

On the description of ancient iron making process at Naikund, Vidarbha Region of India: a thermochemical analysis of megalithic iron smelting

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Abstract: This paper presents a systematic approach to demonstrate ancient iron making practice at one of the earliest iron-smelting sites in India, Naikund, Vidarbha region of India, as far back as 900 *BC*. During the process, maximum temperature attained in the Naikund furnace is estimated to be $\sim 1150\text{ }^{\circ}\text{C}$ to $1250\text{ }^{\circ}\text{C}$ in the reaction zones where solid state reduction of iron followed by separation of the low melting slag phase and metallic iron is predominant. It is observed that the low melting point of the slag phase is possibly by addition of sand or silica and lime stone in the furnace during the iron making process. Furthermore, mass balance studies performed using Rist diagram superimposed with $Fe - C - O$ stability diagram revealed that the minimum charcoal rate was about 1900 kg/ton of iron produced. It can be anticipated that the porous semi-solid metallic iron is hammered to produce the various objects that are used for hunting and agricultural purposes. Our first of its kind approach *via* thermochemical analysis on one of the earliest iron-smelting sites in India, a Naikund furnace, let us produce the evidence of ancient iron making processes in India that

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further open up multitudes of possibilities to investigate the ancient metallurgical structures in India.

Key words: Megalithic Iron smelting, Naikund furnace, Thermo-chemistry, Steel making in ancient India

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1. Introduction

It is believed that the production and use of ferrous products in the Indian subcontinent has a history of palaeolithic age (i.e., 2nd millennium BC). The archaeological excavations conducted at Naikund, one of the earliest iron-smelting megalithic sites, 42 km north-east of Nagpur, Maharashtra, India (Latitude 21.36, Longitude 79.19) (also shown in Google Map in Annexure 1) have shown valuable evidence of iron smelting furnace complete with tuyere, indicating that the origin of ferrous metallurgy is a product of indigenous development and simultaneous beginning of Iron Age at more than one center in the Indian subcontinent [1-4]. This important discovery of the Naikund site led the archaeologists and metallurgists to estimate that this is the only ancient iron-smelting site in India, which is further reflected in all the essential features of the iron smelting technology. Our previous observations [5-7] on metallographic investigations of the wrought iron samples from Mahurjhari, Naikund, Bhagimohari, Khaiwada in the Vidarbha region revealed that the iron objects obtained from these sites must have undergone identical thermomechanical treatments, further indicating the evidence for ancient steel making and hardening treatment around 900 BC. To the best of our knowledge, despite the above studies, the underlying mechanisms (or technology) of steel making process via smelting of iron ores are not understood in great detail. As the slag phase formation during the iron-smelting process is prevalent, it would be interesting to estimate the temperatures corresponding to the slag phase formation process along with reactions corresponding to the temperatures and mass balance.

Keeping this in view, we performed thermochemical investigations and a detailed analysis on slag phase formation during the iron-smelting process in the Megalithic furnace at Naikund. A model of Naikund furnace at Deccan College, Pune (MS) India and its schematic

drawing is shown in Fig. 1 [4]. The supply of air is controlled via clay tubes known as tuyeres with the help of bellows.

2. Experimental Analysis

2.1. Thermochemical Analysis

The thermo-chemical process in iron making comprises a counter current reaction with a downward supply of solid raw material flow from the top flow of gas in a counter direction (i.e., from bottom to top). The process also involves partial melting and separation of the impurities such as silica, limestone or calcium oxide and trace amounts of other oxides. The important reactions of the process are highlighted in Table 1.

2.2. Combustion of charcoal

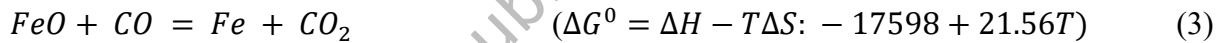
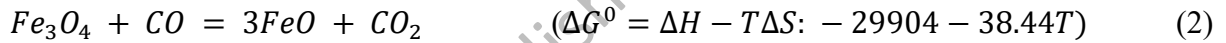
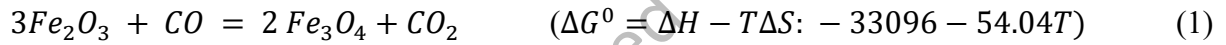
The combustion process of charcoal to form CO and CO_2 , as shown by reaction (1) and (2) in Table 1 takes place in the tuyere zone at the bottom of the furnace. The main reducing agent in the reaction is CO which is formed by the partial oxidation of carbon, while the complete oxidation of CO_2 is expected to provide high thermal energy possibly due to the high exothermic reaction.

