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ON THE ORIGIN OF HIGH PHOSPHORUS CONTENTS IN ANCIENT INDIAN IRON

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Abstract: The excellent corrosion resistance of ancient Indian iron has been attributed to the relatively high phosphorus contents in ancient Indian iron. The possible reason for this high phosphorus content has been explored by analyzing dephosphorization process. The equilibrium distribution of phosphorus between metal and slag phase has been evaluated in ancient and modern irons utilizing thermodynamic and empirical models. Oxygen and phosphorus contents in the metal increased with temperature. At all temperatures, the oxygen and phosphorus contents in ancient Indian iron were higher than in modern iron. The analysis confirmed that the origin of relatively high phosphorus contents in ancient iron is due to the type of slag used in iron extraction (i.e. absence of significant amount of CaO in slag).

Keywords: Ancient Indian iron, phosphorus content, thermodynamics, slag.

1. INTRODUCTION

Ancient and mediaeval Indian iron artifacts are known for their relatively good corrosion resistance. Notable examples are the Delhi iron pillar¹, Dhar iron pillar, iron beams in the Surya temple at Konark, iron pillar at the Mookambika Temple at Kollur, Damascus swords, etc. The good corrosion resistance of the Indian iron artifacts, in general, and Delhi iron pillar, in particular, is due to the unusually high amount of phosphorus present in the samples²⁻⁴. Phosphorus in the metal aids the catalytic formation of a protective amorphous δ -FeOOH layer and/or a protective phosphate layer next to the metal-scale interface^{3,4}. Modern steels do not generally contain more than 0.05% phosphorus because of the problem of intergranular embrittlement (termed as cold shortness) and therefore, the removal of phosphorus from iron is an important industrial concern in modern iron and steel making. Iron, extracted using ancient bloomery furnaces, was the basic raw material utilized for the manufacture of the Delhi iron pillar^{5,6}, in particular, and large iron objects, in general. Therefore, the present analysis does apply to corrosion resistant iron utilized for the Delhi iron pillar. The extracted iron lumps were also used, after suitable heat treatments, for manufacturing agricultural (hoes, spades, sickles and weeding forks), household (knives, ladles, spoons, sieves, saucepans, cauldrons, bowls, dishes, saucers and tripod), building (nails, clamps, staples, sheets, door handles and spikes), tools (anvils, hammers, scissors, saws, chains and smithy tools) and war fare (swords, javelins, armor, helmets and shield bases) items⁷.

Prakash⁷ has analyzed the iron ore reduction reactions in the bloomery furnace and has concluded that conditions favorable for reduction was obtained in the temperature range of 900°C to 1100°C. However, bloomery furnace temperatures were dictated by the requirement of melting the slag. The ancient smelters added SiO₂ as a flux or used a lean siliceous ore so that fayalitic slags (Fe₂SiO₄) were generated in the bloomery furnace. As the presence of lime or alumina increased the melting point of fayalitic slags, ores containing alumina and addition of lime were avoided in the ancient iron making process. The melting point of fayalite is 1205°C while the melting point of FeO-Fe₂SiO₄ eutectic is 1177°C. Therefore, the smelting furnaces were operated at least at 1250°C to 1300°C⁷.

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The gangue material separated out as molten fayalitic slag and red hot solid sponge iron of relatively lower carbon content, was produced. The temperature profiles of traditional Indian bloomery furnaces have been experimentally measured⁸. Raceway temperatures between 1400°C to 1475°C have been measured. Lower temperatures were attained in bloomery furnaces compared to modern blast furnaces because ordinary air was blown through the tuyeres, without any preheating. In modern blast furnace technology, air is preheated to 900°C to 1200°C and temperature in raceway is 2000°C to 2000°C⁹.

The analysis will not consider carbon content in iron because of the relatively low carbon content in bloomery iron, which has been attributed to three causes. As the metal did not remain molten for a long time, pick up of carbon and Si was avoided, and steel compositions were directly obtained. Minor variations in the carbon content was adjusted by controlling the charcoal to ore ratio in the feed materials¹⁰. In the modern blast furnace, the liquid metal is saturated with C and has to be necessarily further refined. Other reasons for the low carbon contents were the high oxygen activity in the iron-rich bloomery slag, and the coating of liquid slag on the metal¹¹.

