

UTILISATION OF INDUSTRIAL AND DOMESTIC WASTES FOR SUSTAINABLE DEVELOPMENT IN IRON AND STEEL SECTOR

A Thesis submitted in partial fulfillment of the requirements for the award of degree of

MASTER OF ENGINEERING IN METALLURGICAL ENGINEERING

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Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature review and original research work by the undersigned candidate, as part of his *“Utilization of Industrial and Domestic Wastes for Sustainable Development in Iron and Steel Sector”* studies.

All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

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ABSTRACT

The demand of Iron and Steel is expected to grow as forecasted by Ministry of Steel. To fulfill this high demand of Iron and Steel in future the resources like Iron Ore, Coal and other minerals will also be high and thus the mineral reserves will be depleted at an alarming rate. So to ensure Sustainable Development in Iron and Steel sector the consumption of mineral reserves needs to be reduced by utilizing the huge amount of wastes generated from an Integrated Steel Plant. An attempt has been made in this direction and some wastes containing high Iron values were first identified by characterization of the waste samples. Plant wastes like BF Flue Dust and Air Cleaning Plant Dust (ACP) are taken to extract the metal values present in them. The mineral values present in BF Flue Dust are utilized by mixing it with Raw Hematite and Raw Magnetite. This Endeavour leads to a considerable reduction in the amount of Raw materials consumed for production of Iron and Steel. The amount of Coal is also depleting at an alarming rate so an attempt has been made to use domestic waste as an alternative for reductant used in Iron and Steel plant. This will lead to a decrease in the consumption of Raw Materials and thus there will be a considerable reduction in the expenditure of the plant. The study of literature of Sugarcane Bagasse showed that it contains good amount of Carbon so an attempt has been made to use it as a potential reductant in Iron and Steel Plant. Lump Hematite Ore is reduced with variable amount of Sugarcane Bagasse and finally the Extent of Reduction is calculated.

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1. Introduction

1. Introduction:

1.1 Scenario of Steel Industry in India:

The Indian steel industry has shown a phenomenal growth in the last few decades. Steel is one of the most basic materials required for industrialization and plays a vital role in the country's economic development. India is lucky since it is endowed with natural resources required for a healthy and vigorous iron and steel industry. India is at present producing nearly [1]. With the liberalization of import tariff on finished steel items the Indian steel manufacturers are able to cut down the cost of production and is competing in the world market. Private industrialists are ready to invest in new steel projects.

Steel industry derives its demand from other important sectors like infrastructure, aviation, engineering, construction, automobile, pipes and tubes etc. With the Indian economy poised for its next wave of growth under the reforms being unleashed in the last one year, there lies tremendous opportunity for the Indian steel industry to prosper and grow exponentially. The steel sector contributes nearly 2% of the country's GDP and employs over 6 lakh people [2]. The per capita consumption of total finished steel in the country has risen from 51 kg in 2009-10 to about 60 kg in 2014-15 and 64 Kg in 2016-17.

A look at the past production figures over the last century attests a significant shift in the geography of Steel making. In 1990, USA was producing 37% of the world steel as against 14% at present. With post war industrial development Asian production now accounts for almost 40%, Europe (including the former Soviet Union) for 36% and North America for 14.5% [3]. Since the late 1960s there has been a leveling off of the rate of growth in steel production, which is partly attributable to greater efficiency in the use of steel and less wastage. Progress in steel making is also indicated from the use of Bessemer converter at the turn of the 19th century to the introduction of oxygen conversion processes in the 1950s and continuous casting in the 1960s. Steel is one of the most recycled non-expendable industrial materials recycled. Material is used in all steel production. Even after decades of use, steel is salvaged and over 40% of steel production is based on recycled material including scraps.

The major steel producers in India are SAIL, TISCO, RNIL, Essar, Ispat Alloy, Jindal Lloyds and Usha Group.

The seven integrated steel plants are:-

- (1)Tata Steel Company
- (2) Bhilai Steel Plant (BSP)
- (3) Bokaro Steel plant (BSL)
- (4)Rourkela Steel Plant (RSP)
- (5) Indian Iron &Steel Company (IISCO)
- (6) Vishakhapatnam Steel Plant (VSP)
- (7)Durgapur Steel Plant (DSP)

1.2 Environmental Management:

Iron and steel industry which comprises, mining of ores, preparation of raw materials, agglomeration of fines in sinter plant, feeding of burden to blast furnace, manufacturing of coke in coke ovens, conversion of pig iron to steel, making and shaping of steel goods, granulation of slag for its use in cement plant, recovery of chemicals from Benzoyl and tar products etc. All the above mentioned operations add to air, water, land and noise pollution [4]. The steel plant slag mainly includes blast furnace slag and steel melting slag (LD process slag). LD slag is a by-product of steel making which comes from pig iron refining process using LD converters and one of the important waste materials in all integrated steel plant. In India the steel melting slag is over 4 million tonne per annum. The amount of steel slag from different steel industries is 150-180kg/t. The total generation per annum is 1.28 million tonne in Steel Authority of India (SAIL), about 0.98 million tonne in Tata Steel. The slag contains variable substances like CaO, Fe and Mn. CaO is an important oxide present in the LD slag which can be used as flux material instead of lime. The blast furnace slag has a long term market in construction and fertilizer industries; Whereas LD slag is not suitable due to high phosphorus content. Till date only 40-50% of LD slag is possible to recycling in India. If removal of phosphorus is possible, LD slag can be recycled in steel making as a flux material. Use of this LD slag not only replace the lime but also avoid heat loss for calcination of limestone. Therefore, the removal of phosphorus from LD slag by reducing not only steel making cost but also the disposal cost. The main co-products from iron and crude steel production are slag, dust, scrap and sludge.

1.3. Waste Generated in Steel Industry: Causes & Effects:

1.3.1. Causes of Waste Generation:

Production of Steel Involves several operations. It starts from naturally occurring raw materials like coal, iron ores & fluxes to produce hot metal in blast furnace, convert hot metal into steel and subsequently to go for rolling of steel into finished product. Several other activities including production of refractory are also performed in varying magnitude inside the steel works. A large

quantity of waste is generated as a sequel to such Activities. To make one-tonne of crude steel even with good raw materials and efficient operation, 5 tonnes of air, 2.8 tonnes of raw materials and 2.5 tonnes of water are required. These will produce in addition to 1 tonne of crude steel, 8 tonnes of moist laden gases and 0.5 tonne of solid wastes [Lean, 1990]. However, in SAIL plants, this figure varies from 820-1,200Kg/tonne of crude steel which is very high [Prothia and Roy, 1993]. In a steel industry, all the three types of waste materials (gaseous, liquid and solid) are generated. The generation of gaseous waste material is the highest but the management of solid waste material is the most intricate. The steel plants of the seventies were characterized by higher waste generation rates associated with massive dumps around the steel works resulting in serious land, water and air pollution.

Over the years, due to technological changes in steel making and strict environmental regulations and legislation emphasis on raw material quality and emergence of new markets coupled with innovative ideas of waste reduction and rescue have resulted in drastic reduction in the quantity of waste generated in steel works from 1,200 Kg to less than 200 Kg per tonne of crude steel and recycling rates have reached 95-97% in some parts of the world [5]. However, the solid waste generation presently in Indian steel industry is in range of 600-1,200 Kg/tonne of crude steel and recycling rate varies between 40- 70% which lead to higher production costs, lower productivity and further environmental degradation. Types of solid wastes generated in an integrated steel plant is shown in Fig 1.1

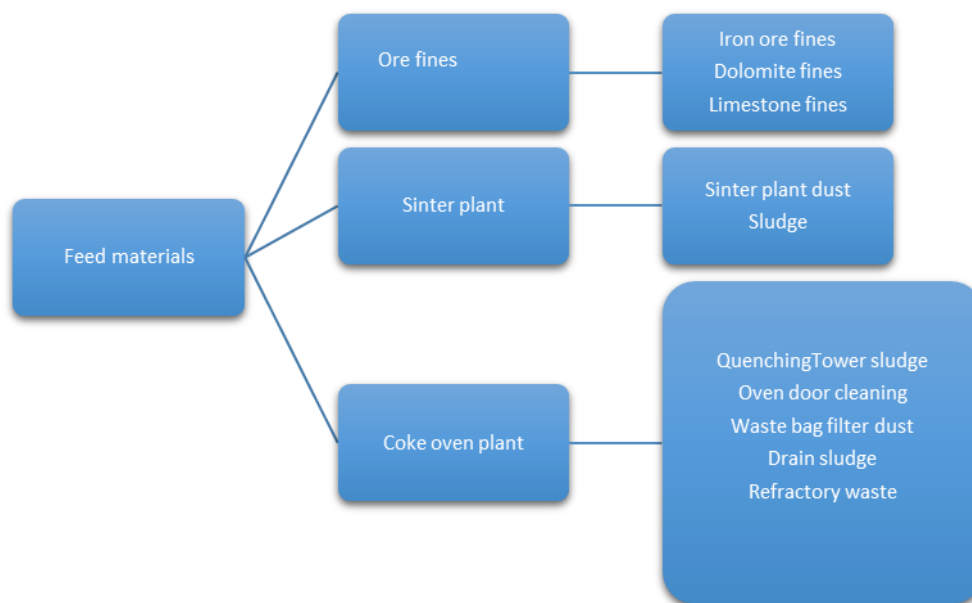


Fig 1.1: Types of Solid Wastes Generated in an Integrated Steel Plant

The generation quantity of various types of waste materials differ from one steel plant to another depending upon the steel making processes adopted and pollution control equipment installed. Generation of major solid wastes from process units and pollution control equipment in case of SAIL (Steel Authority of India Limited) as a whole vis-à-vis other developed countries is given in Fig 1.2.

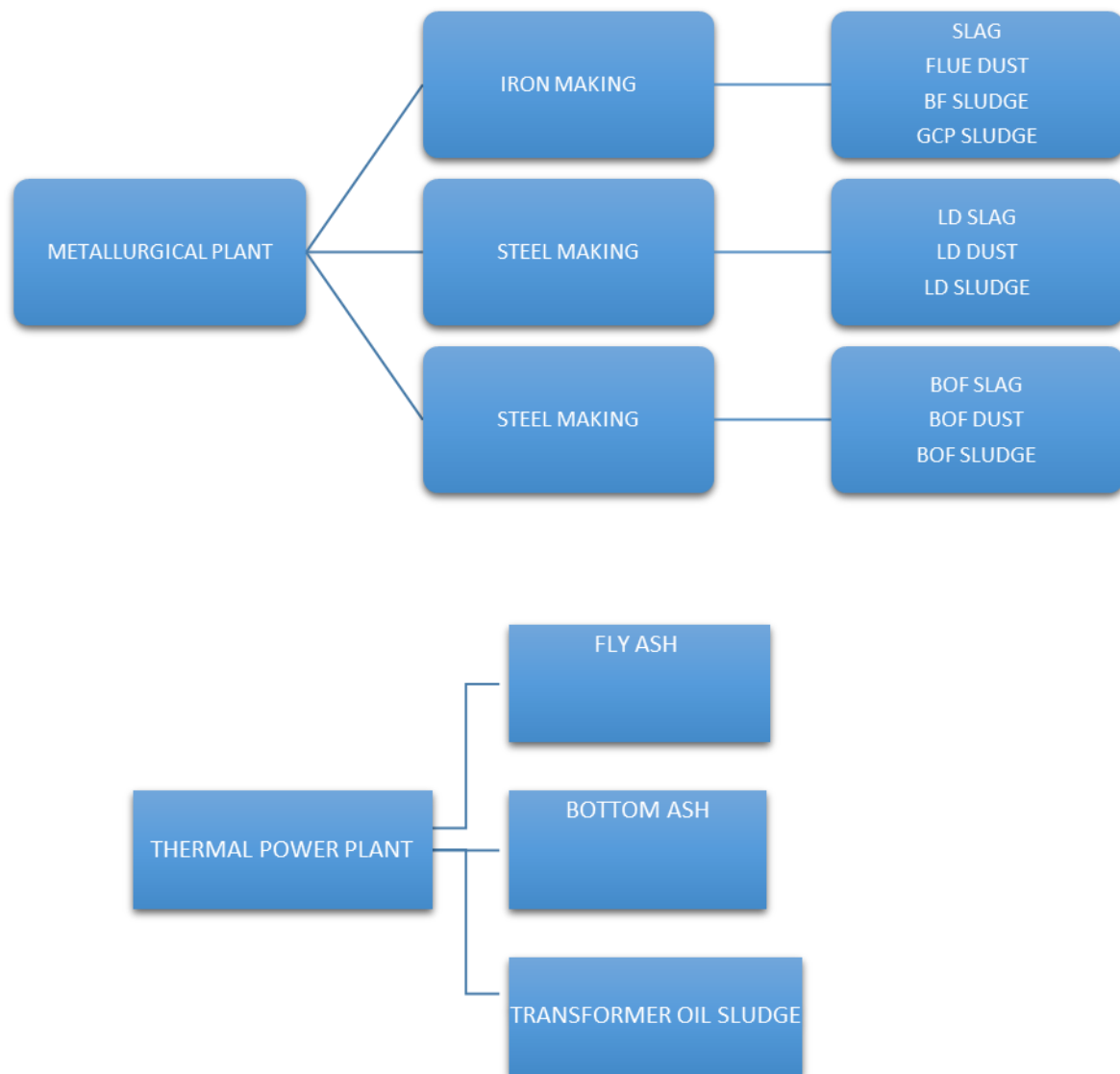


Fig: 1.2 Major Solid Wastes from SAIL Plant

1.3.2. Effects on Environment:

The process of industrialization and continuous exploitation of earth resources for sustainable growth of civilization has depleted the non-renewable resources of the earth thereby adversely affecting the environment.

