Processing of red mud by low temperature microwave hydrogen plasma for production of iron: An eco-friendly technology

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Abstract

Red mud is produced in huge quantities during the processing of bauxite for the production of alumina. So far, few economically attractive processes have been developed for bulk utilization of red mud. Researchers are trying to develop interesting processes and products from this waste material; success achieved so far is restricted to laboratory, pilot scale, isolated or minor volume utilization applications and processes. Red mud of Indian origin contains around 45 – 55 % Fe_2O_3, 11 % TiO_2, 20 % Al_2O_3, 9 % SiO_2 and other associated oxides in minor quantities. Iron being the major component, bulk utilization of red mud will be difficult without an economically and technically viable process being developed for the production of iron from red mud. Indian iron ore containing 45 % Fe_2O_3 is considered as the cut-off grade for the economic production of iron. Accordingly, red mud of Indian origin can be considered as a low grade iron ore. The present study examines the processing of Indian red mud by Low Temperature Hydrogen Plasma for the production of iron in eco-friendly manner at laboratory scale. The iron produced contains 95 % Fe with low carbon and sulphur. Water, which can be recycled, is produced as a by-product of the process.

Key words: Red mud; hydrogen reduction; microwave hydrogen plasma reactor; iron from red mud.

1 Introduction

Red Mud is a byproduct generated during the processing of bauxite with caustic soda utilizing the Bayer process. It is considered as a hazardous material and till today few economically interesting applications or processes have been developed for its bulk utilization. Researchers have tried to produce pig iron from Red Mud by the application of plasma smelting technology [1], production of pig iron and portland slag cement from red mud by application of novel thermal plasma technique [2], production of ordinary Portland cement (OPC) from Red Mud [3], and processing of Red Mud for the production of wood substitute materials [4]. All efforts in this direction have so far been restricted either to laboratory or pilot scale processes. Iron oxide is a major constituent of Red Mud and for this reason it can very well be considered as a low grade iron ore. Red mud of Indian origin contains around 45 – 55 % Fe_2O_3, 11 % TiO_2, 20 % Al_2O_3, 9 % SiO_2 and other associated oxides in minor quantities. The quantum of generation of Red Mud by the alumina industries all over the globe warrants its gainful utilization in bulk quantities. An important option available presenting to researchers is extraction of iron from Red Mud in a most eco-friendly manner.

The reduction of Fe_2O_3 present in Red mud to metallic iron can be achieved either by Carbothermic or Hydrogen reduction processes. The Carbothermic reduction process involves a Blast Furnace route for production. However, this process is not free from pollution and emits large quantities of carbonaceous gases which add to global warming. It has been estimated that for production of one tone of iron, around three tones of green house gases are generated. Under the circumstances, industry have few other alternatives but to follow an eco-friendly (and lower energy cost) path way for production of iron through a Hydrogen reduction process. Researchers elsewhere have tried to produce metallic iron from iron ore employing the Hydrogen reduction process by using hydrogen gas as reductant in a high temperature furnace [5]. This process has limitations, such as it being a time consuming process associated with low yield and moreover, consumption of hydrogen gas was also increased.

The answer to this challenge lies with the state-of-the-art technology for production of metallic iron from iron ores by application of the low temperature Microwave Hydrogen Plasma Reduction route. Through this route, iron was extracted successfully from iron ores as Direct Reduced Iron [6].

Once researchers successfully accomplished such an eco-friendly reduction process, the process know- how was then suitably replicated for production of iron from Red Mud through application of a Low Temperature Microwave Hydrogen Plasma Reduction Process using hydrogen gas as a reductant. The product so obtained contains 95% Fe with low carbon and sulphur. The process is eco-friendly and free from carbon. Moreover, 'water' is generated in the process as a by-product which can be recycled when commercially used.

2 Raw Materials

The Red Mud of Indian origin was used as principal raw material for the study. The mineralogical composition and chemical analysis of Red Mud are furnished in Figure 1 and Table 1 respectively. The other raw materials used for the study were Hydrogen gas of 99.9% purity and Argon gas.

