Production of Green Direct Reduced Iron (DRI) from Red Mud of Indian Origin: A Novel Concept

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Abstract

Red Mud is considered as one of the hazardous waste materials generated during the processing of bauxite for production of alumina using caustic soda employing the Bayer's process. Presently Red Mud is discharged into the nearby Red Mud ponds which are located in the vicinity of alumina refineries. Red Mud of Indian Origin contains around 45-55 % Fe_2O_3, 10.69 % TiO_2, 20.42 % Al_2O_3, 8.72 % SiO_2 and other associated oxides in minor quantities. This composition of Red Mud can be considered as rich source of iron. No significant efforts have been made so far for exploitation of Red Mud for production of iron in commercial scale though some research activities have been reported. R&D activities centered around production of DRI from iron ore have been successfully achieved and reported from this Institute by employing Microwave Hydrogen Plasma Reactor process using hydrogen as reductant at a low temperature of 600-800 ^{o}C. In the present study, similar process has been employed for production of DRI from Red Mud using the same reactor. The DRI produced in the process has been characterized through mineralogical and chemical analysis. The by-product "water" produced in the process can be recycled when the process is carried out in a commercial scale.

Keywords: Red mud, microwave hydrogen plasma reactor, green direct reduced iron, water.

1. Introduction

Red Mud of Indian origin contains around 55% plus of Fe_2O_3 and is considered as a hazardous waste material for the alumina industry which is generated in the order of two tons of Red Mud per one tone of alumina produced from bauxite. The worldwide alumina production is around 58 million tonnes in which India counts for 2.7 million tonnes. India produces around 5.4 million tonnes of Red Mud per annum from its various alumina refineries.

Major players in the Indian aluminium sector are INDAL, BALCO, HINDALCO, NALCO, MALCO, and Vedanta Alumina Ltd. Application of Red Mud for production of different value added items like Portland cement [1, 2], bricks & blocks, tiles, paints & pigments, soil amending agents, fibre reinforced polymer composites for building materials as wood substitutes [3] etc., have been tried out by many researchers throughout the world. However these applications have resulted in partial utilization of Red Mud and bulk utilization of Red Mud still remains as a challenge before the global aluminium community. Since iron constitutes as a major ingredient of Red Mud amounting to around 53.6%, the scope of its recovery for production of DRI is considered as a scientific & technological challenge. Efforts have been made for production of pig iron from NALCO Red Mud by application of plasma smelting technology [4]. Since the processes so far developed for production of pig iron employing Plasma Smelting Technology was not devoid of environmental pollution, the efforts were directed for production of Green DRI by using Microwave Hydrogen Plasma Reactor, considered as a novel and state- of -the -art technology and more so free from environmental hazards. The only by-product that is produced in the process is 'water' which can be recycled for meeting process requirements during scale up of the operation. The process is novel and unique in character and is 100% eco-friendly.

2. Raw Materials

The raw material used for the process was the Red Mud of Indian origin having the following chemical compositions as given in Table 1. The other raw material used for the study was hydrogen gas with 99.9% purity.

Table 1. Typical Composition of Indian Red Mud.

Input Material	Fe_2O_3 (%)	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	MgO (%)	CaO (%)	LOI (%)
Indian Red Mud	53.6	18.9	2.20	4.88	8.29	0.21	0.54	9.30

3. Experimental

The Red Mud of Indian Origin was subjected to crushing and grinding to bring the size up to -100 mesh which was then pelletized to $40X10^{-3}$m diameter and $3X10^{-3}$m height using an electrically operated automatic briquetting press by addition of 1-2% of water with respect to the amount of sample taken for the study. This was then dried in the oven at 100°C for 2hrs. The dried pellet was then subjected to Hydrogen Plasma Reduction in Microwave Hydrogen Plasma Reactor. The experimental parameters like Flow of Hydrogen, Reduction Temperature, Reduction Time, Pressure, and the Power input were studied for the reduction of iron content in Red Mud for production of Green DRI. The raw materials and the products were analysed for their chemical compositions and mineralogical characters. The reduction studies were carried out as per the process flow sheet given in Figure 1.

