ISSN No:-2456 –2165

Characterisation and Reuse Avenues of Blast Furnace Sludge (Solid Metallurgical Waste) and Recycling of Sludge Pond Effluents

Dr. Kalpataru Rout1
Sr. Manager, Quality Control
Neelachal Ispat Nigam Limited,
Duburi, Odisha

Biswajita Mohanty
Research Scholar
P.G. Dept. of Environmental Science
Sambalpur University

Dr. S. K. Pattanayak
Reader & Head
P.G. Dept. of Environmental Science
Sambalpur University

Abstract:-A significant quantity of sludge is generated as waste material or byproduct every day from steel industries. They usually contain considerable quantities of valuable metals and minerals. Transforming these solid wastes from one form to another can be reused either by the same production unit or by different industrial installation is very much essential not only for conserving metals and mineral resources but also for protecting the environment. The present research work discussed the utilization of blast furnace sludge (waste materials) in the production of iron sinter and its optimum utilization. The discharge sludge water may be used after treatment with PAC with a cost competitive price is also discussed.

Keywords:-Solid Waste Recycling, Blast Furnace Sludge, Sludge Pond Effluents, Poly Ammonium Chloride (PAC), Sinter.

I. INTRODUCTION

A. Handling of Waste Issues in Integrated Steel Plants

Over the years, the recovery and the usage of natural resources has been problematic due to a shortage of high quality natural raw materials being experienced all over the world. On the other hand, the disposal of industrial waste or by-products has become more complicated and expensive as a result of the increasing environmental standards and shortages of suitable disposal locations. In the consideration of conserving and extending the resources of quality natural raw materials and increase in environmental awareness, attention is now being focused on the recycling of industrial waste streams or byproducts (Kalyoncu et al., 1999).

Studies and research on metal and waste recycling have shown that as a result of slag processing and usage in different applications, massive stoke piles of such wastes are disappearing and the land occupied by these by-products and waste streams can be reclaimed for other purposes (Zunkel and Schmitt, 1996). These wastes contain some valuable resources and elements such as iron, zinc, lead, calcium, etc., which can be recovered and reused within in steel-making process or can be used as raw materials elsewhere (Shen and Forssberg, 2003; Proctor et al., 2000).

Nearly 1600 - 1700 cum of gas per tonne of hot metal is generated in the blast furnace. Gas generated from the furnace comes out with high amount of dust. To clean the dust a gas cleansing plant is devised which is shown in Fig.1. After emission from the furnace the gas is cleaned in different stages. First stage - gas is send to Dust catcher where 80 % of macro size dust is removed and after dust catcher around 10 gm/nm3 dust remains with gas. Second stage - gas enters to wet ventury washers where gas enters from the bottom and water is sprayed from the top. Here the gas gets cooled from 150-350^{0}C to 45^{0}C and dust content is lowered to 4.5 g / Nm^3. Third stage - gas is further cleaned in wet scrubbers. In some plant have the provision of ESP (electrostatic precipitator) for further cleaning. The final cleaned gas contains 5-10 mg /nm3 and the gas is having high calorific value (750 K cal / Nm^3) due to high amount of carbon monoxide and hydrogen. Due to presence of high percentage of CO and H2, the gas highly explosive and poisonous. In a blast furnace process around the 3 kg of sludge generated per tonne hot metal.

