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Physico-chemical Characterization of Sponge Iron Solid Waste of Maithan Steel Plant – A Case Study

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Abstract: ***Solid waste management has received many challenges that the steel industry faces today. The requirements of "4R" i.e reduce, reuse, recycle and restore the materials for sustainable development by meeting the needs of our present generation without compromising the ability of future generation. India is the largest producer of Direct Reduced Iron in the world. In steel Industry, the production of steel is associated with the generation of solid waste materials like slag, dust, sludge, fly ash etc. Significant quantities of wastes are generated from steelmaking process which is a focus point now-a-days w.r.t its utilization as well as environmental impact. Steelmaking process broadly includes all operations from primary and secondary steelmaking to ingot and continuous casting of steel. At each of these stages of steelmaking process, substantial amounts of wastes are generated. So it is required to minimize and utilize the waste through integrated waste management which has gained special significance in the present scenario, as these wastes have a wide ranging impact on the environment. It is very essential not only for recycling of the valuable metals and mineral resources but also to protect the environment. This paper summarizes and analyzes the generation, composition, characteristics and present status of the utilization of the most of the wastes obtained from sponge iron of Maithan Ispat limited.***

Keywords: sustainable, slag, sludge, environment, recycling

1. Introduction

Sponge iron is a metallic product obtained by reduction of iron oxide in solid state, which is used for manufacturing steel. Steel is manufactured from iron ore mostly using blast furnace (BF) and basic oxygen furnace (BOF) and using electric arc furnace (EAF) in case of manufactured from scrap materials. Molten iron is produced in BF in presence of coke and molten steel is produced in BOF in presence of oxygen [1]. Smelting and refining process involves carbon reduction in BF to produce molten iron and decarburization of molten iron to produce molten steel. After BF and BOF process molten steel is controlled to a target composition and temperature for processing into continuous casting machine to produce rebars, slabs, billets etc. Finally these castings are rolled to the required dimensions in the rolling mill to get finished steel product [2]. Source of solid wastes generated in steel industries is thus coke oven by product plant, sinter plant, refractory materials plant, blast furnace, basic oxygen furnace, steel melting shop, rolling mill. The types of solid wastes in steel industry are mainly classified as coke and coal dust, BF slag, SMS slag, mill scale, scrap, oil sludge, fly ash, acid sludge, refractory wastes etc [1]. Dumping solid waste in open space and excavated land creates pollution in the form of dusts and leachate apart from huge financial liability. Moreover available land is also scarce now-a-days for dumping the solid waste due to alarming growth in human population. A major thrust therefore needs to be given on the scope of reuse of these solid wastes. Presently the production of solid wastes per ton of production of steel is 1.2 ton in India compared to 0.55 ton of that practicing in abroad due to inferior quality of raw materials used. Out of total solid wastes generated in the steel plant in our country 63% are dumped which needs to be recycled or reused to target a clean and green environment with zero waste.

In the conventional integrated steel manufacturing process, the iron from the blast furnace is converted to steel in a basic oxygen furnace (BOF). Blowing oxygen through molten pig iron lowers the carbon content of the alloy and changes it into steel. Steel can also be made in an electric arc furnace (EAF) from scrap steel and, in some cases, from direct reduced iron (DRI). In this process steel scrap along with fluxes (e.g., limestone and/or dolomite) are heated to a liquid state by means of an electric current. During the melting process the fluxes combine with non-metallic scrap components and steel incompatible elements to form the liquid slag. As the slag has a lower density than steel, it floats on top of the molten bath of steel. The liquid slag is tapped at temperatures around 1600 °C and allowed to slowly air-cool forming crystalline slag. Refining of the crude steel is done before casting and the various operations are normally carried out in ladles. As a result, Alloying agents are added, dissolved gases in the steel are lowered and impurities are removed or altered chemically to ensure the production of high-quality steel. The continuous casting operation produces billets, beam blanks, and near-net shape profiles. These semi-finished products are utilized in the rolling mills to produce structural shapes.

