STUDIES ON UTILIZATION AND RECYCLING OF STEEL PLANT FINES BY AGGLOMERATION

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By

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Under the guidance of

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CERTIFICATE

This is to certify that the thesis entitled, “STUDIES ON UTILIZATION AND RECYCLIN OF STEEL PLANT FINES BY AGGLOMERATION”, submitted by Ela Jha in fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Metallurgical Engineering is a bonafide record of investigations carried out by her in the Department of Metallurgical and Materials Engineering, Faculty of Technology and Engineering, M. S. University of Baroda, Vadodara under my guidance and supervision. In my opinion, this has attained the standard fulfilling the requirements of the Ph.D. degree as prescribed in regulations of the University.

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Chapter 1

Introduction

Steel production is the main driving force of economic progress of a country. On 2018 India become second largest producer of steel in the world which is preceded by China [1]. Iron and steel industry's growth in India has been double since last 12 years. India's crude steel production of year 2019 was 111.2 Mt and that was 53.5 Mt in year of 2007. Correspondingly, the per capita steel consumption in India was 43 kg in the year of 2007 which increased to 74.3 kg (72.8 pct) in the year of 2019; still which is much lower than the world average 229.3 kg. The industrial development programmed of any country, by and large, is based on its natural resources. For producing 111.2 Mt crude steel required about 190 Mt of processed iron ore and 237 Mt run of mine ore. At present crude steel capacity in India stood at 142.2 Mt in 2018-19 while production of crude steel reached at 110.9 Mt (78pct utilization) [2].

National steel policy 2017 [3] estimated Indian steel production of 300 Mt will be achieved by 2030-31. To achieve this target, Indian steel plants must have to anticipate latest technologies, increase their production capacities, improve the efficiency of operations, implement latest technologies, utilize raw materials efficiently as well as minimize waste generation [4].

For 300 Mt steel production, there will be requirement of 510 Mt of processed iron ore and 636 Mt run of mine ore per year. India is one of the fortunate countries to have reserves of high-grade iron ores. But with time these reserves of high-grade iron ores are bound to be diluted.

India is amongst the leading producers of iron ore in the world[5].Hematite (Fe_2O_3)and magnetite(Fe_3O_4) are the most important iron ores in India. About 79 pct haematite ore deposits are found in the Eastern Sector (Assam, Bihar, Chhattisgarh, Jharkhand, Odisha and Uttar Pradesh); while about 93 pct magnetite ore deposits occur in Southern Sector (Andhra Pradesh, Goa, Karnataka, Kerala, and Tamil Nadu). Karnataka alone contributes 72 pct of magnetite deposit in India. Of these, hematite is superior because of its higher grade. Indian deposits of haematite ore is within banded iron ore formations occurring as massive, laminated, friable and in powdery form. Another principle iron ore is magnetite that also occurs in the form of oxide. Table 1.2 shows iron ores reserves of India.

Table 1.2: Iron ores Reserves of India (Mt) (as on 1.4.2015) [5]

Type of Ore	**Reserves Category**	**Remaining Resources Category**	**Total**
Haematite	5,422	17,065	22,487
Magnetite	53	10,736	10,789
Total			**33,276**

India has reasonable coal reserves 319,021Mt. Out of which mineable are only 148,788 Mt (i.e.46.6 pct). The coking coal is 19,082 Mt (only 12.8 pct), which is useful for blast furnace iron making. Out of that prime coking is around 4,649 Mt (3.1 pct), medium coking 13,914 Mt (9.4 pct) and semi coking coal is 519 Mt (0.3 pct).Whereas the non-coking coal is 129,112 Mt (86.8 pct), as shown in Table 1.3 [6]. Huge amount of coal fines and coke breezes are also produced during coal mining and coking of coal respectively. These fine cannot be processed in sponge iron/DRI reactors such as Rotary kiln and Rotary hearth.

Table 1.3: Coal Resources of India (Mt) (as on 1.4.2018) [6]

Type of Coal	**Proved/Measured**	**Indicated**	**Inferred**	**Total**
(A) Coking				
Prime Coking	4,649	664	0	5,313
Medium Coking	13,914	11,709	1,879	27,502
Semi-Coking	519	995	193	1,707
Sub-Total (A) Coking	19,082	13,368	2,072	34,522
(B) Non-Coking	129,112	125,697	28,102	282,911
(C) Tertiary Coal	594	99	895	1,588
Grand Total (A + B + C)	**148,788**	**139,164**	**31,069**	**319,021**

However, in a steel industry where several processes are employed using of various raw materials. It is obvious that many valueless substances are generated which are termed as waste materials. Average about 500 kg of solid wastes are generated per tonne of crude steel production [7]. Various solid wastes are blast furnace slag, blast furnace flue dust and sludge, Linz–Donawitz (LD) converter slag, LD sludge, LD dust, mill scale, mill sludge, etc. that are coming out from steel plants.

The utilization of wastes needs to be dealt with in a judicious and sustainable manner. Solid wastes generated from process units are generally characterized by their uniform size and composition. Low moisture content, high levels of metallic and non-metallic values (e.g. CaO, C etc.) content in wastes, which makes these suitable for recycling within the plant or to be sold out to consuming industries. The production of solid wastes per tonne of production of steel is around 1.2 ton in India compared to around 0.55 tonne of that practicing in abroad due to inferior quality of raw materials used and an absence of proper solid waste management practices. Out of total solid wastes generated in the steel plant in our country around 63% are dumped which needs to be recycled or reused to target a zero-solid waste as being done in many developed countries[10]. The huge quantities of iron ore slimes (containing 55 to 60% iron, size < 0.15 mm) collected in tailing ponds, estimated to be 130 Mt (accumulate to the tune of around 10 Mt per year in India) are not being utilized at present [11].

Efforts are being made to utilize the waste materials by proper characterization, beneficiation and agglomeration techniques. The treatment/utilization of steel plant sludge/dusts is still a problem in many countries of the world. Effective utilization of dust and sludge for iron and steel making can be possible after upgradation of iron percent and discard the valueless materials. There is also shortage of coking coal all over the world in general and in particular at India. Large amount of coal fines and coke breezes are generated during coal mining and coking of coal respectively. By incorporating non-coking coal fines or coke breezes with up-gradated dust and sludge are utilized in producing cold bonded iron oxide-coal composite pellets. Using waste-coal composite pellets, metallurgical coke requirement in the ironmaking processes can be reduced.

The iron bearing oxide and carbonaceous material fines are mixed with an appropriate binder and optimum quantity of moisture. The mixture is then pelletized into balls of suitable size.

The composite pellets in cold bonding process are hardened due to physio- chemical changes of the binder in ambient conditions [13] or at slightly elevated temperature (400 to 500K). In cold bonding process, finding a suitable binder is a challenge that ensures the proper physical and mechanical properties of the composite pellet.

The term composite pellet [13] is used here to mean pellet containing mixture of fines of iron bearing oxide and carbonaceous material (i.e. coal/char) which has been imparted sufficient mechanical properties for subsequent handling by cold bonding technique. The prepared cold bonded composite pellet must have enough mechanical strength to withstand high temperature and stresses in reduction furnaces.

1.1 Objective

Looking into the above aspect, the objective of present study is three-fold:

1. Characterization and beneficiation of dust and sludge by using various methods and establishing proper route for beneficiation with good recovery of iron bearing oxide.
2. To prepare composite pellets using various binders by cold bonding techniques in the laboratory and evaluate their properties; this would be a contribution towards development of suitable binder for cold bonding composite pellets.
3. Utilization of composite pellets in liquid metal bath for steel making in induction melting furnace. As well as auxiliary studies as backup investigation with emphasis on isothermal reduction kinetics.

1.2 Methodology

1. Upgradation of flue dust/sludge by various techniques of beneficiation,
2. Characterization of raw materials,
3. Composite briquette and pellet making,
4. Testing of composite briquette/pellet.

Chapter 2

Review of Literature

This chapter deals with the literature review pertaining to utilization of steel plant wastes, especially dust and sludge. It discusses about the various methods of beneficiation of low-grade iron ores for upgradation. A comprehensive review of utilization of dusts and sludge is done. It also discusses about the composite pellets and smelting reduction processes/ technologies. A comprehensive review of different methods, used by investigators in past, for binder selection is done. Further composite pellet making is discussed by using several inorganic and organic binders. It discusses about preparation, reduction kinetics, advantages and uses of composite pellets. A fundamental knowledge of physical, mechanical and thermal behavior of composite pellets, concept of cold bonding, smelting reduction process concepts and understanding of mechanism and kinetics of smelting reduction processes are of utmost importance before advancing through the intricacies of the present study.

Chapter 3

Characterization and Beneficiation (Experimental-I)

This chapter deals with the characterization of raw materials (which include sieve analysis of Steel Plant's wastes (i.e. dust and sludge), chemical analysis of dust and sludge, and proximate analysis of coal etc. By beneficiation methods, an attempt was made to find suitable up-gradation technique to increase the total Fe percentage of dust and sludge; thereby to develop a proper beneficiation method for dust and sludge.

3.1 Characterization and Preparations of Raw Materials

In any experimental work, it is extremely important to characterize the input materials as they provide necessary information required for assessment of the properties of the products. These include evaluation of physical, chemical, and other characteristics of the materials. The sources of raw materials used for experimental work are shown in Table 3.1.

Table 3.1: Sources of Raw Materials

Sources of Iron Oxide (Steel Plant's wastes)	
Steel melting shop dust	Jindal Steel Works, Bellari, Karnataka, India
Steel melting shop sludge	Jindal Steel Works, Bellari, Karnataka, India
Steel melting shop sludge	Vizag Steel Plant, Vishakhapatnam, Andhra Pradesh, India
Coal	
Coal	Procured from local market
Binder	
Lime	Procured from local market (laboratory reagent grade)
Fly ash	Thermal Power Plant, Vanakbori, Gujarat.
Molasses	Procured from local Foundry
Starch	Procured from local market

3.2 Characterization

3.2.1 Size Analysis

Sludge (obtained from Steel Plant) was associated with moisture and non-uniform particles sizes. Since raw materials (i.e. dust and sludge, coal) have non-uniform particles sizes. After drying and grinding at the ball mill, the samples were taken to a suitable size. Size analyses of raw materials were carried out in sieve shaker for 15 minutes. In each case, 100 g sample was taken. Results of size analyses for JSW Dust, JSW Sludge VIZAG Sludge and coal are presented in Tables 3.2, 3.3, 3.4 and 3.5 respectively.

Table 3.2: Size analysis of JSW Dust

ASTM Mesh No.	Particle Size, µm	Weight pct retained	Cumulative pct retained	Cumulative pct passing
85	180	81.7	81.7	18.3
100	150	6.5	88.2	11.8
150	106	7.0	95.2	4.8
200	75	2.3	97.5	2.5
Pan		2.5	100.0	

Table 3.3: Size analysis of JSW Sludge

ASTM Mesh No.	Particle Size, µm	Weight pct retained	Cumulative pct retained	Cumulative pct passing
85	180	65.4	65.4	34.6
100	150	11.1	76.5	23.5
150	106	13.4	89.9	10.1
200	75	5.1	95.0	5.0
Pan		5.0	100.0	

Table 3.4: Size analysis of VIZAG Sludge

ASTM Mesh No.	Particle Size, µm	Weight pct retained	Cumulative pct retained	Cumulative pct passing
85	180	54.8	54.8	45.2
100	150	11.6	66.4	33.6
150	106	17.5	83.9	16.1
200	75	8.2	92.1	7.9
Pan		7.9	100.0	

Table 3.5: Size analysis of Coal

ASTM Mesh No.	Particle Size, µm	Weight pct retained	Cumulative pct retained	Cumulative pct passing
85	180	89.8	89.8	10.2
100	150	6.6	96.4	3.6
150	106	1.5	97.9	2.1
200	75	1.2	99.1	0.9
Pan		0.9	100.0	

3.2.2 Chemical Analysis

The objective of chemical analysis was to determine the chemical composition of the raw materials by different established techniques. Studies were carried out either on the samples as received or after drying if the received samples are associated with moisture. Each material (individually) was thoroughly mixed for homogeneous composition after drying and a representative sample was collected from mixed material for investigation.

