An overview of utilization of slag and sludge from steel industries

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Abstract

Significant quantities of sludge and slag are generated as waste material or byproduct every day from steel industries. They usually contain considerable quantities of valuable metals and materials. It is generally possible to recover some values by physical or chemical mineral processing techniques such as crushing, grinding, classification, hydrocyclone, magnetic separation, flotation, leaching or roasting. Transforming these solid wastes from one form to another to be reused either by the same production unit or by different industrial installation are very much essential not only for conserving metals and mineral resources but also for protecting the environment. This paper analyzes the characterization, beneficiation and utilization aspects of blast furnace flue dust, blast furnace sludge, LD sludge and LD slag generated at modern steel plants.
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Keywords: Steel plant; BF dust; BF sludge; LD slag; LD sludge; Utilization

1. Introduction

Integrated steel plants utilize mostly five materials such as raw materials, air, water, fuel and power to produce steel. During the production of steel, 2–4 t of wastes are being generated per tonne of steel produced. The various solid wastes in the form of slags and sludges that are emerged from steel plants are blast furnace slag, blast furnace flue

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Table 1
Types of solid/liquid waste generated from steel plants

Solid/liquid wastes	Hot metal (kg/t)	Source of generation
Coke breeze	–	Coke oven
Nut coke	–	Coke oven
Coke dust/sludge	–	Coke oven
Blast furnace slag	340–421	Blast furnace
Blast furnace dust/sludge	28	Blast furnace
Sintering plant sludge	–	Sintering plant
LD slag	200	Steel melting shop
LD sludge	15–16	Steel melting shop
Lime fines	–	Steel melting shop
ACP/GCP sludge	–	Steel melting shop
Carbide sludge	–	Acetylene plant
Mill scale	22	Mills
Mill sludge	12	Rolling mills
Refractory, bricks	11.6	Steel melting shop/mills, etc.
Sludges/scales	–	Water treatment plant
Fly ash	–	Power plant

dust and sludge, Linz–Donawitz (LD) converter slag, LD sludge, LD dust, mill scale, mill sludge, acetylene sludge, etc. The solids and liquid wastes generated from a steel plant are shown in Table 1. The composition of these materials vary widely depending on the source of generation but usually contains some useful resources such as iron, carbon, calcium, zinc, lead, etc., which can be recovered and reused in a judicious manner. Besides that, some slag and sludge contain a notable amount of heavy metals and release of them to earth may cause some environmental problems. The harmful components like As, Cd and Hg, etc. are highly objectionable from the pollution point of view. So, the simple disposals of these wastes are becoming less attractive which not only occupies plenty of land but also increases the disposal costs. Therefore, it is desirable to recover the valuables and utilize these wastes. However, detailed scientific investigation is necessary to establish the scope of the problems associated with recovering the valuable materials from different slags and sludge and the proposed utilizations are to be carefully evaluated.

Steel plant slags mainly include blast furnace slag and steel melting slag (open hearth or LD process slag). Various efforts have been made on the utilization of blast furnace and steel slags. These are competitive raw materials for industrial mineral industry. A comparison of the qualities between air-cooled blast furnace slag and natural sand, LD slag and natural sand, LD slag and gravel or crushed stones shows that they are equivalent. The special processing of slag sometimes produces products originating from the rock and mineral industries. Therefore, lot of studies has been made for the concrete, plastering and environmental technology industries (Kolb and Leipold, 1993). Today blast furnace slag has found a wide application in cement production and marketed as Port land blast furnace slag cement (PBFS). Since blast furnace slag contains little iron and high calcium oxide content with similar composition of clinker, it can be safely used along with the clinker and gypsum for production of cement.

LD slag is a byproduct of steel industry, which comes from pig iron refining processing using LD converters. Because of its physical, chemical and mineralogical properties, it can be used as a substitute for aggregates in civil engineering projects. LD slag has the useful components like CaO, MgO with high basicities (CaO/SiO_2) of above 3.0. LD slag therefore has high fluxing capacity and is being charged in the blast furnace due to easy melt and better utilization of calcium values. In the European countries, 30% of such slags are recycled into the blast furnace. However, the most harmful components in the LD slag is P&S which are to be removed before use either in sintering plant or blast furnace. LD slag, used in blast furnace at Bhilai Steel Plant, India was therefore discontinued due to sulphur and phosphorus content (Sharma et al., 1993). The slag is however not suitable in cement making due to the presence of high percentage of iron oxide. In many instances it is usually subjected to metal recovery before its application in steel and iron industries.

Most of the materials of sludge and dusts from steel industries are recycled through sinter making in more advanced countries. The recycled wastes also have some effect on sinter quality, strength and productivity. The recycling is generally controlled depending on the analysis of the waste material. In the direct use of the steel plant wastes, a briquetting plant was commissioned at National Steel Corporation, Great Lake to recycle 300,000 metric tonnes of waste materials such as BOF sludge, BF dust and sludge, LD sludge, mill scale and other materials (Landow et al., 1997). A number of technologies have been developed to allow better utilization of Fe-bearing steel plant fines in primary operations. Methods ranging from simple agglomeration techniques to new hot metal production processes for treating the dust materials are cited which are useful in pretreating the waste materials to make them more amenable to recycling in iron and steel making operations. These processes involve thermal, hydrometallurgical and physical beneficiation methods.