An integrated steel plant unit exhausts several harmful dusts, fumes and substances that are quite injurious to human health, vegetation, crops, landscape, animals, machine life etc. Such discharges contaminate and damage inland waters, environment, soil, food, human settlement and even flora and fauna [4]. Therefore, these wastes could not be left uncared for and that is why threshold limits for such harmful substances have been fixed and industries are required to adhere to these norms.

The environmental impact due to steel production is given in Table 1.1

Sl No	Activities	Environmental Impacts
1	Mining	Dust generation, Air pollution, Noise pollution, Water logging
2	Melting & Refining	Dust generation, Air pollution, Noise pollution, Water logging
3	Casting	Air pollution, Noise pollution
4	Processing	Vegetation, Water pollution, Domestic Animals, Dental and Bone Damage

Table 1.1: Environmental Impact due to Various Activities in an Integrated Steel Plant [4]

1.4 Scope for Utilization of Various Wastes:

The different ways in which different wastes from an integrated iron and steel plant can be utilized is discussed below [6,7,8]: -

□ **Coke Making:**

The main solid wastes generated in the production of metallurgical coke are coal dust, coke dust, tar sludge and acid sludge. Coal dust is recycled back through the coal blend. Coal dust can also be recycled along with coke dust by adding them in the sinter charge mix. Tar sludge is added to the coal blend to improve its density. Acid sludge need to be neutralized before its disposal.

□ **Sinter Making:**

Solid wastes generated in the sinter making are dusts and sludges. Dusts are generated at sinter machine building floors, cyclones and ESP (Electrostatic precipitator). Sludge is generated at the clarifier of the water treatment plant. These dusts and sludges are rich in iron (Fe) and contain good amount of lime (CaO), magnesia (MgO) and carbon (C). These materials are very good materials for recycling back in sinter making. These materials are either blended with iron ore fines or briquetted for recycling.

□ **Pellet Plant:**

The major solid wastes generated in pellet plant are dusts and undersized green pellets. Both of these are recycled back in the pellet feed material.

□ **Blast Furnace Iron Making:**

Solid wastes generated during the Blast Furnace (BF) iron making process are dusts, burden screenings at the stock house, Blast Furnace Slag, Blast Furnace Flue Dust, GCP dust or sludge, Refractory Waste, and Hot Metal (HM) Ladle Skull.

Dusts and burden screenings are recycled back in sinter making.

Most of the BF liquid slag gets granulated and is sold to cement manufacturers for the manufacture of BF slag cement. A small amount of BF slag gets air cooled. The air cooled BF slag is either dumped as landfills or used in road repairs within the steel plant. In either case the iron contamination of the slag is separated and sold for re-melting.

Flue dust and GCP dry dust (in case of dry gas cleaning) are recycled in sinter making. GCP wet sludge (in case of wet gas cleaning) from the clarifier is dried and is either blended with the iron ore fines in the raw material yard or briquetted and recycled in sinter making.

Refractory waste from the ladle repair shop is sold and the same is used by the refractory manufacturer in the manufacture of mortars. HM ladle skull is broken either by dropping weight or by lancing and the broken skull is sold as iron scrap or used in steel melting shop.

□ **Iron Making by Direct Reduction:**

During the iron making process by direct reduction the main solid wastes are char (in case of plants using coal based technology), dusts (both coal and iron), under sized DRI (direct reduced iron) and DRI rejects. Char is used in captive power plant as fuel for the boiler. Coal and iron dusts are used in the sinter plants. Coal dust can also be used in the boiler. Iron dust can also be sold to the cement manufacturers. Under sized DRI is briquetted and used along with DRI in steel melting shop. DRI rejects are recycled back in the process.

□ **Pig Casting:**

During pig casting of hot metal, waste materials like plate jam, runner jam and lime sludge get generated. Plate jam and runner jams are sold as iron scrap after processing. Lime sludge is used for neutralizing purpose.

□ **Basic Oxygen Steel Making:**

The main waste materials in the BOF steel making are converter slag, scrap, waste refractories, converter muck, and gas cleaning plant (GCP) sludge. Except GCP sludge all other waste materials are usually generated in mixed condition which means that during generation one waste material gets contaminated with other waste material. Hence sorting is a very important step for recycling of the waste materials in steel making [7].

GCP wet sludge from the clarifier is dried and is either blended with the iron ore fines in the raw material yard or briquetted and recycled in sinter making.

Converter slag after removal of scrap is recycled in the sinter mix as a replacement for limestone. Converter slag is also used in road repairs, for railway track ballast, and as soil conditioner.

Scrap removed from converter slag as well as from the muck is recycled back in the converter for cooling purpose. Steel scrap also gets generated when there is ladle through or converter through though this phenomenon is very rare.

From converter muck scrap and refractory wastes are removed and balance is used for land fill.

Refractory wastes are usually of two types. First type is which comes out from used converter lining and mainly consists of magnesium carbon refractories. Most of these refractories which are not contaminated are used in the converter for the bottom patching. Second type is ladle refractory wastes. If these wastes are basic, then they are treated similarly to converter refractory wastes. In case they are of alumina then the refractory waste is used for mortar manufacture.

□ **Electric Steel Making:**

Main waste material in the electric steel making is EAF (electric arc furnace) GCP dust, slag, scrap and waste refractories. Magnesia carbon waste refractories are used as slag conditioner in the EAF.

Electric Arc Furnace (EAF) slag owing to its high and high iron content has presently no well-established method for potential recycling [9]. The basicity index (BI) of the slag is generally between 1.2-1.8 which comes under the low hydraulic Merwinite group. Also the Grindability Index, which is a measure for the energy required for grinding a particular material to a given size, is high due to high Iron oxide content. This makes the further grinding and processing of EAF slag energy intensive. The slag has been used as an effective aggregate for road making. Vitrified ceramic tiles have also been developed from the EAF slag.

□ **Continuous Casting:**

Major waste materials generated in the continuous casting process is continuous casting scale, refractory waste, scrap, slag and muck. Here also waste materials are generated in the mixed condition and sorting is needed as the first step for separating different types of wastes.

Continuous casting scale is recycled in sinter plant. Scrap is recycled in the steel making. Other waste materials are used as land fill.

□ **Rolling Mills:**

Major solid waste materials generated in rolling mills are mill scale, refractory waste from reheating furnace, and scrap.

Mill scale is recycled in sinter plant. Scrap is recycled in steel melting shop. Refractory waste depending on the condition either goes for mortar manufacture or is dumped.

□ **Lime Calcining:**

Solid wastes generated at the calcining plant are limestone and dolomite screenings, lime dust and lime fines. Lime dust and lime fines are briquetted and recycled either in sinter plant or steel melting shop. Limestone and dolomite screenings are recycled in the sinter plant.

□ **Thermal Power Plant:**

Major solid wastes generated at the power plant are the fly ash and bottom ash. Fly ash is utilized in the cement production. In some of the plant ash is sent to the ash pond. Ash recovered from the ash pond is utilized in raising the height of the dyke of the ash pond.

1.5 Solid Waste Management:

Waste management of solid wastes consists of generation, prevention, characterization, monitoring, treatment, handling, reuse and residual disposition. It requires a new attitude of the employees and management [13]. Traditional thinking places all the responsibility on a few experts who are in charge for it. The new focus is to make the waste management responsibility for every employee. Importance of solid waste management is what the production oriented managers and workers are to learn. For effective solid waste management, their participation and cooperation is crucial.

Also the commitment of management is necessary and vital for a successful waste management program. Management can demonstrate its commitment by training the employees in waste management techniques, encouraging employee's suggestions, providing resources for the 3 R's activities and measuring and monitoring the waste generation and waste recycling.

The ultimate goal of the management must be the zero solid waste from the plant. For this follow-up and continuous improvements are crucial. Measurement and reporting of waste reduction and achievement of cost saving goals also helpful in improving the working results and the sustained development of the steel plant.



Fig1.3 3'R's of Solid Waste Management

1.6 Need for Waste Classification, Characterization, & Utilization:

The subject of waste is an offshoot of inefficiency on any process. Nature knows no waste. Laws of nature govern the transformation of materials from one state to other. We ascribe the ideals of waste to a given situation according to our intents and purpose. Something unwanted or un-useful is taken as waste [15]. But something unwanted in one situation may be of value in another and unusable in one trade may profitably be used in some other trade. It is left to human brain to devise ways and means, open new vistas of industries and develop new technologies to gainfully utilize the seemingly waste items.

These solid wastes, having wide-ranging impact on the environment are divisible into three basic categories :-

- (1) Waste, which are hazardous and must be treated suitably before throwing them as waste.
- (2) Waste, which are not hazardous, and recovery, recycling and reuse of valuables in it could be done economically.
- (3) Waste which are not hazardous and have little / no value added perspective.

In general case recycling of Wastes which are not hazardous and recovery can be done easily does not creates major problem.

So in this study our main aim will be on the recovery of waste which are not hazardous and where scope of value addition is limited.

Management of waste creates values ethical and aesthetic in nature. It is beneficial from pollution control point of view and even generates revenue. Beneficiation and recycling of waste products

can cater to the needs of the consumer sector. In this competitive industrial age, the aspect of waste control is of paramount importance.

The major solid waste in the form of slag (Blast Furnace Slag, Steel Melting Slag), Dusts (Flue Dust, SMS Dust), Sludge (GCP Sludge from Gas Cleaning plant of Blast Furnace, Acetylene Sludge from Acetylene Plant, Neutralization Plant Sludge and Palm Oil Sludge from Cold Rolling Mill, Acid Treatment Plant Sludge from Silicon Steel Mill), Scale (Mill Scale from Hot Strip Mill) and Ash (Fly-Ash & Bottom ash from thermal power but the present study includes only the Flue-Dust, Fly-Ash, Sinter fines and LD-Slag.

1.7 Use of Sugarcane Bagasse as a Potential Reductant in Iron and Steel Sector:

The use of Sugarcane bagasse as a potential reductant is a good step forward in reducing the consumption of coal as a reductant in Iron and steel sector. Coal being a nonrenewable resource is depleting considerably and from Compositional analysis of Sugarcane bagasse it is found that it contains significant amount of carbon. So using Sugarcane bagasse as a reductant will lead to sustainable development in Iron and Steel sector. The cost of Sugarcane is negligible in comparison to coal so the above step will lead to a considerable reduction in production cost. Sugarcane bagasse will be first processed into a powdered form and then it will be mixed with a quantitative amount of ore sample which can be easily calculated from the reaction stoichiometry.

1.8 Use of Plant and Domestic Waste for Sustainable Development in Iron and Steel Sector:

The present demand of Iron and Steel products leads to depletion of mineral reserve at an alarming rate. Thus it is quite essential to use the mineral values present in the wastes generated in an Iron and Steel plant to achieve Sustainable Development. The processes in an Integrated Iron and Steel Plant generates various wastes like BF Flue Dust, BF Slag, BF Sludge, LD Slag, LD Sludge, ACP Dust, GCP dust, GCP Sludge etc., but in the present work we will use the wastes which contains high mineral values like BF Flue Dust, ACP Dust and some other domestic wastes like Sugarcane bagasse which contains high amount of carbon.

In the present work we will use the carbon present in BF Flue Dust to reduce the hematite present in the Dust and also the extra amount of carbon will be utilized to reduce Iron Ores like hematite and

Magnetite added externally. The presence of carbon and Hematite in BF Flue Dust is confirmed by the XRF analysis of the BF Flue Dust Sample. To utilize ACP Dust, it is reduced by coke dust to get metal values present in the waste. The depletion of coal at an alarming rate is leading to tremendous research in finding alternate reducing agents in the Iron and Steel Sector. Thus an effort has been made in this regard and Sugarcane bagasse as a domestic waste is known to contain high amount of carbon which can be used as a potential reductant.

2. Literature Review

2. Literature Review:

India is the world's second-largest steel producer with production standing at 106.5 MT in 2018[1]. The growth in the Indian steel sector has been driven by domestic availability of raw materials such as iron ore and cost-effective labour. Consequently, the steel sector has been a major contributor to India's manufacturing output. The Indian steel industry is very modern with state-of-the-art steel mills. It has always strived for continuous modernization and up-gradation of older plants and higher energy efficiency levels. Indian steel industries are classified into three categories such as major producers, main producers and secondary producers. India's finished steel consumption grew at a CAGR of 5.69 per cent during FY08-FY18 to reach 90.68 MT [2]. India's crude steel and finished steel production increased to 103.13 MT and 104.98 MT in 2017-18, respectively. In 2017-18, the country's finished steel exports increased 17 per cent year-on-year to 9.62 million tonnes (MT), as compared to 8.24 MT in 2016-17. Exports and imports of finished steel stood at 5.77 MT and 7.13 MT, during April 2018-February 2019 period [2].

The National Steel Policy, 2017, has envisaged 300 million tonnes of production capacity by 2030-31. In 2018, steel consumption of the country is expected to grow 5.7 per cent year-on-year to 92.1 MT. Further, India is expected to surpass USA to become the world's second largest steel consumer in 2019 [3]. Huge scope for growth is offered by India's comparatively low per capita steel consumption and the expected rise in consumption due to increased infrastructure construction and the thriving automobile and railways sectors. Apart from this positive forecast of increase in production in Iron and Steel Sector, the environment is also getting contaminated by leaps and bounds due to the discharge of unutilized plant wastes directly to the environment. Thus stringent measures have been taken by the regulatory bodies to ensure that both development and safety of environment goes hand in hand. The major plant wastes and methods to get rid of them is discussed below.

There are emissions to the atmosphere in the form of dust, fume and steam, acid emissions, fugitive emissions and toxic gases. During refining of Pig Iron into Steel, large quantities of Carbon-Monoxide are produced. Byproduct coke ovens gas contains CO and Hydrogen [4].

Coke ovens are another major source of emissions. About 50 harmful substances are emitted in the atmosphere (some are concentrated and harmful), e.g. benzopyrene and unsaturated hydrocarbons. Flow sheet for Coke ovens is shown in Fig 2.1.