Chemical analysis of Steel Plant's dust and sludge werecarried out by Energy Dispersive X-ray Fluorescence (XRF) Spectrometer (Model: EDXRF-800, Make: Shimazdu, Japan); which is available at Metallurgical and Materials Engineering Department, M. S. University of Baroda, Vadodara.

X-ray fluorescent spectrometer (XRF)is used to determine the Chemical compositions of the samples. The chemical analyses of the Steel Plant's waste samples are shown in Table 3.6. Proximate analysis of coal is carried out in laboratory as per standard method(ASTM D3172) and presented in Table 3.7.

Table 3.6: Chemical analysis of waste samples (as received)

Assay	$Fe_{(T)}$ pct	Fe_2O_3 pct	CaO pct	SiO_2 pct
Dust from Jindal Steel Works, Bellari	38.77	55.39	35.84	5.57
Sludge from Jindal Steel Works, Bellari	51.64	73.77	20.69	2.51
Sludge from Vizag Steel plant, Vishakhapatnam	49.49	70.70	23.29	1.65

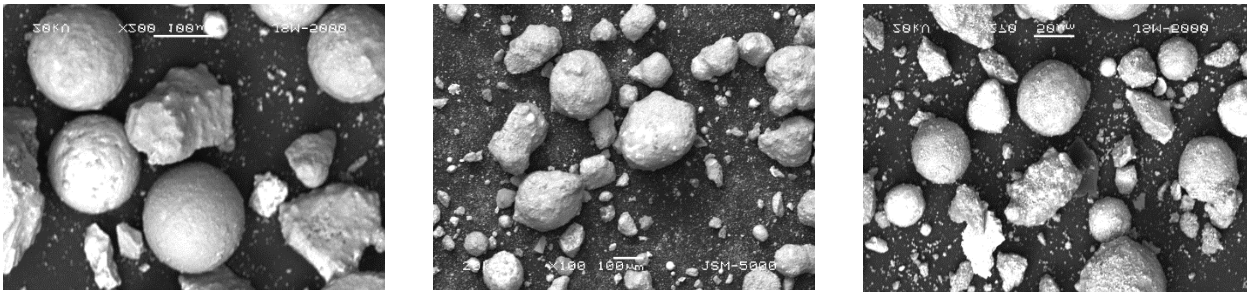
Table 3.7: Proximate analysis of coal samples (as received)

Analyte	Moisture	Volatile Matter	Ash	Fixed carbon
Wt.%	1.0	17.0	20.0	62.0

3.2.3 Microscopic Observation of Raw Materials

Scanning electron microscopy (SEM) is used primarily for the study of surface topography of solid materials. It permits a depth of field far greater than optical or transmission electron microscopy (TEM). Scanning electron microscopic examinations of the powder samples of JSW dust and JSW sludge and VIZAG sludge were carried out to observe the size and shape morphology using JEOL SEM.

Microscopic observation of dust and sludge materials were done by Scanning Electron Microscope (SEM) at Metallurgical and Materials Engineering Department, M. S. University of Baroda, Vadodara. The Scanning Electron Microscopic (SEM) photo-micrographs of JSW Dust, JSW Sludge and VIZAG Sludge are shown in Figure 3.1(a-c). Figure 3.1(a) shows the SEM photomicrographs of JSW Dust sample showing the presence of typically spheroidal shaped particles, some irregular shape particles are also present. JSW sludge and Vizag sludge samples are shown in Figures 3.1(b and c) respectively, that shows spheroidal and irregular shaped particles. The particles are separate from each other.



(a) JSW Dust (b) JSW Sludge (c) VIZAG Sludge

Fig: 3.1: SEM micrographs of JSW Dust, JSW Sludge and VIZAG Sludge sample

3.2.4 XRD Analysis

A few samples were selected for X-ray diffraction studies. XRD analysis of dust and sludge were carried out to identify the phase distribution in the raw material. The results of XRD analysis for JSW dust is shown in Figures 3.2.

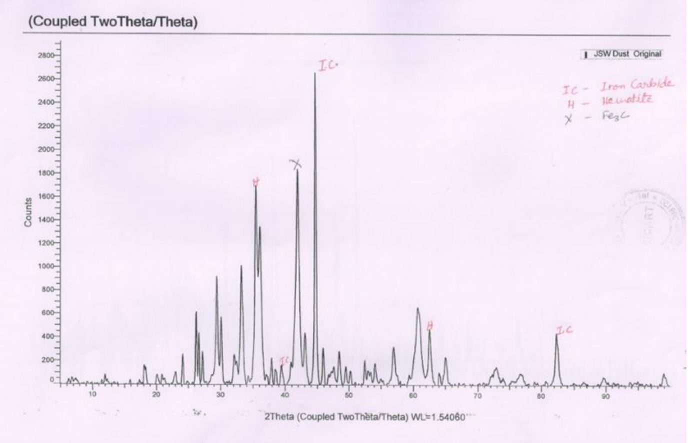


Fig. 3.2: XRD Analysis of JSW Dust (Original Sample)

3.3 Beneficiation

The size distribution of all the wastes were non-uniform; from 66.4 pct in VIZAG sludge to 88.2 pct in JSW dust were found above 150 μm (i.e. 100 mesh). To get uniformity in particle size the dust and sludge was grinded in ball mill up to 150 μm (i.e. 100 mesh).

3.3.1 Single Stage Beneficiation Method

To upgrade the iron (Fe) value in steel plant wastes, many trials are taken for beneficiation processes to discard gangue materials. The beneficiation methods of powder samples were carried out by hydraulic classifier, air classifier and Wilfley table. All the experiments are carried out at Metallurgical and Materials Engineering Department, MSU Vadodara as per the standard procedures. Recovery of iron from wastes were calculated as follows:

$$\text{Iron recovery (pct)} = \left\{\frac{(W_2 \ x \ f_2) x \ 100}{(W_1 \ x \ f_1)}\right\} \qquad \text{....(3.1)}$$

where $W_1$is weight of feed sample, W_2isweightof product after beneficiation,

f_1 is fraction of $Fe_{(T)}$ in feed sample, and

f_2 is fraction of $Fe_{(T)}$ in product after beneficiation.

Further all the beneficiation methods for each sample were compared and it was found that for JSW Dust air classifier was most suitable, total Fe increased from 38.77 to 46.24 pct. Tabling gave good result for JSW sludge, total Fe increased from 51.64 to 60.45 pct. Again, for VIZAG Sludge Tabling was most suitable, total Fe increased from 49.49 to 60.08 pct. However, Air Classifier was very much useful beneficiation process to reduce gangue materials in general and in particular CaO.

3.3.2 Two Stage Beneficiation Methods

Considering the results of individual process on all the three types of waste, a common two stage beneficiation route was developed. The process route, using two stage beneficiation method, was finalised where air classifier was used in the first stage and getting good results; hence the underflow of air classifier was treated again in Wilfley Table. After tabling the concentrate and middling were mixed for final utilization. Figure 3.3 shows the flow diagram of two stage beneficiation route for upgradation of dust/sludge.

The results of two stage beneficiation are given in Table 3.8 to 3.10 for JSW dust, JSW sludge and VIZAG sludge respectively. Maximum increased in total Fe was 63.48 pct (for Tabling concentrate) achieved in JSW sludge; for JSW dust Fe total was upgraded to 61.13 pct (for concentrate + middling of Tabling); and in VIZAG sludge was upgraded to 60.04 pct (for Tabling concentrate) total Fe. Based on total Fe percentage, the two stage beneficiation route is selected.

- Stage 2 recovery is calculated with result of stage 1 as the initial value
- Fe (pct)for (Concentrate + Middling)= $\{\frac{(W_c \text{x } Fe_c + W_m \text{ x } Fe_m) x\ 100}{(W_c + W_m)}\}$ ….(3.2)

where W_c is weight of concentrate, W_m is weight of middling;

Fe_c is fraction of $Fe_{(T)}$ in concentrate, and Fe_m is fraction of $Fe_{(T)}$ in middling.

Table 3.11 shows the final Fe_2O_3, pct considered for pellet production.

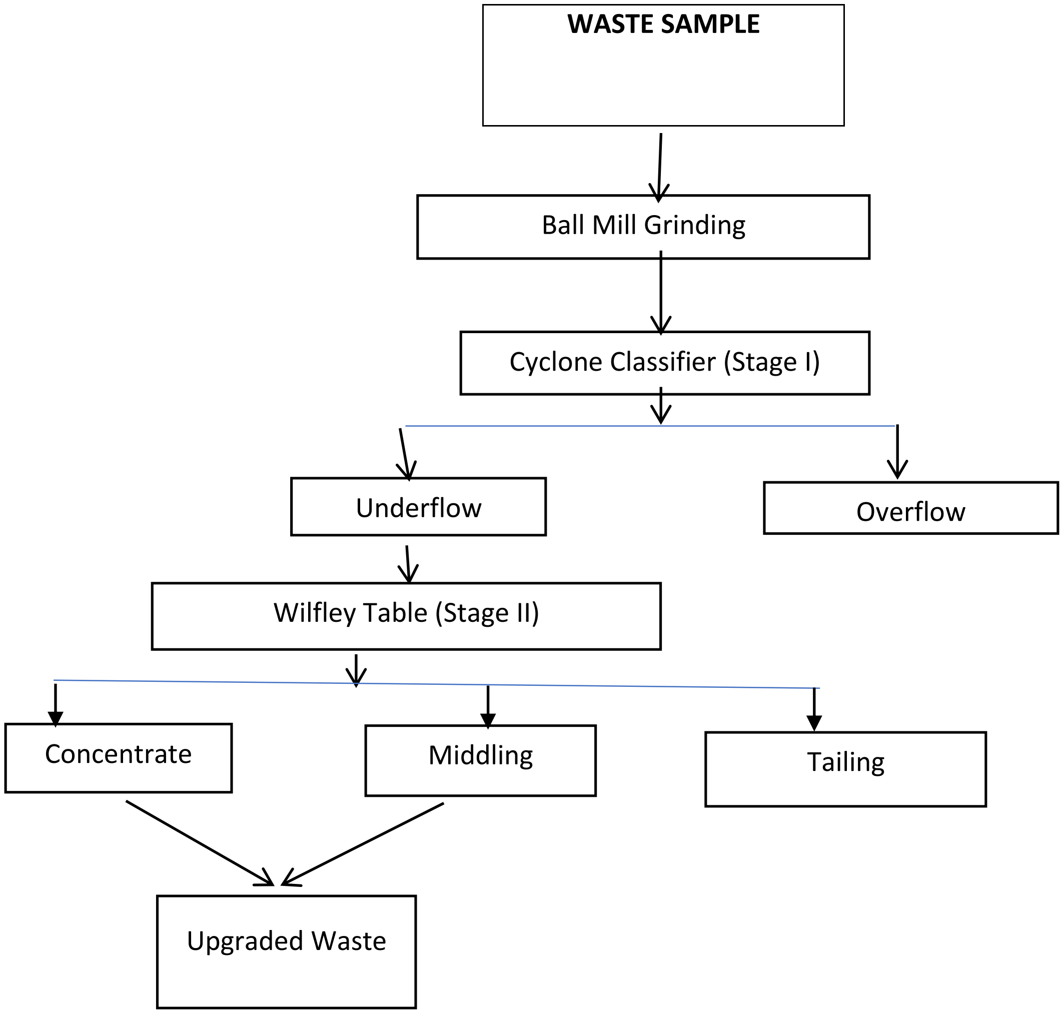


Fig. 3.3: Flow diagram two stage beneficiation for upgradation of dust/sludge

Table 3.8: Result of two stage beneficiations for JSW DUST

Process		**Initial weight, g**	**$Fe_{(T)}$, pct**	**Fe_2O_3, pct**	**Weight retained, g**	**Recovery, pct**
	Original Sample		38.77	55.39		
Stage 1	Air Classifier underflow	200	46.24	66.05	159.26	94.97
Stage 2	Tabling Concentrate	149.26	62.16	88.80	54.55	49.15
Stage 2	Tabling Middling		60.04	85.77	51.35	44.67
Final output	Concentrate + Middling		61.13	**87.33**	105.9	93.8