Sponge iron, customarily called direct reduced iron (DRI) is used as prime metallic in the secondary steel making process using the electric furnace or Induction furnace route. DRI is a substitute to scrap. Sponge iron is produced by reduction of iron ore in the solid phase using either solid (non coking coal) or gas (Reformed natural gas or coal gasification) as reductant. Besides supplying the reducing agents, namely carbon monoxide and hydrogen, the energy requirement for the reduction reaction is also supplied by a part of the reductant as fuel. Sponge iron plants based on two major commercially established processes, namely coal based rotary kilns and gas based shaft furnace reactors. The coal based rotary kilns produce DRI lumps/ pellet being more stable can be stored for longer time. The gas fired shaft furnace produces DRI that needs to be used immediately or converted to blocks of Hot Briquetted Iron (HBI),that can be packed and stored for longer time. Sponge iron constitutes around 3-4% of world's total iron making capacity. Today, India is the largest producer of sponge iron in the world, having 118 plants with an installed production capacity of 11.85 million tons per annum (MTPA); 115 plants are coal based producing 65% of the total production. There are 3 natural gas based plants producing 35% of the total annual production. 100% sponge iron demand of India is met from internal sources. The sponge iron plants in India are located near the source of raw materials. The gas based plants are located along the west coast of Maharastra and Gujarat. The coal based plants are concentrated near iron ore and coal mines of Jharkhand, Orissa, West Bengal, Chattisgarh, Maharastra, Andhra Pardesh, Goa and Karnataka.

In the present study we have taken the solid waste management in the Maithan. Ispat Ltd of Kalingnagar area of Jajpur district of Odisha, India into consideration. The schematic representation of production of Sponge iron and solid waste of Maithan Ispat Ltd is shown in figure 1.

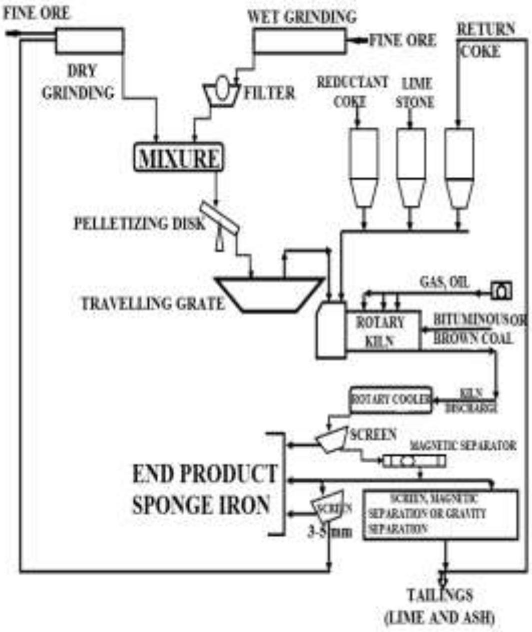

Figure 1: Schematic representation of Sponge Iron Production in Maithan Ispat Limited

2. Materials and Methods

2.1 Study Site

The study was carried out in solid waste dumping site of Maithan Ispat limited, Gopabandhu Marg, Kaling Nagar Industrial complex (KNIC) , Jakhapura in Jajpur district of Odisha, India. Geographical location 20^o 57' – 21^o 3' N latitude and 85^o 59' – 86^o 5'E longitude near duburi mining area of Jajpur district, Odisha, India

In the sponge iron solid waste dumping site, accumulation of solid waste over years resulted in formation of different age series of dumps. For the present study freshly laid dump (D_0), 1 year (D_1), 3 year (D_3) and 4 year (D_4) old dumps were selected. Dump age is expressed as time since the establishment of dump in the site. During dumping of the solid waste, when the dump attains sufficient height, soil of the adjacent area is covered over the dump for stabilization. Thus, D1, D3 and D4 were with soil cover, where as D0 was without soil cover. A natural site adjacent to the waste dumping site was been taken as control site (C) for reference. Location map of Maithan Ispat ltd is shown in figure 2.