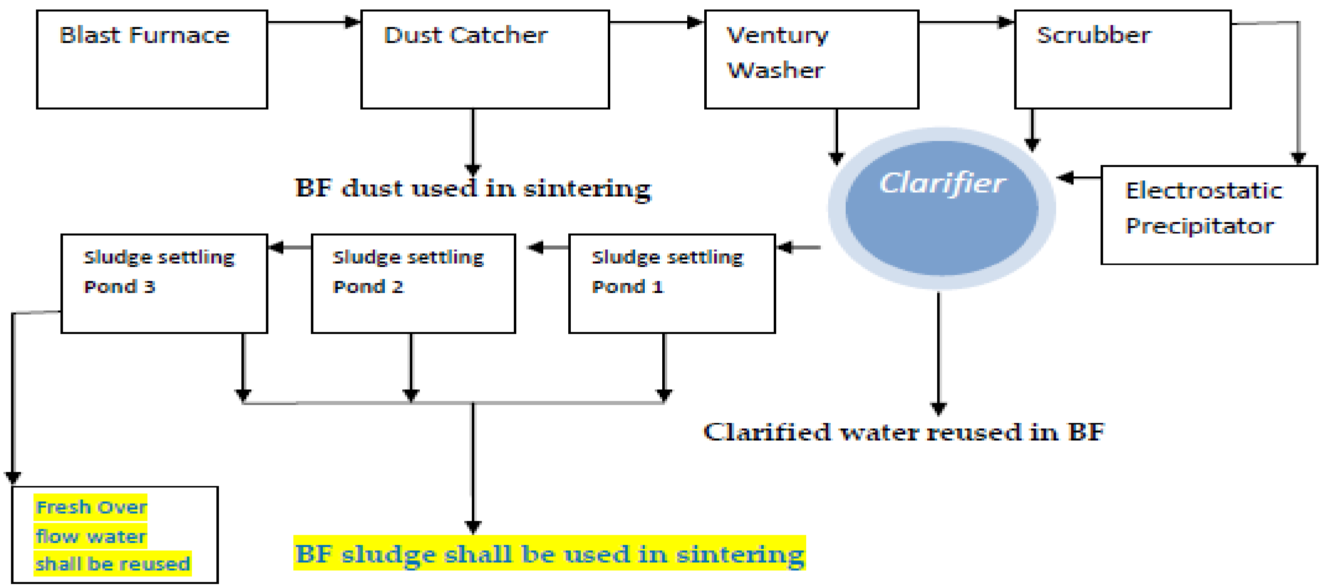

Fig 1: Flow Diagram of Gas Cleansing Plant

B. Use of Blast Furnace Sludge in Sintering

A large quantity of fines is generated in the mines which cannot be charged directly into the Blast furnace. Blast furnace sludge being a fine, cannot be directly recycled in BF and its disposal is very difficult. In order to consume this otherwise waste fine material, they are mixed with Iron ore fines and agglomerated into lumps by a process known as Sintering. Sintering is the process for agglomeration of fine mineral particles into a Porous and lumpy mass by incipient fusion caused by heat produced by combustion of solid fuel within the mass itself.

II. OBJECTIVES

This research work reviews number of technologies in use. The recycling of BF sludge still remains as one of the challenges and there is no adequate literature available. In order to illuminate the problems involved with handling, processing, disposal and treatment of steelmaking wastes including waste gas sludge, the report begins by giving an overview of utilization routes of a number of steel waste materials.

With these objectives, the work plan under this research programme has been structured into two parts:

- Characterization of blast furnace sludge and its utilization potential.
- Recycling of BF sludge pond effluents after treatment.

III. MATERIALS AND METHODS

A. Materials

The study of solid waste of Blast furnace is the main focus of this research pursuit. The waste-rejects were collected at different points of an intergraded iron and steel plant of Kalinganagar Industrial complex, Duburi, Jajpur, Odisha.. 10 no of BF sludge samples are collected from different locations of sludge pond and characterized in respect of their physical and chemical properties and aspects of possible recovery of any value-added products from some of them have been attempted.

B. Methodology

a). Chemical Analysis

The major, minor and trace constituents in different wastes were taken up by wet chemical methods and using different instrumental techniques such as XRF and AAS.

b). X-ray Fluorescence

Major and minor constituents of various sludge and flue dust samples were analysed by XRF spectrometry on Phillips (Axios DY 888) X-ray spectrometer with Scandium and Rhodium targets using pentaerythritol (Al, Si), Thallium Acid Pathalate (Na, Mg), Germanium (P) and Lithium Fluoride (for heavier elements) as analyzing crystals in vacuum medium. International and in-house standards of appropriate compositions were used for calibration. Both major and minor elements were determined by pressed powered pellet technique. The XRF results are cross checked by classical wet chemical methods.

c). AAS:

Analysis of trace constituents like Cu, Ni, Co, Pb, Zn etc. were made with a Varian-Tectron (AA-1475) ABD atomic absorption spectrophotometer fitted with an air acetylene burner. A shielded hollow cathode lamp served as the source of light for the elements to be determined. The absorption measurements were recorded.

IV. RESULT & DISCUSSION

A. Physical Characterization of Blast Furnace Sludge

Blast furnace (BF) sludge is fine-grained and black in colour that soils hand. The black look of the sludge is due to the presence of large volume of unburnt coke particles. They are mostly irregular in shape though a few euhedral grains are uncommon. The bulk density of sludge sample is 0.92 tonne/ m^3. Particle size analysis of sludge was carried out and the data is given in table 1 and depicted in Figure 2.

Size in mm	Wt %	Cumulative %
+ 1 mm to 1.5 mm	43.35	43.35
+ 0.5 mm to 1 mm	11.79	55.14
+ 100 mm to 0.5 mm	14.83	69.97
- 100 mm	30.03	100