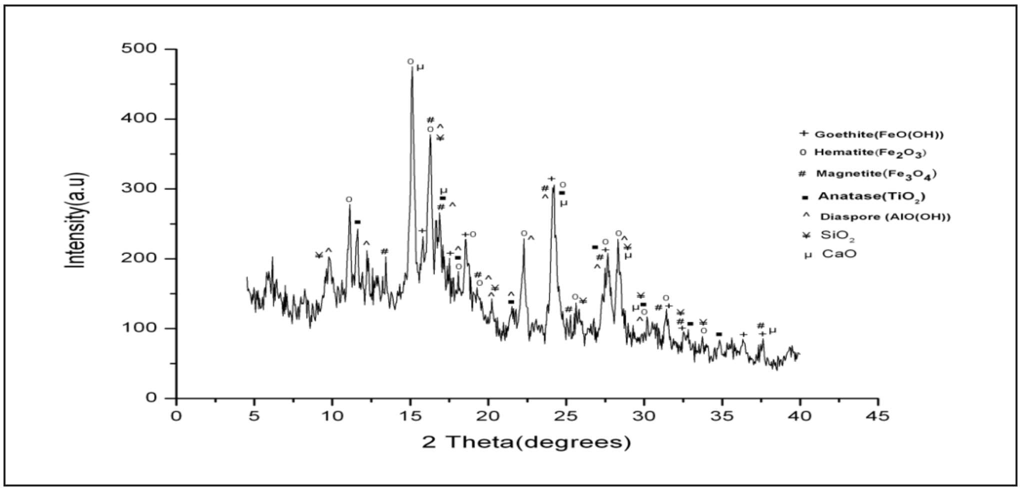

Figure1. Mineralogical Composition of Red Mud of Indian Origin.

Table 1. Typical chemical analysis 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

A Red Mud sample was subjected to crushing and grinding to bring the size to -100 mesh which was then pelletized to 40 mm diameter and 3 mm 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 ^oC for 2 hours. 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 the iron content in Red Mud to produce direct reduced iron (DRI). The raw materials and the products were analyzed for their chemical compositions and mineralogical characters. The reduction studies were carried out as per the process flow sheet given in Figure 2.

3.1 Microwave Hydrogen Plasma Reduction Process

The reduction of the raw Red Mud pellet to produce DRI was carried out in a specially built Microwave Hydrogen Plasma Reactor of 6kW power. The plasma is generated by Microwave assisted thermal plasma process. The Schematic Diagram of Microwave Hydrogen Plasma Reactor with in-situ photograph of the Reactor Chamber is shown in Figure 3**.** 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 temperatures. 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 6 to 8 cm 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 return immediately to hydrogen molecules when they exit from the plasma zone.

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 the 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 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. Table 2 describes the chemical analysis of the reduced red mud pellet. The schematic diagram of the process know how employed is given in Figure 2.

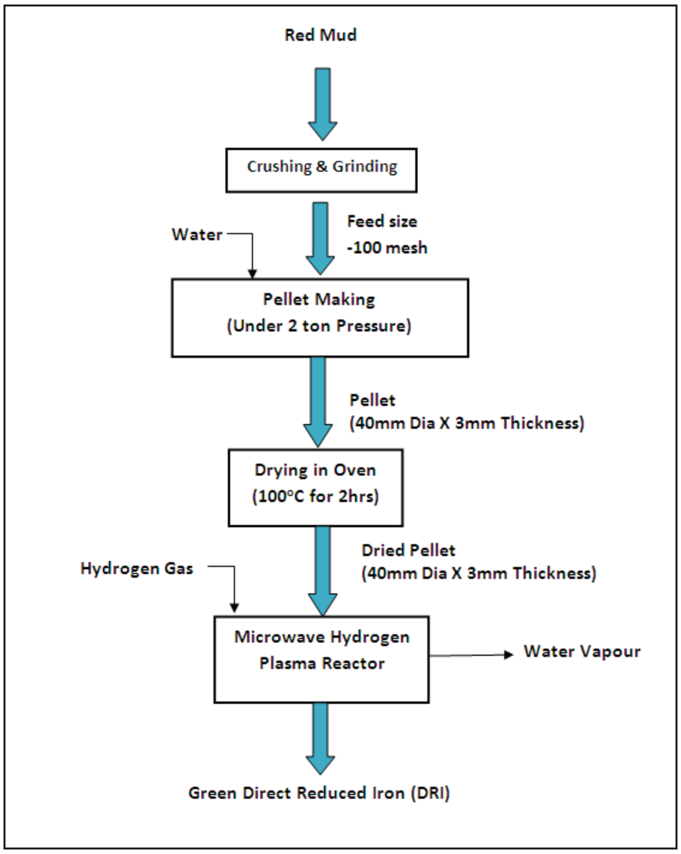

Figure 2. Process flow sheet for the production of green direct reduced iron (DRI) from red mud.