Figure 2: Map showing the location of Kalinga Nagar Industrial Complex (KNIC) and Maithan Ispat Limited Source http://en.Wikipedia.org/wiki/Jajpur district, http://www.mapsofindia.com/maps/orissa/districts/jajpur.htm, accessed on 12th Feb. 2013

2.2 Sample Collection

Waste samples from different age series dump (D_0, D_1, D_3 & D_4) and soil from control site were collected by random sampling method from a depth of 0-15cm by digging pits (15 X 15 X 15 cm^3). For each site, sub-samples were collected from five locations. These sub- samples were brought to the laboratory in sterilized polythene bags and mixed thoroughly to form a composite sample. After sorting out larger pieces of materials, the sample were subjected to sieving in 2mm mesh. Each of the composite samples was divided into three replicates for analysis.

3. Physico-chemical Characterization

Texture of the waste samples was determined by mechanical sieve method [3] and bulk density (g/cm^3) was estimated following the method prescribed in TSBF Handbook (Anderson and Ingram, 1992). The water holding capacity (%) was determined following the protocol proposed [3] and moisture content (%) was measured as the ratio of fresh weight to dry weight of soil expressed in percentage. pH was determined in (soil/water, 1:5) suspension with electronic digital pH meter. Soil organic carbon (mg/g soil) was estimated following titration method of Walkley and Black rapid titration method [3], total nitrogen (µg/g soil) by Kjeldahl method [4] and phosphorous (µg/g soil) content by following the protocol [5].

3.1 Statistical Analysis

The data from physic-chemical analyses were subjected to Analysis of Variance (ANOVA) to test whether the variations between different sites were significant or not. The simple correlation analysis between different parameters and age of the waste dumps were also conducted.

3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) micrographs of collected samples of different age group were recorded with a Jeol Ltd, Japan, Model No 5200 at different magnifications.

4. Results and Discussion

The data related to textural composition (sand, slit and clay percentage), bulk density, water holding capacity, moisture content and pH of waste samples collected from D_0, D_1, D_3 & D_4 and soil sample from control site was presented in Table 1. It was observed that among the waste dumps sand percentage was highest in D_0 and lowest in D_4 showing decreasing trend with increasing age of the waste dumps. The slit and clay percentage was found to be minimum in D_0 and maximum in D_4 showing increasing trend with increasing age of the waste dumps. The correlation between the clay (%) in different waste samples and the age of the waste dumps was noted to be significantly positive ($r = 0.861$, $p < 0.05$). Growth of the root and root exudates inform of organic acid stimulates the weather of coarse particle to finer particles like clay and slit [6, 7]. Vegetation succession in the waste dumps [8] could be a season for increased clay percentage as observed in different mine spoils [9, 10, 11]. Besides, in D_1, D_3 and D_4 there was soil cover in the waste dumps, which also contributed to more percentage of clay in older dumps than in D_0 where there was no soil cover. In absence of vegetation clay particles are more prone to loss [12, 13] and vegetation cover on degraded barren land was reported to check the loss of clay particles [14, 9]. Due to its contribution towards structural stability clay is an important part for soil texture [15, 16]. Thus, the gradual increase in the clay percentage indicated the development of soil structural stability, aggregation and developed resistance to the soil erosion with the increase in the age of the waste dumps.

The bulk density (g/cm^3) was having highest value in D_o and lowest in D_4, showing decreasing trend with increasing age of the waste dump. Bulk density of the control site was found to be less than the waste dumps. Further analysis of variance (ANOVA) indicated that the bulk densities of different sites were observed to be statistically significant ($F = 203.576$, $p<0.001$). The bulk density and the age of the waste dump were found to be negatively correlated ($r = -0.972$, $p < 0.01$) and statistically significant. A decline in bulk density with the age of waste can be interpreted as a reduction in the soil compactness because of the development of soil micropore space [17]. These also detected in SEM figure as shown in figure 3. An increased level of clay fraction contributes to the development of soil micropore space that reduces the soil bulk density. Further vegetation cover on barren land is reported to reduce bulk density and soil compactness [18]. Findings of the present study could be explained by the fact that gradual increase in vegetation cover, accumulation of clay fraction and organic matter led to the development of soil micro-pore space that ultimately reduced the soil bulk density. The water holding capacity (%) of D_0, D_1, D_3 and D_4 were recorded to be 22.96, 27.46, 29.68 and 32.68% respectively.

