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#### Chapter

## Plasma Processing of Iron Ore

Sumant Kumar Samal, Manoja Kumar Mohanty, Subash Chandra Mishra and Bhagiratha Mishra

# Abstract Concern

The depletion of high-grade ore minerals and the scarcity of fossil fuel reserves are challenging factors for metallurgical industries in the future. Also, extensive mining for increased steel demand results in the generation of fines often found unsuitable for use as direct feedstock for the production of metals and alloys. Apart from mines waste, the other major sources of fine minerals are leftover in charge burdens, sludges, and dust generated in the high-temperature process. Sludge and fines generated during beneficiation of ore add to this woe, as the outcomes of beneficiation plants for lean ores show better yield for fine particles. The utilization of lean ore and wastes in iron making requires wide research and adopting new advanced technologies for quality production with time-saving operations. The application of thermal plasma in mineral processing has several advantages that can overcome the current industrial metal extraction barriers. The present study demonstrates the thermal plasma for the processing of different iron-bearing minerals and its feasibility for metal extraction.

**Keywords:** thermal Plasma, blue dust, siliceous iron ore, manganiferous iron ore, recovery

#### 1. Introduction

The global production of crude steel exceeds 1869 million tonnes in the year 2019. Steelmaking viz. carbon steel and alloy steel is a multistep process where iron ore is the starting material used for iron making. Blast furnace iron making is mostly adopted by industries throughout the globe [1, 2]. Production of DRI for smelting in EAF is an alternative for iron ore reduction. There are several problems that persist with the economy of iron and ferroalloys production, and it depends upon three major factors viz. material, process, and product. The characteristics of ore minerals decide the process kinetics, and hence product quality and yield. There are several problems that still persist, as the following needs to be resolved.

i. Ore minerals: The quality of iron ore plays a significant role as the cost of raw ore attributes about 40% of the total production cost. The mined ore needs to be in the specified size range for individual furnace types, which is accomplished by crushing and sizing. The crushing and washing of bulk ore generate a substantial amount of fines viz. micro and macro fines, which cannot be fed directly into a furnace as it affects the porosity of charge burden. Moreover, it increases process cost comprising of agglomeration and heat treatment before extraction.

- ii. Gangue content: The excavated ore always includes gangue contents viz. alumina, silica, and magnesia along with alkali, sulfur, and phosphorus. The type and quantity of gangue affect the entire process kinetics in terms of metallic yield and quality. The primary ore needs to be upgraded through various separation techniques, i.e., physical, gravitational, etc. which is critical for high gangue amounts.
- iii. Mineral phases: The mineral phases present in the ore are of interest as the entire extraction process is dependent on the various minerals present in the parent ore. Minerals in the ore are detected as metal oxides, hydroxides, carbonates, and also associated with gangue as silicates, aluminates. The silicates and aluminates phases are not only difficult to reduce but also consume high flux and energy for which ores with high content of such phases are commonly discarded at the mines site itself. The decomposition of hydroxides and carbonates results in higher coke consumption. The presence of alkali not only affects the process but also has a high impact on refractory linings.
- iv. Process: With the increased demand for steel across the globe in the scenario of unaffordability of high grade ores, research on the applicability of fines, dust, and other industry by-products has become essential in order to control the depletion of earth minerals. These fines are agglomerated through pelletization, sintering, and briquetting routes, which has various drawbacks in terms of production rate, energy consumption, charging, and environmental impact. Ore and agglomerate must be of suitable for minimal transportation loss, hightemperature sustainability, and low disintegration rate. The porosity, density, and crushing strength of agglomerate must be adequate in order to achieve a higher reduction rate and metallic yield. If such properties are not in the predesigned range, it can cost higher and affect smooth operation by promoting fines generation and hinders Boudouard reaction.

The utilization of lean ore and wastes in iron making requires wide research and adopting new advanced technologies for quality production with time-saving operations.