Table 3.9: Result of two stage beneficiations JSW SLUDGE

Process		**Initial weight, g**	**$Fe_{(T)}$, pct**	**Fe_2O_3, pct**	**Weight retained, g**	**Recovery, pct**
	Original Sample		51.64	73.77		
Stage 1	Air Classifier	200	53.25	76.07	162.25	83.65
Stage 2	Tabling Concentrate	152.25	63.48	**90.69**	100.12	78.39
Stage 2	Tabling Middling		59.75	85.36	18.57	13.66
Final output	Concentrate + Middling		62.89	89.84	118.69	92.07

Table 3.10: Result of two stage beneficiation VIZAG SLUDGE

Process		**Initial weight, g**	**$Fe_{(T)}$, pct**	**Fe_2O_3, pct**	**Weight retained, g**	**Recovery, pct**
	Original Sample		49.49	70.70		
Stage 1	Air Classifier	200	47.95	**68.5**	170.08	82.39

Stage 2	Tabling Concentrate	160.0	60.04	**85.77**	73.75	57.72
Stage 2	Tabling Middling		37.36	53.37	37.78	18.4
Final output	Concentrate + Middling		52.36	74.80	111.53	76.12

Table 3.11: Final Fe_2O_3, pct considered for pellet production

Assay →	**Initial $Fe_{(T)}$, pct (f_1)**	**Final $Fe_{(T)}$, pct (f_2)**	**Final Fe_2O_3, pct**
JSW Dust	38.77	61.13	**87.33**
JSW Sludge	51.64	63.48	**90.69**
Vizag Sludge	49.49	60.04	**85.77**

Chapter 4

Briquetting and Pelletizing (Experimental-II)

The fourth chapter discusses the briquettes and pellets preparation and their testing. Taguchi technique was used, for selection of binder proportion in combination. To select the proper binder for pellets preparation, cylindrical shaped briquettes (diameter 9.75 mm and height 13-14 mm) were prepared and tested. Different binders like lime, slaked lime, bentonite, molasses etc. and their combination were used to prepare briquettes and their properties (compressive strength, drop strength and shatter index) were evaluated. From the results of briquettes' strength, pellets were prepared with combined binders (i.e. corn starch and molasses). Isothermal reduction in tubular furnace was carried out and weight loss method was used to find percentage of reduction. The activation energy was also calculated.

4.1 Briquette Preparation

Binders play a very important role in the briquetting/pelletizing process. Binder is that material which serves as a bridge between the particles and thus increases the green or dry strength of the bonded particles.

To select the proper binder for pellets, initially cold bonded briquettes of waste-coal composite briquettes were prepared using a die and punch assembly by giving one impact to the moist powder mixture. The impact force was standardized by proper design of assembly. Diameter and height of the cylindrical shaped briquettes were 9.75 mm and13 to 14 mm respectively. The weight of the briquettes varied between 2.0 to 2.20 g. After green briquettes formation that were exposed to CO_2 gas for 5 minutes (in some cases only) which favored the formation of carbonate bonds between the particles. These briquettes were dried in open atmosphere for 24 hours.

The binder may be organic or inorganic materials. Initial trials for briquettes using various organic and inorganic binders were done only for JSW dust; later, all the other wastes are also used for binder selection.

4.1.1 Testing of Briquettes

The properties of briquettes / pellets of interest are those properties which have bearing on its performance during handling and transportation until it is charged in the furnace, and subsequently on its behavior inside the furnace. The success of the cold bonding process depends heavily on attaining sufficient strength of the composite pellets. Some of the room temperature physical and mechanical properties have been tested and results are reported in this section.

Tests (as per standard procedure) are as follows:

1. Drop test
2. Compression test
3. Shatter test

Trails were done with starch and molasses as binder separately with JSW dust (Table 4.1) and the results were tabulated (Table 4.2). The starch was formed from corn powder. Starch is a carbohydrate. It does not dissolve in cold water and decomposes very easily. The starch has other advantages as binder, such as easy burn out, environment friendly and inexpensive. After careful analysis it was observed the results were promising with starch and molasses when the percentage of binder was more than 5 pct. The combination of binder (starch and molasses) were then tested using design of experiments. It was found that 10 pct starch or 10 pct molasses giving very good results without CO_2 gas passed.

Table 4.1: Different amount of binders used for briquettes

Sr.No.	Binder Composition	Coal
1.	5 pct Starch	As per Stoichiometric calculations
2.	10 pct Starch	
3.	10 pct Molasses	

Table 4.2: Results of briquettes using starch or molasses

Batch No.	**Binder used**	**No. of Stroke**	**Drop No.**	**Shatter Index (pct)**	**Strength (N/Briquette) (Average)**
TB7	5pct Starch	3 strokes	11	22.01	78.4
TB8	10pct Starch	3 strokes	>150	0.52	431.2
TB9	10pct Molasses	3 strokes	>150	0.31	833.0

** CO_2 gas did not pass after briquetting

4.2 Design of Experiments

Experimental work for the briquetting is carried out in such a way that minimum number of experiments can give output as desired. For this *design of experiment* methodology is applied to select the runs of experiment. After the selection of *orthogonal array* and experiment combinations, Taguchi technique was used with two variable (starch and molasses) and three levels (2.5pct, 5.0 pct and 7.5pct of each).

The Taguchi method was developed by Genichi Taguchi, Japan. Taguchi method has been widely utilized in engineering analysis and consist of a plan of experiments with the objective of acquiring data in a controlled way, in order to obtain information about the behavior of a given process[110].The Taguchi design involves orthogonal arrays to organize the parameters affecting particular property of interest and the levels at which they vary. It allows the selection of the necessary data to determine the factors affecting product quality the most with a minimum number of experiments.

Weighted index for the individual outcome for strength and shatter index also for combined properties for pellets are calculated and using that information. Proper combination of starch and molasses, as per required strength and/or shatter index, is selected. Strength and shatter index are complementary properties for pellet. Significance of both the properties may be a compromise between the two. With the help of the Table 4.3, the combination of the two properties according to the rank, finally the proportion of the binder can be selected.

Indexes are calculated as follows:

i) Weighted index for strength = $\frac{\text{Particular strength}}{\text{Max.strength}}$ …(4.1)

e.g. for EE9: Weighted index for strength = [1014.3/1435.7] = 0.7065

ii) Weighted index for shatter index = $\frac{\text{Min.shatter index}}{\text{Particular shatter index}}$ …(4.2)

e.g for EE4 : Weighted index for Shatter index = [0.064/1.488] = 0.043

iii) Total Index = (Weighted index for strength + Weighted index for shatter index) ….(4.3)

Table 4.3: Ranking order considering effect of both outputs

Rank	**Experiment Run**	**Starch (pct)**	**Molasses (pct)**	**Raw Material**	**Strength (N/Briquette)**	**Shatter Index (pct)**	**Weighted index for strength**	**Weighted index for Shatter index**	**Total Index**
1	EE9	7.5	7.5	2	1014.3	0.064	0.7065	1	1.7065
2	EE4	5.0	2.5	2	1435.7	1.488	1	0.043	1.043
3	EE8	7.5	5.0	1	1167.39	0.4	0.8131	0.16	0.9731
4	EE7	7.5	2.5	3	1063.3	0.358	0.7406	0.1788	0.9194
5	EE3	2.5	7.5	3	960.4	0.636	0.6689	0.1006	0.7695
6	EE5	5.0	5.0	3	759.5	0.529	0.529	0.121	0.65
7	EE6	5.0	7.5	1	784.8	0.86	0.5466	0.0744	0.621
8	EE2	2.5	5.0	2	539.0	2.096	0.3754	0.0305	0.4059
9	EE1	2.5	2.5	1	451.26	0.84	0.3143	0.0762	0.3905

4.3 Bonding Mechanism

4.3.1 Corn Starch

The general chemical formula of corn starch is [$(C_6H_{10}O_5)_n$]. Corn starch has semi-crystalline particle structure, the internal area is non-crystalline, while the outer area is crystallized (as shown in Figure 4.1). At the same time, the high relative molecular mass of corn starch and the close reticular formation generated from hydroxyl synthesis by hydrogen bond result in high viscosity[116]. By adding water to the corn starch, swelling take place and viscosity increases; so, the briquettes get a high strength at room temperature. With the temperature rising, the water molecules enter the corn starch, combine with starch molecular and start irreversible swell. When the temperature reaches 110°C, the gelatinization (i.e. it is a process of breaking down the intermolecular bonds of starch molecules in the presence of water and heat) is completed. The original morphological structure of corn starch granules is broken, and the intermolecular interaction is weakened, due to that thoroughly starch spread on the waste concentrate and coal particles. At 200°C corn starch gradually transforms into a continuous solid bridge formation (Figure 4.2), which connected the concentrate and coal particles closely and strength of the composite briquettes increases. Because of mechanical force, the crystal structure of corn starch has been destroyed. The degree of lattice ordering of crystal in crystalline area reduces gradually, which creates a good fluidity of corn starch.

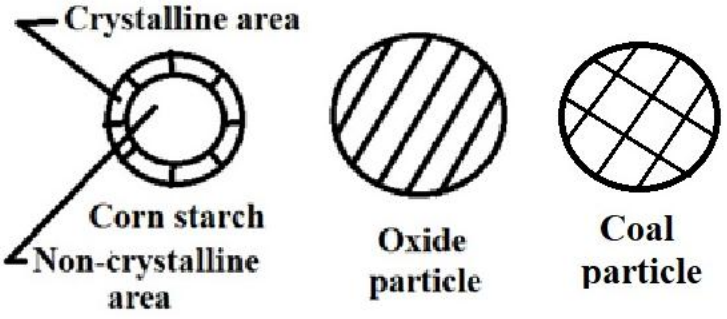


Fig. 4.1: corn starch, waste concentrate and coal particles

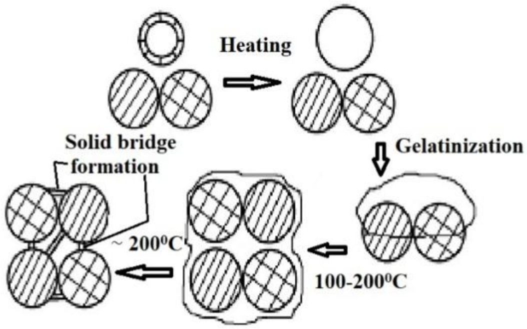


Fig. 4.2: Bonding mechanism of corn starch

Corn starch can improve the composite briquettes strength at room temperature and the strength after drying because of the expansibility after absorbing water and compatibility after gelatinization of corn starch. At 100-200^{0}C corn starch thoroughly spade on the waste concentrate and coal particles and after 200°C corn starch gradually transforms into a continuous solid bridge formation, which connected the concentrate particles and coal particles closely. The strength of composite briquettes/pellets are improved.