Table 1. Size Analysis of Blast Furnace Sludge

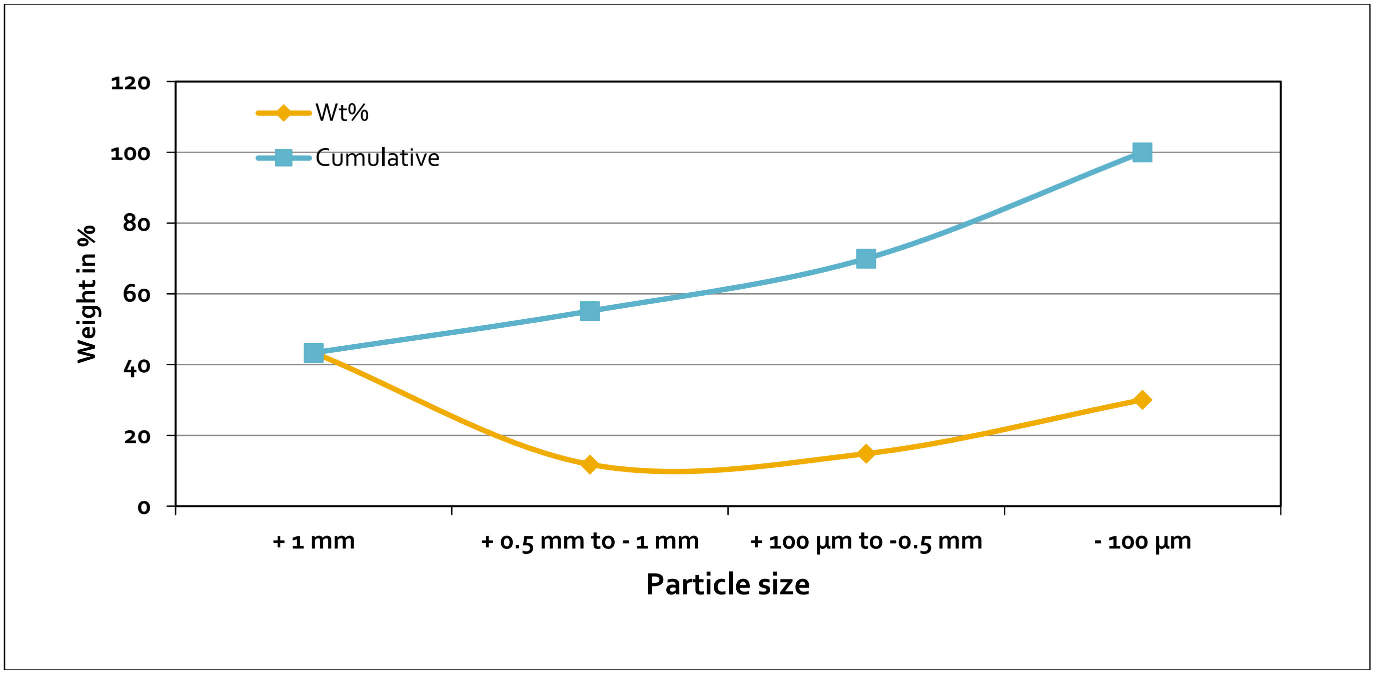

Fig 2 Graphs Showing the Concentration of Different Particle Sizes in the Sludge

The particle size analysis indicates that the +1 mm size and -100µm size particles predominate in blast furnace sludge compared to intermediate size particles (+ 0.5 mm to 1 mm and + 100 mm to 0.5 mm) (Fig.2).

B. Chemical Characterization of Blast Furnace Sludge

The chemical composition of BF sludge collected from sludge yard is discussed below. The major and minor element distribution in the blast furnace sludge sample is shown in Table 2. This is rich in carbon (27.78% fixed carbon), Total Iron (28.16%) and moderately rich in silica (SiO_2-9.07%) alumina (Al_2O_3-5.3%) and calcium (CaO- 8.42%) magnesium (MgO-3.2%). Recycling of BF sludge is being done because of environment concern.

Parameters	Sample nos.										Min	Max	Avg
	1	2	3	4	5	6	7	8	9	10			
T. Fe (%)	23.99	26.02	25.67	28.46	22.32	30.69	28.46	34.22	29.6	32.18	22.32	34.22	28.16
SiO_2 (%)	11.92	8.44	11.6	8.82	8.62	8.06	9.18	8.2	8.3	7.51	7.51	11.92	9.07
Al_2O_3 (%)	5.4	4.79	6.12	5.1	5.06	6.13	6.03	5.18	5.16	4.05	4.05	6.13	5.3
CaO (%)	9.52	8.92	8.2	8.96	8.6	10.03	12.15	5.03	6.25	6.59	5.03	12.15	8.42
MgO (%)	4.62	5.03	4.3	1.21	1.02	3.25	4.26	2.02	1.06	3.4	1.06	5.03	3.02
C (%)	27.8	26.85	26.95	27.84	29.56	23.77	20.69	26.28	36.15	31.92	20.69	31.92	27.78
LOI (%)	33.41	34.91	32.47	35.25	43.89	28.11	27.18	30.65	36.29	31.59	27.18	36.29	33.37

Table 2. Major Elemental Concentration of Blast Furnace Sludge

C. Evaluation of Utilization Potential

The consumption rate of raw materials utilized per tonne gross sinter at studied plant is given in table 3. The maximal uses of raw materials per ton gross sinter are total iron bearing ores, iron ore fines and BF returns.

Items	Unit	Oct, 14	Nov, 14	Dec, 14	Jan, 15	Feb, 15	Mar, 15
Iron ore fines	kg/t GS	864	875	847	830	850	834
Coke breeze+coke dust	kg/t GS	71	80	62	56	61	54
BF returns	kg/t GS	135	125	128	169	173	140
Sinter Returns	kg/t GS	429	233	235	245	330	323
Total Iron bearing	kg/t GS	1428	1233	1210	1244	1354	1303
Limestone	kg/t GS	72	98	64	50	59	56
Dolomite	kg/t GS	91	106	80	71	78	73
Sand	kg/t GS	10	10	7	15	19	18
BF Flue dust	kg/t GS	9	4	10	16	13	19
BF sludge	kg/t GS	9	4	20	46	32	44

Table 3. Specific Consumption of Raw Materials Utilized Per Tonne Gross Sinter.