The process byproduct of mill scale from the rolling process containing >70% Fe is generally recycled into the sintering plant. Generally, 70–100% mill scale containing high iron is being recycled through either briquetting or sintering route with out any difficulties. In some cases, de-oiling of the material is required. Rolling mill sludge is the fine particles, which takes the oil portion along with the rolling cooling water. Recycling of these particles are challenging due to very high oil content. The reduction of oily mill scale sludge along with blast furnace flue dust in laboratory experiments and in a pilot plant rotary kiln has indicated that it is possible to reduce oily mill scale sludge to sponge iron in the rotary kiln (Eriksson et al., 1999).

The extent of generation, characterization and utility of various sludge and slags with a review of number of methods for the recovery of valuables or recycle in the plant from such materials have been summarized.

2. Blast furnace slag

The BF slag is basically inorganic in nature. It contains mainly inorganic constituents such as silica (30–35%), calcium oxide (28–35%), magnesium oxide (1–6%), and Al_2O_3/Fe_2O_3 18–258%. Due to the low iron content it can be safely used in the manufacturer of cement. The chemical and mineralogical composition of Portland cement, blast furnace flue dust and clinker is shown in Table 2. It can be seen that the important constituents of BF slag

Table 2
Chemical composition and mineral logical composition of BF slag, Clinker and Poland cement

Composition (%)	Portland cement	Clinker	Blast furnace slag
Loss on ignition	1.38	1.5	2.25
Insoluble residue	1.18	0.5	–
SiO_2	20.91	21.5	37.14
CaO	62.18	66.6	37.40
Al_2O_3	5.82	5.2	9.15
Fe_2O_3	3.40	2.8	1.05
MgO	2.36	1.0	11.70
SO_3	2.78	1.0	0.37
Mineralogical composition (%)	C_3S-42-46, C_2S-25-27, C_3A-6-10, C_4AF-5-101	C_3S-54-62, C_3A-5-10, C_2S-20-22, C_4AF-10-13	–

such as CaO, SiO_2 and low Fe_2O_3 can contribute to the formation of cement. Two types of blast furnace slag such air-cooled slag and granulated slag are being generated from the steel plants. In India around 40% of this slag is produced in the form of granulated slag. The specific gravity of the slag is approximately 2.90 with its bulk density varying in the range of 1200–1300 kg/m^3. The color of granulated slag is whitish. The air-cooled slag is used as aggregates in road making while the granulated slag is used for cement manufacturing. This has been fully utilized through out the World. It has been proved that around 50% of clinker is replaced by additives like blast furnace granulated slag in the production of cement. Apart from the proven benefits in cement quality such as low heat of hydration, good long term strength, control alkali–silica reaction, resistance to acid, better durability by the addition of granulated slag, it is also a cost saving measure to the cement industries. Air-cooled slag is being used as a substitute for stone, chips for road making in many countries like Australia, France, Holland but it is still under study in India.

2.1. Utilization of blast furnace slag

The blast furnace slag can be used in the preparation of materials such as ceramic glass, silica gel, ceramic tiles, bricks, etc. The devitrification behavior of different sizes of slag-derived glass was investigated using differential analytical techniques to determine the possibility of preparing glass–ceramic materials. The crystalline phases of slag were identified as gehlenite, diopside pyroxene and barium aluminium silicate. The difference in the glass–ceramic texture was observed by treating the sample at different crystallization temperatures. Both acicular and dendritic morphology have been identified in the sample heat-treated at 1050 °C. A slight variation in peak crystallization temperature with particle size indicated a bulk crystallization mechanism (Francis, 2004). The recovery of silica gel from blast furnace slag has been attempted by leaching with H_2SO_4, separation of gypsum, precipitation of silica gel at pH 3.2, followed by the washing of the raw precipitate (Seggiani and Sandra, 2002). The ceramic tile were prepared from granulated blast furnace slag and common clay by mixing calcia:silica ratio at different proportions. The optimum compositions were found to be where calcia–silica ratio were in the range of 0.1–0.3. The mechanical strength and water absorption of the fired specimen were in the range of 28–38 MPa and

2.5–0.1%, respectively. The physical properties of the sintered specimen are explained on the basis of XRD and SEM analysis. Formation of wollastonite in the sintered compacts with finer grain size was found to be an important parameter for increase in strength.

Crystalline and amorphous blast furnace slag can be used as an adsorbent of phosphate from water solutions. The adsorption kinetics measurements confirmed that a model involving pseudo-second-order reactions could describe the sorption of phosphorus on crystalline as well as amorphous slags. The phosphorus sorption follows the Langmuir adsorption isotherm (Kostura et al., 2005).

The adsorption characteristics of blast furnace slag on the removal of lead have been investigated as a function of pH, the metal ion concentration, the particle size and the amount of sorbent. It has been established that the process occurs with increasing pH and the efficient lead removal by granulated slag occurs at pH values lower than precipitation pH values. The equilibrium in the slag lead solution system is described by the Freundlich adsorption isotherm. The percentage of lead removal at equilibrium increases with increasing slag amount but the sorption capacity decreases. Depending on the conditions, a percent lead removal of 97–98% can be achieved. The results obtained could be useful for the application of granulated slag for the Pb-ions removal from industrial waste (Dimitrova and Mehandgie, 1996).

