

ABSTRACT

Steel is the main driving force of economic progress of a country. The steel industry in India is poised to take a huge jump in production of the steel from 111.2 million tonnes (Mt) in 2019 to about 300 Mt by 2030. By producing 106.5 Mt steel, India occupied 2nd position (2018) in the world's steel production. At such a juncture, mindless production boom sans any concern for the environment can ruffle the steel scenario. The industrial development programmed of any country, by and large, is based on its natural resources. For producing 106.5 Mt crude steel required about 182 Mt of processed iron ore and 227 Mt run of mine ore. There are planning for about 300 Mt steel production by India in 2030, that will be required 513 Mt of processed iron ore and 639 Mt run of mine ore. India is fortunate to have reserves of high-grade iron ores. But with time these reserves of high-grade iron ores are bound to be diluted.

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

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

breezes with up-gradated dust and sludge utilized in producing cold bonded iron oxide-coal composite pellets, the metallurgical coke requirement in the blast furnaces can be reduced.

The fines of iron bearing oxides and carbonaceous materials are mixed with a suitable binder and optimum quantity of moisture. The mixture is then pelletized in to balls of appropriate size. In cold bonding process, the composite pellets are hardened due to physio-chemical changes of the binder in ambient conditions or at slightly elevated temperature (400 to 500K). The challenge in cold bonding is to find a suitable binder that ensures the proper physical and mechanical properties of the composite pellet.

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

Interest in composite pellets have grown from the decade of 1980s because of the following advantages:

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

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

There is a shortage of coking coal in India. On the other hand, India has vast reserves of non-coking coal, which is widely available and cheapest reducing agent for iron oxide. Hence, non-coking coal based iron making technology has special relevance for country like India. In fact, the need to make non-coking coal based iron making units economically viable has resulted in the development of SR processes, which do not face sticking problem at high temperature. The SR process exploits faster reduction kinetics at higher temperature due to enlarged specific contact area between reactants in a dispersed phase and increased mass transport rates due to convection and thereby improves productivity. The process make use of non-coking coal in a broad range of composition and accept a wide range of materials including iron ore fines, plant wastes (after beneficiation) such as dusts and sludge or inferior grade ore directly. Their process control is relatively simple and they work out economically at small scale operation catering to varying demands of the market. The process is environmentally acceptable keeping the demands of coming years in view. Some of the upcoming SR processes are Corex, Romelt, HIs melt, Ausmelt, DIOS, Fastmet, Finex, ITmk³ etc. Amongst these Corex, Fastmet/ ITmk³ have already been established at commercial scale.

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

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

Thesis consists of six chapters covering all the relevant information about the steel making wastes (dust and sludge), beneficiation processes, composite pellets, smelting reduction processes and the work that had been done on utilization of steel plant wastes by beneficiation, agglomeration and reduction smelting to produce steel/cast iron.

The first chapter discusses the various types of wastes that are produced during steel making processes and its utilization after beneficiation. It also discusses the definition and advantages of cold bonded composite pellets. Outlines the objectives and plan of work are also presented.

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

The third chapter deals with the characterization of raw materials (which include sieve analysis of dust and sludge, proximate analysis of coal, chemical analysis of dust and sludge etc.). Beneficiation methods, an attempt was made to find suitable upgradation technique for increase in total Fe percentage; thereby developing a proper beneficiation route for dust and sludge. There are different apparatus or instrument used for characterization and beneficiation of raw materials, in particular Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (XRF) Spectrometer are also discussed in this chapter. SEM examination of dust and sludge were initially carried out to find out the morphology (i.e., shape, size and distribution) of the particles.

For this study main raw materials, dust and sludge, were collected from Jindal Steel Works, Bellari; and VIZAG Steel Plant, Vishakhapatnam. Coals procured from local market. The dust and sludge were grinded up to -100 mesh. The ground dust and sludge were

beneficiated using various methods like Air Classifier, Welfley Table and Hydraulic Classifier. Finally, after beneficiation trials, the two methods were finalised. The process route using two beneficiation method is finalised where air classifier was used in the first stage and the underflow was treated again in Wilfley Table. After tabling the concentrate and middling was mixed for further utilization. Maximum increase in total Fe was 52.0 pct achieved in JSW sludge, in JSW dust Fe total was upgraded to 46.2 pct; and in VIZAG sludge was upgraded to 47.9 pct total Fe after air classifier only. Based on total Fe percentage increased (above 60 pct), the two stage beneficiation route is selected. After the two stage beneficiation route, it was observed that in case of JSW dust, JSW Sludge and VIZAG Sludge there was increase in percentage of Fe_2O_3 up to 87.33 pct, 90.69 pct and 85.77 pct from initial Fe_2O_3 55.39 pct, 73.77 pct and 70.70 pct respectively.

The fourth chapter discusses the briquettes and pellets preparation and their testing. Taguchi technique is used, and MINITAB software analysis is discussed for selection of binder proportion in combination. To select the proper binder, cylindrical shaped briquettes (diameter 9.70 to 9.75 mm and height 13 to 14 mm) were prepared and tested. Different binders like CaO, slaked lime, bentonite, molasses etc. and their combination were used to prepare briquettes and their properties (compressive strength, drop strength and shatter index) were tested. It was observed that the highest compressive strength of 1436 N/briquette was obtained for briquettes prepared using 5 pct starch and 2.5 pct molasses as binder in JSW sludge, 1167 N/briquette strength was obtained for JSW dust using 7.5 pct starch and 5 pct molasses as binder and 1063 N/briquette was obtained for briquettes prepared using 7.5 pct starch and 2.5 pct molasses as binder for VIZAG sludge. From these results of briquettes, composite pellets were prepared. Variation in compressive strength was observed mostly by ± 15 pct of the average value. Similarly, the highest drop strength (more than 200 drops) and lowest shatter index value (0.064 pct) were also obtained. Bonding mechanism of corn starch as well as corn starch and molasses are developed.

The iron ore-coal composite pellets were produced using starch and molasses as binder with $\text{Fe}_{\text{tot}}/\text{C}_{\text{fix}}$ ratios as per stoichiometry. The degree of reduction of composite pellets were obtained by reducibility studies. The testing techniques, measurement of degree of reduction for composite pellets, apparatus and procedure are discussed. For measurement of degree of reduction for composite pellets, the weight loss method was used. The loss in weight due to loss of oxygen, carbon and volatile matters were taken into consideration. The isothermal reduction of composite pellets was carried out in nitrogen atmosphere. The reduction studies of composite pellets were analysed, and rate of reduction and activation energy was calculated.

The activation energies are found to be low (49.8–59.28 kJ mol⁻¹) which means, volatile gases (in particular H₂) diffused through porous solid iron oxide particles boundary. Overall reduction was controlled by gasification reactions. Reduced composite pellets were examined by SEM to observe the microstructure of the reduced composite pellets. XRD was carried out to identify the phases present in reduced composite pellets.

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

The sixth chapter contains the summary and conclusions of the present work, and suggestions for further work. The present investigation concludes that the dust and sludge of various steelmaking processes have different in characteristics and hence their beneficiation processes also differ. After beneficiation, upgrading the total Fe percentage, they can be utilized for composite pellets making with coal and subsequently used for steel/cast iron making with high yield.