4.3.2 Corn starch and Molasses

Molasses is a viscous product resulting from refining sugarcane or sugar beets into sugar. Molasses (containing around 50 pct fermentable sugars and 80 pct soluble solids), usually is diluted with an equal amount of water[117] to reduced viscosity. Initially dilute molasses gives a coating on the concentrate particles and coal particles, then due to gelatinization of corn starch which thoroughly spade on the waste concentrate and coal particles; and finally, by solid bridge formation connecting the concentrate and coal particles closely (Figure 4.3).

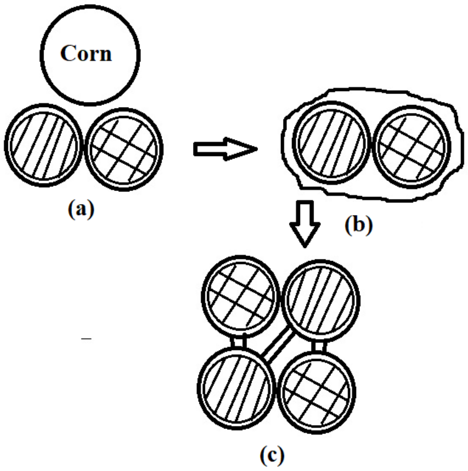


Fig. 4.3: Corn starch-molasses bonding. a) concentrate particle and coal particle coated with molasses, b) corn starch thoroughly spade on the particles, and c) solid bridge formation connecting particles.

Again, chemically corn starch and molasses are form long chain bonding. Reactions of corn starch and molasses are as follows:

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + n\,H_2O = \underset{\text{Glucose}}{n\,(C_6H_{12}O_6)} \qquad \ldots(4.4)$$

$$n\,(C_6H_{12}O_6) = 2n\,(C_2H_5OH) + 2n\,CO_2 \qquad \ldots(4.5)$$

Glucose Ethanol

Again, $$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6 \qquad \ldots(4.6)$$

Molasses Glucose Fructose

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2 \qquad \ldots(4.7)$$

Glucose Ethanol

$$\therefore \quad (C_6H_{10}O_5)_n + C_{12}H_{22}O_{11} + (n+1)\,H_2O = C_6H_{12}O_6 + 2(n+1)\,(C_2H_5OH) + 2(n+1)\,CO_2$$

Starch Molasses Fructose Ethanol …(4.8)

4.4 Pellets Preparation

Figure 4.3 shows the flow diagram for composite pellet making. Binders were selected based on briquettes formation and proper strength of briquettes. Waste-coal composite pellets were prepared using as binder based on Table 4.2, binder proportions (i.e. starch and molasses) were selected for all the three raw materials (Table 4.3) and bulk pellets were prepared according to their compositions.

First mixing of raw materials (waste fines, coal fines, and binders) were done in a porcelain jar rotated at 50 rpm for one hour in a pebble mill. Pellets were prepared in batches using a disc pelletizer (400 mm diameter) which rotated at 17 rpm and angle of pelletizer is 40°. The mixture was fed into the disc manually and water was added by spraying time to time. Total moisture was in the range of 8 to 10 pct by weight of the mixture. The green pellets of nearly 12 to 22 mm sizes were formed. CO_2 gas were not passed to the pellets for hardening. The pellets were dried in open atmosphere for 24 hours. These pellets got hardened in cold bonding process due to physico-chemical changes of the binder in ambient condition. For experimental work, composite pellets were prepared using coals from local sources having Fe_{tot}/C ratio as per stochiometric.

Table 4.3: Selection of binder for pellets

Raw Material	Starch, pct	Molasses, Pct
JSW Dust (1)	7.5	5.0
JSW Sludge(2)	5.0	2.5
VIZAG Sludge (3)	7.5	2.5

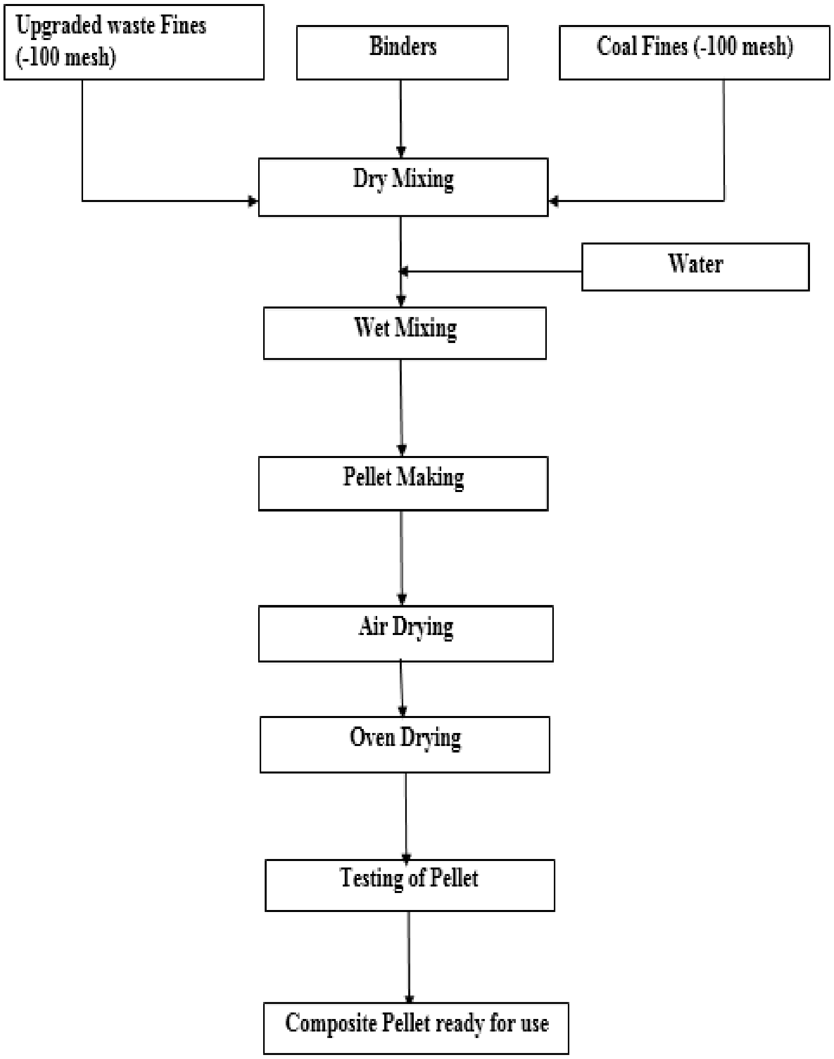


Fig.4.4: Flow diagram of composite pellet making

4.5 Study of Reducibility

The degree of reduction of iron oxide can be obtained by reducibility studies through weight loss method when a gaseous reductant is used. For reduction of iron oxides by carbon, the degree of reduction cannot be found out directly from the weight loss of the sample, since both oxygen and carbon are loosed during reduction. It is not possible to delineate the two unless the released gases are analyzed and their volumes are measured. Accordingly, such reactions have been studied with the help of gas chromatograph attached with the reduction chamber. Even this method runs into trouble when coal is used in place of pure carbon or graphite. Alternatively the reaction product can be chemically analyzed after each test run, but this procedure is time consuming, more expensive and gives only intermittent information. For ore-coal composite pellets, the weight loss of the sample arises not only from oxygen and carbon loss, but also the loss of volatile matters and residual moisture present in pellets[13]. Since only weight loss of the sample is not sufficient, some additional measurements are required for estimating the degree of reduction (α), which is defined as follows:

$$\alpha = \frac{\text{Weight of oxygen removed from iron oxide}}{\text{Total weight of removable oxygen present in iron oxide}} \text{ x } 100 \qquad \text{...(4.9)}$$

Sah and Dutta[96] used the following equation for calculation of fraction of reduction to take care of the loss of volatile matters:

$$f = \left[\frac{4 \text{ x } \{f_{wl} - (f_{coal} \text{ x } f_{vm})\}}{7 \ x \ (f_{ore} \ x \ \rho_{ore} \ x \ f_o)}\right] \qquad \text{...(4.10)}$$

where, f_{wl} is fractional weight loss, = $[(W_i - W_f) / W_i]$,

W_i is the initial weight of the composite pellet,

W_f is the final weight of the composite pellet after reduction,

f_{coal} is fraction of coal present in composite pellet,

f_{vm} is fraction of volatile matters present in coal,

f_{ore} is fraction of waste present in composite pellet,

ρ_{ore} is purity of iron oxide (Fe_2O_3) in waste,

f_o is fraction of oxygen present in pure Fe_2O_3.

4.5.1 Horizontal Tube Furnace

Electrically heated tube furnace was used for reducibility studies. Temperature was controlled by a Pt-Rh thermocouple. Fused quartz tube of diameter 20 mm and length 600 mm was used for the reduction. One end of the tube was connected to the nitrogen gas cylinder for creating inert atmosphere during reduction while the other end of the tube was connected to the water beaker to check the flow of gas. The quartz heating tube was calibrated along the length using Pt-Rh thermocouple to assess the perfect reaction zone within the tube.

The experiments were designed to investigate the reduction kinetics of the composite pellets in isothermal condition at various temperature. Special ceramic boat was prepared for the pellets to be placed into the tube furnace. Pellets were dried at 150^0C for 30 minutes before placing it into the furnace. Two pellets of 12-15 mm diameter were taken simultaneously. Pellets were weighed using electronic balance of 0.001g accuracy. The weights of pellets were in the range of 3 to 7 g. The pellets were placed in high alumina boat, which was put into the preheated tube furnace in nitrogen atmosphere. The reaction time was noted and after reduction the boat was shifted to the cooling zone of the tube and allowed to cool the pellets in the nitrogen atmosphere for 5 minutes. Then the reduced pellets were transferred to the desiccators for further cooling. The cooled pellets were weighted to calculate the fraction of reduction. The variables for Isothermal reduction of composite pellets are shown in Table 4.4.

Table 4.4: Variables for isothermal reduction of composite pellets

Sr.No.	**Variable**	**Number**	**Remarks**
1	Steel plant Waste	3	JSW Dust, JSW Sludge, VIZAG Sludge
2	Coal	1	From local market
3	Temperature (^{0}C)	3	950, 1000 and 1050
4	Time (s)	5	150, 300, 450, 600 and 1200

4.5.2 Measurement of Rate of Reduction (k) and Activation Energy (E)

The fraction of reduction (f) of composite pellets are calculated as per eq. (4.22). Then, f vs t plots are drawn. From the initial straight line of the plot, the slope of the line is found out to know the rate of reduction (k).

Therefore, $k = \frac{df}{dt}$ ….(4.11)

From the rate of reduction (k), the activation energy (E) can be calculated from Arrhenius equation:

$$\text{Rate, } k = A \cdot e^{-(E/RT)} \quad \ldots (4.12)$$

where A is constant, E is activation energy, R is gas constant, and T is absolute temperature.

Therefore, $\ln k = \ln A - (E/RT)$ … (4.13)

Equation (4.25) is used in analyzing the reduction kinetic data. A plot of ln k *vs* 1/T gives slope (E/R) and from the slope of the line, the activation energy (E) can be estimated.

Therefore, the activation energy (E) = [slope x R] … (4.14)

4.6 Results for Reduction of Composite

4.6.1 Results for JSW Dust

Figure 4.5 shows the reduction curve sat various temperatures for JSW Dust composite. From the Figure 4.5, the fraction of reduction increases with increasing in temperature and time. The rate of reduction for JSW Dust at various temperatures are shown in Table 4.5. lnk vs 1/T is plotted for JSW Dust composite (Figure 4.6) and the slope of the line is found out to calculate activation energy. The activation energy for JSW Dust composite is found to be 52.59 KJ/mol.