2.2. Blast furnace flue dust and sludge

Blast furnace flue dust is a solid waste material from the integrated steel plant. The flue dust is a mixture of oxides expelled from the top of the blast furnace, whose major components are iron oxides and coke fines. It also contains silicon, calcium, magnesium and other minor elemental oxides in lesser amounts. The direct recycling of flue dust is not usually possible since it contains some undesirable elements (like zinc, lead and alkali metals) that can cause operational difficulties in the blast furnace. In some cases the particles contain large amount of Zn and Pb as the volatile impurities. It is mainly due to the Pb–Zn containing scrap that is added into the blast furnace. Furthermore, in some cases the dust contains toxic elements (Cd, Cr and As), which make it hazardous and unacceptable for landfill. Therefore, proper characterization followed by a suitable beneficiation method has to be evaluated in order to recycle within the plant.

2.3. Characterization studies of blast furnace flue dust and sludge

The physical and complete chemical analysis of the blast furnace flue dust sample obtained from two steel plants of India is shown in Table 3. The sample contains high level of carbon and iron showing the abnormal accumulation of these two elements. Besides that, the sample contains high percentage of alkalis due to which it cannot be reused in sinter making. The optical emission study (OES) of the blast furnace flue dust sample indicated that iron is present in very high quantities in comparison with the other elements. The associated rare earth elements in the flue dust sample carried out by induction coupled plasma (ICP) are La, Ce, Nd, Pr, Y, Er, Dy, etc. The X-ray diffraction (XRD) study of the BF flue dust sample shows the associated phases of iron metal, gehlenite ($Ca_2Al_2SiO_7$), magnetite, hematite, quartz and wustite in order of abundance (Das et al., 2002a).

Table 3
Physical and chemical properties of typical BF flue dust sample

Constituents	Sample I (%)	Sample II (%)
Carbon	29.90	33.62
Fe_2O_3	51.10	49.50
SiO_2	6.31	8.30
Al_2O_3	5.12	2.54
CaO	4.90	1.96
MgO	0.88	1.33
Pb	0.024	0.019
Zn	0.042	0.028
MnO	0.58	0.02
K_2O	1.22	0.154
Na_2O	0.47	0.07
Fe(T)	35.7	34.62
Bulk density (g/cc)	1.42	1.32
Specific gravity	2.59	2.56
Porosity (%)	45.17	48.53

2.4. Utilization of blast furnace flue dust and sludge

2.4.1. Removal of alkalis from blast furnace flue dust/sludge

The reuse of blast furnace flue dust in sintering plant or blast furnace has been hampered due to the presence of Na, K, Zn, Pb, Cd, S, cyanides, oils, etc. In blast furnace Na, K, S can cause operational difficulties or unacceptable hot metal composition (Ellis, 1999). The performance of blast furnace is strongly affected for presence of alkali due to lowering down the softening and melting temperature of iron ore and sinters. Alkaline elements accumulate in blast furnace due to cyclic reactions and hinder the normal operations, loss of permeability of the burden, cracking of refractory bricks, etc. In addition to this alkali cyanides is likely to be formed cause environmental problems. Zinc has been regarded as a problem because it forms a circuit in the furnace resulting in extra coke consumption. The volatility of zinc and its condensation in cooler region of blast furnace cause serious problems. For dealkalification of blast furnace dust, acid leaching has been suggested to promote increased recycling of iron making. Besides that scrubbing, washing, leaching with $CaCl_2$, NH_4Cl, etc. has been carried out. The study carried out at Regional Research Laboratory, Bhubaneswar, India reveals that it was possible to remove around 75% of Na values by reducing the particle size. However the removal of potassium was restricted to 22% only (Das et al., 2002b).

2.4.2. Recovery of Zn and Pb from blast furnace flue dust and sludge

During the production of pig iron in a blast furnace, Zn- and Pb-containing sludge is being generated. The sludge particles also contain large amounts of iron and carbon that could be recycled in the furnace. However, the Zn content of the sludge is high, and the Zn input to the blast furnace must be limited. Several works have been carried out for the recovery of Pb and Zn values present in the sludge. A hydrometallurgical process whereby the sludge is leached under both acid and oxidizing conditions has been reported. After the

separation of the solids, i.e. carbon and iron from the leaching solution, the latter is passed through an anion exchanger to remove Zn and Pb and then recirculated to the reactor (Van Herck et al., 2000). In some cases selective leaching by sulfuric acid at low concentration and room temperature, gives rise to high recovery of zinc (about 80%) (Zeydabadi et al., 1997). Investigation have been carried out on the use of the NH_4SCN solution, which is produced by the gas emitted from coke furnace to remove zinc from the blast furnace sludge. ZnO reacts with NH_4SCN and forms $Zn(SCN)_2$ which dissolves easily in water (Cho et al., 1997).

Zn from Zn-bearing blast furnace wastes is also separated by froth flotation and wet cyclone methods (Piecuch and Dabrowska, 1983). Experiments have shown that Zn, Pb and other nonferrous metal contents of blast furnace dust can be removed by wet-classifying the dust in a cyclone separator. The dezinced, wet-cleaned blast furnace dust containing around 1% zinc is made into mini pellets as sinter raw materials (Uno et al., 1979). In another attempt by oxidizing–chlorination roasting of blast furnace and steel making converter sludges with $CaCl_2$ for the sublimation of Zn and Pb chlorides it was observed that the degrees of Zn and Pb chloride sublimation were 99.48 and 98.58%, respectively (Shevko et al., 1993).

