

Fundamental Research and Utilization of LD Slag - An Overview

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Abstract: Reduce, reuse, and recycle are important techniques for waste management. These become significant for improving environmental and economic condition of industries. Slag generated from basic oxygen converter (LD-slag) is one of the recyclable wastes in integrated steel plants. It is suitable to be used in road making due to its high hardness and cementing property. Due to its high metallic value (FeO-18%) and lime content (CaO-45%), it is possible to use in BF iron making and steelmaking to replace lime and recover iron. High phosphorous content (1-3%) restricts its use in iron making and steelmaking. The paper gives an overview of different approaches taken worldwide by several investigators for dephosphorisation of LD slag which makes it possible to be reused in iron and steel making.

I. INTRODUCTION

Recently, the industrial sector has grown rapidly, producing a large amount of by-products, which have harmed the environmental balance and have become a major problem for disposal. Slags are undesirable by-products that float above the steel which consist of ionic solutions of molten metal oxides and fluorides. The slags have positive or negative effects on the metal production industry. Components such as SiO_2 , Al_2O_3 and sulfur are considered slag components that reduce the quality of the steel. The slag has a special role in steel production. The slag minimizes heat loss by staying on the liquid steel and protects the metal from oxidation, nitrogen and hydrogen absorption. Waste disposal can best be supported by recycling, reuse of wastes produced in other production processes, and the use of optimization tools and sustainable production theories.

In the recent years, the reuse of waste material has become very important because of the reinforcement of newly environmental regulations, in which waste disposal need to be minimized. Steelmaking operations are specifically concerned by this problem because of the origination of a huge quantity of by-products. These by-products including LD converter slag, fly ash, sludge and alloyed scrap contains some amount of heavy metals that may cause many environmental problems [1]. Therefore, recycling and reuse of waste has become a necessary act in these days due to shortage of dumping space for economic and environmental advantage. In the era of increasing environmental awareness, disposal, recycling and reuse of steel slag wastes with less harming the environment has been a prime concern for the steel industries [2]. LD converter steel slags are industrial by-products resulting from a steelmaking process in oxygen converters (Linz-Donawitz process). Their interesting mechanical properties made it possible to use in civil engineering as natural aggregate replacement in road construction [3-5]. Use of the LD slag will be beneficial because it helps save natural resources [6] and reduces the accumulation of slag grains in every year. Their negative impact on the environment needs to have efficient management system for the wastes coming

from the large-scale industrial plants which can be further used for landfill or reuse [7].

The average rate of generation of LD slag is approximately 150-180 kg per ton of crude steel in India [8]. Researchers also found that this rate of production of LD slag sometimes reaches a high of 200 kg per ton of crude steel [9]. In India, over 12.15-14.58 metric tons of steelmaking slag has been generated in the financial year 2013, and this rate is still increasing with the escalation of steel production. However, it depends on the quality of raw materials and yield efficiency of the steel plants. In India, the utilization of LD slag is a meager 25% compared to a high of 70-100% in other countries [10]. Therefore, disposal of this huge mass of waste slag has become a problem due to environmental and space constraints in the steel plants. The utilization of integrated steel plant waste by an economical and environmental friendly technique will decrease a major portion of the production cost. If these steel plant wastes are reused as a raw material substitute, then it is possible to conserve valuable natural resources like dolomite that are used as fluxing material to reduce the iron in steelmaking and thereby reduce the environmental hazards of mining the ore and reduce slag dumping space [11]. Special processing of slag can produce similar aggregate products originating from the rock and mineral industries. Therefore, much effort has been exerted on utilization of slags as raw materials for infrastructure sector. The LD slag is utilized as a raw material for concrete production, road construction, railway ballast, plastering, and other civil engineering works [12]. Such utilization of the slags will bring in the 3R (reduce, reuse, and recycle) concept to provide an effective and sustainable disposal system for this industrial waste.

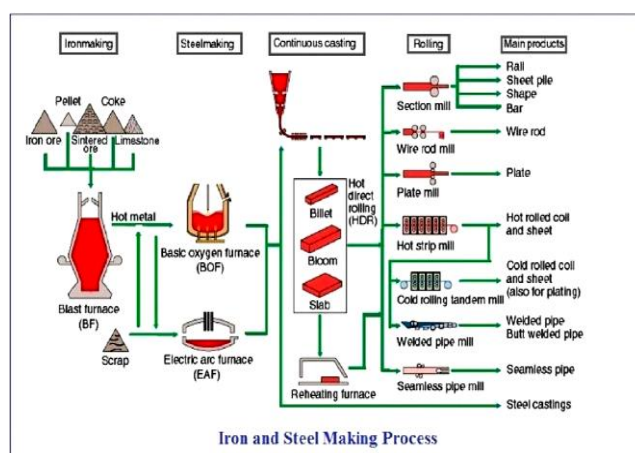


Fig. 1. Flowchart of iron and steel making processes and slag generation in modern steel plant.