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

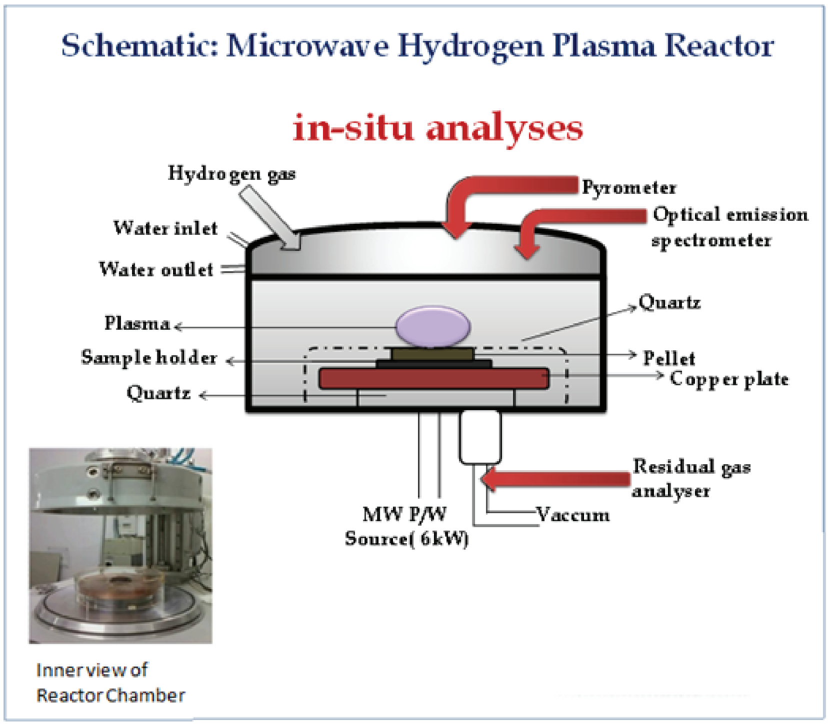

Figure 3. Schematic diagram of microwave hydrogen plasma reactor

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:

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

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

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

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

$$2H_2 + O_2 = 2H_2O \quad (5)$$

$$2Fe + O_2 = 2FeO \quad (6)$$

$$4H + O_2 = 2H_2O \quad (7)$$

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

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. Below 833 K wüstite is unstable and hence magnetite is reduced directly to metallic iron as per reaction (4). It is also known that reactions (2) and (3) are endothermic at any temperature, where as reaction (1) is weakly endothermic in the temperature range 827- 913 K and exothermic at other temperatures.

Figure 4 presents the Ellingham-Richardson Diagram showing the reducing potential of hydrogen (5) in comparison to other reactions, its transformation of FeO to Fe as shown in reaction (6). As seen from Figure 4, molecular hydrogen reduces 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 the hydrogen plasma smelting reduction process, these hydrogen plasma states do also exist for production of iron [7 - 9]. Keeping these in view, efforts were directed at the production of iron from the red mud of Indian origin using the Microwave Hydrogen Plasma Reactor, using various experimental parameters. The results were shown in Table 2.