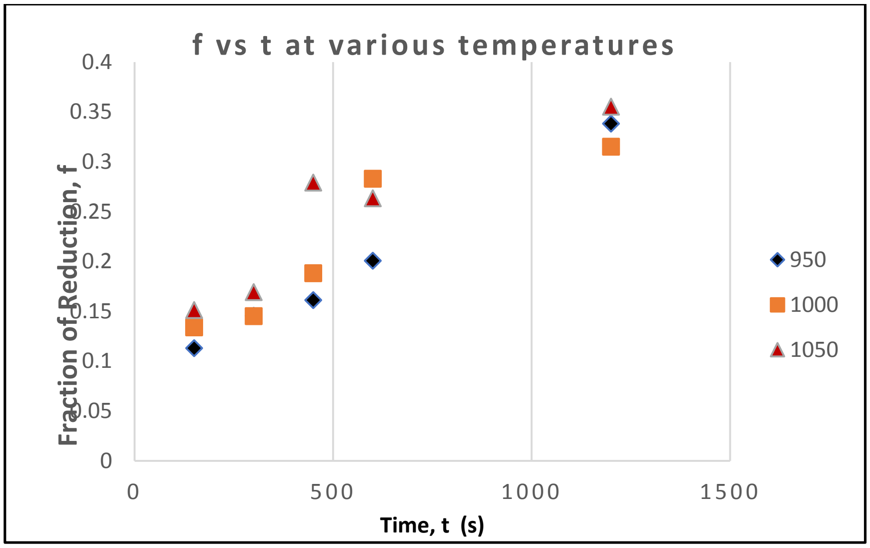


Fig. 4.5: Reduction curve sat various temperatures for JSW Dust composite

Table 4.5: Rate of reduction for JSW Dust composite at various temperatures

Sr.no.	Temp (^{0}C)	Temp (K)	(1/T) x 10^4	Rate, k X 10^4	ln k
1	950	1223	8.18	2.27	-8.39
2	1000	1273	7.86	3.08	-8.09
3	1050	1323	7.56	3.37	-8.00

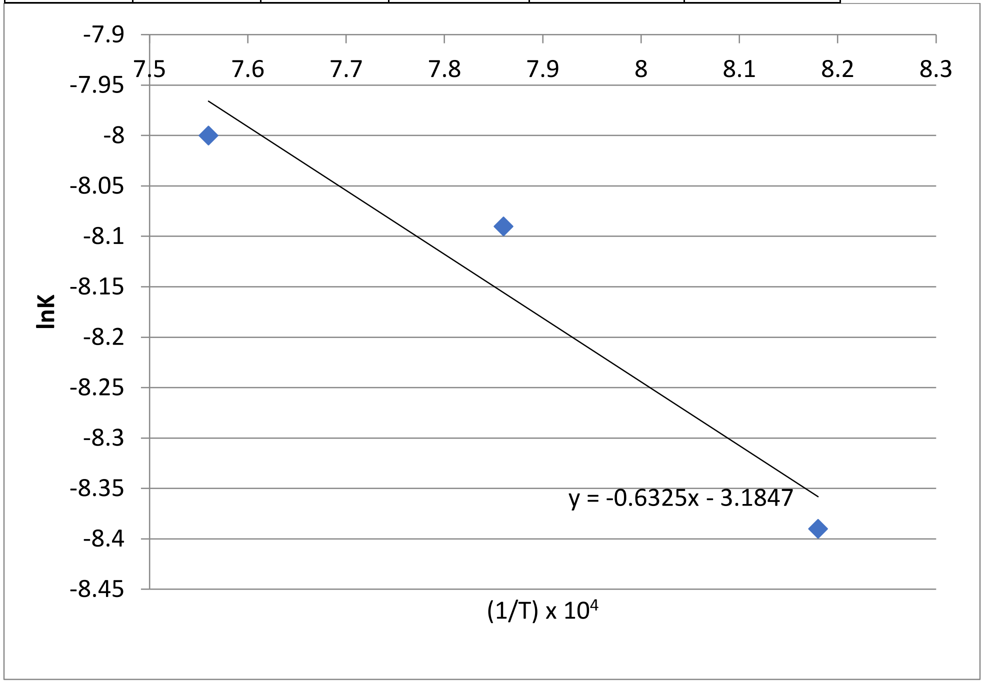


Figure 4.6: Arrhenius plot for JSW Dust composite

4.6.2 Results for JSW Sludge

Figure 4.7 shows the reduction curves at various temperatures for JSW Sludge composite. From the Figure 4.7, the fraction of reduction increases with increasing in temperature and time. The rate of reduction for JSW Sludge at various temperatures are shown in Table 4.6.

lnk vs 1/T is plotted (Figure 4.8) for JSW Sludge and the slope of the line is found out to calculate activation energy. The activation energy for JSW Sludge is found to be 49.8 KJ/mol.

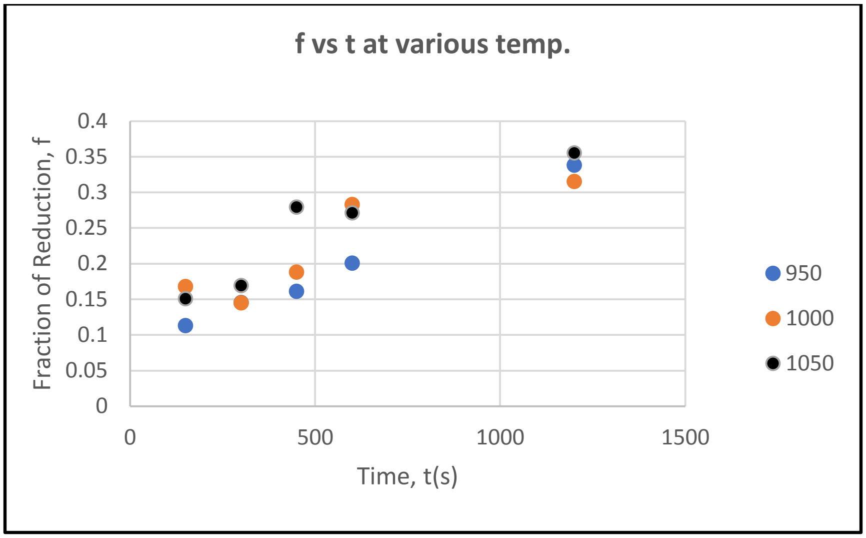


Fig. 4.7: Reduction curves at various temperatures for JSW Sludge composite

Table 4.6: Rate of reduction for JSW Sludge composite pellet at various temperature

Sr.no.	Temp (^{0}C)	Temp (K)	(1/T) x 10^4	Rate, k X 10^4	Ln k
1	950	1223	8.18	7.08	-7.25
2	1000	1273	7.86	9.33	-6.98
3	1050	1323	7.56	10.26	-6.88

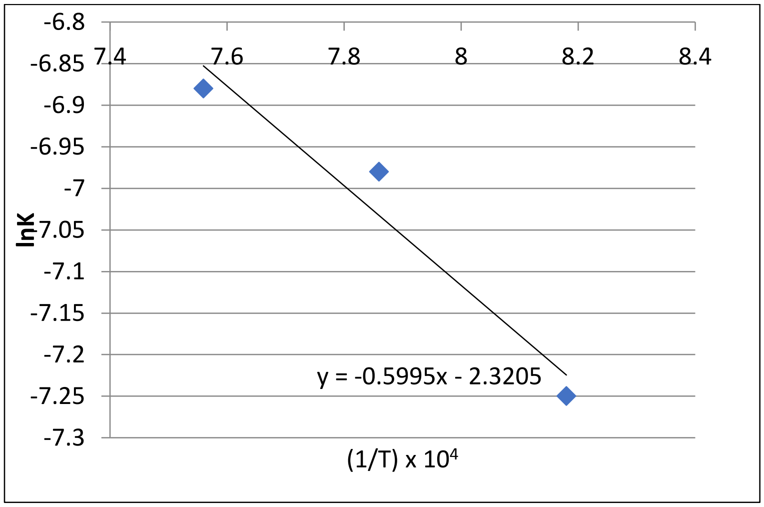


Fig. 4.8: Arrhenius plot for JSW Sludge

4.6.3 Results for VIZAG Sludge

Figure 4.9 shows the reduction curves at various temperatures for VIZAG Sludge composite. From the Figure 4.9, the fraction of reduction increases with increasing in temperature and time. The rate of reduction for VIZAG Sludge at various temperatures are shown in Table 4.7.

Table 4.7: Rate of reduction for VIZAG Sludge composite pellet at various temperature

Sr.no.	Temp (^{0}C)	Temp (K)	(1/T) x 10^4	Rate, k X 10^4	ln k
1	950	1223	8.18	4.29	-7.75
2	1000	1273	7.86	3.78	-7.88
3	1050	1323	7.56	6.79	-7.30

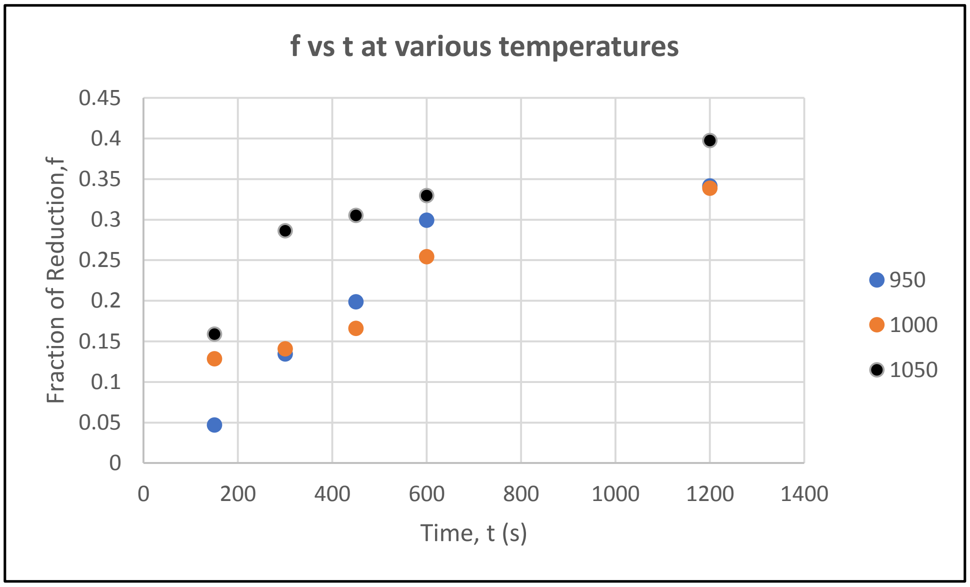


Fig. 4.9: Reduction curves at various temperature for VIZAG Sludge

ln k vs 1/T is plotted (Figure 4.10) for VIZAG Sludge and the slope of the line is found out to calculate activation energy. The activation energy for VIZAG Sludge is found to be 59.28 KJ/mol.