A study was made for the reduction of iron oxides and zinc compounds by the carbon contained in sludge with simultaneous removal of Zn from high-zinc blast furnace sludge. Briquettes of the sludge were fired for different times and at different temperatures. Beside the degree of metalization of iron and removal of zinc it was also possible to evaluate the utilization of carbon contained in the sludge (Fosnacht, 1985).

The use of Waelz kiln (rotary kiln) to reclaim Zn and Pb from blast furnace sludge has been attempted. The material is premixed in wagons, fed into an impact crusher, pelletized and finally put into the kiln. Water, hydrate of lime and coke breeze is added as needed since carbon and basicities help dezincing and reduction of iron oxide. It was possible to volatilize successfully 95% Zn, 95% Pb, 30% sulfur and 30% potassium oxide from a mixture containing 44% Fe, 4.5% Zn, 2% Pb and 7% carbon. About 80% of the final product was −5 mm in size and would have to be sintered (Serbent et al., 1975).

2.4.3. Recycling of blast furnace flue dust and sludge

The dust is generally recycled through sinter making in more advanced countries. The Institute of Gas Technology, USA has developed a fluidized-bed process for recovering direct reduced iron from blast furnace flue dust. Up to 95% of the iron oxides contained in the waste stream could be reduced to elemental iron. The yield of iron depends upon the quantity of iron oxide present in the flue dust and generally ranges from 20 to 30% of the waste stream (Rehmat and Mensinger, 1996). Research program has been started at the Institute of Ferrous Metallurgy at Aachen University of Technology to investigate the possibility of a combined injection of coal and blast furnace flue dust into the blast furnace in order to decrease the deposition of waste material. The direct use of dust leads to a substitution of pellets or briquettes and with it to a decrease of agglomeration costs and energy (Gudenau et al., 1998). In USA and Canada the BF flue dust and the finer mill-scale are generally recycled through the sinter plant. However the steel making wastes have hitherto been almost entirely dumped, owing to their fineness and high Zn, Pb, and alkali content.

Table 4
Carbon and magnetite concentrate obtained from blast furnace flue dust

Constituents (%)	Carbon (wt.%)	Constituents (%) (magnetite)	wt.%
Carbon	79.4	FeO	24.70
Fe_2O_3	5.57	Fe_2O_3	64.38
SiO_2	5.12	SiO_2	1.5
Al_2O_3	3.95	Al_2O_3	2.43
CaO	0.53	CaO	3.80
MgO	0.175	MgO	1.59
Na_2O	0.013	Na_2O	0.016
K_2O	0.077	K_2O	0.05
		Specific gravity	4.1

2.4.4. Recovery of carbon and magnetite from blast furnace flue dust

Extensive characterization and beneficiation studies have been undertaken at RRL, Bhubaneswar to recover valuable products from the solid wastes generated in the steel plants. The studies on blast furnace flue dust from steel plants revealed that it is possible to recover coke fines with more than 80% carbon with 30% yield from these types of flue dusts by column flotation techniques. The coke fines can be either mixed with the coking coal fines or may be agglomerated for recycling. The flotation tailings are rich in ferruginous phases (magnetite) and can be recovered by low intensity magnetic separation technique. A product with 62–65% Fe at a yield of ~30% could be obtained by this process. A flow sheet to recover magnetite from blast furnace flue has been suggested. It was possible to obtain an iron grade of 64.1% Fe with overall recoveries of 48–55%. The quality of carbon and magnetite thus obtained from the blast furnace flue dust sample of a steel plant is shown in Table 4, respectively. The specific gravity of magnetite, which is essential for its use in coal preparation plants, was found to be 4.1 (Das et al., 2002a).

In Katowice steelworks, Poland the blast furnace dust has been used for production of heavy suspension liquid to be used in mechanical treatment of coal. The production cost of the wetting agent from blast furnace dust is several times lower than that of magnetite, which has been used to date (Harris, 1980).

2.4.5. Blast furnace flue dust as an adsorbent

The effectiveness of blast furnace sludge to purify Cu^{2+} containing solutions was studied by determining the adsorption of Cu^{2+} ions from aqueous solution on flue dust. The results suggest that blast furnace sludge is a good adsorbent for Cu^{2+} from aqueous solutions. The adsorption kinetics followed the Langmuir isotherm. The kinetics was similar for temperature and pulp density (Lopez-Delgado et al., 1998). In another study, the adsorption of Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} on the sludge was investigated by determination of adsorption isotherms. Blast furnace sludge was found to be an effective adsorbent for Pb, Zn, Cd, Cu and Cr-ions within the range of ion concentrations employed (Lopez et al., 1995). Blast furnace sludge of two different carbon contents and a metallurgical coke were used to adsorb lead ions from aqueous solutions. High temperature favors the adsorption of lead ions from aqueous solutions on samples with lower carbon content. However, the adsorption capacity of samples with higher carbon contents decreases with increasing temperature. The

increase of adsorption capacity with increasing Fe_2O_3/C ratio in the sludge indicates that under these experimental conditions, the process of lead ion adsorption occurs more strongly on the hematite phase than on the carbon phase (Lopez-Delgado et al., 1998).