It was having lowest value in D_0 and highest in D_4, showing increasing trend with increasing age of the waste dumps. In control site the water holding capacity was 42.20%, which was higher than the waste dumps. The analysis of variance (ANOVA) indicated that the water holding capacities of different sites were observed to be statistically significant at ($F = 167.268$, $p<0.001$). Further the relationship between water holding capacity and the age of the waste dump was positive correlated and statistically significant ($r = 0.943$, $p< 0.01$). Soil texture and organic matter content are the key components that determine soil water holding capacity [19, 20, 21]. The positive correlation of water holding capacity with clay percentage and organic matter content in different age series of mine spoil [11, 22] supports the findings of present study.

Table 1: Textural composition, bulk density, water holding capacity, moisture content and pH of different age series waste dumps and control site (C)

Parameters	D_0	D_1	D_3	D_4	C
Sand (%)	82.95 ± 0.51	76.75 ± 0.25	74.65 ± 0.44	73.14 ± 0.70	61.76 ± 1.24
Slit (%)	7.89 ± 0.61	10.52 ± 0.31	11.78 ± 0.20	12.37 ± 0.50	14.78 ± 0.59
Clay (%)	6.83 ± 0.20	9.78 ± 0.10	10.48 ± 0.30	11.13 ± 0.25	19.82 ± 0.78
Bulk density (g/ cm^3)	1.72 ± 0.04	1.75 ± 0.03	1.52 ± 0.04	1.43 ± 0.02	1.22 ± 0.04
Water Holding Capacity (%)	22.96 ± 1.61	27.46 ± 1.03	29.68 ± 0.55	32.68 ± 0.75	42.20 ± 0.97
Moisture Content (%)	5.62 ± 0.36	6.68 ± 0.36	6.78 ± 0.10	8.02 ± 0.12	11.23 ± 0.29
pH	9.11 ± 0.12	8.21 ± 0.21	7.39 ± 0.12	7.14 ± 0.20	6.42 ± 0.21

Annual average moisture content (%) in different age series waste dumps ranged from 5.62-8.02%, having lowest value in D_0 and highest in D_4 showing increasing trend with increasing age of the waste dumps. In control site the moisture content was 11.23%, which was higher than the waste dumps. The analysis of variance (ANOVA) indicated that the moisture content of different sites was observed to be statistically significant ($F = 232.581.693$, $p< 0.001$). The relationship between the moisture content and the age of the waste dump was positive correlated and statistically significant (r = 0.923, $p < 0.01$). The progressive improvement of the moisture content of the waste dumps with age of waste dumps could be due to the positive influence of the increasing vegetation cover on the waste dump, which prevented the loss of soil water through evaporation by not allowing direct exposure of soil surface to the incoming radiation [23, 24]. In SEM figure it is clear that the bonding in different age series is different and that so why different properties of these samples are found to be different.