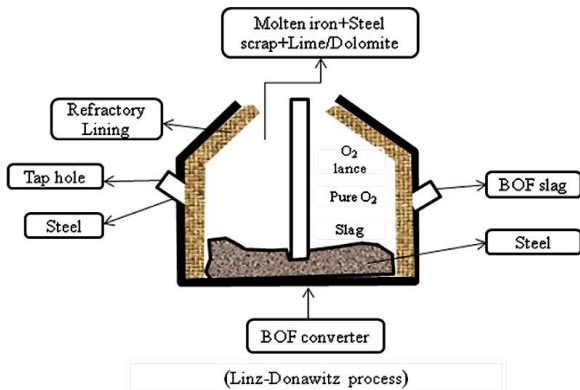


Fig. 2. Schematic representation of the basic oxygen furnace process.

II. PRESENT USES OF LD-SLAG

LD slag bolder is used in road making and floor preparation for its high hardness and cementing property. In Durgapur Steel Plant a major portion of the LD-slag is sold in the form of bolders for roadmaking. Similarly all the steel plants in India are selling more than 50% LD slag for road making and ground filling. Tata Steel's LD- slag has been proved to be an excellent railway ballast material and, as such, is being used by Indian Railways. The lime and magnesia present in LD-slag absorb moisture and CO, from atmosphere to form hydroxides and carbonates respectively which lead to the volume expansion or swelling resulting in crack formation in road and building materials.

LD-slag is used as cement making for replacement of clinker. Although LD-slag usage in cement making is commercialised in China, Indian cement manufacturers are still unwilling to take advantage of the low cost raw material for cement manufacture". LD-slag has higher CaO content in comparison to BF-slag, which acts as an activator and gives better strength. However, presence of P₂O₅ results in corrosion of reinforced materials in concrete structure. If only 10% LD-slag is used in cement, the P₂O₅ content will be around 0.3% which is not so harmful in portland slag cement (PSC), because low P₂O₅ in PSC react; with alkali in slag contributing little strength of cement". Therefore, more than 10% LD-slag use in PSC is not possible. Iron oxide present in LD-slag forms a phase, tetra calcium aluminoferrite (C₄AF) which has an adverse effect on the quality of cement". The total iron oxide content should not be 5%. The ferruginous portion of LD-slag can be separated by magnetic separation technique. However, for magnetic separation, crushing and grinding are required which are very costly. LD-slag is harder to crush compared to lime stone and therefore, it may be difficult to attain the desired fines. At Tata Steel the two staged crushing facility at the raw materials bedding yard has been found to be adequate to crush it to the desired size (90% to $—3\text{mm}$) for sinter making.

LD-slag does not demand heat for calcination when used in sintering. It contains a substantial amount of calcium silicates. Pure di-calcium silicates are high melting compounds (2403K) and so are the solid solutions rich in calcium silicates. This temperature is not attained within a sintered bed. However the presence of iron oxide environment around calcium silicates prevailing in a sinter bed changes the situation. A mixture of 23% di-calcium silicate (2CaOSiO₂) and 77% FeO would melt at around

1553K only. Similarly, the lime rich phases having melting ranges over 2273K, when adequately mixed with iron oxides can have liquidus temperatures of the order of 1473K. Micro-structural observation of laboratory sinter and plant sinter were taken up and found that characteristic micro-structural feature of LD-slag could not be detected in any of these samples. Therefore, it can be said that for all practical purposes, LD-slag got completely assimilated during the sintering. Incorporation of LD-slag has not been found to affect the quality and properties of sinter in terms of size, strength and RBI even up to 40kg per ton of sinter. small-scale industries like foundries and electric arc furnaces.