3.1 Microwave Hydrogen Plasma Reduction Process

The reduction of raw Red Mud pellet was carried out in a specially built Microwave Hydrogen Plasma Reactor of 6kW power for production of Green DRI. The plasma is generated by Microwave assisted thermal plasma process. The Schematic Diagram of Microwave Hydrogen Plasma Reactor with in-situ photograph of Reactor Chamber is shown in Figure 2. The system has provision to inject Hydrogen gas from the top into the chamber through a safety valve and the flow of the gas can be controlled by a mass flow controller. The temperature of the Molybdenum sample holder is measured by means of an IR Pyrometer. The microwave power can be varied to generate the plasma over a range of temperature. The high frequency waves interact with the hydrogen gas to produce the hydrogen plasma. The plasma produced in this manner covers a region up to about $6X\ 10^{-2}$ to $8\ X\ 10^{-2}$ m above the sample. The hydrogen molecules enter the plasma zone and become part of it. The hydrogen molecules under the influence of plasma dissociate in to atomic and ionic forms which reduces the iron oxide present on the surface of Red Mud pellet into metallic iron. These ionic charged particles of hydrogen recombine immediately in to hydrogen molecules when they exit from the plasma zone.

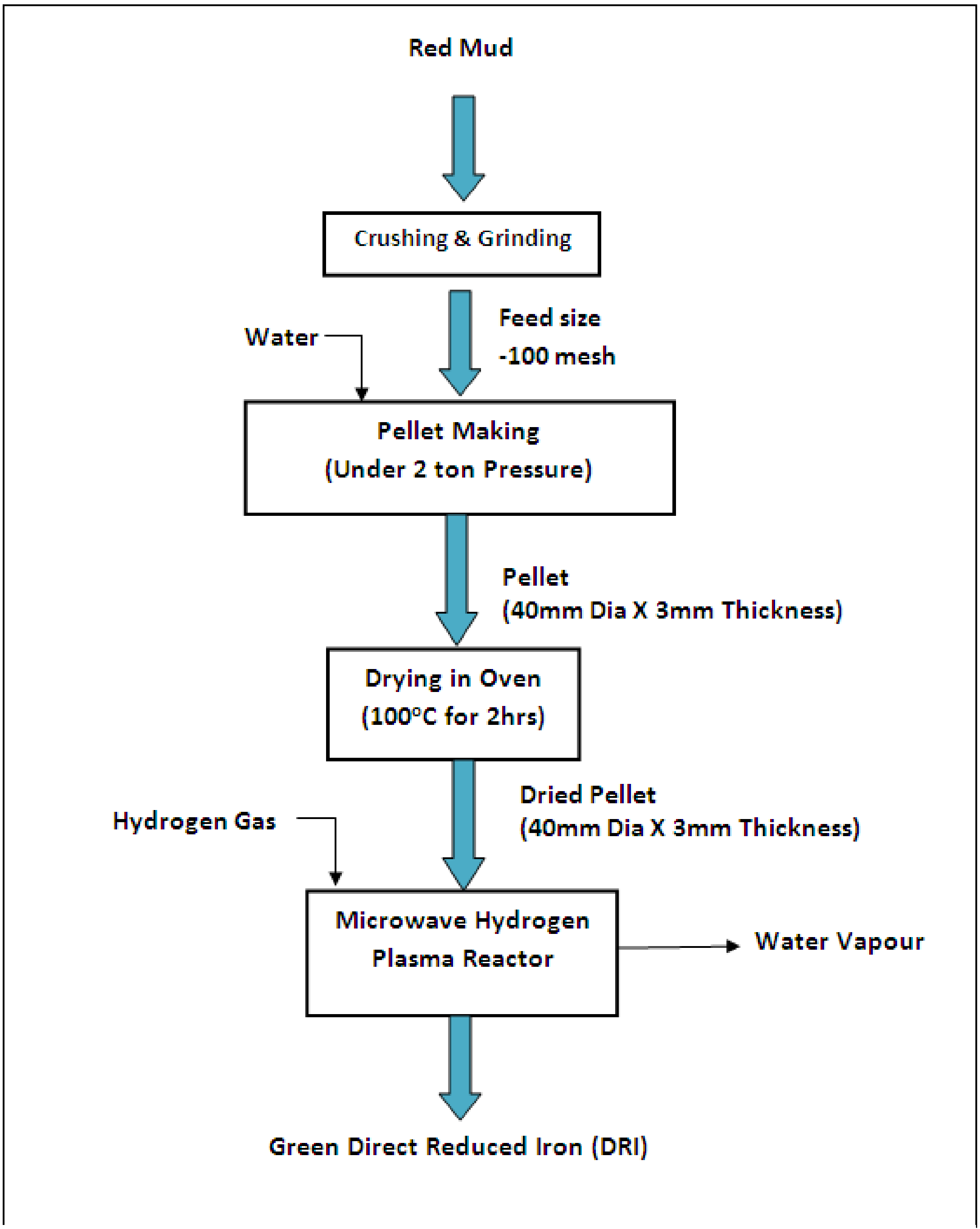

Figure 1. Process Flow Sheet for the Production of Green Direct Reduced Iron (DRI) from Red Mud.

In all the experiments, samples were kept on a Molybdenum sample holder, and the sample holder was in turn placed at the centre of the reactor chamber. Since the rector chamber is water cooled, the outer surface of the chamber remains at room temperature during the experiments. The extent of reduction with variation in process parameters, such as microwave power, hydrogen flow rate, pressure, temperature and time, was recorded by noting the loss in weight of the pellet. After each experiment, the reduced Red Mud pellet sample as shown in Figure 3 was ground and mixed well, and then a representative sample was taken for analysis. An X'Pert PRO-PAN analytical model No. 3040160 was used for X-Ray Diffraction (XRD) studies of the phases in the reduced Red Mud pellet. The quantitative estimation of the phases was done by using the wet chemical analysis procedure for the total iron, metallic iron, ferrous iron, silica and alumina. The Table 2 describes the chemical analysis result of the reduced red mud pellet.

Table 2. Chemical Analysis of Reduced Red Mud Pellet.

Input Material	**Fe(T) (%)**	**Fe(M) (%)**	**FeO (%)**	**SiO_2 (%)**	**TiO_2 (%)**	**Al_2O_3 (%)**
Reduced Red Mud Pellet	87.89	77.95	12.00	7.89	2.44	1.78