#### 2. Plasma

It is not unusual to refer plasma as the fourth state of matter as it is an ionized gas comprised of molecules, atoms, ions (in their ground or in various excited states), electrons, and photons. Plasma possesses a unique property known as quasineutrality since plasma is electrically neutral. In contrast to an ordinary gas, plasma encloses free electric charges that are commonly produced from the gas itself by a variety of ionization processes. In a steady-state situation, the rate of ionization in the plasma is balanced by the rate of recombination. Depending upon the energy content of the plasma, the degree of ionization may be so high that virtually no neutral particles are left, i.e., the plasma becomes fully ionized [3, 4].

#### 2.1 Classification

Since plasma is a broad topic as concerned, all together plasmas are classified into three main categories [5]:

- CTE plasmas (complete thermodynamic equilibrium)
- LTE plasmas (local thermodynamic equilibrium)
- Non-LTE plasmas (nonlocal thermodynamic equilibrium)

Among the above three types, CTE plasmas are used for thermonuclear fusion experiments. The latter two types are used as laboratory plasmas and also implemented for industrial purposes like MINTEK, South Africa. Again according to density and energy, typical plasmas are categorized as shown in **Figure 1**.

Plasmas generated by electron and photon belong to the nonlocal thermodynamic equilibrium category. LTE plasmas are also called as hot plasmas or thermal plasmas and non-LTE plasmas as cold plasmas or non-thermal plasmas. Based on temperature, plasmas are subcategorized into two groups, i.e., low-temperature plasma and high-temperature plasma. Plasmas with temperatures below 10<sup>5</sup> K or in other words, energies less than 10 eV per particle are to be called as low-temperature plasmas. Beyond this limit, it is said to be high-temperature plasma. It is also not unusual for plasma to be called as per its gas name, i.e., oxygen plasma, argon plasma, nitrogen plasma or argon-nitrogen plasma, etc.

#### 2.2 Plasma chemistry

Plasma chemistry refers to the thermodynamic characteristics of various plasma forming gases. Both monoatomic and diatomic gases like argon, helium, neon, nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, air, and a mix-ture of gases are used as plasma forming gases. The relation between energy and temperature of some commonly used monoatomic and diatomic gases are shown in **Figure 2**.

The diatomic molecules require 90 to 200 kcal mole-1 to dissociate between 4000 to 10,000°K, while ionization requires 340 to 600 kcal mole-1 between 10,000 to 30,000°K [5]. The upper practical limit of flame temperature is about



**Figure 1.** *Typical plasmas characterized by their energies and densities.* 





3500°K, where molecules begin to dissociate, while the lower limit of plasma temperatures is about 10,000°K. As most laboratory plasmas are heated electrically, their temperatures will lie in the bottom end of the ionization curve, i.e., above 10,000°K for diatomic gases. For any process operating below 1000°K, an air-fuel flame (~2000°K) or an oxygen-fuel flame (~3000°K) will have a high percentage of energy available for the process. However, for the reaction occurring at 2500°K, only one-sixth of energy contained in an oxygen flame will be available, and rest must be either wasted or recovered in the expensive heat exchangers. On the other hand, a plasma flame composed of atomic nitrogen at 10,000°K would have more than 90% of its energy available above 2500°K. This high energy efficiency may more than offset the economic advantage that combustion energy over electrical energy; certainly, this advantage will increase as electrical energy becomes cheaper while fossil energy gets more expensive. Although by utilizing plasma high temperature can be achieved with the liberation of huge heat energy in a chemical reaction, plasma gases are generally not used as reactants in the reaction.