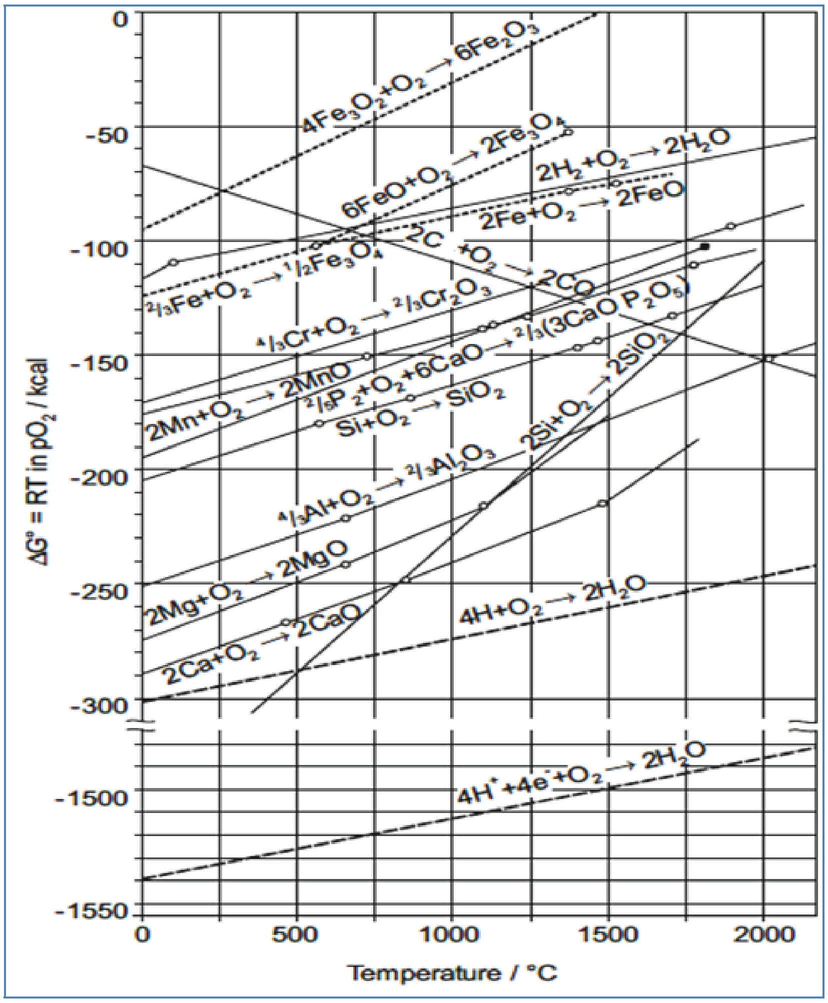

Figure 4. Ellingham-Richardson- Diagram.

4.1 Effect of time

The hydrogen gas starts reacting with the iron oxide present in the red mud pellet from the surface and gradually penetrates 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 this table, it is observed that the percentage reduction of iron oxide to iron present in Red Mud Pellet increases with increasing time. At 120 minutes, reduction is 98.23 %, and that at a low temperature of 300 °C. The XRD results in Figure 5 indicate that over time, the iron peaks become prominent, 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: 750 W, Pressure: 5.33 kPa, 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