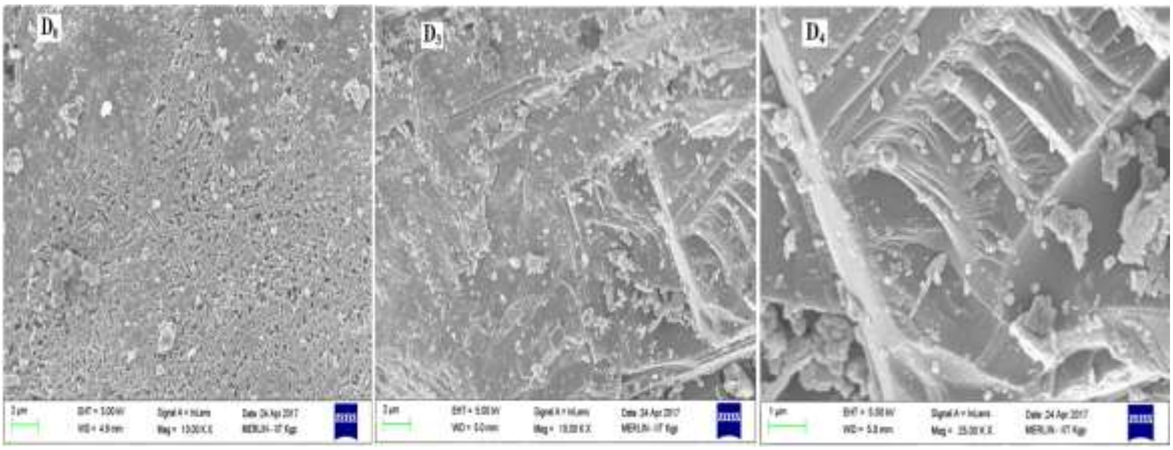

Figure 3: SEM of Fresh sample D_0, D_3, D_4

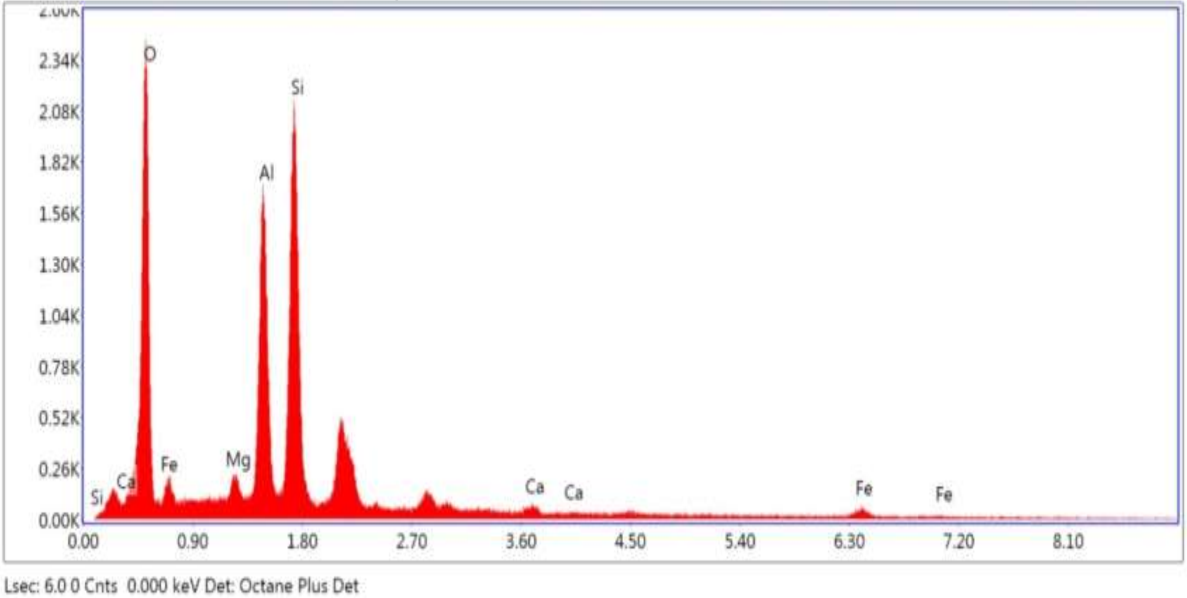

Figure 4: EDAX of Sludge Waste Sample Collected

Table 3: eZAF Smart Quant Results of collected Sludge Waste Sample

Element	Weight%	Atomic%	Net Int.	Error %	K ratio	Z	R	A	F
O K	38.75	52.73	5,072.04	6.50	0.26	1.08	0.97	0.62	1
Fe L	1.46	0.57	66.80	27.31	0.01	0.8	1.11	0.7	1
Mg K	0.74	0.66	141.84	23.02	0.01	0.98	1	0.87	1.02
Al K	21.85	17.65	3,918.51	4.15	0.19	0.94	1.01	0.92	1.01
Si K	35.08	27.22	5,436.60	4.26	0.30	0.96	1.01	0.89	1
Ca K	2.16	1.17	95.35	31.43	0.02	0.88	1.03	0.98	1.02

pH of the waste dumps was recorded to be in alkaline range. The highest value of pH (9.11) was in D_0 and lowest (7.14) was in D_4, showing decreasing trend with increasing age of the waste dumps. In control soil pH was recorded to be 6.42. The analysis of variance (ANOVA) indicated that the pH of different sites was observed to be statistically significant at ($F = 89.20$, $p < 0.001$). The relationship between the pH and the age of the waste dump was negatively correlated and statistically significant (r = -0.842, $p < 0.05$). The alkaline pH of waste dumps was due to dolomite, which is one of the raw materials for sponge iron production. The residues of dolomite in form of CaO in the sponge iron solid waste resulted in high pH [25]. It is confirmed from figure 4 in which the presence of calcium is shown. However with increasing age of the waste dumps there was gradual decline in the pH value. Organic matter is usually considered to lower soil pH by releasing H+ associated with organic anions, by nitrification or by an increased cation exchange capacity and corresponding increase in exchangeable acidity

