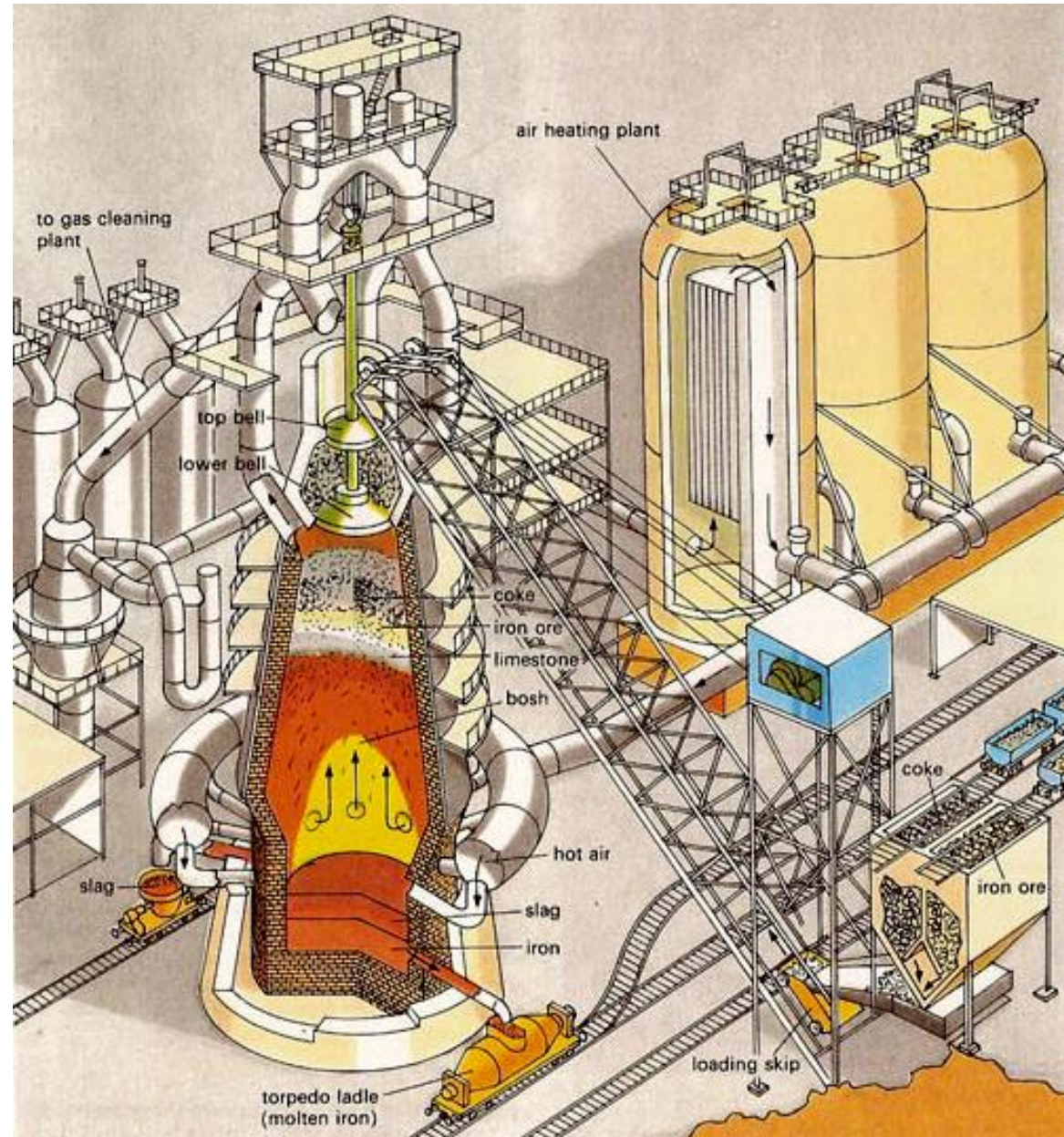
➤ **Iron ores** are pelletized & sintered before use in furnace.

➤ **Limestone (*kireç taşı*)** is a rock having high proportions of **calcium carbonate ($CaCO_3$)**. It is used as a flux to react with and remove impurities in molten iron as slag.

➤ This waste slag is lighter than iron in weight, so it floats on top of iron and helps protect the iron from oxidation.

➤ It is drawn off periodically, and hauled away in slag cars.

➤ **Coke (*kok kömürü*)** is obtained after burning certain soft coals **without air** in **a coke oven**.

➤ It is hard, brittle, porous material having 85-90% carbon together with some ash, sulphur, and phosphorous.

➤ Coke serves two functions in the reduction process:
  ▪ It is a fuel supplying heat for the chemical reactions
  ▪ It produces CO to reduce the iron ore