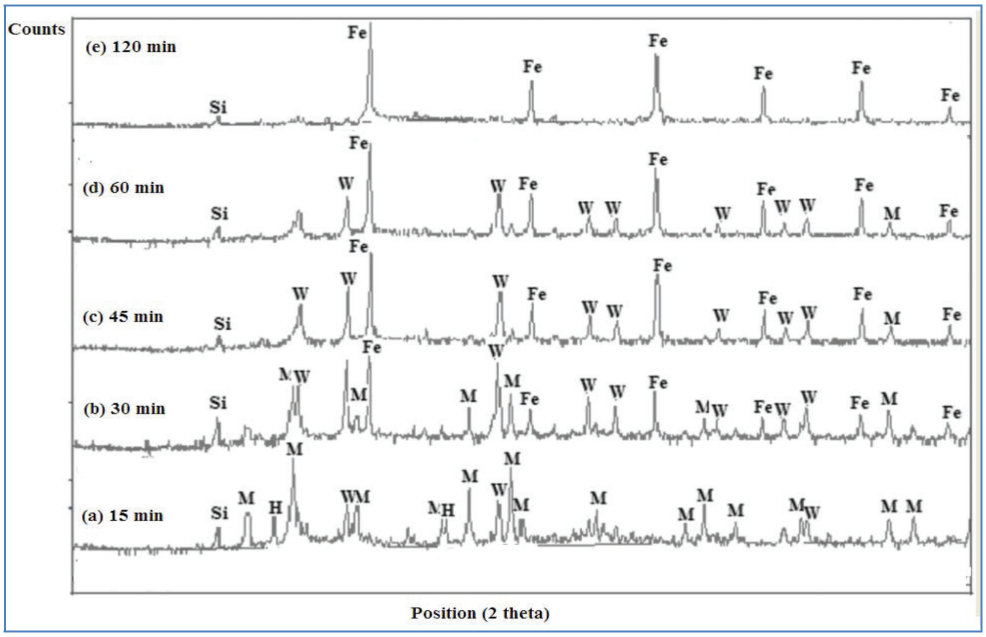

Figure 5. XRD Diffraction plots for red mud pellet reduced by Microwave Hydrogen Plasma at various time intervals.

4.2 Effect of temperature

As seen in Table 3, even at a low Temperature of 300 ^oC, 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 the red mud pellet. The results obtained from these studies are shown in Table 4 , which indicates that the percentage reduction in the pellet increases from 70.56 to 99.3 with increase in temperature from 300 to 800 ^oC, keeping reduction time a constant 60 minutes. From the results of Tables 3 and 4, it can be concluded that the percentage reduction of iron oxide is faster at a higher temperature (800 ^oC) than at 300 ^oC. 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: 750 W, Pressure: 6.66 kPa, hydrogen flow rate: 3.33 x 10 $^{-6}$ m^3s^{-1}).

Sl.No	Temperature (^oC)	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

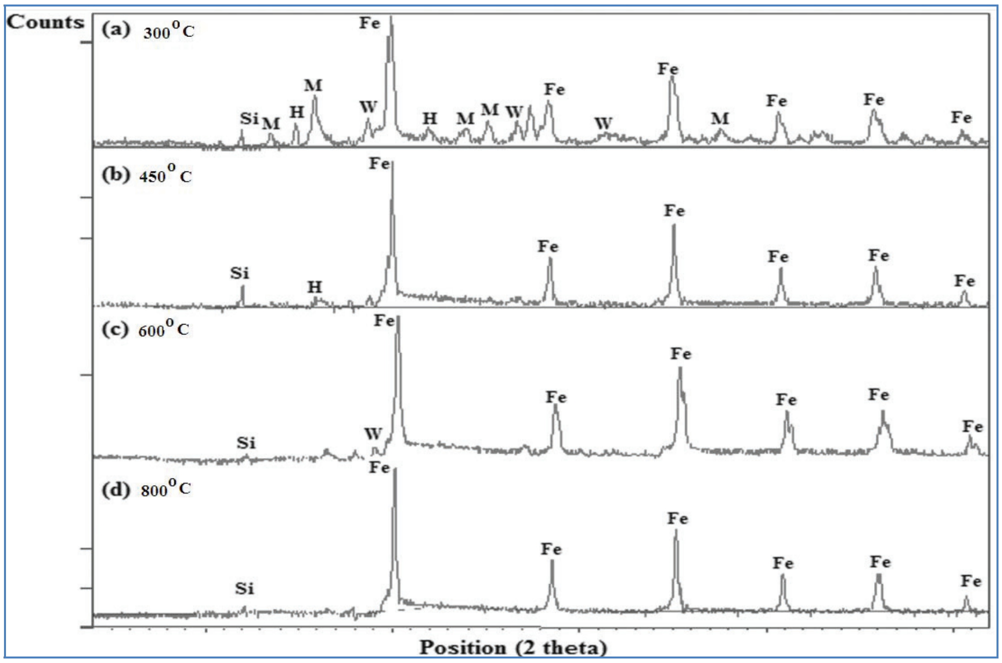

Figure 6. XRD Diffraction plots for Red Mud Pellet reduced by Microwave Hydrogen Plasma at various temperatures.