III. RECYCLING OF LD-SLAG

LD-slag may be used in refining of steel or in ironmaking due to its high metal value and lime content. It may also be used as a fertilizer due to its high phosphorous content. Presently it is neither used in steel melting and iron making nor in fertilizer making. To use this slag in melting or in iron making, dephosphorisation is required, whereas, to use it in fertilizer making, high phosphorus contents are required. In this age of competitiveness to minimize production cost, a good step can be taken to reuse LD-slag in steelmaking and ironmaking process. The phosphorus content of the blast furnace usually ranges from 0.1 to 0.3 % depending upon the type of burden used, whereas the bulk of quality steels must have phosphorus level below 0.02%. Thus almost 90% phosphorus present in the hot metal is removed as and magnesia which can easily substitute almost equal amount of limestone in the Blast furnace burden provided phosphorus is removed from the slag. However, the phosphorus content of hot metal will increase. if phosphorus is present in the recycled slag. This will require additional consumption of flux at later stage. Therefore, steelmaking slag for recycling must have low (<math><0.01\%</math>) phosphorus. An alternate approach for producing low-P (<math><0.01\%</math>) steelmaking (BOF) slag could be pretreatment of hot metal before it is sent to converter. The removal of phosphorus from hot metal is much easier due to its relatively lower temperatures (1573-1623K) compared to the removal in BOF where high temperatures (1873-1993K) prevail. However, intensive desiliconization of the hot metal is a prerequisite for an effective dephosphorization. Therefore, removal of phosphorus from Steelmaking slag is a better option to make it recyclable to Iron making processes. Several attempts for the dephosphorisation have been made to address this problem which are Physical Process, Chemical Process, Physico-Chemical Process.

IV. UTILIZATIONS OF LD SLAG

Use for soil stabilization and as a soil conditioner. LD slag is used as a soil additive to improve its physicochemical properties and in situ stabilization of Cu and other trace metals in a sandy Cu contaminated soil. It was found that soil pH increases with a higher incorporation rate of LD slag and allows bean growth, foliar Ca concentration, and further reduced foliar Cu concentration below its upper critical value, thus avoiding excessive soil EC and Zn deficiency [16]. Experiments have found that the soil pH increases from 5.3 to 6.4 with the use of 7500 kg of slag per hectare, the second year response being higher, i.e., 41% increase in the soil pH with 3000 kg slag per hectare

[17]. This is in the natural range and shows a positive effect on mustard and wheat seedling growth. Thus, this can be used in rural agriculture for better plant growth [18]. The Government of India, Ministry of Finance, has issued a circular (Circular No 553/49/2000-CX New Delhi, October 18, 2000) notifying that LD slag may be used as a soil conditioner after certain processing such as crushing, washing, and addition of rock phosphates. LD slag contains 29% calcium in the form of CaO. LD slag also contains phosphorous in the form of P₂O₅. Thus, use of LD slag has a limiting to ground limestone and is used regularly to reduce the need of liming on acidic soil [19]. Steel slag has also been used as amendment for metal-contaminated soils after proper environmental assessment.

Use as a fertilizer. Attempts have been made in Tata Steel, India, to use LD slag after grinding to 300 mesh as a soil conditioner in paddy fields, tea gardens, etc. [20]. Nippon Kokan Corporation (NKK) Japan has developed a process to produce eco-friendly slow-release potassium silicate fertilizer from the slag that shows less release effect rather than conventional fertilizers [21]. Many experimental works have been conducted for the production of fertilizers from LD slag, semi-calcined dolomite, and ammonium sulfate, and their agricultural applications for agro-forestry and pasture farming. The potential economic benefits of applying this new fertilizer to the soil were also evaluated [22]. According to soil type and agricultural use, by adding a concentration of LD slags between 1.5 and 5.0 tons/ha it is possible to achieve an increase in soil pH and hence to improve the soil quality and productivity. Experimental works were also carried out using pulverized LD slag for growing vegetables and crops like tomato, potato, onion, spinach, and wheat in acidic soil [23].

Use for road making and floor preparation. With increasing environmental awareness, the waste utilization of steel plants has become an attractive alternative to disposal. For the sustainable development of the steel industry, innovative environmental solutions should be applied. Nippon Slag Association in Japan is using LD slag in port and harbor construction [24]. LD slag boulders are used for floor preparation and in road making for its high hardness and cementing properties. Many steel plants are selling more than 50% of LD slag for construction and ground filling. The LD slag has proved to be an excellent railway ballast material and is being used by Indian Railways. In the Durgapur Steel Plant (Steel Authority of India), the LD slag is sold in the form of boulders for road making. Due to the presence of lime and magnesia, LD slag absorbs moisture and CO₂ from the atmosphere to form hydroxides and carbonates, which leads to volume expansion or swelling in road

or building materials. This problem can be overcome by weathering the slag for a duration of 6 to 9 months for the hydration of free lime before its use [25].