Coal

Coke Oven

Limestone

Coke

Iron Ore

Blast Furnace

Slag

Molten Iron
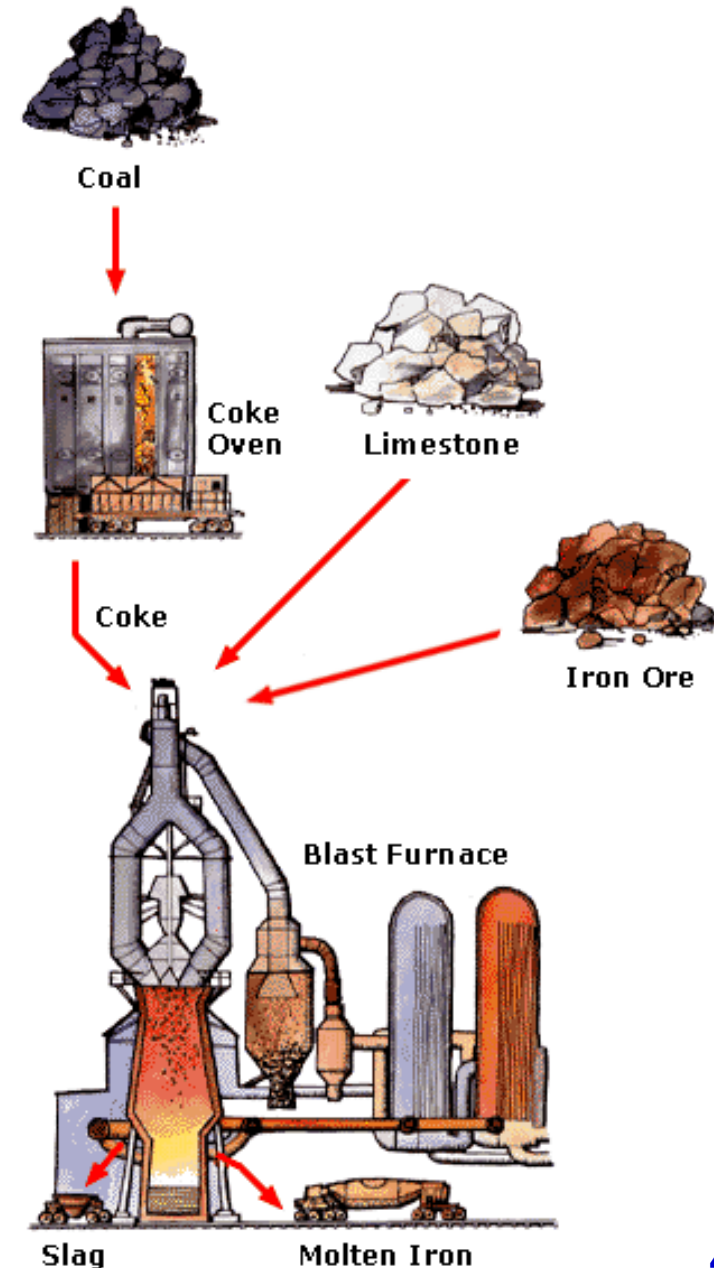
➤ In blast furnace, **iron ore is reduced** by combining it **with coke**. In other words, oxygen is removed from iron ore and combined with carbon. Thus, metallic iron is released from its oxides.

➤ Charge is raised to **hoppers** via skip cars on inclined rails, and raw materials enter furnace through hoppers until the entire furnace is filled with charge.

➤ Cross-section of the furnace increases towards **bosh region**. Charge is compressed at lower-bosh region due to smaller cross-section, and this compression supports the weight of the material above.

➤ Air is blown in through **tuyeres** at bottom of furnace. Before this, it is preheated to 600-800 °C (in stoves of refractory bricks) in order to increase the efficiency of production. To reduce erosion, the shell of furnace is water cooled.

Skip car

Charge hoppers

~200°C

~700°C

CO_2

Alternating layers of iron ore and coke

Reduction zone

~1200°C

Heat absorption zone

Fusion zone

Hot air

~2000°C

Combustion zone

Molten slag

Molten iron

Production of Pig Iron

C : coke (85-90% carbon with impurities)
Fe_2O_3 : iron(III) oxide (ferric oxide – hematite)
Fe_3O_4 : iron(II,III) oxide (magnetite)
FeO : iron(II) oxide (ferrous oxide)
$CaCO_3$: limestone (calcium carbonate)
CaO : lime (calcium oxide)
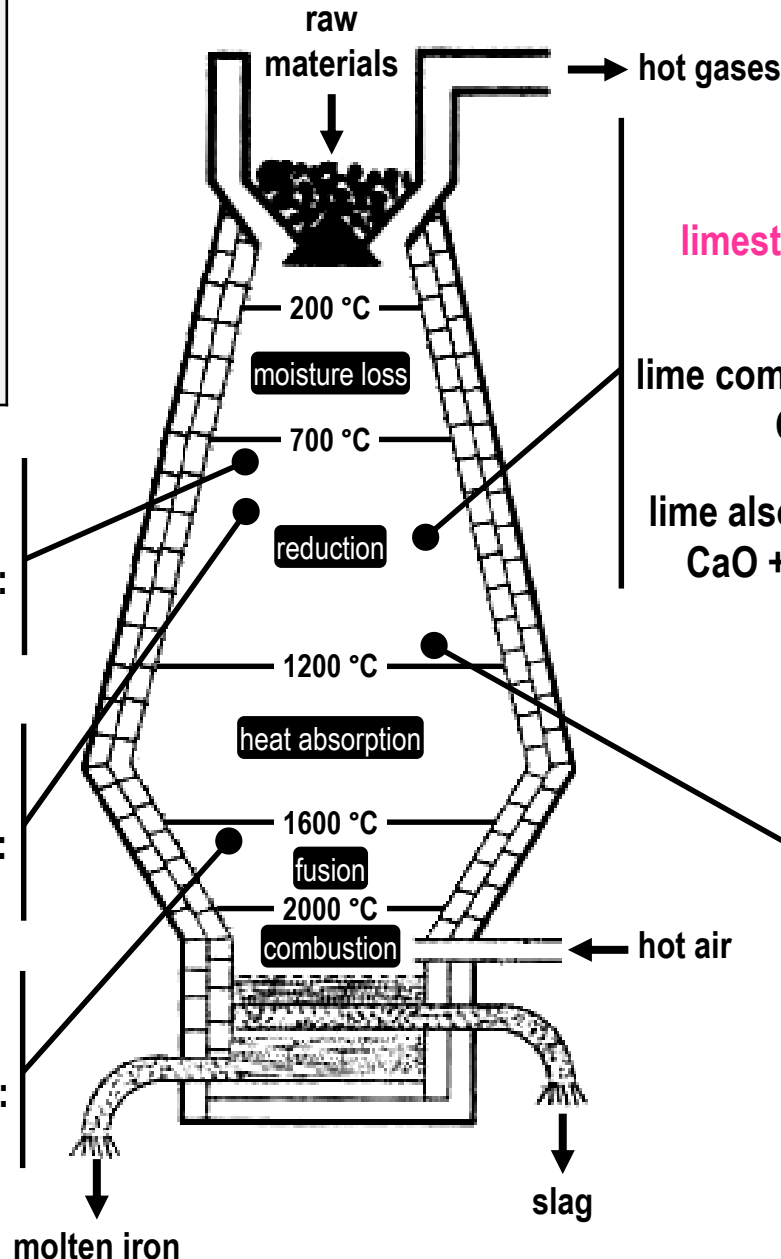$CaSiO_3$: slag (calcium silicate)
SiO_2 : silica in iron