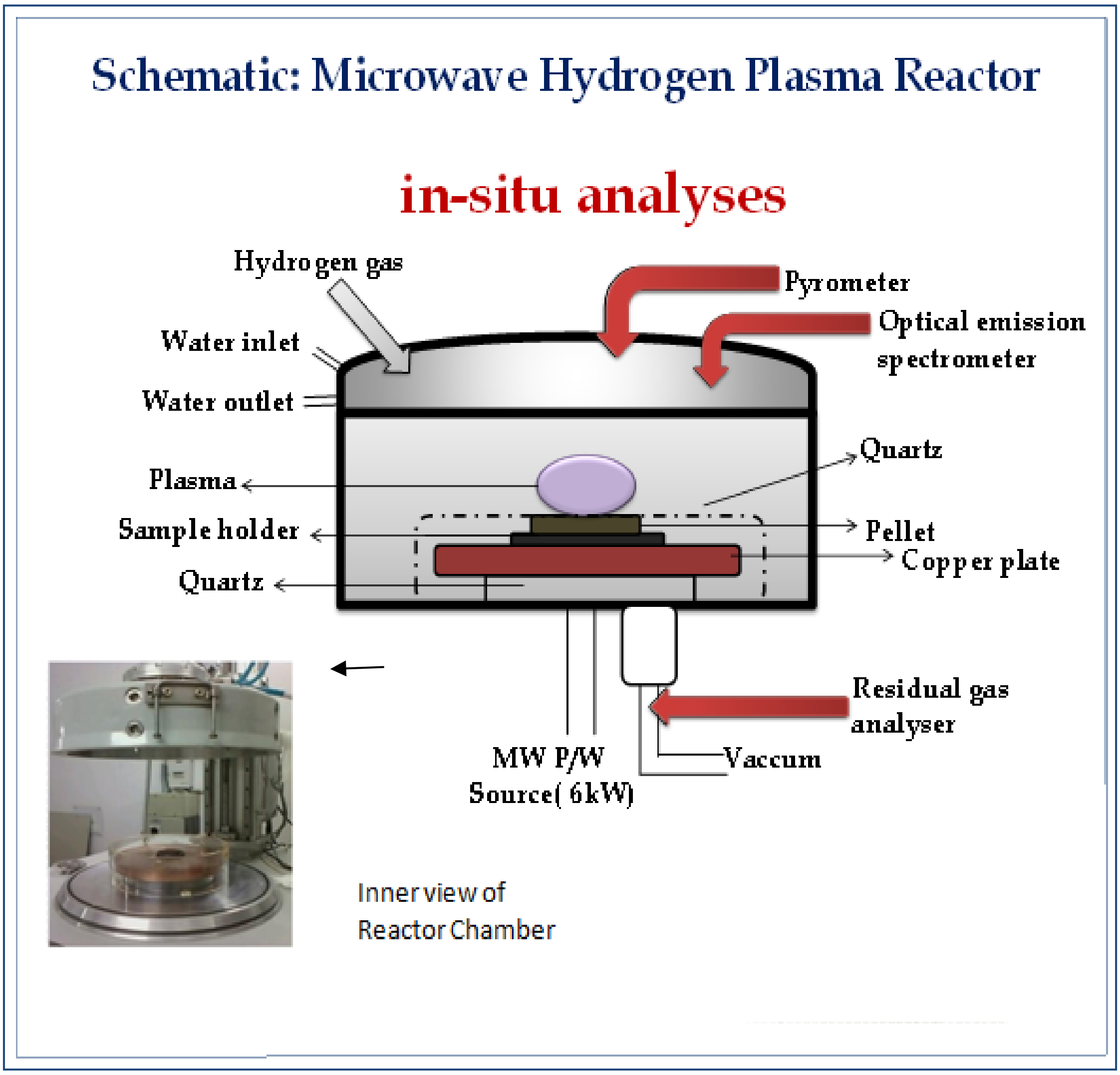

Figure 2. Schematic Diagram of Microwave Hydrogen Plasma Reactor with in-situ photograph of Reactor Chamber.

