CHAPTER 2

UNDERSTANDING “IRON”

An Appraisal of Iron

Iron (Fe) is the fourth most abundant element in the earth making up 5% of its crust. Among the metals, it stands second in abundance to Aluminium. One of the most useful of all metals, iron is best known for its use as a high-strength structural material, for steel manufacturing and for its magnetic properties. It is rarely found in the metallic state and generally occurs in its compound form, that is, as ores. This chapter introduces the metal iron, the types of iron ores, their distribution in the Indian sub-continent, properties of iron and its alloys followed by the Iron-Carbon Equilibrium Diagram and an account of industrial production of iron and pre industrial iron working.

Types of Iron Ores

An ore is a geochemical anomaly in which the abundance of an element is concentrated many times over its average crystal abundance. In ore deposits, the valuable metal is found either in native form or combined as discrete minerals forming chemical complexes with sulphur, oxygen and carbonate (Newman 1965). Native iron of terrestrial origin is rare. In the native state of meteorite, iron content is more than 90%. A few exceptions are in the form of grains and pellets in some of the basaltic formations. As it is less in quantity, its extraction is difficult (Coghlan 1956) suggesting that this would have been an insignificant source to the prehistoric people. The
economic ore deposits vary in size from few thousand tons to several million tons. The iron content in different ores varies from a maximum of 70% to as low as 30% (Table 2-1).

Table 2-1: Amount of iron content in major iron ores

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Colour</th>
<th>Metallic Iron Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>Red</td>
<td>69.94</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>Black</td>
<td>72</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>Brown</td>
<td>48.3</td>
</tr>
<tr>
<td>Limonite</td>
<td>Fe₂O₃ₙ(H₂O)</td>
<td>Brown</td>
<td>60-65</td>
</tr>
</tbody>
</table>

Bateman (1955) has identified the common impurities in iron ore. These are silica, phosphorous, manganese, sulphur, alumina, water and titanium. Economically good ores have less silica, alumina, lime and magnesia. To decide whether an ore body is economically advantageous to work with or not, four major factors are taken into consideration. These are its easy availability, the nature and amount of minor constituents in them, the way the principal mineral is combined with the minor constituents and the geographical location of the ores (Hodges 1964). However, for the ancient smelter, the easy availability of the ore would have mattered more than its quality or quantity.

Iron has great affinity for oxygen and therefore the most plentiful and important of iron ores are oxides followed by carbonates and sulphides. It combines readily with oxygen to form oxides; FeO, Fe₃O₄ and Fe₂O₃, of which Fe₂O₃ is the most stable one. The relatively pure minerals of iron are hematite (Fe₂O₃) and limonite (Fe₂O₃ₙ(H₂O)). Both contain high
proportions of iron and are relatively free from sulphur and phosphorus. The magnetic oxide of iron namely magnetite or lodestone (Fe$_3$O$_4$) is a mixture of two oxides, that is, ferrous oxide (FeO) and ferric oxide (Fe$_2$O$_3$). There is possibility of the presence of magnetite whenever these two oxides are present together. Carbonate ores (FeCO$_3$) have low content of iron. Sulphide ores, pyrites or marcasite (FeS$_2$) and pyrhotite (Fe$_7$S$_8$) were presumably less attractive to ancient man. It is difficult to assess which of the factors mentioned mattered in the choice of ore by the ancient smelter.

Metalliferrous minerals as ore deposits are unevenly distributed throughout the world. Magnetite ores occur in the form of thick beds and irregular masses in igneous and crystalline rocks, while hematite occurs as beds inter-stratified as sedimentary constituent of many mineral veins. Limonite appears in the form of bog iron as irregular sheets in lake-basins and marshy lands. Formation of a mineral deposit is an episode or a series of episodes in the geological history of a region and reflects three broad categories:

1) igneous activity,
2) sedimentary process and
3) metamorphism

Based on the mode of formation, Bateman (1955) classified the ores into various types such as:

(a) Sedimentary ore formed by deposition and precipitation of ore forming minerals, which are carried and transported in solution.
(b) Crystalline ores formed from magnetic concentrations where crystallisation of the ore forming minerals occurs.