raw materials → hot gases

200 °C
moisture loss
700 °C
reduction
1200 °C
heat absorption
1600 °C
fusion
2000 °C
combustion

← hot air

molten iron

slag

❺ **around 900 °C**

limestone decomposes into lime:
$$CaCO_3 \rightarrow CaO + CO_2$$

lime combines with silica to form slag:
$$CaO + SiO_2 \rightarrow CaSiO_3$$

lime also removes sulphur from iron:
$$CaO + FeS + C \rightarrow Fe + CaS + CO$$

❷ **after 700 °C**

iron(III) oxide is reduced to **iron(II,III) oxide**:
$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$

❸ **around 850 °C**

iron (II,III) oxide is reduced to **iron(II) oxide**:
$$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$$

❹ **before 1200 °C**

iron(II) oxide is reduced to iron:
$$FeO + C \rightarrow Fe + CO$$

carbon dioxide is re-reduced:
$$C + CO_2 \rightarrow 2\ CO$$

❶ **around 1650 °C**

coke unites with oxygen of hot air:
$$2\ C + O_2 \rightarrow 2\ CO$$

➤ **Molten iron** (at the bottom of blast furnace) contains **carbon** (3.0-4.5%), **silicon** (4%), and **manganese** (up to 1%) as well as some other unwanted impurities (such as **sulphur** and **phosphorous**). These are later removed to some extent during steel making process.

➤ Production of pig iron is an intermediate stage in the manufacture of steel. The iron is tapped at intervals and collected in a transfer car which is insulated to keep the iron hot. Then, it is moved to the steel furnace and added to the charge of steel scrap with limestone.

➤ Sometimes, the iron is not made into steel. Instead, it is **poured directly into moulds**. Before the introduction of pig casting machines, the iron was poured into open sand moulds consisting of a groove or through with many small moulds on each side (reminding one of **sow and pigs**), hence the name is **pig iron**. Iron pigs are melted in cast iron foundries and in steel mills.

➤ Iron from ore can be directly reduced to produce **sponge iron** in a solid state reduction at 750 °C using natural gas or some other reductant.

$$Fe_2O_3 + CO \rightarrow 2\ FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$
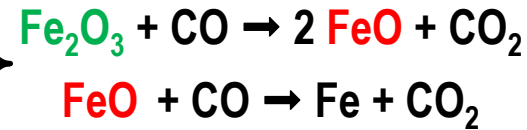
➤ This iron has a spongy appearance, and it can be converted to steel using an electric process.

➤ Solid state, low temp. reaction makes it possible to mine and produce this iron from very remote areas in very small quantities.

➤ Considerable research has gone into development of this technology, and small-size steel plants were constructed (such as **HyL**, **Midrex**, **SL/RN**, **Accar**).
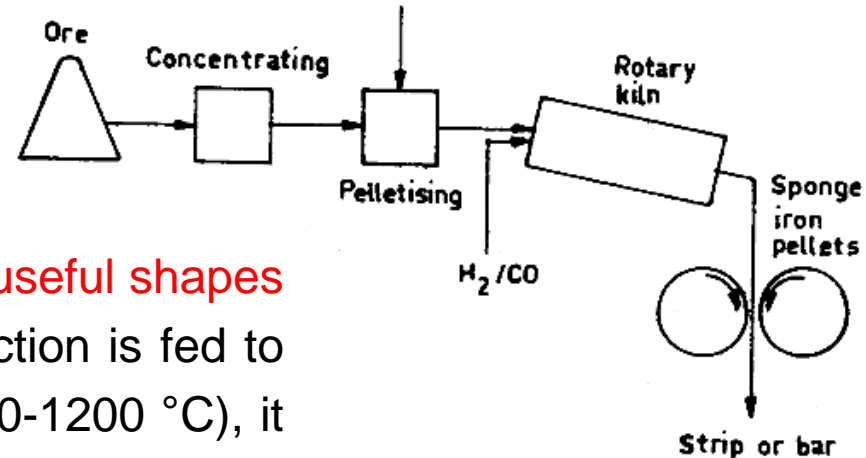
➤ Recent development is converting sponge iron into useful shapes by **sintering & pressing**. Sponge from direct reduction is fed to a large-dia rotary kiln. After gaseous reduction (1100-1200 °C), it is passed into small-gap rolls to have 80% reduction in thickness.