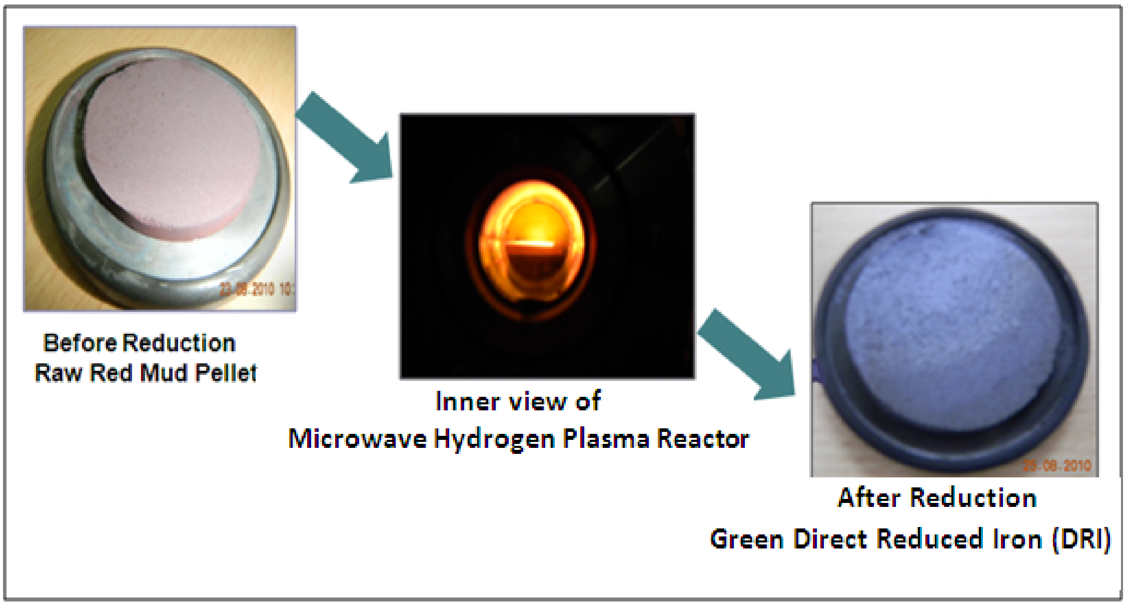

Figure 3. Microwave Hydrogen Plasma Reduction of Raw Red Mud pellet for production of Green Direct Reduced Iron (DRI).