The aim of the present communication is to explicate the causes for the unusually high amounts of phosphorus in ancient Indian iron. Phosphorus contents in iron, in equilibrium with slag of known composition, will be theoretically estimated using empirical and thermodynamic methods. As limestone is a major constituent of modern blast furnace charge, the presence of lime in modern slags is invariably considered in all the empirical models. Thermodynamic models, on the other hand, provide the thermodynamic equilibrium partitioning of phosphorus between the metal and the slag, based on available thermodynamic data. It must be pointed out that these models have been developed for systems under equilibrium, whereas, in practice, iron and steel making operations occur under non-equilibrium conditions. Nevertheless, these models provide ideas about limiting and approximate compositions to be anticipated under equilibrium conditions.

The limitation of applying analyses, developed for modern iron making, must also be stated. The models presented in the following sections apply to metal and slag being in the liquid state. The traditional furnaces were operated to obtain molten slag. Iron was essentially produced by solid state reduction. However, as the ore particles descended down the traditional furnaces, evidences (dendritic microstructures characteristic of solidification) are available that suggest metal particles melt partially during their descent in front of the tuyeres⁸. The particles were in the molten state for a relatively short time due to the small extent of this region. In this regard, the contact between the iron and slag particles have to be also understood¹¹. The ore particles reached the high temperature region of furnace before they were completely reduced. Silica from the ore/ash reacted with remaining iron oxide and formed the slag. The slag contained relatively higher FeO because complete reduction was not achieved. This liquid slag coated the metal, preventing further metalloid pickup. Excess slag ran down the charcoal bed to the hearth, till it reached the lower temperature region and then solidified. This solidified slag formed a crucible on which the reduced iron particles settled down, and sintered slowly into a highly porous mass, called the bloom. The interstices of the iron blooms were filled with slag and some charcoal pieces.

2. DATA UTILIZED

Slag compositions in ancient and modern iron making processes are required in order to estimate the equilibrium distribution of P between the slag and the metal phases by empirical and thermodynamic methods. Elvin has reported, in detail, the iron-making

process employed by the Agarias, a group of tribal people of Madhya Pradesh, who were primarily involved in iron making by heredity¹². The Agarias smelted iron by the traditional bloomery process that was extant in ancient India¹². This process has been described in great detail based on modern-day observations at a few places in Bihar and Madhya Pradesh^{7,8}. This is also supplemented by other observations in the past two centuries¹³⁻¹⁹.

A brief review of the traditional process is provided. Locally available ore was generally used. Elwin¹² reported that low grade ores were preferred by Agarias even when rich ore was found in the vicinity. This was governed by the nature of the smelting process (i.e. need to generate molten fayalitic slags), as described earlier. The ore was beneficiated by gravity separation with water, using a sloping pan made in the bank of river. The black ore particles were left behind while the light silicious matter was washed away. They were then dried in the sun. The charcoal, that was used for reduction, was also prepared with special care. The preferred woods for making charcoal were hard woods like teak and sal. The bloomery furnace was essentially a shaft furnace. Several different types have been reported in the literature^{7,8,13-19}. For example, three different types have been classified by Percy¹⁷: (a) circular section with conical shaft (250 mm to 350 mm in diameter at base tapering to 100-200 mm at top, 600 mm to 1200 mm high) with separate openings for slag and metal. The blast from the pair of bellows was directly introduced into the furnace by tuyeres. (b) cavity made in bank of clay of cylindrical shape (375-400 mm dia and 750 mm tall). Slag was tapped from the opening at the bottom while metal was extracted from the top of the furnace. A row of such furnaces could be made in one bank of clay. (c) cavity scooped in the side of a clay mound (450 mm x 450 mm square section but sometimes rectangular with height 1800 to 2100 mm). The front wall, about 150 mm thick, was removed and replaced as desired. Slag was tapped periodically from the perforations in the base plate. When the iron rose to the height of the tuyeres at the end of 12-16 hours, the base plate was removed and the lump of iron weighting 70-90 kgs removed. The furnace used by the Agarias was a squat structure, 600 mm above the ground level and 270 mm below the ground, with a shaft diameter of about 300 mm. An inclined platform was also provided for piling up of charge which the bellow operator raked into the mouth of the furnace⁸. Before the first smelting operation, the furnace was dried thoroughly and the cracks in the furnace wall were repaired. The tuyeres were positioned in the bottom and the slag holes created in the temporary wall. The furnace was either partly or completely filled with charcoal and lighted by introducing burning cinder through tuyeres. Air was blown by operating the bellows. The first charge of ore was made as the charcoal burned. Charcoal and ore were alternatively charged periodically. The ratio of ore to charcoal varied between 1: 1 to 1: 1.5. The collection of slag was checked by probing with a wooden stick through the tuyeres. After the third or fourth charge the slag hole was pierced open and the slag was tapped. The hole was then sealed with charcoal, ash or sand. Slag was tapped periodically after every charge. Between 8 and 15 charges of ore and charcoal were made in one cycle. Each cycle took between 3 to 6 hours. After the last charge, the burden was allowed to descend to half the furnace height before the blowing was stopped. The temporary wall was broken and the iron bloom was pulled out with tongs. It was then hammered gently with a hammer to squeeze out the slag entrapped between iron particles. If the bloom was large, it was sheared with an axe. This bloom was further processed by blacksmiths.