Blast furnace flue dust is a waste material from steel industries and may be used to remove heavy metal ions from aqueous solutions. It was found to be a good adsorbent for divalent copper and lead ions from aqueous solutions. The carbon, metallic iron and aluminosilicate phase present in the flue dust sample are responsible for the removal of metal ions. The amount of copper removal is higher at higher temperature. On the other hand the removal capacity of Pb(II) ion is comparatively low. The adsorption kinetic was rapid over an initial time period followed by the slower rate at final stage. It follows both Freudlich and Langmuir adsorption isotherms and appears more or less of physical nature. Blast furnace flue dust is a waste material from steel industries and may be used to remove heavy metal ions from aqueous solutions. This technique can be exploited in treating industrial waste and cleaning water (Das et al., 2002a).

3. LD slags

Great amounts of slags from steel plants are produced through basic oxygen furnace and LD furnace. The main purpose of LD process is to convert the molten pig iron and steel scraps into high quality steel. In India, the generation of steel melting slag is over 2 MT per annum. The amount of steel slags from different steel industries are 150–200 kgs/t of steel produced.

3.1. Characterization of LD slag

The chemical composition of typical LD slag samples generated at steel plant is shown in Table 5. The main components are Fe, CaO, and SiO_2. The high content of CaO in the slag can be used to substitute for a part of limestone as fluxing material to reduce the iron in steel making cost. Many steel plants of the World utilize LD slag as the replacement of limestone.

Table 5
Chemical composition of LD slag

Constituents	Percent	
	Sample 1	Sample 2
SiO_2	12.16	12.0
Al_2O_3	1.22	1.58
FeO	26.30	27.89
CaO	47.88	50.0
MnO	0.28	–
MgO	0.82	1.50
P_2O_5	3.33	3.35
S	0.28	0.30
LOI	7.54	–
Na_2O	0.036	–
K_2O	0.071	–

Table 6
Major phases present in steel slags

Phases	wt.%
Tricalcium silicate (C$_3$S), Ca$_3$SiO$_5$	0–20
Dicalcium silicate (C$_2$S), Ca$_2$SiO$_4$	30–60
Other unethed silicates	0–10
Magnesiocalciowustite	15–30
Dicalcium aluminoferrite (Ca$_2$(Fe, Al, Ti)$_2$O$_5$	10–25
Magnesium type phase (Fe, Mn, Mg, Ca) O	0–5
Lime phase (Ca, Fe) O	0–15
Periclase (Mg, Fe) O	0–5
Fluorite CaF$_2$	0–1

Steel slags contain higher amount of P&S, which seriously affects the direct recycling to iron and steel making process. The X-ray diffraction studies of two steel plant slags carried out in our laboratory reveals that, the major phases of LD slag are dicalcium ferrite, calcium aluminate and wustite. The major phases present in LD slag as reported in other parts of World are given in Table 6 (Goldring and Juckes, 1997). Steel slags also contain some reactive mineral phases such as 2CaO·SiO$_2$, 3CaO·SiO$_2$ and free CaO and MgO.

The electron probe micro analysis (EPMA) study of the LD slag sample was carried out to know the association of phosphorus in LD slag and the results are shown in Table 7. There is some variation with respect to Fe, Ca, Al and Mn content. Most of the analysis relates to very low MgO content and hence not reflected in EPMA study. However, it is evident that P content in the slag is more attached to the calcium phase than the iron phase. No separate phase of phosphorous could be identified either in XRD or micro photographic studies.

3.2. Utilization of LD slag

LD slag can be utilized in many areas such as soil conditioners, fertilizers, recovery of metal values, etc. Experiments were conducted using pulverized LD slag for growing vegetables like tomato, potato, onion, spinach, and crops like wheat, in the acidic soil (Maslehuddin et al., 2003). The results show that by adding a concentration of slag of between 1.5 and 5.0 t/ha, according to soil type and its agricultural use, it is possible to achieve a proportional increase in the soil's pH as well as changes to the exchange complex. The result is improved quality and soil productivity. Production of fertilizers from steel manufacturing byproducts such as LD slag, semi-calcined dolomite and ammonium sulfate

Table 7
EPMA analysis of LD slag (P-rich)

P	Ca	Mn	Al	Na	Ti	Fe	K	Si
1.49	46.20	2.30	1.61	0.01	0.93	26.2	0.11	15.45
3.56	64.4	0.28	0.18	0	0	1.10	0.28	31.11
3.15	58.8	0.99	0.24	0	0.08	1.98	0.22	30.3
0.88	31.17	5.8	1.94	0	0.27	35.51	0.11	12.52
0.67	33.52	5.53	6.20	0.1	4.03	9.86	0.72	35.9

and their application in agricultural systems, viz. pasture farming, agro-forestry and forestry have been studied. The influence of these materials on the chemical composition of soil, grass and to the potential economic benefits of applying these new fertilizers to the soil were also evaluated (Lopez Gomez et al., 1999).

3.3. Recycling of metal values

In addition to the fluxing characteristics of LD slag, the recovery of metal values from slag was carried out by different techniques. Smelting reduction technique was applied for the recovery of valuable metals such as vanadium and chromium from LD slag using a Tamman furnace. The degree of metalization of slag was 98% at 1600 °C at 30 min of time (Park et al., 1994). The slag is also reduced in an electric furnace to separate the slag and metal. The recovery of metal values from steel slag was carried out by addition of small quantity of mineral additive into the molten slag followed by crystallization of the slag. The additive acts as nuclei for the crystallization of dicalcium silicate in the slag (Weiss et al., 1987). The breaking of slag produces 65–80% slag and 10–15% chips.