#### 2.3 Generation of plasma

Thermal arc plasmas are generated by striking an electric arc between two or more electrodes. They are characterized by high current densities (greater than 100 A/cm<sup>2</sup>) and are more luminous than other types of discharges, especially when operated at atmospheric pressure and above. Thermal arcs can be initiated in several ways. Two common methods are electrode contact, which produces a short circuit, or pre-ionization of the gap between electrodes by a high-frequency spark. The cathode must be heated beyond 3500 °K, at which point the thermionic emission of electrons begins, generating the charge carriers that create the plasma state [3]. Cold cathodes are cylindrical and made of heavily cooled copper, iron, or copper alloy while high-temperature cathodes are usually rod-shaped and made of thorium, tungsten, or graphite. Thermal arc plasma torches can operate in two modes, i.e., non-transferred and transferred arc. If the plasma torch having two electrodes designed in such a way that hot gas emerges through one electrode and then heated by the flame is called non-transferred. If there is only one electrode in the torch and



#### Figure 3.

Schematic diagram of transferred and non-transferred plasma torches.

material to be heated/melted acts as another electrode, then it is said to be transferred. The schematic of both transferred and non-transferred arc plasma torches are shown in **Figure 3**.

#### 2.4 Application of plasma

In the last two decades, plasma has claimed to be an emerging solution to numerous processes due to its unique features and hence implemented in various sectors [4, 6–10]. Plasma finds significant industrial applications viz. melting, smelting, smelting and reduction, remelting and refining, spark plasma sintering, surface modification, and surface coating.

#### 2.5 Advantages of plasma over conventional processes

Although there are a lot of many advantageous aspects behind the utilization of plasma, some of the important features are given in **Table 1**.

#### 2.6 Application in iron making

Many researchers investigated the applicability of plasma in iron and steel making [9, 11, 12]. In general, plasma is used as a heat source instead of reductant itself, as the percentage of the degree of reduction lags behind when utilized as a reductant. The selection of the type of plasma and preferred operating parameters, along with the type of reductant, is a crucial factor that needs to be considered sensibly in relation to the treating of material. The wrong choice can affect both troubleshooting and also processing costs.

Criteria for selection must be based on answering many questions, which comprises;

- i. Type of reducing agent (carboneous or any other)
- ii. Type of plasma forming gas (inert, self-reducing, self-burning or helps in burning)

High efficiency	Since a huge amount of energy in the form of heat is available by utilization of plasma, high throughput can be achieved.
Long-range of melting materials	Since high temperature can be achieved in a reaction by using plasma, almost all materials can be melted in this process. Although its commercial use to melt and process metals is well known, the method is less known as a method of melting glass.
Feed capability	This process is independent of the size, shape, and composition of feed material.
Transient process	Due to the release of huge heat energy that a particular reaction requires at a specific temperature, plasma stands ahead of any other process to respond to the changes in a shorter period.
High energy fluxes	Higher temperatures with extreme jet velocities and greater thermal conductivities of plasma gases are the key factors that result in high energy fluxes. Smaller furnace dimensions with high smelting capacity are a unique aspect of using plasma.
Independent energy source	The flexibility of control over feed rate and power independently and input power is not limited by the electrical conductivity of feed material to be melted or smelted. Hence greater freedom of choice with respect to charge composition is available by using plasma.
Gas flow control	Unlike combustion systems, the gas flow rate, temperature, and energy input are not interdependent, and gas flow rate and temperature can be controlled separately irrespective of energy input.
Gas environment control	Energy can be provided to the system with desired oxygen potential to ensure oxidizing, reducing, or inert gas conditions independently without taking temperature into account.
Electrical energy- intensive process	Minimization of the usage of fossil fuel energy and conservation of fossil fuel can be made.
High energy transfer to slag layer	Plasma jet is directed towards slag layer and significantly increases the metallization rate.
Purity level in product	The purity level of the final product through plasma processing is very high.

#### Table 1.

Advantageous aspects of thermal plasma.

iii. Type of process (melting, smelting or smelting reduction)

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iv. Process duration
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v. Process environment (open-air, inert or vacuum)

vi. Feed rate

vii. Power control

#### 3. Description of the plasma furnace

The schematic diagram of 30 kW DC extended arc plasma reactor used for this study is shown in **Figure 4** [13].