Elwin has provided the slag composition from one such Agaria furnace and interestingly he has also provided the chemical analyses of the iron extracted from the same furnace¹². Similar slag compositions have also been reported by Turner¹⁸. The slag composition reported by Elwin will be used as the model ancient Indian slag composition (Table I). The

Table I. Typical composition (wt.%) of an ancient and a modern iron making slag

Slag component	Ancient slag	Modern slag
Silicon dioxide (SiO ₂)	18.00	16.00
Wustite (FeO)	53.40	20.00
Haematite (Fe ₂ O ₃)	10.01	00.00
Manganese dioxide (MnO)	09.75	05.00
Magnesium oxide (MgO)	02.01	04.00
Alumina (Al ₂ O ₃)	09.02	00.00
Carbon (C)	00.28	00.00
Titanium dioxide (TiO ₂)	00.30	00.00
Calcium oxide (CaO)	00.40	52.00
Phosphorus pentaoxide (P ₂ O ₅)	00.45	03.00

slag composition does not add to 100% and this was accounted for while estimating the mole fractions from the weight fractions. In the same table, a representative modern blast furnace slag composition has also been provided. Elwin also reported that the composition of iron extracted from the Agaria furnace after smelting was 0.780 C, 0.025 Si, 0.140 P, 0.100 Mn and traces of S.

3. THERMODYNAMIC MODELS

Different thermodynamic models of partitioning of phosphorus between the metal and slag differ in their

assumptions regarding the nature of slag. The modern theories have, in general, been characterized as ionic or molecular. The molecular theory assumes that the acidic and basic components of the slag are associated in the form of molecules²⁰. As lime is quantitatively the most preponderant component of modern slags, the molecular theory assumes the association of lime (CaO) with the acidic components. Models based on ionic theory to determine the phosphorus contents will be highlighted because thermodynamic data to apply molecular theory for fayalitic slags were not available.

The ionic theories of slag assume that the oxides completely dissociate in the slag solution. Earlier models based on the ionic theory, like Temkin's model, assumed that the slag solution completely dissociates into non-interacting ions of same charge that were distributed in a completely random manner²⁰. Later models, like Flood's model, considered equilibrium between elements dissolved in metal phase and their ions in the slag, assuming ideal behavior in slag and non-ideal behavior in metal. The interactions between the different cations present in the slag, which were assumed to be distributed in a matrix of oxygen anion, have been considered in later modifications of the ionic theory of slags²¹.