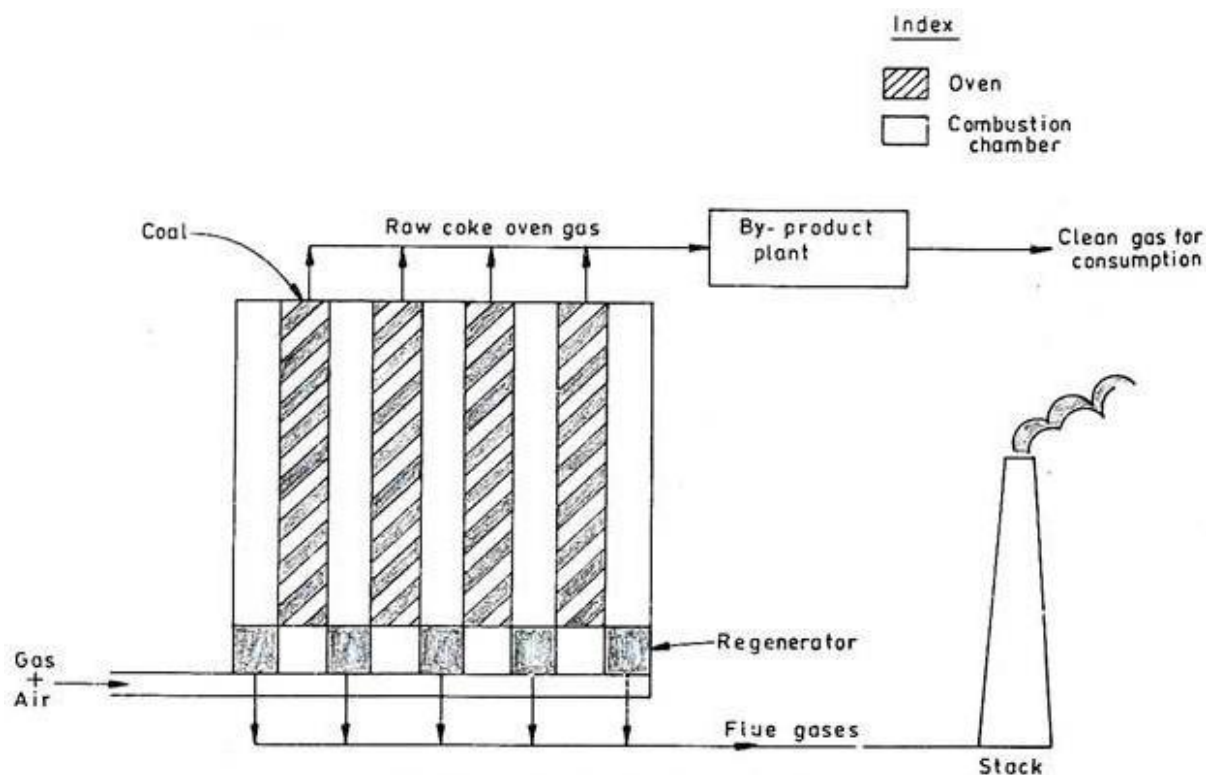


Fig 2.1: Process Flow Sheet for Coke Oven Batteries [4]

The most acute problem in the whole of steel industry is from secondary emissions. Steel industry has been able to a large extent reduce the emission of dust. However, less effort has been made against controlling the gaseous pollutants.

Carbon-monoxide control has till date no abatement system. A modern sinter plant with a surface of 400 m² emits some 2 million m³/h of waste gas with about 1% CO into the atmosphere. Dilution and dispersion is achieved through tall chimneys commonly used in sintering plants.

For removal of Sulphur Oxides, efficient processes are being used in Japan and consist of washing the fumes with a lime or a basic solution (calcium or ammonium hydroxide) and of obtaining as a byproduct gypsum or ammonium sulphate.

The desulphurization yield is about 90% for an initial content of about 400 ppm SO₂. The level of SO₂ in exhaust gases from sintering plants (400ppm) is comparable to that from coal an oil-fired power stations after desulphurization and much lower than those power stations which do not desulphurize their stack gases.

Scrubbing techniques for nitrogen oxides exist in Japan but have only begun to be applied on an industrial scale in some coking or sintering plants.

It appears preferable to seek alternatives of improving process techniques (better regulation of combustion in reheating furnaces) rather than to utilize sophisticated techniques for NO_x removal.

Certain classical particulate removal techniques seem adequately efficient for the trapping of the gaseous components of fluoride (HF), e.g., dissolution in vent scrubbers, trapping in dust cake on bag filters

The major wastes produced in integrated steel plants include BF Iron Slag Steel Melting Shop (SMS) Slag accounting for nearly more than half a ton for each ton of steel produced in ISPs [5]. Most of the steel plants are utilizing 100% of the iron slag produced (mostly in cement making and some portion as aggregate, both of which are permitted in BIS or IRC Standards Specifications) while others are closer to reach the 100% utilization.

The utilization of SMS (particularly LD) slag is limited due to its

- Phosphorous content
- High Free lime content and
- Higher specific weight.

To resolve these issues, Ministry of Steel has constituted a Task Force for promotion and utilization of Iron and Steel Slag. A meeting of the task force was held on 30th September, 2016 under the chairmanship of Joint Secretary (Steel), which was attended by all major steel plants in public & private sector and associations. In this meeting, all the issues related to slag were deliberated upon and action plans were evolved. Ministry of Steel has written to Indian Road Congress for development of codes and procedures allowing use of SMS slag as road aggregates, Research Designs and Standards Organization (RDSO) for framing standard for use of iron and steel as rail ballast, Ministry of Environment and Forest & Climate Change for considering making mandatory the use of iron and steel slag in road making, rail ballast and also to all the ISPs for setting up of commercial plant to produce processed SMS slag.

The quantum of research in the field of waste management in Iron and Steel Industry has been voluminous in major steel producing nations of the world. But, in India, it is still in infant stage. Further, the spectrum of solid waste generated by iron and steel plants is quite large & diversified but the R & D work pertaining to them is not equipoise. In the fields of few waste products like metallurgical slag, dust/sludge, considerable research work has been done while some other waste like acetylene sludge and palm oil sludge have received scant to no attention in the field of R& D. Moreover, a large bulk of literature on waste is available in form of seminar/synopsis/workshop proceedings which have limited circulation. As such it would be an uphill task to peep back into the historical aspect of its scientific research development against the backdrop of the present state of the art. Besides the following core literature reviewed, some pertinent references are cited in various chapters dealing with different types of waste.

A large number of literatures are available on total management of waste generated from a Steel plant focusing on different aspects of pollution measures, safe disposal and recirculation etc. In an attempt of recycling of waste from an Integrated Iron and Steel plant the work of Prince Kumar Singh, Avala Lava Kumar, Pravan Kumar Katiyar, Rita Mauryaon [6] Agglomeration behavior of steel plants solid waste and its effect on sintering performance leads into the conclusion that the agglomeration properties of the flue dust and sludge fines are more appropriate in combined form in comparison to individual of flue dust and sludge. The pellets having good strength were found in the case of mixed pellets (50% of each, flue dust and sludge) by using bentonite binder with very high productivity value as 75 of disc pelletizer.

Advances made by Christof Lanzerstorfer, Michaela Kröppl of University of Applied Sciences Upper Austria School of Engineering/Environmental Science on Air classification of blast furnace dust collected in a fabric filter for recycling to the sinter process leads to great results in efficient recycling of BF Dust [7]. They concluded that the residue from totally dry cleaning of blast furnace top gas contains zinc and other components which are not wanted in the sinter feed material so their allowed concentration is restricted. Therefore, a reduction of the concentration of these components in material recycled to the sinter plant is often required. Air classification is a simple process that can be applied for separation of the dust into a low-contaminated fraction for recycling and a highly contaminated fraction for discharge [8]. The separation of a dust sample from a dry blast furnace top gas cleaning filter into five dust classes with subsequent chemical analysis of these dust classes enabled the calculation of enrichment factors dependent on the dust particle size. The linear regression of the data gave good correlation coefficients for most components as expected, the

unwanted volatile components like zinc, alkali metals and chloride are increased in the finest dust classes, whereas the valuable components like carbon (represented by the LOI) and iron are more evenly distributed [10,11]. A large number of literatures are available on total management of waste generated from a Steel plant focusing on different aspects of pollution measures, safe disposal and recirculation [9]. Major noteworthy contributions on overall waste management are by Leonard (1997), Padhi et al. (1999), Chatterjee (1993), Rechner (1995), Basu (1997), Mukharjee and Chakrabarty (1999) etc.

The process permits utilization of carbon content from the waste as a reductant. Study carried by Reddy et al (1996) indicated the probability of recovery of 60% carbon values from flue dust through conventional flotation technique [12]. Parrat and Aumonier (1996) explained the techniques used for upgrading metal extraction from slag.

The work on Effective Utilization of Blast Furnace Flue Dust of Integrated Steel Plants by B. Das, S. Prakash, P. S. R. Reddy, S. K. Biswal, B.K.Mohapatra, V. N. Misra from Regional Research Laboratory (Council of Scientific and Industrial Research), Bhubaneswar leads to the conclusion that Solid waste material generated at steel plants should be well characterized with respect to undesirable as well as valuable components [13]. The extent of recovery of values or recycling within the steel plants can be enhanced by beneficiating the wastes.

The work on Solid Wastes Recycling Through Sinter-Status at Tata Steel by U. S. Yadav, B. K.Das, Ashok Kumar and H. S. Sandhu from Tata Steel, Jamshedpur leads to the conclusion that Integrated steel plants generate several by-products, categorized as waste [14]. Wastes are rich in iron, flux and fuel values. Sinter plants provide opportunities for recovering values from wastes or converting the 'waste to gold'[15]. Flux fines, LD slag and sludge, BF dust, mill scale etc. are being recycled up to the extent of 100 kg/t-sinter without considering iron ore and sinter returns from the blast furnace [16] . Approximately 27000 tonnes of various solid wastes are recycled every month through sinter replacing around 80-90 kg of prime material/t sinter. The total annual saving to the company due to waste recycling translates to Rs. 25 Crores [17].

The research on Application of air classification for improved recycling of sinter plant dust by Christof Lanzerstorfer from University of Applied Sciences Upper Austria, School of Engineering/Environmental Sciences Leads to the conclusion that in sinter plants the dust collected from the off-gas is recycled back to the feed material as long as the chloride content of this dust is below the plant-specific limits [18]. In many sinter plants part of the dust has to be excluded from recycling to avoid an up-cycling of chloride. In this case the dust from the last field of the EP is

usually discharged to landfill. In this study it has been shown that air classification can be applied for separation of the dust into a fraction with low chloride content for recycling and a highly concentrated fines fraction not for recycling. For optimization of the classification several variants were investigated [19]. Depending on the requested fraction of dust for recycling and required chloride discharge classification of the mixed dust from the EP or classification of the dust from the rear fields of the EP can be chosen [20].

Experimental analysis on the use of BF-sludge for the reduction of BOF-powders to direct reduced iron (DRI) production by D. Mombelli, C. Di Cecca, C. Mapelli, S. Barella and E. Bondi gives us significant knowledge of the fact that BF Flue Dust contains significant amount of carbon which can be used to reduce the amount of reductant added externally to the Blast Furnace or a certain tonnage of production [21]. In this work the use of BF sludge as a reducing agent for the reduction of BOF powders has been investigated. The different briquettes have been cold-bonded using hydrated lime and molasses as a binder, hot briquetted at 700 °C, before being roasted in both air and argon, respectively. The experimental campaign demonstrates the feasibility of the use of BF-sludge as C-source [22]. The iron oxides in the briquettes can be almost completely reduced to produce direct reduced iron featured by porous morphology. The formation of sponge iron was observed for all the blends investigated [23]. The average metallization ratio was 50-60% and 60-80% for air and argon roasting, respectively. This offers the possibility to use BF-sludge for DRI production with a wide range of iron-rich powders composition. The production of such self-reducing briquettes can decrease the overall amount of disposed wastes, generating a significant economic advantage. The use of BF sludge as a C-source reducing agent can lead to an important reduction of coke use, with beneficial effects on human health and the environment [24].

The industrial development programmed of any country, by and large, is based on its natural resources. Production of 72 Mtpa finished steel would require about 123 Mtpa of iron ore. Table 1 shows the status of iron ore reserve in India, ranking sixth in the world, according to estimate by Indian Bureau of Mines, Nagpur as on 1st April 2000 [25]. However, with the increasing mining activity and exports of high grade ores; high grade reserves are slowly and steadily getting depleted. Indian Iron ore deposits are also soft and friable in nature hence large amount of fines are generated. The data for Iron Ore Reserve in India is shown in Table 2.1.

Grade	A. Lump s (%)	B. Fines (%)	C. Lump s & Fines (%)	D. Prospect ive Resourc es (%)	E. Other s (%)	Total Hematite [A+B+C+D +E] (%)	Magnet ite (%)	Total Resourc es Mt (%)
High	915.28 (7.09%)	139.22 (1.08%)	409.1 (3.17 %)	-----	-----			
Medium	2822.9 (21.87 %)	2506.9 (19.42 %)	421.2 2 (3.26 %)	-----	-----			
Low	1131.9 (8.77%)	1325.5 (10.27 %)	331.7 5 (2.57 %)	-----	-----			
Unspecifi ed	533.23 (4.13%)	354.19 (2.74%)	116.6 5 (0.9%)	-----	-----			
Sub- total	5403.3 (41.87 %)	4325.8 (33.52 %)	1278. 72 (9.9%)	1480 (11.47%)	417.9 (3.24 %)	12905.79 (100%)	10682.2 1	23588
						(54.71%)	(45.29 %)	(100%)

Table 2.1: Iron Ore Reserve in India [5]

Now, to utilize these valuable mineral containing wastes, agglomeration technique is used. The agglomeration is a process which uses fine particles, added with binders or other additives to form pellets, briquettes or nodules (sinter) [26]. This process is mainly used to produce iron ore pellets which supply the blast furnaces. The performance of a pelletizing circuit requires physical processes such as regrinding, hydro classification, screening, mixing and usage of balling discs or drums to form the pellets [27]. The quality of the end product is also influenced by the addition of specific additives and their methods of addition.