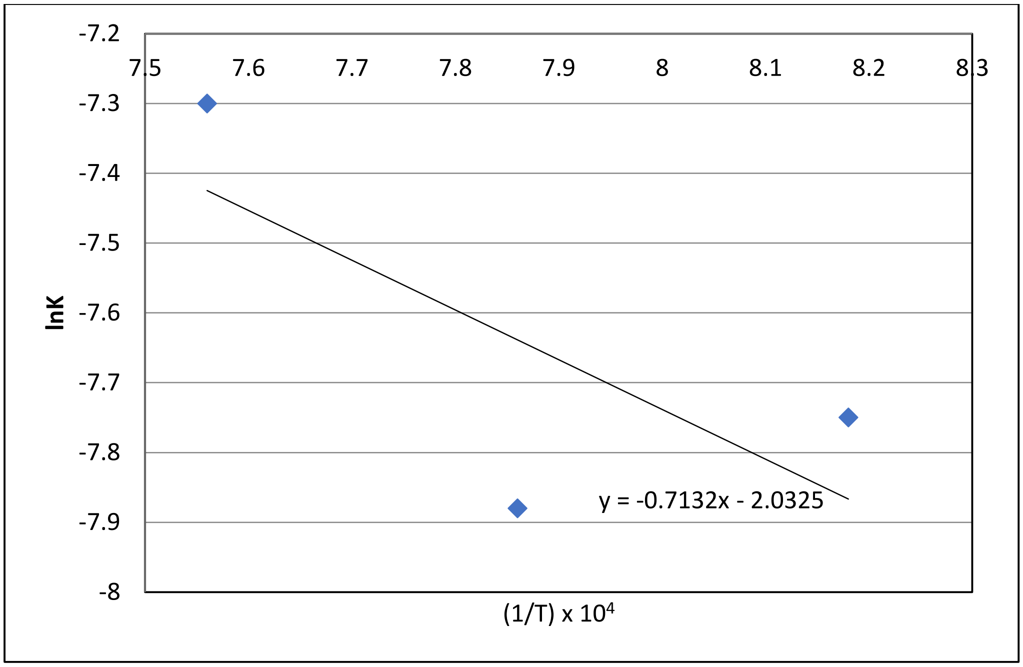


Fig. 4.10: Arrhenius plot for VIZAG Sludge

Table 4.8: Values of Activation Energies for All the Composite Pellets

Sr.No.	Steel Plant Waste	Activation Energy, KJ/mol
1.	JSW Dust	- 52.59
2.	JSW Sludge	- 49.80
3.	VIZAG Sludge	- 59.28

The computed values of activation energies (Table 4.8) are found to be low (49.8 to 59.28 kJ mol^{-1}) which means, volatile gases (in particular H_2) diffuse through porous solid iron oxide particles boundary. Overall reduction is controlled by gasification reactions [$C (s) + CO_2 (g) = 2CO (g)$ and $C (s) + H_2O (g) = CO (g) + H_2 (g)$]. In all cases, lower activation energies obtained may be due to the catalytic effect of freshly reduced iron and gangue present in waste, influence the gasification rate.

These above values are comparable to the values of activation energies reported in the literatures. Wang et al. [118] obtained activation energy 68.95 kJ mol^{-1} for iron ore-hard coal (low volatile content) pellet. Goswami et al. [119] obtained activation energy 60.75 kJ mol^{-1} for fluxed composite pellets. They observed a mixed kinetic model where reduction is initially diffusion controlled and later on chemical reaction controlled. For non-isothermal reduction studies of composite pellets, it was reported [120] that when temperature is lower than 1,073 K (800^0C) , the reaction is controlled by interface chemical reaction; when the temperature is higher than 1,173 K (900^0C), the reaction is controlled by diffusion ($E = 57.3$ kJ mol^{-1}).

4.7 XRD and SEM

XRD were carried out on reduced composite pellets to identify the phases present in reduced composite pellets. Figure 4.11 shows XRD peaks for JSW Dust. The result shows the presence of sharp peaks of different phases. The XRD peaks confirm the topochemical pattern of reduction (i.e. $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$) occurred in the composite pellets.

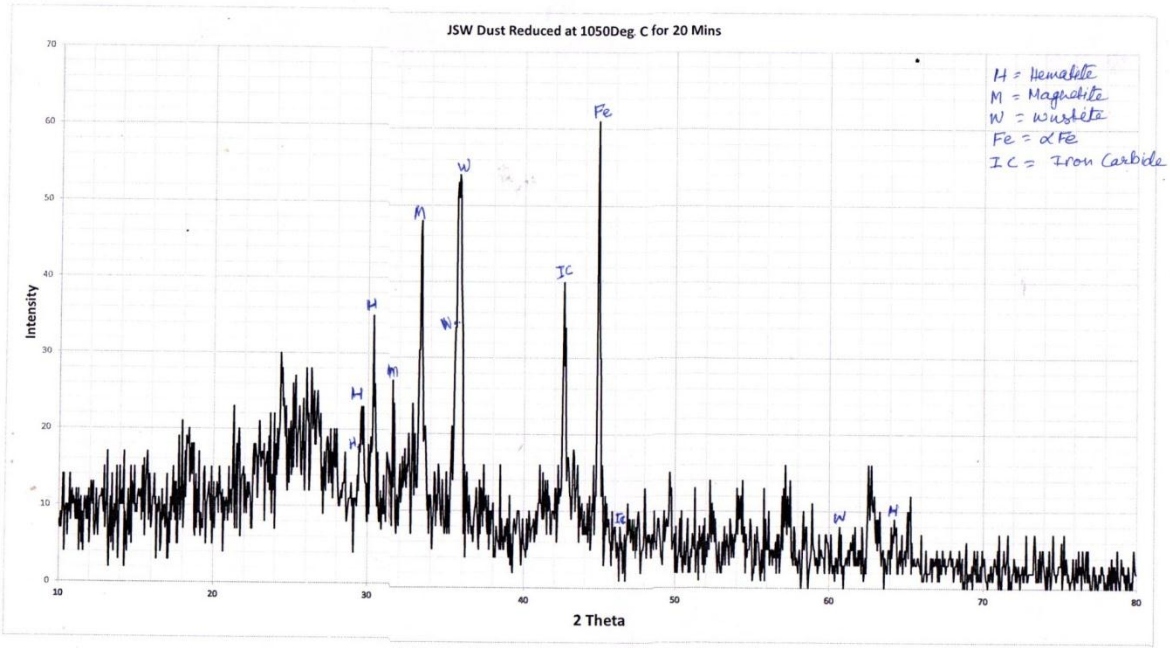
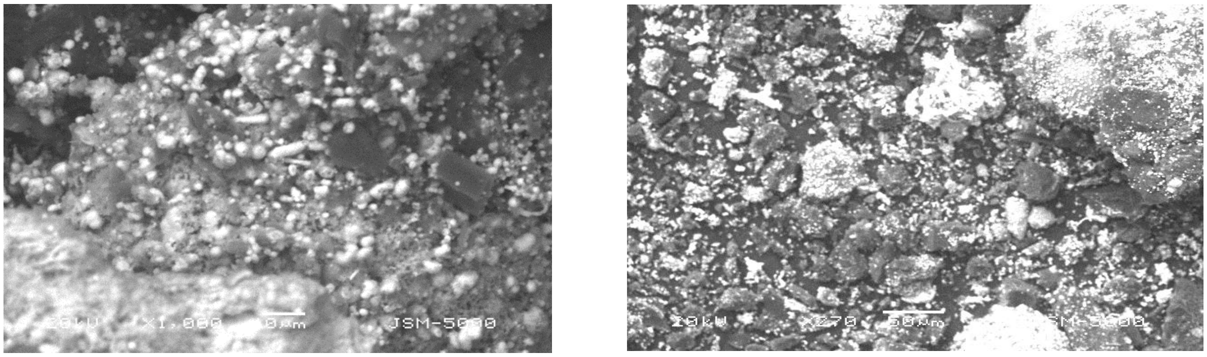


Fig. 4.11: XRD of reduced JSW Dust composite at 1050^0C for 1200 s

Reduced composite pellets were examined by SEM to observe the microstructure. The SEM micrographs (Figure 4.12) confirmed the presence of reduced metallic Fe in reduced composite pellet samples. Fine metallic particles (without sinter) were confirmed the homogeneous reduction mechanism. But the topochemical pattern of reduction in the composite pellets were not found in micrographs.



(a) (b)

Fig. 4.12: SEM micrographs of reduced (a) JSW Dust and (b) VIZAG Sludge composite samples at 1050^0C for 1200 s(5000X)

Chapter 5

Smelting Reduction (Experimental III)

The fifth chapter deals with the analysis of experimental data generated on smelting reduction of the composite pellets made from upgraded waste. The dissolution behavior of the individual pellet as well as bulk dissolution of the pellets are discussed in terms of yield and other output of the smelting reduction.

5.1 Smelting Reduction

The need for an alternate ironmaking technology arises out of the demand to conserve the depleting reserves of good quality coking coal, to make use of non-coking coal reserves dispersed across the country and to take advantage out of large price differences between imported metallurgical coal and non-coking coal. The scenario forced innovators to look for alternative coal-based iron production routes[95]. In order to overcome the above, scientist and technologists have been working for quite some time specially in the second half of last century to develop suitable process of ironmaking, called smelting reduction (SR) process, using non-coking coals and iron ore[15].

5.2 Smelting Reduction of Composite Pellet in Induction Furnace

Smelting reduction of waste-coal composite pellets was carried out in a laboratory induction furnace at Metallurgical and Materials Engineering Department of M. S. University of Baroda. The experiments were designed to investigate i) dissolution behavior of composite pellets in molten bath, and ii) bulk dissolution of composite pellets in molten bath to produce steel/cast iron and to assess the recovery of iron.

5.2.1 Dissolution Behavior of Composite Pellet

Initially the furnace crucible was filled with mild steel scrap. Before switching on the furnace, the demineralized water circulation through heating coil and induction panel was set on. The crucible was filled with steel scrap and furnace was switched on with initial power supply of 4 to 5 kWh and gradually raised to 10 kWh. Within half an hour the steel scrap was melted and chemically homogenization took place. Sample of liquid metal was taken for analysis. Now liquid metal bath was ready to receive the composite pellet. To study the dissolution behaviour of composite pellets in molten bath, a single composite pellet was put in the molten bath and was visually observed that how the composite pellet dissolved in the molten bath and the time required for complete dissolution was noted. This was repeated several times. It was observed that the16-17 mm diameter composite pellets completely dissolved in the molten bath at an average 27 seconds.

5.2.2 Bulk Dissolution of Composite Pellets

Table 5.1 shows the variables for smelting reduction of composite pellets in induction furnace. The experiments were carried out to observe the bulk dissolution of composite pellets in molten bath to produce steel/cast iron and to assess the recovery of iron (in terms of yield). Initially the furnace crucible was filled with mild steel scrap. The switching on the furnace as described earlier, within half an hour the scrap melted and formed molten bath i.e. hot heel. A small amount of liquid molten metal, as sample, was collected for initial chemical analysis of the melt. Composite pellets were charged in small batches to hot-heel. Preheating of pellets took place due to the radiation from hot heel and subsequently reduction and dissolution of pellets occurred in hot heel. Some amount of lime powder was added for easy slag formation. After complete dissolution of pellets and slag-off, the liquid molten bath was allowed to homogenize for some time. The fluidity of molten metal increased with time which led to the homogenization of bath due to convective stirring within liquid molten bath. Slag was removed with the help of steel (TMT) rod. Liquid molten metal was poured in earlier prepared sand mould. The casting was knocked out after solidification and samples were cut for chemical analysis and testing.

Recovery of iron (i.e. yield) was calculated as follows:

$$\text{Iron yield (\%)} = \frac{\boldsymbol{Iron\ present\ in\ product\ x\ 100}}{\boldsymbol{Total\ iron\ present\ in\ the\ charge}}$$

$$= \frac{\boldsymbol{Total\ iron\ in\ output\ as\ cast\ sample\ x\ 100}}{\boldsymbol{Total\ iron\ from\ scrap + Iron\ from\ composite\ pellet + Iron\ from\ starring\ rod}}$$

$$= \frac{(W_5\ x\ F_6)\ x\ 100}{\{[(W_1 - W_2)\ x\ F_1] + (W_3\ x\ F_2\ x\ F_3\ x\ F_4) + (W_4\ x\ F_5)\}} \qquad ...(5.1)$$

Where W_1 = Weight of MS scrap, kg

W_2 = Weight of sample taken for chemical analysis before pellet addition

F_1 = Fraction of Fe present in initial melt

W_3 = Weight of composite pellets charged, kg

F_2 = Fraction of iron oxide present in composite pellets

F_3 = Fraction of purity of iron oxide

F_4 = Fraction of Fe present in iron oxide (i.e. 112/160 = 0.7)

W_4 = Weight of TMT rod dissolved during stirring the melt, kg

F_5 = Fraction of Fe present in TMT rod

W_5 = Weight of product, kg

F_6 = Fraction of Fe present in product

Table 5.1: Variables for Smelting Reduction of Composite Pellets

Sr. No.	Variable	Number	Remarks
1	Steel plant Waste pellet	3	JSW Dust, JSW Sludge, VIZAG Sludge
2	Steel Scrap	1	From Local Market
3	Percentage of Pellets charged	4	5%, 10%, 15%, 20%
4	Fe_{tot}/C	1	3.11 (as per stoichiometry)

5.3 Results of Bulk Dissolution of Composite Pellets

5.3.1 JSW Dust

Table 5.2 shows carbon (in product) and iron yield variation with addition of JSW dust composite pellet.

