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GEO-CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF SOLID WASTE MATERIALS GENERATED FROM METALLURGICAL FURNACES- A CASE STUDY

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ABSTRACT

The production of steel is associated with the generation of huge amount of solid waste materials like slag, dust, sludge, etc. Significant quantities of wastes are generated from steelmaking process which is a focus point now-a-days with reference to (w.r.t) its utilization as well as environmental impact. Steelmaking process broadly includes all operations from primary and secondary steelmaking to ingot and continuous casting of steel. At each of these stages of steelmaking process, substantial amounts of wastes are generated. Thus minimization and utilization of waste through integrated waste management has gained special significance in the present scenario, as these wastes have a wide ranging impact on the environment. The solid waste generation, presently in Indian steel industry is in the range of 450 - 550 kg/t of crude steel and recycling rate varies between 40 - 70 % which lead to higher production costs, lower productivity and further environmental degradation. It is very essential not only for recycling of the valuable metals and mineral resources but also to protect the environment. In advance countries, the solid waste generation has been brought down below 200 Kg per tonne of crude materials and the recycling and reuse rates are above 90% approaching almost to 100% level. This paper summarizes and analyzes the generation, composition, characteristics and present status of the utilization of the most of the wastes generated from the steelmaking processes. The aim of the paper is to explore the various developments for total recycling of solid waste generated from steel industry, so that the vision for making "*clean & green steel with zero waste*" can be achieved for survival and growth of steel business in future.

Key Words: Minimization, utilization, zero waste, survival, steel business

INTRODUCTION

The production of steel in steel plant involves several operations starting from use of natural raw materials, like iron ore, coal and flux in production of hot metal and further processing of hot metal into steel and subsequently, rolling of steel into finished products in the rolling mills. Quantities of solid wastes generated in steel melt shops are a cause for concern as their nature is quite variable and diversified (Nayak and Pal 2001). The waste materials like slag, dust, sludge, etc. have a wide range of impact on the environment. For example some metals are essential for biotic function (micronutrients such as Cu), but when present at higher concentrations, may detrimentally affect the health of organisms (Gadd 2010). Other metals are non-essential and toxic in trace amounts (e.g. Hg, As) (Kalis et al. 2006, Kapustka et al. 2004). Metals are also of environmental concern as, unlike organic contaminants, they do not biodegrade; rather they are stored and released from various geochemical forms as environmental conditions change (Sakan et al. 2007). Earlier these wastes were either dumped or thrown out in the open space but now with rising concern for the environment and lack of space for the dumping of such huge wastes, new technologies are being explored to tackle these wastes as they contain concealed resources. Solid waste is the unwanted or useless solid materials generated from combined residential, industrial and commercial activities in a given area. It may be categorized according to its origin (domestic, industrial, commercial, construction or institutional); according to its contents (organic material, glass, metal, plastic paper etc); or according to hazard potential (toxic, non-toxin, flammable, radioactive, infectious etc.)

Over the years, due to technological improvement in steelmaking and strict environmental regulations, emphasis on raw material quality and new markets coupled with innovative ideas on waste reduction and reuse have resulted in drastic reduction in the quantity of waste generated in steel works from 1,200 kg to less than 200 kg per tonne of crude steel and recycling rates have reached to 95 - 97 % in some parts of the world (Dykstra et al. 2000). Few steel industries have approached to cent percent waste utilization without discharge of any waste to environment. In India, as per the draft National Steel Policy, 2012 / 2015, the crude steel production is planned to be increased from present 100 Mt/yr to 300 Mt/yr and therefore, the waste management system needs to be further strengthened for making successful and economically viable efforts for 100 % utilization of all wastes (Cherh 2008).