Use in cement making for replacement of clinker. In India, cement manufacturers are unwilling to take advantage of the LD slag as a low cost raw material for cement manufacture, whereas its use in cement making is commercialized in China. At Tata Steel, India, a project was initiated in collaboration with Lafarge India for use of LD slag for cement making [20]. In a comparison of LD slag and BF slag, LD slag has higher CaO content and acts as an activator and gives better strength, though the presence of P₂O₅ creates corrosion in reinforced concrete structure. If

only 10% LD slag is used in cement, then the P₂O₅ content will be around 0.3%, which is not so harmful in Portland slag cement (PSC), because low P₂O₅ in PSC reacts with alkali contributing additional strength of cement [26]. Thus, it is not possible to use more than 10% LD slag in PSC. Due to the presence of iron oxide in LD slag, it forms a phase, tetracalcium, aluminoferrite which has an adverse effect on cement quality. This ferruginous part of LD slag can be separated by magnetic separation [27].

Use in sinter plant after removal of phosphorus. Removal of phosphorus from LD slag is a better option for recyclable iron making processes. Many authors prefer physical processes like magnetic separation, flotation, dual phase separation, etc. for the same. In magnetic separation study, particles with high magnetic susceptibility are separated by a light magnetic field, and weaker magnetic particles will be separated by a strong magnetic field. Therefore, heterogeneous magnetic fields of different intensities can separate different particles. However, this is not a very effective way of dephosphorization [28-29]. A number of workers have performed chemical treatment (pyrometallurgical) of LD slag [30]. Phosphorus is also removed through evaporation by adding silicon to the Fe-P-C alloy obtained slag with carbon. During reduction of converter slag in an electric furnace, it is possible to form two different phases: one metallic and other nonmetallic [31]. The reduction of phosphorus in molten slag containing 8.3% Al₂O₃ and 3.5% P₂O₅ with basicity of CaO/SiO₂ of 1.1 at 1735 K, 1823 K, and 1893 K has been studied. It shows that temperature has an effect on the reduction of phosphate by graphite. The possibility of reduction of phosphorus by CO gas at 1823 K and the increase in reduction rate with increasing CO gas flow rate has also been investigated. It was concluded that the reaction rate of P₂O₅ was not controlled by diffusion of the P₂ gas phase product but by the chemical reaction [32].

Use in recovery of different metal values. The metal values recovery from LD slag was carried out by different techniques. Out of these techniques, the smelting reduction technique was carried out for valuable metals recovery, i.e., vanadium and chromium using a Tamman furnace. The recoveries of metal from LD slag are as high as 98% at 1600°C in 30 min [38]. This process was carried out by addition of a small quantity of mineral additive to the molten slag followed by crystallization of the slag. The additive acts as nuclei for crystallization of dicalcium silicate in the slag, and the breaking of slag produces 65–80% slag and 10–15% chips [39]. It was also reported that the most harmful components in LD slag are phosphorus and sulfur, which are to be removed before use either in the sintering plant or the blast furnace. In the Bhilai Steel Plant, India, LD slag was used in the blast furnace but later discontinued due to the high sulfur and phosphorus content [40]. However, the slag is not suitable in cement making due to the presence of a high percentage of iron oxide. The study has been carried out by magnetic separation techniques, and it was found that the combination of low and high intensity magnetic separation of ground LD slag at 63 μm in the wet process is effective.

Use for wastewater treatment. The use of steel slag in industrial wastewater treatment has received intensive attention in recent years. Due to the porous structure and large surface area of steel slag, it is easy to separate from water due to its high density. A high adsorption capacity of

steel slag was observed in the treatment of mercury-containing seawater [41]. The steel slag has been used as a low cost adsorbent for arsenic in aqueous systems, showing 95–100% removal efficiency at pH 2. The removal mechanism included the co-precipitation of the analyte from the solvent and its adsorption in CaCO₃ [42]. The removal of copper from wastewater using steel slag was conducted by adsorption and precipitation [43]. Additionally, steel slag can be used as a separate adsorbent to remove aqueous ammonium nitrogen [44], phosphorous [45], and phenol [46].