➤ The products have similar mechanical properties of conventional low carbon steel, but the structure is quite different.

Ore — Concentrating — Pelletising — H_2/CO — Rotary kiln — Sponge iron pellets — Strip or bar

➢ In ancient times, before the advent of steel and pig iron, iron was produced by a direct process whereby the ore was heated in a forge to white heat to remove impurities. Charcoal fire in the forge was not hot enough to melt the iron, thus the result was **a pasty mass of spongy iron** that was then hammered to remove molten gangue or slag. Wrought iron is never cast; instead it is hammered, pressed, or forged.

➢ Wrought iron was used extensively before modern steel making processes (such as bars, plates, rails and structural shapes for bridges, boilers and many other applications). It has **particularly been used where the parts are to be forged or welded**.

➢ Wrought iron was made by **puddling process**: pig iron was melted in open hearth furnace. Iron oxide was added so that carbon and other impurities were removed by iron oxide slag. The mass of iron was removed and squeezed to remove the slag, but much of slag remained in the iron. The result was low-carbon, fibrous (due to trapped slag), soft iron.

➢ Today, **Aston process** is used: molten pig iron and steel are poured into open hearth furnace in a prepared slag. This cools the metal to a pasty mass, and it is squeezed in a hydraulic press. The slag is distributed in iron matrix as threads and fibers in rolling direction. This imparts excellent ductility to wrought iron. In addition, it has good machinability and corrosion resistance.
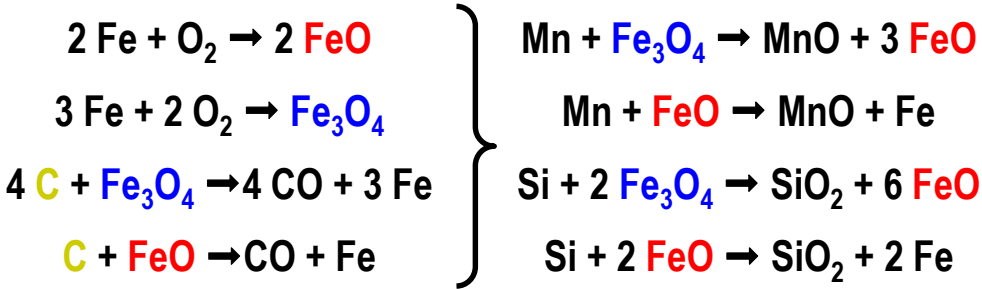

The Puddling Furnace

Iron

fire

Puddling bar
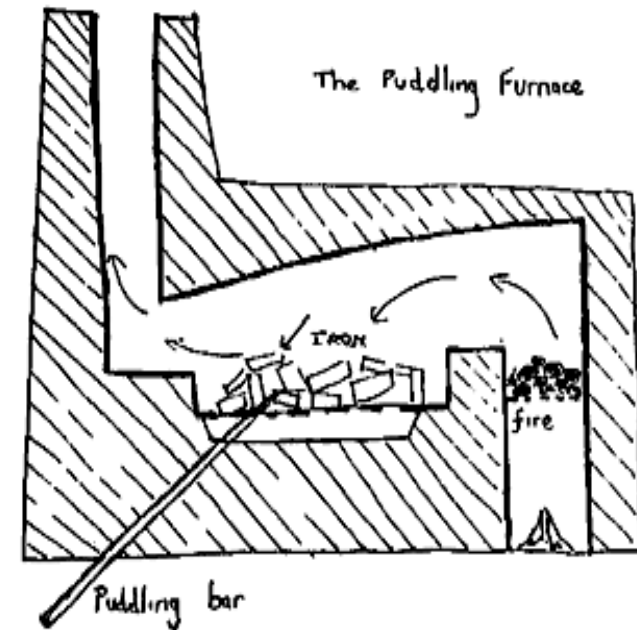
➤ Since pig iron contains too many impurities, it must be refined to produce steel or cast iron of various types. **Steel** is simply an alloy of iron with most of its impurities removed (containing 0.03 - 2% carbon, plus other alloying elements).

➤ Over 90% of steels is **plain carbon steel** (having less than 1% carbon with little manganese to control sulphur and other impurities). The rest is all other **alloy steels**.

➤ **Major steel making processes** (with their use in percentages):

   1. Bessemer-Thomas: 0% (not generally used today due to its product of inferior steel)

   2. Basic Oxygen Furnace (BOF): 60% (majority of steels are produced by this process)

   3. Open Hearth (Siemens-Martin): 15% (superior to Bessemer-Thomas)

   4. Electric Processes: 25% (for producing high quality & special purpose steels)

➤ These processes are classified **depending upon the formation of slag**:

   ▪ **Acidic process:** the slag with **high silica**

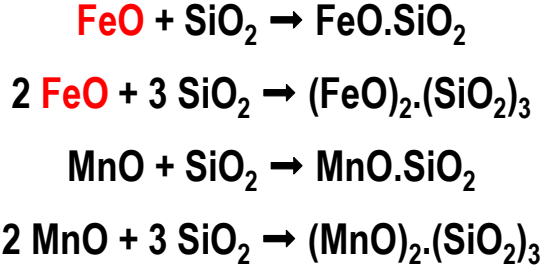   ▪ **Basic process:** the slag with **high lime**