One of the major concerns of world steel plants are the disposal of wastes generated at various stages of processing [28]. The global emphasis on stringent legislation for environmental protection has changed the scenario of waste dumping into waste management. Because of natural drive to be cost effective, there is a growing trend of adopting such waste management as would convert wastes into wealth, thereby treating wastes as by-products.

Stringent environmental norms and concerns over the consumption of energy have forced the steel industries to find an alternative feeding burden for iron making process. In this perspective, iron oxide ore cold bonded-self reducing coal composites are gaining popularity due to increase of reduction kinetics even with decreasing reducing agent and specific energy consumption. Several researchers have investigated the use of this burden material in the blast furnace and for the alternative iron making route. The viability of using vegetable peels and other domestic wastes is also discussed in this work [29].

Sugarcane bagasse is the fiber that remains after the sugars have been extracted. As an agro-industrial residue, sugarcane bagasse (*Saccharum officinarum*) is another source of lignin raw material. Chemical composition of sugarcane bagasse is similar to the other plant cell walls [30]. Each class of plants, grasses, softwoods, and hardwoods produces lignins rich in one type of the phenylpropane repeat unit. Sugarcane bagasse lignin has a higher proportion of H-type lignin, *p*-hydroxyphenyl, and hence a lower methoxy content than softwood and hardwood lignins[31]

The domestic wastes present around us are abundant and can be utilized in an efficient manner to add value to our society. Domestic wastes like Vegetable peels, Plastics, Sugarcane Bagasse are known to contain significant amount of Carbon which can be used as an alternate to Coal and Coke in Iron and Steel Industry. The depletion of Coal at an alarming rate is demanding such measures for Sustainable Development in the Iron and Steel Industry. The Compositional analysis of Sugarcane Bagasse confirmed the presence of Cellulose(61.53%) and Lignin (38.46%) [32].The percentage of Carbon present in cellulose and lignin is studied and finally the amount of Carbon present in Sugarcane Bagasse is calculated.

3.Scope of Work

3.Scope of Work:

Blast furnace flue dust contains valuable amounts of carbon and iron. In addition to coke fines, the flue dust also contains fines generated from BOF slag, limestone and pellets, and as a result it contains basic oxides such as CaO and MgO as well as a considerably high amount of Fe₂O₃.

Also Air Cleaning Plant Dust (ACP) from the Sinter Plant has considerable amount of Fe content and the other copious amounts of silica (SiO₂), alumina (Al₂O₃) but the main significance due to which it is used in the project is the absence of carbon.

The main purpose of this research is to recover the iron content in the flue dust and ACP dust with the help of briquettes. We are considering reduction of iron oxides through the formation of briquettes as the iron content required is less than the iron content required for the making a pellet or sinter and also it is cost effective. These cold bonded briquettes made mainly from iron oxides and carbonaceous material such as coke. The coke content already present in the flue dust helps in the reduction process. These briquettes can be charged in the blast furnace with the feed material.

An Integrated Iron and steel plant produces a lot of wastes and based on the quantity of metal values specially iron present in the waste we are going to work on Blast Furnace Dust, Air Cleaning Plant Dust. The considerable amount of carbon present in the blast furnace dust is also utilized to reduce the externally added raw Hematite and Magnetite ore in varying proportions. A process is formulated after keeping in mind the consumption of coal at alarming rate to use Sugarcane Bagasse as an alternative reducing agent in Iron and steel sector.

This recovery of iron content by forming briquettes is advantageous in the following ways:

- Reduction the amount of iron ore and coke (feed material) charged.
- The coke content already present in the briquettes decreases the coke content required for the reduction to be carried out.
- Better reducibility due to higher strength of the briquettes and uniform size.
- Cost reduction.
- . The characterization of Blast Furnace Flue Dust revealed that the loss on ignition in the flue dust is high and itself contains 25% carbon.

4. Methodology

4. Methodology:

To utilize the plant wastes containing significant amount of carbon and/or Iron like Blast Furnace Flue Dust and Air Cleaning Plant Dust, the following methodology discusses how these wastes are mixed with hematite and magnetite in various proportions and reduced to get Iron. Use of Sugarcane Bagasse, a domestic waste, as an alternative reductant will also be discussed.

4.1 Reduction of Blended Blast Furnace Flue Dust with Raw Hematite:-

- Blast furnace flue dust (BF dust) sample is prepared below standard sieve size of 150 mesh.
 - Raw hematite ore is crushed using jaw crusher and roll crusher after that it is finally pulverized to obtain the desired size of the raw ore.
 - Hematite ore is sieved using sieves of various sizes and 150 mesh size is preferred for further processing.
 - XRF analysis of the sieved Ore is carried out for the composition.
 - XRD of BF Dust revealed that carbon available in BF Dust is more than sufficient to reduce and recover the Iron available in the BF Dust. So the extra carbon present is utilized to reduce the hematite containing considerable amount of Iron.
 - Blending of BF Dust and hematite ore in varying proportion is performed.
 - Binding agents such as molasses, water, bentonite (4% of total mixture) is added.
 - Briquettes are prepared individually by adding varying percentage of hematite and then reduction in a tube furnace is carried out at a temperature of 1000⁰C and for about 60 minute.
 - Extent of Reduction (EOR) which is a measure of the quality of reduction process is calculated.
 - To substantiate the trend shown in EOR.
 - Finally, XRD of the reduced sample is carried out.

- Optimization of hematite percentage with respect to BF Dust is carried out.

4.2 Reduction of Blended Blast Furnace Flue Dust with Raw Magnetite: -

- Raw Magnetite ore is crushed using jaw crusher, roll crusher and is finally pulverized using a pulverizer to obtain desired size of the Ore.
- BF Dust and magnetite ore is prepared under 150 mesh size using sieves of various mesh size.
- XRF analysis of the sieved Ore is carried out for the composition.
- Blending of BF Dust and Magnetite Ore in varying proportion is performed.
- Binding agents such as molasses, water, bentonite (4% of total mixture) is added.
- Briquettes is prepared individually by adding varying percentage of Magnetite and then reduction in a tube furnace is carried out at a temperature of 1000⁰C and for about 60 minutes.
- EOR is calculated.
- To further validate the above results XRD of the samples is carried out.
- Optimization of Magnetite percentage with respect to BF Dust is carried out.

4.3 Reduction of Blended Air Cleaning Plant Dust with Coke Dust: -

- Air Cleaning Plant Dust is subjected to XRF for compositional analysis.
- ACP Dust is blended with coke dust. The amount of coke dust is varied and mixing of ACP Dust is carried out with 5% less than Stoichiometric amount of carbon, Stoichiometric amount of carbon, 5% more than Stoichiometric amount of carbon, 10% more than stoichiometric amount of carbon.
- Reduction of the above mixture is carried out in a tube furnace at 1000⁰C for 60 minutes.
- EOR for the above sample is evaluated.
- XRD of the reduced sample is performed

- .Optimum condition is found out for the above reduction processes so as to make it industrially viable.

4.4 Reduction of Raw Hematite by Sugarcane Bagasse: -

- Sugarcane Bagasse is subjected to pyrolysis for up to 150⁰C for 60 minutes to remove moisture and other materials to get carbon rich residue.
- From the literature it is clear that the Sugarcane Bagasse mainly contains Cellulose (61.53%) and Lignin (38.46%). The percentage of Carbon in Cellulose and Lignin are 44.44% and 63.4% respectively. Thus, the total amount of Carbon in Sugarcane Bagasse is found out to be 51.45%.
- The degree to which Sugarcane Bagasse is able to reduce the hematite ore lump is studied by adding variable amount of sugarcane bagasse i.e. stoichiometric(ST) amount of Sugarcane bagasse required for reduction, 30% more than stoichiometric (ST) amount of Sugarcane bagasse required for reduction.
- EOR for the above sample is evaluated.
- XRD of the reduced lump sample is performed.

4.5 Extent of Reduction:

Extent of Reduction is defined as the ratio of actual reduction to the standard reduction. Actual reduction of the sample is measured from the loss in weight after reduction and standard reduction is measured from the total loss of oxygen from the Ore sample after reduction.

5. Equipments

5.Apparatus and Instruments:

5.1 Weighing Balance:-

Weighing balance machine is measuring equipment for determining the weight of an object with digital display in the present study. It is a class of balance designed to measure weights in the sub-milligram range. The capacity of the balance is 1000 gm and the readability is 0.01gm. The measuring pan of weighing balance (0.1 mg or better) is inside in a transparent enclosure with doors to suppress the effect of dust and fluctuation due to air & current in the room during operation. This enclosure is often called a draft shield. A picture of the instrument is shown as in Fig 5.1



Fig 5.1: Weighing Balance

5.2 Jaw Crusher:

In a Jaw Crusher compressive force is used for breaking of ore, rock and mineral. A Jaw Crusher consists of a set of vertical jaws, one jaw is kept stationary and is called as fixed jaw. The other jaw is called as swing jaw and it moves back and forth relative to fixed jaw by a cam or pitman mechanism. The volume or cavity between the two jaws is known as the crushing chamber. The movement of the swing jaw is quite small, since complete crushing is not performed in one stroke. The machine basically contains two parts called front part and rear part. The front part of the machine contains the crushing zone with a plate and suitable teeth. The rear part contains the motor part which runs the crusher. The front part is connected with the rear part by a wheel and a belt. A picture of the instrument is shown in figure 5.2.

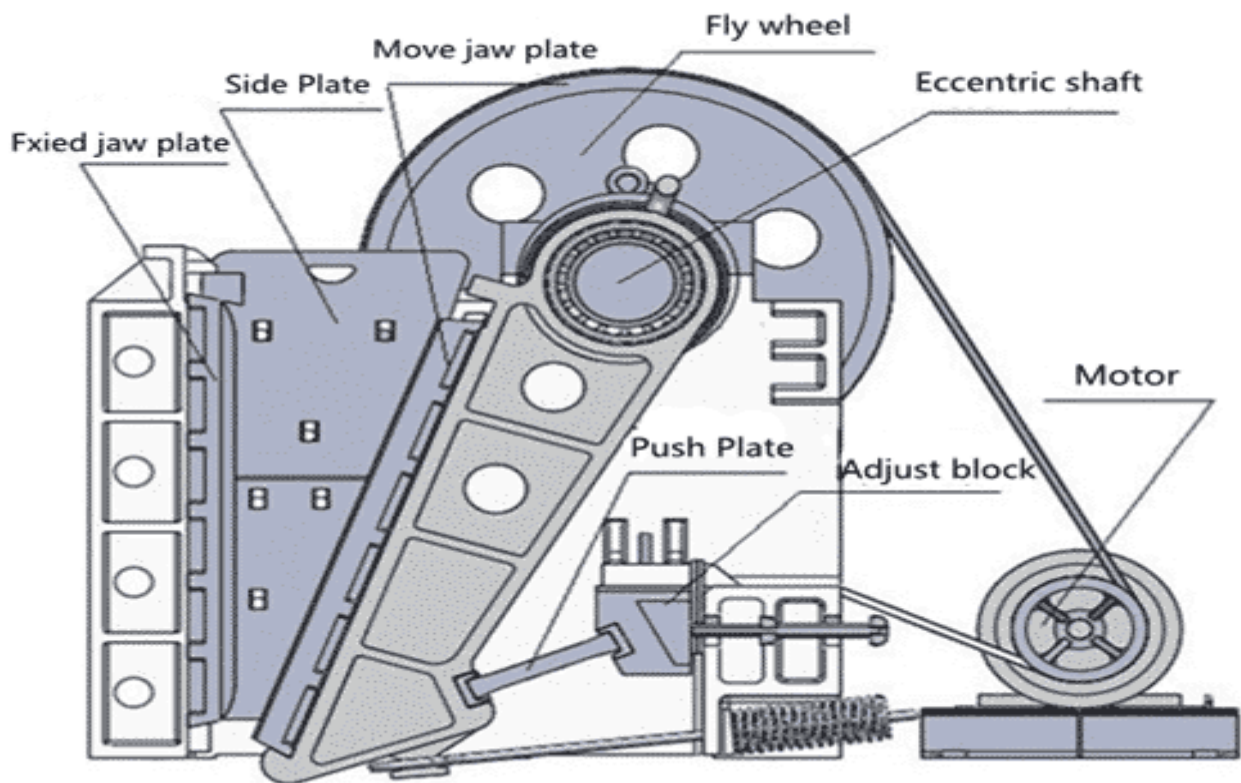


Fig5.2: Jaw Crusher

5.3 Roll Crusher:

The Roll Crusher is suitable for coarse and medium crushing. Roll crushing is carried out after the operation of jaw crusher i.e. the final product size of jaw crusher is further decreased by roll crusher. The material feeding granularity is very big and the material discharging granularity is adjustable in Roll Crusher. It is able to crush materials with compression strength less than 160 MPa. The final products are generally fine. The materials fall from the feeding mouth into the space between the two rollers and are squeezed & crushed and afterwards final products fall naturally. If there are some super-hard materials or materials that cannot be crushed, the rollers of the roll crusher can automatically yield relying on the hydraulic cylinder or the spring. Thus it increases the gap between the two rollers, and then such material will fall, consequently, the machine will be protected from being damaged. A picture of the instrument is shown in figure 5.3