On top of the reactor, the plasma torch is attached in the downward direction. The plasma torch contains a hollow cylindrical graphite crucible with 145 mm outer diameter, wall thickness 15 mm, and 300 mm high that serves as the anode. A hollow graphite rod of 400 mm long and 5 mm inner and 35 mm outer diameter serves as the cathode. The graphite rod end is tapered to a conical shape for superior



**Figure 4.** *Schematic diagram of DC extended arc plasma reactor.* 

electron emission. The hollow structure of the cathode has been designed to have provisions for gas flow. The material to be processed was placed in the anode crucible bed, and the arc was initiated by shorting the cathode and the crucible bottom wall (graphite plate). The arc length was increased by raising the cathode rod up suitably within the crucible to heat the charge placed in the crucible. The power supply and power control unit is designed to vary the necessary voltage and current, enabling easy and smooth control of experimental conditions. Voltage and current can be altered over a range of 0–100 V and 0–500 A, respectively. The gas supply unit facilitates plasma forming gases, i.e., oxygen, argon, nitrogen, methane, coke oven gas. Besides, the mixture of above gases can be utilized as plasma forming gas. Gas flow control consisting of digital indicators helps in not only measuring gas flow rate but also governing a suitable flow of gases as per experiment performed and stands as a key parameter. The gas flow rate can be varied from 0 to 15 LPM. Heat insulating materials are placed in between the steel casting and reaction chamber.

Several prerequisite steps have to be done before feeding samples into the reaction chamber. Initially, the crucible was cleaned in order to avoid any other material contained in the crucible to be reacted with samples. The hollow tapered graphite rod was fitted in such a way that it points towards the center of the reaction chamber. After checking no leakage in the crucible, it was placed in the space provided in steel casting. Bubble alumina was poured in spacing between the reaction chamber and reaction chamber that acts as a heat-insulating medium. The power supply was then provided, and proper arcing between cathode and anode was tested. The gas supply is then connected to the cathode passage, and plasma forming gas was purged into the reaction chamber for 1 minute to displace atmospheric air. After that, the power supply and plasma forming gas supply both supplied simultaneously, and the required voltage and current maintained. Then sample feed was poured into the hot reaction chamber as per our requirement.

#### 4. Plasma processing of iron-bearing minerals

The present study demonstrates the plasma processing of three iron-bearing minerals viz. blue dust, siliceous type iron ore, and manganiferous iron ore.

#### 4.1 Plasma processing of blue dust

Blue dust is the purest form of iron oxide mineral (hematite) abundantly available in many states of India. For the present study, blue dust of Koira origin, Odisha, India, was collected, which is in fine form (150  $\mu$ ). The chemical analysis of blue dust is given in **Table 2**. The ore is mainly composed of Fe<sub>2</sub>O<sub>3</sub>, and XRD analysis also confirmed the presence of single mineral hematite.

Plasma smelting operations were carried out for mixtures of blue dust and coke in argon and nitrogen ionizing atmosphere [14]. The coke percentage in charge mixture (500 gm) was varied from 5–20%. The plasma gas flow rate was maintained at 2.5 LPM.

The highest recovery rate exceeding 86% was achieved for using nitrogen as plasma forming gas. The recovery rates in argon plasma are comparatively less than those of nitrogen plasma. It is because of the diatomicity of  $N_2$  gas, which liberates higher energy flux than the monoatomic gas Ar. The loss of Fe in the process involves loss accounted for in charging and splashing of metal droplets due to the high velocity of the plasma jet in the course of smelting. The loss of metal splashing is further minimized by adjustment of power input and controlling gas flow rate. The recovery rate attains 95% maximum in closed furnace type arrangements.

As the gangue in blue dust is low, the metallization (Fe) occurs in the absence of complex slag phases. Blue dust with different carbon percentages (i.e., 5, 10, 12, 15, and 20) smelted by using nitrogen plasma shows the change of ferrite, ferritecementite to fully pearlite structure, which can be attributed to the Hull-Mehl model of pearlitic transformation [15]. The silica in blue dust in the high reducing atmosphere reduces into SiO, observed in smelting tests as fumes. The smelting duration for the conversion of  $Fe_2O_3$  into Fe was 17 minutes, which is several hours in BF iron making. Moreover, blast furnace limits the direct charging of blue dust to avoid lowering the porosity of charge burden, which increases process cost and affects smooth operation.