Acidic Process

➤ **Non-metallic oxides** oxidize iron into **iron(II) oxide** & **iron(II,III) oxide** which subsequently oxidizes **C**, **Mn**, **Si** (**P** is not oxidized as it would be reduced again in the presence of **SiO$_2$**):
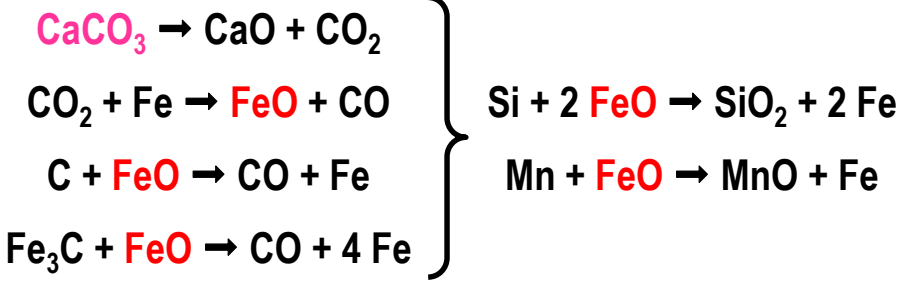
$$2 Fe + O_2 \rightarrow 2 FeO \qquad Mn + Fe_3O_4 \rightarrow MnO + 3 FeO$$

$$3 Fe + 2 O_2 \rightarrow Fe_3O_4 \qquad Mn + FeO \rightarrow MnO + Fe$$

$$4 C + Fe_3O_4 \rightarrow 4 CO + 3 Fe \qquad Si + 2 Fe_3O_4 \rightarrow SiO_2 + 6 FeO$$

$$C + FeO \rightarrow CO + Fe \qquad Si + 2 FeO \rightarrow SiO_2 + 2 Fe$$

➤ Such oxides **form slag** which floats over molten steel protecting it from excessive oxidation:

$$FeO + SiO_2 \rightarrow FeO.SiO_2$$

$$2 FeO + 3 SiO_2 \rightarrow (FeO)_2.(SiO_2)_3$$

$$MnO + SiO_2 \rightarrow MnO.SiO_2$$

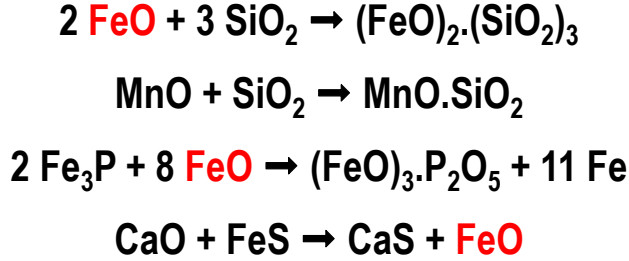$$2 MnO + 3 SiO_2 \rightarrow (MnO)_2.(SiO_2)_3$$

➤ Refractory lining is **acidic (silica)** since it would otherwise react with the bath producing cracks.

Basic Process

➤ **Metallic oxides** oxidize impurities. **Limestone** is added as oxidizing agent unless oxygen is blown in the process (as in Bessemer process):

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CO_2 + Fe \rightarrow FeO + CO \qquad Si + 2 FeO \rightarrow SiO_2 + 2 Fe$$

$$C + FeO \rightarrow CO + Fe \qquad Mn + FeO \rightarrow MnO + Fe$$

$$Fe_3C + FeO \rightarrow CO + 4 Fe$$

➤ **Slag forming** reactions are as follows. <u>The third reaction</u> only takes place if slag is very basic and only slightly oxidizing (presence of **Si** reduces **P**, and it goes back to steel). In addition, **S** can be partially reduced in <u>the last reaction</u>.

$$2 FeO + 3 SiO_2 \rightarrow (FeO)_2.(SiO_2)_3$$

$$MnO + SiO_2 \rightarrow MnO.SiO_2$$

$$2 Fe_3P + 8 FeO \rightarrow (FeO)_3.P_2O_5 + 11 Fe$$

$$CaO + FeS \rightarrow CaS + FeO$$

➤ Refractory lining is **magnetite** or **dolomite**.

➤ In both acidic and basic processes, the oxidizing agent is **iron(II) oxide (FeO)** although it is produced early in acidic process, and hence the time required for refining is shorter.

➤ Basic process has much more severe oxidizing condition, thus it is likely that some of FeO is present in steel which forms cellular structure around ferrite crystals reducing its strength.

➤ Therefore, all being equal, acidic steel is probably more desirable.

➤ In most cases, too much carbon is burnt out during refining. Thereby, carbon content of steel is raised by adding **ferromanganese** (72-80% **Mn**, 6-8% **C**) or **spiegeleisen** (15-20% **Mn**, 4-6% **C**). They may be added during refining in acidic process whereas in basic process it is added in the ladle rest (which reduces phosphorous). **Carburisers** also act as deoxidizers.

➤ **The refined steel** is produced through oxidation, and hence it may (in most cases it does) contain oxygen in the form of iron oxide and dissolved gas. This can be tackled by:

- Deoxidation (killed steel)
- Rimming (rimmed steel)

Killing

➤ It is done by adding silicon (ferrosilicon) or aluminum, which form SiO_2 or Al_2O_3 by reacting with **iron oxide** or **oxygen**:

$$Si + 2\,FeO \rightarrow SiO_2 + 2\,Fe$$

$$2\,Al + 3\,FeO \rightarrow Al_2O_3 + 3\,Fe$$

Rimming

➤ **Manganese** is added in the form of ferromanganese which forms manganese iron oxide. During solidification, pure iron solidifies at the surface of the mold leaving the molten steel in the middle as enriched with carbon. Manganese iron oxide reacts with carbon to form **CO**.