(c) Replacement ores- hydrothermal solutions carrying iron ore minerals replace the original calcareous rock.

(d) Residual ores- when undesired constituents of rocks or mineral deposits are removed during weathering, under favourable condition iron accumulates.

The important iron ore deposits in India occur as sedimentary, crystalline, and residual formations (Krishnan 1964). In ancient iron-formations, the dominant iron minerals are goethite, berthierine, chamosite, greenalite, stilpnomelane, siderite, pyrite, magnetite and hematite (Greensmith 1989: 165).

Distribution of Iron Ores

Iron ore deposits of India are found associated with a number of geological formations, namely; Pre-Cambrian, Cuddapah, Vindhyan, Gondwana, and Deccan. Of these, the Pre-Cambrian is considered most important and comprises some of the largest hematite and magnetite deposits in India (Krishnan 1964).

Some of the richest iron ore deposits in the country occur in Madhya Pradesh, Rajasthan, Bihar, West Bengal, Mysore, Goa and Salem (Tamil Nadu). In eastern India, siliceous limonite in Tipan series of Assam, limonite deposits in Burdwan District of West Bengal, high-grade hematite
deposits in Mayurbhanj, Singhbhum, Keonjhar and Badoni in Bihar indicates rich iron ore deposits. In the north-west, rich ore deposits occur at Chapri, Jannpur and Dhanota of Punjab (magnetite and hematite bands), and extensive deposits at Alwar, Jaipur and Jodhpur Districts of Rajasthan. In central India, rich and extensive deposits of banded hematite/quartzite occur at Bastar, Durg, Chanda, Jabalpur, Bailadila, Rajahra, Dalli, Asolay, Pipalgaon and Lohar in Madhya Pradesh. The Deccan and Ratnagiri in Maharashtra; south Guntur, Cuddapah and Kurnool in Andhra Pradesh; Dharwar series in Karnataka; and hematite-quartzite series in Salem in Tamil Nadu represents high iron ore deposits. However, such type of commercial deposit of iron is absent in Gujarat.

Properties of Iron and its alloys

Every metal has a definite geometrical order in the internal arrangement of its atoms/ions (the constituent particles) which is referred to as crystal structure. The space lattice of any metal is comprised of innumerable conjugate unit cells inside which the atoms are arranged in a definite order giving a regular repetition of pattern in three dimensions. Thus, in each crystal, the atoms are spaced in a characteristic pattern. The main three types of such arrangements of metallic space lattice are, viz., Body Centred Cubic (BCC), Face Centred Cubic (FCC) and Hexagonal Close Packed (HCP). During melting of the metal, this orderly lattice breaks down and the arrangement of the atoms becomes haphazard (Nayak 1985).

Many metals including iron are subject to crystalline transformations in the solid state upon changes in their temperature. The different modifications of
the same metal are designated as alpha (\(\alpha\)), beta (\(\beta\)), gamma (\(\gamma\)) and delta (\(\delta\)). Iron exists in all these four aforesaid forms. Of this, alpha, beta and delta have Body Centred Cubic and gamma-iron has Face Centred Cubic structure. Iron may exist in different allotropic forms in the solid state depending upon the temperature to which it is heated. When iron cools at a temperature below 1535\(^{\circ}\)C, it slowly passes from liquid to solid state forming delta iron (Body Centred Cubic crystal lattice), which is stable above 1400\(^{\circ}\)C. At 1390\(^{\circ}\)C, the delta iron transforms to gamma iron. Gamma iron is non-magnetic (Face Centred Cubic lattice); stable between 912\(^{\circ}\)C-1390\(^{\circ}\)C and dissolves carbon to form a solid solution. At 910\(^{\circ}\)C, gamma iron is transformed into beta iron (of Body Centred Cubic lattice). At 768\(^{\circ}\)C, beta transforms to soft alpha-iron/ferrite (the chief constituent of pure wrought iron), possessing magnetic property. The beta iron (paramagnetic state of alpha iron) occurs between 910\(^{\circ}\)C and 768\(^{\circ}\)C. (Fig: 2.1)