4. Results and Discussions

There is no doubt that hydrogen can be used as a reducing gas in direct reduction processes. A careful analysis of the literature shows that iron oxides can be reduced by hydrogen gas and in this contest, a series of relevant reactions are as follows:

$3Fe_2O_3 + 3\ H_2 = 2\ Fe_3O_4 + 3\ H_2O$ ---------- (1)

$w/(4w\text{-}3)Fe_3O_4 + H_2 = 3/(4w\text{-}3)Fe_wO + H_2O$ ---------- (2)

$Fe_wO + H_2 = w\ Fe + H_2O$ ---------- (3)

$Fe_3O_4 + 4\ H_2 = 3Fe + 4\ H_2O$ ---------- (4)

$2H_2 + O_2 = 2H_2O$ ---------- (5)

$2Fe + O_2 = 2FeO$ ---------- (6)

$4H + O_2 = 2H_2O$ ---------- (7)

$4H^+ + 2O^{2-} = 2H_2O$ ---------- (8)

It has been shown that molecular hydrogen is a good reductant for iron oxides, which follows the reactions (1)-(3). In these reactions, w is the atomic ratio of iron to oxygen in wüstite and is known to vary from 0.95 along the wüstite-iron boundary to 0.85 along the wüstite-magnetite boundary. Bellow 833K wüstite is unstable and hence magnetite is reduced directly to metallic iron as per reaction (4). It is also known that reactions (2) & (3) are endothermic at any temperature, whereas reaction (1) is weakly endothermic in the temperature range 827- 913K and exothermic at other temperatures.

Figure 4 presents the Ellingham-Richardson Diagram showing the reducing potential of hydrogen (5) in comparison to other reactions, is transformation of FeO to Fe as shown in reaction (6). As seen from Figure 4, molecular hydrogen reduced Fe_2O_3 and Fe_3O_4 quite easily, though ΔG^o values for reactions (5) & (6) are much closer. However, it is also seen from the Figure 3 that ΔG^o values for reactions (7) & (8), involving atomic and ionic hydrogen species respectively, are very high and negative in comparison to reaction (5), which involves molecular hydrogen. The two species H and H^+ are provided by the plasma. In other words, in the plasma state, both H and H^+ can coexist. In hydrogen plasma smelting reduction process, these plasma states of hydrogen do also exist for production of iron [5 – 10].

Keeping these in view, efforts were directed for production of Green DRI from the Red Mud of Indian origin which contains good amount of iron oxide using Microwave Hydrogen Plasma Reactor. Experiments were conducted to ascertain the possibility of reduction of iron oxide present in Red Mud in to iron using various experimental parameters. The results were shown in Table 2.

