PREFACE

Steel is the largest (1600 million ton in 2015) produced metal in the world and India is the 3rd largest global steel producer (90 million ton in 2015). These steel plants are the major source of solid waste materials like slags from blast furnace and LD plant, fly ash / bottom ash from power plant, iron ore slimes from ore washing plant, coal/coke from coke ovens etc.

The production of one million ton of crude steel, causes generation of around 20,000-25,000 ton iron ore slime, 6000-7000 ton coal combustion residues (fly ash/ bottom ash), 850-950 ton BF slag , 350-450 ton steel making slag, 50-65 ton flue dust, 35-50 ton mill scale, 125-135 ton scrap, 85-90 ton lime and dolomite fines.

It is estimated that the total solid waste generation is about 84% in the form of iron ore tailings (fines/ slime) and coal combustion residues (fly ash / bottom ash) and remaining 16% constitute all other solid waste including slag. These solids waste cause adverse impact on their disposal to environment and economy.

The loss of valuable metals affects metal production economy while dumping expenses and cost adds to the product cost. These solid waste dump yard are known for their pollution and health hazard which cannot be ignored now a days due to the strict legal framework enforced by the government.

The literature survey revealed that the above wastes (Iron ore slime & Bottom ash/ Fly ash) are being used for land filling and conversion into some value added products in few countries. However, the partial or bulk utilization of such waste is still an academic issue in India.

The present study deals with the partial utilization of iron ore slime and bottom ash for the preparation of value added products.

The thesis comprises of EIGHT chapters.

Chapter-1 presents a brief introduction along with literature review on generation, types, properties and applications of iron ore slime and Bottom Ash.

The extensive literature survey was conducted on various efforts made globally during 1990 to 2015 to utilize such solid waste indicating that work has not been done extensively in the following areas:

1. Bottom Ash utilization for building bricks has been partially attempted.
2. Bottom ash as a bed filter material has not been attempted.
3. Bottom ash and iron ore slime for making insulation bricks (value added products for industries) have not been explored.
4. Iron ore slime and bottom ash for the production of Ferro-alloys have not been tried.

This chapter also gives the following expected benefits from the present study:

1. Exploration of solid waste from integrated steel plant (ISP).
2. Preparation of value added products from solid waste material for the use as furnace insulation bricks, building bricks, bed filter material and ferro-alloys.
3. Protection of environment by avoiding solid waste dumping, promoting sustainable development.
4. Improved economy of the plant.

Based on the literature survey and considering the above possible benefits, the present work was undertaken. The solid waste available from Indian Steel Plant was selected for the study to be relevant Nationally. The study was planned to be conducted as (a) Characterization of waste (i.e. iron ore slime and bottom ash) followed by (b) Bed filter material suitability test (c)

Development of bricks (building as well as insulation) making process utilizing iron ore slime and bottom ash with using two different methods, i.e. Geopolymerization & Firing respectively. (d) Extraction of metallic constituents of iron ore slime and bottom ash using Electric Arc furnace (EAF) under environment of Nitrogen plasma and Hydrogen plasma respectively.

Chapter-2 deals with the characterization of the raw materials with respect to Physiochemical, Geotechnical as well as Bed filter suitability.

The various studies resulted in the following observations:

(a) The type of combustion process greatly varies the properties of bottom ash, although the origin of coal used remains same. Bottom ash is a source of silica and alumina which could be utilized as a potential material for manufacturing useable products.

(b) The bearing strength and shear strength of fluidized bed combustion (FBC) bottom ash is better than the pulverized coal combustion (PCC) bottom ash which suggests its possible use for sub layers for pavements and road. Due to porous popcorn like structure of PCC bottom ash, the permeability is more than FBC which could not be used in making embankments of canals, dams etc.

(c) The study concludes that the FBC bottom ash could be used as an effective bed filter material for making ash dykes compared to sand as well as PCC bottom ash.

Chapter-3 deals with the utilization of bottom ash for making building bricks production through geopolymerization technique. In these experiments, two types of bottom ash were used having particle size <75 µm. The different molar NaOH solution along with Na_2SiO_3 were added while making the brick sample by pressing in a hydraulic press followed by curing at different time and temperature. The cured samples were characterized for their different property evaluation such as strength, water absorption, density etc. The tentative mechanism of geopolymerization was established based on the results of different properties as well as XRD and FT-IR analysis.