When temperature of the metal drops (on cooling) below a certain critical value the metal begins to solidify. In this process, small crystals begin to form nuclei throughout the liquid. As cooling continues, more and more atoms attach themselves to the nuclei in the arrangement of the crystal habit typical of the metal. One might expect metals of cubic habit to solidify ultimately in the form of cubes. But, since there is a great dissipation of heat at the corners of cubes than elsewhere, there is a tendency for atoms to become attached to the corners of each cubic nucleus. As a result, radial arms develop at the corners of the nuclei. These in turn develop secondary arms and so on, resulting in the formation of crystal skeleton like a fern.
Fig: 2.1 Allotropic Transformation of Iron
tree, that is, a dendrite. On further cooling, these dendrites will grow until they come in contact with the adjacent ones. The remaining liquid metal between the branches of the dendrites will solidify to fill the spaces. Ultimately, each dendrite will become a polyhedral crystal with its surface having contact with adjacent crystals. These crystals, which are irregular in boundary, are usually referred to as grains.

The rate of cooling is of great importance as it governs the size, shape and arrangement of the grain of a metal. When a pure metal cools very slowly, the nuclei will be more or less evenly distributed throughout the metal. As a result, the grains will be of approximately the same size and roughly equiaxial. If cooling is rapid, solidification starts at a number of different points and a larger number of grains develop producing a finer grain structure.

Since the atoms of a metal are arranged in a regular lattice, there are planes of weakness running through the lattice. Thus, when a metal is hammered lightly, whole volumes of lattice may become momentarily deformed and return to their original position after each blow. Under heavier hammering these volumes of lattice may become permanently deformed. As a result the crystal grain may take up a new shape. This kind of distortion is known as slipping. Slip lines are visible under the microscope as fine parallel lines traversing the grains of the metal which are formed by the slipping of a part of the grain over the other in different directions. As a result of slipping under severe hammering, the grains themselves become flattened.
The iron-carbon equilibrium diagram facilitates one to understand different microstructures. Each microstructure is characteristic of a definite range of composition and a particular temperature. Hence, the constituents of microstructures vary according to the variations in alloying element and temperature (Figure 2.2).

In the figure 3.4, above the line ABCD (area I in the diagram), the alloy is in homogenous liquid state. “A” is the melting point of pure iron (δ-iron). Point H represents the maximum solubility of carbon (0.1% carbon) in δ-iron at 1490°C. As carbon content increases melting point decreases and at point B, austenite (γ-iron) starts forming. Curve JE represents lowering of melting point. At point E, at 1130°C, the maximum solubility of carbon is 2%. “C” is the eutectic point and at this point the mass solidifies to a mixture of austenite and cementite. Complete solidification of the alloy occurs below the line HJECF. Alloys containing 0.18%-2% carbon become solid along the part of the solidus HJE. Those with from 2%-4.3% carbon are completely solid on line EC. The solidification of the last portions of the liquid phase enriched in carbon (4.3%) takes place along this line. All the liquid is completely solidified at 1130°C, at the same time crystals of austenite containing 2% carbon (Point E) and cementite containing 6.67% carbon (Point F) separates. The solubility of carbon in γ-iron decreases as iron cools down and cementite separates from the solid mass. Carbon in the austenite decreases along ES. The point S corresponds with 0.82% of...
Fig: 2.2 Iron-Carbon Equilibrium diagram showing phases and microstructures.
carbon. At 912 °C, the γ-iron changes to α-iron. The carbon dissolved in γ-iron depresses the transition point of γ-iron into α-iron along GS, S being the eutectic point, the remaining austenite is converted into pearlite (a mechanical mixture of α-iron and cementite) (Weinstein 1970).

If a molten alloy of iron and carbon containing less than 0.85% carbon is allowed to cool slowly, it will solidify at a relatively high temperature forming austenite. On further cooling, the carbon is ejected from the space lattice of the iron and ferrite is formed. The ejected carbon combines with some of the iron and gets distributed in the ferrite matrix as finely laminated grains known as pearlite. If the original alloy contains exactly 0.85% carbon, no grains of ferrite will be formed, but instead, the whole material will be composed of pearlite. When the mixture contains more carbon in the range of more than 0.85% and less than 1.8% grains of iron carbide, cementite, will be formed by infilling the pearlite eutectoid.