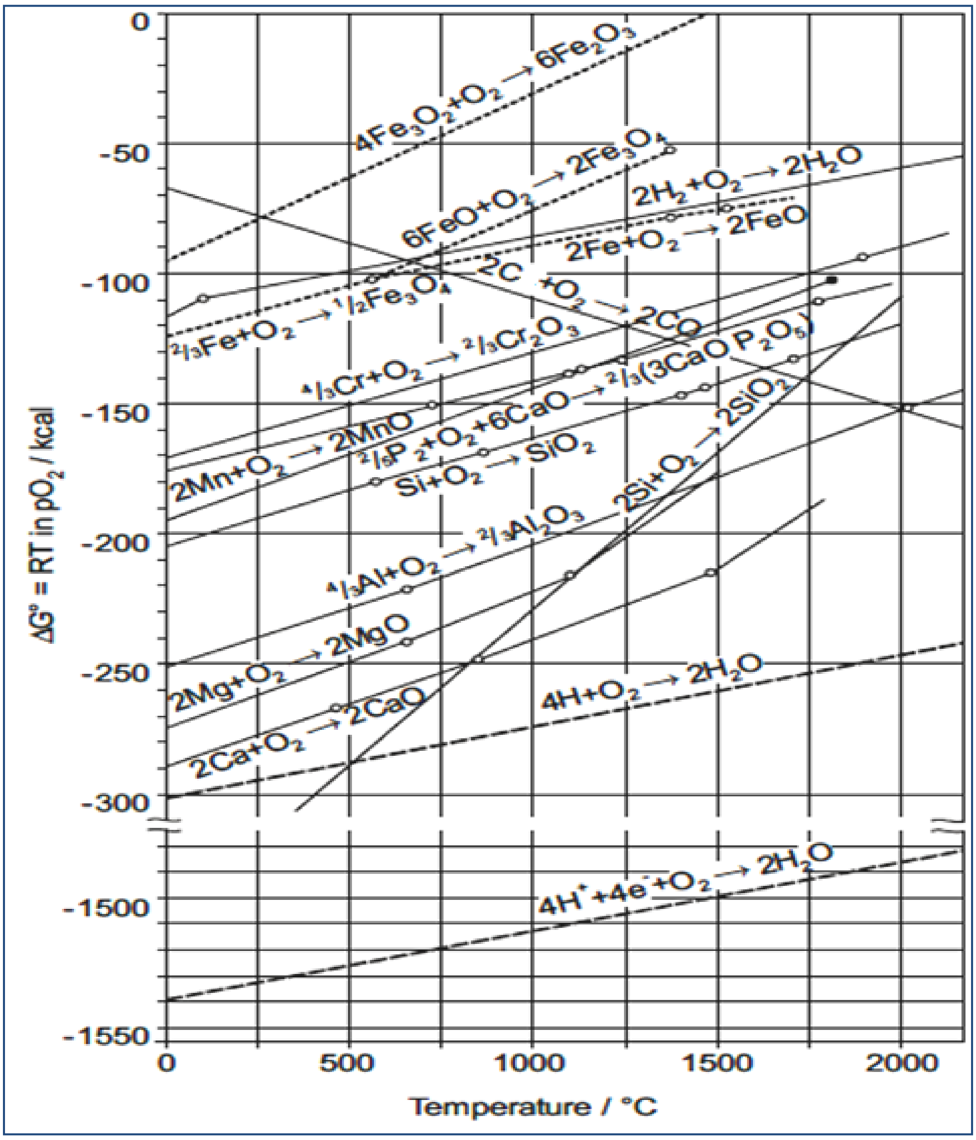

Figure 4. Ellingham-Richardson Diagram.

4.1 Effect of Time

The hydrogen gas starts reacting with the iron oxide present in the Red Mud Pellet from the surface itself and gradually it penetrates inside the body of the pellet for which reduction time plays an important role. The experiments were carried out at various reduction time intervals keeping other parameters constant as shown in Table 3. From Table 3, it is observed that the percentage reduction of iron oxide present in Red Mud Pellet into iron increases with increase in time and at 120 minutes, it becomes 98.23 % and that too at a low temperature of 300°C. Further, the XRD results at Figure 5 indicate that how over the passage of time, the iron peaks gets prominence and its presence is established.

Table 3. Reduction of compacted Red Mud Pellet by Microwave Hydrogen Plasma at various time intervals (Temperature: 300°C, Microwave Power: 750W, Pressure: 5.33 X 10^3 Pa, Hydrogen Flow Rate: 3.33 x 10^{-6} m^3s^{-1}).

Sl.No	Time (min)	Initial weight (g)	Final weight (g)	Reduction (%)
1	15	15.023	14.170	20.18
2	30	15.015	13.150	45.69
3	45	14.910	12.460	64.30
4	60	14.910	12.210	70.56
5	120	14.920	11.210	98.23