Being a reducing gas, CO removes oxygen (O) from iron oxide (Fe_2O_3) present in the iron ore, thus sets free pure iron (Fe), however, CO_2 , being inert during the process, does not react with (Fe_2O_3). The complete conversion of carbon (C) into CO_2 is possible due to the excess supply of oxygen (O). Therefore, it is of vital importance that a sub-stoichiometric and optimum supply of O and charcoal be maintained in the furnace so that charcoal is partially oxidized to CO . However, caveat here is that charcoal or C combustion

provides both reducing gas and heat energy for the process, and the heat produced by CO_2 formation is much higher than the heat produced by CO formation (see the enthalpy difference in the reactions below). Therefore, the formation of CO_2 is essential so as to attain the required temperature for the melting or partial melting of slag phase though the estimation of quantity of required CO_2 (a stoichiometric proportion) is a timely topic and beyond the scope of the present study.

2.3. Reduction of iron ore

The reduction of iron ore by CO is a step-by-step procedure that starts with conversion of hematite (Fe_2O_3) to magnetite (Fe_3O_4) followed by transformation of wustite (FeO) to metallic iron. The above procedure is presented in the below reactions 1 – 3.



It can be also evinced that the reduction of most of the Fe_2O_3 and Fe_3O_4 takes place in the temperature range 500 – 600 °C, following to which the reduction of FeO commences in the temperature range of 900 – 1000 °C where the high concentration of CO is prevalent (see the gray band/zone in Fig. 2). This eventually results in the establishment of dynamic equilibrium between FeO reduction and CO consumption followed by Boudouard reaction, which is endothermic in nature, as presented below. At this stage, most of the iron oxides get reduced to metallic iron, and formation of the slag phase is evident in the tuyere region. The various stages of reduction process and thermodynamic conditions can be evinced from the $Fe - C - O$ stability diagram shown in Fig. 2, which further suggests that the concentration of CO

required for the reduction of different ores. For ex., the concentration of CO required for the reduction of Fe_2O_3 is less than 10%, while it is 20 – 30% for Fe_3O_4 and 70% for FeO .

2.4. Formation of slag phase

The formation of slag phase during the process takes place simultaneously with FeO reduction in high temperature combustion zone (i.e., in tuyeres zone), where the part of unreduced FeO is expected to react with the impurities present in the iron ore and charcoal to form the slag phase. It is believed that during ancient smelting processes, the temperature did not reach the pre-defined melting point of iron (1537 °C), and the final product in the furnace is expected to be a semi-solid, which is the mixture of metallic iron and slag phase. This semi-solid mixture of metallic iron and slag phase is difficult to separate, and therefore, sand or silica is often added purposefully to separate metallic iron from slag phase, and subsequently to form the fayalite phase ($FeSiO_2$), which has a melting point of about 1200 °C, as shown in the phase diagram in Fig. 3 [8]. The formation of fayalite is evident from the analysis of entrapped slag found in the archeological samples of iron objects found in this region [9]. Melting point of the slag phase can decrease further due to the presence of limestone or calcium oxide to form the Kirschsteinite ($CaFeSiO_4$) phase. The $CaFeSiO_4$ is then expected to react with $FeSiO_2$ to form complex slag system known as $Ca - Fe$ Olivines having a melting point around 1130 – 1150 °C, as shown in Fig. 4 [10]. Some of the main sources of calcium oxide in the slag phase are impurities in iron ore, charcoal, or added as a flux such as sand and limestone. The iron ore found in this region contains high phosphorus, that further remains untreated in the metallic iron phase. However, the iron artifacts found in this region showed a wide range of variation in phosphorus content from 570 – 2300 ppm [9-11], indicating that some amount of phosphorus removal had taken place in many of the ancient iron samples during smelting