➤ This process uses pear-shaped converter **(Bessemer Converter)** with a capacity of 15-20 tons. It is filled with molten pig iron when it is in horizontal position. Pig iron is usually melted in **a cupola** before charging in the converter.

➤ The converter is turned to its vertical position, and compressed air (about 125 atm) is blown in through **tuyeres** which oxidizes all impurities to produce steel.

➤ The oxidation of carbon and silicon is an exothermic reaction (i.e. the heat keeps the steel molten). For low phosphorous iron, acidic process is used which takes about 10 minutes to oxidize the impurities.

➤ The quality of steel from this process is not very good, and hence this process is not commonly used.
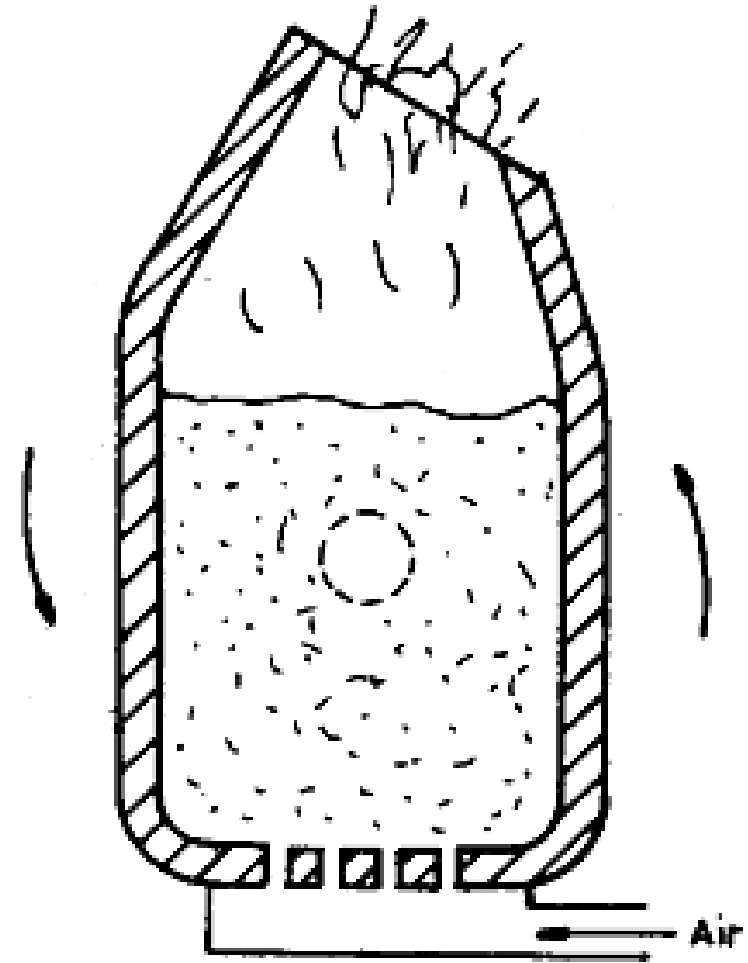
➤ Use of air in Bessemer process leads to high nitrogen steels, which is not desirable for certain applications. Basic oxygen process uses 98% pure oxygen instead of air. Basic oxygen converter resembles Bessemer converter, except that it is closed at the bottom.

➤ Molten metal in converter is refined by blowing pure oxygen at high pressures (higher than 800 atm) into the melt using water cooled lances. The agitation ensures uniform refining, and oxygen oxidizes the impurities and forming a slag.

➤ This is a basic process. It has the advantage of using 25% scrap as raw material to avoid excessive heat, and is faster than open hearth process (about 300 tons/hour).

Oxygen Lance
Refractory Lining
Slag

➤ The quality of steel is very good (due to low content of hydrogen and nitrogen). The further modification is to add lime powder into oxygen jets when using high phosphorous charge.

➤ **Lintz-Dowatz (L/D) process** is commonly used for steel making.

➤ **Kaldo and Rotor processes** are the same as L/D, except that converter works in horizontal position instead of vertical. Largest proportion of steel is produced by these processes.
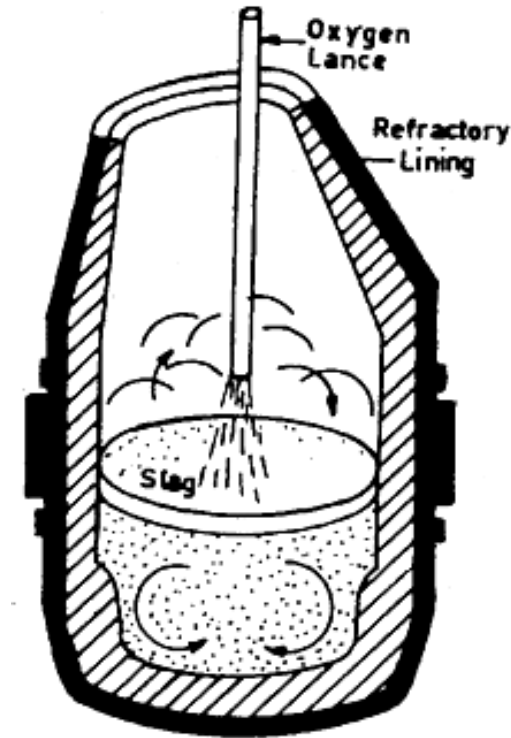
➤ In this process, steel is produced by heating molten pig iron, scrap, iron ore and other elements (such as **ferrosilicon** and **flourspar** to make slag viscous) in the furnace.