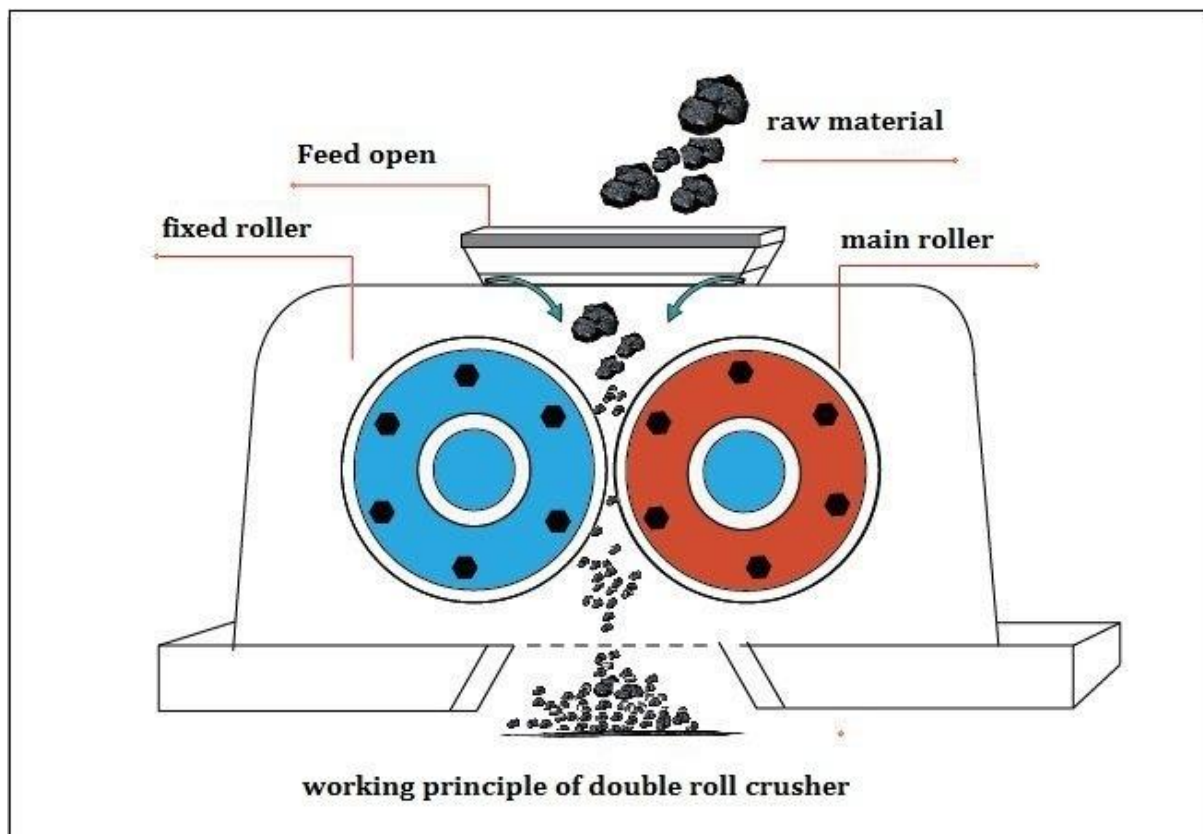


Fig 5.3: Roll Crusher

5.4 Pulverizer:

A Pulverizer or grinder is a mechanical device for the grinding of many different types of materials. A pulverizer is used to reduce the size of lump ores into fines which is also called comminution process. To obtain very fine size of ore pulverizer is generally used. The device consists of rotating devices which in contact with ores are able to exert sufficient force required to break the lump ore. The image of a pulverizer is shown below



Fig 5.4 Pulverizer

5.5 Reduction Furnace:-

Reduction experiments are carried out in a conventional resistance furnace (up to 1623K) containing silicon carbide as heating element with PID controller. Size of alumina tube is 50mm outer diameter (O.D) and 40 mm inner diameter (I.D) with length (L) 700mm. Heating zone in the furnace is around to 10 cm. Alumina boat with length around to 100 mm is used for sample holding in isothermal heat treatment. At first the temperature is raised to desire temperature and quickly the boat is inserted carefully in the heating zone. The temperature is calibrated and standardized by using aPt/Rh thermocouple. The furnace has closed environment (closed with cork on both ends). After the experiment the sample is cooled in the furnace to room temperature. A picture of the reduction tube furnace is shown below in Figure



Fig 5.5: Reduction Furnace

5.6 X – Ray Fluorescence:-

The structure of hematite was analyzed by XRF. X-ray spectrometer with Scandium and Rhodium targets using pentaerythritol (Al, Si).ThalliumAcidPathalate (Na, Mg), Germanium (P) and Lithium Fluoride (for heavier elements) as analyzing crystals in vacuum medium. International and in-house standards of appropriate compositions were used for calibration. Both major and minor elements were determined by pressed powered pellet technique.

5.7X –Ray Diffraction:-

X-ray diffraction technique is non-destructive analytical equipment which reveals information about the major phase, crystal structure and chemical composition with formula of ore. This technique is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. In the present study phase analysis is carried out by X-ray diffraction spectrometer with Bragg-Barentano geometry (RigakuUltima III, Japan) of raw ore and several treated products (oxidized, reduced). The equipment is based on this equation Here ' d ' is the spacing between diffracting planes, ' θ ' is the incident angle, ' n ' is any integer, and ' λ ' is the wavelength of the beam. Cu ' $K\alpha$ ' (λ -1.54) is the source of x-ray with operating current and voltage of 40 kV and 30mV respectively. The scan is continued from 20 to 90 degree with 5⁰/min. Samples are crushed and fined by mortar & pastel about to 5 gm and ultrafine sample are spread over in a quartz holder and then put in the holding position of the equipment. Data is collected after comparing the positions and intensities of peaks with those of the corresponding standards by PDF database (PCPDF-WIN software, JCPDS-International Center for Diffraction Data. The following showing diffraction instrument as in Fig:



Fig 5.6: X- Ray Diffractometer

5.8 Scanning Electron Microscopy: -

A Scanning Electron Microscope (SEM) is a type of electron microscope that provides us the images of the sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that containing information about the sample's surface topography, composition, and other properties such as electrical conductivity. For SEM- EDX analysis the finely powdered sample is taken on carbon tape which is mounted in a sample holder. For polished sample first of all a little thicker sections of ore is cut by a rock cutter and then the sections are mounted on glass slides by araldite. Now the sections are polished well by different methods and stages of dry and wet polishing until a stainless highly glossy surface is made. Then the glass slide is cut to size (made smaller) to be fit in the sample holder of SEM. Before analysis the sample is coated with conductive material(palladium) with JEOL JFC -1600 Auto Fine Coater. The morphological study is investigated by JEOL JSM-8360 Scanning Electron Microscope (Japan). Surface morphology has significant characteristic to study the samples in the present study. The morphological characteristics are generally changed after various treatments of the raw ore. Here in the study, raw, oxidized, reduced and pre-treated ores are analyzed. Elemental mapping of a selected location and point analysis are carried out to know the mineral composition and presence of various elements in the grain. The shape and size of the sample are found by this study. Energy dispersive X-ray spectroscopy (EDX) is an analytical technique used for the element analysis or chemical characterization of a sample. It is the measurement of X-rays emitted during electron bombardment in an electron microscope (SEM) to

determine the chemical composition of materials on the micro- and nanoscale. By determining the energies of the X-rays emitted from the area being excited by the electron beam, the elements present in the sample are determined (qualitative analysis). The rate of detection of these characteristic X-rays is used to measure the amounts of elements present. If the electron beam is restored over an area of the sample, then EDX systems can also acquire X-ray maps showing spatial variation of elements in the sample. The elemental mapping of a specific polished section and fine sample is carried out along with SEM on OXFORD Instrument model no 7582 (England) with INCA software.



Fig 5.7: Scanning Electron Microscopy

6. Results and Discussions

6.Results and Discussions:

6.1 Characterization of Raw Materials:

6.1.1 Blast Furnace Flue Dust:

Blast furnace flue dust samples are collected from Vizag steel plant. Characterization of the sample is carried out using X Ray diffraction. The collected samples are sieved below 150 mesh size after which it is subjected to XRD. The compositional analysis of the sample is carried out using XRF. XRD Plot of Blast Furnace Flue Dust Sample is shown in Fig 6.1.

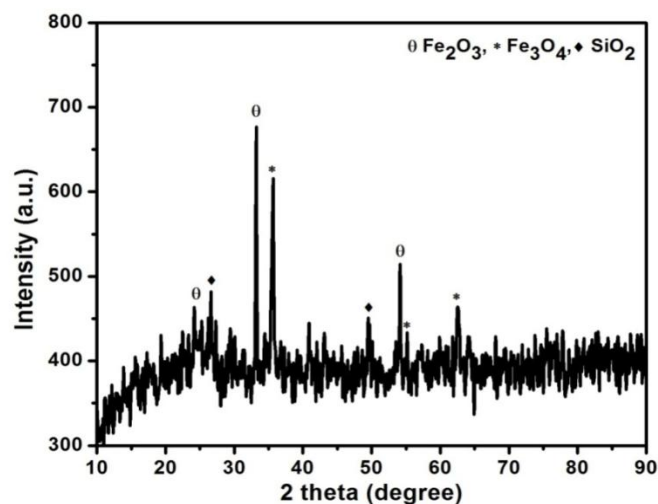


Fig. 6.1: XRD Plot of Blast Furnace Flue Dust Sample.

It can be noticed from the XRD plot that the main phase of iron present is hematite and other minor phase present are of SiO₂, Al₂O₃ etc.

XRF Analysis of Blast Furnace Flue Dust:-

The XRF analysis of the BF flue dust was carried out, which gave us the composition of the BF dust as given below in Table 6.1

Sl. No.	TOTAL FE	SiO ₂	Al ₂ O ₃	MgO	CaO	TiO ₂	Mn	S	P	LOI

%	30.62	4.48	1.01	1.95	5.53	0.06	1.95	.087	.003	40
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Table 6.1: XRF Analysis of the BF Flue Dust Under Evaluation

6.1.2 Air Cleaning Plant Dust (ACP):

Sintering plant dust arrested by electrostatic precipitator known as Air Cleaning Plant Dust in an integrated iron and steel company is perceived as a precious secondary material to steelmaking process, due to the presence of important elements to the industry such as, Fe and C with an attractive concentration.

The air cleaning plant dust sample was collected from Vizag steel and it was subjected to XRD analysis and the analysis revealed the following result. The Compositional Analysis of ACP is shown in Table 6.2

Compositional Analysis of ACP Dust:-

Sl.No	Constituent	Wt %
1	ZrO ₂	0.005
2	TiO ₂	0.313
3	Mn	0.067
4	SrO	0.000
5	SiO ₂	10.289
6	S	0.745
7	P ₂ O ₅	0.181
8	Na ₂ O	0.082
9	MgO	2.723
10	K ₂ O	0.252
11	Iron oxide (Fe ₂ O ₃)	55.799

12	Cl	0.162
13	CaO	15.739
14	Al ₂ O ₃	6.483
15	Cr ₂ O ₃	0.018
16	PbO	0.000
17	BaO	0.025
18	LOI	7.116
	Total	100

Table 6.2: Compositional Analysis of ACP Dust under Evaluation

6.1.3 Raw Magnetite:-

XRD analysis of Raw Magnetite:-

The XRD plot shows that two major phases are present in Raw Magnetite.

1.Magnetite (Fe₃O₄)

2.Alumina (Al₂O₃)

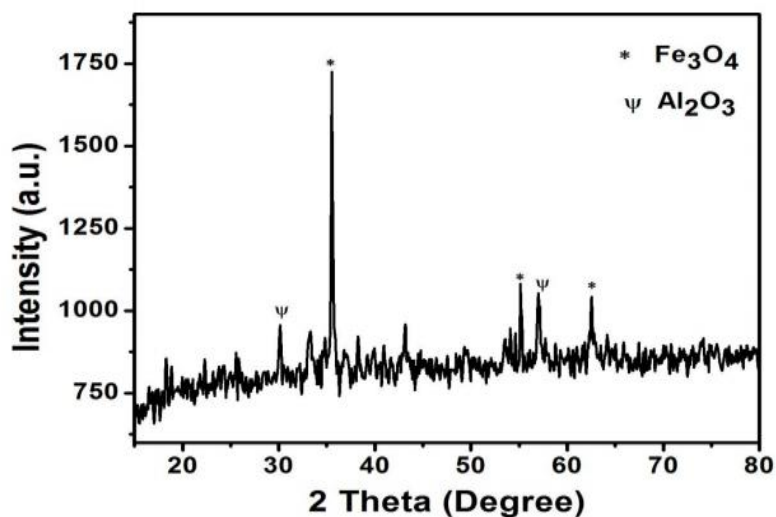


Fig. 6.2: XRD Plot of Raw Magnetite Sample.

XRF analysis of Raw Magnetite ore:-

The XRF analysis of Raw Magnetite ore revealed the following compositional data. The XRF data clearly indicates that the ore chiefly comprises of ferrous oxide.

Constituent	Fe(Total)	TiO ₂	Al ₂ O ₃	SiO ₂
Percentage	54	0.06	6.25	6.7

Table 6.3: XRF Analysis of the Raw Magnetite under Evaluation

6.1.4 Hematite ore (HMO): -

Hematite ore has been collected from Visakhapatnam Steel Plant (VSP), Visakhapatnam. At VSP, Iron ore is received from Bailadila mines, Chattisgarh of M/s. National Mineral Development Corporation.

6.1.4.1 XRF analysis of Raw Hematite Ore (HMO):

Element/ Compound	Fe(T) O ₂	Si O ₂	Al ₂ O ₃	Ti O ₂	Mn O	Mg O	Ca O	Na ₂ O	P ₂ O ₅	S	K ₂ O
Concentration (%)	64.39	4.0	2.26	0.1	0.06	0.25	0.3	0.02	0.0	0.	<0.0
		2		8			9		9	1	1

Table 6.4: XRF Analysis of Raw Hematite Sample under Evaluation

Wave length dispersive x-ray fluorescence (WDXRF; PAN Analytical) has been used to characterize hematite ore and is depicted in Table 6.4. The composition of this collected ore is found to contain 64.39 wt% of Total Fe along with 4.02 wt% of SiO₂ and 2.26 wt% of Al₂O₃.