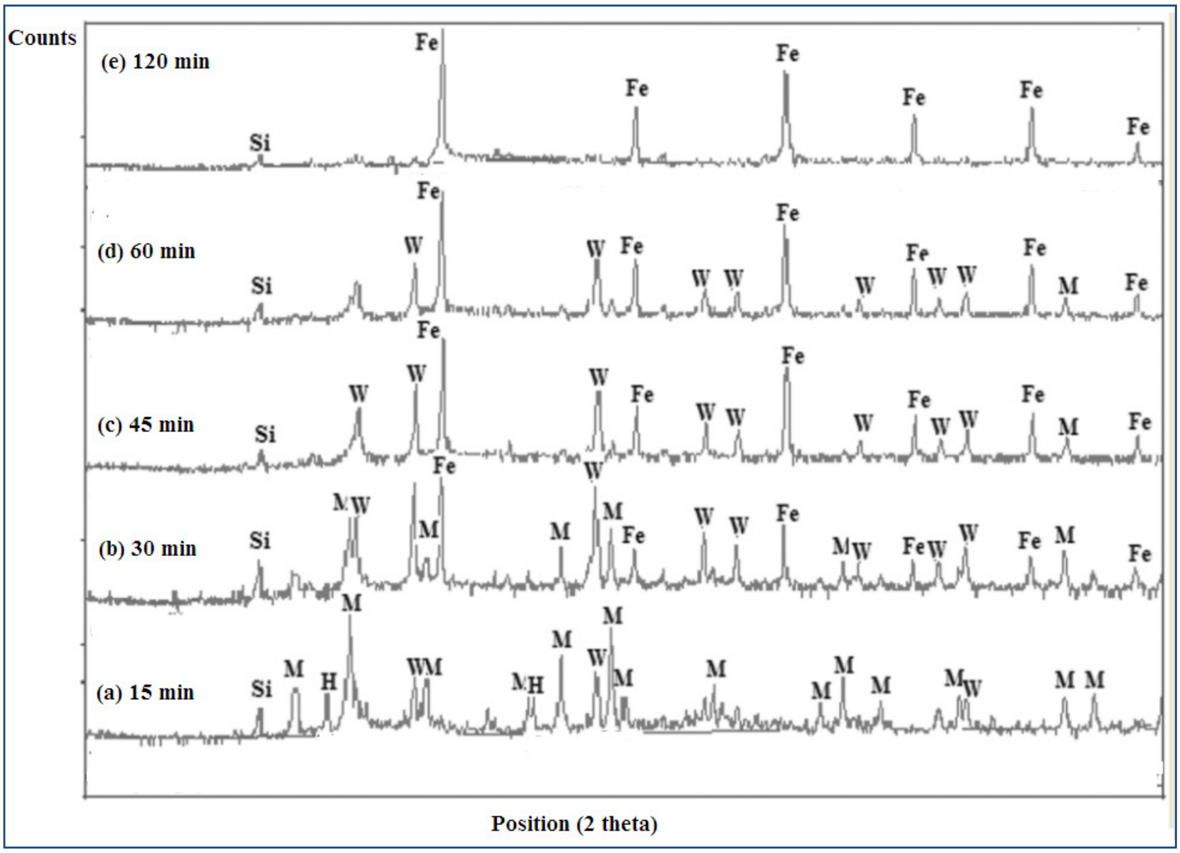

Figure 5. XRD Diffraction plots for Red Mud Pellet reduced by Microwave Hydrogen Plasma at various time intervals.

4.2 Effect of Temperature

As seen in Table 3, even at a low Temperature of 300°C, a percentage reduction of 98.23 was achieved at a time interval of two hours duration. Accordingly, further experiments were carried out to see both the effect of temperature and time on percentage reduction of iron oxide present in Red Mud pellet. The results obtained from these studies are shown in Table 4 , which indicates that percentage of reduction of iron oxide present in Red Mud Pellet increases from 70.56 to 99.3 with increase in temperature from 300 to 800°C keeping reduction time 60 minutes as constant. From the results of Table 3 and Table 4, it can be derived that percentage reduction of iron oxide is faster at a higher temperature (800°C) than at 300°C. It may be because of the fact that more and more of excited hydrogen species are taking part in the reduction process as temperature gradually increases. The XRD results indicate the prominence of iron peaks with variation in temperature (Figure 6).

Table 4. Reduction of compacted Red Mud Pellet by Microwave Hydrogen Plasma at various Temperatures (Time: 60 min, Microwave Power: 750W, Pressure: 6.66 X 10^3 Pa, Hydrogen Flow Rate: 3.33 x 10^{-6} m^3s^{-1}).