3.4. Other applications

The LD slags are suitable materials for the base and sub-base layer of road because of the hard characteristics. Investigations on the mineralogy and physical properties of LD slag have shown that it would make an excellent road stone. Experiments on the weathering of slag, both on the laboratory scale and in stockpiles, have shown that the free lime levels will drop to a near-constant nonzero value after 9–12 months. The LD slag of various ages has been used in the construction of the wearing course of several works and public roads. Nippon Slag Association in Japan is researching converter slag utilization in port and harbor construction and the use of EAF oxidizing slag as concrete aggregate (Ozeki, 1997). A major area for utilization of LD slag is in ballast for railway tracks. The slag sample from Indian steel plants have been tested and found to satisfy the railway satisfaction for ballasts.

3.5. Removal of phosphorus from LD slag

In order to utilize more LD slag either in blast furnace or sintering plant it is desirable to remove the phosphorus content from the LD slag. The study results through electron probe micro analysis and liberation analysis reveals that P occurs predominantly in dicalcium phase. It has been reported that high gradient magnetic separation studies (HGMS) was able to separate around 50% of the P value from the LD slag. It was also possible to remove around 70% of phosphorus from slow cooled slag by HGMS. It is reported that slow cooling of LD slag promotes the mineral grain growth and formation of calcium phosphate as fine-grained crystal (Fregeau-Wu et al., 1993). The preliminary dephosphorization method of hot metal outside the steel making furnace was investigated to obtain extra low phosphorus steel and to utilize the LD slag more effectively. Hot metal with a phosphorus content of 0.09–0.16% was treated in a ladle with a dephosphorization agent consisting of LD slag and iron oxide or lime and iron oxide, and the phosphorus content of hot metal was reduced to 0.020–0.060 or 0.003–0.020%, respectively. By refining the dephosphorized hot metal

in the LD converter, extra low phosphorus steel having a phosphorus content of less than 0.005% was obtained (Thomas, 1983).

Several studies have been undertaken in this laboratory for the removal of phosphorus from LD slag. In flotation studies the slag sample was ground to below 100 µm size by laboratory ball mill. Sodium oleate was used as the collector where as gum acacia was employed as iron depressant. As no froth had appeared at lower pH values, all the flotation studies were carried out at alkaline pH. The results of the studies indicated that by increasing the collector concentration the weight of the concentrate increases but the grades of the P, Fe and CaO are equally distributed in both float and nonfloat fractions. The other methods such as magnetic separation, classification were met with limited success with respect to the removal of phosphorus from LD slag (Das et al., 2002b). Different methods other than physical beneficiation studies such as smelting by induced furnace and plasma smelting studies were carried out to remove the phosphorus content from LD slag. In two of the plasma studies the basicities was maintained at 2.50 and 2.25 by the addition of quartz into it. It was possible to obtain 1.2–1.3% of P in the slag phase where as the P content in the metal phases were as high as 2.92%. Beside the smelting studies, roasting with NaCl, Na_2CO_3 followed by leaching in dilute HNO_3 were also carried out. It was possible to remove around 50% of the phosphorus values at all the temperature range studied in which the material has to be ground to a finer size.

Specific bacteria such as *A. niger hyphomicrobiumt* and *B. mucilaginosus* are being used for the removal of P from ores, sludges, etc. Hence, a preliminary study on bacterial leaching for the removal of P from LD slag was carried out. The studies were undertaken by using a specific bacteria for P dissolution namely *Frateuria aurentia*. The studies were undertaken at 10% (v/v) inculation. It was possible to remove around 72.17% P from the LD slag (Pradhan et al., 2005).

4. LD sludge

The fine solid particles recovered after wet cleaning of the gas emerging from LD converters in the sludge form are termed as LD sludge. During this process the furnace emits very fine iron oxide particles that are removed from the waste gases by a wet scrubbing process. This waste may contain high levels of CaO, Zn, Pb, etc. depending upon the type of limestone and chemistry of scrap used during the process of steel making. At steel plants, the high moisture content of the LD sludge (35–40%) is a major obstacle in its recycling to the sinter plant. It becomes sticky and forms agglomerates after long exposure to the atmosphere. Therefore, LD sludge has to be optimally dried and made handleable before recycling. In order to meet the strict environmental requirements, it has become necessary for steel plants to develop a process of recycling this waste material. The sludge contains appreciable quantities of iron and lime and is therefore quite suitable for recycling in the sinter plant.