Phosphorus in the liquid metal phase in equilibrium with P₂O₅ in the slag phase can be represented by the following equilibrium reaction:



The equilibrium constant (K_p or K_1) and the standard free energy change (ΔG^0) for the above reaction are given by the following expressions^{20,21}

$$K_p = K_1 = \frac{a_{P_2O_5}}{a_{P(m)}^2 * a_{O(m)}^5} \quad (2)$$

$$\Delta G_1^0 = -RT \ln K_p = -705420 + 557.472T \quad (\text{Joules}) \quad (3)$$

where T is the temperature in degree Kelvin. Henceforth, the subscript in the free energy indicates the equation to which it is applicable. The activity of P₂O₅ can be further expressed as:

$$a_{P_2O_5} = \gamma_{P_2O_5} * X_{P_2O_5} \quad (4)$$

where, $X_{P_2O_5}$ is the mole fraction of P_2O_5 and $\gamma_{P_2O_5}$ is the activity coefficient of P_2O_5 in the multicomponent slag in equilibrium with metal. It can be noted that, in order for dephosphorization to proceed, $a_{P_2O_5}$ should be low (i.e. the acidic P_2O_5 has to be neutralized by some basic component in the slag).

In order to estimate the phosphorus content in metal utilizing equation 2, the oxygen content in the metal and the activity coefficient of P_2O_5 must be available. The methods to obtain oxygen contents would be presented first, followed by the estimation of P contents.

3.1 Oxygen content in metal

The estimation of oxygen content in the iron is related to the equilibrium between oxygen in metal solution and oxygen in slag solution. At any temperature, there is a limit to the amount of oxygen that can dissolve in iron. The maximum amount of oxygen that can dissolve in a metal under equilibrium conditions is determined by the solubility limit estimated from empirical studies²²⁻²⁴. Nevertheless, in practice, equilibrium conditions are almost impossible to achieve and iron and steel making processes normally occur under non-equilibrium conditions. Therefore, the amount of oxygen present in dissolved state in the metal is always less than the saturation value, which is attained only under equilibrium conditions. The amount of oxygen dissolved under non-equilibrium conditions can be correlated to that under equilibrium conditions using thermodynamic relations. The amount of oxygen dissolved in metal is governed primarily by the following reaction²²⁻²⁴



The equilibrium constant for the above reaction is given by the following expression:

$$K_5 = \frac{a_{Fe(l)} \cdot a_{O(m)}}{a_{FeO(s)}} \quad (6)$$

where $a_{Fe(l)}$ is the activity of liquid iron in metal phase, $a_{O(m)}$ is the activity of oxygen in metal phase and $a_{FeO(s)}$ is the activity of FeO in a slag in equilibrium with liquid metal.

When liquid iron is saturated with oxygen, $a_{FeO(s)} = 1$. Assuming that the metal solution obeys Henry's Law ($a_{O(m)} = [O]$), the above equation modifies to

$$K_5 = [O]_{sat} \quad (7)$$

where $[O]_{sat}$ is the oxygen content of the metal under equilibrium conditions. Under conditions of nonsaturation, the equilibrium constant is given by:

$$K_5 = \frac{[O]}{a_{FeO(s)}} \quad (8)$$

where $[O]$ is the oxygen content of the metal under non-equilibrium conditions. Therefore, combining equations 7 and 8, the oxygen content of the liquid iron at a given temperature under condition other than saturation is related to the oxygen content at saturation by

$$[O]_{sat} = \frac{[O]}{a_{FeO(s)}} \quad (9)$$

The oxygen content of liquid iron at saturation as a function of temperature (1803K to 2233 K²⁴) is given by

$$\log[\%O]_{sat} = -\frac{6380}{T} + 2.765 \quad (10)$$

Therefore, the equilibrium solubility of oxygen in metal in equilibrium with slag of known FeO content can be expressed as:

$$\log[O] = \log a_{FeO} - \frac{6380}{T} + 2.765 \quad (11)$$

The above expression has been obtained utilizing the empirical co-relation of saturation oxygen solubility in iron with temperature²⁴. Alternatively, the oxygen content can be determined theoretically from the known free energy change as a function of temperature (1540K to 2000K²¹) for the oxygen partitioning reaction (i.e. equation 5) and this is given by

$$\ln[O] = \ln a_{FeO} - \frac{15407.7459}{T} + 6.9749 \quad (12)$$

In order to estimate the oxygen content by the above two equations, a_{FeO} is required. This can be obtained from the regular solution model²¹. The activity of FeO present in slag solution in equilibrium with the metal is