To use blue dust in BF, agglomeration and heat treatment are required. Although stiff vacuum extrusion briquetting avoids heat treatment, binder requirement is still essential. The cement and bentonite binder adds cost and also requires unnecessary slag generation and separation from the purest Fe<sub>2</sub>O<sub>3</sub> ore.

The direct smelting of blue dust in thermal plasma has several advantages over conventional processes in terms of cost-saving operation, purity level in hot metal, and high production rate. The production cost will be much less for industrial large scale furnace and by using cheap gases such as methane, coke oven gas, etc.

#### 4.2 Plasma processing of siliceous type iron ore

For this study, partially reduced briquettes made from iron minerals were collected from an industry in the vicinity of Rourkela, Odisha, India. Briquettes upon solid state reduction at 1250°C are partially melted which hinders further reduction at higher temperatures. The industrial trial of such briquettes in mini BF suggested its infeasible use for iron making due to high FeO loss in slag. The chemical composition of the briquette sample is given in **Table 3**.

The amount of silica and alumina in the briquette is about 16% in cumulative. XRD analysis detected wustite (FeO), fayalite ( $Fe_2SiO_4$ ), and hercynite ( $FeAl_2O_4$ ) as major phases in the briquette sample. The presence of such phases suggests the high affinity of FeO towards silica and alumina for which low melting fayalite forms, melts early and hinders CO gas passage to the core. Partial melting of briquette also affects the furnace operation and increases flux addition, and hence increases the process cost.

Constituents	In Wt. %
Fe <sub>2</sub> O <sub>3</sub>	96.87
SiO <sub>2</sub>	0.45
Al <sub>2</sub> O <sub>3</sub>	0.21
MgO	Trace
LOI	1.48

In Wt. %
72.2
8.6
7.2
0.63
1.4
0.4
9.57

#### Table 3.

Chemical composition of briquette.

Here, an attempt was made for the utilization of these briquettes for the value addition with maximized extraction [16]. Since plasma processing does not restrict the slag chemistry, briquettes were smelted with and without flux (CaO). Initial trials with flux addition targeting melilite slag (CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) improved Fe recovery in metal. For the CaO/SiO<sub>2</sub> ratio in the range of 0.9–1.0, metallic yield exceeds 88%. The flow characteristics of such slag allow a better reduction in the slag layer where unreduced Fe-oxides are more promptly metalized.

Another approach was aimed at the direct smelting of briquettes without adjustment of slag chemistry. Since the briquettes are composed of fayalite, additional coke was provided for the reduction of silicon along with iron. These briquettes were smelted for a longer period than previous slag practice. The metallic recovery was appreciably higher, i.e., exceeds 94% by using nitrogen as plasma forming gas.

Phase and microstructure evolution confirms the formation of the iron silicide (Fe<sub>3</sub>Si) phase in the alloy along with Fe. These ferrosilicon alloys can be used for deoxidation purposes, which is of greater value than metallic Fe.

This study suggests that the utilization of silicate-based iron minerals are more suitable for ferrosilicon production rather than iron making. Although the energy consumption is a little higher for FeSi production from these briquettes, flux consumption and melting of excess slag can be eliminated. Moreover, the product (FeSi) cost puts importance on its feasible production.

#### 4.3 Plasma processing of manganiferous iron ore

Manganiferous iron ore is the type of lean manganese ore containing a maximum about 10–15% of Mn. These are of less importance in ferromanganese production; however, reduction roasting and magnetic separation improve Mn/Fe ratio. The primary objective of such a process is to reduce Fe<sub>2</sub>O<sub>3</sub> into Fe<sub>3</sub>O<sub>4</sub>, which easily

separates as magnetic particles. However, the feasibility of the upgrading process becomes questionable when both iron and manganese oxides are in associated form, i.e., bixbyite (Fe, Mn)O<sub>3</sub> mineral.