➤ It is superior to Bessemer process (not restricted to low phosphorous iron & uses steel scrap as charge).
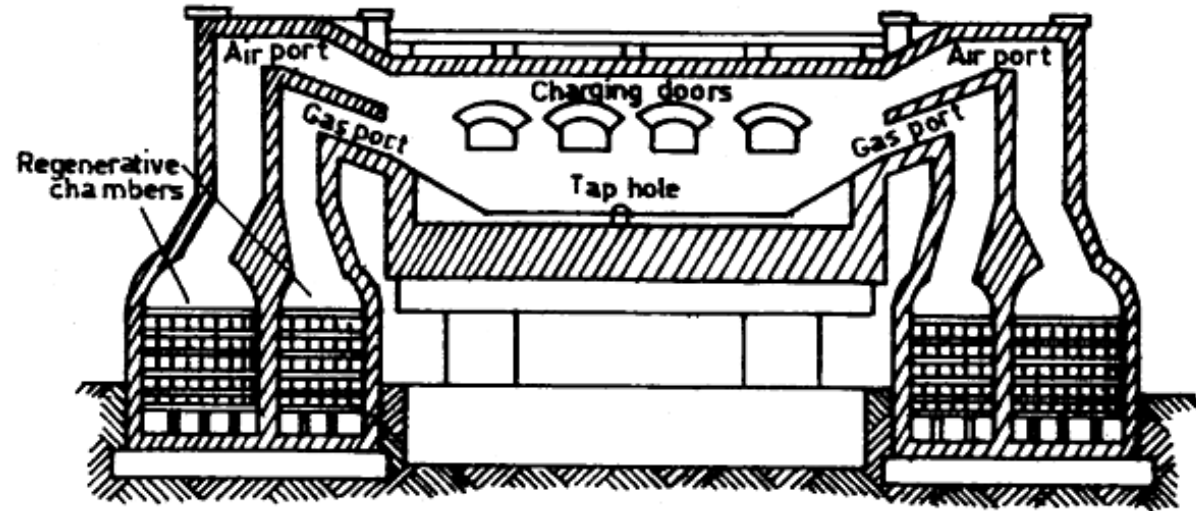
➤ Sufficiently high temperatures are obtained by using **regenerative furnaces** (the exhaust gases are used to heat up brick walls, which in turn supplies heat to the incoming gases).

➤ These furnaces produce 100-375 tons per heating of 8-10 hours. The flow of gases and air is alternated in every 15-20 minutes. Mostly basic process is used with limestone as flux.

➤ Although the quality of steel is good, limited amount of steel is produced by this process. Sometimes **duplex process** is used (acid Bessemer and basic open hearth are combined). Impurities (such as **Mn** and **Si**) are removed by Bessemer process followed by the removal of **S** and **P** in open hearth. However, duplex process is not very common.

➢ Electric steel making is employed when extremely high quality steel is required and electrical energy is cheap and plentiful. **Alloy steels**, **tool steels**, **stainless steels** and **steel castings** are produced by these processes.

➢ In such processes, pig iron and cold scrap are added as usual with other desired elements. The heat is provided by electrical energy in few ways. Atmosphere and temperature can be controlled precisely, and there is no excessive oxidation from furnace gases so that the steel composition can be manipulated accurately.

Electric Arc Furnace

➢ Electricity from one electrode passes through an arc into the charge, and through another arc to other electrode.

➢ Usually a charge of graded-steel scrap is melted under basic slag (lime) to remove **P**. Second basic slag is used to remove **S** and to deoxidize the steel in the furnace.

➢ Capacity of furnaces may be **200 tons** with production rate of **40 tons/hour** and power of **50,000 KWh**. **Graphite electrodes** (up to Ø760 mm, over 24 m long) are used. Operating potential is **40 V**, and current exceeds **12,000 A**.

Consumable Carbon Electrodes

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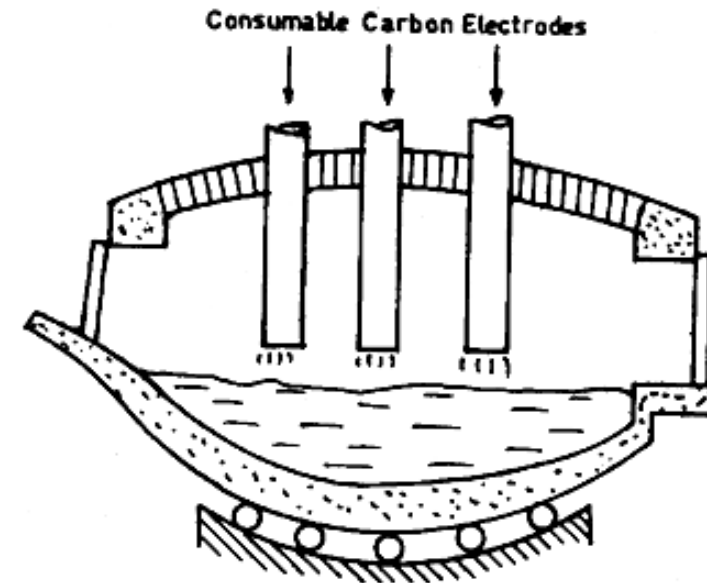
Induction Furnace

➤ A coil is wound around a crucible, and a high current in the coil heats the metal which forms the secondary of a transformer. Alternating current in the primary coil creates magnetic field and produces **an eddy current** in the metal.