D. Behavior of Blast Furnace Sludge on Total Iron Ore Fines Per (Kg /Tonne) Sinter

As given in table 2, the percentage of total iron in blast furnace sludge varies from 22.32% to 34.22% and the average percentage is 28.16%. So use of BF sludge has an important impact on specific consumption of iron ore fines in sinter burden to make 1 tonne of gross sinter which is cleanly depicted in Fig. 3. But in NINL the use of BF sludge in sinter burden varies from 0.53% to 2.81% for the month of October–2014 to March–2015. So the specific iron ore consumption per tonne gross sinter decreases. More the iron content in the BF sludge less will be the specific consumption of iron ore fines for sinter making for better productivity of sinter plant.

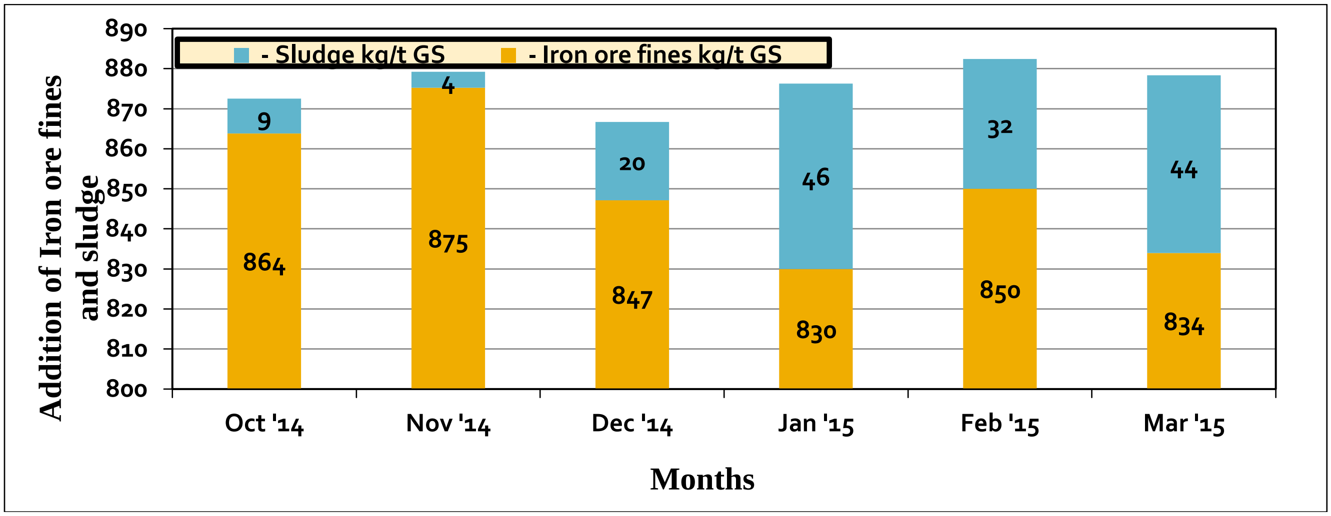

Fig. 3 Iron Ore Fines Per Tonne Gross Sinter Vs Blast Furnace Sludge Per Tonne Gross Sinters

E. Behavior of Blast Furnace Sludge on Silica Content in Sinter Making

It is clear that the silica percentage varies from 7.51 to 11.92 and the average percentage of SiO_2 in BF sludge is 9.07 (Table 2). As silica is an acidic impurity, there is a requirement of basic flux in order to make the feasible slag bond in sinter. In general the silica content of sinter varies from 5-6 % and it mostly comes from iron ore fines, lime stone fines, dolomite fines etc. Major contributor for silica in sinter is iron ore fines. For better sinter making the alumina /silica ratio should be less than 1. So BF sludge is used as replacement of iron ore fines to some extent as the alumina/silica ratio is 0.58.

F. Behavior of Blast Furnace Sludge on Alumina Content in Sinter Making

The alumina percentage in BF sludge varies from 4.05 to 6.13 and the average percentage is 5.3 (Table 2). The presence of alumina in sinter has an adverse effect on sinter making. Generally the % of alumina in sinter blend between 2.5-3%. More the alumina in the sinter more will be the RDI(Reduction degradation index). The major contributor for alumina in sinter is iron ore fines which are a major source in sinter raw mix. As we have used 0.45 to 2.92% of BF sludge in sinter raw mix/tonne gross sinter it has negligible effect of alumina on sinter property.