$$a_{FeO} = X_{FeO} * \gamma_{FeO} \quad (13)$$

where X_{FeO} is the mole fraction of FeO in slag and γ_{FeO} is the activity coefficient of FeO in the slag. The activity coefficient of the FeO, in a multi-component slag, in equilibrium with metal (1540K to 2000K²¹) is

$$\begin{aligned} RT \ln \gamma_{FeO} = & -18600 X_{FeO_{1.5}}^2 + 7110 X_{MnO}^2 - 41480 X_{SiO_2}^2 + 33470 X_{MgO}^2 - 31380 X_{CaO}^2 \\ & + 44930 X_{FeO_{1.5}} X_{MnO} - 93140 X_{FeO_{1.5}} X_{SiO_2} + 17740 X_{FeO_{1.5}} X_{MgO} \\ & + 45770 X_{FeO_{1.5}} X_{CaO} + 40580 X_{MnO} X_{SiO_2} - 21340 X_{MnO} X_{MgO} + 67780 X_{MnO} X_{CaO} \\ & + 58570 X_{SiO_2} X_{MgO} + 60670 X_{SiO_2} X_{CaO} + 102510 X_{MgO} X_{CaO} (J) \end{aligned} \quad (14)$$

Using the above expression activity coefficients, $\log \gamma_{FeO}$, for ancient and modern slags were calculated to be $-91.032/T$ and $26.863/T$ respectively.

The oxygen contents in ancient and modern irons as provided by equations (11) and (12) have been plotted as a function of temperature in Figure 1. The results from both the models were mutually consistent and the differences were marginal. The oxygen content in iron increased with temperature. At all temperatures, oxygen content was higher for ancient iron when compared to that in modern iron. Interestingly, Igaki has related the corrosion resistance of ancient iron objects to the high oxygen contents in the metal²⁵. The present calculations indicate that higher oxygen contents must obtain in ancient iron

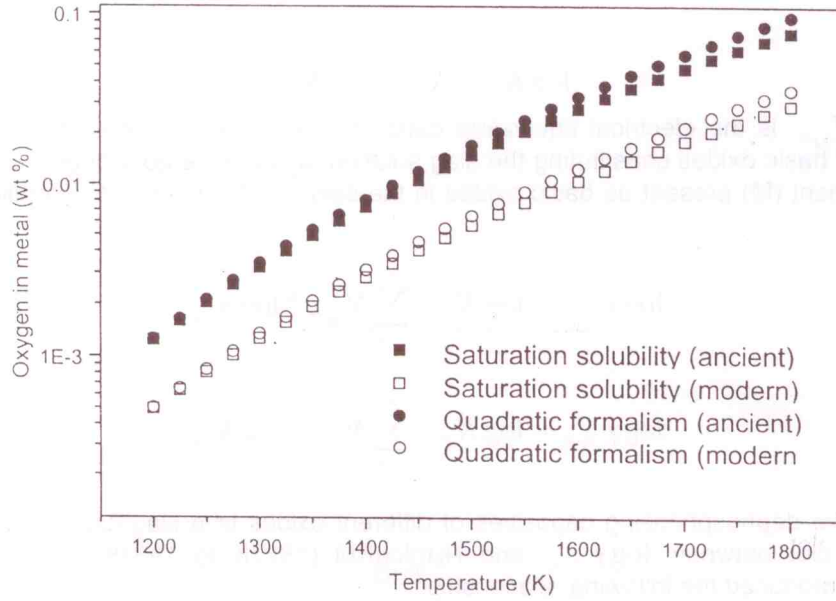


Fig.1. Oxygen content as a function of temperature in ancient and modern iron.

compared to modern iron and this is again related to the type of slag used in the iron-making process.

3.2 Phosphorus content in metal

Two different ionic theories for estimating phosphorus content in metal would be illustrated.