6.1.4.2 XRD Analysis of Hematite Ore:

The phases present has been analyzed by using x-ray diffractometer (XRD; RigakuUltima III) with the help of Cu-K α radiation and is shown in Fig below.

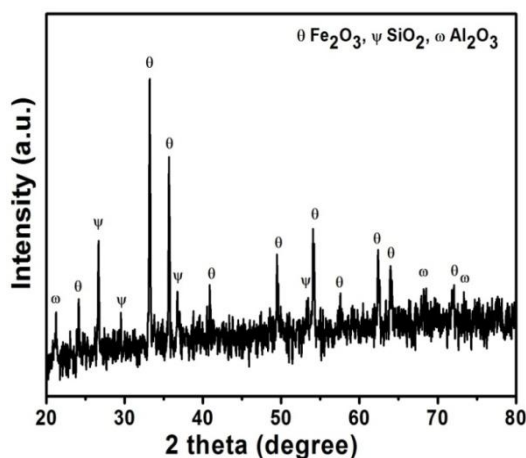


Fig. 6.3: XRD Plot of Raw Hematite Ore Sample.

From the XRD Plot of Hematite Ore Sample it is very clear that Hematite, Silica and Alumina are the major phases.

6.1.5 Coal:

Boiler grade coal was used in these experiments. This coal was supplied by Vizag steel plant along with the ultimate analysis of coal. TG-DTA, proximate analysis and XRD of the coal was performed for its characterization.

6.1.5.1 Proximate analysis of Boiler Grade Coal:

Component	Percentage (%)
Fixed Carbon	28.08
Volatile Matter	28.31
Moisture	7.40
Ash	36.21

Table 6.5: Proximate Analysis of Boiler Grade Coal

6.1.5.2 TG/DTA analysis of Coal:-

The TG/DTA study of boiler grade coal is shown below.

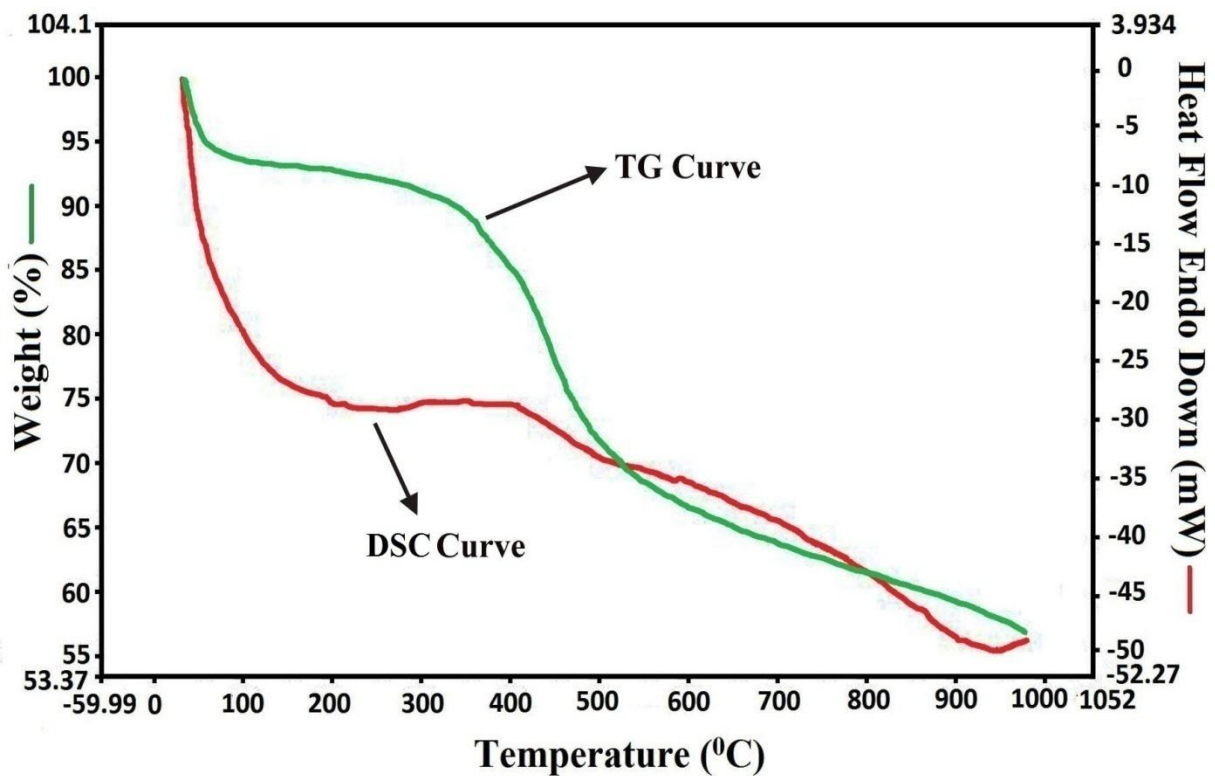


Fig 6.4: TG/DTA Analysis of Boiler Grade Coal

The green line is the TG (Thermo Gravimetric) curve and the red line is the DSC (Differential Scanning Calorimetry) curve. The nature of the weight loss conforms to the data from the proximate analysis of the boiler coal. The graph shows a weight loss up to 383K, which is obviously the expulsion of the moisture (7-8 %) in the coal. The major weight loss from 673K to 823K is the removal of the volatile matter (25- 30 %). This is the single most important step during the gasification. The weight loss on further increasing the temperature occurs at a very slow rate due to soot formation or mild oxidation by the trace amount of oxygen present in nitrogen which is used as a shielding gas in the experiment.

6.2 Characterization of Binders:-

Binders play a crucial role for the mechanical strength of the briquettes. Here, bentonite, molasses and lime have been used as binders and its corresponding characterizations are summarised here under.

6.2.1 Bentonite:-

There are two types of Bentonite, namely, swelling type or Sodium Bentonite and non-swelling type or Calcium Bentonite. Sodium Bentonite is usually referred to as Bentonite, whereas Calcium Bentonite is called Fuller's earth. Excellent plasticity and lubricity, high dry-bonding strength, high shear and compressive strength, low permeability and low compressibility make Bentonite commercially viable. Sodium Bentonite is well suited as a binder in the preparation of pellets and in foundry. Owing to high green strength resulting from its property to absorb and then release moisture, Bentonite is used in iron ore palletization. Bentonite is collected from Tata steel plant, Jamshedpur, Jharkhand, India. The typical composition of sodium bentonite is tabulated in Table 5.8. The proximate analysis at different temperatures for a period of 60 minutes is also performed and shown in Table 6.6.

Typical constituents	Contents
SiO ₂	59.10%
Al ₂ O ₃	18.60%
CaO	1.90%
MgO	4.00%
K ₂ O	0.30%
Na ₂ O	2.50%
Moisture	6-12%
Swelling Index	22-26 (ml/2g)
Loss on Ignition	8.90%
Water absorption rate	>580%
PH	10-10.5
Cation Exchange Capacity	75-85 meq/100g

Table 6.6: Composition of Bentonite

6.3 Results on briquetting and Reduction of BF Flue Dust with Hematite Briquettes:

6.3.1 Blending and Briquetting of BF Flue Dust and Hematite for Reduction:

The sample after characterization was prepared for briquette formation. The Blast Furnace Flue Dust was mixed with variable percentage of hematite i.e. 20%,30%,40% and 50% of hematite and briquettes of each of these composition was prepared by adding suitable amount of binder and moisture. The following table shown below shows few parameters which can directly indicate the optimal amount of hematite to be mixed with a suitable amount of Blast Furnace Flue Dust for efficient utilization of the available carbon. This operation will lead to reduction in the amount of reductant charged conventionally. Various Parameters for BF Flue Dust and Hematite Briquettes are shown in Table 6.7.

Sl No	BF Dust(%)	Hematite(%)	Initial wt. (gm)	Final wt. (gm)	Extent of Reduction
1	70	30	9.963	6.926	84.87%
2	60	40	10.248	7.023	91.45%
3	50	50	9.868	6.658	95.59%
4	40	60	7.915	5.668	90.39%

Table 6.7:- Various Parameters for BF Flue Dust and Hematite Briquettes

XRD plots of reduced Blast Furnace Flue Dust and Hematite briquettes

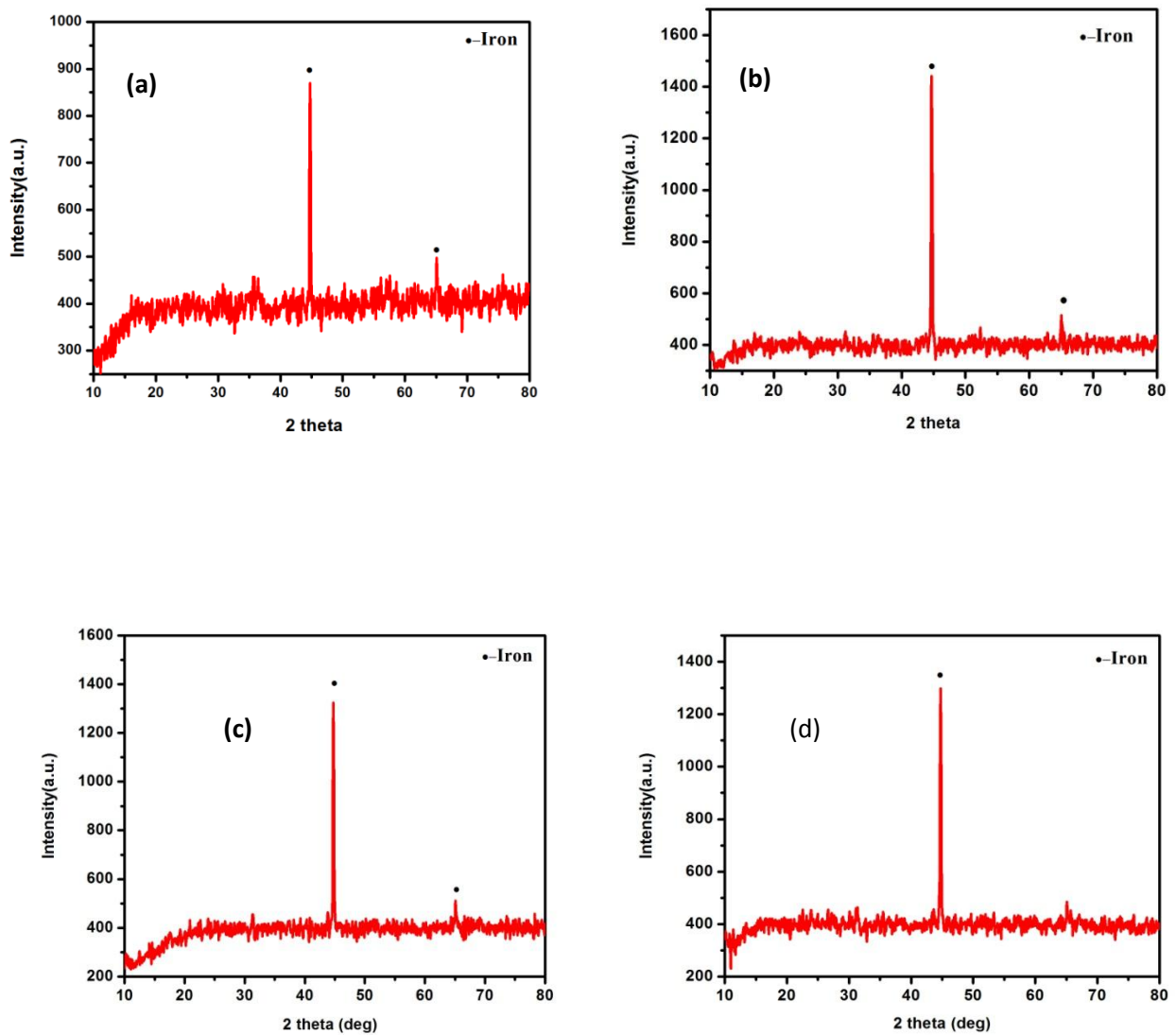


Fig. 6.5: XRD plot of BF Flue Dust sample containing Different percentages of Hematite i.e.

(a) 70%BF Dust and 30% Magnetite, (b) 60%BF Dust and 40% Magnetite, (c) 50%BF Dust and 50% Magnetite, (d) 40%BF Dust and 60% Magnetite.

From the above XRD plots it can be seen that peak of iron is prominent in each of the above sample but the intensity of the peak which is a measure of quality of reduction is different and it can be

seen that it is maximum for the sample containing a mixture of 60% BF Flue Dust and 40% hematite. The peak intensity for the samples containing 50% BF Flue Dust and 50% hematite and 70% BF Flue Dust and 30% hematite are also high showing that the reduction has occurred up to a good extent. For the sample containing 40% BF Flue Dust and 60% hematite the reduction has occurred up to a lesser extent which is justified by a low intensity peak of Iron.

6.4 Results of Briquetting and Reduction of BF Flue Dust with Magnetite Briquettes:-

6.4.1 Blending and Briquetting of BF Flue Dust and Magnetite for Reduction:

The Blast Furnace Flue Dust was mixed with variable percentage of magnetite i.e. 40%,50% and 60% of magnetite and briquettes of each of these composition was prepared by adding suitable amount of binder and moisture. The following table shown below shows few parameters which can directly indicate the optimal amount of magnetite to be mixed with a suitable amount of Blast Furnace Flue Dust for efficient utilization of the available carbon. This operation will lead to reduction in the amount of reductant charged conventionally and also this will ensure utilization of low grade ores like Magnetite for sustainable development in Iron and Steel Sector.