A prepared section of low carbon steel, cooled slowly will allow a more accurate estimate of the quantity of carbon present. Steel of very low carbon content (0.02%) consists of ferrite alone as light coloured grains of varied sizes and shapes on the etched surface. The size and shape of the ferrite grains depend upon the kind of deformation in rolling or by forging. As carbon content increases, pearlite as lamellar or granular structure appears as light and dark stripes. As the proportion of carbon increases, the amount of pearlite also increases.

When steel is cooled rapidly (i.e., quenched) the sudden cooling does not give time for the complete rearrangement of the austenite solid solution. Under these conditions, fine needle-like crystals of martensite, are
produced. Martensite is a super-saturated solid solution of carbon in iron. It is exceptionally hard and can even scratch glass. A slightly slower rate of cooling achieved by quenching in oil produces a structure of finely laminated ferrite and cementite known as troostite, which differs from pearlite only in the degree of fineness of lamellae. The structure of troostite (ferrite + cementite) is generally too fine to be observed under normal magnifications. Martensite and troostite are formed only when the steel has been heated sufficiently to allow the carbon to enter the space lattice of iron. Quenching of steel below the critical temperature of 720°C will not produce these constituents (Fig: 2.3) (Coghlan 1956).

Steel containing martensite and troostite is hard but brittle. Tempering can relieve this brittleness to some extent. Gentle heating of quenched steel at low temperature converts martensite to troostite. At higher temperatures (above 450°C) a new constituent, sorbite, is produced. This component is clearly visible under normal magnification. When carbon dissolves in austenite, a wrought iron object will show a core of ferrite and pearlite with cementite. Hence, according to the carbon content and temperature, pearlite or mixtures of pearlite with cementite or any other constituent may be formed in iron/steel.
Fig: 2.3 Equilibrium for Iron-Carbon alloys indicating various kinds of steels and transformation on quenching. (After Coghlan 1956)
A common feature of objects produced from wrought iron is the inclusion of stringers or fibres of slag. During the process of forging, these are flattened and elongated and their presence gives the metal its characteristic fibrous appearance. Sulphur and phosphorus are other clearly visible impurities. Sulphur will combine with iron to form ferrous sulphide, a brittle, yellow-brown material that gets deposited at the grain boundaries.

**Corrosion**

Corrosion is a destructive alteration of metal by electrochemical reaction with its environment. Iron objects are highly sensitive to corrosion. The presence of moisture and naturally occurring soluble salts in the soil, its degree of acidity or alkalinity, porosity (aeration) and electrical conductivity also accelerates corrosion. Rusting is the formation of hydrous ferric oxides. Appearance of orange and red components as the first products of corrosion is a characteristic feature of rusting (Plenderlith 1956). These components, which are initially mixtures of ferric and ferrous hydroxides, turn to hydrated ferric oxide on further corrosion. Varying porosity allows electric current to flow, leading often to catastrophic forms of corrosion.

One of the most common causes of heavy corrosion is often traced to the presence of a certain sulphate reducing bacteria called *Sporovibrio desulphuricus* and sheet forming bacteria called *Galliionella ferriginea* (Plenderlith 1956). The *Sporovibrio desulphuricus* reduces the surface area
of the iron from sulphates to sulphides. The most common feature of heavily corroded iron i.e., blistered structure of tubercles is formed by the action of sheet forming bacteria.

Another factor that initiates corrosion is the effect of heat treatment on the object. Carbon steels, which are quenched from high a temperature show martensite. Heating at a low temperature and subsequent cooling causes martensite to decompose to iron carbide (cementite) and low carbon ferrite. This two-phase structure sets up cells with different potentials and accelerates corrosion reaction.

It is appropriate at this point to discuss the various processes involved in the extraction of iron.