The progress on technological aspects, process options for enrichment of input materials and solid waste management in Indian steel industry are moving at much slower pace than desired. In order to sustain the present competitive market and for further growth in future, it is essential to use technological innovations and putting R & D efforts in order to reduce waste generation and further for its recycling to steel plants (Hagni and Hagni 1991). Modern trend steel industries are focusing on eco-friendly technologies for making clean & green steel with zero waste to environment to make steel business a sustainable and successful venture.

The most important environmental issues are that the world facing today is the issue of waste management and disposal of waste. This problem crosses all international borders and influences the lives of all the people of the world. Poor solid waste management is a threat to public health and causes a range of external costs. However, solid waste management in the developing countries has received lesser attention from policy makers and researchers than the other environmental problems, such as air and water pollution (Jha et al. 1999). Waste management encompasses everything from collection and handling to disposal by incineration, landfill and other methods, and recycling. Also included are the serious associated implications for the health of people and the environment. As waste producing activities proceed and intensify, the world community will be faced with hard choices on how to best manage and dispose of wastes. These decisions should be based on hard science and sound management practices (Karakus and Hagni 1991). However, there are geopolitical dimensions to be found in the decision-making process of waste management and disposal. India is the second largest nation in the world in population i.e 1.21 billion accounting for nearly 18% of world's human population, but it does not have enough resources or adequate systems in place to treat its solid wastes. Improper solid waste management deteriorates public health, causes environmental pollution, accelerates natural resources degradation, causes climate change and greatly impacts the quality of life of citizens (Das et al. 1996). In this research paper we have tried to do mineralogical and geo-chemical characterization of waste material generated from metallurgical furnaces (Iron Making & Steel Making) and also waste material generated from thermal power plant. The results of the above investigation have been synthesized to find out the amenability of the waste materials to upgrade and further utilization.

MATERIALS AND METHODS

Study Site

The study was carried out in solid waste dumping site of Maithan Ispat limited, Gopabandhu Marg and Mideast Integrated Steel Limited (MISL)-MESCO Kaling Nagar Industrial complex (KNIC) , Jakhapura in Jajpur district of Odisha, India. Geographical location 20° 57' – 21° 3' N latitude and 85° 59' – 86° 5'E longitude near Duburi mining area of Jajpur district, Odisha, India which is shown in Fig. 1.

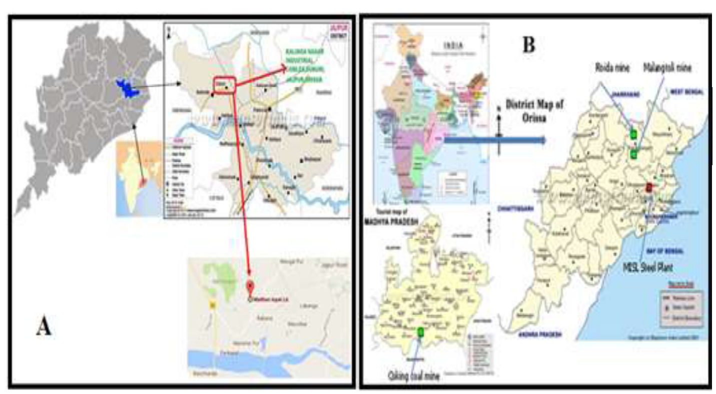

Fig. 1. Map showing the location of Kalinga Nagar Industrial Complex (KNIC) with Maithan Ispat Limited (A) and Mideast Integrated Steel Limited (MISL) – MESCO (B)
Source: http://en.Wikipedia.org/wiki/Jajpur district, http://www.mapsofindia.com/maps/orissa/districts/jajpur.htm, accessed on 12^{th} Feb. 2013

Collection of Samples

Blast Furnace Slag

Blast Furnace Slag (BF) is formed when iron ore or iron pellets, coke and a flux (either limestone or dolomite) are melted together in a blast furnace. When the metallurgical smelting process is complete, the lime in the flux combine chemically with the aluminates and silicates of the ore and coke ash to form a non-metallic product called blast furnace slag. During the period of cooling and hardening from its molten state, BF slag can be cooled in several ways to form any of several types of BF slag products. This slag is collected from MISL (MESCO)

1. **Granulated slag**: - Blast Furnace Slag is rapidly cooled by large quantities of water to produce a sand-like granule that is primarily ground into cement commonly known as GGBS (Ground Granulated Blast Furnace Slag).