Sl. No	BF Dust (%)	Magnetite(%)	Initial Wt. (gm)	Final Wt.(gm)	Extent of Reduction
1	70	30	9.926	7.728	64.22
2	60	40	10.235	7.233	90.30
3	50	50	9.829	7.066	92.16
4	40	60	9.668	7.015	96.24

Table 6.8:-Various Parameters for BF Flue Dust and Magnetite Briquettes

XRD analysis of BF Flue Dust and Magnetite Briquette samples after reduction:

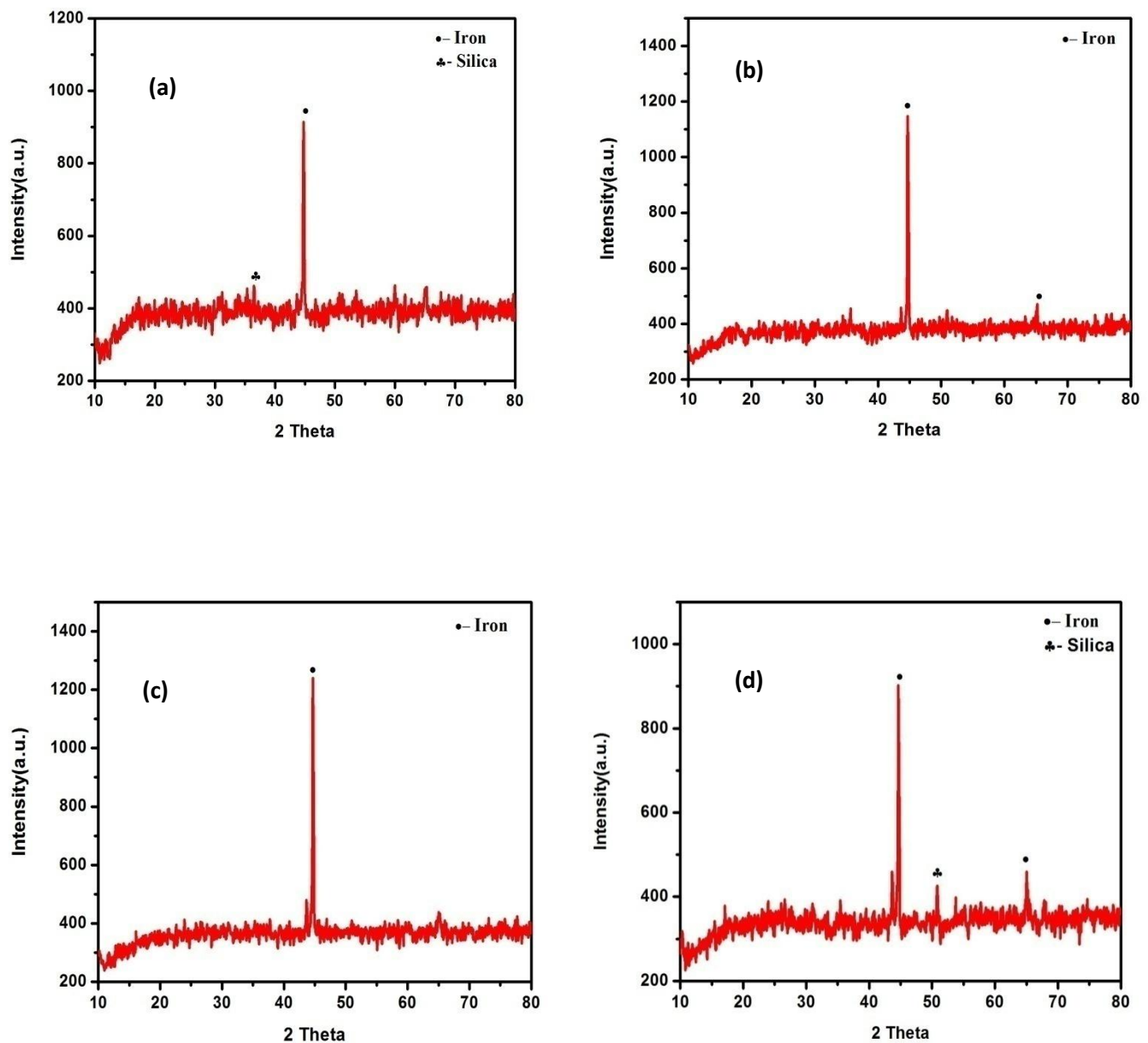


Fig. 6.6: XRD plots of reduced Blast Furnace Flue Dust and Magnetite briquettes containing (a) 70% BF Dust + 30% Magnetite, (b) 60% BF Dust + 40% Magnetite, (c) 50% BF Dust + 50% Magnetite, (d) 40% BF Dust + 60% Magnetite.

From the XRD plot of the Blast Furnace Flue Dust and Magnetite briquettes it can be seen that Iron peak is predominant in all of the above samples, but the intensity of Iron peak is maximum for the mixture containing 50% BF Dust + 50% Magnetite. Apart from iron silica phase can also be observed in some mixtures.

6.5 Results on briquetting and Reduction of ACP Dust with Coke Dust:-

The XRD and XRF plot of ACP Dust confirmed considerable amount of Iron in the form of Fe_2O_3 and to extract that metal value, the ACP Dust is briquetted with varying amount of Coke Dust. The varying amount of Coke Dust taken here ensures the optimal utilization in reducing the Iron Oxide present in ACP Dust. Coke dust is added to ACP in different proportions: 5% less than Stoichiometry (St), Stoichiometry, 5% more than stoichiometry, 10% more than stoichiometry. The reduction of the briquettes is carried out under the same conditions. The Extent of Reduction of reduced samples are calculated followed by characterization. Various Parameters for ACP Dust and Coke Dust Briquette are shown in Table 6.9

Sl No	Variation in carbon percentage	wt of ACP Dust(gm)	wt of coke dust(gm)	Initial wt(gm)	Final wt(gm)	Wt loss(gm)	Extent of Reduction (%)
1	5% less than st.	10	1.629	11.100	9.270	1.830	54.954
2	stoichiometric amount	10	1.715	10.926	7.844	3.082	94.026
3	5% more than st.	10	1.801	11.083	7.864	3.219	96.814
4	10% more than st.	10	1.887	11.732	8.330	3.402	96.658

Table 6.9: Various Parameters for ACP Dust and Coke Dust Briquette

XRD Analysis of reduced ACP sample

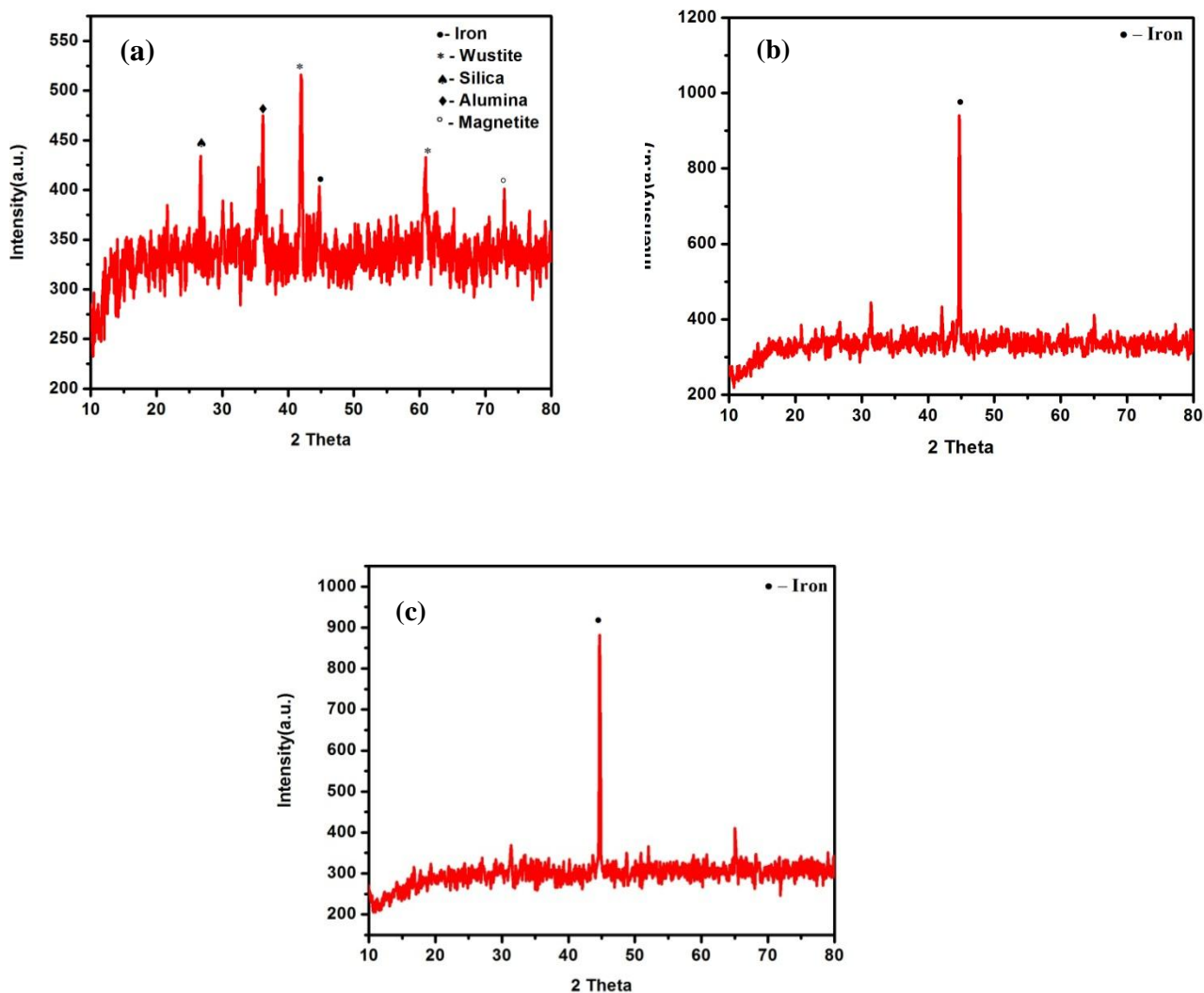


Fig. 6.7: XRD plot of reduced Air Cleaning Plant Dust sample containing (a) 5% less than stoichiometric amount of carbon, (b) stoichiometric amount of carbon, (c) 5% more than stoichiometric amount of carbon respectively.

From the XRD plot of the above samples it can be seen that prominent iron peak is present in all of the above sample but the Iron peak intensity is maximum for the sample containing stoichiometric amount of carbon. For the sample containing 5% less than stoichiometric amount of carbon apart from Iron phase like Wustite, Magnetite, Alumina and Silica are also present because the reduction has taken place to a lesser extent compared to other samples.

6.6 Results on briquetting and Reduction of Sugarcane bagasse with Lump Hematite Ore: -

The Sugarcane bagasse contains considerable amount of carbon which can be directly used to reduce hematite. In this study we will delve into the mechanism by which this reduction process takes place by carrying out the reduction of hematite with varying percentage of sugarcane bagasse. The data shown in the table below shows the parameters of the reduction process of a certain amount of hematite with varying amount of sugarcane bagasse i.e. stoichiometric(St.) amount of Sugarcane bagasse required for reduction, 30% more than Stoichiometric amount of Sugarcane bagasse required for reduction. Various Parameters for Hematite Lump Ore and Sugarcane Bagasse Reduction are shown in Fig 6.10

Wt of Lump Hematite Ore (gm)	Wt of Lump Hematite Ore after reduction (gm)	Wt of sugarcane bagasse (gm)	Loss in wt (gm)	Extent of Reduction (%)
8.581	7.383	3.451(St.)	1.198	58.95
8.300	6.770	4.340(+30%St.)	1.530	80.46

Table 6.10: Various Parameters for Hematite Lump Ore and Sugarcane Bagasse Reduction

XRD Analysis of Reduced Sample

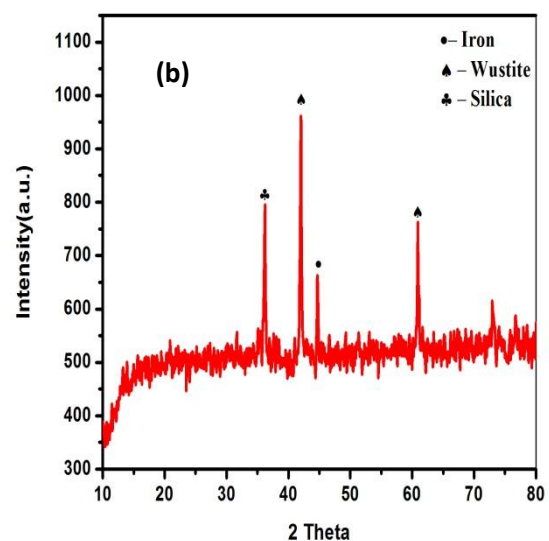
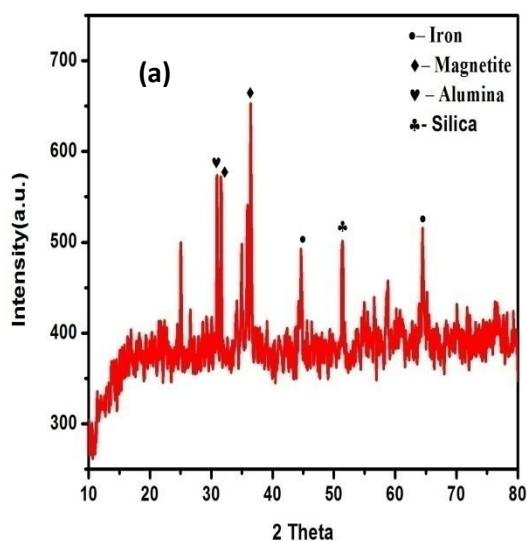


Fig 6.8: XRD plot of lump Hematite Ore reduced with (a) Stoichiometric amount of Sugarcane Bagasse and (b) 30% more than Stoichiometric amount of Sugarcane Bagasse.

From the XRD plot shown above it is very clear that the Iron peak intensity is high in case of 30% more than Stoichiometric amount of Sugarcane Bagasse and thus the quality of reduction in this case is good. The sample containing Stoichiometric amount of Sugarcane Bagasse also contains Magnetite phase which means that the quality of reduction is not optimal and some other phases like silica and alumina were also present.