Sl.No	Temperature (°C)	Initial weight (g)	Final weight (g)	Reduction (%)
1	300	15.023	14.170	70.56
2	450	15.015	13.150	89.7
3	600	14.910	12.460	91.6
4	800	14.910	12.210	99.3

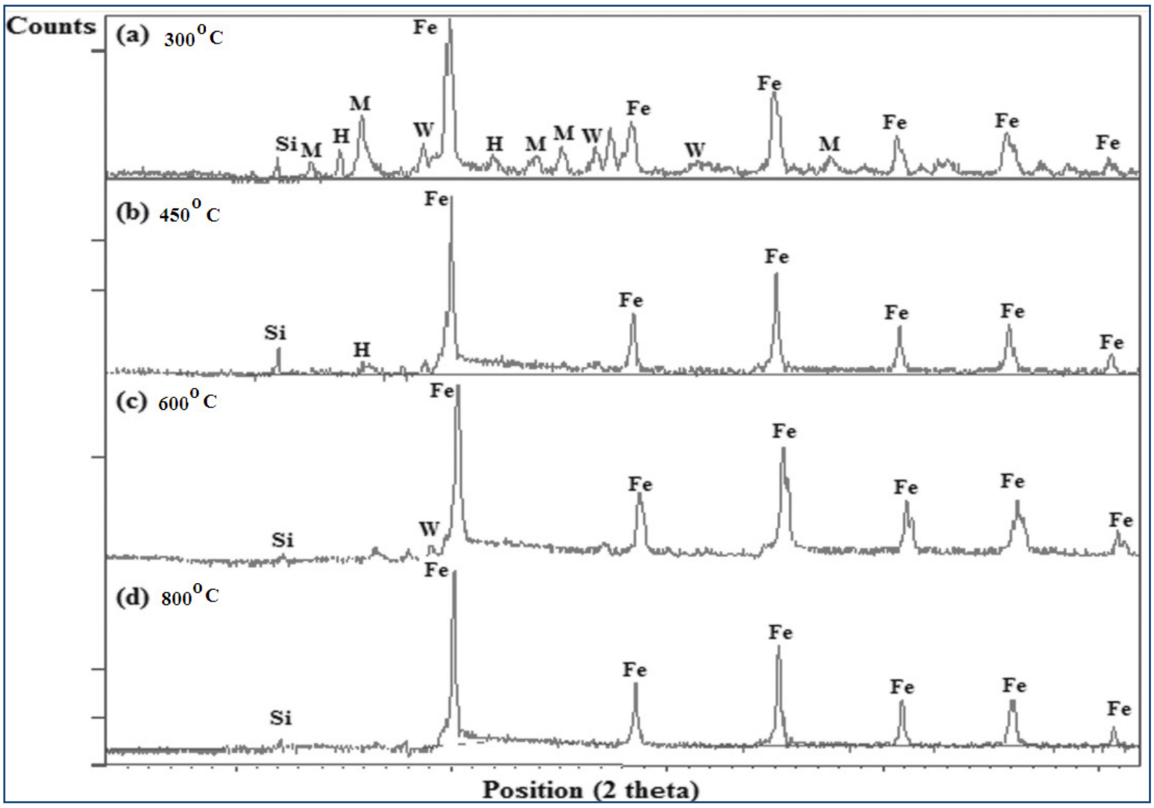

Figure 6. XRD Diffraction plots for Red Mud Pellet reduced by Microwave Hydrogen Plasma at various temperatures.

5 Eco-friendly Process

The conventional process of iron making through DRI route has limitations. It requires higher temperature of around 1200°C to convert iron oxide in to metallic iron. In the other hand, the present process needs low temperature of around 300°C only to carry out the reduction and is more energy and cost effective. Furthermore, the process is green in character as it is carbon free and environmental friendly and generates 'water' in the process as a by-product which can be recycled when used in the commercial process.

6 Conclusion

From the above experimental evidences and observations, it can be concluded that Red Mud containing around 53.6% Fe_2O_3 and some appreciable quantities of Al_2O_3 and other associated metal oxides in minor quantities, can very well be reduced to Green DRI by application of Microwave Hydrogen Plasma technology.

The process has been successfully established in the laboratory scale and needs to be scaled up to pilot scale of operation before its commercial feasibility is established. CSIR-IMMT, Bhubaneswar, Odisha, India is in possession of laboratory scale technology for production of Green DRI from Red Mud of Indian origin and the know-how is readily available for commercial exploitation.

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