2. **Air-cooled Slag**: - Blast furnace slag is allowed to slowly cool by ambient air, is processed through a screening and crushing plant and is processed into many sizes for use primarily as a construction aggregate.

Steel Making Slag

Steel making slag is an unavoidable by-product in Iron & Steel making. It is essentially a mixture of metal oxides and silicon dioxide i.e. silicate. However, Iron & Steel Slag is non-metallic in nature and does not contain hazardous materials. These slags are collected from Moithan Ispat Limited. These are SMS slag, SMS sludge and Fly ash.

Characterization

Bulk Density

It is defined as the mass of many particles of the material divided by the total volume they occupy. The total volume includes particle volume, inter-particle void volume, and internal pore volume.

Procedure

- Slag sample size of 25 – 50mm is taken.
- A container of known volume is taken.
- Sample is completely filled in container till top.

$$\text{Bulk density} = \frac{\text{Wt. of the sample}}{\text{Volume of Container}}$$

Porosity

Porosity is a measure of how much of a rock has open space. This space can be between grains or within cracks or cavities of the rock.

Procedure

- Initial weight of sample is noted down.
- Sample of 100g is taken and dipped into water completely.
- Slag is allowed to be in 350mL water for 1 day.
- Volume of sample is found out by volume of water displaced.
- Final weight of sample is noted down.

Porosity is calculated by following equation

$$\%\text{Porosity} = \frac{\text{Volume of water absorbed}}{\text{Volume of slag}} \times 100$$

pH analysis

Determination of pH plays an important role for utilization process plan. According to their acidic and basic nature their utilization is carried out.

Procedure

- 5g of powered slag is taken.
- 20mL of water is used to dissolve slag powder.
- Now water is filtered using filter paper.
- Filtered water is left for 15 minutes.
- A litmus paper is dipped into water.
- Change in colour of litmus paper is compared with standard colour chart

Scanning Electron Microscopy (SEM)

The morphological characteristics of different samples were observed by using a scanning electron microscope (Hitachi S4800, Japan.). An Energy Dispersive X-Ray Analyser (EDX or EDA) is also used to provide elemental identification and quantitative compositional information.

X-ray diffraction (XRD)

X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. XRD monitoring diffraction performed on Philips PW-1847 X-ray crystallographic (Utah, Saltlake city) unit equipped with a Guinier focusing camera CuK_2 radiation.

RESULTS AND DISCUSSION

Bulk Density

Bulk density is a property of powders, granules, and other "divided" solids, especially used in reference to mineral components (soil, gravel), chemical substances, (pharmaceutical) ingredients, foodstuff, or any other masses of corpuscular or particulate matter. It is not an intrinsic property of a material and can change depending on how the material is handled. Bulk density is more for SMS slag and granulated slag than air cooled slag. For fly ash and SMS sludge it is very less (Table 1).

Table 1.Bulk density of different samples

	Granulated slag	Air Cooled slag	SMS slag	Fly Ash	SMS sludge
Wt. of the sample taken	792.5 g	490 g	802.5g	8 g	11 g
Vol. of the container	250 mL	250 mL	250mL	250 mL	250mL
Bulk Density	3.17 g/mL	1.96 g/mL	3.21 g/mL	0.032 g/mL	0.044 g/mL

Porosity

Permeability is a measure of the ease with which a fluid (water in this case) can move through a porous rock. It is found that granulated slag is more porous than SMS slag as well as air cooled slag (Table 2). So these can use for filling of low lands and which can be made easy to grow green vegetation.