G. Behavior of Blast Furnace Sludge on Calcium Content in Sinter Making

The percentage of CaO in BF sludge varies from 5.03 to 12.15 and the average percentage is 8.47 (Table 2). Presence of CaO in BF sludge act as a basic flux and plays an important role for making feasible slag bond in sinter by counteracting the effect of SiO_2 in input feed material. So there is a need of adding lime stone for fluxing effect and to decrease the melting point of gangue content of input feed materials because of presence of CaO in BF sludge and it has fluxing effect. Its use in sinter burden can minimize the use of lime stone which is clearly evident from Fig;4.

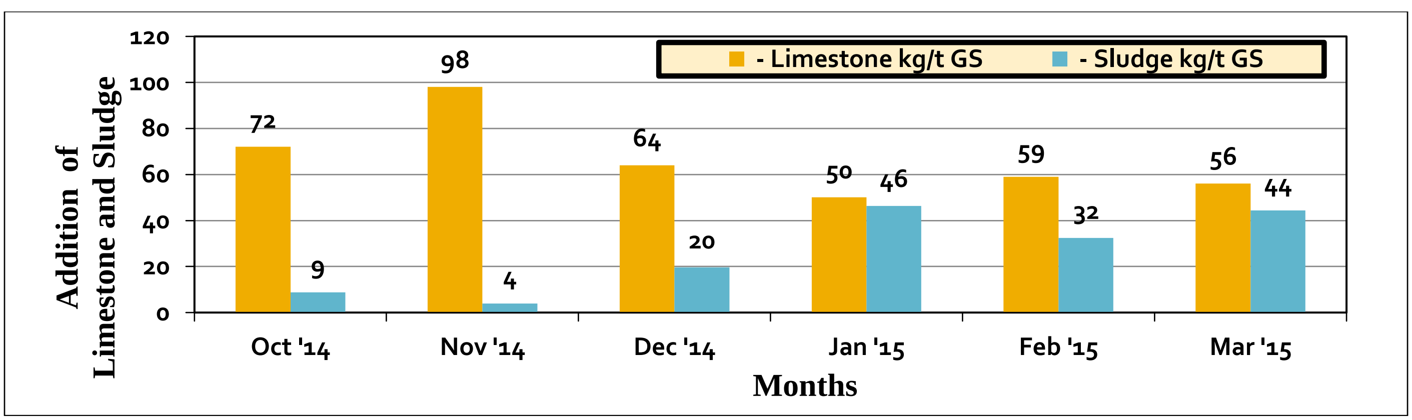

Fig .4 Consumption of Lime stone Vs Blast Furnace Sludge Per Tonne Gross Sinter

H. Behavior of Blast Furnace Sludge on Magnesium Content In Sinter Making

The magnesium content in BF sludge varies from 1.06 to 5.03 and the average percentage is 3.02 (Table 2). Presence of MgO in BF sludge make the slag more fluid in blast furnace so there is a clear separation of metal and slag in BF and more separation of sulphur from metal to slag. In general the MgO percentage in sinter is 2-2.5,as the BF sludge contain 3.2% MgO. By its use in sinter burden the use of dolomite can be minimized in sinter raw mix as evident from Fig. 8.