4.1. Characterization studies of LD sludge

The chemical analysis of typical sludge sample being generated at steel plant is shown in Table 8. The sample contains around 61–64.1 of Fe and 9–10% of CaO. It is evident form

Table 8
Chemical analysis of the LD sludge sample

Constituents	Percent	
	Sample 1	Sample 2
Fe (total)	64.12	61.0
FeO	79.58	76.93
Fe_2O_3	2.79	1.43
CaO	8.9	10.59
MgO	0.38	0.38
SiO_2	0.71	1.97
Al_2O_3	0.32	0.95
P	0.101	0.126
MnO	0.10	0.24

the chemical analysis that, the iron is mostly present in divalent state due to reduction during the operation. Due to very high iron and appreciable amount of CaO content, it is a good raw material for recycling to iron and steel industries. It has been observed that the Al_2O_3 content is far lower than iron ore is an added advantage to reuse in steel plant. The size and elemental distribution of LD sludge is shown in Table 9. The size and elemental distribution of LD sludge is shown in Table 9. The Fe, CaO and acid insoluble are equally distributed in all the size fractions. Hence separation of either Fe or CaO by simple classification technique is not possible. The X-ray diffraction study of the LD sludge sample is shown in Fig. 1. The X-ray diffraction studies were carried out to identify the different mineral phases in the sample. The XRD peaks of the three samples, viz: (i) bulk sample, (ii) sample calcinited at 950 °C and (iii) products obtained on magnetite separation. The different mineral phases identified are hematite, quartz, wustite, calcite and metallic iron. These studies were supported by the microphotographs. Most of the iron-rich phase including Fe-metals appears globular. The calcite occurs in irregular shaped fragments showing rhombohedral cleavage. The metallic globules are often encircled by thin layer of glassy phase. Secondary magnetite grains often coagulate and appear in spherical shape. Skeletal growth of Fe-metal over wustite base is occasionally noticed. The calcite fragments sometimes enclose Fe-metallic prills but usually appear as broken fragments. The microphotographs are shown in Fig. 2(A–F).

Table 9
Size and elemental distribution of the as received LD sludge sample

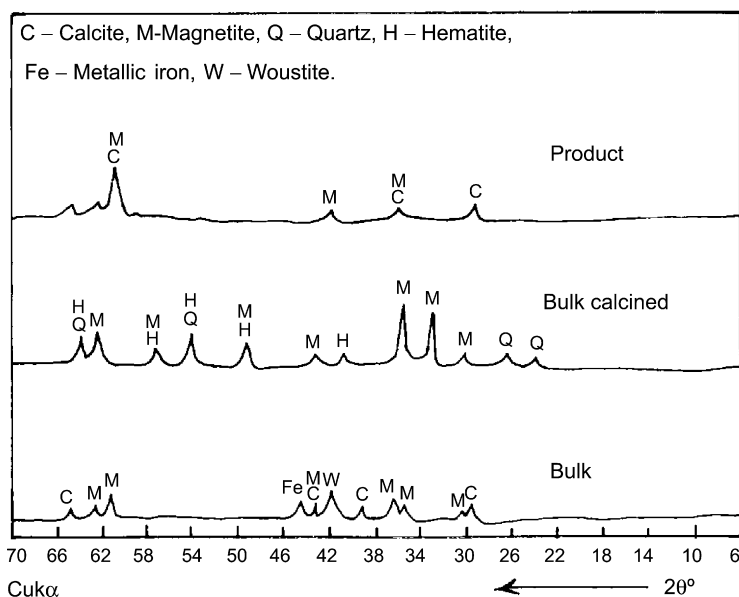| Size (μm)	wt.%	Fe (%)	Acid Ins (%)	CaO (%)
+1000	9.8	65.34	0.79	9.75
+500	12.9	63.7	0.40	9.0
+300	4.0	65.34	0.58	8.75
+150	4.4	62.82	0.80	9.5
+75	0.5	61.9	1.21	13.0
+45	6.8	63.38	1.29	10.0
−45	61.6	64.2	0.69	9.5
Head	100	64.16	0.71	8.62

Fig. 1. X-ray diffraction studies of LD sludge: C, calcite; M, magnetite; Q, quartz; H, hematite; Fe, metallic iron; W, woustite.

4.2. Utilization of LD sludge

In order to maximize the use of LD sludge in sinter making, pre pelletisation of LD sludge is highly essential. Pilot plant trials successfully demonstrated the viability of recycling million of tons of steel plant dusts and sludge that are now typically land filled, and typically converting them into useful products, i.e., hot metal for steel production, zinc-rich raw material for the nonferrous metal industry, and slag for road bed and cement production. The pilot plant trials and subsequent feasibility study showed that steel plant waste oxides could be smelted in an environmentally sound manner for an attractive return on investment (Sarma et al., 1996).

The carbothermic reduction of sludges without addition of coal under nitrogen atmosphere for conversion to metallic iron has been reported. The results indicated that increasing the weight ratio of sludge, size of solid sample, carbon content, density of solid sample or reaction temperature could increase the reduction rate (Chen et al., 1992). However for direct use of this type of sludge briquetting or pelletisation is important to agglomerate the fines.