Use in CO₂ capture and flue gas desulfurization. CO₂ is one of the primary greenhouse gases and a large contributor to climate change. Thus, carbon capture and storage (CCS) research has been the focus of CO₂ reduction technology. With the current CO₂ sequestration routes, mineral CO₂ sequestration is regarded as a potentially important technology due to its benefits such as environmental friendliness and permanent trapping of CO₂ in the form of carbonate and without the need for post-storage surveillance for CO₂ leakage [47]. CO₂ gas is stored by allowing magnesium or calcium oxides in silicate minerals to react with carbon dioxide and form carbonates in mineral carbonation [48]. It is possible to store CO₂ in carbonate form using steel slag slurry under mild conditions of temperature and CO₂ pressure though steel slag contains a large amount of CaO [49]. The method of flue gas desulfurisation includes wet, dry, and semi-dry processes, among which the wet limestone/lime method is most widely used. It was also concluded that agglomeration gas desulfurization with steel slag was feasible [50]. The experiment was carried out on wet flue gas desulfurization with scrap slag powder residue. It was inferred that a more than 60% wet desulfurization rate could be achieved with a reasonable design and suitable operation by using steel slag. However, this technology is still limited to the laboratory research stage [51]. From this study, it can be confirmed that LD slag may be used in different fields due to its various properties.

Important Properties, Uses, Advantages, and Disadvantages of LD Slag

Properties	Uses	Advantages	Disadvantages
Resistance to heavy load, durability	Concrete, asphalt, ballast, road base	Greater hardness, better adhesion, greater stability and reduced wear	Greater weight compared to natural rock
Free drainage, resistance to skidding, inertia, hydraulic property	Ballast, road base, terrain preparation, base course materials	Greater hardness, better Adhesion	Impact on logistics and transport costs
Basicity/CaO content	Cement, agricultural use	Replacing the use of clinker, reducing energy consumption and CO ₂ emissions	Emissions of airborne pollution in the form of dust, gases, noise, and vibration when operating machinery
Soluble P ₂ O ₅	Fertilisers/s oil conditioner, agricultural use	Amending acid soil and improving plant growth	Possible leaching of heavy metals, potential risk to biosphere

V. CONCLUSIONS.

LD slag is one of the important waste materials generated in steel plants. Besides its use as road making and cement producing, it can very well replace lime addition to the steelmaking route due to its high lime content. However, the presence of phosphorous in it is quite high which restricts its utilization in iron and steelmaking. The amount of phosphorous can, however, be reduced by physical and chemical means.

New technologies and/or the improvement of existing technologies have been investigated and developed in order to achieve the ambitious target of “zero-waste” in the incoming years. The effective utilization of LD slags turns into a high-value added product and allows improving the steel plant competitiveness. Due to its high lime content, LD slag can replace lime addition in steelmaking. It can also be used for road making and floor preparation, cement making for replacement of clinker, and recovery of metal values. The phosphorus-enriched slag can also be used as a fertilizer for agricultural purposes and as a soil conditioner for acidity correction of soil. The presence of endemic phosphorus in LD slag is sometimes high, which restricts its reutilization in iron production and steelmaking. The amount of phosphorus can be reduced by physical, chemical, and biological means. As phosphorus is intimately associated with other elements in slag, bioleaching may be an ideal approach for its removal from the LD slag. Also it is possible to use LD slag for recovery of metal values, CO₂ capture and flue gas desulfurization and wastewater treatment through LD slag by applying alternative techniques. However, dephosphorization consumes fluxes and produces a high phosphorus slag, which again needs to be disposed of. Therefore, reuse and recycling of LD slag after removal of phosphorus seems to be a better approach. This will not only solve the present-day problem of LD slag but will also lead to the achievement of zero waste status and sustainable utilization of byproducts of the steel industry.

A detailed study on steel manufacturing with waste management of LD slag reveals that it can be cost effective if handled properly. For reuse of LD slag, after tapping of heat, the slag can be treated under a slow cooling process. The three phases (dicalcium silicate, dicalcium ferrite, and wustite) can be separated. After separation, the iron-rich portion (wustite) can be recycled for iron manufacture or steelmaking, and the lime-rich portion (dicalcium ferrite) can be converted to Mg–Mn-wustite by adding a mixture of metallic powder and coke breeze. If the P content is within tolerable limits in dicalcium ferrite, it can be used directly in iron manufacture or steelmaking. The P-rich portion (dicalcium silicate) can be used for fertilizer making. On the other hand, LD slag can be used for land filling after checking its long-term leaching properties.

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