3.2.1 Flood's Model

As stated earlier, the equilibrium constant for the dephosphorization reaction (1) is given by

$$K_p = \frac{X_{P_2O_5}}{[P]^2 \cdot [O]^5} \cdot \gamma_{P_2O_5} \quad (15)$$

Thus,

$$K_p = K'_p \cdot \gamma_{P_2O_5} \quad (16)$$

where K'_p is the value of equilibrium constant K_p under ideal Raoultian behavior.

$$\log \gamma_{P_2O_5} = \log K_p - \log K'_p \quad (17)$$

However, for each cation in the slag solution ²⁰

$$\log K'_p = N'_{M^{2+}} \cdot \log K_M \quad (18)$$

or

$$\log K_p = N_{MO} * \log K_M \quad (19)$$

where $N_{M^{2+}}$ is the electrical equivalent cation fraction of each cation, N_{MO} the mole fraction of basic oxides constituting the slag solution, and K_M the equilibrium constant for each element (M) present as basic oxides in the slag²⁰. Thus, eqn. 17 modifies to the following:

$$\log \gamma_{P_2O_5} = \log K_p - \sum_{i=1}^n N_{M_i^{2+}} * \log K_{M_i} \quad (20)$$

or,

$$\log \gamma_{P_2O_5} = \log K_p - \sum_{i=1}^n N_{MO_i} * \log K_{M_i} \quad (21)$$

The relative dephosphorizing capacities of different oxides in a slag can be determined from the plot between $\log \gamma_{P_2O_5}$ and $N_{MO} \log K_M$ (1823K to 1933K)^{20,23}. One such approach produced the following relationship^{20,23}

$$\log \gamma_{P_2O_5} = -1.12 \sum_{i=1}^n N_{MO_i} * \log K_{M_i} - \frac{42000}{T} + 23.58 \quad (22)$$

where

$$\sum_{i=1}^n N_{MO_i} * \log K_{M_i} = 22N_{CuO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} - 2N_{SiO_2} \quad (23)$$

It must be noted that $\gamma_{P_2O_5}$ has been obtained in an empirical manner in the Flood's model. The phosphorus content for ancient and modern iron determined by using equations 11, 15 and 22 have been provided in Figure 2.

3.3 Quadratic Formalism

The activity coefficient of the i^{th} component, γ_i , in a multi-component slag can be expressed²¹

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k + I' \quad (24)$$

where X_i is the cation fraction of the i^{th} component, α_{ij} is the interaction energy between the i^{th} and the j^{th} cations, and I' is the factor relating the activity coefficients of the hypothetical regular solution and the real solution. This approach is known as quadratic formalism²¹. According to this regular solution method, the equilibrium relation of phosphorus in slag and metal is given by the following equations:

$$P + 2.5 Q = (PO_{2.5}) (R.S.) \quad (\text{Joules}) \quad (25)$$

The equilibrium constant and standard free energy for the above reaction are:

$$RT \ln K_{25} = RT \ln \left[\frac{X_{PO_{2.5}}}{a_P a_O^{2.5}} \right] + RT \ln \gamma_{PO_{2.5}(R.S)} \quad (26)$$