**Mining**

Mining is the process of recovering the minerals from the earth’s crust, including such minerals of organic origin as coal and petroleum. Mining covers extraction of ores containing valuable minerals, metals or other substances, which are procured from the ore by subsequent processing (Newman 1965). Modern mining is a costly and complicated business. It begins with locating probable mineral veins that can produce enough of the desired substance to justify the high cost of extraction. Present day mining methods fall into three categories; 1) placer mining, 2) open-pit mining, and 3) underground mining. The major mining operations are surface mining, shaft mining, slope mining and drift mining (Helsey 1977). Surface mining is restricted to surface outcrops. Shaft mining is done by making narrow
adits/slopes driven into the ore body. Openings of such mines are one meter in diameter in order to let just one person crawl inside with the support of ropes. Elliptical shafts are used for supporting the roof.

Ore dressing

Ore dressing is the treatment of concentrating the valuable constituents that is enriching the metal, content by mechanical or physical methods. In this process, the gangue of the ore separates to improve the physical character of the ore charged in the furnace. It begins with simple hand picking or releasing the mineral by crushing the rock or magnetically separating the ferrugenous minerals. Further cleaning of the freshly ground ore is done by agitating the same in running water, whereupon, the lighter gangue material suspended in the flowing water is carried further and separated. The denser ore material get trapped in grooves set in the floor across the flow of the water, by virtue of the difference in specific gravity of the gangue and mineral. Some ores could be smelted directly after dressing (benefication).

Roasting

Roasting chemically converts sulphides, chlorides and carbonates to oxides and drives off water of crystallisation, thereby facilitating subsequent smelting. For a majority of the ores, some preliminary treatment (roasting) is beneficial and in some cases, essential. Sometimes, roasting is carried out before crushing in order to facilitate that operation. The roasting after crushing is more advantageous as it creates greater surface area for
complete reaction. Both dressing and roasting are necessary from the chemical point of view to enhance the yield of iron. In roasting, the temperature should be moderate with oxidising conditions.

Smelting

Smelting is a pyro-chemical process for the extraction of metal or metallic compound from an ore in a state of fusion. Extracting iron from ores and preparing it for use involves the conversion of natural iron-bearing minerals into metallic iron. In the smelting process, pure iron is obtained by heating the ore using charcoal. At high temperatures and under optimum supply of oxygen, charcoal is converted to carbon monoxide that reduces iron oxide to iron. Apart from iron oxides, iron ores contain oxides of silicon, manganese and magnesium as impurities. Hence, the main criterion for smelting iron is the reduction of ore (usually hematite or limonite), with carbon monoxide.

Manufacture of Iron

The main process for production of iron is through the blast furnace. In the blast furnace, high operating temperatures enable the production of molten iron. The raw materials required for the production of iron (pig iron) in the blast furnace are iron ores, fuel and flux. Pig iron is manufactured by smelting iron ore in a blast furnace using a fuel (usually coke, which supplies heat for the operation and acts as a reducing agent), a flux (generally limestone, which combines the gangue of the ore with the ash of
the fuel to form a fusible slag) and a blast of hot air, which supplies the necessary oxygen for the combustion of the fuel.

The blast furnace plant consists of
(i) the blast furnace
(ii) appliances for sending up the ore, fuel and flux to the top of the furnace and charging them into the furnace
(iii) blowing engines for sending the blast of air
(iv) the stoves for heating the blast
(v) the water pumping plant for supplying the large quantities of water needed for cooling the furnace walls and for steam raising
(vi) the appliances for cleaning the blast furnace gas
(vii) plant for generating power from the furnace gas and
(viii) appliances for the disposal of pig iron and slag (Swarup and Rastogi 1977:).

The smelting room of a modern blast furnace comprises of a throat, stack/shaft, body, bosh and hearth. The throat is cylindrical in shape and it receives the charge and carries off the gases. The stack below it is conical in shape and tapers outward to the next lower section that facilitates the descent of the materials being smelted and the distribution of the gases throughout the furnace. Body is the widest section and it connects the stack with bosh. Bosh converges down towards the hearth. The lowest part of the hearth is cylindrical in shape. Tuyeres are inserted at the top of the hearth (Weinstein 1970:23-24).