Table 5.2: Carbon (in Product) and Iron yield variation with composite pellet charged for JSW dust

Heat No.	Pellet Charged, pct	Carbon, pct	Iron yield, pct
1	5.26	1.29	90.66
2	11.10	1.45	98.23
3	17.65	0.97	94.44
4	24.93	3.44	87.58

5.3.2 JSW Sludge

Table 5.3 shows carbon (in product) and iron yield variation with addition of JSW Sludge composite pellet.

Table 5.3: Carbon (in Product) and Iron yield variation with composite pellet charged for JSW Sludge

Heat No.	Pellet Charged, pct	Carbon, pct	Iron yield, pct
5	5.28	1.45	93.95
6	11.33	1.32	94.31
7	17.62	1.45	96.12
8	24.93	2.59	91.51

5.3.3 VIZAG Sludge

Table 5.4 shows carbon (in product) and iron yield variation with addition of VIZAG sludge composite pellet.

Table 5.4: Carbon (in Product) and Iron yield variation with composite pellet charged forVizag Sludge

Heat No.	Pellet Charged, pct	Carbon, pct	Iron yield, pct
9	5.28	1.43	94.52
10	13.38	1.23	81.93
11	17.66	1.45	98.33
12	24.96	1.97	93.11

Figures 5.1 and 5.2 shows comparison of carbon (in product) and iron yield with addition of different composite pellets. Above 20 pct addition of composite pellets to the molten metal formed cast iron, due to higher carbon input along with composite pellets. There was some carbon dissolved from graphite crucible, due to more times were spend for dissolving the total composite pellets.As addition of composite pellets increases, carbon in product also increasing in general. Above 20 pct addition of composite pellets to the molten metal, in general, iron yield decreases due to loss of iron in slag.

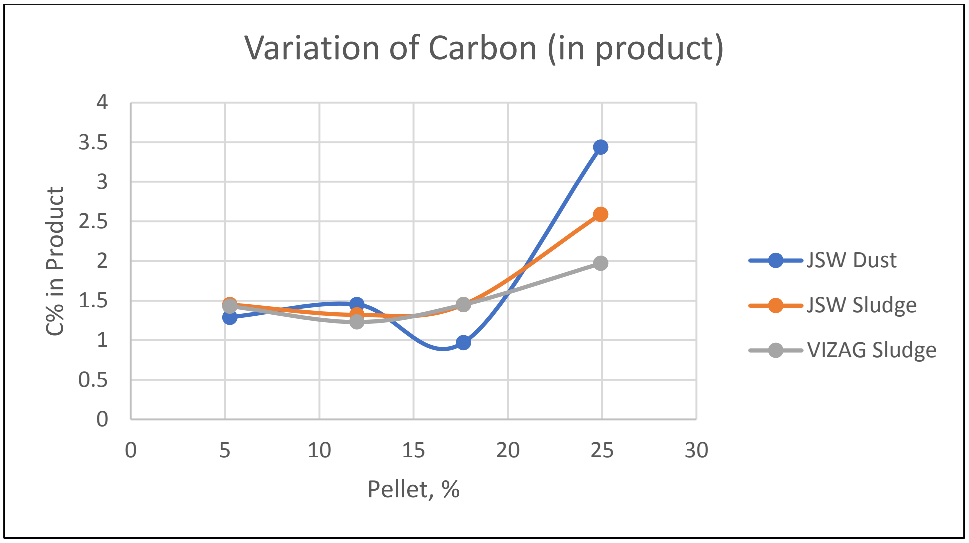


Fig. 5.1: Variation of carbon (in product) with addition of composite pellets

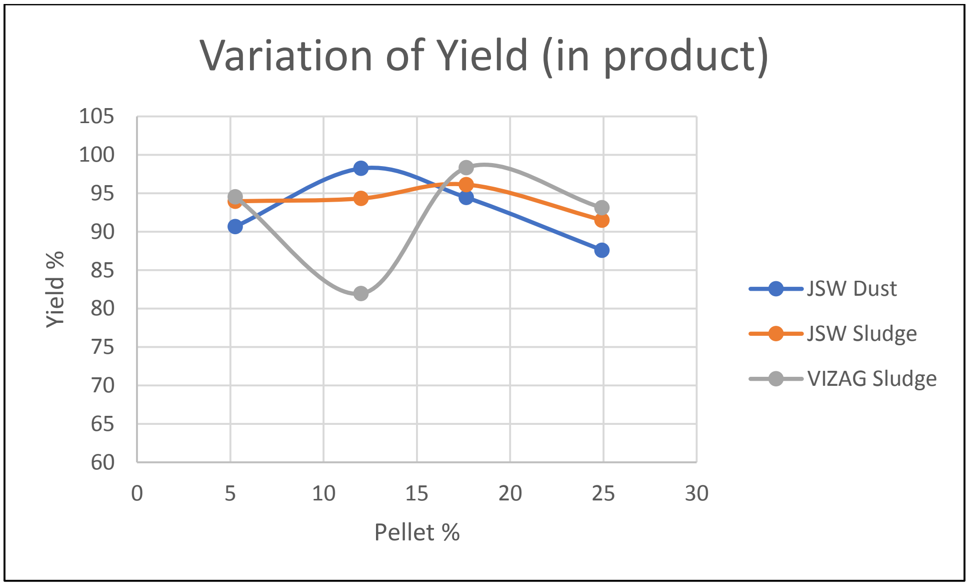
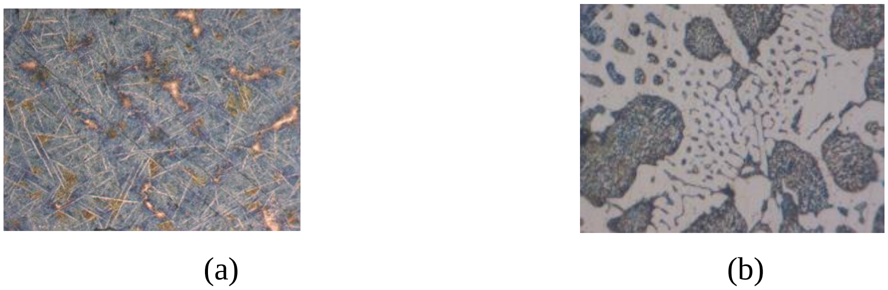


Fig. 5.2: Variation of iron yield with addition of composite pellets

5.7 Microstructure of Products (i.e. Steel/Cast Iron)

The solidified samples were first normalized at 850^{0}C for1hourand then the microstructural studies were carried out. Microstructure was observed under microscope using 2% NITAL as etchant and 100X magnification. The microstructure of steel/cast iron produced in all 12 heats and few are shown in Figure 5.3 to 5.5.



(a) (b)

Fig. 5.3: Microstructure of product by addition of JSW Dust composite pellet to the melt at (a) 5.26 pct, (b) 24.93 pct (100X)

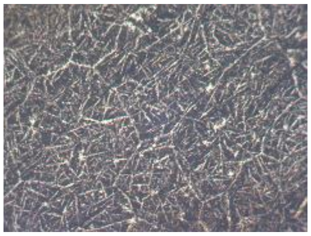


Fig. 5.4: Microstructure of product by addition of JSW Sludge composite pellet to the melt at 11.33 pct (100X)

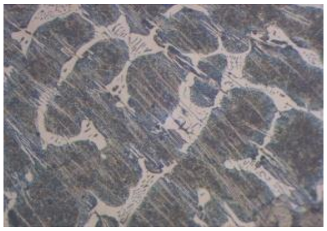


Fig. 5.5: Microstructure of product by addition of Vizag Sludge composite pellet to the melt at 17.66 pct (100X)

Figure 5.3 (a) shows more of pearlite and less of cementite (1.29 pct C) and Figure 5.3 (b) shows more of cementite and some pearlite (3.44 pct C). Figure 5.4 shows cementite at grain boundary and pearlite (1.32 pct C). Figure 5.5 shows more cementite percentage with pearlite (1.45 pct C). The microstructure reveals that as the percentage of composite pellets increases in the molten steel the cementite percentage also increases which is the result of increase in the carbon percentage of steel/cast iron produced.

Chapter 6

Summary and Conclusions

6.1 Summary

Steel is the main driving force of economic progress of a country. The industrial development programmed of any country, by and large, is based on its natural resources. There are planning for about 300 Mt steel production by India in 2030, that will be required 513 Mt of processed iron ore and 639 Mt run of mine ore. India is fortunate to have reserves of high-grade iron ores. But with time, these reserves of high-grade iron ores are bound to be diluted.

However, in a steel industry where several processes are employed using of various raw materials. It is natural that many valueless substances are generated which can be termed as waste materials. The waste can be categorized in terms of solid, liquid and gases. The solid wastes are from process units and also from pollution control units. The process wastes, dust and sludge from pollution control unit, are the area of attention. Solid wastes generated from process units are generally characterized by their uniform size and composition. Low moisture content, high levels of metallic (i.e. Fe) and non-metallic values (e.g. CaO, C etc.) content in wastes, which makes these suitable for recycling within the plant or to be sold out to consuming industries.

Efforts are being made to utilize the waste materials by proper characterization, beneficiation and agglomeration techniques. The treatment/utilization of steel plant sludge/dusts is still a problem in many countries of the world. Effective utilization of dust and sludge for iron and steel making can be possible after upgradation of Fe percent and discard the valueless materials. There is also shortage of coking coal all over the world in general and in particular at India. Enormous amount of coal fines and coke breezes are generated during coal mining and coking of coal respectively. By incorporating non-coking coal fines or coke breezes with up-gradated dust and sludge utilized in producing cold bonded iron oxide-coal composite pellets, the metallurgical coke requirement in the blast furnaces can be reduced.

The term composite pellet is employed here to mean pellet containing mixture of fines of iron bearing oxide and carbonaceous material (i.e. coal) which has been imparted sufficient green strength for subsequent handling by cold bonding technique. The prepared cold bonded composite pellet should have sufficient mechanical strength to withstand high temperature and stresses in reduction furnaces. Interest in composite pellets have grown from the decade of 1980s because of the following advantages:

1. Utilization of cheaper resource and pollution control,
2. Very fast reduction rate due to intimate contact between reductant and oxide particles,
3. Reduction in energy consumption for production because cold bonded composite pellets do not require induration,
4. Promising prospect for iron making at small scale with higher production rate,
5. Because of their uniform size and convenient form, composite pellets can be continuously charged into the furnace leading to higher productivity, and
6. Consistent production quality as the chemical composition of composite pellets does not change.

The concept of Smelting Reduction (SR) process of iron ore, an alternative to blast furnace technology was initiated around 1970. The SR processes involving both reduction and smelting are very similar to blast furnace in which all the reactions take place in a single reactor. Most of the smelting reduction processes involve by removal of oxygen from the iron ore in the solid state (initially) followed by further removal of remaining oxygen in the liquid phase reduction reaction. Ideally, a smelting reduction process should have 100 pct reduction of iron oxides in the liquid state in a single stage in a single reactor.