Table 2. Porosity of different samples

	Granulated slag	Air cooled slag	SMS slag
Volume of water taken	250 mL	250 mL	250 mL
Volume of water after dipping the sample	272 mL	265 mL	262 mL
Volume of the sample	22 mL	15 mL	12 mL
Water absorbed by sample	11.45 mL	0.270 mL	0.234 mL
% of porosity	52 %	1.8 %	1.95 %

pH analysis

As slag is used as soil conditioner it is very important to know their nature. Generally slag formed is acidic in nature and these acidic slag are harmful than alkaline slag (Table 3). To make the acidic slag into alkaline, these are treated with limestone. If the substance is found out to be acidic it is used in the places where alkalinity is more and vice versa. Granulated slag and air cooled slag may be used in alkaline soil as soil conditioner with fertilizer whereas SMS slag can be used as a soil neutralizer for highly acidic soils in areas such as Eastern India; its use as a fertilizer has also been well-established.

Table 3. pH of different samples.

Samples	pH	Remark
Granulated slag	4.1	Acidic
Air cooled slag	4.3	Acidic
SMS slag	12.2	Basic

SEM

SEM studies have brought out the characteristics of the various mineralogical phases. In electron microscopy, the image formation is due to the scattering of electron beam scans over the sample. In general this study brings out the size, shape and micro morphology of minerals and their textural patterns. The chemical composition of the slag is dependent upon the composition of the available iron ores, flux stones, and fuels, and on the proportions required for efficient furnace operations. The blast furnace must be charged with uniform raw materials if the iron produced is to be consistent in quality. This procedure also ensures uniformity in the composition of the slag.

According to EDAX studies it is found that both granulated slag (Fig. 2 a) and air cooled slag (Fig. 2b) contain calcium and silicon more weight percentage than that of magnesium, aluminium and sulfur. So this slag is not harmful for environment. Similarly SMS slag (Fig. 2 c) and SMS sludge (Fig. 2 d) contain more weight percentage of oxygen, aluminium, silicon than Fe, Mg, K, Ca etc. It is interesting Ti is found 2.56 (Wt%) in SMS slag while Au is obtained 23.37 (Wt%) in SMS sludge. It is not profitable to extract gold from SMS sludge. In fly ash (Fig. 2e) weight percentage of oxygen, aluminium, silicon found more than that of Fe, Mg, Ca. These slags are sold by authority to other company.

XRD

The different phases of the slag identified in order of abundance, from their X-ray diffraction pattern includes