[26, 27]. Gradual leaching with time, mixing of waste with soil in the waste dumps (except D0) and addition of organic matter by vegetation succession might have resulted in declining pH

Organic carbon (mg/g soil), total nitrogen (µg/g soil) and $NaHCO_3$ extractable phosphorous (µg/g soil) content of D_0 was at non-detectable level, where as it was having minimum value in D_1 and maximum value in D_4, showing increasing trend with increasing age of the waste dumps as shown in Table 2. In control soil the level of organic carbon, total nitrogen and $NaHCO_3$ extractable phosphorous were higher than the waste dumps. In D_0 there was only solid waste freshly released from the industry which basically contained klin dust, iron residues, unburned coal and dolomite residues [28, 29, 30]. Thus, organic carbon, total nitrogen and extractable phosphorus were not detected in D_0. However, in D_1, D_3 and D_4 there was soil cover from control site and also vegetation growth on the waste dumps.

Table 2: Organic carbon, Total nitrogen and Extractable Phosphorus content in waste samples of different age series waste dumps and in control site (C)

Parameters	D_0	D_1	D_3	D_4	C
Organic Carbon Mg/g Soil	ND*	1.31 ± 0.21	2.03 ± 0.25	3.13 ± 0.54	13.25 ± 0.70
Total nitrogen µg/g Soil	ND*	89.52 ± 3.94	122.81 ± 12.02	390.52 ± 37.90	1538.42 ± 43.18
Phosphorous µg/g Soil	ND*	51.08 ± 2.61	94.37 ± 9.96	182.61 ± 7.55	751.22 ± 26.98
C : N	ND*	22.22	21.45	9.81	9.42

The nutrients present on the control soil get mixed with the waste and input of litter from vegetation component resulted in increased level of organic carbon. There have been reports about the increase in the level of organic carbon along with the restoration of the degraded soil [31, 9]. With the increasing age of the waste dumps there was also increase in the number and diversity of the leguminous plants resulting in increased level of total nitrogen in the waste dumps. Besides, the establishment of mycorrhiza [32] and activity of other phosphate solubulizing microbes in the waste dumps might have resulted in the increased level of extractable phosphorous. The ratio of organic carbon to total nitrogen (C:N ratio) was found to be maximum in the D_1 (22.22) and minimum in D_4 (9.42), showing decreasing trend with increasing age of the waste dumps. The decreasing trend of C: N ratio with increasing age of the waste dumps substantiated to the fact that there was relatively more accumulation of nitrogen than that of carbon.

5. Conclusion

It is concluded that the physicochemical data of 0 to 4 years old sponge iron solid waste dumps, with the increase in the age of the waste dumps there was amelioration of different physicochemical parameters of the waste dumps. It is revealed that there is reclamation of the waste dumps due to soil supplementation and development of vegetation. Further comparison of 4 year old waste dump (D_4) with that of the natural control site the sponge iron solid waste dumps will take more time to reach to the state of natural site. In the present study it was observed that over a period of 4 years soil organic carbon was showed an annual increase of 772µg/g waste. The corresponding figure for nitrogen and phosphorous was 79 and 38.4µg/g waste respectively. This annual rate indicated the pace and progress of reclamation process in the sponge iron solid waste dump. If the pace is going to be sustained it will take 18 to 20 years to reach to the level of natural control site. It is important to note that the natural vegetation succession on the process of reclamation of the waste dump will convert it into a natural ecosystem which can give a zero effect of solid waste to the environment and create a clean and green surrounding around us. Now Maithan Ispat ltd is selling this waste to different companies for another novel use.

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