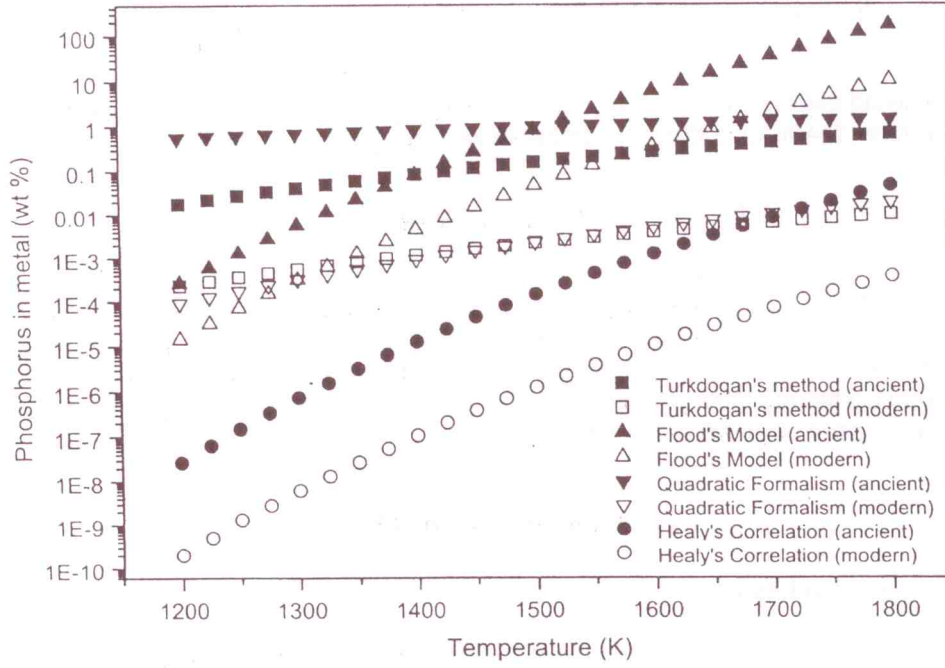


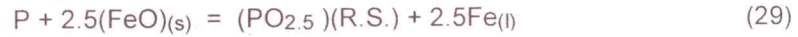
Fig. 2. Phosphorous content as a function of temperature in ancient and modern iron.

$$\Delta G_{25}^0 = -326520 + 162.88T \quad (27)$$

The activity coefficient of the $PO_{2.5}$, in a multi-component slag, in equilibrium with metal is²¹

$$\begin{aligned} RT \ln \gamma_{PO_{2.5}} = & 31380X_{FeO}^2 + 14640X_{FeO_{1.5}}^2 - 251040X_{CaO}^2 - 37660X_{MgO}^2 + 83680X_{SiO_2}^2 \\ & + 1920X_{FeO}X_{FeO_{1.5}} - 251040X_{FeO}X_{CaO} - 102510X_{CaO}X_{MgO} + 94140X_{FeO}X_{SiO_2} \\ & - 140590X_{FeO_{1.5}}X_{CaO} - 20090X_{FeO_{1.5}}X_{MgO} + 65680X_{FeO_{1.5}}X_{SiO_2} - 188280X_{CaO}X_{MgO} \\ & - 33479X_{CaO}X_{SiO_2} + 112960X_{MgO}X_{SiO_2} \quad (J) \end{aligned} \quad (28)$$

Combining equation 5 and 25, the equilibrium relation between phosphorus in metal phase with iron oxide in slag is obtained:



$$RT \ln K_{29} = RT \ln \left[\frac{X_{PO_{2.5}}}{a_P a_{Fe(l)}^{2.5}} \right] \ln \gamma_{PO_{2.5}(R.S.)} \quad (30)$$

$$\Delta G_{29}^0 = -6280 + 17.908T \quad (\text{Joules}) \quad (31)$$

The conversion factor between the activities of liquid P_2O_5 and hypothetical liquid $PO_{2.5}$ can be derived based on the following equilibrium²¹



$$\Delta G_{32}^0 = 52720 - 230.706T(J) \quad (\text{Joules}) \quad (33)$$

$$RT \ln a_{P_2O_5(l)} = 2RT \ln a_{PO_{2.5}(R.S.)} + 52720 - 230.706T \quad (\text{Joules}) \quad (34)$$

$$RT \ln \gamma_{P_2O_5(l)} = -RT \ln X_{P_2O_5(l)} + 2RT \ln X_{P_2O_5} + 2RT \ln \gamma_{P_2O_5(R.S.)} + 52720 - 230.706T \text{ (Joules)} \quad (35)$$

The following expression for phosphorus in metal in equilibrium with that in slag at a given temperature (1540K to 2000K²¹) can be derived using eqns. 30 and 35.

$$\ln[P] = 33.47 - 2.5 \ln[O] + 0.5 \ln a_{P_2O_5} - \frac{42423.62}{T} \quad (36)$$

The value of γ_{FeO} for modern and ancient slags has been already listed and $\log \gamma_{P_2O_5}$ for ancient slag was calculated to be $1154.765/T$ and that for modern slag was $-5499.114/T$. $X_{P_2O_5}$ for ancient slag were calculated to be 0.0043 and for modern slag it was 0.0251. The phosphorus contents for ancient and modern iron determined by utilizing equation 36 have been provided in Figure 2.