process. Therefore, it can be construed from the above observations that the produced slag had high phosphorus capacity and calcium oxide yielding $Ca - Fe$ Olivine slag that has low melting point. The slag melting or softening temperatures are very important for the iron making process, since it acts as a thermal reserve zone, and limits the maximum temperature of the process. This indeed (i.e., lower slag melting temperature) makes the process more fuel efficient, with better productivity and quality of the iron produced. Therefore, the complex slags such as $FeSiO_2$ or $Ca - Fe$ Olivine begin to liquefy and subsequently flow downward leaving behind the spongy iron. This product (spongy iron) is known as iron bloom. As this bloom iron is a product of solid state reduction at low temperature, it has small amount of impurities. These iron blooms are further heated to red-hot temperature, and skillfully hammered to obtain desired shapes (i.e., ancient weapons).

3. Thermal energy and mass balance

3.1. Thermal energy balance

The combustion of charcoal takes place in the tuyere zone or combustion zone, that has the highest temperature in the furnace. This temperature can be estimated by Adiabatic Flame Temperature (AFT) considering no heat loss to the surroundings [12]. The estimation of AFT does not consider the heat losses through the refractory wall and various endothermic reactions such as decomposition of lime stone, solution loss reaction, and latent heat of melting, therefore AFT indicates the maximum temperature attained in the combustion zone of the furnace.

The metallic phase formed by reduction separates out from the oxide phase or slag phase that do not have a fixed melting point, however it does have a definite temperature range for melting (i.e., between softening or melting temperature to complete melting temperature).

Since slag melting involves significant amount of heat absorption due to latent heat of melting, without much increase in temperature, it acts like a thermal reserve zone in the furnace, such that the temperature in the combustion zone of the furnace is limited to a temperature slightly above the melting start or softening temperature of the slag.

3.2. Estimation of adiabatic flame Temperature (AFT) in the furnace

To describe the process, and evaluate the heat and mass balance calculations, several reactions are combined together, and the amount of nitrogen coming with oxygen during air blow is also considered. The combustion of charcoal in the furnace can produce both CO_2 and CO . At high temperatures above $1000\text{ }^{\circ}\text{C}$, almost 100% CO is produced as shown in Fig. 2. High temperature gas formed due to combustion of charcoal can supply both heat energy to preheat the ore and reduction of iron oxides. Material and heat balance for combustion and reduction of iron ore are given below:

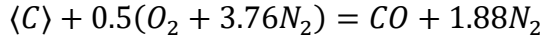
Thermochemical data;

- Considering no preheating, the initial gas temperature is $25\text{ }^{\circ}\text{C}$ or 298 K .
- AFT is indicated by T_f ($^{\circ}\text{C}$)
- Thermochemical data [13], for specific heat in $\text{J/mol} \cdot \text{K}$ are as follows:

$$C_{pCO} = 28.41 + 4.10 \times 10^{-3}T; \quad C_{pCO_2} = 44.14 + 9.04 \times 10^{-3}T;$$

$$C_{pN_2} = 27.87 + 4.18 \times 10^{-3}T; \quad C_{Fe} = 24.48 + 8.45 \times 10^{-3}T$$

We can calculate the T_f from the thermodynamic data taking into account change in enthalpy (ΔH) due to the overall reaction, and specific heat (C_p) values of the product, where oxygen along with inert gas nitrogen in air have to be considered for heat balance. For the partial combustion of charcoal to CO we get;

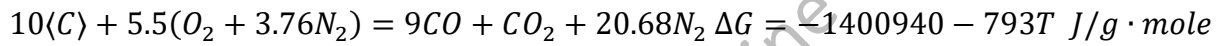


$$\Delta G = -111700 - 88T \text{ J/g} \cdot \text{mole}$$

From the heat balance, we can calculate the T_f , by solving eqn. (5) given below:

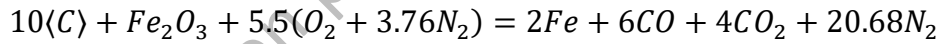
$$-\Delta H = 111700 = \int_{298}^{T_f} (C_{pCO} + 1.88C_{pN_2})dT$$

From the calculation of T_f from the above equation we get $T_f = 1244^\circ\text{C}$, which may not be sufficient for providing the extra heat energy for melting the slag phase. Therefore, we can consider some amount of CO_2 formation, which is more exothermic to provide the extra heat. Considering 90% CO and 10% CO_2 formation, and by combining the equations for CO and CO_2 formation to get;



This gives a much higher T_f around 1415°C . Therefore, the calculation shows that some amount of CO_2 formation is essential to provide the required thermal energy for the process.

Finally, we can combine the reactions of combustion of charcoal to 90% CO and 10% CO_2 gas to reduce the iron ore from haematite to metallic iron, as shown in reaction 6.



$$\Delta G = -1510940 - 795T \text{ J/g} \cdot \text{mole}$$

The combined reaction of charcoal combustion and reduction of iron oxide let us estimate the T_f around 1345°C . Since this temperature is lower than the melting temperature of iron, the product will be solid state iron, which is porous due to the removal of oxygen and other impurities such as slag and can be designated as sponge iron. The slag is anticipated to be in a semi-solid state due to the formation of the low melting slag phase such as FeO , or complex Olivine. The T_f only indicates the maximum temperature, that can be attained when there is no heat loss, however, in actual case such as the Naikund furnace, once the slag melting or

softening temperature is reached, heat absorption occurs due to the latent heat of melting, thereby restricting the temperature to slightly above the slag melting or softening temperature. Here we have considered 10% CO_2 formation, however with an increase in the amount of CO_2 , T_f will also increase, which further indicates the high amount of melting of slag. The thermal profile inside the furnace involving the high temperature tuyere zone or combustion zone is schematically shown in Fig. 5.

3.3. Mass balance

Mass balance for reducing one gram mole of iron is given by the Rist diagram [9] illustrated in Fig. 6, over which $Fe - C - O$ phase stability diagram is superimposed, thus to analyze the process methodically. The positive O/Fe in this diagram is from Fe_2O_3 reduction, while the negative O/Fe indicates the incoming oxygen atoms from the blast. The efficiency of CO utilization is limited by the chemical pinch point W for FeO reduction. According to the prevailing conditions and thermodynamics, reduction of FeO takes place when CO/CO_2 ratio is 4:1 or more (i.e., CO is above 80% in the flue gas). The O/C ratio for 80% CO gas is estimated to be 1.2, from which the charcoal rate to produce one ton of metallic iron can be estimated. The charcoal rate obtained from the Rist diagram analysis is the minimum charcoal rate under the given condition.

As the outlet gas composition of Naikund furnace is not known, we can only estimate the process by thermochemical analysis. The variation of flue gas composition in the furnace outlet is represented by the three points A , B and C in Fig. 6. Considering the middle line with outlet composition B , that further represents the standard case we have studied, we can calculate the ratio for $6CO$ and $4CO_2$ at outlet, which further suggests a ratio of O/C as 1.4 (Fig. 6). From this we can also calculate the charcoal rate, considering 70% C in charcoal

along with remaining impurities and volatile matter. This further indicates the efficiency of iron extraction process around 70% and estimated charcoal rate of about 2200 kg/ton of iron produced. For the case A, with lower O/C ratio, we can consider $6CO$ and $3CO_2$ at the outlet, which further let us estimate the O/C around 1.33, and a charcoal rate of about 2000 kg/ton of iron. For the case C, with higher O/C ratio, we further consider 50% CO at outlet (i.e., $6CO$ and $6CO_2$), which gives O/C around 1.5, and charcoal rate of about 2700 kg/ton of iron produced.