The agglomeration studies carried out at Regional Research Laboratory indicated that, LD sludge as such do not give enough strength of the briquettes. However it was possible to get adequate green strength as well as the crushing strength so as to recycle in the plant by using LD sludge in combination with mill scale. The combination of binders plays a vital role in the formation of the agglomerates. In order to have sufficient green strength for pellet making, a minimum of 2% lime and 6% of organic binder is required. Drying
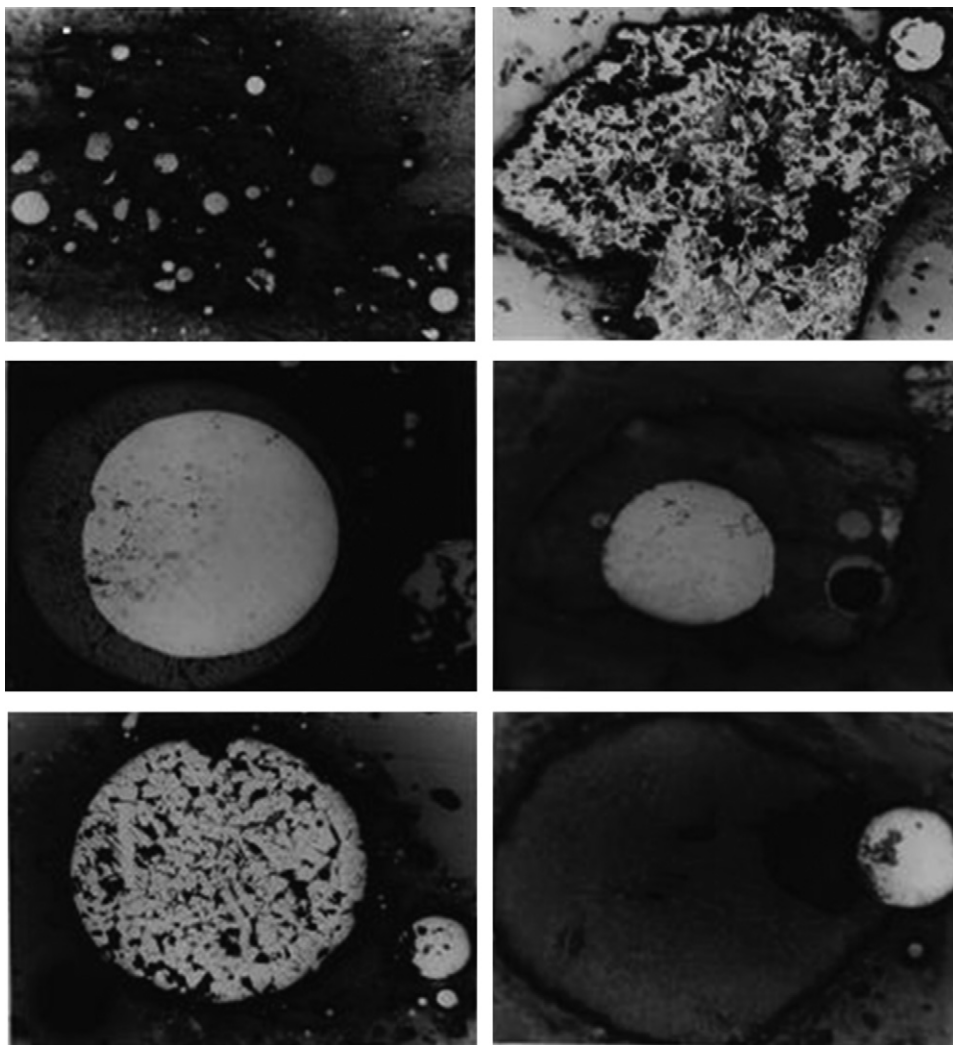
Fig. 2. The micrographs of LD sludge (from top). (A) Calcite with irregular shaped fragment. (B) Metallic globules encircled by thin porous glassing phase. (C) Secondary magnetite. (D) Skeletal fragment enclosed. (E) Fe metal prills. (F) Broken fragments of calcite.

Table 10
Pelletisation study of LD sludge

Serial no.	Organic binder (%)	Lime (%)	Inorganic binder (%)	Green strength (no. of drops)	Crushing strength (kg/pellet)	
					Naturally cured	Dried
1.	3	1	6	2	1.25	3.1
2.	6	2	6	2	6	10.9
3.	6	2	8	5	12.2	31

of pellets at 110 °C for 1 h, the crushing strength of the pellets increased considerably. It was also observed that around 8–9% of inorganic binder is required for making pellets. The pelletisation study of LD sludge is shown in Table 10.

5. Conclusions

A large amount of various sludge and slags are being generated from blast furnace and steel melting process at integrated steel plants. Studies carried out on different solid waste materials plants have indicated that most of the valuable products can be recovered by simple physical or chemical beneficiation techniques. The use of blast furnace slag should be enhanced in cement making to reduce the cost of cement manufacturer. The studies carried out on blast furnace flue dust generated at steel plants have indicated that most of the carbon values can be recovered either by cell or column flotation techniques. Fine magnetite with more than 64% Fe can be recovered from B.F. flue dust by low intensity magnetic separation techniques. Harmful components like alkalis, Zn, Pb present in the flue dust sample should be removed for its effective utilization in sinter making. LD slag can be a substitute for limestone in blast furnace operation. As phosphorous is intimately associated with other elements in the slag bi-leaching may be an ideal approach for its removal from LD slag. It is possible to recover iron values from LD slag by applying mineral processing techniques. It can be used as fertilizer for agricultural purpose and soil conditioner for acidity corrector of the soil. Beneficiation studies such as classification, magnetic separation and flotation were carried out to remove the phosphorous content from LD slag have met with limited success.

The agglomeration of LD sludges could be the ideal approach to maximize its use in sinter feed and thereby increase in the productivity of the sinter plant. The briquetting and pelletisation of LD sludge using organic and inorganic binders in combination with mill scale are the ideal approaches in recycling into the plant. The process of micro-pelletisation followed by sintering may be considered for their utilization in the steel plants.

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