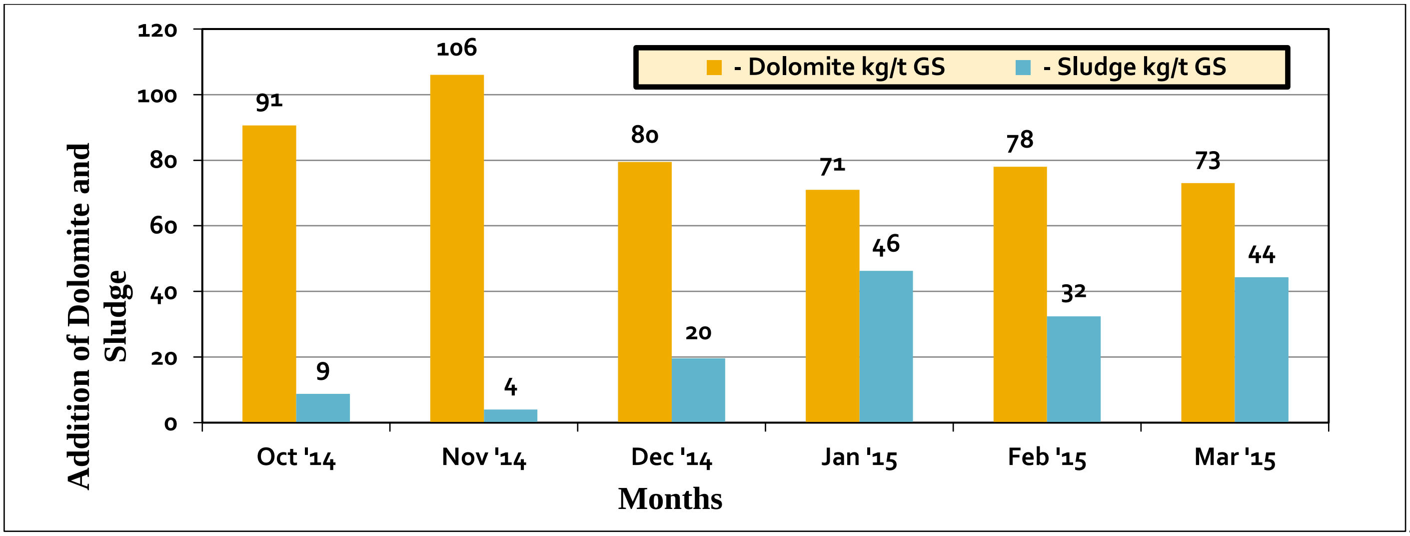

Fig .5 Consumption of Dolomite Vs Blast Furnace Sludge Per Tonne Gross Sinter

I. Behavior of Blast Furnace Sludge on Coke Rate in Sinter Making

The carbon content in BF sludge varies from 20-69 to 31.92 and the average percentage of carbon in BF sludge is 27.78 (Table 2). In sinter burden coke breeze is used as fuel. More the total carbon content in BF sludge more will be the internal heat generation for sinter making and it increases the tumbler index which is an important cold strength parameter of sinter. BF sludge contain 27.78% of total carbon so its use in sinter making can minimize the specific consumption of coke breeze / tonne gross sinter as it is evident from Fig. 6.

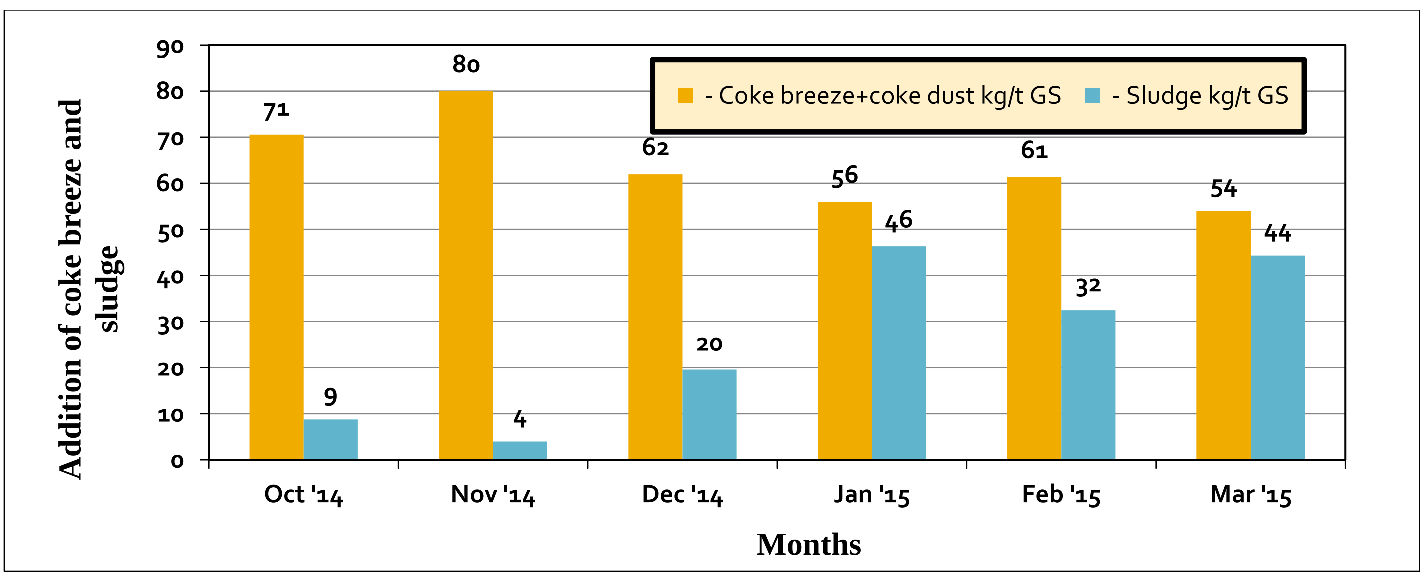

Fig .6 Consumption of Coke breeze Vs Blast Furnace Sludge Per Tonne Gross Sinter

J. Benefits of Sintering by Using Blast Furnace Sludge:-

BF sludge plays an important role by saving coke consumption and it is environment friendly also. Some of the benefits of the use of BF sludge are

- Less the coke breeze consumption, less will be the FeO in sinter.
- FeO content affects both reducibility and reduction degradation index.
- For a given basicity, lower FeO content in sinter improves sinter reducibility and softening behavior.
- FeO content in sinter should be kept at 6.7% to maintain higher strength.
- FeO strength level should not exceed 8% as that affects the fuel rate in blast furnace considerably due to inferior reducibility.
- The important property of sinter is cold strength which includes sinter granulometry, strength and consistency in chemistry. In sinter the state of dispersion of hematite, magnetite and calcium ferrite in a glassy silicate govern its strength. The slag phase contributes to the bonding strength of sinter through partial melting.
- Cold strength of sinter is generally represented by measuring Tumbler index (TI). The best sinters have ISO strength indices between 70 and 80.
- TI values of sinter should be high as low values affect the gas permeability inside BF. By the use of BF sludge we found that there is no deviation in TI and AI index of sinter.
- So BF sludge can be used upto 5% without affecting the sinter property.