The results obtained suggested that Geopolymer bricks of bottom ash are feasible by adding sodium silicate and sodium hydroxide. Rate of geopolymerization was quicker initially in case of FBC bottom ash than PCC as dissolution was not required for FBC type because of free state of silica and alumina. Although geopolymerization is slightly more in case of FBC, yet PCC bottom ash is more suitable for strength development due to presence of hard aluminium silicate phase. Up to 65 °C, geopolymerization increases and then decreases because of higher rate of geopolymer gel formation that restricts the further dissolution of ash particles. Increasing NaOH concentration ensures more geopolymerization up to 10M but further addition decreases this action because of highly viscous NaOH layer covering surface and thus restricting further geopolymerization.

Chapter-4 deals with the utilization of iron ore slime & bottom ash for making insulation bricks by the firing route. The bricks made by a hydraulic press with the varying iron ore slime and firing temperature were tested. The parameters like fineness of bottom ash, moulding pressure, holding time and moisture content were kept constant based on the preliminary test conducted before the present experiments.

The results concluded that for the preparation of bricks, iron ore slime acts as an effective binder due to its fineness which increases green strength of the bricks made from even coarser bottom ash. Increasing firing temperature and iron ore slime content increases the strength inside the bricks due to formation of lower melting constituents. For the same reason, water absorption and porosity decreased and density increased. Due to porous structure in PCC bottom ash, strength as well as density decreased and porosity increased with respect to FBC bottom ash. The presence of iron oxide in iron ore slime forms iron silicate and iron aluminium silicate phases in the presence of silica and alumina at high temperature which imparts fired strength drastically in the bricks. The bricks produced in this study could be used for insulation in low to medium temperature applications (max 600°C). Thus, this bricks could be effectively utilized at the cold facing side of the furnace wall.

Chapter-5 deals with the second option of bulk utilization of this solid waste, which needs high temperature tool for extraction of metals (i.e. Si & Al) present as silica and alumina which is reducible at high temperature. The literature indicated that plasma arc furnace could be used for such study. Such type of transferred arc plasma (TAP) furnace is very costly and the supplier for this type of furnace (laboratory scale) was not found in India. In view of this, it was decided to fabricate the furnace indigenously in the laboratory for this study. The literature provided different inputs for the furnace design and fabrication. The fabricated furnace was fully characterized for smooth functioning by observing the parameters like arc length, energy consumption, graphite electrode consumption, sound level as well as lining erosion, before taking up trials for the study of smelting reduction behavior of solid waste. The results concluded that fabricated furnace is well designed and suitable for smelting reduction studies. Nearly 200°C increased melt temperature and ~10dB lower sound levels were observed with nitrogen plasma arc compared to a normal arc. Hydrogen plasma increases more than 100°C melt temperature generating ~5 dB sound than nitrogen plasma. Lower energy and electrode consumption were noted with nitrogen plasma arc melting than normal arc melting. The lower energy consumption and higher electrode consumption were observed in the case of hydrogen plasma in comparison to nitrogen plasma. The higher plasma arc temperature resulted in shorter meltdown time than normal arc with smoother arcing. Hydrogen plasma created more heat, reducing meltdown time and lower energy consumption but simultaneously increased graphite electrode consumption, crucible wear and sound level.

Chapter-6 deals with the behavior of smelting reduction of iron ore slime and bottom ash, in a fully characterized TAP furnace yielding ferro-alloys. These experiments were performed using different process variables such as: mixture ratio (bottom ash: iron ore slime), charge form (pellet and powder), reductant type (char/coal/graphite), reductant ratio (stoichiometry), charge layer thickness, crucible type (graphite/ magnesite), arc type (normal/ N_2 and H_2 plasma), as well as smelting time (10-80 min). The products, i.e. metal, slag and dust were analyzed to understand the mechanism of smelting and improve the yield of the product.

The present investigation indicated the feasibility of plasma arc smelting of iron ore slime and bottom ash to produce iron- aluminum- silicon alloy. The partial recovery of aluminum and silicon in the metal bath is indicative of carbothermic reduction of alumina and silica in the charge at plasma arc temperature. The recovery of aluminum and silicon due to carbothermic reduction under plasma arc appears to be affected by various operating parameters such as temperature, stoichiometric ratio of carbon in reductant, form of feeds (pellet/powder), charge material quantity, type of feed (bottom ash/ bottom ash + iron ore slime) and crucible lining. In the present investigation, the limited experimentation has indicated the following trends.

(a) Higher temperature by using hydrogen plasma appears to give increased recovery of aluminium and silicon in the bath.