4. Concluding remarks

In summary, this work presents a systematic investigation on the thermochemical analysis of megalithic iron smelting process to investigate the ancient iron making process at Naikund, Vidarbha region of India, around 900 BC. An attempt has been made to demonstrate the understanding of ancient craftsmen and smelters about the process, their keen observations, skilled efforts and development. The important findings of the present exercise can be summarized below;

- First and foremost, combustion of charcoal provides both thermal energy and reducing gas for the process, and the $Fe - C - O$ phase stability diagram shows 80% CO or above is required for FeO reduction, however, adequate amount of CO_2 formation is also essential for the high thermal energy requirement of the process.
- The AFT for the combined reaction of charcoal combustion and reduction of Fe_2O_3 to metallic iron is estimated to be 1345 °C, where the formation of solid state porous iron (or sponge iron) can be evinced.
- Separation of the metallic iron and the slag phase is essential to produce the finished iron objects. Therefore, low melting slag phase formation is essential to easily separate the

slag and the metallic phase, which is achieved by the addition of sand and limestone to produce, thus to produce the low melting FeO and $Fe - Ca$ Olivine phase that have melting points around $1205\text{ }^{\circ}\text{C}$ and $1140\text{ }^{\circ}\text{C}$, respectively. This is evident from the entrapped slag analysis, and presence of CaO in the slag as a major step for the removal of phosphorus from the ancient iron samples.,

- The thermochemical and mass balance analysis performed from the Rist diagram .superimposed over $Fe - C - O$ phase stability diagram indicates $6CO$ and $6CO_2$ are the two outlet gasses produced during the process with high O/C ratio (i.e., 1.5%), that further produces $2\text{ g} \cdot \text{mol}$ of metallic iron at a charcoal rate of 2700 kg/ton of iron, demonstrating the 70% efficiency of metallic iron production process.
- In the same vein, charcoal rate can vary based on different process parameters. For ex., for lower O/C ratio (1.33%), where $6CO$ and $3CO_2$ yields the charcoal rate 2000 kg/ton of iron.

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List of Figures

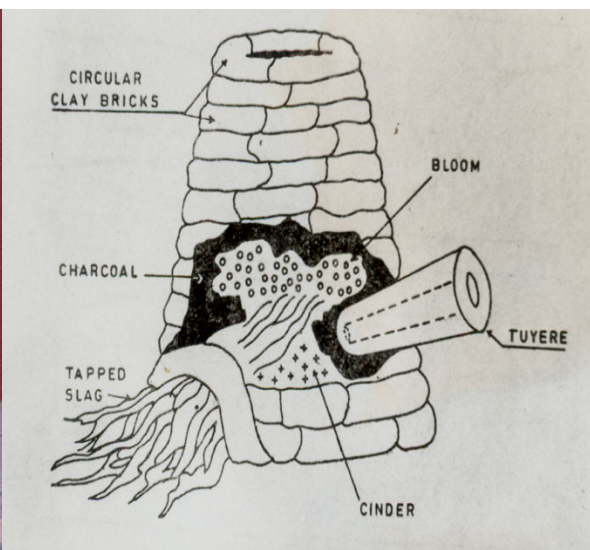


Figure 1: Model of Naikund furnace at Deccan College, Pune (MS) INDIA and its schematic drawing [Adopted from Gogte, Department of Archaeology and Museums, Government of Maharashtra and Deccan College, Pune, 1982, 52 – 59 [4]].