K. Sludge Pond Water Analysis and Its Future Reuse

The sludge pond water is alkaline and characterized by high turbidity, TDS, Conductivity, Hardness, Calcium and magnesium (Table 4). An experiment was conducted to examine the effectiveness of polyaminechloride in the reduction of turbidity of sludge pond water because turbidity is an expression of all the above parameters.

Sl. no.	Parameter	Value
1	pH	8.31
2	Turbidity	192 NTU
3	TDS	306 mg/L
4	Conductivity	613µS/cm
5	Hardness	168mg/L
6	Calcium	105mg/L
7	Magnesium	129mg/L
8	Phosphate	6.86 mg/L
9	Zinc	0.19mg/L
10	Iron	0.25mg/L
11	TSS	45mg/L

Table 4. Values/Concentration of Different Physico-Chemical Parameters of Sludge Pond Effluent

L. Experimental Study for Reduction of Turbidity by Using Polyamine Chloride:

1lit of water sample was taken for this experimental study. Then stirring activity was carried out at 40 rpm at different dosing rate of PAC. Finally the parameters were measured after retention time of 15minutes and the results are given in table 8, presented in figures 13 and 14 and discussed below.

Dose PAC in (ppm)	pH	Turbidity (NTU)	TDS (ppm)
0	8.3	192	306
30	8.2	180	305
60	8.1	140	304
90	8	100	303
120	7.8	60	302
160	7.6	40	301
180	7.5	10	300
210	7.4	5	300

Table 5. Experimental Study f Sludge Pond Water By Adding Polyamine Chloride

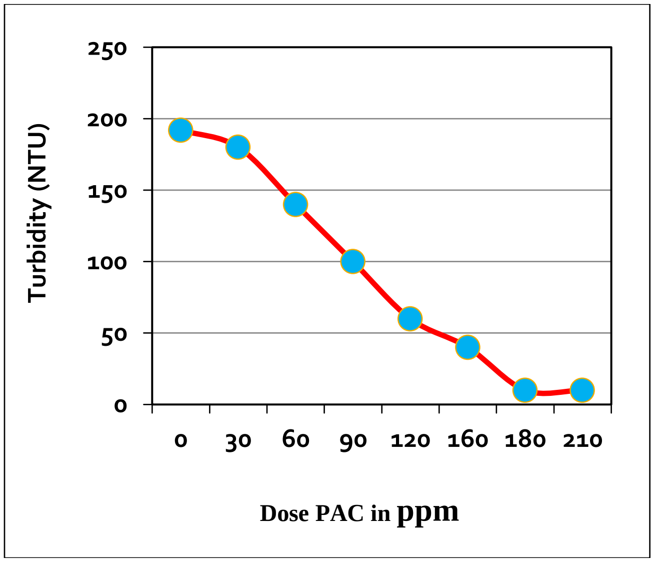

Fig .7 Turbidity vs Dose of PAC

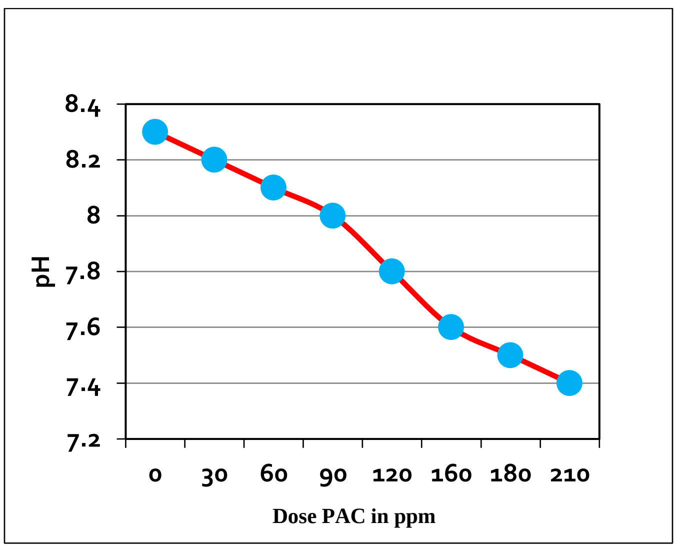

Fig .8 pH vs Dose of PAC

M. Cost Implication Study for Reducing Turbidity:

A calculation for cost effectiveness of PAC use in reducing turbidity of pond sludge water was carried out as follows.

- Turbidity of raw sludge water= 192 NTU
- Final turbidity after using of 180 ppm PAC = 10 NTU
- Sludge water discharge / hr = 35 m^3
- Sludge water discharge / day = 840 m^3
- Quantity of PAC required = 0.1512 tonne (180ppm/litre sludge water)
- Price of 1tonne of PAC = Rs 10,000
- Price of 0.1512 tonne of PAC = Rs 1512
- Price of 1m^3 make up water = Rs 4.50
- Price of 840m^3 make up water = Rs 3780
- Price saving in % term = (3780 – 1512) x 100= 60 %
  3780

From the above pilot study it is implied that the discharge sludge water may be used after treatment with PAC with a cost competitive price. The price evaluation module implies there is a 60% saving with respect to input cost price of water. More or less the PAC treated sludge may also be used in sinter making. It is may be considered for future study. Since there is no appreciable change in TDS of input and output water quality, hence output water can be recycled for industrial use instead of throwing to waste water cycle.