As an alternative, these ores are subjected to smelting for obtaining FeMn alloy with low Mn content. It is a cost-saving operation, and smelting operations can be carried out even in BF. The complexity arises for such ores with high gangue amount, which affects the extraction kinetics by forming silicates, aluminates, and/or complex mixtures phases.

In the present study, lean manganese ore was collected from Joda valley, Odisha, India. The ore is in fine form and is being discarded as waste at the mines site itself. The initial assessment of the ore through wet chemical analysis indicated that the ore contains about 17% of alumina and 9% of silica. The Mn content in the fines is about 12%, which falls into the manganiferous category. The reduction studies of such briquettes evidenced the formation of hercynite, galaxite, fayalite-manganon, and spessartine phases at different temperatures. These phases lower the reducibility of the ore and also deteriorate the physical and mechanical properties of the agglomerate.

Here an attempt was made to utilize these fines directly in thermal plasma, avoiding any agglomeration. Smelting of such ores by using other technologies results in poor Mn recovery (≈30%) and high FeO loss into slag; flux addition was essential.

The smelting of ore with flux addition targeting melilite and mayenite slags in ionizing atmosphere improved Mn recovery and was 80% maximum. Although plasma arc provides high energy flux, the slag chemistry also governed the process kinetics. By adjusting slag chemistry to a too basic slag lowered the activity of silica and alumna; however, the formation of high melting silicate compounds such as dicalcium silicate and tricalcium silicate increases the viscosity of the slag. The flowability of such slag hinders carbon contact with metal oxides and hence lowers the reducibility.

In the current scenario, ferromanganese production follows rich slag and discard slag practices. The rich slag retained in primary smelting (low fluxing) is further smelted in another step to produce silicomanganese or ferro-silicomanganese. In discard slag practices, the slag retained in primary smelting, which contains less than 15–30% MnO, is discarded.

The present study refers to the discard slag practice followed by plasma smelting with the highly basic slagging operation. As the ore contains high alumina, primary smelting similar to rich slag practice will result in slag with alumina bearing compounds, which will be difficult to reduce in the secondary smelting for obtaining silicomanganese. Moreover, the cost of smelting these high melting compounds will increase reductant, energy consumption, and also lower the furnace refractory life cycle.

The extraction of metals from these types of complex ores in single-stage smelting operation should be chosen in such a way that the slag can be used in secondary products such as cement.

#### 5. Hydrogen plasma

In iron making, coke is used as a heat source and reductant. The application of plasma in iron making lowers  $CO_X$  emission for being used as plasma as a heat source. The reducibility of metal oxides by solid carbon or CO gas is lower than that of H<sub>2</sub>. The use of methane as plasma forming gas is beneficial over argon or nitrogen from a cost perspective. However, ecofriendly gas emission in iron making is only

possible through hydrogen plasma processing; the exit gas is water vapor, which reduces environmental pollution and will be much beneficial in impurity-free metal production [17, 18].

At present, research projects are being carried out for hydrogen reduction of iron ore in a pilot-scale, such as HYBRIT [19]. The primary installation of such reactors costs high; continuous improvements are essential. The primary beneficiation of iron ores will improve the purity of iron ore, which in turn will reduce the cost of the process.

#### 6. Conclusion

The importance of plasma in iron making is discussed considering different types of ore minerals and its various aspects of processing. The freedom in size, composition, and smelting conditions required for complex ore minerals fits into the processing of iron ore in thermal plasma. The use of coke as a heat source in conventional iron making processes can be eliminated with the application of thermal plasma. The recovery rate and purity level in hot metal extracted from complex mines waste is noticeable higher by using thermal plasma. The future eco-friendly hydrogen plasma processing is of interest. Moreover, the use of hydrogen plasma can result in carbon-free metal/alloys, which can lower production costs by avoiding decarburization.

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