6.7 Graph Showing plot for variation of EOR for different test case:

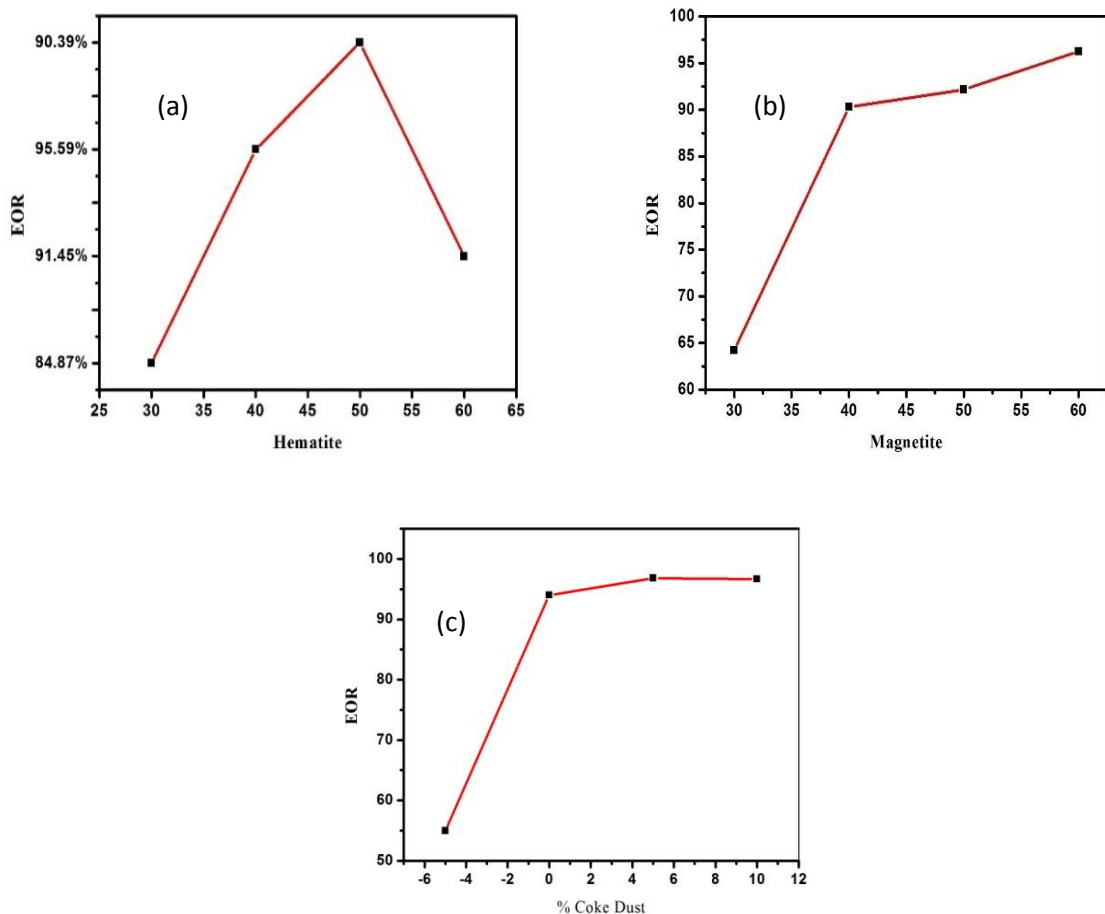


Fig 6.9: Graph showing the variation of EOR in case of (a) BF Flue Dust mixed with Hematite (b)BF Flue Dust mixed with Magnetite (c) ACP Dust mixed with Coke Dust

From the above graph it can be seen that in case of (a) the EOR is increasing as the percentage of hematite is increasing from 30% to 50%, but finally there is a decrease in the EOR as the Hematite percentage is increased further from 50% to 60% because the fixed amount of carbon available in BF Flue Dust is consumed and it is not available for further reduction.

In case of (b) the EOR is increasing with increase in the percentage of Magnetite being added to BF Flue Dust and the maximum EOR is found at the composition of 40%BF Flue Dust and 60% Magnetite.

In Fig (c) as the amount of Coke Dust being added to ACP Dust is increased there is an increase in EOR and after 5% more than stoichiometric amount of Coke Dust addition, there is very little variation in EOR. Thus the carbon present in 5% more than stoichiometric amount Coke Dust is sufficient to reduce the Iron Oxide present in ACP further Coke Dust addition is not improving the quality of Reduction.

7. Conclusion

7. Conclusion:

- The extent of reduction for Blast Furnace Flue Dust sample mixed with Hematite, increased as the percentage of hematite was increased from 30% to 50% and finally there was a decrease in extent of reduction as the Hematite percentage was increased from 50% to 60%. The decrease in extent of reduction after 50% is due to the fact that as BF Flue Dust contains a fixed amount of carbon and that amount is not sufficient to reduce the Hematite after more than 50%. There was a prominent peak of Iron in the XRD plot of the reduced sample of the mixture containing BF Flue Dust and Hematite confirming the reduction process.
- For the reduction of the mixture containing BF Flue Dust and Magnetite variations were made in the briquette mixture. The extent of reduction increased as the Magnetite percentage was increased from 30% to 50% and finally there was a decrease in Extent of Reduction as the Magnetite percentage was increased from 50% to 60%. The decrease in Extent of Reduction after more than 50% Magnetite is due to the fact that the fixed amount of carbon present in BF Flue Dust was unable to reduce the extra amount of iron oxide present in the Magnetite.
- The reduction of ACP Dust was carried out by adding varying percentage of Coke Dust i.e. 5% less than Stoichiometric amount of Coke Dust, Stoichiometric amount of Coke Dust, 5% more than Stoichiometric amount of Coke Dust and 10% more than Stoichiometric amount of Coke Dust to study the effect of amount of Coke Dust on the quality of reduction. The extent of Reduction increased as the amount of coke dust was increased from less than 5% to more than 5% and finally there was a decrease in the Extent of Reduction as the Coke Dust was increased to 10% more than of Stoichiometric amount. The decrease in Extent of Reduction after 5% more than Stoichiometric amount of Coke Dust addition is because all the Iron Oxide present in ACP Dust was optimally reduced by the Coke Dust and extra addition of Coke Dust thereafter was just making the ACP Dust a limiting reagent.
- The reduction of Hematite ore lump with varying amount of Sugarcane Bagasse was carried out. Two samples of Lump Hematite Ore were taken one containing the stoichiometric amount of sugarcane bagasse and the other containing more than 30% of the stoichiometric amount of bagasse and it was found that the extent of reduction improved as the sugarcane bagasse was taken in more than stoichiometric amount. The increase in extent of reduction is because the Carbon available in the stoichiometric amount of Sugarcane Bagasse was not sufficient to reduce the iron oxide present in Lump Hematite Ore and extra addition of

Sugarcane Bagasse ensured better reduction. The XRD plot of the reduced sample showed that the peak intensity of Iron is higher in 30% more than

- Thus the above Endeavour of utilizing the wastes by briquetting shows good potential to be adopted in the industries generating a lot of wastes so that sustainable development in the Iron and Steel Sector can be achieved and use of domestic wastes like Sugarcane Bagasse as an alternative reductant also shows good potential to be used in future and thus reduce the consumption of Coal.

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9. Appendix

9. Calculations:-

9.1. Calculation on Reduction of Blast Furnace Flue Dust with Hematite:-

9.1.1. Calculation on EOR:-

EOR for 50% BF Flue Dust sample mixed with 50% of Hematite

Initial weight of unreduced briquette sample = 9.868gm

Final weight of reduced briquette sample = 6.658gm

Loss in weight after reduction = 3.21gm

Reduction Rate = $3.21/9.868 = 32.52\%$

LOI for BF Flue Dust = 40%

Amount of oxygen in Hematite = 13.8gm

Amount of oxygen in BF Flue Dust = 7.719gm

Total oxygen = 21.519gm

Amount of carbon in 50% BF Flue Dust sample = $25*0.5 = 12.5$ gm

Total loss for 100% reduction = $12.5+21.519 = 34.019$ gm

EOR for the given reduction process = $(32.52/34.019)$

$= 95.59\%$

9.2. Calculations on Reduction of BF Flue Dust with Magnetite:-

9.2.1. Calculation on EOR:-

EOR for the BF Flue Dust sample mixed with stoichiometric amount of Magnetite

Initial weight of unreduced briquette sample = 9.738gm

Final weight of reduced briquette sample = 7.162gm

Loss in weight after reduction = 2.576gm

Reduction Rate = $2.576/9.738 = 26.45\%$

LOI for BF Flue Dust = 40%

Amount of oxygen in magnetite = 12.34gm

Amount of oxygen in BF Flue Dust = 6.17gm

Total oxygen = 18.515gm

Amount of carbon in 40% BF Flue Dust sample = $25 \times 0.4 = 10$ gm

Total loss for 100% reduction = $10 + 18.515 = 28.515$ gm

EOR for the given reduction process = $(26.45/28.515)$

= 92.76%

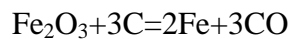
9.3. Calculations on Reduction of ACP Dust with Coke Dust:-

Amount of iron oxide present per 100 gm of ACP = 55.8gm

Loss on Ignition = 7.16%

Actual amount of Fe_2O_3 present per 100gm of ACP = 60.09gm

The stoichiometric reaction for the reduction of ACP is given by



From the given reaction amount of total iron present in 60.09gm of iron oxide can be calculated as $(112/160 \times 60.09) = 39.06$ gm

The amount of carbon required to reduce 60.09 gm of iron oxide = $(36/160 \times 60.09) = 13.529$ gm

To reduce 100 gm of ACP 13.529 gm of carbon is required. Thus to reduce 10 gm of ACP 1.352gm of carbon is required.

For 10 gm of ACP amount of coke dust required = $(1.325/.788) = 1.715$ gm

Amount of coke dust for 5% less than stoichiometric amount = 1.629gm

Amount of coke dust for 5% more than stoichiometric amount = 1.801gm

Amount of coke dust for 10% more than stoichiometric amount = 1.887gm

9.3.1. Calculation on EOR:-

EOR for the ACP sample containing stoichiometric amount of coke dust

Initial weight of unreduced briquette sample = 10.926gm

Final weight of reduced briquette sample = 7.844gm

Loss in weight after reduction = 3.082gm

LOI for ACP = 7.16%

Amount of Fe_2O_3 in 10gm ACP = 6.009gm

Amount of oxygen in 6.009gm of $\text{Fe}_2\text{O}_3 = (48/160 * 6.009) = 1.8027\text{gm}$

Thus standard reduction of the briquette sample = $(1.8027/6.009 * 100) = 30\%$

Actual reduction of briquette sample = $(3.082/10.926 * 100) = 28.2\%$

EOR for the given reduction process = $(28.2/30 * 100) = 94.026\%$

9.4. Calculations on Reduction of Lump Hematite Ore with Sugarcane Bagasse :-

Percentage of Cellulose in Sugarcane Bagasse = 61.53 %

Percentage of Cellulose in Sugarcane Bagasse = 38.46 %

Percentage of Carbon in Cellulose = 44.44 %

Percentage of Carbon in Lignin = 63.4 %

Total Carbon in 100 gm of Sugarcane Bagasse = $(61.53 * 0.44 + 38.46 * 0.634)$

= 51.45%

For Sample 1

Wt. of Lump Hematite Ore = 8.581

Wt. of Fe_2O_3 in Lump Hematite Ore = $0.92 * 8.581 = 7.894\text{gm}$

Carbon required to reduce this $\text{Fe}_2\text{O}_3 = (36 * 7.894 / 160) = 1.776\text{gm}$

Sugarcane Bagasse required to reduce this $\text{Fe}_2\text{O}_3 = (100 \times 1.776 / 51.45) = 3.451 \text{ gm}$

For Sample 2

Wt. of Lump Hematite Ore = 8.300

Wt. of Fe_2O_3 in Lump Hematite Ore = $0.92 \times 8.300 = 7.636 \text{ gm}$

Carbon required to reduce this $\text{Fe}_2\text{O}_3 = (36 \times 7.636 / 160) = 1.718 \text{ gm}$

Sugarcane Bagasse required to reduce this $\text{Fe}_2\text{O}_3 = (100 \times 1.718 / 51.45) = 3.339 \text{ gm}$

Now, 30% more than Stoichiometric amount of Sugarcane Bagasse = $(1.3 \times 3.339) = 4.340 \text{ gm}$

9.4.1. Calculation on EOR:-

1. For Stoichiometric amount of Sugarcane Bagasse:

Wt. of Lump Hematite Ore = 8.581 gm

Wt. of Lump Hematite Ore after reduction = 7.383 gm

Loss in Wt. = 1.198 gm

Wt. of Fe_2O_3 in Lump Hematite Ore = $0.92 \times 8.581 = 7.894 \text{ gm}$

Amount of oxygen in 7.894 gm of $\text{Fe}_2\text{O}_3 = (48 / 160 \times 7.894) = 2.3689 \text{ gm}$

Amount of oxygen in 100 gm of Ore = $(48 / 160 \times 7.894) = 23.689 \text{ gm}$

Actual Reduction = $(1.198 / 8.851) = 13.96\%$

Extent of Reduction = $(13.96 / 23.68) = 58.95\%$

2. For 30% more than stoichiometric amount of Sugarcane Bagasse:

Wt. of Lump Hematite Ore = 8.300 gm

Wt. of Lump Hematite Ore after reduction = 6.770 gm

Loss in Wt. = 1.530 gm

Wt. of Fe_2O_3 in Lump Hematite Ore = $0.92 \times 8.300 = 7.636 \text{ gm}$

Amount of oxygen in 7.636 gm of $\text{Fe}_2\text{O}_3 = (48 / 160 \times 7.636) = 2.290 \text{ gm}$

Amount of oxygen in 100gm of Ore= $(48/160*7.636) = 22.908\text{gm}$

Actual Reduction = $(1.530/8.300) = 18.433\%$

Extent of Reduction = $(18.433/22.908) = 80.46\%$.