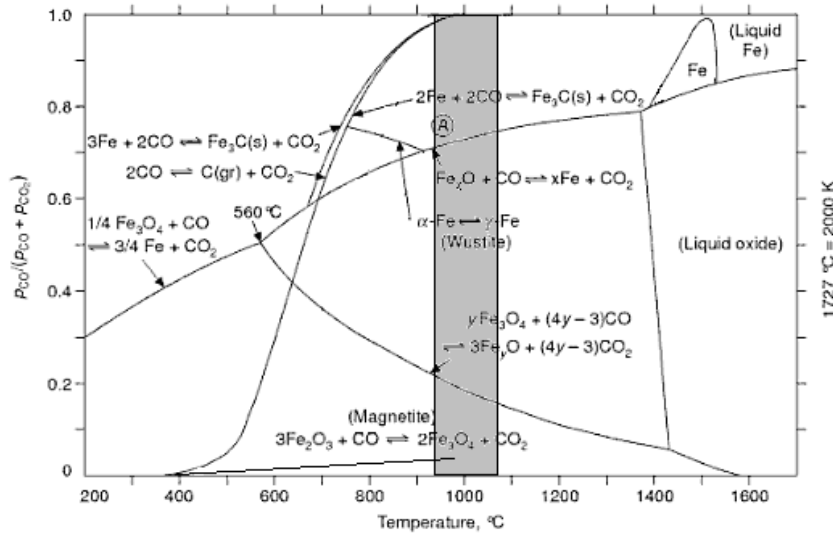


Figure 2: *Fe – O – C* equilibrium diagram showing the optimum conditions for the furnace operation.

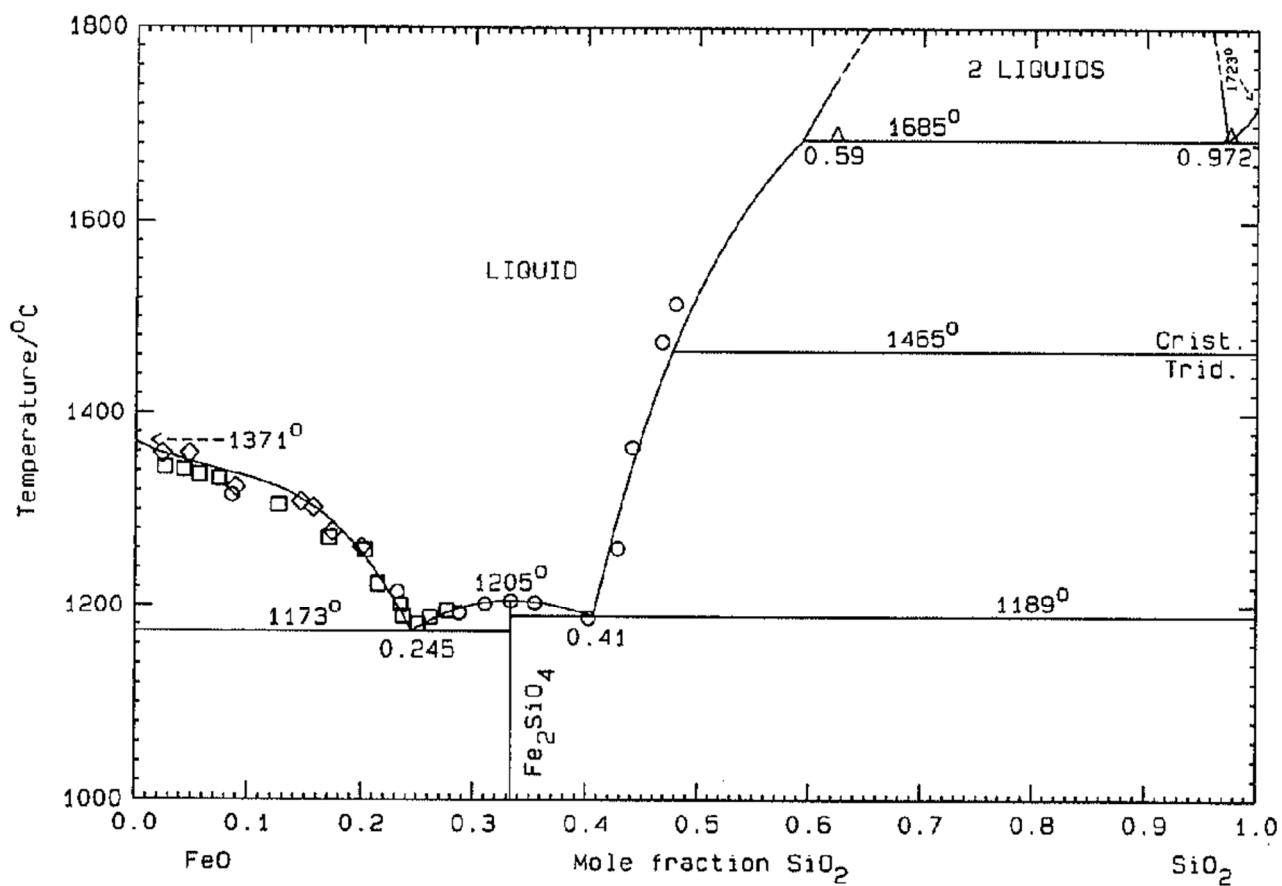


Figure 3: The $FeO - SiO_2$ phase diagram showing low melting fayalite (Fe_2SiO_4) phase formation [Adopted from Mukhopadhyay and Lindsley, American Mineralogist, 68 (1984) 1089-1094 [8]].