V. CONCLUSION

Management of waste is an integral component of management of environment, as much as an important part of business opportunities. Metallurgical industries are energy intensive and mostly environment subjective. Life cycle assessment of a typical product from any metallurgical industries reveals significant environmental impacts from “Cradle to Grave” operations. An integrated steel plant consumes large variety and quantity of resources raw materials and energy for producing steel and in this process of conversion generates substantial quantities of solid, liquid and gaseous waste.

Blast furnace sludge (upto 5%) can be recycled in sinter process without affecting the sinter properties required for BF operation. This waste contains both hematite and carbon and being relatively poor in alkali content, it can be blended with iron fines in sinter making.

The discharge sludge effluent can be used after treatment with PAC with a cost competitive price. From the price evaluation module there is a 60% saving with respect to input cost price of water. More or less the PAC treated sludge may also be used in sinter making.

Management of solid waste has two important objectives of national interest such as utilization of waste converting it into wealth through recovery of valuables and secondly minimization of the detrimental impact of waste generation on the ambient environment. This study is an attempt towards achieving this goal.

REFERENCES

[1]. Basu. G. S., Sarka.r P. K., Sharma. R. P., Ahemad. A., and Dhillon. A.S. (1997) Recycling & reuse of solid waste at Tata Steel. Tata Search, pp.118-120.

[2]. Chaudhary. P., Chaudhary. M. K., Gupta. S. S., Das. B. K., and Sandhu. H. S. (2001) Use of Pre pelletised LD Sludge in iron ore sintering. Tata Search, 107.

[3]. Das. B., Prakash. S. Reddy. P.S. and Misra. V.N. (2007) Resources, Conservation and Recycling 50, p.40.
[4]. Diz, H.R. and Novak, J.T. (1998). Fluidized bed for the removing iron and acidity from acid mine drainage. J. Environ. Eng, 124, pp.701-708.
[5]. Fosnacht. D.R., (1981), Recycling of ferrous steel plant fines. State-of-the-art, Iron Making and Steel Making, 8 (4), pp.22-25.
[6]. Jenke, D.R. and Diebold, F.E. (1983). Recovery of valuable metals from acid mine drainage by selective titration. Water Res, 17, pp.1585-1590.
[7]. Jouhari. A.K., Datta. P.S. and Misra.V.N. (2003). Mineral Processing and ExtractiveMetallurgy (Trans. Inst. Min. Metall. C), 112, p.65.
[8]. Kalyoncu, R.S. (1999). Slag-Iron and steel: U.S. Geological Survey Mineral Commodity Summaries, pp.94-95.
[9]. Mohan, D., and Chander, S. (2001). Single component and multi-component adsorption of metal ions by activated carbons. Colloid. Surf, 177, pp.183-196.
[10]. Motsi, T., Rowson, N.A., and Simmons, M.J.H. (2010). Adsorption of heavy metals from acid mine drainage (AMD), by natural Zeolite. The University of Birmingham, Unpublished Thesis.
[11]. Nakano. M., Okada. T., Hasegawa. H., and Sakakabara. M. (2000) ISIJ International, 40, p238.
[12]. Nivedita. S. S., Mohapatra. B. K., Das. B., and Paul. A.K. (1999). Characterization of dust from iron and steel making furnaces at the Rourkela Steel Plant. Orissa, for their processing, Proceedings of ISBAN, 1999, pp. 62-68, RRL, Bhubaneswar, India.
[13]. Van Herck. P., Vandecasteele. C., Swennen. R., Mortier. R. (2000). Zinc and lead removal from blast furnace sludge with a hydrometallurgical process. Environmental Science and Technology, 34, 17, , pp. 3802–3808.
[14]. White, D.A., and Siddique, A. A. (1997). Removal of manganese and iron from drinking water using hydrous manganese dioxide. Solvent Extr. Ion Exc, 15, pp.1133-1145.
[15]. Wilkin, R.T., and McNeil, M. S. (2003). Laboratory evaluation of zero valent iron to treat water impact by acid mine drainage. Chemosphere, 53, pp.715-725.
[16]. Zabban, W., Fithian, T., and Nabevak, D.R. (1972). Converting AMD to potable water by ion exchange treatment, Coal Age pp.107-111.
[17]. Zeydabadi. B.A., Mowla. D., Shariat. M.H., and Fathi Kalajahi J. (1997). Zinc recovery from blast furnace flue dust. Hydrometallurgy, 47, 1, pp.113–125.
[18]. Zunkel, AD., and Schmitt RJ. (1996). Dealing with EAF dust: environmental regulations and treatment processes. In: 9th International Mini-mill Conference, 12-14 March 1996, Cincinnati, USA Metal Bulletin Monthly‟s. p.23.