➤ Penetration of eddy current depends upon the frequency, and a frequency of **500-2000 Hz** is generally used.

➤ Capacity of furnaces usually ranges from **few kilograms to 5 tons**.

➤ High quality bearing and tool steels are produced by this process.

Refractory bricks

Water

Electral wirings

Water

➤ Another method of heating the charge (which is sometimes used) is to make the charge a career of electricity. The charge is heated due to its **electrical resistivity** when electricity is passed through it (just like an electrical coil is heated when current is passed through it).
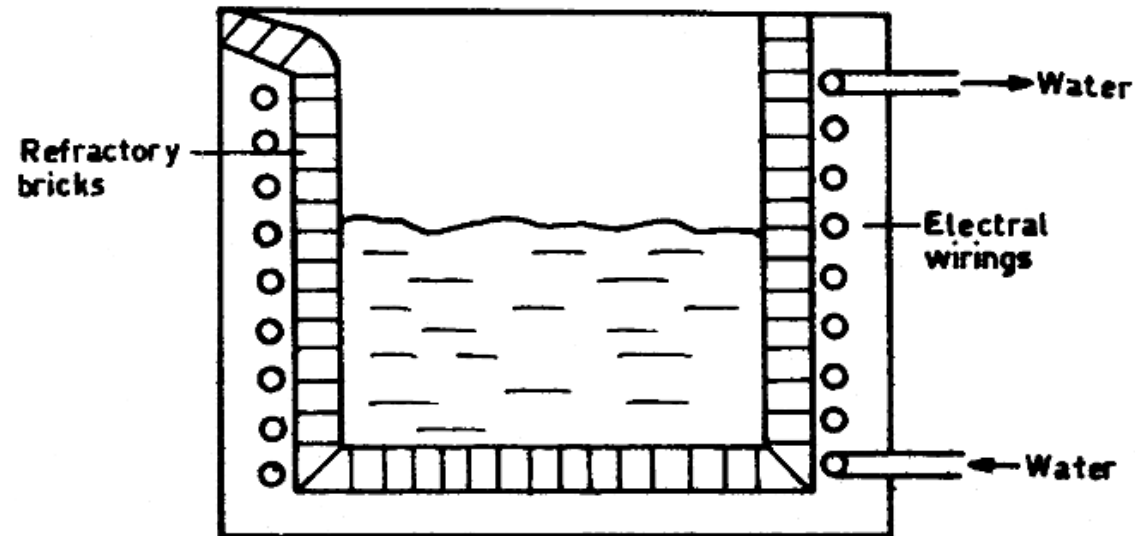
➤ As a result of deoxidation and incomplete removal of impurities, the molten steel has either dissolved impurities (Mn, Si, P) and gases or suspended non-metallic inclusions.

➤ These impurities remain in their positions through cooling and transformation to ferrite and pearlite structures. The dissolved impurities may strengthen ferrite or may react with other elements to form inclusions and other phases depending upon the nature of the impurity.

➤ **Manganese: promotes depth of hardening**, but **also liable to quench cracking**. It may dissolve in ferrite to give solid solution strengthening; or it may form carbides, sulphites or manganese-silicate inclusions.

➤ **Silicon:** present in most steels (**usually less than 0.2%**), and **generally beneficial**.

➤ **Sulphur:** Should be kept in low amounts (**< 0.05%**). Exists as sulphide (MnS or FeS). **FeS** forms brittle, low melting point, yellowish brown film around solid steel crystals and causes the metal to split when forged. **MnS** is a dove grey colored inclusion which is only slightly soluble in iron and segregates into large globules irregularly distributed throughout steel.

➤ It is plastic at high temperatures, and elongates into fibers during rolling without impairing mechanical properties. It may improve fatigue characteristics by enveloping brittle oxides.

➤ **Phosphorous:** has powerful tendency to segregate. The amount should be **max. 0.05%** (more than that is dangerous and should be avoided by keeping its content below 0.05%).

➤ It forms a compound which dissolves in iron up to 1.7%, but in the presence of 3.5% **C** its solubility is reduced to 0.3% and the excess forms a brittle eutectic found in cast irons.

➤ In rolled steels, areas containing high **P** are elongated into bands (ghost bands), which are characterized by the absence of pearlite (weak due to presence of **P**). In some specific cases, **P** is beneficial (e.g. in tin plates and for fire welding of spades).

➤ **Dissolved carbon & nitrogen:** cause strain aging after cold rolling in mild steels. They also affect the ductility as shown through impact tests.

➤ After steel making processes, the steel is poured into ingot moulds. These cast ingots are preheated (soaked) at 1200 °C. Then, they are formed into blooms, billets, and slabs.

➤ **A bloom** has square cross-section with min. size of 15 x 15 cm.

➤ **A billet** (smaller than bloom) has square cross-section from 4 cm up to the size of a bloom.

➤ **Slabs** with rectangular sections (min. 25 cm wide & 4 cm thick) are rolled from either ingot or bloom. The width is always 3 to 4 times the thickness. Plates, skelp and thin strips are rolled from slab.

➤ **Other shapes** are produced from slabs, blooms, and billets.

Slabs — Plates — Skelp — Pipe and tubing — Large diameter pipe

Blooms — Structural shapes — Strip — Tin plate

Rails — Tube rounds — Seamless pipe

Billets — Bars — Wire rods — Wire — Cold drawn bars