(b) The recovery of aluminium and silicon in the bath was found to increase with carbon content in the mix upto certain level (stoichiometry). Further addition did not affect much recovery.

(c) The higher metals recovery (Al and Si) during smelting was noted with powder form of the feed compared to pellet form.

(d) Increased metals recovery was observed with larger quantity of batch charge of feed material possibily due to increased bed thickness.

(e) The metal recoveries were found to be higher in case of charge having iron ore slime and bottom ash in comparison to only bottom ash which may be due to Fe-Si metal raining from top layer helping in higher yield.

(f) The higher metal recovery was noted with the use of graphite crucible in comparison to magnesite crucible which may be due to the dissolved carbon in the melt which acted as a reductant.

Chapter-7 presents the issues arising from the studies conducted during smelting reduction of iron ore slime and bottom ash under plasma environment. The two major parameters indicating the process economy in TAP furnace are Energy and Graphite consumption. Environmental consideration mainly depends on sound generation as well as generation of dust, fumes and gases.

The results concluded that the least energy consumption observed in the case of plasma in comparison to normal arc is due to the excess heat generation. Graphite crucible and powder charge decreased the energy consumption due to the excess carbon dissolution in the melt through the graphite crucible accelerating the reduction reaction. Graphite crucible material as well as powder charge decreases the heat loss by conduction and radiation and decreases the energy consumption. Increasing reactivity and stoichiometry of carbon increases the reduction reaction hence decreases the energy consumption. The graphite consumption follows the similar trend as regards the energy consumption in all cases, except arc type. In the case of nitrogen plasma, least graphite consumption was observed, whereas slight increase in graphite consumption due to reaction with hydrogen was noted in hydrogen plasma case. Powder charge and increased charge bed height surrounding the arc decreases the sound level. Graphite crucible easily discharges the current, resulting in the lower sound. Plasma decreases the sound level due to the fact that plasma gas creates easy path of electron transfer. Hydrogen plasma increases sound due to burning of hydrogen gas.

Chapter-8 presents the overall Summary and Conclusions derived from the present study, which are listed below:

- FBC bottom ash material characteristics are found to be suitable material for bed filter in Ash dyke.
- The bottom ash (FBC/PCC) has been found to be suitable material for making light-weight building bricks using geopolymer techniques.
- The iron ore slime and bottom ash mixture have been found to be suitable for making the insulation bricks.

The limited experiments conducted have given the feasibility of smelting iron ore slime and bottom ash in a plasma arc furnace to produce iron-aluminum-silicon alloy.

- The significant recovery of aluminum and silicon in the melt is indicative of carbo--thermic reduction of alumina and silica in the iron ore slime and bottom ash. However, further work is required to optimize the recovery of metals during the smelting process.

Based on the present studies following fruitful conclusions may be drawn:

1. The characteristics of fluidize bed combustion (FBC) bottom ash materials are found to be a suitable for using as bed filter in ash dyke.

2. Both types (FBC and PCC) of bottom ash have been found to be the suitable material for making lightweight building bricks using geopolymer techniques.

3. The iron ore slime and pulverized coal combustion (PCC) bottom ash mixture has been found to be more suitable for making insulation bricks compared to FBC bottom ash.

4. The limited experiments conducted have given the feasibility of smelting iron ore slime and bottom ash in a plasma arc furnace to produce iron-aluminium-silicon alloy.

5. The significant recovery of aluminium and silicon in the melt is indicative of carbothermic reduction of alumina and silica in the mixture of iron ore slime and bottom ash. However, further work is required to optimize the recovery of metals during the smelting process.

Scope for future work

In the light of the observations made during the present investigation, further work may be undertaken in the following areas:

- The field trials may be conducted while making dykes using FBC bottom ash as filter bed materials in place of conventional sand particles.

- In light of the encouraging results of making building bricks using FBC and PCC bottom ash by geopolymeric technique, the further work may be conducted in making required size bricks to test its properties in the form of lightweight bricks as a building material.

- The preparation of insulation bricks using PCC bottom ash may be undertaken for making regular sized bricks in large numbers to test its techno-economic feasibility for industrial application.
- In view of the feasibility of smelting, mixture of iron ore slime and bottom ash in plasma arc furnace to produce iron aluminium silicon alloy, further work may be undertaken in exhaustive manner to examine the effect of various smelting parameters in enhancing the recovery of reduced metals by regulating operating parameters. During such studies, efforts may also made to study the kinetics of smelting reduction process.