The ore, fuel and flux are charged into the furnace from the top in the required proportions. Air is blown in near the bottom through a number of
symmetrically placed pipes called tuyeres. The air rises up through the charge and the gases formed are removed from the top. The stack, which receives the solid charge at the top gradually widens downward to allow the easy descent to the charge which expands on being heated by the rising current of hot gases (Fig: 2.4). In a short time, the hot gases pass through the furnace and heat the column of charged material to high temperatures. At the furnace throat, the temperature equals 300°C-350°C and it gradually increases at the lower levels. Highest temperature (1700°C-1750°C) is at the upper part of the hearth near the tuyeres. The carbon in the coke burns according to the reaction:

\[ \text{C} + \text{O}_2 = \text{CO}_2 \]  \hspace{1cm} (1)

The large amount of heat evolved in this reaction and the carbon dioxide produced, almost completely decomposes when it comes in contact with hot coke.

\[ \text{CO}_2 + \text{C} = 2\text{CO} \]  \hspace{1cm} (2)

Upon contact with the rising gases, the charged materials first lose their hygroscopic water content followed by their chemically combined water. The dehydrated lumps of charge become more porous. The hydrated iron oxide in hematite \((n\text{Fe}_2\text{O}_3.m\text{H}_2\text{O})\) is converted to ferric oxide \((\text{Fe}_2\text{O}_3)\).

Thermal decomposition of the carbonates in the flux and in certain kinds of iron ores (siderite) occurs in the middle and lower sections of the stack. The temperature at the beginning and completion of this decomposition depend
Fig: 2.4 Flow diagram of Blast furnace operation.
upon the nature of the carbonates and the size of lumps, for example the decomposition of limestone to form lime, according to the reaction:

\[ \text{CaCO}_3 = \text{CaO} + \text{CO}_2 \]

The decomposition of lime takes place at 900°C - 1000°C. Siderite decomposes to form magnetite by the reaction at a lower temperature (400-500°C)

\[ 3\text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO} \]

Reduction by carbon monoxide begins in the stack and proceeds in steps from Fe₂O₃, Fe₃O₄ and FeO as shown in the following reactions:

\[ 3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \]
\[ \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2 \]
\[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \]

The reaction, which produces metallic iron as the end product is called indirect reduction of iron and proceeds at moderate temperatures (500°C-900°C) with the evolution of heat.

In the presence of incandescent coke and at higher temperatures (above 1000°C-1100°C) not only does iron ore reduces to metallic iron but regeneration of carbon monoxide proceeds rapidly. The process is represented by the following reactions:
\[
\begin{align*}
\text{FeO} + \text{CO} &= \text{Fe} + \text{CO}_2 \quad \text{(8)} \\
\text{CO}_2 + \text{C} &= 2\text{CO} \quad \text{(9)}
\end{align*}
\]

The simultaneous activity of these two chemical reactions enables the formation of metallic iron and is called direct reduction. It is assumed that about 60% of iron is produced in the blast furnace by reaction (1) and rest 40% by reaction (2). Metallic iron formed in the blast furnace is initially in the solid state (spongy iron), since it has a high melting point \(1539^\circ\text{C}\). In the presence of carbon, the spongy metallic iron is gradually carburised by the reaction:

\[
3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2 \quad \text{(10)}
\]

and its melting point is lowered to \(1150^\circ\text{C} - 1200^\circ\text{C}\). The resulting carburised iron contains 1.8-2% of carbon. This carburised iron drops down on the well of the hearth. During the time of the aforesaid activity, iron absorbs additional carbon to a concentration of about 3.5-4%, that is, the usual carbon content of liquid pig iron.

The reduction of impurity elements such as manganese (Mn), silicon (Si), and phosphorus (P) from the charge take place simultaneously in the blast furnace along with the reduction and carburisation of iron. The following reaction occurs only in presence of solid carbon.

\[
\begin{align*}
\text{MnO} + \text{C} &= \text{Mn} + \text{CO} \quad \text{(11)} \\
\text{SiO}_2 + 2\text{C} &= \text{Si} + 2\text{CO} \quad \text{(12)}
\end{align*}
\]
Phosphorus present in the charge undergoes reduction in the presence of iron ore gangue (SiO₂) by solid carbon. For example, phosphorous present in the charge as phosphoric calcium salt undergoes the following reduction:

$$\text{P}_2\text{O}_5.(\text{CaO})_4 + 5\text{C} + 2\text{SiO}_2 = 2\text{P} + 2(\text{CaO})_2\text{SiO}_2 + 5\text{CO}$$

The above reaction proceeds easily in the blast furnace resulting in the passing of high amount of phosphorus into the pig iron.