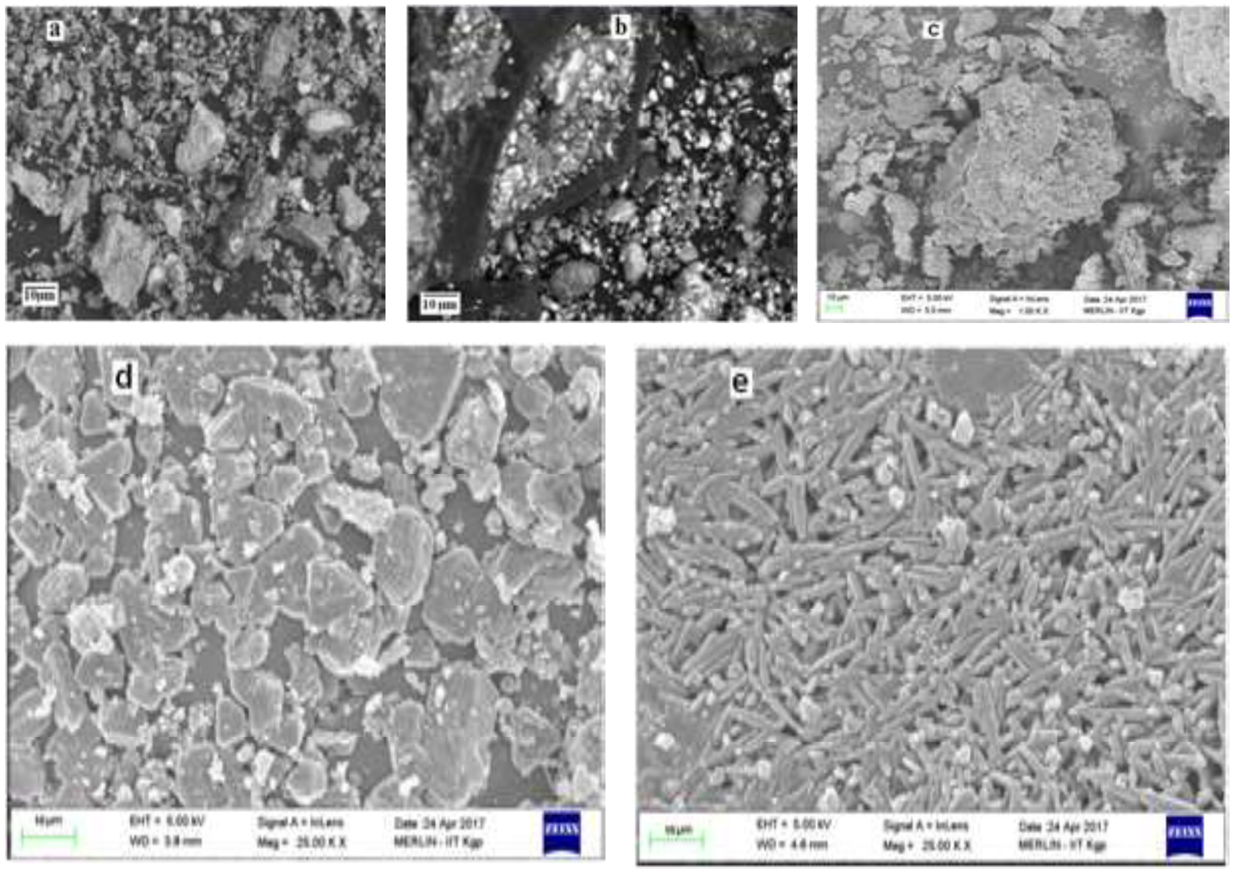

Fig.2.SEM of granulated slag (a), air cooled slag (b), SMS slag (c), SMS sludge (d) and fly ash (e)

Hematite, Quartz, Magnetite, Wustite , Wallastonite and Rankinite shown in Fig. 3 for granulated slag, Fig. 4 for air cooled slag and Fig. 5 for SMS slag.