4.3 Reaction mechanism at the surface of the red mud pellet

In the Microwave Hydrogen Plasma Reactor, the hydrogen gas passes from the top of the reactor through the plasma zone and comes in contact with the surface of the Red Mud pellet. At the surface of the pellet, the gas-solid reaction takes place. Figure 7 indicates the path way of the reaction mechanism from raw red mud pellet to iron. In the context of gas-solid reaction, in addition to ionic and atomic species of hydrogen, the role of vibrationally excited hydrogen molecules has also been emphasized in the literature [2]. It has been reported that vibrationally excited hydrogen molecules stimulate the chemical process through their surface dissociation and diffusion of hydrogen atoms into the crystal structure of iron oxide present in Red Mud pellet. The experimental data of P. Rajput et al [2] provide evidence to the presence of vibrationally excited hydrogen molecules. Therefore, similar reaction mechanism may also be happening at the surface of the red mud pellet for the production of iron. Accordingly, it can be concluded that vibrationally excited hydrogen molecules are probably the species responsible for reduction of iron oxide present. Another alternate possibility may be the contribution of the atomic and ionic species of hydrogen plasma as a catalyst to drive reduction of iron oxide in the pellet. However, more studies are required to obtain further insight with respect to reaction mechanism at low temperature.

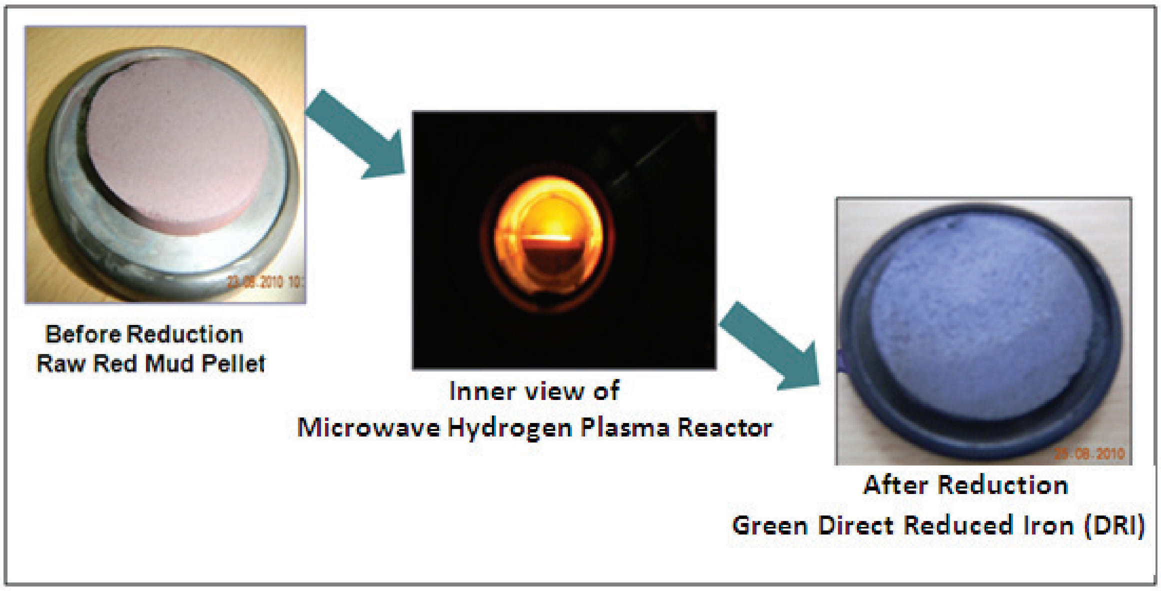

Figure 7. Microwave Hydrogen Plasma Reduction of raw red mud pellet for production of Green Direct Reduced Iron (DRI).

5 Eco-friendly Process

The conventional process of iron making through DRI route has limitations. It requires a high temperature of around 1200 ^{o}C to convert iron oxide in to metallic iron. The process presented here on the other hand, needs only a temperature of around 300 ^{o}C to carry out the reduction and is more energy and cost effective. The process is green in character as the central process 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. Conclusions

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 iron by the application of Microwave Hydrogen Plasma technology.

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

7 Acknowledgement

The authors are grateful to Prof. (Dr.) B. K.Mishra, Director, CSIR-IMMT, Bhubaneswar for his cooperation and guidance in the R&D work and giving permission for publication of the paper. The authors are also grateful to the Indian aluminium industries for providing Red Mud samples for carrying out the investigation.

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