Slag forms in two stages in the blast furnace. Primary slag forms approximately at the level of the furnace body or lower part of the stack on the basis of a fusible mixture of several oxides, namely, lime, silica, alumina and iron oxides. From the foregoing components, certain proportion of liquid ferrous slag is formed at 1160°C-1200°C. As it runs down into the hearth, the primary slag gets heated to higher temperatures. At this stage, its chemical composition changes as it dissolves coke ash, fluxes and the remainder of the ore gangue. The ferrous oxide that remains in the final blast furnace slag is very scanty and rich in lime, magnesium oxide and alumina. By using converters, open-hearth furnaces and electric furnaces, steel is made out of pig iron in modern steel making industry.

Pre-Industrial Iron working:

Pre-industrial iron working (that is iron smelting and forging) was prevalent as a cottage industry in the sub-continent until the beginning of the 19th century and still survives in some remote corners of the country. The Geological Survey memoirs and records, District Gazetteers and traveller's
accounts provide information regarding pre-industrial smelting. The distribution of pre-industrial smelting centres is related to the distribution of suitable ores. Various types of pre-industrial iron smelting furnaces have been reported in India. Here, an effort has been made to broadly outline the techniques of pre-industrial mining, ore dressing, and smelting practised in different parts of the sub-continent and specifically in Gujarat.

The iron ore deposits in India were available right from the surface and hence little mining was required. The pre-industrial smelters could get iron not only from large deposits but also from ferruginous laterite and quartz iron-ore deposits (Chakrabarti 1992:125). In most regions, magnetite ore was preferred over hematite wherever both were available in abundance. Low-grade ores were generally preferred over high-grade ores probably due to their softness and their easily crushable nature. The high-grade ores would require higher smelting temperature than the low-grade ones (Tripathi 1994:242).

There are regional variations in mining practices. According to Holland (1892) the mining in Salem (Tamil Nadu) “was even more wasteful than smelting”. The mining was never more than three feet deep. Even pieces of pure magnetite were rejected on account of their greater hardness and compactness. The primitive miners of Salem selected only well disintegrated and weathered pieces of quartz-magnetite schist. Elwin (1942) and Joshi (1970) have described the mining practices by iron smelting tribes (Agarias) in Chottanagpur Plateau and in parts of Orissa. Joshi has reported that Agarias carried the ore in specially made baskets locally called 

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pieces and packed them into the *dadu* or *tukna*. Digging was carried to a depth of six to seven feet.

The practices of *ore dressing* in different parts of the sub-continent were more or less the same irrespective of the type of ore (Holland 1892, Joshi 1970). The first step in ore dressing was *hand picking* of the ore that took place at the mining area itself, which was then broken into smaller fragments by *crushing* with a flat hammer. The crushed material was accumulated and *winnowing* it against a strong wind. In parts of south India, the ore was further enriched through density separation by washing of finer particles of quartz in the river. The Agarias *roasted* (Fig: 2.5) the ore in an ordinary fire of wood and bark.

The technique of *smelting* varied greatly from area to area, although the basic principle remained the same. Variations can be observed in size and shape of the furnace, types of tuyeres and bellows, slag disposal techniques and metal refining technology. The provision for draining away slag stands as the criteria for classifying the furnaces. Each tribe had its own distinct working and furnace design, though the basic principle remains the same. Percy (1864: 254-270) explains three basic types of iron smelting furnaces. The first is circular in form, 2-4 feet high and made of tempered clay. There are two openings at the bottom- one for removing the cinder and sponge iron and the other for inserting tuyeres. The second type of furnace was a cavity made of clay, in a bank two and a half feet deep. At the bottom were two openings facing each other through one of which the tuyeres were inserted. The third type of furnace was again a cavity scooped out in the side of a clay mound.
Fig: 2.5 Pre-Industrial Roasting
(After Agricola 1955)
McWilliam (1920) records slag tapping furnaces at Mirjati in Chottanagpur area where a simple tuyer was provided on one side for tapping the slag. Cleere (1963) refers to three types of furnaces viz., Kamar Joda, Chingle Becha and Jiragora furnaces. The Jiragora type is the most common and was used by Agarias (Fig: 2.6). In Jiragora type (Fig: 2.7), the shaft was tapering towards the top and had three openings. One opening was at the top and the rest at the bottom. The top opening was used for feeding ore and charcoal. Often, a machan (a bamboo platform), resting on poles and plastered with clay was erected, level with the top of the furnace. The smaller and longer openings at the bottom were respectively for maintaining the blast and retrieving the bloom and slag.