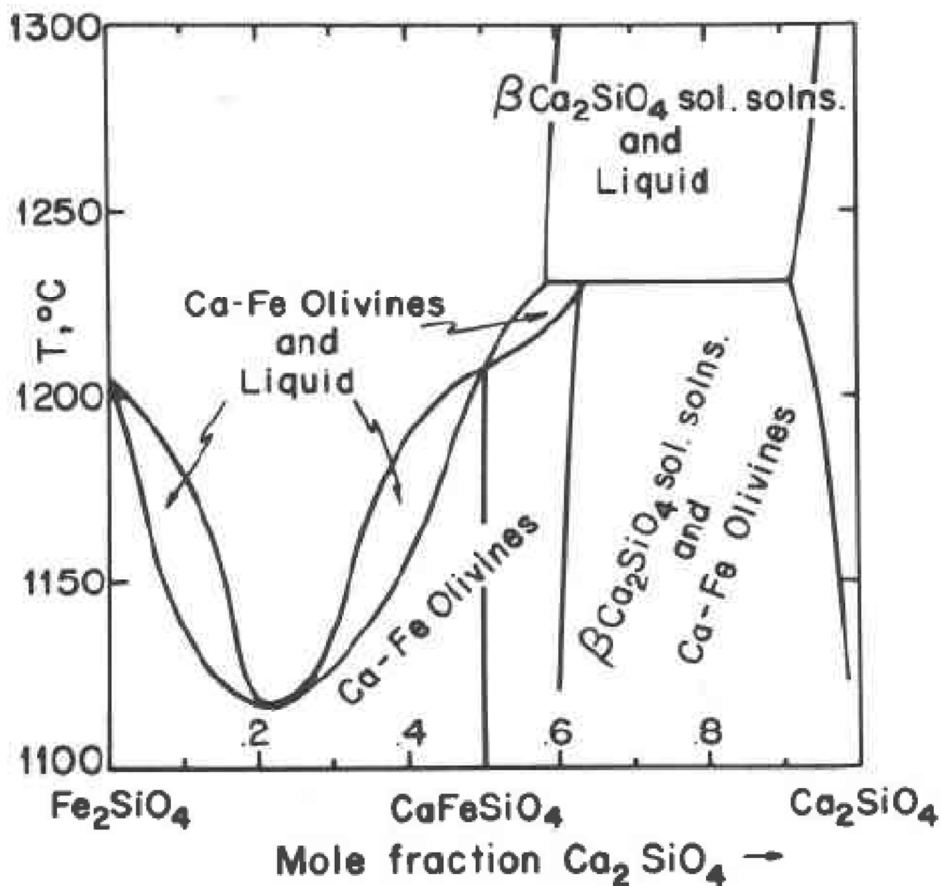


Figure 4: The $\text{CaSiO}_4 - \text{FeSiO}_4$ system showing the formation of low melting $\text{Ca} - \text{Fe}$ Olivines [Adopted from Ping et al., ISIJ International, 33 (1993) 26-35 [10]].

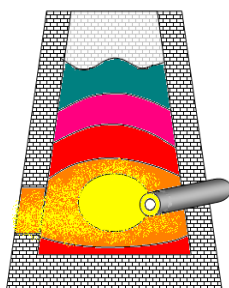


Figure 5: Schematic representing the various temperature zones in the Naikund furnace [Adopted from Gogte, Department of Archaeology and Museums, Government of Maharashtra and Deccan College, Pune, 1982, 52 – 59 [4]].