There is a shortage of coking coal in India. On the other hand, India has vast reserves of non-coking coal, which is widely available and cheapest reducing agent for iron oxide. Hence, non-coking coal based iron making technology has special relevance for country like India. In fact, the need to make non-coking coal based iron making units economically viable has resulted in the development of SR processes, which do not face sticking problem at high temperature.

The composite pellets, produced from steel plant dust or sludge (after beneficiation), can be utilized as the feed material for smelting reduction. Rate of production is expected to be higher with composite pellets due to high degree of pre-reduction to the smelting reactor. There have been very few studies for the utilization of various steel plant wastes in the steel making process. However, the dust and sludge are used in steel making at some places, but the productivity is not good by using directly. There are a few published literatures on utilization of steel plant dust and sludge. Looking into the above aspect, the objective of present study was three-fold:

1. Characterization and beneficiation of dust and sludge by using various methods and establishing proper route for beneficiation with good recovery of iron bearing oxide.
2. To prepare composite pellets using various binders by cold bonding techniques in the laboratory and evaluate their properties; this would be a contribution towards development of suitable binder for cold bonding composite pellets.
3. Utilization of composite pellets in liquid metal bath for steel/iron making. As well as auxiliary studies as backup investigation with emphasis on isothermal reduction kinetics.

To achieve the set objectives, the overall study consisted of four parts:

i) Characterization of raw materials,
ii) Beneficiation of waste materials to upgrade iron content,
iii) Selection of binder for waste-coal composite pellet making,
iv) Fundamental studies on isothermal reduction of waste-coal composite pellets, and Bulk dissolution of composite pellets in molten bath to produce steel/cast iron.

Therefore, it was decided to carry out the beneficiation of the waste to enrich iron content. Preparation and testing of waste-coal composite briquettes / pellets were done. Isothermal reduction of waste-coal composite pellets and investigation on reduction smelting of composite pellets in liquid metal bath were done. Some auxiliary studies as back-up investigations with emphasis on kinetics, for better understanding of reduction behavior of composite pellets were also done.

The following raw materials were selected and procured for the present study:

Sources of Iron Oxide (Steel Plant’s wastes)	
Steel melting shop dust	Jindal Steel Works, Bellari, Karnataka, India
Steel melting shop sludge	Jindal Steel Works, Bellari, Karnataka, India
Steel melting shop sludge	Vizag Steel Plant, Vishakhapatnam, Andhra Pradesh, India
Coal	
Coal	Procured from local market

Binder	
Lime	Procured from local market (laboratory reagent grade)
Fly ash	Thermal Power Plant, Vanakbori, Gujarat.
Molasses	Procured from local Foundry
Starch	Procured from local market
Charge material for induction furnace	Steel scrap (procured from local market)

Chemical analysis of waste samples were done using Energy Dispersive X-ray Fluorescence (XRF) Spectrometer. The proximate analyses of coal was done according to the standard method. The Scanning Electron Microscopic (SEM) examination of waste sample were carried out using JEOL SEM (Model: JSM-5610 LV) coupled with Oxford Energy Dispersive Analytical X-ray (EDAX) system. The waste powder sample showed the presence of mostly spheroidal shaped particles. XRD of the waste samples showed the waste were amorphous in nature. A wide variation in particle size was observed in sieve analysis of the samples.

The ground dust and sludge were beneficiated using various methods like Air Classifier, Welfley Table and Hydraulic Classifier. Finally, after beneficiation trials, two stage beneficiation route was selected. After the two stage beneficiation route, it was observed that in case of JSW dust, JSW Sludge and VIZAG Sludge there was increase in percentage of Fe_2O_3 up to 87.33 pct, 90.69 pct and 85.77 pct from initial 55.39 pct, 73.77 pct and 70.70 pct of Fe_2O_3 respectively.

To select the proper binder, cylindrical shaped briquettes (diameter 9.70 - 9.75 mm and height 13-14 mm) were prepared and tested. It was observed that the highest compressive strength of 1436 N/briquette was obtained for briquettes prepared using 5 pct starch and 2.5 pct molasses as binder in JSW sludge, 1167 N/briquette strength was for JSW dust using 7.5 pct starch and 5 pct molasses as binder and 1063 N/briquette was obtained for briquettes prepared using 7.5 pct starch and 2.5 pct molasses as binder for VIZAG sludge. From these results of briquettes, composite pellets were prepared. Variation in compressive strengths were observed mostly by ±15 pct of the average value. Similarly, the highest drop strength (more than 200 drops) and lowest shatter index value (0.064 pct) were also obtained.

The iron ore-coal composite pellets were produced using starch and molasses as binder with Fe_{tot}/C_{fiX} ratios as per stoichiometry. The degree of reduction of composite pellets were obtained by reducibility studies. For measurement of degree of reduction for composite pellets, the weight loss method was used. The loss in weight due to loss of oxygen, carbon and volatile matters were taken into consideration. The isothermal reduction of composite pellets was carried out in nitrogen atmosphere. The reduction studies of composite pellets were analysed, and rate of reduction and activation energy was calculated. The activation energies were found to be low (49.8–59.28 kJ mol^{-1}) which means, volatile gases (in particular H_2) diffused through porous solid iron-oxide particles boundary. Overall reduction was controlled by gasification reactions. Reduced composite pellets were examined by SEM to observe the microstructure of the reduced composite pellets. XRD was carried out to identify the phases present in reduced composite pellets.

The experiments for smelting reduction of composite pellets were done in an induction furnace of 5 kg capacity at temperature 1723 ± 10 K. The process deals with the bulk dissolution of composite pellets into the molten bath and iron recovery was calculated in terms of yield. During smelting reduction, it was observed that the 16-17 mm diameter composite pellets completely dissolved in 24 to 30 seconds. The maximum yield 98.2 pct for JSW Dust composite and 98.3 pct for Vizag Sludge composite were obtained.

In summary, the present investigation has demonstrated effective recycling and utilization of steel plant waste like BOF Dust and sludge. Beneficiation of dust and sludge was done to increase the Fe pct of raw materials. Beneficiation methods were selected such that there was no chemical used. This investigation also demonstrated smelting reduction of composite pellets in an induction furnace a feasible alternative route to produce hot metal using dust and sludge. The investigation on kinetics and dissolution behavior of composite pellets in liquid metal bath gave insight for fundamental and fair understanding of the reduction behaviour of waste-coal composite pellets. The metal, produced in smelting reduction, has reasonable iron yield up to 98.3 pct. The present studies also demonstrate an effective way of utilization of BOF dust and sludge for extracting metal which is of vital concern for resource conservation and pollution control. Using cold bonding technique, composite pellets of sufficient green strength were produced. This is a contribution towards development of suitable binder for cold bonding technology.

6.2 Conclusions

1. The steel plant wastes (like JSW dust, JSW sludge and VIZAG sludge) can be easily beneficiated for the upgradation of the iron (Fe) values.
2. For single stage beneficiation method: i) JSW dust improved the iron (Fe) values from 38.77 pct to 46.24 pct by Air Classifier with 94.97 pct recovery; ii) JSW sludge improved the iron (Fe) values from 51.64 pct to 60.45 pct by Tabling with 56.83 pct recovery; and iii) VIZAG sludge improved the iron (Fe) values from 49.49 pct to 60.08 pct by Tabling with 51.2 pct recovery.
3. It was observed that Air Classifier was the most suitable beneficiation method for all the samples and the next common beneficiation technique was Wilflay Table, so the first stage in two stage beneficiation was Air Classifier and then Wilfley Table (if it is needed) in the second stage. For better recovery concentrate and middling were mixed together.

4. For two stage beneficiation method (i.e. Air Classifier was used in the first stage and the underflow of Air Classifier was treated again in Wilfley Table): i) JSW dust improved the iron (Fe) values up to 61.13 pct (concentrate + middling) with 93.8 pct recovery; ii) JSW sludge improved the iron (Fe) values up to 63.48 pct (concentrate) with 78.39 pct recovery; and iii) VIZAG sludge improved the iron (Fe) values up to 60.04 pct (concentrate) with 57.72 pct recovery.
5. After two stage beneficiation method, it was observed that in case of JSW dust, JSW Sludge and VIZAG Sludge there was increase in percentage of Fe_2O_3 up to 87.33 pct, 90.69 pct and 85.77 pct from initial 55.39 pct, 73.77 pct and 70.7 pct of Fe_2O_3 respectively.
6. During trails for binder selection, it was found that TB3 (with 7.5 pct fly ash, 5 pct lime and 5 pct molasses) gave good green drop strength (8) and dry drop strength (24), but TB6 (with 7.5 pct fly ash, 5 pct slake lime and 5 pct molasses) gave higher compressive strength (107.8 N/briquette) and as well as good shatter strength (7.17); that means slake lime was more effective to form calcite due to CO_2 passing.
7. Further trails with starch and molasses as binder were done with JSW dust. Taguchi technique was used for selection of binder proportion for pellets making. It was found that E2 (with 2.5 pct starch and 5 pct molasses) gave highest strength (1196.82 N/briquette) and lower shatter index (0.18).

8. During reducibility study of pellet, it was found that fraction of reduction increases with increasing in temperature and time for all three materials. The fraction of reduction for pellet was increased with time of heating and rise in temperature. Initially the fraction of reduction was very low which may be due to the release of volatiles, which was slow process. But later on-the fraction of reduction increased with time, which might be attributed to the faster gas-solid reactions at high temperature.
9. The activation energies for reduction were found - 52.59, - 49.80 and - 59.28 KJ/mol for JSW Dust, JSW Sludge and VIZAG Sludge composites respectively.
10. The activation energies for composite pellets reduction were found to be low (49.8–59.28 $kJ\ mol^{-1}$) which means, volatile gases (in particular H_2) diffused through porous solid iron-oxide particles boundary. Overall reduction was controlled by gasification reactions.
11. From XRD, it was confirmed that the reduction took place in topochemical manner, i.e. stagewise reduction (i.e. $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$).
12. It was also confirmed that the presence of metallic iron in reduced composite by SEM.
13. It was observed during smelting reduction that the composite pellets were completely dissolved easily at the molten bath.
14. It was also observed that the 16-17 mm diameter composite pellets completely dissolved in the molten bath at an average 27 seconds. That means dissolution rate of composite pellet is very fast. Hence, production rate would be faster.
15. As addition of composite pellets increased during smelting reduction, carbon content in product also increased in general.
16. It was observed that above 20 pct addition of composite pellets to the molten metal formed cast iron, due to higher carbon input along with composite pellets. There was also some carbon dissolved from graphite crucible, due to more time were spend for dissolving the total composite pellets.
17. The maximum yields were obtained 98.2 pct, 96.1 pct and 98.3 pct for JSW Dust composite, JSW Sludge composite and Vizag Sludge composite respectively.
18. Above 20 pct addition of composite pellets to the molten metal, in general, iron yield decreased due to loss of iron in slag.
19. It is possible to charge composite pellets as feed material in Smelting Reduction Process to get faster steel/cast iron production.

20. An alternate method of iron/steel making is possible by charging composite pellets as feed material.

6.3 Suggestions for Further Work

1. TG-DTA of composite pellet should be carried out at a single heating rate and at different heating rates.
2. The waste-coal composite pellets produced in present study have good dry strength but swelling behavior and strength after reduction were not studied. Such specific investigations are essential for better understanding of the pellet properties and their behavior in reduction/smelting furnaces.
3. Economic evaluation of the smelting reduction of composite pellets by conducting trials at pilot plant level is required for commercialization in future.
4. By adding composite pellets in melt, it is possible to get steel directly by controlling the Fe_{tot}/C_{fix} ratio in composite pellet. Since dissolution rate of composite pellet is very fast, after complete dissolution of composites, oxygen lancing can be done to the liquid bath to control carbon and phosphorous in the bath and desulphurization can be carried out in the ladle.
5. By proper heat balance calculation, it is possible to design the reactor to produce steel directly by continuous charging of composite pellets.

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