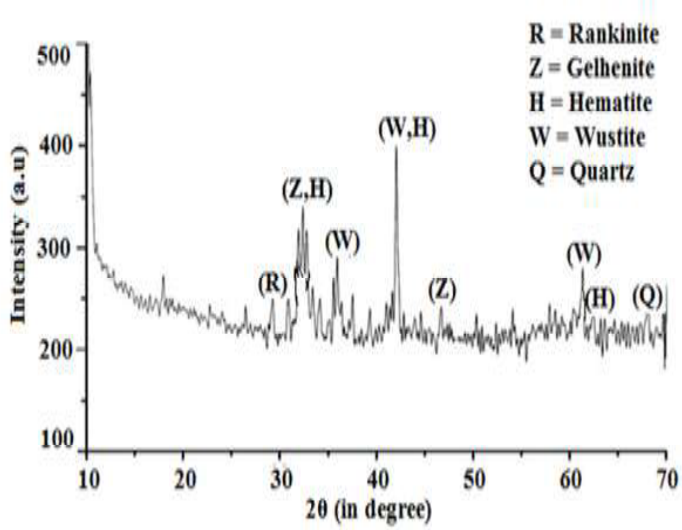

Fig. 3. XRD of granulated slag

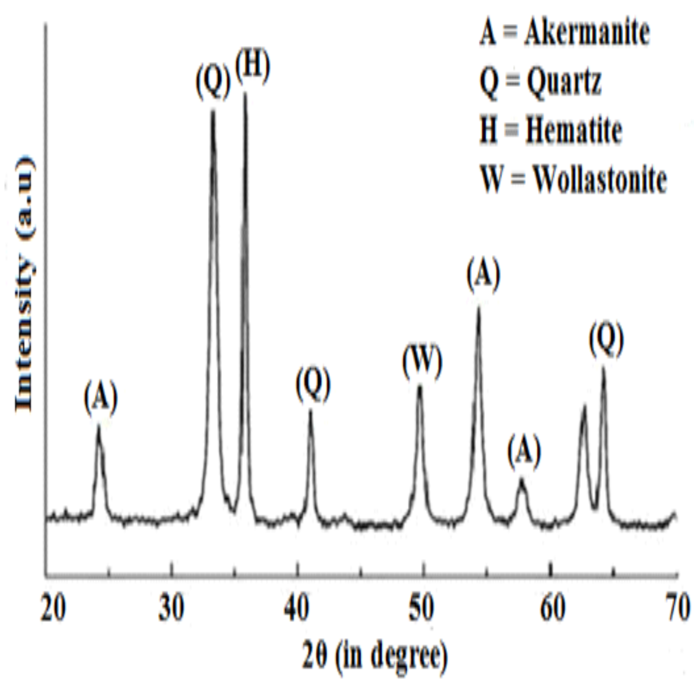

Fig. 4. XRD of air cooled slag

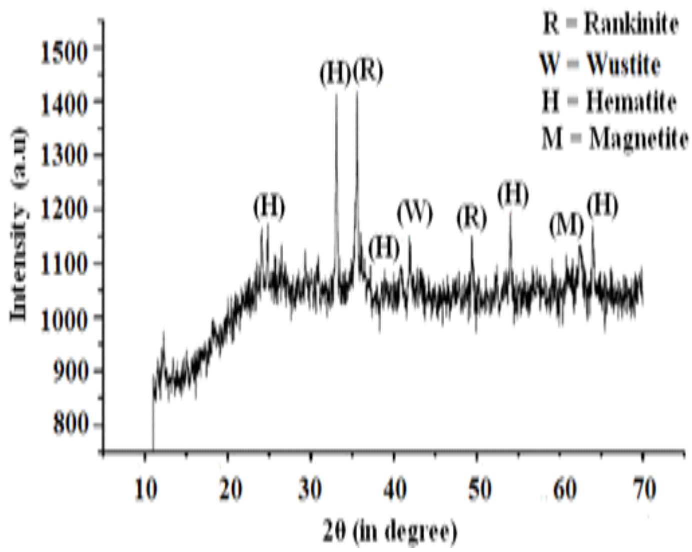

Fig. 5. XRD of SMS slag

CONCLUSION

Development of steel industry is focusing on "Clean, green and sustainable technology" for its survival, development and growth. The sustainable technology development means improvement of the quality of life for everyone and generation to come without making any harm to environment. Steelmaking slag is a by-product of the steelmaking process. XRD, SEM is done along with bulk density, porosity and pH has been determined. From these results we concluded the following applications of wastes obtained from steel plant. Almost all steelmaking slag that produced is effectively utilized for material in road construction and other civil engineering projects, calcium-oxide-based reformer like ground improvement, soil improvement etc and raw materials for cement, fertilizer. Many of these uses represent natural substitutes for man-made material. In future researchers can develop new functions for steelmaking slag and further expanding its application. Air Cooled Slag can be used in all types of construction aggregate applications in addition to manufacture of mineral wool, cement and glass and as a soil conditioner. Granulated blast-furnace slag production is quite small and can be used in road base and fill construction. Steelmaking slag can be used as source of iron and flux materials in blast furnaces. Management of solid waste reduces or eliminates adverse impacts on the environment and human health and supports economic development and improved quality of life.

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