4. EMPIRICAL MODELS

4.1 Healy's Co-relation

Many co-relations have been developed for P partitioning between slag and metal based on empirical studies both on laboratory and plant scale. The most popular among them is Healy's correlation, developed from empirical data from modern steel plants. The phosphorus content²⁶ in metal, [P], is correlated with the phosphorus content in slag, (P), by the expression²⁶

$$\log \frac{(P)}{[P]} = \frac{22350}{T} - 16.0 + 0.08(\text{wt. \% CaO}) + 2.5 \log(\text{wt. \% Fe}_{total}) \quad (37)$$

where the weight percent CaO and total Fe in the slag have been considered. The effects of other oxides like MnO, MgO, etc. have not been incorporated in this correlation, because modern steel making slags generally contain CaO in large proportions. The P contents determined have been presented in Figure 2.

4.2 Turkdogan's Model

Turkdogan²⁴, assuming the slag to be ionic in nature, derived the following relations for slag/metal phosphorus reaction, over a wide range of slag composition and temperature (1350K to 2000K), based on independent experimental data.

$$K_{PO} = \frac{(P) * [O]^{-2.5}}{[P]} \quad (38)$$

$$\log(K_{PO}) = \frac{21740}{T} - 9.87 + 0.071 * BO \quad (39)$$

where T is the temperature in Kelvin and BO is the slag basicity that incorporates the effect of the basic oxides. It was determined by empirical studies that the basic oxides present in the steel making slags, the phosphate capacity is strongly affected by the

amount of CaO and CaF₂ in the slag and lesser by the MgO content²⁴. The contribution of the major basic oxides to the phosphate capacity has been empirically given as²⁴

$$BO = \%CaO + \%CaF_2 + 0.3\%MgO \quad (40)$$

The expression for oxygen content as given in equation 11 can be combined with equations 38 and 39, and the P content in metal (1350K to 2000K) is given by

$$\log[P] = \log(P) - 2.5 \log(FeO) - 2.5 \log a_{FeO} + 3.8775 - 0.071 * BO - \frac{7415}{T} \quad (44)$$

The phosphorus content in the slag, (P), is known from the composition of the slag (Table 1). The results obtained using this expression for ancient and modern irons have been presented in Figure 2.

5. DISCUSSION

Ancient Indian iron always possessed higher phosphorus than modern iron at all temperatures. While the variation of P content with temperature was not drastic in the case of the quadratic formalism method, it was significant in the Flood's method. Some factors promoting phosphorus removal from the metal are high slag basicity, low operation temperature and a highly fluid slag.

The above estimations indicate that the origin for higher P contents in ancient iron is due to lack of CaO in the slag. The major basic component in ancient Indian iron making slags was FeO²⁷ which aided dephosphorization. The optimal amount of FeO in slag and its implications for ancient slag will be briefly addressed. At higher silica contents, the activity of FeO decreases due to the formation of iron silicates. With increase in amount of lime in slag, the activity of FeO again decreases because it combines with lime. FeO has two functions in a slag, one as a basic oxide and other as an oxidant. The oxidizing power of the slag is determined by the amount of FeO in it. FeO is required to oxidize phosphorus. On the other hand CaO determines the basicity of the slag and is required to fix P₂O₅ in slag as 3CaO.P₂O₅. Although FeO can also fix P₂O₅ in slag as 3FeO.P₂O₅, CaO is the stronger among the two in terms of dephosphorizing capacity. With increasing amounts of FeO in slag, the effect of CaO is diluted. The optimum combination of FeO and CaO will vary with the overall slag composition. It is known that when FeO is present more than 20% in the slag, it leads to phosphorus reversal, because dilution of CaO becomes dominant²⁰. As ancient Indian iron making slags were rich in FeO (around 45-50%) and poor in CaO, this resulted in relatively high phosphorus contents in ancient iron.

6. CONCLUSIONS

The origin for the high phosphorus contents of ancient Indian iron has been explored by considering thermodynamic and empirical models for partitioning of P between metal and slag. All methods provided consistently higher values of phosphorus content in ancient iron when compared to modern iron for all temperatures. It is concluded that the low lime content of ancient slags (because limestone was not used in the charge) resulted in higher P contents in ancient Indian iron.

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