Kamar Joda and Chingle Becha both are more primitive than the general type of primitive iron-smelting furnaces described by Percy and others in Indian context (Ghosh 1964). At Kamar Joda, the temperature did not exceed 1100°C and there was no provision for the tapping of slag. The lump was drawn when it was hot. When cool, it was cut into pieces and reheated in a forge and shaped into objects (Fig: 2.8).

Pre-industrial furnaces were in operation during nineteenth century in Kathiawar. The principal metal was iron and smelting was done at Khambalia and Badra Districts and remains of iron smelting furnaces are still visible near Naganath (Majumdar 1965: 22). Ironsmiths of the Khambhalia town are renowned for their skill (Imperial Gazetteer 1909: 400). Iron ores of considerable richness suitable for smelting is reported from Surat, Rewa Kantha, Panchmahals, Kaira, Ahmedabad, Kathiawar and Kutch (Chakrabarti 1992:131). There are some early evidences of Iron smelting in Kutch area earlier than pre-industrial times, but later it seems to
Fig: 2.6 Agaria Iron Smelters of Central India.  
(After U. Ball 1880)
Fig: 2.7 Agaria Jiragora Furnace
(After Tripathi 1994)
Fig: 2.8 Kamarjoda and Chinglebeche pre-Industrial Furnaces
(After Tripathi 1994)
have become extinct, as during pre-industrial times, these mines remained unworked (Imperial Gazetteer 1909: 333). Traces of old, unused iron-smelting areas are found in Godhra, Palanpur and Shivrajpur. Iron mines were worked near the town of Kapadavanj in Early Historic times. Lateritic ores as ferric oxide or in other forms seemed to have been used as they are available throughout the northern portion of peninsular Gujarat. Iron exists at Valsad and early heaps of slag have been reported from Padri area of Surat. After the impact of foreign iron, native industry came into disuse (Majumdar 1965).

Jacob (1843: 98-104) in his report to the Royal Asiatic society opined that iron ore was chiefly found in the north-western part of peninsular Gujarat. According to him, there were six "foundries" running at a time "during the fair season" in this region. He visited two of these - Ranawao in Rana's Taluka and Ranpur in Porbandar State. The location of iron smelting at these places was determined by their proximity to Barda hills where both charcoal and ore were easily available.

Jacob further describes long and narrow furnaces covered by masonry and lined with clay to maintain the temperature for smelting in the furnaces. Out of the two openings on either sides of the furnace, one was meant for working of the bellows and the other for the removal of the slag. Charcoal and coal were fed alternately. Bellows made of bullock skin sewn round bamboo hoops in vertical rings were used for supplying air. He recorded that two smelting operations were conducted per day and the output was 40% of the ore. The lump from the furnace was heated in a forge and broken into pieces that were made into small bars for the market. According to him, two varieties of iron were produced - *chontia* (inferior variety -
produced from inferior ore) and *marka* (a better variety). Jacob records six foundries constantly working throughout the fair season and other three working occasionally.

The furnace in Kathiawar peninsula was based on an entirely different concept that appears to have been developed and perfected locally without any external influence (Watt 1890). The furnace used here was rectangular in cross-section and horizontal in layout. This furnace resembles the reverberatory furnace known in pre-industrial Europe and runs on a similar principle. The essential feature of this furnace is that the flame produced by the blast through inclined tuyeres is applied on the ore, which was kept in a separate chamber.

With this understanding of modern as well as pre-industrial iron production the next chapter outlines the methods used to study the iron objects recovered from some excavated Early Historic sites in Gujarat.